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University of Zagreb

FKITMCMXIX

in cooperation with

Hrvatske vode, Legal entity for water management (HR)
Department of Civil & Environmental Engineering, College of Science, Engineering and Technology, Jackson State University (USA)
Croatian American Society (HR)
Slovenian Biomass Association (SLO)
ODRAZ, Sustainable Community Development (HR)

3rd International Symposium on Environmental Management

Towards Sustainable Technologies



Conference Proceedings

October 26 - 28, 2011
Faculty of Chemical Engineering and Technology, Zagreb, Croatia

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Towards Sustainable Technologies
October 26 – 28, 2011, Zagreb, Croatia



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PREFACE

The Book of papers entitled "Conference proceedings of SEM2011" presents 53 papers reviewed and revised from 59 initially submitted for the "3rd International Symposium on Environmental Management" (SEM2011), held on October 26-28, 2011 in Zagreb, Croatia. Approximately 250 environmental professionals and experts, involved in the application of environmental assessment and management in businesses, scientific organizations, and governmental and non-governmental agencies, attended at the SEM2011.

Thematic units included papers matched the topics presented at the Symposium. Papers presented within *Environmental Management – Towards Sustainable Technologies* are focused to the issues such as economical instruments and aspects of environmental protection, including the case study of environmental performances; the problem of commercialization of water sources and services, application of the green economy as a competitive economy - Croatia's way to EU. Papers dealing with the *Sustainable Energy Production* and *Renewable Energy* topics are covered mostly by foreign participants (based on wind, biogas and solar cells). The topics *Soil and Forestry* cover removal of pesticides and soil degradation processes. There are also several papers focused on soil protection and management issue. Thus, Croatian soil system database, soil conservation strategy in Europe and Hungary are presented, as well as new results and achievements of the joint project between Croatian and Hungarian scientists. Furthermore, within this topic the papers dealing with *Solid Waste Management*, presenting the problem of Croatian landfills, as well as problems related to the same topic in developing countries, are also included. Waste management issue is also covered by several case studies and scientific papers dealing with problems such as electrochemical treatment of landfill leachate, chemical recycling of postconsumer PET bottles, detoxification of tobacco waste and designing the reactor system, and the handling of sewage sludge and sludge generated by different industrial processes. *Water and Wastewater Management* are covered by several case study papers, presenting the ways how to solve the problems by application of novel processes such as microwave and ultrasonic irradiation, efficiency of pilot-scale wetland for the treatment of wastewater. Also, this section includes papers related to adsorption, recovery of perfluorinated surfactants from waste water and removal of glucocorticosteroides and anesthetics from water with RO/NF membranes; the synthesis and characterization of new environmentally friendly materials, such as fly ash, primarily used as an additive in cement industry, and zeolites, which can be used for the managing of water and air pollution. Within the section *Green Economy, Green Chemistry and Green Technologies* and *Sustainable Building* several papers present the latest achievements and trends in sustainable building and construction in Croatia but in the world too. These papers point out the new approach and new materials in construction, how to use renewable energy sources and materials, but also report the latest EU directives within legislative in sustainable construction and alternative processes for removing organic sulfur compounds from petroleum fractions.

Furthermore, the Conference Proceedings presents the approach to designated area zoning focusing in particular on the selection of methodology and concepts for achieving balance between environmental protection and economical and social development in Croatia. One of the very important subjects today, the *Education for Sustainable Development* related closely to environmental issues, is covered by the case study from Hungary and presenting training methods for purchasing officers to facilitate green procurement. Among topics Risk Assessment & Management and Environmental Management very interesting paper "A Comparative Analysis of Universities using Sustainability Indicators" appears and a case study from Croatian ceramic industry is presented as well. With increasing globalization problems, there is also increasing interest in environmental prevention and protection. Environmental management integrates many scientific and other professional disciplines all together and shows an essential link between life and nature, increasing consumer society and environment. Nowadays, environmental programs are oriented to sustainability conceived by environmental engineers and managers providing more and better solutions for the problems in environment.

Hence, the wide and variety areas of presented papers in the Conference proceedings clearly demonstrate the importance of multidisciplinary and interdisciplinary approach to the solving of problems within environmental management in all spheres of every day life. We hope that the book provides enough interest data, results, new achievements and pro-active approaches within environmental management to any of readers' vocation and the field of interest.

Editors: Natalija Koprivanac, Hrvoje Kušić and Ana Lončarić Božić

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SOIL DEGRADATION PROCESSES AND EXTREME SOIL MOISTURE EVENTS, AS ENVIRONMENTAL PROBLEMS IN THE CARPATHIAN BASIN

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Abstract

Soils (the geological strata–soil–water–near surface atmosphere–biota–ecosystem continuum) are the most important – conditionally renewable – natural resources in the Carpathian Basin. Society uses (and sometimes misuses) soil resources, utilizing three specific and unique soil characteristics: multifunctionality, productivity and resilience. Consequently, the rational and sustainable use, protection and conservation of soil resources – maintaining their multifunctionality – are priority tasks of biomass production and environment protection and are key elements of sustainable development.

As a result of greatly varied soil forming factors and soil formation/degradation processes a rather heterogeneous, sometimes – even in micro-scale – a mosaic-like soil cover has developed in the Carpathian Basin. The natural conditions in the Carpathian Basin (particularly in the lowlands and plains) are generally favorable for rainfed biomass production. These conditions, however, show extremely high, irregular, consequently hardly predictable spatial and temporal variability, often extremes, and sensitively react to various natural or human-induced stresses. The main constraints are:

(1) Soil degradation processes: soil erosion by water and/or wind, acidification, salinization/ sodification, structure destruction and compaction, biological degradation.

(2) Extreme moisture regime: simultaneous hazard of flood, water logging, over-moistening and drought sensitivity.

(3) Unfavorable changes in the biogeochemical cycles of elements, especially of plant nutrients and environmental pollutants (organic matter decline; leaching–accumulation; fixation–release; (im)mobilization).

Soil processes can be controlled (to a certain extent) and their unfavorable/harmful economical/ecological/social consequences can be prevented or at least moderated on the basis of real prognoses, sensitivity and stress tolerance analyses based on a comprehensive soil database, information and monitoring system.

Water resources are limited. According to the long-term hydrogeological forecasts, the probability, frequency, duration and seriousness of extreme hydrological situations and the hazard of their harmful consequences are expected to increase. Water will be the key factor of sustainable multipurpose (food, fodder, industrial raw material, alternative energy) biomass production, agricultural and rural development, and environment protection. Consequently, the increase of water use efficiency will be a key element of sustainable development. It is an important fact that soil is the largest potential natural water reservoir. In many cases, however, the efficient use of this huge water storage capacity is limited either by reduced infiltration or poor water retention resulting in evaporation and/or filtration losses and extreme hydrological events (as flood, water logging, over-moistening or drought) with their harmful (sometimes catastrophic) consequences. All efforts should be taken consequently for an efficient soil moisture control: to help infiltration into and water storage within the soil in plant-available form. Most of these measures are – simultaneously – efficient elements of environment protection.

Keywords: *soil multifunctionality; soil fertility; soil resilience; soil moisture control; water logging hazard; drought sensitivity*

1. INTRODUCTION

Soils are the most important – conditionally renewable – natural resources in the Carpathian Basin. Consequently, their rational and sustainable use, protection and conservation, maintaining their desirable multifunctionality, are priority tasks of biomass production and environment protection and are key elements of sustainable development.

2. ELABORATION

2.1. Natural Conditions

The natural conditions of the Carpathian Basin (particularly the lowlands and plains) are generally favourable for rainfed biomass production [1,2]. These conditions, however, show high and irregular, consequently hardly predictable spatial and temporal variability, often extremes and sensitively react to various natural or human-induced stresses. The generally favorable agro-ecological potential is mainly limited by three soil factors:

- Soil degradation processes [3,4]
- Extreme moisture regime: simultaneous hazard of flood, water logging, over-moistening and drought sensitivity [5,6]
- Unfavorable changes in the biogeochemical cycles of elements, especially of plant nutrients and environmental pollutants

The comprehensive assessment and efficient control of these phenomena are the primary tasks of multipurpose biomass production, environment protection and sustainable rural development.

2.2. Limiting Factors of Soil Multifunctionality and Soil Degradation Processes

The main limiting factors of soil multifunctionality/fertility/productivity in Hungary are shown in Fig. 1. [7]. The most important soil degradation processes in the Carpathian Basin (similarly to Europe) are summarized in Fig. 2.



Figure 1. Map of the limiting factors of soil fertility in Hungary

Legend: 1. Extremely coarse texture (8% of the total area of Hungary). 2. Acidity (12.8%). 3. Salinity and/or sodicity (8.1%). 4. Salinity and/or sodicity in the deeper layers (2.6%). 5. Extremely heavy texture (6.8%). 6. Peat formation (1.7%). 7. Erosion (15.6%). 8. Shallow depth (2.3%)

In spite of the large and increasing extension of degraded lands in all continents, it can be stated that soil degradation is not an unavoidable consequence of intensive (but rational!) agricultural production and social development! Because of soil resilience most of these soil degradation processes can be prevented, eliminated or at least moderated. But it needs permanent control and widely adopted soil (and water) conservation technologies, as indispensable elements of sustainable site-specific precision soil management.

In the last years the revolutionary development of in situ and laboratory analytics, remote sensing, informatics, computer technology, GIS/GPS applications, etc. have given opportunity for the control of soil degradation processes on the basis of an up-to-date comprehensive environment/soil database [8].

This was the aim of the GLASOD (Global Assessment of Soil Degradation) and PHARE-MERA international projects; and this is in the focus of the European Soil Conservation Strategy [9]. In Hungary – based on all available soil information – the "environmental sensitivity/susceptibility/ vulnerability of soils to various soil degradation processes were comprehensively analyzed, giving a good scientific basis for the development of the Hungarian Soil Conservation Strategy [10].

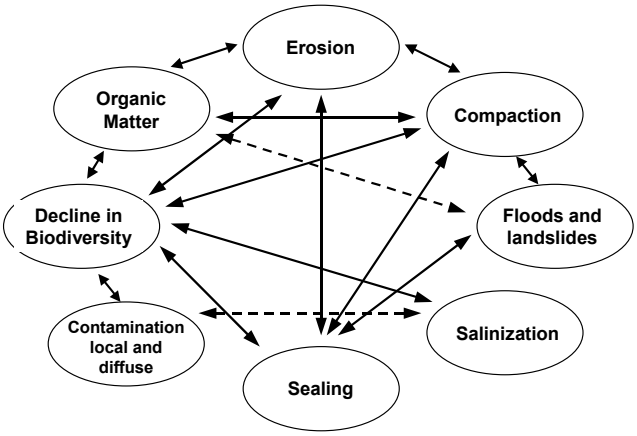


Figure 2. The main soil degradation processes in the Carpathian Basin

2.3. Extreme Moisture Regime

It can be predicted with high probability that in future water will be the determining (hopefully not limiting) factor of food security and environmental safety in the Carpathian Basin [11,12]. Consequently, the risk reduction of extreme hydrological events and soil moisture regimes, and the increase of water use efficiency will be the key issues of soil and water management, biomass production.

2.3.1. Limited Water Resources

The water resources are limited and an increasing water demand must be satisfied from these limited resources [12].

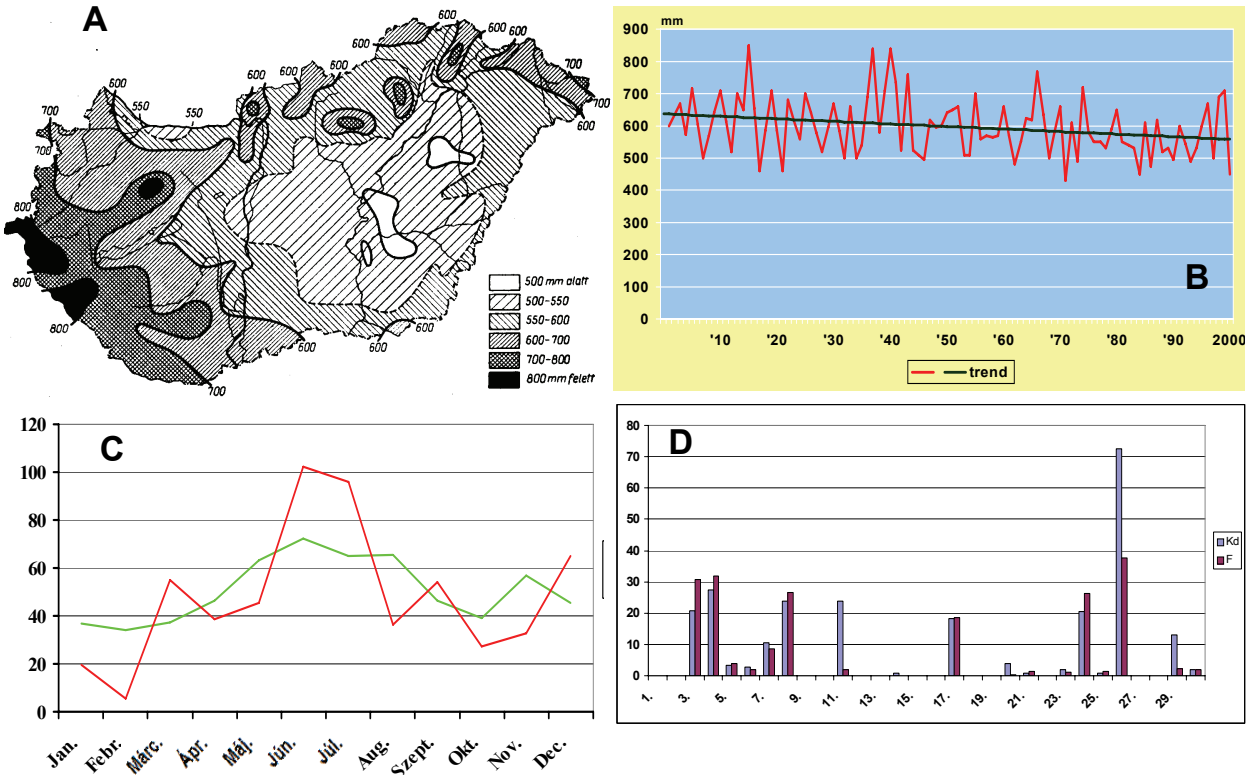


Figure 3. Territorial and time distribution of atmospheric precipitation in Hungary: (A) Geographical distribution of the 100-year average annual precipitation, (B) Average annual precipitation in Hungary in the 20th century, (C). Monthly distribution of the long-term average and 2008 annual precipitation, (D) Daily distribution of monthly precipitation (May 2008) at two nearby meteorological stations

The average 500–600 mm annual precipitation in the Pannonian Plains shows extremely high territorial and temporal (Fig. 3) variability – even at micro-scale. Under such conditions a considerable part of the precipitation is lost by surface runoff, downward filtration and evaporation. Precipitation will not be more in the future. On the contrary, it might be less and its spatial and time variability is expected to increase. It results in increasing risk (frequency, intensity) of extreme weather events (high intensity rains, droughts etc.) with their hydrological (flood, water logging, over-moistening), ecological (droughts, crop damages, yield reduction) and environmental (erosion–sedimentation, infrastructure damages, landscape destruction) consequences. The available quantity of surface waters (rivers) will not increase, particularly not in the critical low-water periods. A considerable part of the subsurface waters (especially in the poorly drained lowlands) is of poor quality (high salinity, alkalinity, sodicity), threatening with harmful salinization/sodification processes. The over-exploitation of groundwater may result in serious environmental deterioration: "desertification symptoms" appear.

2.3.2. (Hydro)Physical Properties of Soils

There are two additional reasons of extreme soil moisture regime:

- the heterogeneous microrelief of the "flat" lowland
- the highly variable, sometimes mosaic-like soil cover and the unfavorable physical and hydrophysical properties of some soils [13,14].

According to our comprehensive assessment 43% of Hungarian soils can be characterized by unfavorable, 26% by moderately (un)favorable and 31% by favorable moisture regime, as illustrated by Fig. 4., indicating the main reasons of various moisture conditions.

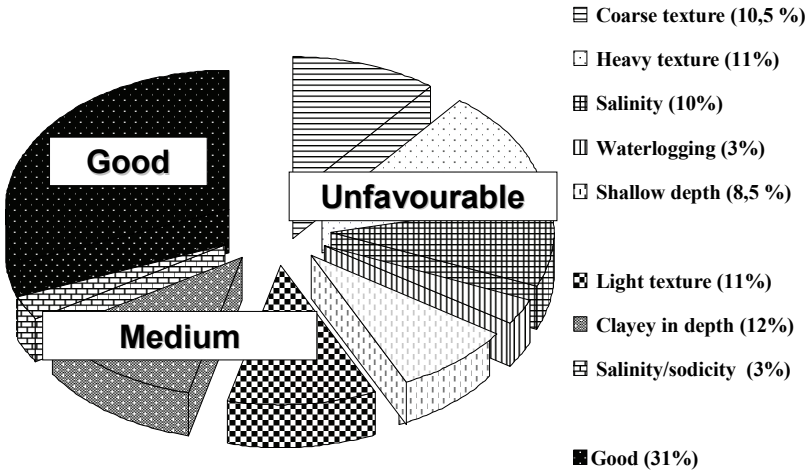


Figure 4. Moisture regimes of soils in Hungary and their reasons

In the last years a comprehensive soil survey–analysis–categorization–mapping–monitoring system was developed in Hungary for the exact characterization of hydrophysical properties, modelling and forecast of water and solute regimes of soils. The system was used efficiently in the planning, implementation, operation, maintenance and control of land use and agricultural water management activities [13,14]. The schematic map of these soil hydrophysical categories (quantitatively characterized) is presented in Fig. 5.

2.4. Soil as Water Reservoir – Extreme Hydrological Events

Under the given natural conditions it is an important fact that soil is the largest potential natural water reservoir (water storage capacity) in the Carpathian Basin. The 0–100 cm soil layer may store about half of the average annual precipitation and about 50% of it is „available moisture content".

In many cases, however, this huge *potential* water storage capacity is not utilized because of:

- limited infiltration due to water saturated pore volume: frozen topsoil; nearly impermeable soil surface or near surface soil horizon;
- poor water retention.

As a consequence of these limitations the risk/hazard of extreme hydrological/soil moisture events (as flood, water logging, over-moistening vs. droughts) are characteristic features in the Carpathian Basin and occur with increasing frequency and intensity, often in the same year on the same area.

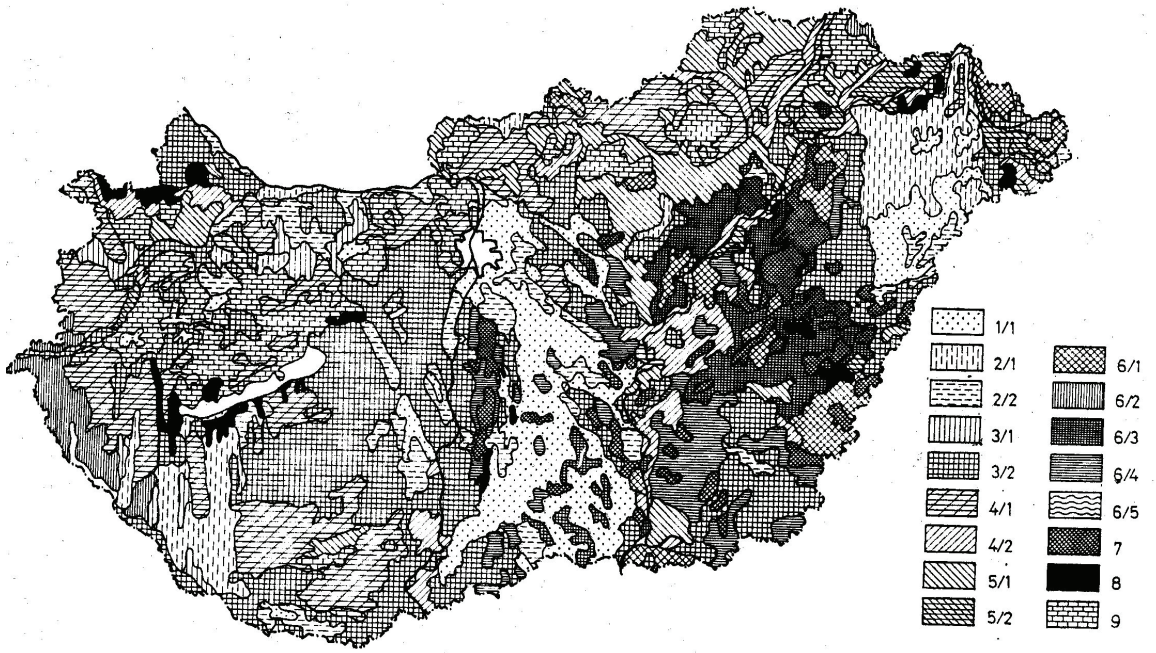


Figure 5. Hydrophysical characteristics of soils in Hungary

Legend: 1.Soils with very high IR, P and K; low FC; very poor WR. 2. Soils with high IR, P and K; medium PC; and poor WR. 3. Soils with good IR, P and K; good FC; and good WR. 4. Soils with moderate IR, P and K; high FC; and good WR. 5. Soils with moderate IR, poor P and K; high PC and high WR. 6. Soils with unfavourable water management: very low IR and K. 7. Soils with extremely unfavourable water management due to high salinity/sodicity: extremely low AMR, IR and K. 8. Soils with good IR, P and K; and very high FC (organic soils). 9. Soils with extreme moisture regime due to shallow depth. *The main profile variants:* (1) texture becomes lighter with depth (soils formed on relatively light-textured parent material): 2/1, 3/1. (2) uniform texture within the profile: 1/1, 2/2, 3/2, 4/2, 5/2. (3) relative clay accumulation in the horizon B: 4/1, 5/1. Profile variants of category 6: 6/1: highly compacted, heavy-textured soils with poor structure; 6/2: pseudogleys; 6/3. deep meadow solonetzes and solonetzic meadow soils; 6/4: soils with salinity/sodicity in the deeper horizons; 6/5: peaty meadow soils

2.5. Unfavorable Changes in the Biogeochemical Cycles of Elements

Soil moisture regime has distinguished significance in soil productivity. It determines the water supply of plants, influences the air- and heat regimes, biological activity and plant nutrient status of soil. In most of the cases it determines the agro-ecological potential; the biomass production of various natural and agro-ecosystems; environmental sensitivity and the hazard of soil and water pollution. Extreme hydrological situations and soil moisture regime result in unfavorable changes in the biogeochemical cycles of elements (plant nutrients, pollutants) [6,14].

2.6. Control of Extreme Moisture Regime

The control of extreme field water cycle requires a special “two-way” (“double faced”) soil moisture control in the Carpathian lowlands. Because the “active” water management actions, such as irrigation and drainage are faced with serious economical and environmental limitations [5] all efforts have to be taken

- to reduce evaporation, surface runoff and filtration losses
- to increase the available moisture content of the soil: to help infiltration; increase the water storage capacity; reduce the immobile moisture content
- to improve the vertical and horizontal drainage condition of the soil profile or the given area (prevention of over-saturation and water logging)

Most of these „moisture management actions” are – at the same time – efficient environment control measures [5,6].

3. CONCLUSIONS

Sustainable and rational land use, soil and water management, including the risk reduction of extreme hydrological events and soil moisture regime requires continuous actions. This permanent control may prevent, eliminate or at least reduce undesirable soil processes and their harmful

economical/ecological/environmental/social consequences; and may satisfy the conditions for the „quality maintenance" of this "conditionally renewable" natural resource.

Control – with priorities of preventive actions – can be efficient only on the basis of comprehensive database, risk assessment, impact analysis and prognosis.

REFERENCES

[1] I. Láng, L. Csete, Zs. Harnos, Agro-ecological potential of Hungarian agriculture, (In Hungarian) Mezőgazdasági Kiadó, Budapest, 1983.
[2] Gy. Várallyay, Soil as a fundamental medium of agro-ecosystems, (In Hungarian) KLÍMA-21 Füzetek, 37 (2004) 33–49.
[3] E. Michéli, Gy. Várallyay, L. Pásztor, J. Szabó, J., Land degradation in Hungary. In: Land Degradation. (Eds.: J. R.. J. Jones, L. Montanarella.) JRC Ispra, 2003, 198–206.
[4] Gy. Várallyay, Soil degradation processes and their control in Hungary. Land Degradation and Rehabilitation, 1 (1989) 171–188.
[5] Gy. Várallyay, Soil degradation processes and extreme soil moisture regime as environmental problems in the Carpathian Basin. Agrokémia és Talajtan, 55 (2006) 9–18.
[6] Gy. Várallyay, Extreme soil moisture regime as an increasing environmental problem in the Carpathian Basin. In: Tessedik Sámuel Főiskola Tudományos Közlemények, 7 (1) (2007) 47–54.
[7] I. Szabolcs, Gy. Várallyay, Limiting factors of soil fertility in Hungary, (In Hungarian) Agrokémia és Talajtan, 27 (1978) 181–202.
[8] J. Szabó, L. Pásztor, Zs. Suba, Gy. Várallyay, Integration of remote sensing and GIS techniques in land degradation mapping, Agrokémia és Talajtan, 47 (1998) 63–75.
[9] Gy. Várallyay, Soil conservation strategy in EU and in Hungary, (In Hungarian) Agrokémia és Talajtan, 54 (2005b) 203–216.
[10] T. Németh, P. Stefanovits, Gy. Várallyay, Hungarian National Soil Conservation Strategy, (In Hungarian) Ministry of Environment Protection and Water Management, Budapest, 2005.
[11] I. Pálfai (Ed.), The role and significance of water in the Hungarian Plain, (In Hungarian) Nagyalföldi Alapítvány, Békéscsaba, 2000.
[12] L. Somlyódy, Strategy of Hungarian water management, (In Hungarian) MTA Vízgazdálkodási Tudományos Kutatócsoportja, Budapest, 2000.
[13] Gy. Várallyay, Water storage capacity of Hungarian soils, (In Hungarian) Agrokémia és Talajtan, 54 (2005a) 5–24.
[14] Gy. Várallyay, Soil degradation processes and extreme hydrological situations as factors determining the state of the environment, (In Hungarian) KLÍMA-21 Füzetek, 62 (2010) 4–28.

BIOGAS IMPROVEMENT THROUGH YEAST USE IN HIGH PRESSURE HOMOGENIZER (HPH)

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Abstract

The energy market has surged in the recent past. Their prices are becoming unbearable for the common people in spite of its hazardous state it tends to be creating for the world's climate coupled with present unrest in some of the oil producing nations of the World. To overcome these effects of greenhouse gas emission, global warming and degradation, energy situation needs to be changed. Hence renewable energy is now thought to be an alternative. Biogas is classified as one of the bioenergy from renewable energy source [RES] which is different from others; fossil fuels and nuclear source in that it is clean and environmental friendly. The demand for biogas in particular is expected to double in the next ten years worldwide as it can be produced and stored easily when needed; hence biogas from renewable energy source is considered as the most efficient and environmentally beneficial in terms of energy. To further boost these and meet the increasing need of the society, this paper tends to focus on one of the ways, Biogas production can be improved upon using the High Pressure Homogenizer via yeast and as a material for biogas production, it is being analyzed through cells breakage and release of protein via mechanical means through the application of stress externally on the HPH wherein the resultant is further analyzed for light intensity using the UV spectrophotometer in the comparison of the product released after the centrifugation to remove the solid from the liquid. This is assumed that breaking the microbial walls of microbes in the yeast releases organic material which further enhances the increment of methane and bioethanol production.

Keywords: *biogas, energy, fossil fuel, High Pressure Homogenizer (HPH), yeast*

1. INTRODUCTION

The current energy crisis across the globe need to be changed as this has been as result of the falling fossil fuels quantity and the general unrest across most of the oil producing countries of the world as well as the rising prices of crude oil. Also, the damaging effects of these products to the world all over, need to be considered which has now surpass finding corrective measure to them.

As part of these solutions, biomass has being termed to play a phenomenal role for future energy supply mainly through thermochemical, physiochemical and biochemical transformations mainly as well as by conventional combustion [1]. In the production of biogas, apart from anaerobic digestion (AD), High Pressure Homogenizer (HPH) has also now been considered wherein cell disruption technology has been carried out in the laboratory and at the industrial level using yeast. Yeast is of interest in this study due to its workability and high protein content that are released which aid the production of biogas in the process; hence it is considerably preferred to other biomass materials and the yeast in this regards; is the bakers' yeast with the scientific name as *Saccharomyces cerevisiae*. The process applied here is the mechanical means of HPH which are generally considered appropriate for large scale disruption as against the non-mechanical which could be physically, chemically or enzymatically in the rupturing of the cell [2]. Cell disruption is thought to be the breaking apart of the yeast structure to effect release of intercellular product, which thus allows subsequent recovery [3,4].Basically on a normal scale, mechanical means are non-specific but their efficiency tends to be higher and their application broader in comparison with the other means of cell disruptions [5]. The developmental process cannot be isolated from further downstream in its procession as a result of the operation affecting the suspension physical properties such as the viscosity, density and particle size thereby influencing the subsequent solid-liquid separation step [6]. Microorganisms produce two basic types of biological compounds; the extracellular or the intercellular; the former are excreted into a growth medium while the latter are retained inside the cytoplasm of the cell [5,7]. Despite this, the yeast cell wall's nature is dependent wholly on the organism type and external growth conditions like presence of certain chemical compounds in the environment,

cultivation temperature and composition of the growth medium as well as its phase and the specific rate of growth [8,9].

Homogenizer has been studied extensively by different authors and researchers, depending on the homogenizer that is in application, most homogenizers today exceed pressure of 150 MPa [10] and [11,12] considers homogenizer pumps to be operating at pressures in the region between 50 and 120 MPa and as such, function by pumping liquid through a spring loaded ring seal. On this basis, the Homogenizer for consideration in this paper is the APV-Gaulin HPH and its main functionalities are the inlet, the gap and the exit region; these regions holds the valve seat, impact ring and the valve head respectively.

1.1. Yeast (*Saccharomyces cerevisiae*) Analysis

Yeast are considered to be eukaryotic unicellular microorganism which are widely distributed in the environment naturally [13] and their cell sizes are usually between 5-10 μ in diameter, these cells do not form filaments or a mycelium; they remain as single unit as cells [14]. Their cells division is by budding and they are facultative anaerobes. They are having long history in human's life; hence have been thought to be the first domesticated microorganism due its ability to be used in brewing since the civilization days of Babylonian and Sumerian way back between 6000-2000 BC.

Yeast are widely used in the industry, in fact; their cells are used as sources of food, vitamins and growth factors, this is because they are cultured for cells themselves, for cell components and for the end products that they produce during the fermentation of alcohol [14]. Yeast budding makes it multiply as a single cell through its divisions or by direct division as fission, that is; *Schizosaccharomyces* or former as *Saccharomyces* and through sexual reproduction form by what is known as asci; which has up to eight haploid ascospores. This could be in the form of cells conjugation of opposite mating types [13]. These ascospores form together with the adjoining nuclei and multiply via vegetative divisions or as with certain yeast, fuse with other ascospores [15].It has been useful due to its commercial significance and value and it is having a long history as the organisms have been utilized in the fermentation of sugars in rice, wheat, barley in the production of alcoholic beverages as well as in the bakery industries, in these cases, the most commonly used type of yeast is the *Saccharomyces cerevisiae* referred to as the baker's yeast [16], where its fermentation gives off ethanol and CO_2 through the sugar that is present in the flour, and most recently as a source of CO_2 which aid the production of biogas due to its high protein contents.

1.2. Classification

Generally, most cell biologists have often use the term 'yeast' as a synonym for *Saccharomyces cerevisiae* and the reason has been *S. cerevisiae*, called the bakers' yeast has been by far the most studied and with the best characterization in terms of unicellular eukaryote [17], but yeast classifications, can be achieved through delimitation that are based upon by their common properties, like when living things are being classified and for this purpose, characteristics of living organisms should be considered based on the previous published papers [18]. Also, biochemical methods have been used as test in yeasts classification; this is where the yeast strains are based to some degree on their ability to ferment certain sugars [19]. The system was reorganized as its fermentation ability only examine the genus *Saccharomyces* and as such, could not be validated on number of yeast strains due to the fermentative ability but limited to only the *Saccharomyces cerevisiae* and *Saccharomyces carlsbergensis* group [20]. Despite the information wealth on its genetics and molecular biology, *S.cerevisiae*is sometimes not viewed favorably as a host for recombinant protein expression due to perception that it has lower secretory capacity as compared *P.pastoris* and other yeasts classified [21]. These are further analyzed as a result of their utilization; with the different species being compared either as; methanol, lactose, starch, xylose or alkane and fatty acid utilizing. Particularly, *P.pastoris;* this has been utilized to produce over 300 foreign proteins since 1984 [22, 23].

2. ELABORATION

2.1. Materials and Methods

The experiments were conducted using the conventional APV- Gaulin High Pressure Homogenizer (HPH) and baker's yeast. The supplied baker's yeast was refrigerated for freshness originally and subsequently broken into beaker when ready to be used as it was as a block of fresh yeast, weighing 950 g. Using the following composition; the solutions A, B and C where prepared.

(i) *Solution A* (0.1 M KH_2PO_4 + 0.15 M NaCl), this is equivalent of 1 L
13.6 g of KH_2PO_4weighed into beaker and dissolved using the deionised water, also; 8.8 g of NaCl weighed into beaker and dissolved using the deionised water, both mixed together and filled to the 1 L mark. This was repeated thrice for 3 L of solution to be obtained.

(ii) *Solution B* (0.1 M K_2HPO4 + 0.15 M NaCl)
4.6 g of KH_2PO_4weighed into beaker and dissolved using the deionised water, also; 1.8 g of NaCl weighed into beaker and dissolved using the deionised water, both mixed together and filled to the 200 mL mark.

(iii) Solution C obtained through gradually adding Solution B to Solution A until the pH scale of 5.3 was attained.725 mL of solution C added to the 950 g broken yeast and mixed using the electric mixer.

The impact ring valve used here was 9.758 mm in diameter. Since the pump results in the pressure built up, this comes as a result of the piston being powered in the pressure rise [10]. Different torque were applied at different time during coupling before the HPH is turned on, lower values are started with, to see the rise in pressure. The mixed yeast when passed through, flow through the compressed entrance known as the gap region and are adjustable through sequential increment by the user and this then, leaves the gap region via the exit way in the direction of the impact ring and then through the outlet (Figs. 1. and 2.) [5,10].

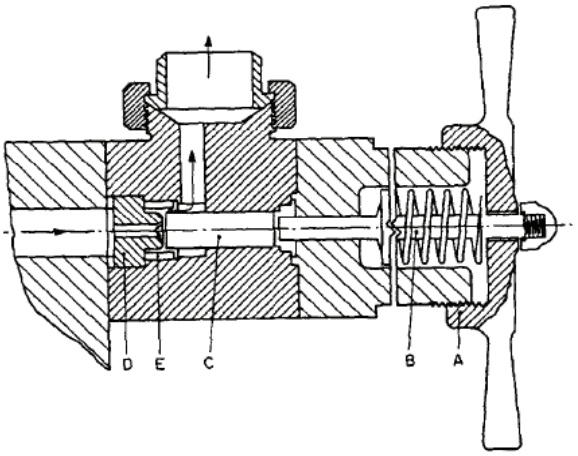


Figure 1. HPH discharge valve unit, this is controlled by hand wheel assembly, A, which through a spring loaded valve rod, B, positions the valve, C in relation to the valve seat, D. During discharge, mixed yeast passes via the valve and its seat and impinges on an impact ring, E [5].

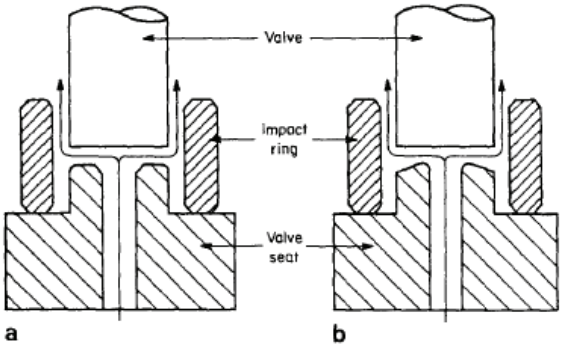


Figure 2. Details of the seat valves (a) 'Flat unit' (b) 'Knife-edge unit' [5]

When in operation, HPH was cleaned up and allowed to run for half an hour, then 2 L deionised water ran through for proper cleaning and when almost completely empty through the conical section, before the mixed yeast suspension (1695 mL is poured through. 600 mLof the suspension was collected at outlet as waste originally before another 500 ml of the concentrated suspension is taken in a different measuring tube at 40 MPa pressure. This was acceptable for the avoidance of contamination and impurities from the HPH. The hand wheel bar was closed as the pressure raises over 40 MPa to prevent burst up since the maximum on the dial gauge is 60 MPa as the cells in the yeast at that point becomes suddenly deformed under the intense pressure, making the slurry slightly smaller. As the pressure rises, the cell expands

which will result in the cell wall rupturing due to the high tensile stresses generated momentarily [4,24]. 200 mL of the solution homogenized was taken and diluted through adding 800 mL of phosphate buffer pH 5.3 (Solution c) to form a solution for protein concentration measurement, this was to ensure that the concentration was same as the composition of the 500 mL of the homogenized sample. Six 250 mL centrifuge tubes were weighed on the pan; content, tube and cap to 90 g; the content was filled in the tube as diluted and undiluted (3 each) and labeled as such, that is; diluted and undiluted, the equal weight of the tubes was necessary to balance the centrifuge machine as required during the spinning process of the machine and prevent damages being made to set of equipment. The centrifuge set to run at 13,000 rpm for an hour and the temperature adjusted accordingly to the room temperature and on completion, the centrifuged liquids are separated from the solids for protein analysis, while the solid residuals left in the tube after the separation of the liquid are the unbroken yeast cells and debris, and are considered as waste. The separated liquid were emptied into beaker and filtered to test tubes at the rate of 200 ml and 2000 mL of the solutions respectively to three test tubes each labeled as diluted and undiluted with the diluted part mixed by 1800 mL of pH 5.3 phosphate buffer solution. 500 mL of the solution is taken into cuvette with 2000 ml blue biuret solution (protein reagent), and after ½ hour, the cuvette is placed into the spectrophotometer, but before then, this should be set to wavelength (λ) of 550, position the cuvette so the light beam will pass through the clear sides (Fig. 3.). The door will not close properly if the cuvette is in the wrong position (Fig. 4.). The amount of light that penetrates the filtered homogenized yeast solution that has been centrifuged is known as transmittance and is expressed as the ratio of the intensity of the transmitted light measure by the photodiode, I_t, and the initial intensity of the light beam, Io, as expressed by the formula [25];$T = I_t / I_o$.

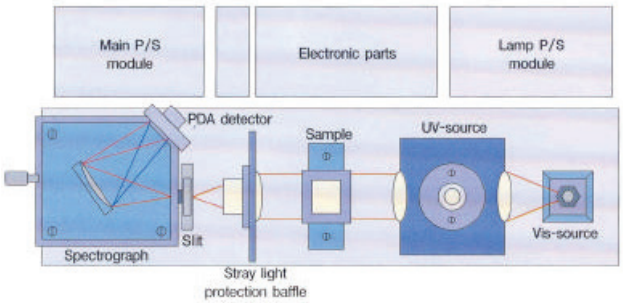


Figure 3. schematic of PDA Spectrophotometer[25]

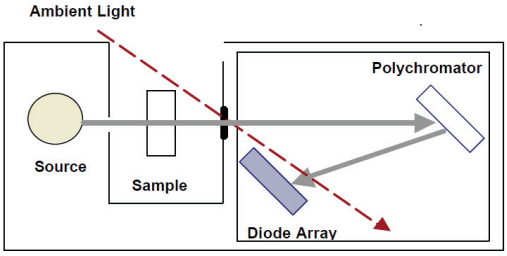


Figure 4. Reasons for minimal stray light effects[25]

Ring Size – 9.758 mm, this is the impact ring that lies between the valve seat and the valve head within the HPH. For the purpose of cell disruption, the prepared suspension was kept in a refrigerator at 4 °C and this resulted in the optimum concentration of the suspension that was homogenized and collected at 40MPa, to give maximum cell disruption during the homogenization and after the centrifugation [26 ,27]

2.3. Results and Discussion

Table 1 and Fig. 4. both indicate the pressure of Yeast/ Water released variations with the applied torque on the impact ring during the homogenization. The torque applied through the use of wrench was increased in sequence through 1 to 8 and water shows linearity in its plot (Fig. 4.), while the plot for yeast suspension shows an exponential value with $R^2 = 0.9622$. This suggests that increase in the applied torque on the impact ring on the valve seat leads also to an increase in the resultant pressure due to the decomposition of the cell that rupture before exiting the chamber, as there will be need for the cells to maintain high pressure since the cells deformation through direct pressure will not be sufficient because of the elastic and compressible properties of the bakers' yeast [10]. Invariably, turbulence plays a very

important role in this discussion, as [28] hypothesized it as having the greatest influence on disruption in a homogenizer.

Table 1. Yeast/Water pressure analysis using the HPH compared with the applied Torque on impact ring

Pressure (MPa), Yeast	10	13	14	16	18	26	36	40
Pressure (MPa), Water	0.5	6	7	8	12	13	14	15
Torque (Nm)	1	2	3	4	5	6	7	8

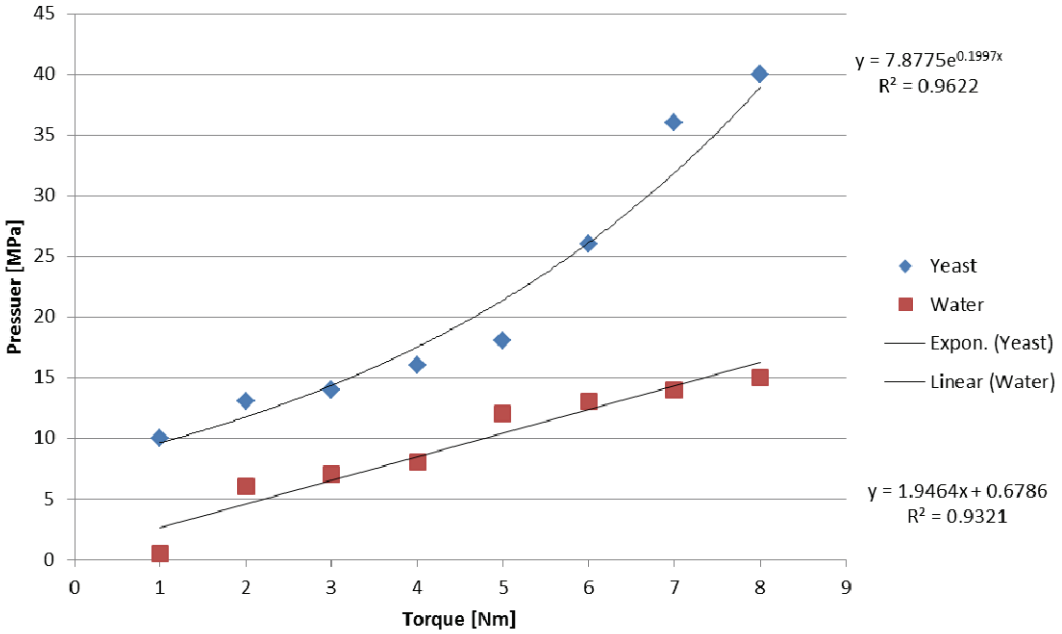


Figure 5. Pressure on Yeast/Water compared with the applied Torque on impact ring within the HPH Compartment.

With microbial cell like bakers' yeast it is a different scenario as this will now become complex due to the eddy current that will be involved which will cause the bond to be broken in the form of the Van der wall forces of attraction that is present which on the contrary would not have been able to break down causing fragmentation to the entire cell wall completely even with the applied torque and pressure on the yeast being homogenized.

The rise in the water pressure, should not have been, this happened so due to the clean-up of the HPH after each use of passing the yeast solution through the inlet, gap and exit region. Even though it is cleaned up for about half an hour, there will still be left over of some of the yeast that has not been completely removed and as a result, this will build up cavitation on the HPH which when used on the next level of torque applied, raises the pressure of water. This cavitation tends to drop the water pressure below that of the yeast at a given temperature, wherein bubbles of vapor will form at the nucleation sites tends to be favorable. As the bubble continue its built up, and as the external pressure is applied, there will be time when there will be balance in which the forces tending to enlarge the bubble equates that tending to reduce it as gases are trapped in, this in turn would cause an increase in the pressure of the yeast and so a high pressure comes as a result to oppose the surface tension force tending to reduce its size [10, 28].

While in Table 2 and Fig. 6., depicts the samples; diluted and undiluted suspension of yeast that has been centrifuged. Both have originally been diluted and the diluted was further diluted by 2000 ml of solution C (Phosphate buffer) at the pH of 5.3 before 500 ml reagent solution was added to both set. These were allowed to stay for half an hour before being passed through the UV Spectrophotometer for protein analysis. When done, the results obtained were as shown in Fig. 6. and Table 2. This suggests that the diluted solution had more concentration of protein when brought under the UV spectrophotometer as compared to the undiluted, with greater percentage of protein content released.

Table 2. Spectrophotometer Readings: Showing the absorbance rate of protein release (Light Intensity) between diluted/undiluted homogenized yeast

Samples	1	2	3	4	5	6
Undiluted	0.210	0.270	0.323	0.339	0.357	0.423
Diluted	0.781	0.782	0.785	0.799	0.812	0.850

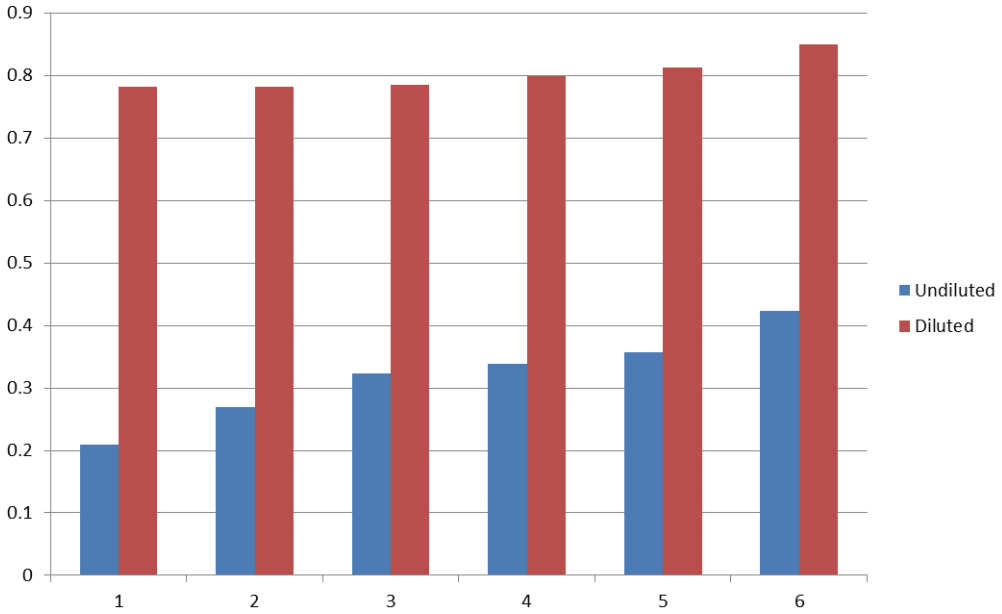


Figure 4. Diluted and undiluted homogenised yeast samples compared after the centrifugation

3. CONCLUSIONS

Cell disruption and high pressure homogenization, has been studied for years now but not until the advent of climate change and renewable energy as regards finding ways towards its curbing that its studies has become prominent in its protein analysis for biogas production. Recently, most of the microorganisms and feedstock have all been developed in the processing of biogas and of all these, *Saccharomyces cerevisiae*(baker's yeast) surpasses them all in terms of its originality and protein contents that are released during homogenization and that in turn improves the production of biogas. High pressure homogenizer is thought to be the best for yeast and other unicellular organisms in the cell disruption for biogas production but has not been evident or proven that this process of cell disruption do not damage or destroy protein contain in them, but its use has been satisfactorily deployable and economically viable to reduce production cost as well as improving the GHG emissions control.

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REFERENCES

[1] C. Nzila, J. Dewulf, H. Spanjers, H. Kiriamiti, H. Van Langenhove, Biowaste energy potential in Kenya, Renewable energy 35 (2010) 2698-2704.
[2] R. W Lovitt, M. Jones, S.E Collins, G.M Coss, C.P Yau, C. Attouch, Disruption of bakers' yeast using a disrupter of simple and novel geometry, Process Biochemistry 36 (2000) 415-421.
[3] A.P.J. Middelberg, Process-scale disruption of microorganism. Biotechnol. Adv. 13 (1995) 491-551.
[4] I.Z. Shirgaonkar, R.R. Lothe, A.B. Pandit, Comment on the mechanism of microbial cell disruption in high-pressure and high-speed devices, Biotechnol. Prog. 14 (1998) 657-660.
[5] J. Geciova, D. Bury, P. Jelen, Methods for disruption of microbial cells for potential use in the dairy industry – a review, International Dairy Journal 12 (2002) 541-533.

[6] Y. Chisti, M. Moo-Young, Disruption of microbal cells for intercellular products. Enzyme Microb. Technol. 8 (1986) 194 -204.
[7] T. Charinpanitkul, A. Soottitantawat, W. Tanthapanichakoon, A simple method for bakers' yeast cell disruption using a three-phase fluidzed bed equipped with an agitator. Bioresource Technol. 99 (2008) 8935-39
[8] I. W. Sutherland, The bacteria wall and surface. Process Biochemistry 10(3) (1975) 4-8.
[9] C.R. Engler, C.W. Robinson, Effects of organism type and growth conditions on cell disruption by impingement. Biotechnology letters, 3(2) (1981) 83-88.
[10] A. Clarke, T. Prescott, A. Khan, A.G. Olabi. Causes of breakage and disruption in a homogeniser. Applied Energy, 87 (2010) 3680-3690
[11] P.J. Hetherington, M.P. Dunhill, M.D. Lilly. Release of protein from bakers' yeast. Trans Inst. Chem. Eng. 49 (1971) 142-148.
[12] H. Shutte, M.R. Kula, H.J. Rehms, G. Reed. Biotechnology Bioprocessing, vol. 3, second ed. Weinheim: VCH, 1993.
[13] G.M. Walker. Yeast, Encyclopedia of microbiology, third ed., 2009, pp. 478-491.
[14] H.J. Pfaff, The Life of Yeasts, in: A. Sertkaya, Investigation of cytocidal effect of K5 type yeast killer protein on sensitive microbial cells, (2005), pp. 1-3.
[15] R.K. Mortimer, C.R. Contopoulou, J.S. King. Genetic and physical maps of *Saccharomyces cerevisiae*, Yeast (Edition 11) 8 (1992) 817-902.
[16] R.B. Wickner, In the Molecular and Cellular Biology of the Yeast *Saccharomyce*, (eds.) J.R. Broach, J.R. Pringle, E.W. Jones, Cold Spring Harbor Laboratory Press, New York, 1991, pp.263-296.
[17] B.S. Glick, Cell biology: Alternatives to baker's yeast, Current Biology 6 (12) (1996) 1570-1572.
[18] T. Tsuchiya, Y. Fukazawa, M. Taguchi, T. Nakase, T. Shinoda. Serologic aspects on yeast classification, Mycopathologia et mycologia applicata 53 (1974) 77-91.
[19] A.S. Schultz, L. Atkin, C.N. Frey, The biochemical classification of yeast strain, (1940) 339-346.
[20] M.N. Stelling-Dekker. Monograph of the yeast species maintained at the central bureau of mold cultures. The Spore-forming yeasts (1931); (1), in: A.S. Schultz, L. Atkin, C.N. Frey. The biochemical classification of yeast strain (1940); pp. 339 – 346.
[21] S. Muller, S. Sandal, P. Kamp-Hansen, H. Dalboge, Comparison of expression systems in the yeasts *Saccharomyces cerevisiae*, *Hansenulapolymorpha*, *Klyveromyceslactis*, *Schizosaccharomycespombeand Yarrowialipolytica*. Cloning of two novel promoters from *Y. lipolytica*. Yeast 14 (1998) 1267-1283.
[22] D.R. Higgins, J.M. Cregg (Eds): Pichia Protocols, Humana Press, Totowa, NJ, 1998.
[23] G.P.L. Cereghino, J.L. Lin Cereghino, A.J. Sunga, J.M Cregg, Expression of foreign genes in the yeast Pichiapastoris. Genet. Eng.: Principles and Methods 23 (2002) 157-169.
[24] J.S.G. Brookman, Further studies on the mechanism of cell disruption by extreme pressure extrusion. Biotechn. Bioeng. 17 (1975) 465-479.
[25] H. Choi, Advantage of Photodiode array. (http://www.hwe.oita-u.ac.jp/kiki/ronnbunn/paper_choi.pdf)
[26] S.S. Save, A.B. Pandit, J.B. Joshi. Use of hydrodynamic cavitation for large scale microbal cell disruption. Food and Bioproducts Processing 75 (1997) 41-49.
[27] S.S. Save, A.B. Pandit, J.B Joshi. Microbial cell disruption: role of cavitation, Chem. Eng. J. 55 (1994) 67-72.
[28] M.S. Doulah, J.S.G. Brookman, T.H. Hammond. A hydrodynamic mechanism for the disintegration of Saccharomyces cerevisiae in an industrial homogeniser. Biotechno. Bioeng. 17 (1975) 845-858.

THE IMPORTANCE OF WIND SHEAR COEFFICENT AND AIR DENSITY FOR THE ESTIMATION OF WIND ENERGY PRODUCTION

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Abstract

In this study, based on the formula used in the calculation of wind energy potential, the effects of variations in wind shear coefficient and air density to the wind energy potential calculations depending on various factors have been investigated for the case in Turkey, in Central Anatolia, at Yunak Region. Under the scope of this study, to analyze the energy production under different circumstances, two different wind turbine models (GE 2.5 MW and GE 1.5 MW), different Hellmann coefficients (α) (0.25, 0.2 and 0.14) and standard air density value (1.225 kg m^{-3}) and annual average air density value of the region (1.09 kg m^{-3}) have been taken into account. Eventually, as seen from the calculations, extrapolating the wind data to the hub height and the air density value affect the wind energy production estimation. For this reason, all these variables must be considered before performing the investments.

Keywords: *Air density, Hellmann coefficient, wind energy production estimation, wind energy*

1. INTRODUCTION

Nowadays, the electrical energy demand of developing countries gradually increases. Turkey does not have sufficient reserves to meet its electrical energy needs in terms of its own energy resources. Therefore, Turkey draws a dependent profile on foreign resources regarding electrical energy production. The must-have items of energy policies can be ordered as; Sustainable production of electrical energy, having redundant resources for electrical energy production, diversity of the energy resources, clean and cheap use of energy resources. By taking all these issues into consideration, wind energy which is the one that Turkey has a good potential among the renewable energy resources have great importance for Turkey. However, at this point, it is important to use this valuable potential possession accurately and in an efficient manner. It is very important to analyze the wind characteristic of the region in order to acquire the maximum wind potential from the site. During the analysis of the regions wind characteristics, hourly average, daily average, monthly average, seasonal average values are needed. Also, the spatial variation of the wind vector information is required. Generally, the wind measurements are performed at elevations such as 10 m and 30 m. However, the modern wind turbine hub heights are such as 60m, 70m ... 100m and over the measurement heights.

Therefore, the recorded values obtained from the measurements have to be shifted to hub heights by several methods. Wind Power Law is the most widely used method. Wind Power Law [1]:

$$\frac{v_2}{v_1} = \left(\frac{h_2}{h_1} \right)^{\alpha} \tag{1}$$

where; v_1 and v_2 are the measurement wind speed at the heights h_1 and h_2 respectively. α is the wind shear coefficient.

In order to make this calculation, a constant wind shear coefficient will be decided by assessing the different cases at the Table 1 [1]. Hence, this leads to differences in the estimated production forecasts. Additionally, in many studies while calculating the wind energy potential of the region, the average value for air density is considered as ρ = 1.225 kg m^{-3} (at sea level, air temperature is 15ºC). However, studies show that as well as the instantaneous change in wind speed, the change in air density is also a factor that should not be ignored [2-4]. In addition to these factors, the temporal variation of the wind vector, heavy rain, hail, frost, lightning strikes and snow are factors that should not be ignored in wind energy production. Thus, in the light of all this information the wind turbine selection and micro-sitting can be done for the region where a wind energy power plant is planned to be constructed.

In this study, based on the formula used in the calculation of wind energy potential, the effects of variations in wind shear coefficient and air density to the wind energy potential calculations depending

on various factors have been investigated for the case in Turkey, in Central Anatolia, at Yunak Region. Under the scope of this study, to analyze the energy production under different circumstances, two different wind turbine models (GE 2.5 MW and GE 1.5 MW), different Hellmann coefficients (α) (0.25, 0.2 and 0.14) and standard air density value (1.225 kg m^{-3}) and annual average air density value of the region (1.09 kg m^{-3}) have been taken into account.

Table 1. Wind Shear Coefficient of Various Terrains

Terrain Type	Wind shear coefficient
Lake, ocean and smooth hard ground	0.10
Foot high grass on level ground	0.15
Tall crops, hedges, and shrubs	0.20
Wooded country with many trees	0.25
Small town with some trees and shrubs	0.30
City area with tall buildings	0.40

2. ELABORATION

2.1. Wind Characteristic Values of the Region

In this study, the hourly mean wind speed data recorded at 10 meters from Yunak region, where the coordinates are 38° 47′ 16,26" north and 31° 56′ 54,51" east, received from Turkish State Meteorological Service (TSMS) between the years 1986 and 2007, have been used to investigate the wind characteristics of the region. In Table 2, the average temperature, average air density and average wind speed values between the years 1986 and 2007 were presented. In Figure 1, the annual average wind speed values which are recorded at the height of 10 meters during the total 22 years in between 1986 and 2007 were given. As shown in Fig. 1., in the year of 2001 the highest wind speed was observed as 4.24 m s^{-1}, while the lowest wind speed was 3.40 m s^{-1} which recorded in 2006. In Fig. 2., considering the data of 22 years the average monthly wind speeds are presented. The lowest monthly average speed of 3.41 m s^{-1} was observed in October and the highest monthly average speed of 4.53 m s^{-1} was obtained in March. Regarding the data for the years 1986 - 2007, the seasonal average wind speeds for winter, spring, summer and autumn are 3.73 m s^{-1}, 4.79 m s^{-1}, 4.04 m/s and, 3.59 m s^{-1}, respectively.

Table 2. Average temperature, air density and wind speed values for the years 1986-2007

Average Temperature (˚C)	Average Air Density (kg m^{-3})	Average Wind Speed (m s^{-1})
11.04	1.09	3.89

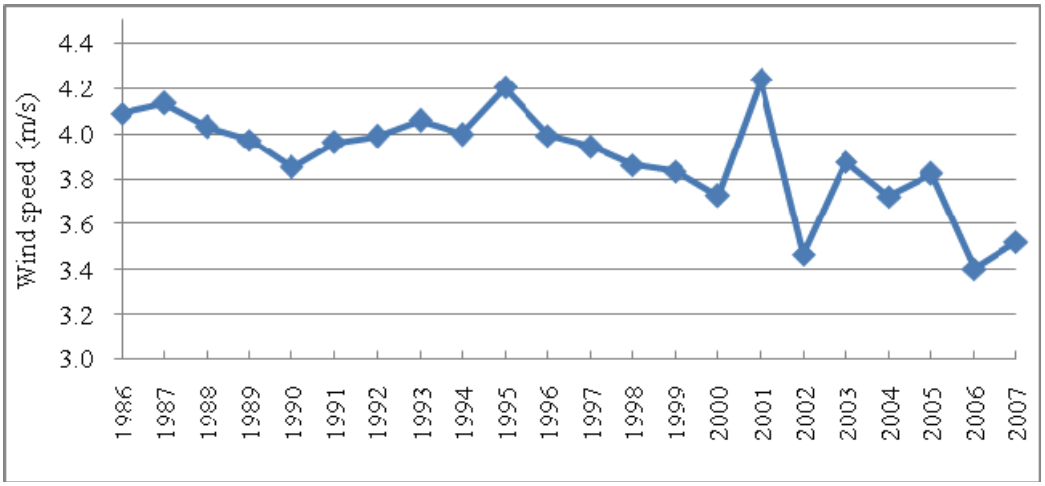


Figure 1. Annual average wind speeds for Yunak region 1986-2007

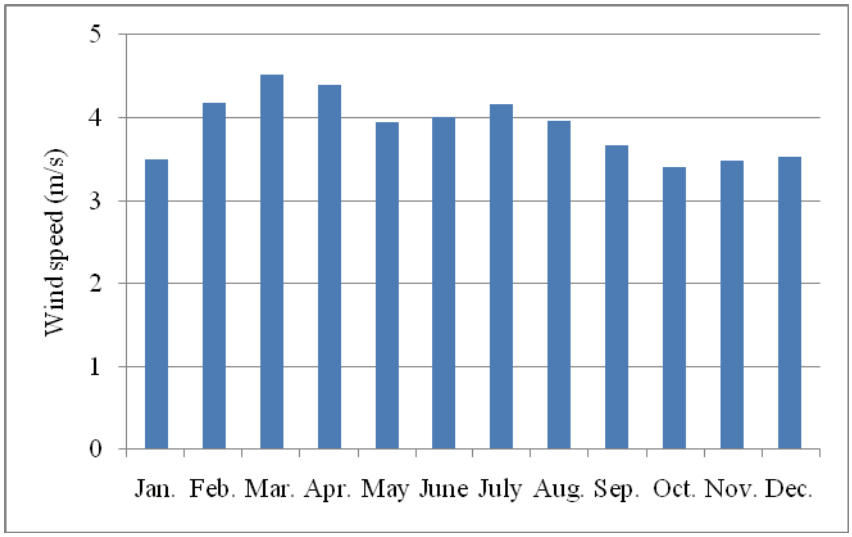


Figure 2. Monthly average wind speed for Yunak region 1986-2007

2.2. The Effects of Air Density and Wind Shear to the Wind Energy Production

Wind energy is directly proportional to the cube of wind speed and air density. Besides wind speed and air density are spatial and temporal variables [3]. Air density can be defined as mass per unit volume of air and varies as a function of time and location. The change in air density with respect to the altitude has to be considered in wind energy studies. In practical calculations, the value of air density is considered as 1.225 kg m^{-3} (P = 1013.25 hPa pressure at sea level and 288 K). Regarding the most common simple equation, wind power is directly proportional to the air density. Therefore, a reduction in air density causes a decrease in wind power. Fig. 3. shows that the higher the altitude the lower the wind power due to a decrease in air density. This means that the wind speed at 3000 m has to be higher than the sea level in order to equilibrate the power reduction with respect to air density [5]. When Fig. 3. is evaluated, it is clearly seen that for the average height of 1000 m which is Yunak region's average height, the air density value is approximately 1.10 kg m^{-3}. The measurements recorded at Yunak region show that the value of air density is 1.09 kg m^{-3}.

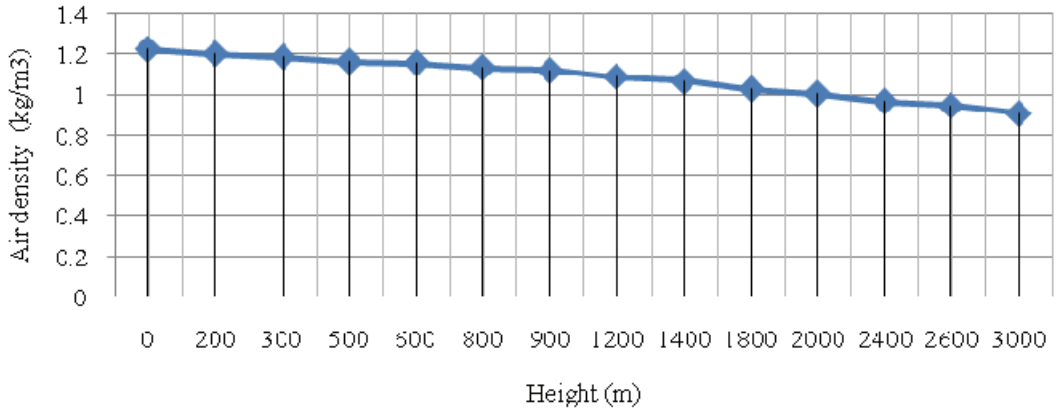


Figure 3. Variation of air density with respect to altitude

The wind turbines power production depends on wind speed and air density and the variations in air density also affects wind turbines electric power generation. With the increasing air density, the possible power production also increases. A significant proportion of power production decreases when the air density declines. On the other hand, wind shear coefficient is another parameter that affects the wind energy production. Wind shear coefficient is used to extrapolate the measured wind speeds at measuring station tower height to the hub height of the wind turbine.

In this study, the hourly wind speed data of Yunak region which is received from TSMS for the years 1986 - 2007 is used. Within the frame of this study, the analyses of energy production were made in two different wind turbine models that are GE 2.5 MW and GE 1.5 MW. Additionally, different Hellmann coefficient values (α) (0.25, 0.2 and 0.14) were applied by also considering the standard air density

(1.225 kg m^{-3}) and the area value of the annual average air density (1.09 kg m^{-3}). With respect to all these various parameters 12 different situations were obtained and shown in Table 4. Wind speed values recorded at 10 meters height, were extrapolated to 100 and 80 meters by taking into account different Hellmann coefficients. Using the power curves of the wind turbines the potential energy productions are calculated for different air density values. In Table 3, the energy production values and capacity factor values are also given for 12 different situations obtained from the total 22 years. In case the 1.5 MW wind turbine is selected, wind turbine capacity factor value varies between 19% and 30.9% depending on the air density and wind shear coefficient. For the case of 2.5MW wind turbine, the turbines capacity factor value varies in between 21% and 37.2%.

Table 3. Eenergy production and capacity factor values for 12 different situations

Situations	Turbine type	Wind shear coefficient	Air density (kg m^{-3})	Electricity Production (MWh)	Capacity factor (%)
1	1500 kW	0.14	1.225	60269	20.9
2		0.2	1.225	75799	26.2
3		0.25	1.225	89225	30.9
4		0.14	1.09	54866	19.0
5		0.2	1.09	69722	24.1
6		0.25	1.09	82734	28.6
10	2500 kW	0.14	1.225	108192	22.5
11		0.2	1.225	137990	28.6
12		0.25	1.225	163564	34.0
10		0.14	1.09	101035	21.0
11		0.2	1.09	131055	27.2
12		0.25	1.09	157333	32.7

The effect of air density on energy production using 2.5 MW wind turbine for α = 0.25, α = 0.2 and α = 0.14 are shown in Fig. 4. The effect of wind shear coefficients on the annual energy production for the standard air density 1.225 kg m^{-3} and also for 1.09 kg m^{-3} is given in Fig. 5.

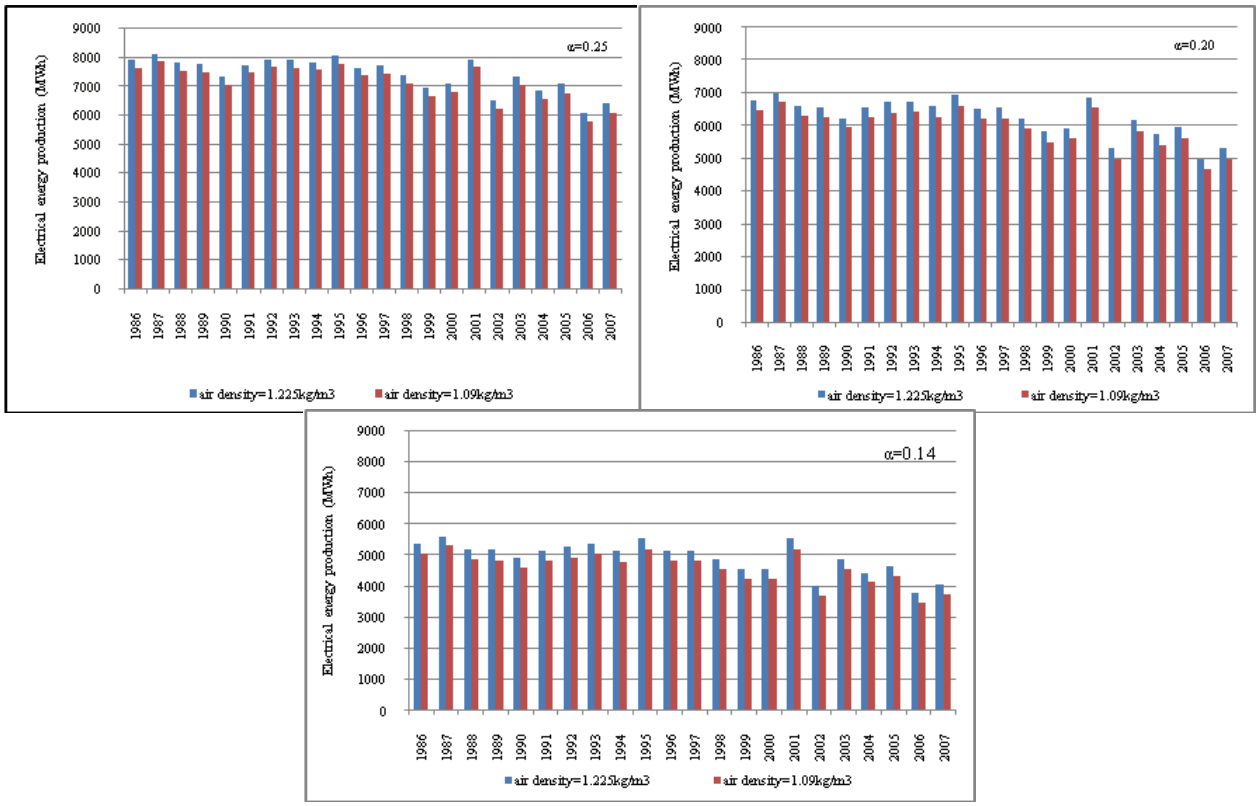


Figure 4. The effect of air density on energy production using 2.5 MW wind turbine

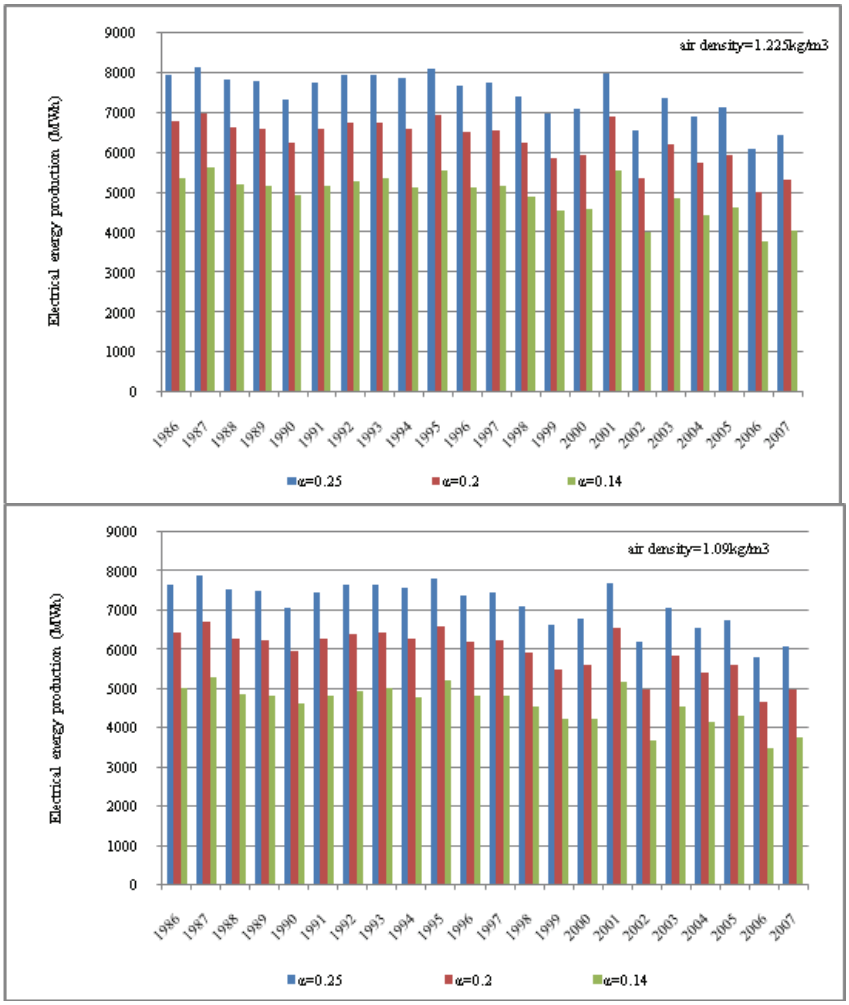


Figure 5. The effect of wind shear coefficients on energy production using 2.5 MW wind turbine

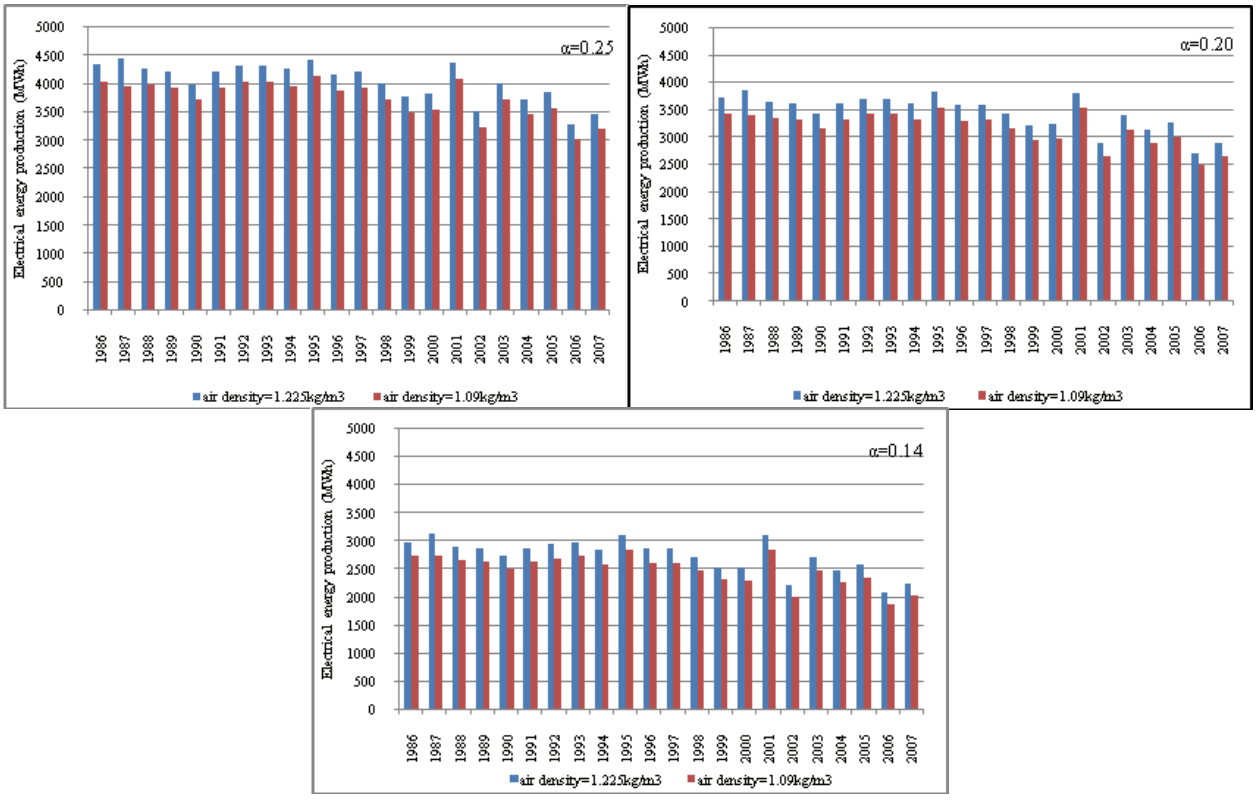


Figure 6. The effect of air density on energy production using 1.5 MW wind turbine

The effect of air density on energy production using 1.5 MW wind turbine for α = 0.25, α = 0.2 and α = 0.14 are shown in Fig. 6. The effect of wind shear coefficients on the annual energy production for the standard air density 1.225 kg m^{-3} and also for 1.09 kg m^{-3} is given in Fig. 7.

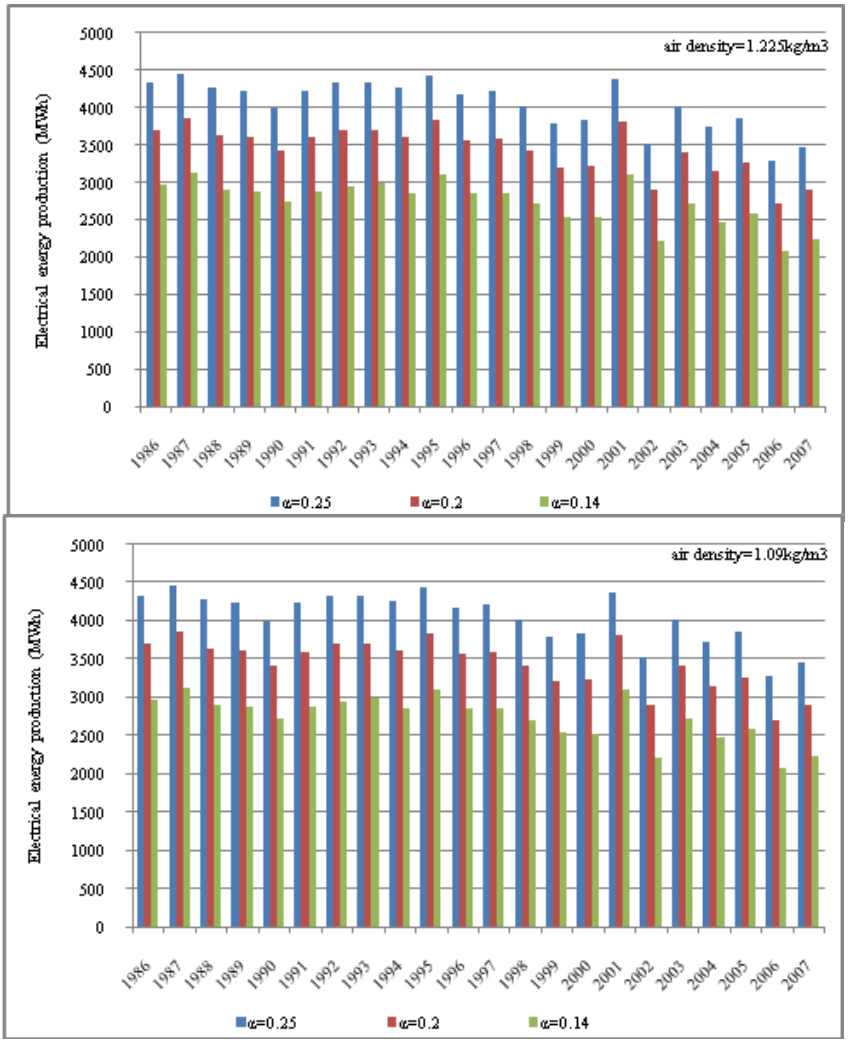


Figure 7. The effect of wind shear coefficients on energy production using 1.5 MW wind turbine

3. CONCLUSIONS

Within this study, the effects of wind shear coefficient and variations in air density on wind energy production estimations have been analyzed. The study was carried out to the data recorded at 10 meters belonging to the years in between 1986 – 2007 and received from TSMS of Yunak region. The hourly average wind speed, pressure and temperature records were used for two different wind turbine types. In consequence of the calculations the following results were obtained for the different turbines.

In case the 2.5MW wind turbine was selected;

- When the air density was taken 1.225 kg m^{-3} and wind shear coefficient (α) were 0.25 and 0.20, the estimated energy production was higher 51% and 28% than α value was taken as 0.14.
- When the air density were selected as 1.09 kg m^{-3} wind shear coefficient (α) were 0.25 and 0.20, the estimated energy production was above 56% and 30% than α value was taken as 0.14.
- When the air density was selected as 1.225 kg m^{-3}, instead of the average air density of site 1.09 kg m^{-3} estimated energy production was achieved 4%, 5.3% and 7.1% more for the cases of 0.25, 0.20 and 0.14 wind shear coefficient, respectively,

In case the 1.5MW wind turbine is selected;

- When the air density was taken 1.225 kg m^{-3} and wind shear coefficient (α) were 0.25 and 0.20, the estimated energy production was higher 48% and 26% than α value was taken as 0.14.

- When the air density were selected as 1.09 kg m^{-3} wind shear coefficient (α) were 0.25 and 0.20, the estimated energy production was above 51% and 27% than α value was taken as 0.14.
- When the air density is selected as 1.225 kg m^{-3} instead of the average air density of site 1.09 kg m^{-3}, estimated energy production was achieved 7.9%, 8.7% and 9.9% more for the cases of 0.25, 0.20 and 0.14 wind shear coefficient, respectively,

Eventually, as seen from the calculations, extrapolating the wind data to the hub height and the air density value affect the wind energy production estimation. For this reason, all these variables must be considered before performing the investments. Otherwise, payback periods will delay and the investors will suffer a loss. Apart from these, meteorological factors such as; heavy rain, hail, frost, lightning strikes, snow and high temperature also affect the production of wind energy. Before the installation of the wind power plant, the inspections must be done to observe if these meteorological events occur or not. In this way it is possible to minimize the effects of such events on energy production.

REFERENCES

[1] M.R. Patel, Wind and Solar Power Systems. CRC Press, 1999.
[2] Z. Şen, A.D. Şahin, Regional assessment of wind power in western Turkey by cumulative semivariogram method, Renewable Energy. 12 (1997), 169-177.
[3] Z. Şen, Stochastic wind energy calculation formulation, Journal of Wind Engineering and Industrial Aerodynamics. 84 (2000), 227-234.
[4] J.W. Reed, Wind power climatology of the United States, SAND78-1620, 1979.
[5] H. Dobesch, G. Kury, Basic Meteorological Concepts and Recommendations for the Exploitation of Wind Energy in the Atmospheric Boundary Layer, ENAIRGY, Vienna, Austria, 2000.

WIND ENERGY TECHNOLOGY MONITORING IN PATENT DOCUMENTS

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Abstract

Energy and environmental protection are a mainstay of the global development, particularly of the economic, social and policy development. The renewable energy resources will have a decisive role for the economic and environmental sustainability of the mankind in the near future.

The paper is giving an overview of the state of the art of the wind energy technology in patent documents, and their future trends.

With the purpose of identifying the numerous, insufficiently exploited possibilities of applying technical information found only in patent documents, particularly for the purpose of development and business, by way of some illustrative examples of the wind energy technology the paper is showing the output of data analysis and data collection and interpretation methods. Such data analysis may be a significant indicator of the strategic decision making, in case of assessing the investments in development and technological trends, planning the appearance on the market, in licensing and investment projects respectively.

Keywords: *wind energy, patent search, patent documents, patent monitoring*

1. INTRODUCTION

Collected over centuries, technical knowledge could be found in books, manuals, encyclopedia, project documentation, professional and scientific publications etc. Most of that knowledge is accessible on internet making it a predominant source of common knowledge.

However, based on professional opinion, 80% of all technical knowledge is stored in patent documents exclusively. Number of patent documents, mostly patent applications increase continuously and annual average increase during last decade was 6%.

In order to enhance usage of information collected in millions of patent documents, national patent offices, international offices for intellectual property and private firms, developed specialized data bases for searching patent documents also through internet. Nowadays, searching patent documents, along with other sources, is used for business purposes and as starting point in planning research and development project.

2. ELABORATION

2.1. Wind Energy Patent Applications

Wind energy, as a renewable energy source, generated, during a last decade, a number of inventions like in any other technical field. However, there hasn't been much interest in seeking patent protection in many countries. Interest rose during some periods in history, but a significant increase happened after Kyoto meeting 1997, and after implementation of Kyoto agreement in 2005.

Number of patent applications in Europe increased by 51% in 2009. Seventy percent of these applications were filed by residents of the US, Germany and Denmark, with nearly a third of them coming from General Electric.

2.1.1. Patent Databases and Patent Searching

Patent databases, besides containing a predominant share of technical information, also have another great advantage, being significantly better organized than any other source of documented technical solutions, including databases of professional and scientific literature as well. A part of patent databases, specifically those of national and regional offices and the World intellectual property organization, is freely accessible on the Internet, whereby a free of charge search has been provided for the highest number of published patent documents.

In order to better understand the task of patent databases search, it has to be perceived what data are contained in each patent document as a rule. These are as follows:

- *The number of patent application* is a unique number composed of data country code or of an organization as addressees (to who the application is addressed), and the numeric character distinguishing such an application from any other existing patent document. Such number is subsequently added a status of document indicating the phase of granting right procedure.
- *The filing date of application* is particularly relevant information, and in case of the first patent application it is a priority date as well, being a date from which are valid the applicant's legal rights.
- *The name of invention* corresponds as a rule to its contents, but it is not always sufficiently informative. Therefore, it has been updated or modified in some commercial patent databases in order to remove such a deficiency.
- *The applicant's name or title* identifies the owner of rights to an invention, and this may be a company, organization and any other legal or natural person, including the inventor. There may be several applicants.
- *Addresses of all applicants*, including their country of residence or domicile
- *The names of all inventors* who are always natural persons. At the inventor's particular request his/her name and data shall be omitted form the patent application.
- *Addresses of all inventors,* including their country of residence or domicile.
- The attorney's name or title, if any.
- *The attorney's address*.
- *Priority right data* in case it is not the first patent application. Such data contain the number or numbers of the first applications, their filing date(s) and data country code or of a regional office where filed.
- *Designated countries* in applications filed with the regional offices or international organizations, present a list of countries in which patent protection is to be requested. Such information is non-committal, and it may be modified by the applicant pending proceeding.
- *The publication date* is another particularly relevant date. Following its publication, the patent becomes a part of the state of the art, i.e. of the accumulated fund of technical knowledge. From the publication date the patent application is accessible to the public, and it may be found in the official gazette of the Office where patent grant procedure is conducted or in patent databases. Between the patent application date and its publication date usually pass 18 months. This is the reason why new technical achievements are shown in databases with such a delay.
- *The publication number* is a unique alphanumeric character of the published document, and depending of the legislation of a particular country or a region where patent granting procedure is conducted, it may be identical or not to the patent application number.
- *The abstract of patent application* is a short, abbreviated presentation of its full contents, and it is officially published with a majority of already mentioned data. Similarly to the name of invention, the abstract of patent application is not always sufficiently informative. In some commercial patent databases it is therefore updated or modified in order to remove such deficiencies.
- *The International patent classification* is a specific, language autonomous system of identifying the patent application, thereby allocated to a designated technical field. The patent application may be allocated several classification symbols. The classification procedure is conducted by patent examiners, experts for designated technical fields. A systematic classification of patent documents is one of the most relevant elements for the subsequent efficient use of patent databases.
- *Description of the invention* is a particularly informative part of the patent document, but its contents may be searchable as plaintext by way of the advanced commercial patent databases only.
- *Patent claims* are a particularly relevant part of the patent document uniquely defining what is to be protected. Similarly to the description of invention, patent claims may be searchable as plaintext by way of the advanced commercial patent databases only.
- *Citations of data sources* also emerge in patent documents, although not so often and not in such a scope as in technical literature. The search option and citations analysis is a characteristic of very advanced patent databases.

From the above mentioned it is evident that with the necessary search abilities, reliable data may be found of the particular invention or of the concerned patent document. It is less evident how to find data required for more complex analyses. For the solution of any such problem it is primarily necessary to set the objectives to be achieved, the strategy and the mode of solving the problem. The example of such an analysis is described further on, related to the field of alternative energy sources.

2.2. Patent Search and Data Retrieval

In order to perform a thorough search of patent documents which would result in a more comprehensive dataset, there are few steps that have to be followed. Purpose of use of results has to be determined, after which a proper database has to be selected, and, finally, search strategy has to be defined and thoroughly checked for any inconsistencies. There isn't a general rule for every search, but it rather has to be modified for different purposes. Fig. 1. shows one of many ways to define a proper path for search, retrieval, and finally analysis of patent data. Analysis of technical aspects represents a thorough data mining and is believed the most thorough as it includes analysis of specific embodiments in numerous patent documents. This type of analysis, if properly conducted; could serve as an objective basis for research and development projects.

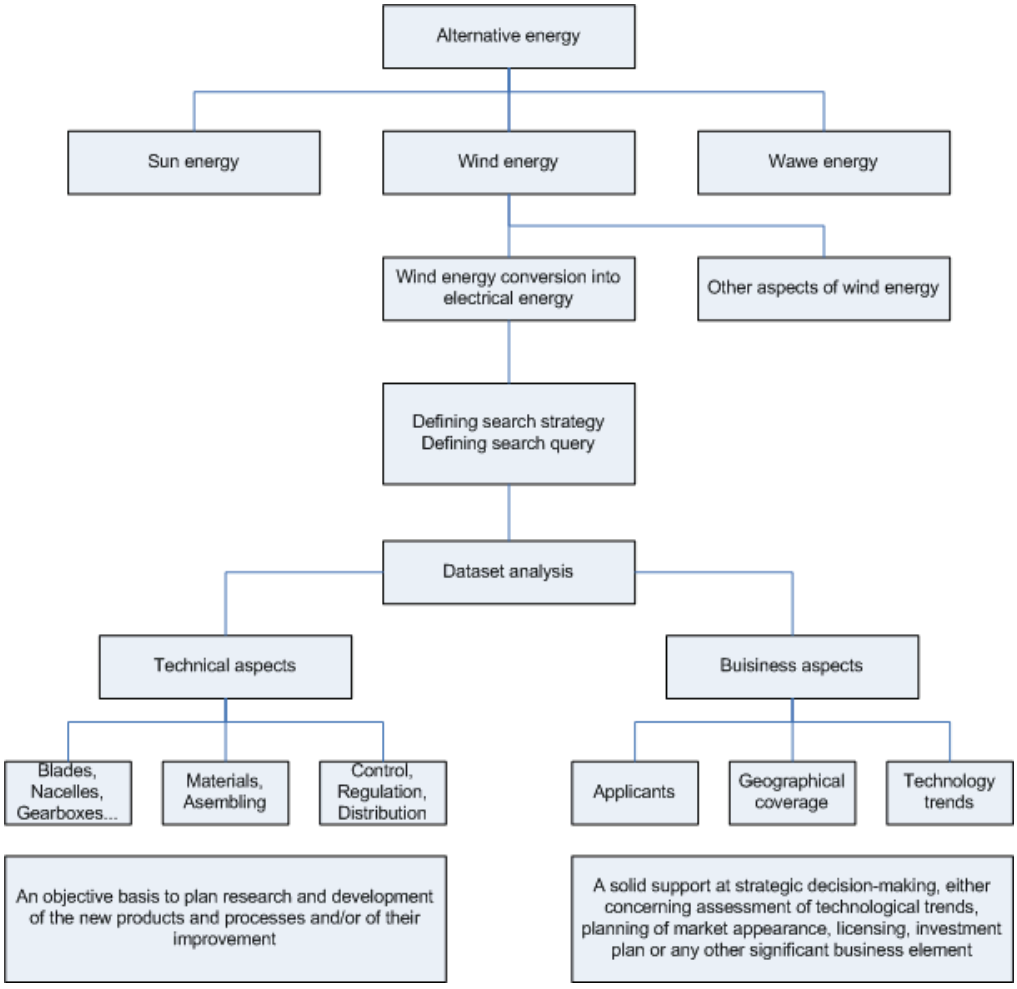


Figure 1. Diagram of an approach to search and analysis of patent documents

This work is limited to analysis of bibliographic data on a general technical level of wind turbines/wind motors.

2.2.1. Search Strategy

Defining search strategy largely depends on purpose and later use of data retrieved by search and analysis. Therefore, in order to conduct a proper search, it is necessary to define the purpose of the analysis results. After that it is much easier to define a proper search strategy, which is usually a set of keywords and their corresponding synonyms. Additionally, and quite often used tool in narrowing down a search are other bibliographic data, such as applicant/assignee, inventor, relevant dates (publication,

application, priority date). Even more usual tool for narrowing the search are patent classification codes like IPC, ECLA, UCLA and F- & FI-terms (International Patent Classification, European Patent Classification, United States Patent Classification and Japanese classification respectively).

2.2.2. Database and Search

A commercial patent database Thomson Innovation [1[has been selected for this purpose. Covering more than 80 million patent documents from around the world it offers tools for searching and extracting only data relevant for the search. It was decided that all available data collections will be searched using only IPC and ECLA symbols for given technical field as described in Table 1.

Table 1 Patent classification symbols used in search with description

Patent classif. symbol	Description
F03D	Wind motors, Controlling wind motors, Adaptations of wind motors for special use, Combinations of wind motors, Details, component parts, or accessories, Mounting structures
Y02E 10/76	Wind turbines, Blades or rotors, Components or gearbox, Control of turbines, Generator or configuration, Nacelles, Offshore towers, Onshore towers, Power conversion electric or electronic aspects for grid-connected applications concerning power management inside the plant, e.g. battery charging/discharging, economical operation, hybridization with other energy sources

Search resulted in 67 332 records found, which was a data subset used in all further analysis. MS Office Excel has been used for analysis of retrieved data. Subset has not been additionally filtered for patent family members, therefore, all patent publications were included in further analysis.

Although being one of the most comprehensive patent databases in the world, dataset retrieved might include some noise due to incorrect classification symbols or other less obvious errors. Nevertheless, dataset retrieved is considered to be a representative sample, and noise is considered non-significant. This study did not include non-patent sources such as scientific literature etc.

2.3. Data Analysis

For many years, technical area of wind energy utilization didn't attract much interest in research and development. This is confirmed also in patent databases, when analyzed over longer period of time (Fig. 2).

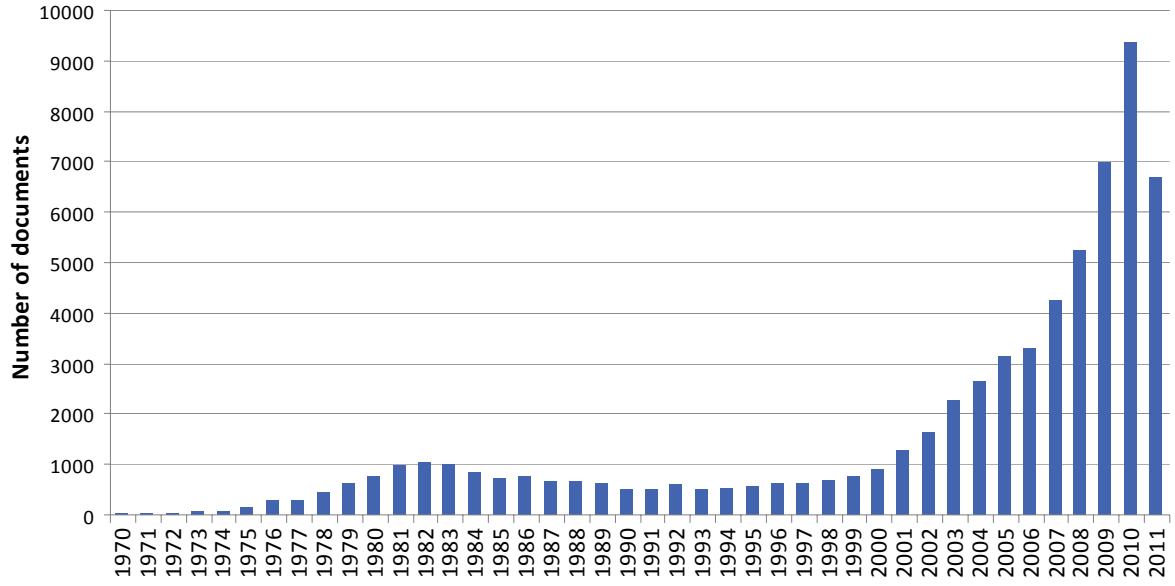


Figure 2. Patent publishing trends from 1970 until 2011.

Until mid 1970's patent publications were under 100 per year. In 1975 there is an increase in published patent documents indicating that there's an increase also in research and development in this area. In 1982 technology has peaked which resulted in decrease of published documents in the following decade. Although, R&D has decreased, number of inventions still remained over 500 publications per year. A huge increase in R&D activity begins in 1997 and has remained until today. It is understood that policy makers do make a change in innovation, as patenting in all "green technologies" increased after Kyoto meeting in 1997.

Going further into detailed analysis of original sub-set, another type of data is usually used to determine present state of the art. Country code is good indicator of intensity of R&D in a specific country, especially if combined with other bibliographic data in a patent document.

Fig. 3. shows a change in number of published patent documents for 15 selected offices before and after 2005. The data presented clearly indicate that specific countries like China, South Korea, and United States are of major interest either as a market or as centers of R&D, or both. Additionally there is an increase in publishing EP documents, which indicates that there is an increased activity in at least one of 39 countries, members of the European Patent Organisation.

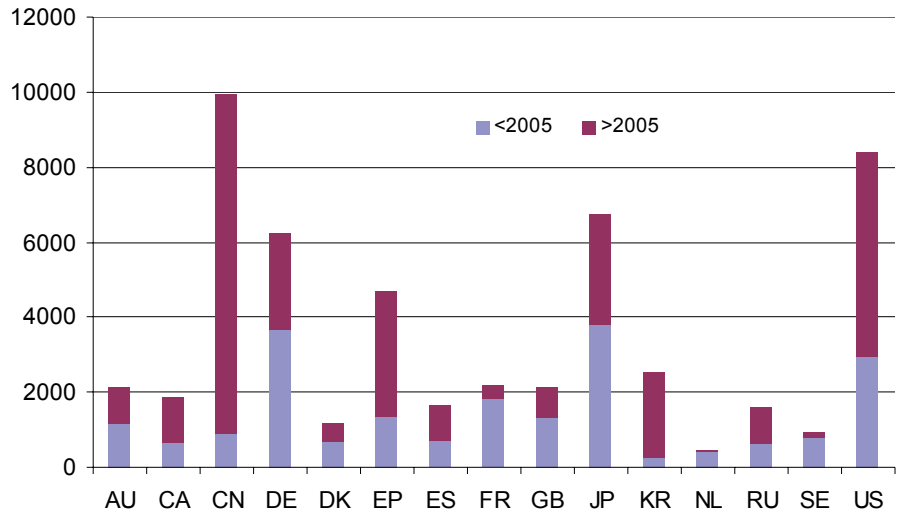


Figure 3. Number of published patent documents for selected offices before and after 2005

Statistical data from some sources [2] show that world market for wind energy is rapidly increasing. Patent data analysis shows that number of states in which a patent protection is sought is bigger than ever. Fig. 4. represents number of states that have published patent documents in given technical area. During 2009 and 2010 there has been an expansion in protection of inventions, which means that applicants are expected to enter these markets, if not already.

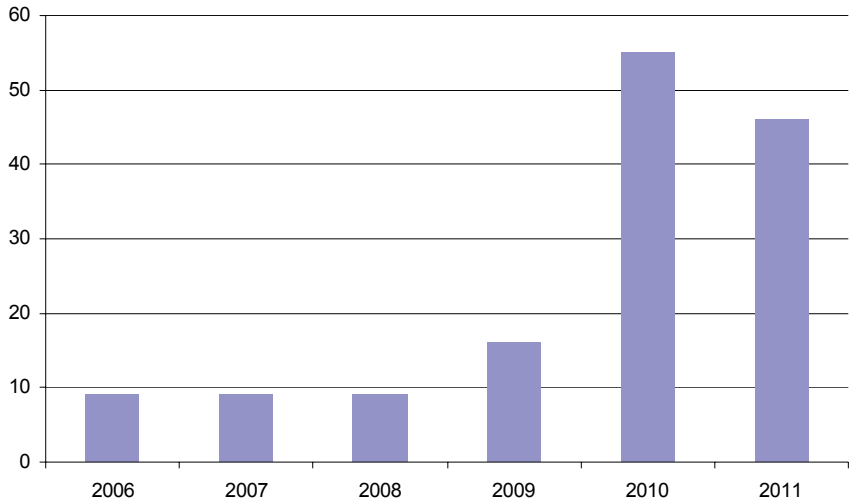


Figure 4 Number of designated states for the previous 5 years

Additional analysis might give extra information on specific markets or countries. If China is taken as a target for analysis (Fig. 5.), it is interesting to take into account legislation when considering a tremendous increase in patent activity. Obvious increase in patent documents would be expected, as total world number is increasing too. However, China hasn't been target market always, but has rather shown increase from 2005 onward, the same year that the first Chinese Renewable Energy Law was passed [2], and entered into force a year later. Not only that patenting activity increased in China, but market began to rapidly grow.

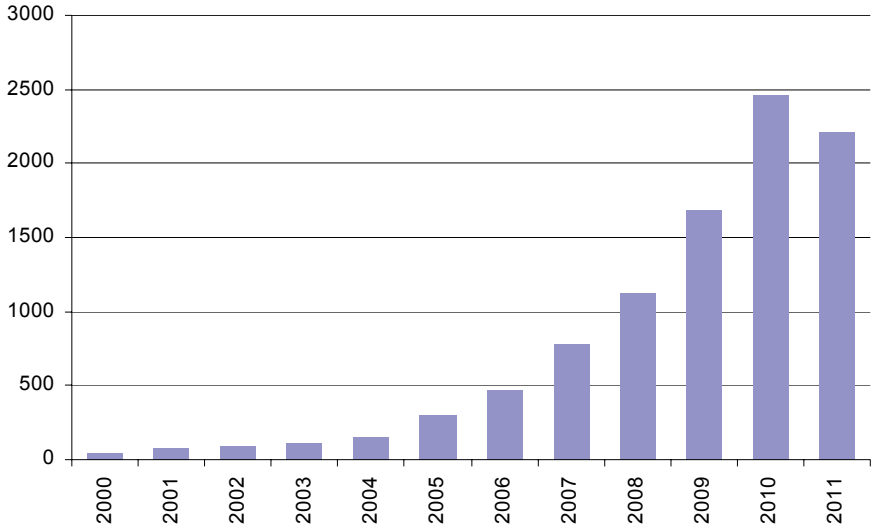


Figure 5. Number of published Chinese patent documents last 12 years

Another very useful aspect is to analyze priority data which gives a clue where is the centre of innovation capability. Table 2 shows how many Chinese published patent documents claim Chinese priority (Chinese inventors), and non-Chinese priority (inventors from the rest of the world). Again, a large increase is present after 2005 due to change in legislation, giving more incentive to inventors.

Table 2 Claimed priorities in published Chinese documents before and after 2005

Country code	Before 2005	After 2005	Total
CN	716	6770	7486
Non-CN	190	2271	2461

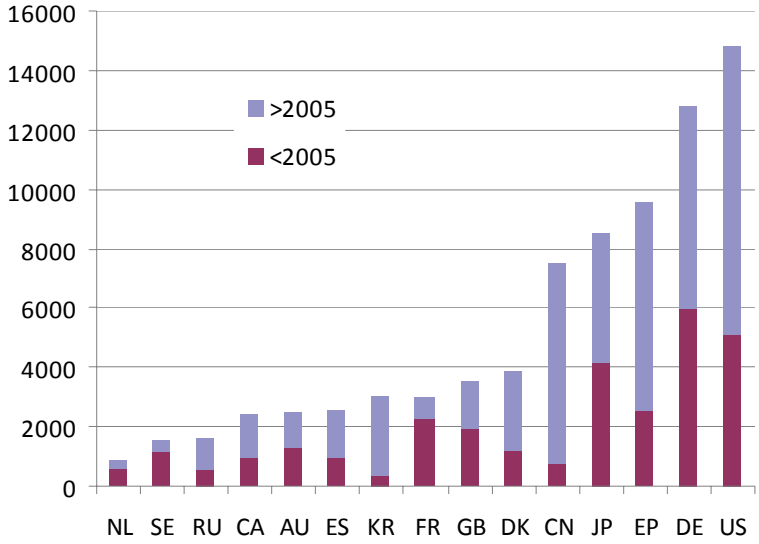


Figure 6. Number of patent documents claiming priority for selected countries

When put into global context this data analysis gives a hint which countries are leading researching centers worldwide (Fig. 6.). It has to be cleared that although some countries show decrease in claimed priorities it is usually the case that applicants chose to file their priority application at regional office like European Patent Office, hence decrease in number of claimed national priorities. Distinction has to be made between U.S., German and Japanese inventors who have been present in this technical field before 2005, and those whose activity is emerging after 2005, like Chinese and Korean.

Finally, analysis could be also made on specific applicants giving an insight on which companies or individuals are the most important in given technical field, are applicants conducting research and development on their own or do they collaborate with other inventors, where is their R&D being done, etc. Some of the above mentioned aspects are analyzed below, making it possible to draw few conclusions. Fig. 7. shows most active applicants worldwide giving an insight on "who is who" in wind technology for the last 7 years.

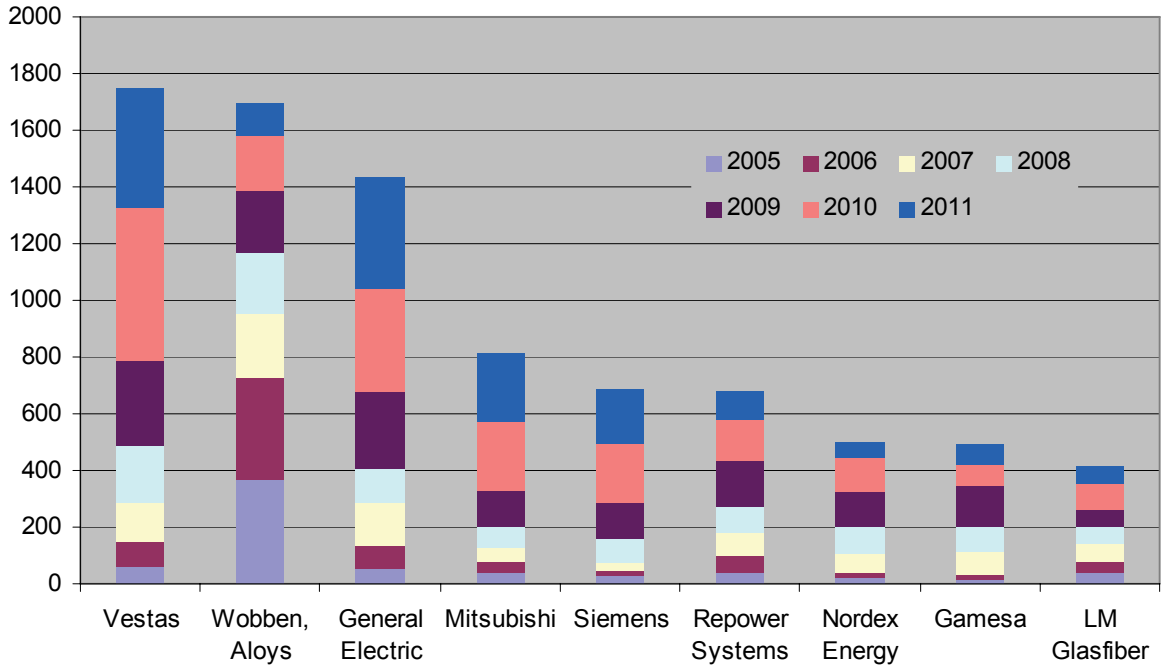


Figure 7. Number of patent documents by applicant by year

Further analysis of other bibliographic data would give additional information on some business aspects for selected applicants. For example, Table 3 shows claimed priority country codes for General Electric Company as applicant which means that almost 90% of their applications were firstly filed in United States. Probably, most of their R&D is done in United States.

Table 3 Claimed priority country codes for General Electric patent documents

Country code	Documents	Percentage
US	810	87.19%
DE	60	6.46%
EP	54	5.81%
CN	3	0.32%
GB	2	0.22%

Table 4 Claimed priority country codes for Vestas patent documents

Country code	Documents	Percentage
DK	707	75.61%
EP	130	13.90%
GB	47	5.03%
US	32	3.42%
WO	7	0.75%
SG	4	0.43%
DE	3	0.32%
CN	3	0.32%
NL	2	0.21%

Similarly, as shown in Table 4, Vestas files its applications mostly in Denmark and through European Patent Office, which usually means that most of their R&D is done in Denmark. This type of conclusion could be further verified if analysis was made by country of inventor.

3. CONCLUSIONS

Post Kyoto time period shows large increase in patent activity. This indicates that policy, both national and international, make impact on research and development. Influence is two-fold: through more rigid legislation concerning ecological influence, on one hand and through incentives and tax reductions/feed-in-tariffs, on the other hand. This combination ensures that R&D as well as commercial utilization of wind energy has good basis for mass production and commercialization.

It is obvious that wind motors technology area hasn't yet peaked and is expected to grow. Further analysis is needed in order to get an insight to specific sub-areas of this area which would make it possible to see which technical aspects of wind motors still have some space for improvement regarding R&D, and which have matured.

REFERENCES

[1] http://www.thomsoninnovation.com/
[2] Global Wind Report 2010, GWEC, http://www.gwec.net/fileadmin/images/Publications/GWEC_annual_market_update_2010_-_2nd_edition_April_2011.pdf

SUSTAINABLE ENERGY MANAGEMENT – SOLAR ENERGY AND THERMAL STORAGE TECHNOLOGIES

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Abstract

The foremost global challenges facing the energy market today are growing environmental concerns, especially climate change, economic development and energy security. Developing and deploying more efficient and less environmentally damaging energy technology is critical to achieve objectives of energy security, environmental protection and economic and social development. Solar energy is the most important renewable energy source that waits to be exploited to meet the global challenges of the energy market. This paper attempts to give an overview of the recent thermal energy storage technologies used in solar applications around the world with the emphasis on two Mediterranean countries: Turkey and Slovenia that are cooperating on three years joint project with the title: Thermal Energy Storage for Efficient Utilization of Solar energy.

Keywords: *thermal energy storage, solar energy, Slovenia, Turkey*

1. INTRODUCTION

Sun is a continuous energy source of the earth. Solar energy is so abundant that one hour of sun shine on earth covers world energy demand for an entire year [1]. Storage of thermal energy is very important in conserving available solar energy because of its intermittence. For example, solar energy is available only during the day and applications that collect excess heat during sunshine hours require heat storage in order to make it accessible for the night or other periods (clouds or fog). When deciding for a certain technology or method of storage following considerations should be taken into account: the temperature range, over which the storage has to operate, the capacity of the storage, heat losses from the storage, the rate of charging and discharging, cost of the storage unit, energy density [kJ kg^{-1}] or volumetric energy capacity [kJ m^{-3}] and length of time during which energy can be stored with acceptable losses. Storage of only a few hours is essential in most applications and is referred as short term storage, whereas in some applications long term storage of a few months may be required.

2. ELABORATION

2.1. Thermal Energy Storage Technologies

Thermal energy can be stored as a change in internal energy of a material as sensible heat, in which the temperature of the storage material varies with the amount of energy stored, as latent heat, which makes use of the energy stored when a substance changes from one phase to another by melting (as from solid to liquid), as thermo-chemical heat, or combination of these (Fig. 1.).

2.1.1. Sensible Heat Storage

In Sensible Heat Storage (SHS), thermal energy is stored by raising the temperature of a solid or liquid. SHS systems utilize the heat capacity and the change in temperature of the material during the process of charging and discharging. The amount of stored heat depends on the specific heat of the medium, the temperature change, and the amount of storage material which is represented with the Equation 1. SHS are simpler in design than latent heat or bond storage systems, but the disadvantage is that they are bigger in size. This is the reason why an important criterion in selecting a material for SHS is ρc_p value (equation (1)). Another disadvantage is that energy is not stored or delivered at a constant temperature.

$$Q = \int_{T_i}^{T_f} m c_p \, dT = m c_p (T_f \quad T_i) \tag{1}$$

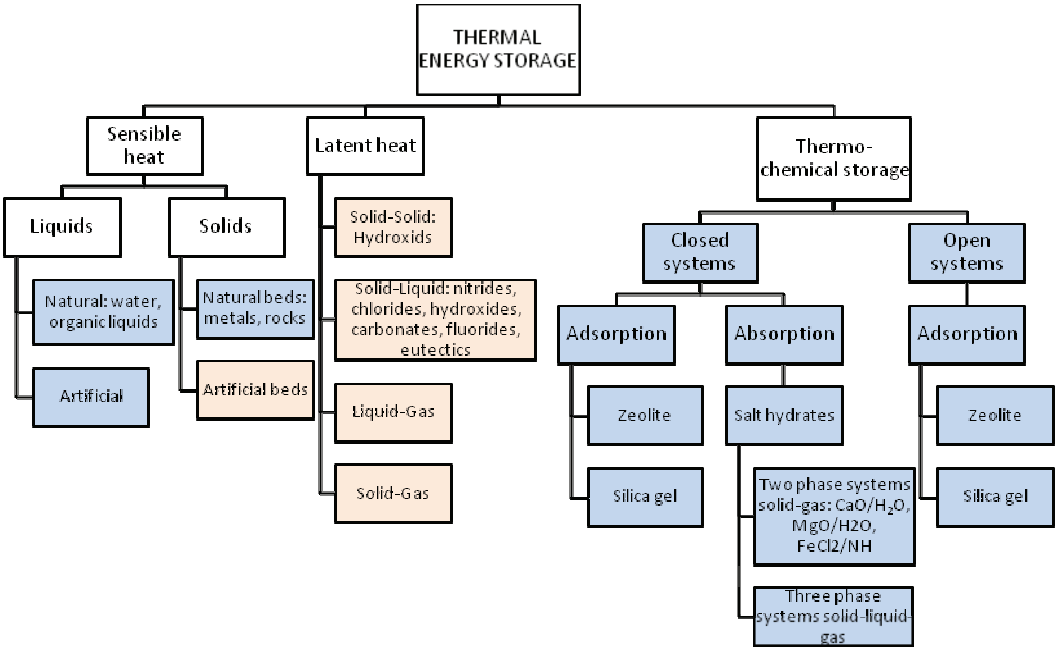


Figure 1. Thermal energy storage technologies

A variety of substances have been used in such systems, where water seems to be the best available liquid because it is inexpensive and has high specific heat. Other liquids are organic liquids (heat transfer oils), certain inorganic molten salts, liquid metals, etc. Other possible form of substances is solid state. In this case rocks (for air heating applications), metals, ceramics are being used.

2.1.2. Thermo-Chemical Storage

In this case heat is used to produce certain chemical reaction and therefore energy is stored in bond reactions between chemical compounds. For a cyclic process, the products of the reaction or sorption process have to be reconverted to the original compound in an exothermic reaction, where heat can be utilized for the load. The amount of heat stored depends on the amount of storage material, the endothermic heat of reaction, and the extent of conversion (equation 2). The chemical produced can often be stored cold (without losses), for a long time and can often be transported easily. In spite of these advantages, bond energy storage systems are not as common as sensible heat storage and latent heat storage and are being proposed for use in the future for medium and high temperature applications.

$$Q = a_r m \Delta h_r \tag{2}$$

2.1.3. Latent Heat Storage

Latent heat storage uses a phase change material as a storage medium. A phase change material (PCM) is a substance with a high heat of fusion which is capable of storing and releasing large amounts of energy (equation 3).This can be accomplished through solid-liquid, liquid-gas, solid-gas and solid-solid phase transformations, but the only two of practical interest are the solid-liquid and solid-solid [2].In solid–solid transitions, heat is stored when the material is transformed from one crystalline to another. This transition generally has smaller latent heat and volume changes than solid–liquid transition. Solid-liquid transformations have comparatively smaller latent heat than liquid-gas. However, these transformations involve only a small change in volume (< 10 %). Solid-liquid transition has proved to be economically attractive for use in thermal energy storage systems [2]. For solar heating and for heat load levelling applications materials that melt between 15°C and 90°C can be applied.

$$Q = m a_m \Delta h_m + \int_i^m m c_p dT + \int_m^f m c_p dT = m\left[a_m \Delta h_m + c_{sp}(T_m - T_i) + C_{lp}(T_f - T_m)\right] \tag{3}$$

PCMs have two important advantages as storage media: they can offer an order-of-magnitude increase in heat capacity, and for pure substances, their discharge is almost isothermal. For example, in the case of water, as much as 80 times of energy is required to melt 1 kg of ice as to raise the temperature of 1 kg of water by 18˚C.

A classification of PCMs is given in Fig. 2. They can be classified into the following major categories: inorganic compounds, organic compounds and eutectics of inorganic and/or organic compounds. Inorganic compounds include salt hydrates, salts, metals and alloys, whereas organic compounds are

comprised of paraffins, non-paraffins and polyalcohols. Some requirements for PCMs: large latent heat, high thermal conductivity, melting temperature in the practical range of operation, congruent melting with minimum sub cooling, chemical stability, low costs, nontoxic and non-corrosive.

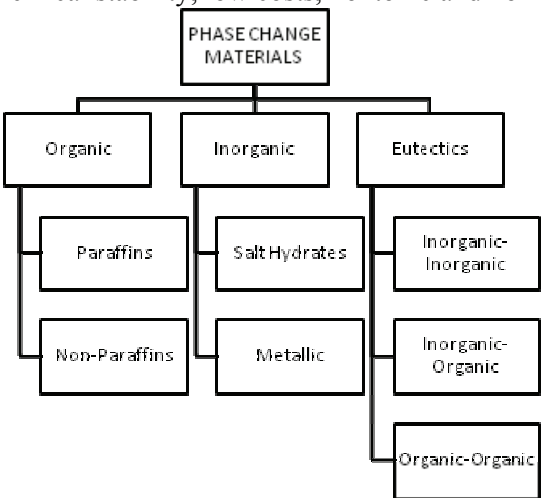


Figure 2. Classification of PCM materials

Table 1. Comparison of different possibilities of heat storage

	Advantages	Disadvantages
Sensible heat storage	• Simple design	• Size of the systems • Not isothermal storage process
Latent heat storage	• Isothermal storage process • High storage density	• Price • Low thermal conductivity • Almost no convection
Thermo-chemical storage	• High energy density • Cooling and heating possible (systems act as a heat pumps)	• Complexity • Expensive compounds • Relatively high temperature required • Limited experience with long-term operation

2.2. Solar Energy Use in Turkey

Turkey is located in a relatively advantageous geographical location for solar energy. Fig. 3. shows total solar radiation distribution of Turkey [4]. Especially Mediterranean and Aegean Sea coast has a very high potential for utilization of solar energy. Turkey's average annual total sunshine duration is calculated as 2.640 hours (daily total is 7.2 hours), and average total radiation as 1.311 kWh m^{-2} per year (daily total is 3.6 kWh m^{-2}) [4].

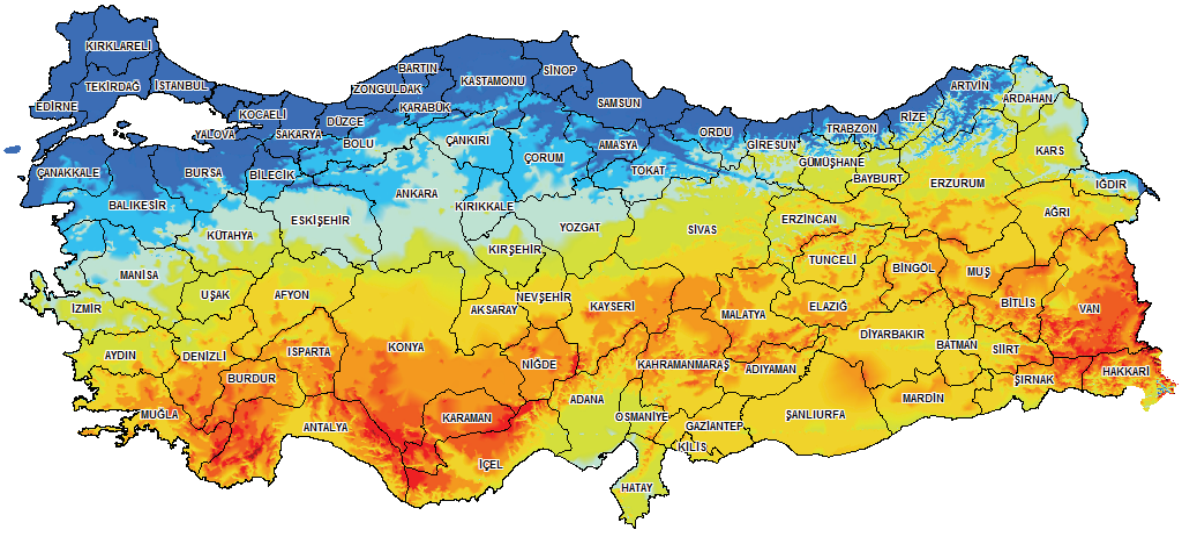


Figure 3. Total solar radiation distribution of Turkey [4].

The solar energy use in Turkey amounted to 0.4 Mtoe in 2008. Two-thirds of this was used in the residential sector and the rest in industry [5]. Main solar energy utilization in Turkey is with flat plate glazed collectors. In a recent report on Solar Heat Worldwide 2011 carried out for 53 countries, total capacity of flat plate collectors in operation in Turkey by the end of 2009 is 8424.5 MWth, which corresponds to about 12 million m^2 of total collector area. The corresponding calculated CO_2 emissions reduction is about 3 million tons per year. Turkey is reported to have the fourth highest total installed capacity among these countries [6]. Considering the estimated technical potential for solar energy of 380 TWh, or 32.6 Mtoe in Turkey [5], only slightly more than two per cent of this potential is utilized.

2.2.1. Examples of Solar Energy Storage Technologies in Turkey

Solar thermal applications apart from hot water systems that utilize flat plate collectors are at R&D stage in Turkey. The first solar house built for experimental purpose was back in 1971. Table 1 shows the solar houses in Turkey. It can be seen that the performance of these solar houses has been increasing with new systems. Thermal storage systems in the solar houses given in Table 1, all use sensible heat.

Table 1. Solar houses in Turkey [7]

Solar House	Location, Year of construction	Type	Thermal storage	Heat transfer fluid	Solar energy covering heating load (%)
MTA	Marmaris, 1971	Passive	Trombe wall	Air	30
MTA Chemistry Lab	Marmaris, 1981	Active	Gravel	Air	NA
Cukurova University	Adana, 1981	Passive	Greenhouse+Trombe wall	Air	NA
Ege University	Izmir, 1991	Passive	Greenhouse	Air	85
Ege University – Gama type	Izmir, 1990	Passive	Greenhouse+Trombe wall	Air	85
Hacettepe University	Ankara, 2003	Active+Passive	Gravel	Air	NA
METU	Ankara, 1980	Active+Passive	Water+Greenhouse	Water	22.4
Ankara Municipality	Ankara, 1993	Passive	Air	Air	73
TUBITAK guesthouse	Antalya, 1996	Passive	Greenhouse+Trombe wall	Air	NA
Erciyes University	Kayseri, 1996	Active	Water	Air	84.5
Erciyes University with floor heating	Kayseri, 1998	Active	Water	Water	86
Erciyes University Sports Hall	Kayseri, 2001	Active	Water	Air	73
Denizli PAU	Kayseri, 2007	Passive	Trombewall+Water	Air+Water	NA
Diyarbakır	Diyarbakır, 2007	Passive	Greenhouse+Trombe wall	Air	NA

In the following passive solar project, thermal energy storage in microencapsulated phase change materials (PCMs) together with insulation materials was utilized to decrease heating and cooling load of a test cabin of 4 m^2 floor area in Adana, Turkey (Fig. 4(a). Two different PCMs – Micronal 5001 – BASF (melting point 26ºC and latent heat 110 kJ kg^{-1}) and Micronal 5008 - BASF (melting point 23ºC and latent heat 110 kJ kg^{-1}) - were used. Macro-packages of PCM in rectangular shape (0.35×0.30 m^2) and thickness 0.05 m were prepared using Aluminium foil. Total amount of PCM used was 3.5 kg. As insulation material Izopan –IZOCAM, which is a sandwich panel of glass wool in between aluminium layers was used. The energy conservation was 7% for cooling and 23% for heating as a result of using PCM macro-packages lined on the walls as shown in Fig. 4(b) [8].



Figure 4 (a). Test cabin used (b). Microencapsulated PCM packages installed in the cabin [8]

Another R&D project for a greenhouse heating and cooling does not use solar collectors, but uses greenhouse itself as the solar collector. Two separate greenhouses with polyethylene covers, each having an area of 360 $m^2$and growing tomatoes at Cukurova University, Adana research farm have been used. The first greenhouse has been heated and cooled by Aquifer Thermal Energy Storage (ATES) technology. The solar heat accumulated in the greenhouse through the use of fan coils and perforated ducts shown in Fig. 5. is injected into aquifer. By doing this greenhouse was cooled down in summer time. In the second control greenhouse a conventional heating system has been used without any cooling. Two wells - a cold and a warm well – were operated for the ATES greenhouse. The wells had a depth of 80 m, casing diameter of 0.40 m and the distance between the wells was 100 m. The schematic diagram of the system is shown in Fig. 6. The monitoring results show that 68% energy conservation and 40% increase in yield of products were realized. Apart from the electricity used for fans and pumps, "0" fossil fuel was consumed [9].



Figure 5. Fan coils and ducts used for extracting solar heat from greenhouse [9]

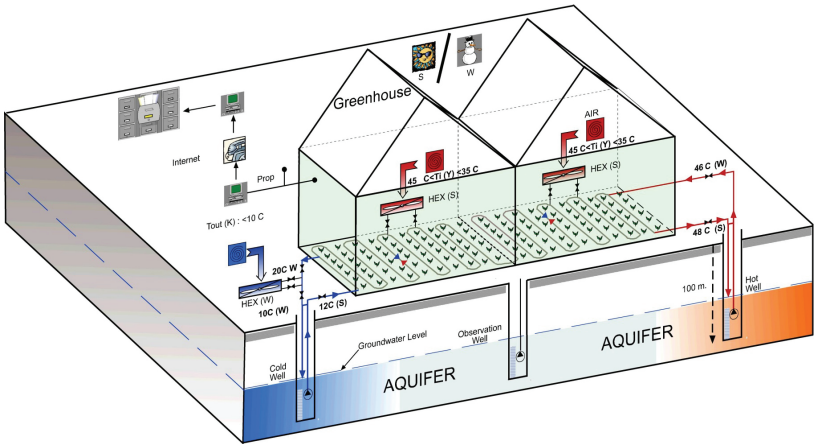


Figure 6. Aquifer thermal energy storage system used in greenhouse [9]

There are few commercial solar heating and cooling projects. In Southern Turkey, the solar cooling system of a hotel and resort complex in Sarigermehas was in operation since 2003. The system not only supplies solar cooling but also solar pool and space heating and solar-powered steam generation for the hotel laundry. Parabolic through collectors, shown in Figure 7, are used to collect the sun at a temperature of 180 – 250˚C [10].

2.3. Solar Energy Use in Slovenia

In Slovenia we have installed 100.000 $m^2$of solar energy collectors or 0.05 m^2 per inhabitant, if some data has been considered as a base (Switzerland 0.02m^2, Austria 0.09m^2). Only short-term thermal energy storage is now being used in households in Slovenia in larger scales. These are used for preparing of warm sanitary water and for heating. On the seasonal storage (aquifers) in Slovenia we still do not have a operating system, where we would be using heat from aquifer on renewable manner. Measurements of environmental data have been realized in Slovenia for many years. Among others measurements, solar radiation is one of the most predominant. Data are given in the book *Solar radiation in Slovenia* [10]. Fig. 7. presents annual solar radiation in Slovenia.

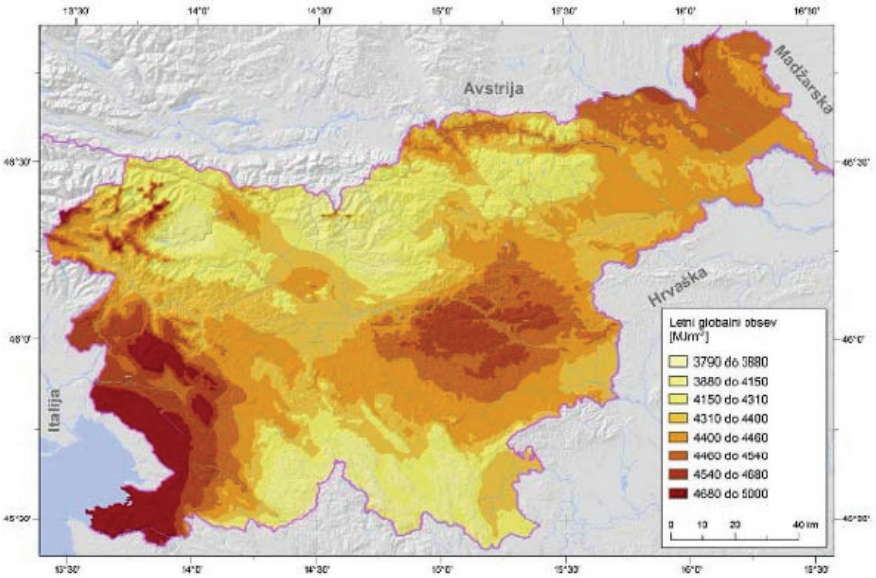


Figure 7. Potential of solar energy in Slovenia

2.3.1. Examples of Solar Energy Storage Technologies in Slovenia

In the next pages some examples of solar energy use in Slovenia are presented. Most of them are collected in the frame of EU funded project Solarge [11].

2.3.1.1. Hotel Delfin, Izola, 140 sqm | 90 kW_{th} | 2001

In year 2001 the hotel was renovated. Roof was sloped before, is now flat and supports four fields of solar collectors, which are designed exclusively for heating of salt water in internal and external swimming pools. The heat storages have integrated tube heat exchangers and they are connected to the compensation pool, where fresh sea water is added and disinfected. Storage volume is 15 m^3.



Figure 8. Photos of solar system in Izola

2.3.1.2. Dom starejših občanov Preddvor, 144 sqm | 100 kW_{th} | 1990/2000

Elderly home Preddvor is home of 190 guests, mainly pensioners and disable peoples. There are two residential buildings, an older one (1860) and a newer one, built in 1990. The buildings are well maintained, still not thermal insulated. Since 2003 the buildings are heated by biomass district heating plant. Storage volume is 8.4 m^3.



Figure 9. Photos of solar system in Preddvor

2.3.1.3. TermeČatež / Hotel Žusterna, Koper, 600 sqm | 420 kW_{th} | 2001

The solar system is built at hotel Zusterna at the seaside. It is used for heating of the outdoor swimming pool and was installed during the renovation in 2001. The whole roof of an indoor swimming pool is used as solar roof with unglazed solar collectors. The costs of the solar collector were only 40.2 € m^{-2} because only additional costs for stainless steel piping and pump was paid. Storage volume is 2 m^3.



Figure 10. Photos of solar system in Žusterna

2.3.1.6. Research project- PCM solar wall

A facade construction designed for storing the heat of solar radiation falling on the absorber plate with PCM was developed in the Laboratory for Heating, Sanitary and Solar Technology at the Faculty for Mechanical Engineering in Ljubljana [12]. The wall consists of six main components. The wall construction operates on the following principles. Short-wave solar radiation passes through glass with TIM (Transparent Insulation Material) (1,2) which at the same time prevents convective and short-wave radiation heat transfer. Black paraffin wax (3) in a transparent plastic casing made of polycarbonate absorbs and stores energy mostly as latent heat. The air for the house ventilation is heated in the air channel (4) and is led into the room. Insulation (5) and plaster (6) are standard elements in the room.

3. CONCLUSIONS

For efficient utilization of solar energy, compact and cost-effective storage systems with high energy storage density are essential. There is an urgent need to exploit the solar energy to meet the growing energy demand and to sustain the life on earth. Solar energy is abundant in Turkey and in Slovenia, but current applications are limited to solar domestic hot water utilization. R&D on other solar applications is increasing in recent years. Once solar systems are mass produced like conventional, fossil energy

systems, and integrated into buildings, thus replacing conventional systems they will become competitive. A corrective pricing mechanism, such as a carbon tax, will also help competitiveness.

REFERENCES

[1] H.Ö. Paksoy, Thermal Energy Storage Technologies for Solar Applications, Solar Future 2010 Conference, Istanbul, Turkey, 11-12 February, 2010.
[2] S. Sharma, K. Sagara, Latent Heat Storage Materials and Systems: A Review, International Journal of Green Energy. (2010) 1-56.
[3] M. M. Farid, A. M. Khudhair, S. A. Razack, S. Al-Hallaj, A review on phase change energy storage: materials and applications. Energy Conversion and Management , (2004) 1597-1615.
[4] General Directorate of Electrical Power Recourses Survey and DevelopmentAdministration of Turkey home page (www.eie.gov.tr).
[5] Energy Policies of IEA Countries – Turkey 2009 Review, International Energy Agency Publications, OECD/IEA, Paris, 2010.
[6] W. Weiss, F.Mauthner, Solar Heat Worlwide – Markets and Contribution to Energy Supply in 2009, International Energy Agency Solar Heating and Cooling Program, 2011.
[7] http://www.yenienerji.info.
[8] Y. Konuklu, H. Ö. Paksoy, Phase Change Material Sandwich Panels for Managing Solar Gain in Buildings, J. Sol. Energy Eng. Volume 131, Issue 4, 041012, 2009.
[9] B. Turgut, H. Ö. Paksoy, S. Bozdağ, H. Evliya, H. Y. Dasgan, K. Abak, D. Dikici, Aquifer Thermal Energy Storage for Greenhouse Climatization CLIMA 2010. Antalya, Turkey, Congress May 9-12, 2010.
[10] D. Kastelec, J.Rakovec, K. Zakšek, Solar energy in Slovenia, SAZU 2007.
[11] http://www.solarge.org/index.php.
[12] U. Stritih, Heat transfer enhancement in latent heat thermal storage system for buildings, Energy and buildings 35 (2003) 1097 – 1104.

PESTICIDE ROOT ZONE MODEL FOR AGRICULTURAL SOILS

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Abstract

A one-dimensional Pesticide root zone model (PRZM) approximated by the method of lines and finite-differences that accounts for pesticide fate in the crop root zone is applied. PRZM model investigates effects of distribution of rainfall and water evapotranspiration, water convection and diffusion in soil as well as pesticide biodegradation within and immediately below the plant root zone. The model is given by coupled second order partial differential convection-dispersion equation and biodegradation with time-variable boundary conditions.

Adsorption/desorption studies are very useful for providing essential information on the mobility of pesticides and their distribution in the soil, water and air. Adsorption data can also be used for comparative and modelling purposes. The objective of this research was to determine the parameters of non-linear adsorption isotherms (Freundlich, Langmuir and Temkin) for atrazine by fitting the adsorption experimental data to the isotherm models and implementation of Freundlich isotherm in PRZM model in order to simulate atrazine dissipation in the corn field from Slavonski Brod (Croatia).
Keywords: *pesticide root zone model (PRZM), atrazine, adsorption isotherm*

1. INTRODUCTION

Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] is *s*-triazine herbicide widely used in crop production. The fate and behaviour of this herbicide in agricultural soils are influenced by various physico-chemical and biological processes, including sorption dynamics, degradation, plant uptake, volatilization, surface runoff and leaching [1]. Transport of pesticides through the unsaturated zone of soils is mainly controlled by biodegradation and sorption kinetics. Pesticide mineralization or degradation kinetics in soils is described in pesticide transport models including a first-order approach, e.g. HYDRUS model, PESTRAS model, PRZM model [2-6].

A one-dimensional Pesticide root zone model (PRZM) is applied as a research or a management tool which allows dynamic simulations of pesticide fate in the crop root zone. PRZM includes modelling of phenomena as microbial transformation, water transport through soil layers, irrigation, simulation of soil temperature distribution, volatilization and vapour phase transport in soils [6].

Sorption dynamics is one of the major environmental factors that determine the fate of a pesticide in soils and its potential for leaching and biodegradation [7]. The most important soil parameters for studying the adsorption/desorption processes are organic matter content, organic carbon content, clay content, soil texture and pH for ionisable compounds [8]. Freundlich, Langmuir and Temkin adsorption isotherms are often used to describe the overall sorption characteristics of a particular soil at equilibrium, in an investigated pesticide concentration range [9].

The aim of this research was determination of parameters for Freundlich, Langmuir and Temkin atrazine adsorption isotherms in corn field on location in Slavonski Brod and to simulate dissipation behaviour of atrazine by applying PRZM model.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Chemicals

Technical atrazine (97.4 % purity; Herbos, Croatia) was used for adsorption experiments. All chemicals used for HPLC analysis were of analytical grade. Pure atrazine (99 %) was purchased as standard of Pestanal quality from Riedel-de Haën, Sigma-Aldrich, Seelze, Germany.

2.1.2. Soil

Soil samples that have not been previously treated with atrazine (0-30 cm layer) were collected from corn field in Slavonski Brod (Croatia). Physical and chemical characteristics of the soil are presented in Table 1. Soil was homogenized, air-dried at room temperature and milled.

Table 1. Physical and chemical characteristics of corn field soil in Slavonski Brod

soil	clay, %	silt, %	sand, /%	organic matter content, %	organic carbon, %	organic nitrogen %	pH
Slavonski Brod	18.0	74.2	7.8	3.69	1.25	0.29	5.62

2.1.3. Adsorption Experiments

The atrazine adsorption on soil from corn field in Slavonski Brod was determined using the standard equilibrium method according to the OECD guideline 106 [8]. Soil samples (2 g) were mixed with 10 mL of 0.01 mol L^{-1} $CaCl_2$ solution containing atrazine at concentrations of 0.5, 1, 3, 6 and 9 mg L^{-1}.

The samples were shaken (200 rpm) for 16 hours in order to establish equilibrium and then centrifuged at 15300 rpm for 10 minutes. The atrazine concentration remaining in the supernatant at equilibrium was determined using HPLC technique. Blank and control samples were prepared on the same way without atrazine and soil. The amount of atrazine adsorbed on soil particles (μg g^{-1}) was calculated as the difference between the initial atrazine concentration in the solution (μg mL^{-1}) and the atrazine concentration remaining in the supernatant at equilibrium (μg mL^{-1}).

For determination of atrazine adsorption parameters, Freundlich, Langmuir and Temkin adsorption isotherm models were used.

Freundlich isotherm is used to describe heterogeneous system [11], equation (1):

$$q_e = K_f \cdot C_e^{1/n} \quad (1)$$

where:

q_e – amount of adsorbed atrazine per unit mass of sorbent (soil), μg g^{-1}
C_e – atrazine concentration remaining in the solution at equilibrium, μg mL^{-1}
K_f – the Freundlich adsorption constant which represents soil adsorption capacity, μg $^{1-1/n}$ $(mL)^{1/n}$ g^{-1}
n – Freundlich constant, indicates how favourable the adsorption process is.

In case of $n = 1$, K_f is defined as K_d (mL g^{-1}), atrazine partition (distribution) coefficient.

Langmuir isotherm is based on the assumption that maximum atrazine adsorption corresponds to a saturated monolayer of atrazine molecules on the soil surface with no interaction between the sorbed molecules [11], equation (2):

$$q_e = q_{max} \cdot b \cdot C_e/(1 + b \cdot C_e) \quad (2)$$

where:

q_{max} – maximum amount of atrazine per unit mass of sorbent (soil), μg g^{-1}
b – constant related to the affinity between the atrazine and soil, mL μg^{-1}

Temkin isotherm is generally given in the following form [11], equation (3):

$$q_e = B \cdot \ln(A \cdot C_e) \quad (3)$$

where:

A – Temkin isotherm constant, mL μg^{-1}
B – $B = RT/b$, where b is the Temkin isotherm constant related to sorption heat, J mol^{-1}
R – gas constant, 8.314 J K^{-1} mol^{-1}
T – temperature, K

Parameters of Freundlich (K_f, n), Langmuir (q_{max}, b) and Temkin (A, B) isotherms were evaluated using the linearized form of the given models. Atrazine partition (distribution) coefficient K_d is calculated from the expression equation (4):

$$K_d = m_{ads} \cdot V_0/m_R \cdot m_{soil} \quad (4)$$

where:

m_{ads} – mass of adsorbed atrazine, μg
m_R – mass of atrazine in the solution at adsorption equilibrium, μg
m_{soil} – mass of the soil, expressed in dry mass of soil, g.
V_0 –initial volume of 0.01 mol L^{-1} $CaCl_2$ solution containing five different atrazine concentrations, mL

2.1.4. HPLC Analysis

For the determination of atrazine concentration (initial and equilibrium), high performance liquid chromatography (HPLC) method is applied. Analysis was performed on a Varian Prostar system (Model 230, USA) and UV diode array detector (UV DAD) (Varian, Prostar 335, Australia). The chromatographic column was Luna C_{18} (5 ěm, 250 x 4.6 mm, Phenomenex, UK) with quard column C_{18} 4 x 3mm I.D. (Phenomenex, UK). The solvents were acetonitrile and 10 mmol L^{-1} phosphate buffer (pH 7) with mobile phase flow rate 1 mL min^{-1}.

Atrazine was identified by its retention time and UV spectrum which was compared to the known standard

2.1.5. PRZM Model

PRZM model accounts for rainfall distribution, plant evapotranspiration, pesticide flux, pesticide biodegradation and water table flux (Fig. 1).

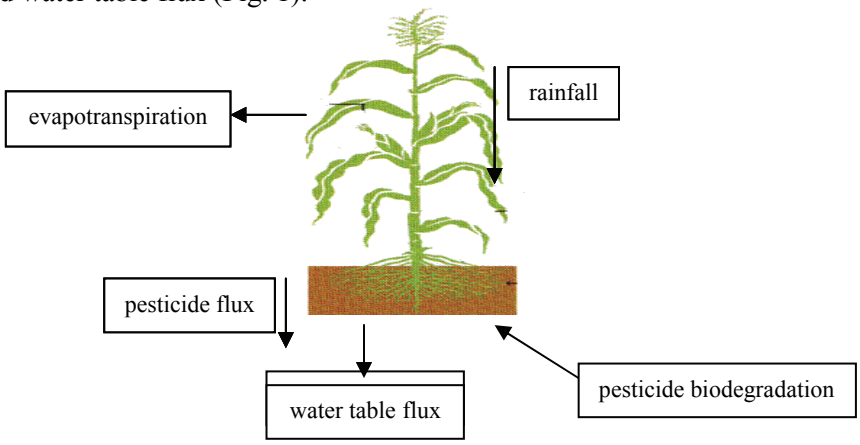


Figure 1. Schematic diagram of PRZM (pesticide root zone model) and the main transport fluxes

PRZM is complemented with partial differential convection-dispersion equation to model the pesticide transport and water influx due to rainfall [2], equation (6):

$$R \cdot \partial C_P/\partial t = D_{ef} \cdot \partial^2 C_P/\partial x^2 - v(t) \cdot \partial C_P/\partial x + (1/\theta) \cdot \partial C_{P,total}/\partial t_{deg} \quad (5)$$

where:

C_P – pesticide concentration in liquid phase, mg L^{-1}_{liq}
t – time, days (d), hours (h)
R – pesticide retention or retardation factor
D_{ef} – dispersion coefficient, m^2 d^{-1}
x – distance, m
v – averaged water-pore velocity, m d^{-1}
θ – liquid phase fraction, (L_{liq} L^{-1}_{total})
$C_{p,total}$ – pesticide concentration in solid and liquid phase
$\partial C_{P,total}/\partial t_{deg}$ – change of the total pesticide concentration due to degradation

Retention or retardation factor is given by [2] equation (6):

$$R = 1 + \rho_b \cdot K_d/\theta \quad (6)$$

where ρ_b is the soil bulk density, kg L^{-1}.

Degradation by microbial culture is given with equation. (7) [10]:

$$dC_P/dt = - k_{PX} \cdot \gamma_X \cdot C_P/(C_P + K_P) - k_P \cdot C_P \quad (7)$$

where:

k_{PX} – reaction rate constant which refers to the conversion of pesticide P and concentration of microbial biomass γ_X, mmol g^{-1} h^{-1}
γ_X – microbial biomass concentration, g L^{-1}
K_P – biocatalytic saturation constant which refers to pesticide P, mmol L^{-1}
k_P – reaction rate constant which refers to the physical conversion of pesticide P, h^{-1}.

Growth and decay of microbial culture is given by the expression [10], equation (8):

$$d\gamma_X/dt = \mu_{Xm} \cdot \gamma_X \cdot (1 - \gamma_X/\gamma_{Xm}) \cdot C_P/(C_P + K_{ag}) - k_d \cdot \gamma_X \quad (8)$$

where:

μ_{Xm} – maximum specific biomass growth rate, h^{-1}
γ_{Xm} – theoretical maximum of microbial biomass concentration, g L^{-1}
K_{ag} – biocatalytic saturation constant of biomass growth referring to pesticide P, mmol L^{-1}
k_d – biomass decay rate, h^{-1}

The soil dispersion parameters are taken from literature [2]. Degradation parameters are taken from [10]. PRZM balance equation (eq. 5) was integrated by the method of lines with finite differences using software WR *Mathematica* 6.0. For simulation purposes, the integration region from 0–0.3 m (soil layer depth from corn field in Slavonski Brod) was divided into three depths (0.003; 0.15; 0.3 m) and simulated during 50 days after atrazine applications at three arbitrary dosage levels (1.5; 3; 4.5 L ha^{-1} with atrazine concentration 0.5 kg L^{-1}) with assumed constant temperature of 25 ºC. Calculated value for atrazine partition (distribution) coefficient is included in eq. 6 to calculate the retention (retardation) factor.

2.2. Results and Discussion

The adsorption models are investigated experimentally in atrazine equilibrium concentration range from 0.5-9 μg mL^{-1}. The relationship between the amount of adsorbed atrazine (q/μg g^{-1}) and atrazine concentration at equilibrium (c_f/μg mL^{-1}) is presented in Fig. 2. These experimental data are approximated with three theoretical adsorption models (Freundlich, Langmuir, Temkin) and the model parameters are estimated from linearized form of these models using Least Square Method available in *Excel* 2007 (Table 2).

Table 2. Parameters of Freundlich, Langmuir and Temkin adsorption isotherm models

Soil	Freundlich isotherm		Langmuir isotherm		Temkin isotherm	
	K_f/μg$^{1-1/n}$ (mL)$^{1/n}$ g^{-1}	n	q_{max}/μg g^{-1}	b/mL μg^{-1}	A/mL μg^{-1}	B
Slavonski Brod	1.57	1.12	21.32	0.084	3.33	2.35

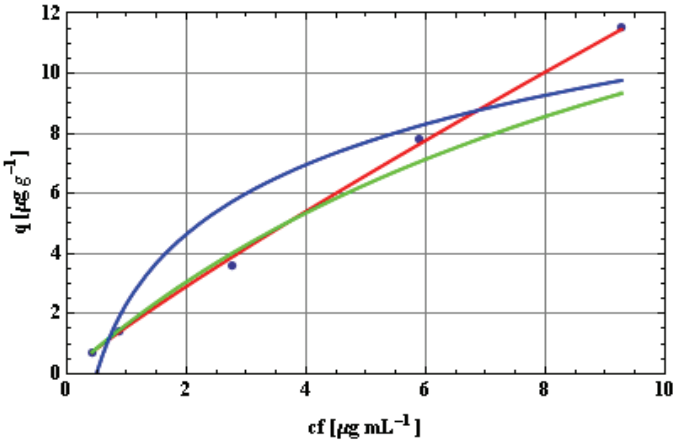


Figure 2. Comparison between experimental data and modelled adsorption isotherms for atrazine in corn field soil at location of Slavonski Brod. (•) experimental values, (—) Freundlich isotherm, (—) Langmuir isotherm, (—)Temkin isotherm.

To resolve which of the model is the most suited, SSE (sum of squares errors) between experimental values of adsorbed atrazine and the predicted values are evaluated. It was found that standard errors for Langmuir and Temkin (0.593; 1.675 μg g^{-1}) are for an order of magnitude larger than Freundlich (0.086 μg g^{-1}). Atrazine partition (distribution) coefficient, K_d, is calculated based on eq. (4) and the mean of five K_d values (1.6 mL g^{-1}) is applied in PRZM model (eq. 6) in order to evaluate atrazine dissipation in the Slavonski Brod corn field. Inlet conditions for PRZM model are given by the rainfall distribution (Fig. 3) measured at the same location provided by Meteorological and Hydrological Institute of Croatia [12].

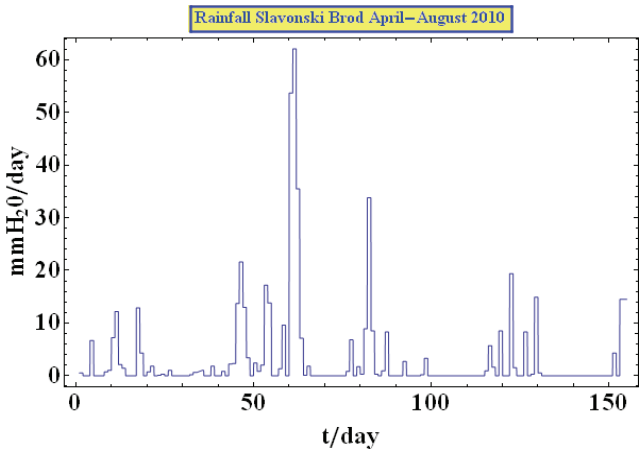


Figure 3. Rainfall distribution in a corn field near Slavonski Brod during 2010

According to the simulation results (Fig. 4) it can be concluded that atrazine dissipated efficiently in the top soil depth (0.003 m) with range of half-life constants from 2 to 4 days, which is significantly lower, compared to available literature data for untreated soils. The effects of atrazine diffusion and convection are also shown in soil depth. At half depth (0.15 m) atrazine concentration reaches maximum values after 55 days at significantly lower concentrations (4–10 μg L^{-1}) also showing the significant effect of atrazine application concentration. At the depth of 0.3 m the breakthrough curve appears after 45 days and shows an increase in concentration from 0.0004 to 0.0012 μg L^{-1} which is 3-fold lower compared to half depth.

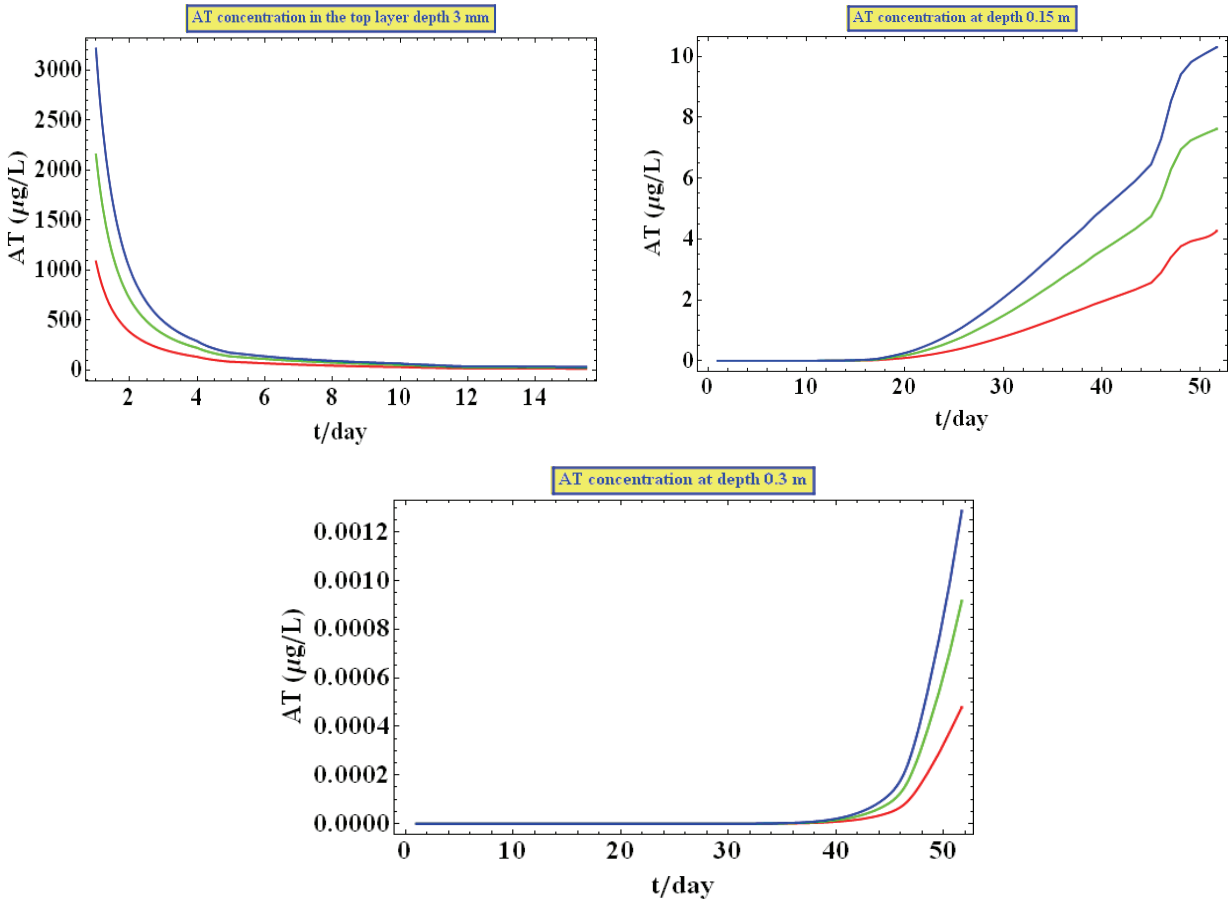


Figure 4. Simulations of transient atrazine concentrations through the soil depth (0.003; 0.15; 0.3 m) in the Slavonski Brod corn field ((—) 1.5 L ha^{-1} of applied atrazine, (—) 3 L ha^{-1} of applied atrazine, (—) 4.5 L ha^{-1} of applied atrazine)

3. CONCLUSIONS

The adsorption studies confirmed Freundlich isotherm to be the best model for description of atrazine adsorption in agricultural soil with standard error 0.086 μg g^{-1}.

Freundlich adsorption isotherm is implemented in evaluation of the dispersion effects such as retention factor, effective diffusivity and water-pore velocity which is a part of dispersion phenomena included in PRZM model.

By applying PRZM, soil pesticide mobility, dissipation and its persistence can be estimated and included in soil management

REFERENCES

[1] M. Arias-Estévez, B. Soto-González, E. López-Periago, B. Cancho-Grande, J. Simal-Gándara, Atrazine Sorption Dynamics in Acid-Surface Soils, Bull. Environ. Contam. Toxicol. 75 (2005) 264–271.

[2] K. Cheyns, J. Mertens, J. Diels, E. Smolders, D. Springael, Monod kinetics rather than a first-order degradation model explains atrazine fate in soil mini-columns: Implications for pesticide fate modelling, Environ. Pollut. 158 (2010) 1405–1411.

[3] J. Simunek, M.T. Van Genuchten, M. Sejna, 2005. The HYDRUS-1D Software Package for Simulating the One-dimensional Movement of Water, Heat and Multiple Solutes in Variably-saturated Media, Version 4.05. Department of Environmental Sciences, University of California Riverside, Riverside, California, USA.

[4] A. Tiktak, A.M.A. van der Linden, F. Swartjes, 1994. Pestras: A One Dimensional Model for Assessing Leaching and Accumulation of Pesticides in soil. RIVM report 715501003, Bilthoven the Netherlands

[5] I.G. Dubus, S. Beulke, C.D. Brown, B. Gottesburen, A. Dieses, Inverse modelling for estimating sorption and degradation parameters for pesticides, Pest Manage. Sci. 60 (2004) 859–874.

[6] L.A. Suárez, PRZM-3 Model, EPA/600/R-05/111 (2005).

[7] I.D. Kovaios, C.A. Paraskeva, P.G. Koutsoukos, A.Ch. Payatakes, Adsorption of atrazine on soils: Model study, J. Colloid Interface Sci. 299 (2006) 88–94.

[8] OECD Guideline for the Testing of Chemicals, Adsorption-Desorption Using a Batch Equilibrium Method, 2006, http://www.oecd.org/dataoecd/9/11/33663321.pdf

[9] M. Dehghani, S. Nasseri, S. Amin, K. Naddafi, M. Taghavi, M. Yunosian, N. Maleki, Atrazine adsorption desorption behavior in Darehasaluie Kavar corn field soil in Fars Province of Iran, Iran J. Environ. Health. Sci. Eng. 2 (2005) 221-228.

[10] M. Bošnjak, N. Udiković Kolić, I. Petrić, D. Cihlar, D. Hršak, Integrated approach to mathematical modelling of atrazine degradation in different reaction systems, Food Technol. Biotechnol. 48 (2010) 392–403.

[11] B.H. Hameed, J.M. Salman, A.L. Ahmad, Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones, J. Hazard. Mater. 163 (2009) 121-126.

[12] http://meteo.hr/index.php

THE ASSESSMENT OF CHOSEN TOOLS TO SOIL PROTECTION

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Abstract

The project aimed to test the effectiveness of policy instruments for protection of agricultural land. The aim is to define the main factors of degradation of agricultural land. The project deals with the status of guidelines for the protection of agricultural land and analyzes the critical points of its protection in relation to the application of policy instruments according to the individual components of government and executive authorities. A guide for finding connections to the application of land resources protection policies was knowledge from studies and our own research of knowledge identified mainly find out on a questionnaire drawn up for different interest groups in relation to agricultural land. Land consolidation and GAEC were analyzed deeply as two selected policy instruments. Questionnaires conclusions provide an overview, what kind of tools were set for soil protection, how they work, if there is obtain some feedback and evaluation tools. The project results are proposals to improve soil conservation policies and the way of their promotion and experience obtain in the area of policies evaluation in the CR.

Keywords*: policy cycle, agriculture land protection, policy instruments*

1. INTRODUCTION

The policy of land resources protection is slowly getting to the front of government and general public interest. The cause of interest for land can be sought particularly in soil eco-services, which plays an important role for its production and ecological functions. The protection of land resources should definitely be addressed in wider connections with links to the instruments of the Common Agricultural Policy of EU. The protection of agricultural land is one of the most complex political and legal issues, thanks to the large number of stakeholders, often their different interests and a necessity to build social consensus approach to agricultural land.

The key role in the implementation of soil policy has a proper value of soil, that doesn´t rest only on a current economic value, but also on prediction of land value in the future and creation of public goods, which can also be understood as a specific easement in legal relations.

The research question of this task was aimed at assessing of the degree of policy instruments effectiveness to protect agricultural land in CR. Soil conservation has also gaps in the European Union, such as the absence of regulation in force, focused exclusively on the protection of agricultural land. Draft Framework Directive on soil protection has been discussed for years, but not agreed. The character of soil protection at European level is highly fragmented and consists mainly in the downward pressure on the intensity of farming.

The national legislative in the CR as a result of harmonization follows the European framework of protection as the mandatory minimum level of protection. There are many direct and indirect instruments for land protection that can be generally classified into groups of regulatory, incentive or other instruments. The aim was to prepare an analysis of soil protection policy's implementation of in the Czech Republic.

Prescriptive policy [1, 2] describes a theory of rules, emphasizing the importance of legitimacy attributed to the rules for conditional efficiency that the measure is implemented with.

2. ELABORATION

2.1. Theoretical Overview

The survey was done in the CR and targeted at a central and a regional level. The central level was represented by Ministry of Agriculture, Central Land Office and Payment Agency of CR. The regional level was represented by landscaping designers, consultants, regional agencies.

2.1.1. Typology of Public Policy Tools

Public policy tools that can influence changes in the external environment have relatively wide spectrum and can be classified in several ways. One possibility is cutting tools stimulatory and restrictive. Another division is using a tool to direct (e.g. investment grants to companies expanding in problem regions, the provision of state contracts, etc.). Indirect instruments are changing the business and socio-economic climate in selected regions, e.g. by investments into social infrastructure, supporting institutions, increasing education, in the typology of policy instruments based on a study of the theory of political economy [1] and other available literature [2, 3, 4].

Categories used in the study were published in a study SoCo project [2], it is following overview:

- Mandatory instruments
- Incentive-based measures
- Awareness raising measures
- Private initiatives

There have been described in more detail, namely tools Land consolidation and GAEC in the article.

Land consolidation is implementing to improve landscape water regime and soil erosion protection. Making design landscaping is the intersection of the interests of landowners, public interest and other legitimate right or interests defended in the cadastral territory.

GAEC is a part of the cross-compliance, that was accepted on 1st January 2009, between years 2010 and 2011 leads to the gradual expansion. GAEC 2 is focused to water erosion [6, 7] and it is the subject of a detailed survey. GAEC 2 was extended in 2011 to slightly vulnerable soil erosion, it is necessary to observe a technology in soil-crop cultivation in wide rows.

Evaluation of policy instruments was performed by analysis of available literature. Conclusions from literary sources were supplemented by an investigation into the interviews with specialists at a central regional and a local level. A questionnaire should answer the question, "What are the causes of inefficiency of soil protection and why it cannot remove it?" The analytical framework of the research was the policy cycle, going from problem identification, through design instruments to the implementation, evaluation and the feedback. The questions in the questionnaire contain mainly open questions, where respondents have enough space to express themselves. The questionnaire is structured in four parts: identifying the problem and conditions, the draft policy instruments, implementation and management tools, evaluation and feedback of policy instruments. The answers of respondents with quantifiable data were summarized in a table list, the open answers are used as source for conclusions or answers are used as direct quotations.

Work package:

A. To identify all the important types of soil degradation, including sealing

B. To identify existing policy instruments that can reduce soil degradation

C. Assign each type of degradation corresponding to the existing policy instruments

D. Choose one key type of degradation and a corresponding policy instrument

E. Data collection through an interview

F. Evaluation of survey data and a conclusion

G. Proposals for a change in policy

2.2. Results

Most respondents were from regional offices from Land office and an agency´s level, interviews were held face to face.

2.2.1. To Identify all the Important Types of Soil Degradation

2.2.1.1. Soil Sealing

Land decreases accelerate significantly in the last 15 years, now it is about 15 ha per day. Losses of agricultural land are mostly of high quality soils and irreversible [5].

2.2.1.2. Water Erosion

Water erosion is caused by the destructive activities of raindrops, surface runoff, followed by loose soil particles transported by surface runoff. The intensity of water erosion is due to the nature of precipitation and surface runoff, soil conditions, the morphology (slope, length and shape of slopes), vegetation conditions and the wy land use, including use agro-technologies. The extent of water erosion in the CR was 1780 thousand ha, it is 42% of agricultural land.

2.2.1.3. Wind Erosion

There are dry and warm climate areas mostly at risk; it represents 23 % of agricultural land in the CR.

2.2.1.4. Decline in Organic Mater

The disposals soil organic matter occurs when losses exceed inputs of organic matter. There are two reasons, lack of application of manure and compost on the field and inappropriate crop rotations with a lack of humus-producing crops leading to degradation of the soil's nutrient reserves.

2.2.1.5. Soil Compaction

Use of heavy machinery in wet weather conditions or on saturated fields causes soil compaction. Soil compaction decreases transformation and restoration capabilities soil reduces the efficiency of sanitation. The compaction of soil in some cases associated with increased mobility of hazardous substances as a result of acidification (acidification).

Table 1. Overview of policy instruments to protect the soil and the type of instrument

Policy instrument	legislation	type
Law on Soil Protection	334/1992.	MI
Decree of ME* on Soil protection	13/1994	MI
National implementation of the Nitrates Directive	103/2003	MI
National implementation Water Framework Directive	254/2001	MI
Law on Protection of Nature and Landscape	114/1992	MI
Law on environment	17/1992	MI
Law on fertiliser	156/1998	MI
Sewage Sludge Directive	SMR 3	MI
Building act	183/2006	MI
National Environment Monitoring System, established under the Law for Preservation of Environment	Prom. SG.91/25 2002	MI
Law on Forest	289/1995	MI
Law on Land Consolidation and on Land Settlement Boards	139/2002 and 309/2002	MI
GAEC 1,2	Cross Compliance	MI
GAEC 3,4	Cross Compliance	MI
GAEC 5	Cross Compliance	MI
GAEC 6,7,8,9	Cross Compliance	MI
GAEC 10	Cross Compliance	MI
Less Favoured Area and N2000*	RDP*** axis II	IM
Agri-environment schemes, organic farming	RDP axis II	MI
Agri-environment schemes, care of meadows and pastures	RDP axis II	MI
Agri-environment schemes, care of landscape	RDP axis II	MI
Land consolidation	RDP axis I	MI
Initiatives and projects	Interreg, aj.	MI
Advisory system	Organize by MoA****	MI
Public opinion		ARM
Leader	RDP axis IV	ARM

Source: own investigations,

* ME – Ministry of Environment,** Natura 2000, *** Rural development plan 2007-2013, **** MoA – Ministry of Agriculture

2.2.1.6. Loss of Soil Biodiversity

Soil biodiversity is defined as the variability among living organisms in soil and the ecological complexes of which they are a part. It includes diversity within species, between species and ecosystems.

2.2.1.7. Acidification

The process of acidification is associated with soil compaction. It is a very slow degradation process, where the natural processes of acidification increased human activity (limiting calcium). Causes of acidification produce excesses of nitrogen in soil, acid precipitation, in limiting the cultivation of legumes, limiting the application of calcium fertilizers, etc.

2.2.1.8. Contamination

Human activities lead to undesirable enrichment of soils with various substances, especially risk elements (heavy metals) and organic pollutants. Risk elements are usually a problem of old chemical factories and storages. Organic pollutants are a problem of hygiene soil since the widespread use of herbicides, insecticides and other synthetic and natural organic substances in industry and agriculture.

2.2.1.9. Soil Salinity

Causes of soil salinity are application of excessive volumes of mineral fertilisers or dry areas.

2.2.1.10. Landslide and Flooding

Landslide and flooding are frequent type of degradation in the Czech Republic. Cause the slope and soil profile properties. Although so far there has been no catastrophic scale in the Czech Republic has recorded thousands of local landslides. Risk to the landslide slope is usually more than 22.

2.2.2. To identify Existing Policy Instruments that Can Reduce Soil Degradation

Mandatory instruments (MI), Incentive-based measures (IM) and awareness raising measures (ARM) are shown in Table 1, private initiatives were not included in this investigation.

2.2.3. Assign to Each Type of Degradation Corresponding to the Existing Policy Instruments

Degradation processes in agricultural soils were evaluated by a group of experts, depending on how effective is on the scale:

0 - the tool does not solve the degradation
1 - degradation of marginal utility solves
2 - tool is partly focused on the degradation
3 – tool is mainly focused on the degradation

The most effective focus on protecting land is in the area of hazardous materials contamination. Instruments incentive and awareness is primarily devoted to GAEC 1.2, it is soil erosion and the effectiveness of other instruments to protect the soil is low. Completely inadequate protection of soil loss in the area - sealing. Only the public interest in some cases can be the only actor to prevent construction on a green field site (industrial zone). None of degradation was identified as effectively protected by some type of tools. Results of expert´s assessment are given in Table 2.

Table 2. Summary evaluation of the effectiveness of policy instruments to protect soil against degradation

Degradation	MI	IM	ARM
Soil sealing	0.35	0.43	1.00
Water erosion	0.71	1.43	0.5
Wind erosion	0.35	1. 00	1.00
Decline in organic mater	0.29	0.57	0
Compaction	0.24	0.57	0.5
Loss of soil biodiversity	0.47	0.71	0
Contamination	0.76	0.86	0.5
Landslide and flooding	0.41	0.71	0.5
Soil salinity	0.29	0.14	0

Source: own investigations,
MI - Mandatory instruments, IM - Incentive-based measures, ARM - Awareness raising measures

Respondents answered in the questionnaire at the question: "How do you judge significance and extent of these types of degradation?" The results are in Table 3.

Table 3. Summary assessment of soil degradation load in CR (*last decades*)

Respondents	1	2	3	4	5	6	7	8	9	10	11	12	13	average
Soil sealing	5	5	3	5	5	4	5	3.5	4.5	5	3.5	5	2.75	4.33
Water erosion	4	4	4	4	4	3.5	4.5	3.5	2.75	3	2.5	3	3.25	3.54
Wind erosion	3	3	2	3	4	1	2.5	0	0	3	1	3	1.75	2.10
Decline in organic mater	4	4	0		4	3	3	3	3.25	2.75	4	3	2.5	3.32
Compaction	4	4		3	3	3	2.5	2	2	2.25	3	3	2.25	2.83
Loss of soil biodiversity	3	3	4	2	4	2	3	2	0	2.75	4	2.5	2.5	2.67
acidification	0	3	0	0	2	2	2.5	0	1	2	2	2.5	2	1.90
contamination	0	2			2	2	2	1.5	2.5	2	1	1.5	3	1.95
Landslide and flooding	3	3	4	2	3	3	2	3.5	1.75	2.5	3	3	2.5	2.79
Soil salinity	1	1		1	2	1	1	1	2	0	2	1.5	2	1.29

Source: own investigations

Sealing is usually an irreversible loss, but a government in the the CR no protect efficiently and effectively ruins national wealth - land. Respondents stated that we are losing natural resources and too often we build on a green field and there is no use of brown fields. In addition, there has been a very negative trend of increasing soil degradation and water erosion identified by reduction of organics in the soil. Both of this degradation also closely correlated together, because by reducing the proportion of soil organic matter there is increasing a soil susceptibility to water and wind erosion.

2.2.4. Choose one Key Type of Degradation and Corresponding Policy Instrument

Key type of degradation was chosen as a water erosion, because it is expressively influenced by agricultural activities. Two policy instruments have been chosen, the first of them is a land consolidation, because it was identified by experts as the most effective for more types of degradation and the second is GAEC 2, because it is specialized on water erosion.

2.2.5. Data Collection through Interview

Data collection has started in July 2011 until today. The interviews will be completed in October 2011. The partial results show that there are serious gaps and barriers to protect soil. The most problems are in policy evaluation and effective feedback.

2.2.5.1. Policy Formulation

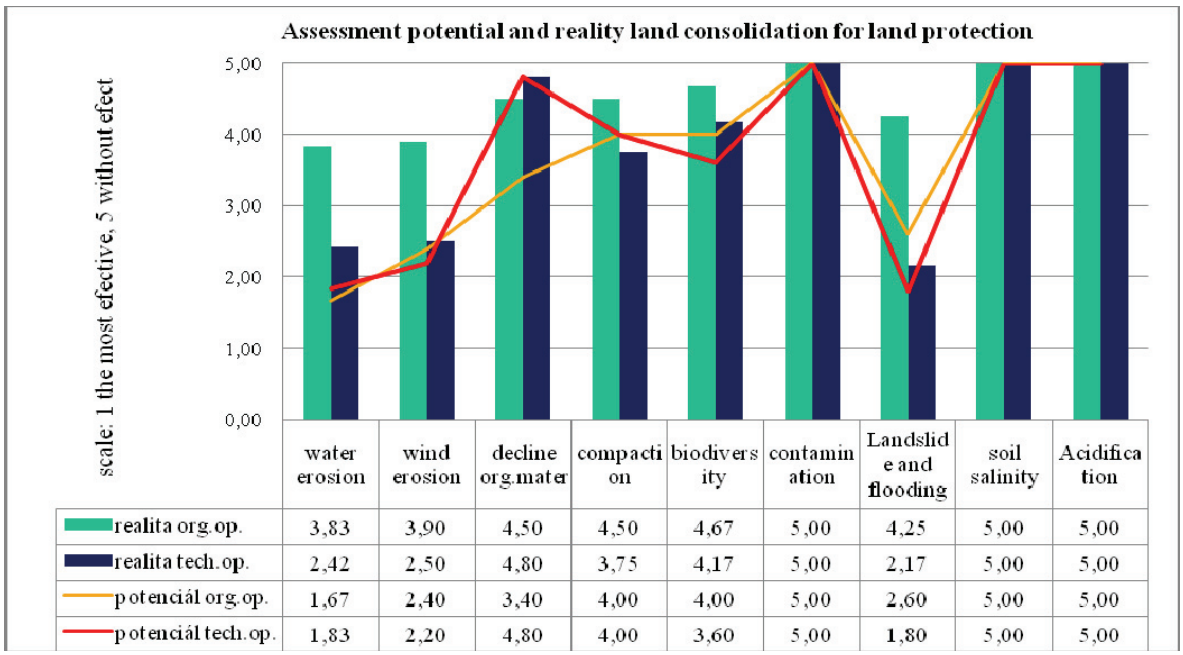
Policy proposals have been based on adequate knowledge of the impact of agriculture on soil degradation from existing studies, surveys and experience of those actors who prepared the policy and it continues to be governed. Experience shows the most frequent erosion: water and wind erosion. In other areas, lower level of understanding. There are prepared, organized and methodically prepared specialists (especially engineers and staff of Land Offices) for correct targeting land consolidation guidelines. Barriers were identified pressures caused by the most intense and uncontrolled sale of state land, which makes it difficult to enforce the plans of common facilities (including measures to protect the land). The results are given in Fig 1. The investigation confirmed that the realization of technical measures has a high efficiency. Organizational measures (agricultural engineering, grassing, etc.) have high efficiency, but they are not implemented. The organizational arrangements are considered potentially more effective against erosion.

2.2.5.2. Proposal of Policy Instrument

Land consolidation

Communication among the various actors in designing measures took a form of written materials, a commented version of the proposals; it was possible to a limited extent, to enter into proposals for organized workshops and working meetings. Feedback was limited to gathering information about number of old and new parcels and so on. Regional and local workers were not informed about their comments.

Ministry of Agriculture published (2010) "Technical standard document of common facilities plan in land consolidation" [8], where they are ready to change. During 2011 is possible to discuss this material on an open platform. The plan of common facilities is proposed in only one cadastral area. The interests of soil conservation have political boundaries; it is the reason why some measures are not implemented.



	water erosion	wind erosion	decline org.mater	compacti on	biodivers ity	contamin ation	Landslid e and flooding	soil salinity	Acidifica tion
realita org.op.	3,83	3,90	4,50	4,50	4,67	5,00	4,25	5,00	5,00
realita tech.op.	2,42	2,50	4,80	3,75	4,17	5,00	2,17	5,00	5,00
potenciál org.op.	1,67	2,40	3,40	4,00	4,00	5,00	2,60	5,00	5,00
potenciál tech.op.	1,83	2,20	4,80	4,00	3,60	5,00	1,80	5,00	5,00

Source: own investigations

Figure 1. Assessing of the potential and reality of common facilities plan in land consolidation, which can affect soil conservation

GAEC2 erosion measure

There is an advantage -a very good process mapping of soil erosion. Definition of areas threatened by erosion conducted easily, but a problem was how to promote more complicated measures and principles to practice. Complicated managements were replaced by simple and less effective. The implementation was difficult, there were a lot of appeal in farmers, but all have been processed. It has been well managed in the e.g. complaints out mistakes in LPIS was about 70 % of unjustified complaints. On the other side, there was no evaluation of the GAEC on vulnerable land, it was not quantified and published an economic impact to an economy farm. Consultants were not well involved in the implementation process. The implementation process ran quickly for farmers, there was a lot of new information.

2.2.6. Evaluation of Survey Data and Conclusion

2.2.6.1. Land Consolidation

Respondents said that mainly helps them the process designers of soil conservation by helpful communication with good explanation requirement to protect land and landscape. Support for Mayor and Land Authority is also very important. Cooperation in community and a public opinion play an important role for farmers. Most respondents said they feel the chaos in agricultural policy that does not motivate farmers to protect the soil (high reduction in livestock, commodity prices, changing the rules). Good users achieved good economic results in the LFA with a simple or 3-4 rotations crops. State policy does not lead to diversity of agricultural production, varied the cropping pattern with legumes. A very critical view was recorded on the method and the extent of state land sales. Another barrier mentioned by respondents was the lack of monitoring. Nobody knows what happens with common facilities after implementation, i.e. how the owner cares about them and maintain in good condition. Most of the new common facilities (roads, trees in line, green belts) require continuous maintenance. The new owner (municipalities) often does not manage enough money in thier budget.

2.2.6.2. GAEC2 Erosion Measure

Negotiations were intensive and very difficult. The working group gave proposals for the Monitoring Committee. The ground of the study was an expert attitude of research institutes and professional practice. Finally there was found a compromise, but it was not easy. The main response was to focus to

the practical implementation of proposed measures. The problems consisted mainly of the feasibility of proposed technology.

2.2.6.3. Policy assessment

The weakest of the political cycle is a policy evaluation. There is not set a transparent assessment of effects and impacts of soil policy at present time. Land consolidation is a multi-targeted, reorganizing of ownership, elimination of deficiencies in the land. Monitoring is focused more to the details of the ownership relations than on soil-effects. GAEC is introduced the first year, it is too early to make impact assessment, but it seems that preparations for the evaluation will be more in depth. The idea is that the results of the function of instruments used to adjust the policy and the policy cycle has been closed.

3. CONCLUSIONS

Preliminary conclusions of the work are follows: The rapid sale of state land to prevent state land in the country by implemented measures within the landscaping. Active Land authorities have drawn up plans for a land protection process with functional criteria of landscape. The landscape plan for the soil and water protection should be drawn for the whole area of the CR and should have mandatory conditions for a regional level and funding. One of the results of such plan must be a reserve of state land for soil conservation, flood protection and water retention in the landscape.

A recommendation for soil protection policy is to provide funds for the after care of new built facilities (roads, polders, ditches, etc.). Financial support would help municipalities and owners to realize maintenance and bring the benefit for surrounding society.

It is necessary to establish a monitoring and evaluation in terms of impact assessments for the protection of soil and landscape.

The final conclusions of the study will be conducted after the conclusion of the survey and final evaluation. To prepare proposals for changes in policy instruments will be a workshop and group work.

REFERENCES

[1] B. G. Peters J. Pierre, Handbook of public policy, University of Melbourne, 2006.

[2] SoCo Project Team, Joint Research Centre – Institute for Prospective Technological Studies, *Final report on the project 'Sustainable Agriculture and Soil Conservation (SoCo*), Luxembourg: Office for Official Publications of the European Communities, 2009, ISSN 1018-5593, ISBN 978-92-79-12400.

[3] E. Ostrom, Understanding Institutional Diversity. Princeton, NJ, USA: Princeton University Press, 2005.

[4] Winter a May (Winter SC, May PJ.. Motivation for Compliance with Environmental Regulations. Journal of Policy Analysis and Management 20(4): 675–698.) 2001

[5] J. Vopravil, Vývoj A Degradace Půd V Podmínkách Očekávaných Změn Klimatu, 2010.

[6] Nařízení vlády NV 479/2009

[7] http://eagri.cz/public/web/mze/dotace/kontroly-podminenosti-cross-compliance/dokumenty-ke-stazeni/rok-2011/rok-2011-1.html

[8] L.Střítecký et al., Technický standard v plánu společných zařízení v pozemkových úpravách, Vydává: Ministerstvo zemědělství – Ústřední pozemkový úřad, Těšnov 17, 117 05 Praha 1, Č.j. 10749/2010-13300

PROBLEMS OF THE DEVELOPMENT OF SUSTAINABLE FORESTRY AND MAINTAINING SOIL FERTILITY IN LITHUANIAN SEA-SHORE REGION

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Abstract

Forests cover about 35 % of terrestrial area of Lithuania. Every year forested land increased by 0.2 % on the average during the last 70 years. However due to the political-administrational and economic changes of that period, the management of the forested landscapes became an important and difficult task nowadays. Numerous small owners cannot guarantee a long-term use of their property because of lack of motivation, knowledge and skills, which impedes the harmonious development of forestry. Another obstacle is the primitive understanding of biodiversity, even among the professional foresters. That was inherited from the traditional forestry, which for many years of the 20th century was orientated towards the economic benefits mostly.

Forests were grown in about 138,000 ha in the Sea-shore region in 2009 making 26.5 % of total area. One national and three regional parks with special environment protection regime are located in this region. Sea-shore region distinguishes among other regions by one of the least area under the forest coverage and comparatively larger part of less fertile soils in Lithuania. About 52.4 % of forest land is managed by the state, but the private forest area increases from year to year. The increase is mostly fulfilled by the afforestation of less favoured land abandoned from the agricultural sector: that makes about 42,000 ha or 8.1 % of the total Sea-shore region area. Soils in this region vary from the almost neutral to the strongly acid Luvisols, Albeluvisols, Dystric, Fluvisols and Gleysols. The soil fertility is less than average in Lithuania due to the specific conditions: increased precipitation level and leaching of nutrients, lowlands, high ground water table and dominating of substrate with light textural composition. In order to maintain more sustainable forestry sector and soil fertility, some territories have to be afforested from 5 % to 20 % and more dependently on the area of abandoned land. The overall task for Sea-shore region is to reach 34 % of the total forest land area. The completion of land reform, new directions of wood industry sector development and climate change are among the other problems and challenges to be adapted and/or fulfilled in near future.

Keywords: *sustainable management, forested land**, s**oil fertility, abandoned land, afforestation*

1. INTRODUCTION

In EU until now there is no uniform forestry management model. Most of the studies are focused on either the ecological, economic or social aspects of the forest management, but also its important to integrate these into a decision-making process aimed at achieving sustainability of forest management [1-3]. Thus in such situation national models are developed according to the local conditions, existing traditions and general trends of EU forestry development. Lithuania is still in the search for ways to optimize its forestry management by looking for solutions to the dilemma of public-private forests ratio and to expediency of structural reforms of existing forestry districts [3]. Different ownership of forests has some advantages and disadvantages. The not fulfilled yet Land reform is one more obstacle [3, 4]. The objective of this work is to reveal the most important problems that impede the attempts of the developing sustainable forestry in Lithuania nowadays, with focus on the environmentally sensitive Sea-shore region with lower than average area under the forest cover and less fertile soils as compared with other regions of Lithuania.

2. ELABORATION

2.1. Materials and Methods

Statistical data on the forested land at the municipality and forest enterprises levels was obtained from the State land registry forest inventory and National forest inventory databases [5,6]. Cartographic GIS method („ArcView GIS 3.2a“ program) was used to analyze spatial differences in the distribution

of area of forest land, both already covered and planned to be afforested. Supplemental data on the protected areas and resources as well as public opinion on forest resources management was obtained from the materials of Lithuanian Statistical department, Ministry of Environment and Lithuanian Institute of Forestry [4-7]. Data on soil fertility was obtained from the State Land Foundation (previuosly Lithuanian Institute of Land Use and Survey) [8]

2.1.1. Theory and/or Calculation

There are numerous scientific publications on the theme of sustainable development and management of natural resources, including the forest: most of them are with both theoretical and practical research background. In Lithuania some guidance and principles of optimized spatial development of forests were described and suggested rather early, in the eighties of 20th century [9]. Further the schemas and ideas of this complex study were developed and supplemented with new content, but still are actual nowadays. The main spatial axes – urban and nature frames, as recreation or conservation belts are the integrated components of sustainable spatial structure of Lithuania regions. But prerequisite for it is that regional policy making could be organized by constructive, conservative and temperate scenarios [9]. Thus, for more sustainable balance between cultural/human ecosystems and more natural ecosystems there is a need not only to increase the forested land area in the country, but also to reach more even its spatial distribution in certain localities. The land abandoned from agricultural sector (usually less favored) is one of the options to reuse it for afforestation purposes. Areas of such land were calculated on the neighborhood level in each municipality of Sea-shore region using National Statistical and State Land Foundation data from 2005. In total 7 municipalities and 35 neighborhoods were analyzed in the region. Data on the forested land area was obtained from 2005, 2009 and 2010, thus they reflect the recent situation, but in order to describe the changes in time-scale and to forecast situation in near future, the trend from 1938 till 2020 was calculated.

2.2. Results and Discussion

2.2.1. Tasks and Problems of Development towards Sustainable Forestry

Sustainable forest policy goals in Lithuania are described in the Forest Law, Forest Policy, Implementation Strategy, and the summarized version of these tasks is presented in the Fig. 1.

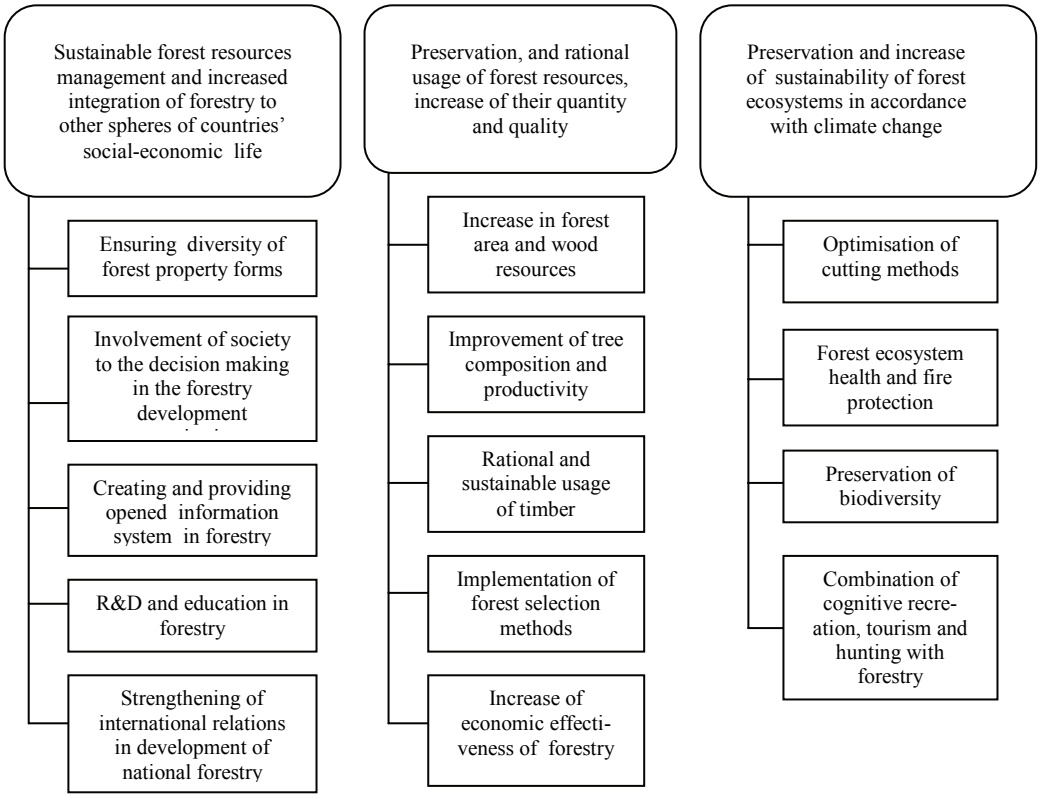


Figure 1. The summarized objectives and tasks for sustainable forestry development in Lithuania [6-8]

One of the objectives is to "establish a legal framework for the forest management in all types of forest ownership, based on common principles of sustainable development" [7]. But in the practice there

are many obstacles to reach these tasks. The largest obstacle is related to the not-yet completed Land reform and its consequences after the changes of Lithuania political system in year 1990 up to now (Fig. 2).

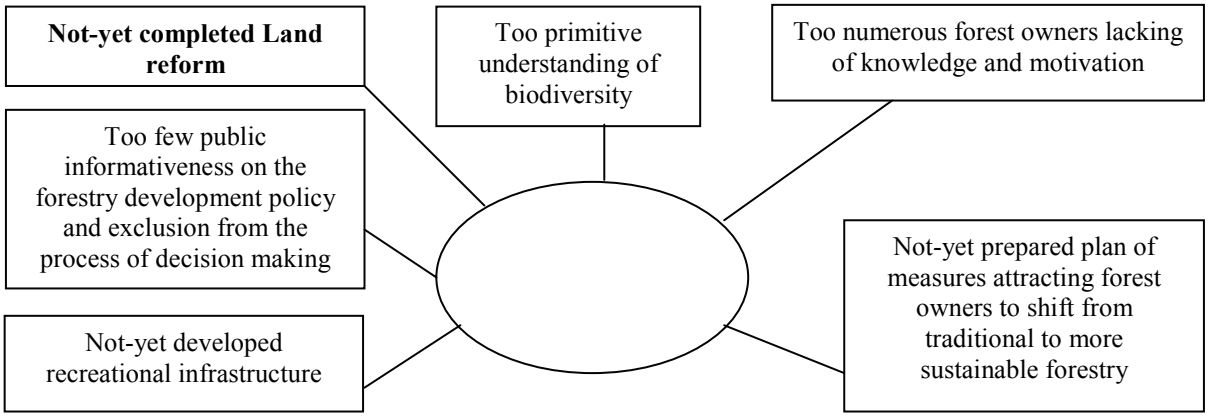


Figure 2. Recent problems of sustainable development of forestry in Lithuania as indicated in available sources of information [3,4,7,11]

Recently about 52.4 % of forest land is managed by the state, but the private forest area still increases from year to year. There were more than 250,000 of private forest owners with 829,4 thous. ha of forest land (with average 3.3 ha forest size) in Lithuania in 2010 [6]. They are spread in all the municipalities, but mostly concentrated in the eastern part of Lithuania. From year 2000 different education courses started to be organized for those owners, who have not professional background in forestry [3]. But as surveys showed, still large percentage of them are lacking of basic knowledge, and thus are not motivated to do essential changes in forest management. Additionally, the primitive understanding of biodiversity is dominating even among the professional foresters. To improve the situation, a transition toward adaptive learning and participatory governance as a means of facilitating conservation efforts is proposed [11].

According to the results of social inquiry of population, fulfilled by the Institute of Forestry in 2003 and 2006 [4], there are many problems of development more sustainable forestry in Lithuania. The main of them, as mentioned in the answers of respondents, are: 1). too large cuttings, particularly in the private forests; 2). afforestation is not enough qualitative; 3). in many places not-yet developed recreational infrastructure. In general, more active and motivated to get knowledge on forest development policy and principles were older respondents, than younger. There was difference in distribution of answers from survey in 2003 and 2006 on the question, which are managing better, private owners or state forest enterprises: in 2003 majority of respondents considered that these are state enterprises, and in 2006 – those private owners. The both surveys revealed, that people are not informed enough neither about the forestry development plans and policy, nor involved in the decision making process. Thus it is evident, that in order to make the principles of sustainable management understandable to all whom it might concern, there is a need for better prepared educational system and measures in sustainable forestry, with implemented demonstration areas, where different owners, stakeholders, state foresters, scientists and public representatives could work together using participatory research and learning methods (Fig. 2). New directions of wood industry sector development and climate change are among the other problems and challenges to be adapted and/or fulfilled in near future.

2.2.2. Changes in the forest cover

Forests covered about 35 % of terrestrial area of Lithuania or 33.1 % of the total area in 2010 [6]. Though forested land decreased after the World War II as compared with 1938, later, during the last 70 years, it was increasing by 0.2 % every year on the average (Fig. 3).

The common trend of forested land area in Lithuania shows the increase in 2020 till about 34-35 %.

The total area of Sea-shore region (previous Klaipėda county territory) occupies 5746 km^2. Forest land extended in about 138,000 ha in 2009 making 26.5 % of region's area. At the same time, the country's average reached 32.9 % in 2009, thus the more sustainable development of Sea-shore region needs first of all to extend the forested land area here, much more than in other regions of Lithuania (Fig. 4).

One of the new approaches to analyse the spatial consequences on forest of Klaipėda county was the modelling of spatio-temporal forest cover changes by remote sensing, between 1986 (just before the end

of Soviet Union) and 2005. Measures and analysis of forest land cover changes in the Klaipėda county were made by the use of different spatial and geographical data: satellites images (from 1986 and 2001) and airborne color photography (from 2005). The results of remote sensing methods showed that forest area in Klaipėda district increased from 20.5 % in 1986 to 23.9 % in 2005 [12]. These results were close to those obtained at the Statistical department.

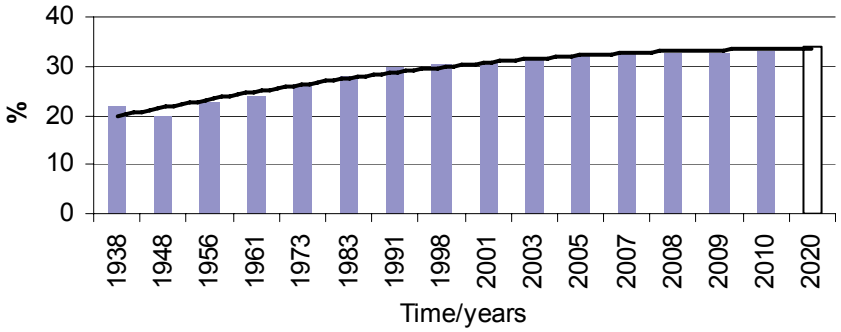


Figure 3. Changes in the forest land area (in % of total area) in Lithuania from 1938 to 2010 with trend and forecasted area for the year 2020.

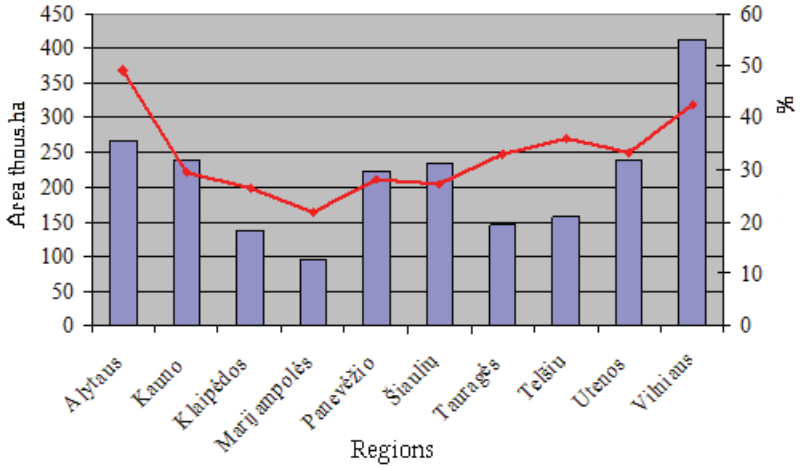


Figure 4. Forested land area in Lithuania counties/regions, in % and thous.ha in 2009 [5]

How the forested land was distributed within the municipalities of Sea-shore region from 2004 to 2009, it is demonstrated in the Table 1.

The least forested land area is characteristic to Skuodas district municipality due to the more developed traditional agriculture here and the most forested – to Neringa municipality, the area of this is extending entirely within the territory of Kuršių Nerija National park. There was no increase in forested land area from 2006 to 2009 in all regions, and this is disadvantage, because Sea-shore region is one with the least forested area in Lithuania.

Besides this, three regional parks with special environment protection regime are located in the Sea-shore region. Total protected area in the region makes 135,282 thousands ha or 26.0 % of total area: this is higher than Lithuania average (15.0 %). The overall task for Sea-shore region, according to the National forest development programme [7] is to reach 34 % of the total forest land area till 2025.

Table 1. Changes in the forested land area of Sea-shore region in % on the municipalities level in 2004-2009 [5].

Year	Municipalities							
	Klaipėda urban	Klaipėda district	Kretinga district	Neringa	Palanga urban	Skuodas district	Šilutė district	Weighted average in total region
2004	16.3	23.8	33.1	84.1	39.9	15.4	22.1	24.7
2005	20.5	25.9	34.4	84.1	40.1	19.5	22.3	26.3
2006	20.6	26.0	34.6	84.1	39.9	19.8	22.3	26.5
2007	20.6	26.0	34.6	84.1	39.9	19.8	22.3	26.5
2008	20.6	26.0	34.6	84.1	39.9	19.8	22.3	26.5
2009	20.6	26.0	34.6	84.1	39.9	19.8	22.3	26.5

2.2.3. Soils and their fertility

The parent materials of soils in Lithuania vary in the age and genesis, the most common being Quaternary deposits of Glacial origin. These deposits support a great variety of soils and a complicated soil cover in Lithuania. Preliminary estimates show that Albeluvisols occupy 30 % of the country, Luvisols 27 %, Cambisols 13%, Arenosols 12%, Podzols 11%, mainly in forest areas, and Gleysols and Histosols 5.3% in the depressions [13]. Gleyic Albeluvisols and some Dystric soils which are formed on materials low in carbonate and deeply leached loamy deposits, predominate in Western Lithuania, in the Sea-shore region. Soils here vary from the almost neutral to the strongly acid Luvisols, Albeluvisols, Fluvisols, Arenosols and Gleysols. Lithuanian soils are classified on the basis of fertility scoring of utilised agricultural area. The soil map prepared by the specialists of State Land Foundation, demonstrating average fertility scoring of the utilized agricultural area in the municipalities, is shown in Fig. 5 [14].

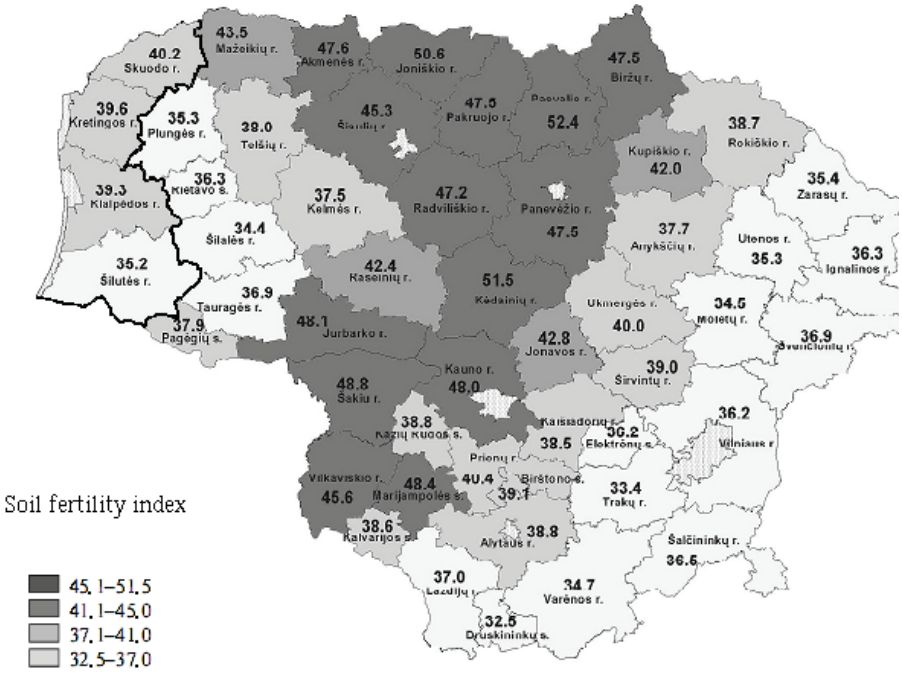


Figure 5. Distribution of soil fertility scoring in Lithuania' municipalities (Sea-shore region marked with bold boundary line) [8].

The given figures show that fertility scoring of utilized agricultural area in the counties varies between 32.7 and 44.8. The utilized agricultural area of most counties (except that of Utena) has average fertility rate (in general, such fertility scoring is between 34 and 45). There is no utilized agricultural area in Lithuania with very high fertility scoring, and fertility scoring of Utena county utilized agricultural area is slightly lower than the average. The soil fertility in Sea–shore region is less than average in Lithuania due to the specific conditions: increased precipitation level and leaching of nutrients, low relief, high ground water table and textural composition of substrate (Fig. 5). Particularly low fertility is characteristic to the soils of Šilutė district municipality, where the lighter soil texture is widely spread.

According to the National forest development program till 2025 [7], there are about 42,000 ha of less favored soil with fertility score 32 and less in the Sea-shore region: this area could be firstly used for the afforestation (Table 2).

The largest areas of less favoured land are characteristic to Šilutė district municipality (17732 ha) and the least – to Kretinga district municipality (5513 ha), thus the largest potential of afforestation can be planned in Šilutė district municipality, where the recent forest land could increase by 9.3%

Table 2. The areas of less favoured agricultural land in the municipalities of Sea-shore region (in ha and % of total agricultural land area) [7,8]

Municipality	Agricultural land in ha	Less favoured agricultural land area in ha and % of total agricultural land area	
Klaipėda district	71825	10137	14.1
Kretinga district	50764	5513	10.9
Skuodas district	63183	8633	13.7
Šilutė district	118558	17732	15.0
Total	304328	42015	13.8

2.2.4. Potential of the forest land development

While solving questions of land management in large scale the forest planning problem is tough necessarily, especially the problem of forest cover enlargement. According to geoqualimetry methods and obtained results at Vilnius University [15], from sustainable development point of view forest cover enlargement is the most topical in Vilkaviškis, Šilutė, Radviliškis, Joniškis, Kelmė, Pasvalys, Tauragė, Pakruojis, Marijampolė districts. One of the mentioned districts – Šilutė district municipality – is located in the south of Sea-shore region, where agricultural landscapes and flat relief of Nemunas river delta is extending. The potential afforestation was estimated on the neighbourhood level of each municipality in accordance to the area of less favoured and abandoned agricultural land of Sea-shore region (Fig. 6). The map shows, that the greater concentration of such a land characteristic to the neighborhoods of Šilutė and Klaipėda district municipalities, thus the afforestation here has the higher potential.

There is one more reason, why its important to increase forested area in the traditional agricultural landscape with light soil texture soils, like in Šilutė district municipality: the possibility to decrease soil deflation. The geoecological impact of forest to the nearby landscapes is considered to be extended till about 250 m from the forest line towards the neighboring landscapes [16]. This impact first of all is reflected in the changes of microclimate (wind, humidity, temperature, and precipitation and evaporation regime) and different soil properties, such as soil pH, organic matter content, soil density, hydrological properties, etc. [17]. There are positive and negative aspects of this impact from the point of view of agricultural farming. But the positive impact, directly related to the reduced soil deflation and water erosion, is particularly important for the agricultural landscape with light soil texture domination.

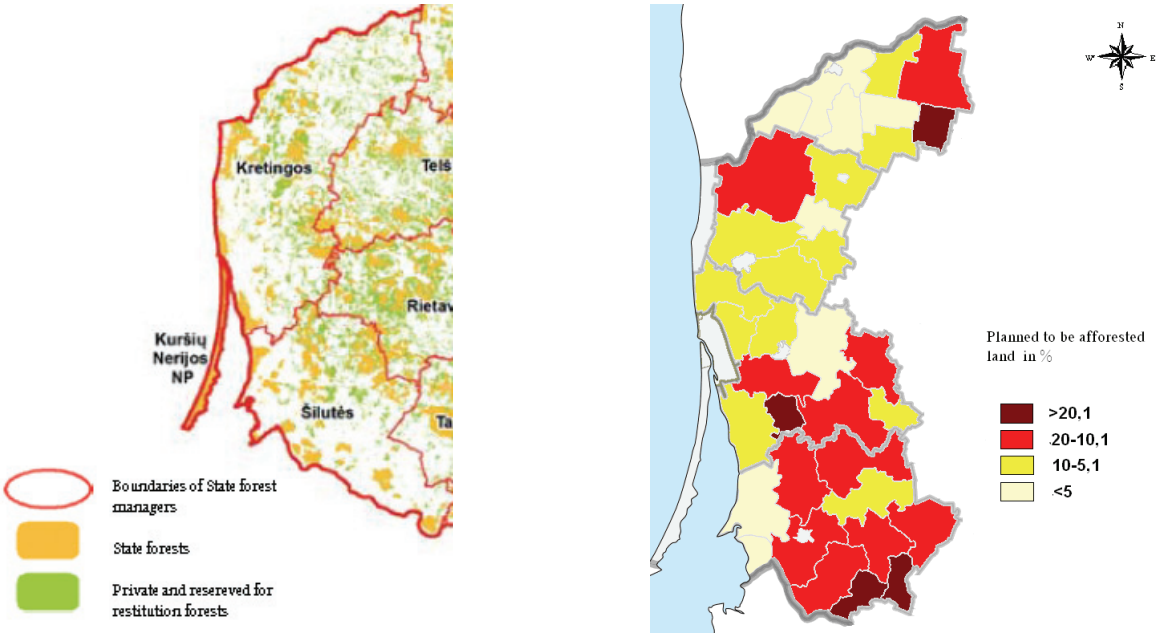


Figure 6. Recent forest land distribution within Kretingos and Šilutės State forest enterprises and Kuršių Nerijos National Park (NP) (left) [6] and the planned to be afforested land areas in the neighborhoods of Sea-shore region in % until 2020 (right).

3. CONCLUSIONS

After analysing of results above, few conclusions might be drawn:
1. Among the problems of more sustainable forestry development in Lithuania, one of the main is not-yet completed Land reform and its consequences.
2. Nowadays there is a need for better prepared educational system and measures in sustainable forestry in Lithuania, with implemented demonstration areas, where owners, stakeholders, state foresters, scientists and public representatives could work together using participatory research and learning methods.
3. Soils in the municipalities of Sea-shore region are less fertile as Lithuania average, thus in order to maintain them, the afforestation in less favoured or abandoned from agricultural sector land is an essential measure to optimize and sustain more diverse landscapes.
4. In order to increase forested land area in the Sea-shore region, the higher afforestation untill 2020 is planned in the neighbourhoods of Šilutė and Klaipėda district municipalities, where the largest areas of less favoured or abandoned from agricultural sector land are located. Afforestation could be implemented within agricultural landscapes with lighter soil texture in order to reduce soil deflation and water erosion.

REFERENCES

[1] E.Rametsteinera, M.Simula, Forest certification—an instrument to promote sustainable forest management? Journal of Environmental Management 67 (2003) 87–98.
[2] V.K. Varma, I.Ferguson, I.Wild, Decision support system for the sustainable forest management, Forest Ecology and Management 128 (2000) 49-55.
[3] V.Domarkas, A. Varapnickas, Miškininkystės vystymo Europos Sąjungoje tendencijos ir Lietuvos miškų ūkio valdymo aktualijos, Viešoji politika ir administravimas, 16 (2006) 41-56.
[4] N.Kupstaitis, S.Tumidaj, Ką mano visuomenė apie Lietuvos ir Europos miškus? Baltijos miškai ir mediena (2006) gruodis, Aplinkos ministerijos Miškų departamentas; http://www.medis.lt/bmm-straipsnis.cfm?id=617.
[5] Aplinkos Ministerija. Lietuvos miškų ūkio statistika (2009) www.amvmt.lt/images/veikla/stat/miskustatistika/ 2009

[6] Lithuanian forest map, Forest cadastre of the Republic of Lithuania (2010) www.amvmt.lt/images/veikla/stat/miskustatistika/2010/
[7] Nacionalinė miškų ūkio plėtros programa iki 2025 m., Aplinkos ministerija /projektas/ http://www.am.lt/VI/files/0.687588001296461465.pdf
[8] VĮ Valstybės Žemės Fondas, http://www.vzf.lt/Apie-mus-677.html
[9] P.Kavaliauskas, N.Rilys, Lietuvos TSR kompleksinė gamtos apsaugos schema laikotarpiui iki 2000 metų, Žinija, Vilnius, 1988.
[10] P.Kavaliauskas**,** A concept of sustainable development for regional land use planning: Lithuanian experience, Technological and Economic Development of Economy 14 1 (2008) 51–63.
[11] M. Lazdinis, P. Angelstam, I .Lazdinis, Maintenance of Forest Biodiversity in a Post-Soviet Governance Model: Perceptions by Local Actors in Lithuania, Environmental Management 40 (2007) 20-33. DOI: 10.1007/s00267-005-0387-8
[12] S.Gadal, J.Lekavičiūtė, Remote sensing processing consequences of political and economical changes on Klaipėda county forests (1986-2005), Human resources – the main factor of regional development, Journal of Social sciences, Klaipėda university, Klaipėda 4 (2011) (in press)
[13] V.V.Buivydaite, Soil survey and available soil data in Lithuania, in: R.J.A.Jones, B.Hauškova, P.Bullok and L.Montanarella (Eds.), Soil resources of Europe, second edition, European Soil Bureau Research Report 9, Office for Official Publications of the European Communities, Luxembuorg, 2005, pp. 207-224.
[14] Report of the Republic of Lithuania in accordance with the requirements of Article 19(2) of the Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC; http://www.19_2_lithuania_en.pdf
[15] R.Žalkauskas, P.Kavaliauskas, Motivation of forest cover enlargement topicality in respect to sustainable development, Miškininkystė 2 56 (2004) 21–38.
[16] A.Dilys, D.Pivoriūnas, Vakarų Lietuvos miškų geoekologinio poveikio charakteristika, Geografijos metraštis 31 (1998) 309–317.
[17] A.Buciene, Impact of forest on the crop yield and soil agrochemical properties, in: Windbreaks and Agroforestry, International Symposium, Hedeselskabet, Denmark, Viborg, 1993, pp. 218-220.

NITRATE REMOVAL IN THE CONTINUOUS-FLOW STIRRED REACTOR

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Abstract

The presence of excess nitrate in natural water resources is determined and therefore the EU water legislation set a Nitrates directive to reduce and prevent water pollution. As a result, the new methods for nitrate removal are studied and the use of attached bacterial cells was investigated for effective nitrate removal. The main objective of the present study was the use of acclimated bacterial cells that were interacted with natural powdered clinoptilolite and the resulting biozeolite particles (B-NPC) were applied in the continuous-flow stirred reactor for establishing stable and efficient nitrate removal from the surface water (SW). The nitrate removal was monitored in the first set of experiments at different dilution rates (0.027, 0.043, 0.095, 0.429, and 0.755 1/h) in order to achieve the optimal dilution rate. In the first test set, nitrate ions were found in the effluent only at dilution rates of 0.429 and 0.755 1/h. The removal of 100 mg NO_3^--N/L from the SW with B-NPC (9% w/w) was monitored during 21 days and complete and efficient removal was achieved at pH of 7-8 and 20-25 °C. Finally, the use of B-NPC in the continuous-flow stirred reactor was demonstrated as an efficient method for nitrate removal from the surface water.

Keywords: *Clinoptilolite, Continuous-flow stirred reactor, Denitrification, Mixed bacterial culture, Nitrite accumulation*

1. INTRODUCTION

The nitrogen (N) containing compounds are an increasingly important global issue as N flowing through ecosystems has multiple impacts on terrestrial, aquatic and atmospheric environments [1,2]. In agricultural areas, the excess N can leach to groundwater and ultimately enter surface waters through different discharges like under-field tile drainage and ditches or the discharge of shallow groundwater to surface waters. Therefore, many land management approaches have been proposed to reduce N losses, such as improved efficiency of N use, managing N inputs through soil tests, land management plans and controlled drainage [3,4]. Integrating wetland and riparian buffers into the agricultural landscape have also been demonstrated as a potentially useful way to reduce N losses to surface waters [5], but different methods for permanent removal of nitrate and nitrite are still being investigated [6-9]. Low-cost and simple technologies are needed to reduce nitrogen due to its well known harmful impacts. For example, an excess of N in the aquatic environment could lead to many environmental problems including acidification of freshwater bodies, eutrophication and associated hypoxic zones, adverse health effects for aquatic organisms and production of greenhouse gas such as N_2O [10]. Furthermore, high nitrate concentrations in drinking water can also be hazardous to human health. In acid conditions in the stomach (digestive system), the nitrite ions formed from nitrate ions may cause the appearance of cancers, through the formation of nitrosamines or nitrosamides [11]. The presence of nitrite ions can also be the cause of the methaemoglobinemia (or blue baby disease) for newborn infants, which corresponds to the loss of the oxygen-carrying ability of haemoglobin [12].

The most widely understood process of permanent nitrate removal is heterotrophic denitrification, in which microorganisms converts nitrate (NO_3^-) to N gases using a carbon (C) source as the electron donor and for growth [13,14]. This process was mostly studied in different reactors usually named denitrifying bioreactors. Denitrifying bioreactors are reactors that contain microbes and carbon substrates which are added into the contaminated water to serve as a C and energy source for supporting the microbial growth and the conversion of nitrate to nitrogen gases. At the microbial scale, the rate of heterotrophic denitrification is generally controlled by concentrations of oxygen (O_2), nitrate and nitrite and C [15]. The availability of a degradable organic C source to drive denitrification becomes critical where nitrate is present in excess. Present organic C promotes denitrification; firstly, by providing an anoxic environment through the oxidation of organic compounds and, secondly, by acting as an electron donor. In water

treatment systems, this C source could be part of the water stream, but also could be supplemented as liquid C sources such as acetate, ethanol or methanol [16,17]. Furthermore, the presence or addition of phosphate salts in the SW could improve reactor performance in water treatment systems [18].

The use of different bioreactors is broadly studied and among them the use of free dispersed cells could cause problems in the operation of bioreactors due to the blockage of flow lines and clogging of filters, while separation of biomass from the treated effluents, is beset with technical difficulties, rendering the treatment procedure cost-prohibitive [19]. This has led to an increase of interest in the entrapment of microbial cells as immobilized preparations. Some studies have therefore, investigated microorganisms immobilized in hydrogels such as carrageenans and ca-alginates, in order to improve denitrification and achieve efficient nitrate removal [20-23]. But several disadvantages associated with gel entrapment include limitations in the rate of diffusion, insufficient mechanical strength leading to breakage of gels and dispersal of biomass, lack of open spaces for cell growth, and prohibitive cost of application [24,25]. These difficulties can be overcome by immobilizing the microbial biomass within the highly porous and strong matrix, such as different polymer granules or natural materials like zeolites [20]. The zeolite as naturally occurring porous aluminosilicate minerals has a large specific surface area and cation exchange capacity [8,26-28]. Their abundance and low cost in many regions together with their mechanical strength makes them favourable for application in many different processes which are applied in order to remove pollutants and improve water quality. The modified zeolite was recently investigated for removal of nitrate from water through adsorption or ion exchange and as a fertilizer carrier to control nitrate release [6,8, 27-29]. Additionally the interaction of zeolite and microorganisms were applied for phosphate removal [30]. Therefore, the use of clinoptilolite-rich zeolite as support material for bacterial growth seems to be promising for heterotrophic denitrification and removal of nitrate from water.

In the present paper the previously adapted microbial culture interacted with natural zeolite and the resulting biozeolite particles were used for investigation of nitrate removal in the continuous-flow stirred bioreactor. To investigate denitrification in the continuous-flow stirred bioreactor the selected $MeOH/NO_3$-N value was applied and a simplified kinetic analysis was performed for quantitative comparison of nitrate degradation and methanol consumption. At first, different dilution rates (D) were investigated and then in the second set of experiments, the efficiency and stability of the process were monitored for 22 days. During the last part of the second set of experiments, the raw surface water was used (without addition of phosphate salts) in order to determine the impact of phosphate addition on microbial community functions and the denitrification performance.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Microorganisms, Zeolite and Surface Water Solution

Microorganisms originated from the active sludge of the wastewater treatment plant Anamet, Savski Marof, Croatia and the agricultural soil sample (Lastovo, Croatia). The active sludge (100 mL) and 50 g of the soil were mixed and filtered (blue band filter). The obtained biomass was washed twice, diluted to 50 mL with the SW solution, and used in the acclimation tests and then for nitrate removal in a batch denitrification study [31]. The acclimated mixed bacterial culture was refrigerated at 4 °C and stored until use.

The zeolite used in the study was a natural powdered clinoptilolite (NPC), obtained from the Zlatokop deposit in Vranjska Banja, Serbia. The NPC was washed with redistilled water in order to remove the surface dust, dried at 105 °C for 24 h and grain size fractions smaller than 0.063 mm were used for interaction with the mixed bacterial culture.

The prepared SW solution consisted of K_2HPO_4, (2.5 g/L) and KH_2PO_4, (1 g/L) and raw surface water from the Bjelovar region up to 1 L. Prior to use, the SW was sterilized at 121 °C for 15 min. During the second test set, the raw surface water from the Bjelovar region was used without addition of phosphate salts and sterilization. The stock nitrate solution ($NaNO_3$ solution containing 10 g NO_3^--N/L) and methanol were added separately to the sterile SW solution or to the raw SW to provide initial nitrate-N concentration of 100 mg NO_3^--N/L and CH_3OH/N mass ratio of 3:1, respectively. All the reagents used during the tests were of an analytical grade level.

2.1.2. Preparation of Biozeolite Particles (B-NPC) and Experimental Set-up

In a 0.5 L sterile reaction bottle 200 g of NPC was weighed and the acclimated suspension of the mixed bacterial culture was pumped and recirculated with a peristaltic pump through the bottle for 48 h. The NPC with bacterial cells (B-NPC) was filtered (blue band filter) and washed with a sterile 0.9% NaCl solution. The wet B-NPC was stored at 4 °C until use.

The denitrification tests with the use of the B-NPC were conducted in a 0.25 L sterile reactor containing 19 g of the B-NPC and the SW medium up to 210 mL. The initial nitrate concentration and CH_3OH/N mass ratio of 100 mg NO_3^--N/L and 3:1 were set by addition of the stock nitrate solution and methanol to the sterile SW solution, respectively. The MeOH/NO_3-N mass ratio of 3:1, was selected according to previous investigations and in order to avoid carbon-limited conditions [31]. After preparation, the reactor was sealed, punctured with 2 needles (one for sampling and the other for removal of produced gas) and placed on the magnetic stirrer at 100 rpm. The agitation speed of 100 rpm was set for feed SW solution mixing and in order to avoid outflow and loss of B-NPC. The investigation of the denitrification process in the continuous-flow stirred reactor began as a batch test and after complete removal of nitrate from the SW, the overflow pipe was opened and continuous flow of feed began at different flow rates into the bottom of the reactor. The SW used as feed solution was prepared daily and checked for nitrate-N, nitrite-N, chemical oxygen demand (COD) and DO concentrations. Incubation was conducted at 16-25 °C, pH 7.2 and an agitation speed of 100 rpm under anoxic conditions.

In a second set of experiments the nitrate removal was monitored for 22 days with a gradual increase of the dilution rate. During this experiment after 16 days, influent SW solution was used without sterilization and addition of phosphate salts. The use of raw surface water was investigated in order to determine the impact and the need to add phosphate salts.

2.1.3. Analytical Methods

During the predetermined time intervals, the samples were taken with a sterile syringe, filtered through a Chromafil filter (0.45 μm), immediately processed for pH and dissolved O_2 (DO) measurements, and then used for nitrate, nitrite and COD analysis. Immediately after sampling, the DO concentration, pH and temperature were monitored by the Seven Go dissolved oxygen meter SG6, Mettler-Toledo (Schwerzenbach, Switzerland) and pH-meter WTW pH 330 (Weilheim, Germany), respectively. Nitrate and nitrite concentrations were determined by the chromotropic acid method and by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride respectively, at spectrophotometer Hach DR/2400 (Hach Company, Loveland, Colorado, USA) [32,33]. COD were determined according to the Standard methods [32]. The denitrification kinetic analysis applied for calculation of the denitrification rates during this study was given in our previous paper [34]

2.2. Results and Discussion

Denitrification in the continuous-flow stirred reactor was monitored in the first set of experiments at different dilution rates (0.027, 0.043, 0.095, 0.429 and 0.755 1/h) in order to achieve the optimal dilution rate and efficient nitrate removal (Fig. 1). Each test started as a batch and when nitrate was completely reduced (in approximately 6-7 h), continuous flow of feed solution began. Nitrate N and nitrite-N in feed solution were usually 99 – 122 mg NO_3^--N/L and 0 – 0.02 mg NO_2^--N/L, respectively. The DO was between 6.00 – 8.20 mg O_2/L and average pH and COD values were 7.28 and 540 mg O_2/L. In the first test set, nitrate ions were completely reduced in the reactor at almost all investigated dilution rates. The nitrate concentration of 0.12 mg NO_3^--N/L was recorded in the effluent at the steady state, at D = 0.755 1/h (Fig. 1B). In the course of tests, the maximum of nitrite generation was up to 0.11 mg NO_2^--N/L, the nitrite was subsequently completely reduced or at the end of the process in the SW, the presence of 0.01 mg NO_2^--N/L was determined. Generally, accumulated nitrite was low in comparison to the initially present nitrate and has no significant impact on the denitrification, as revealed from an earlier study [35]. During seven days of the first set of experiments at different dilution rates, the volumetric denitrification rates (Vol. K_{den}) were increased from 2 to 74 mg NO_3^--N/Lh. (Fig. 2).

The methanol was added to provide an external C source for the bacterial denitrification and as shown in Fig. 2 the COD removal was in the range of 65.06 – 86.76%. The highest COD removal was achieved at D of 0.095 1/h and 0.755 1/h along with nitrate removal higher than 99.52%. Even when nitrate and COD loading rate were increased almost 25× during this test set, the nitrate was almost completely removed. This unexpectedly high efficiency of the bioreactor could be explained by the presence of B-NPC or by the increased activity of mixed bacterial culture that interacted with clinoptilolite. In addition, it has been demonstrated that the addition of zeolite improves the performance

of the denitrification process [36]. Obviously this interaction of bacteria and zeolite enables effective nitrate removal.

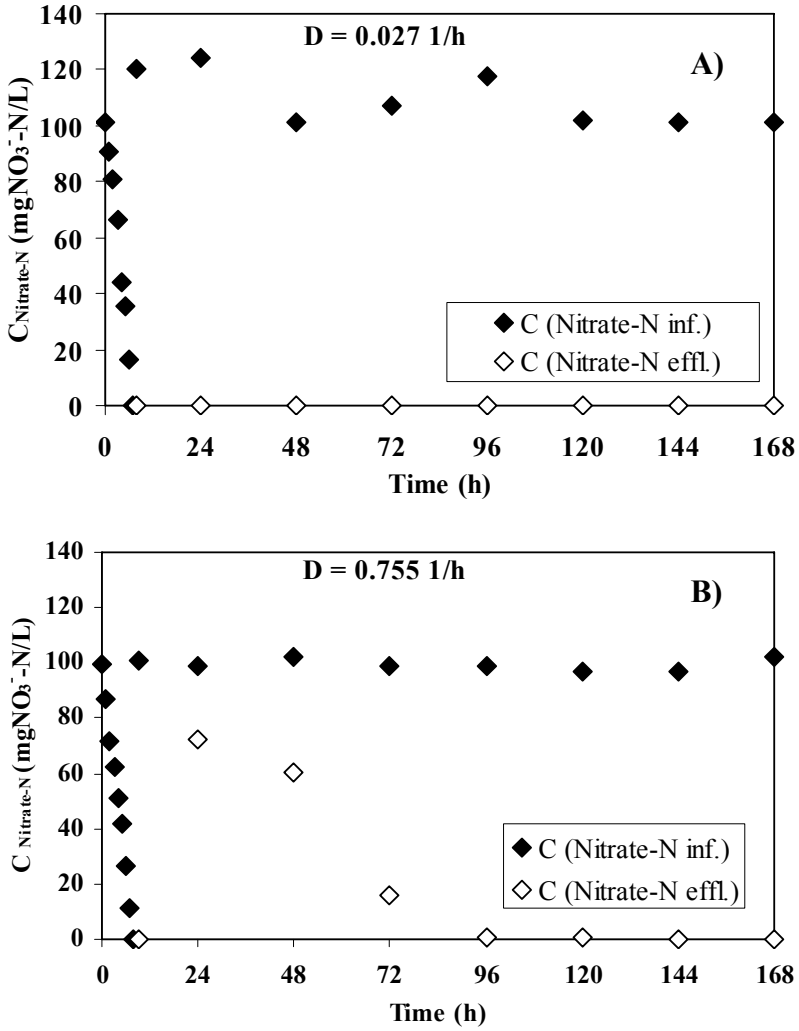


Figure 1. Nitrate profile during denitrification in the continuous-flow stirred reactor. Nitrate concentrations in influent and effluent at the dilution rate of 0.027 1/h (A) and 0.755 1/h (B)

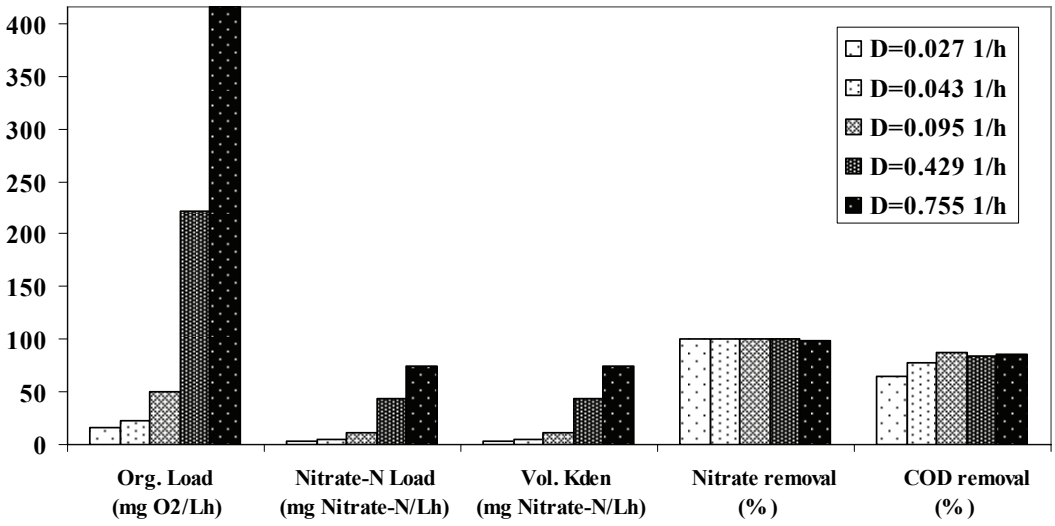


Figure 2. Parameters determined during denitrification at different dilution rates in the continuous-flow stirred reactor: Organic and nitrate loading rates, volumetric denitrification rates and nitrate and COD removal

In the second test set, denitrification started at the dilution rate of 0.429 1/h, since the previous test had shown that the effluent at the dilution rate of 0.755 1/h contained nitrate. During 8 days of continuous flow effluent nitrate-N was lower than 0.9 mg NO_3^--N/L, and therefore on the 9th day D was increased to 0.755 1/h (Fig. 3). Nitrate concentration in the effluent increased within the following 24 h to 11 mg NO_3^--N/L but in the next few days it was lowered to 0.5 mg NO_3^--N/L. After 12 days of continuous operation, the system reached the steady state and the process was monitored over another 10 days (Fig. 3A). After some fluctuations during the first 12 days, the nitrate-N and nitrite-N concentrations in the effluent were between 0.2 – 0.47 mg NO_3^--N/L and 0 – 0.057 mg NO_2^--N/L respectively. At that period nitrate and COD removal were in the range of 87.77 – 99.91% and 75.72 – 96.33%, with average values of 98.42% and 84.96%, respectively. The COD removal observed during this prolonged denitrification was generally higher than the values observed during the previous test set.

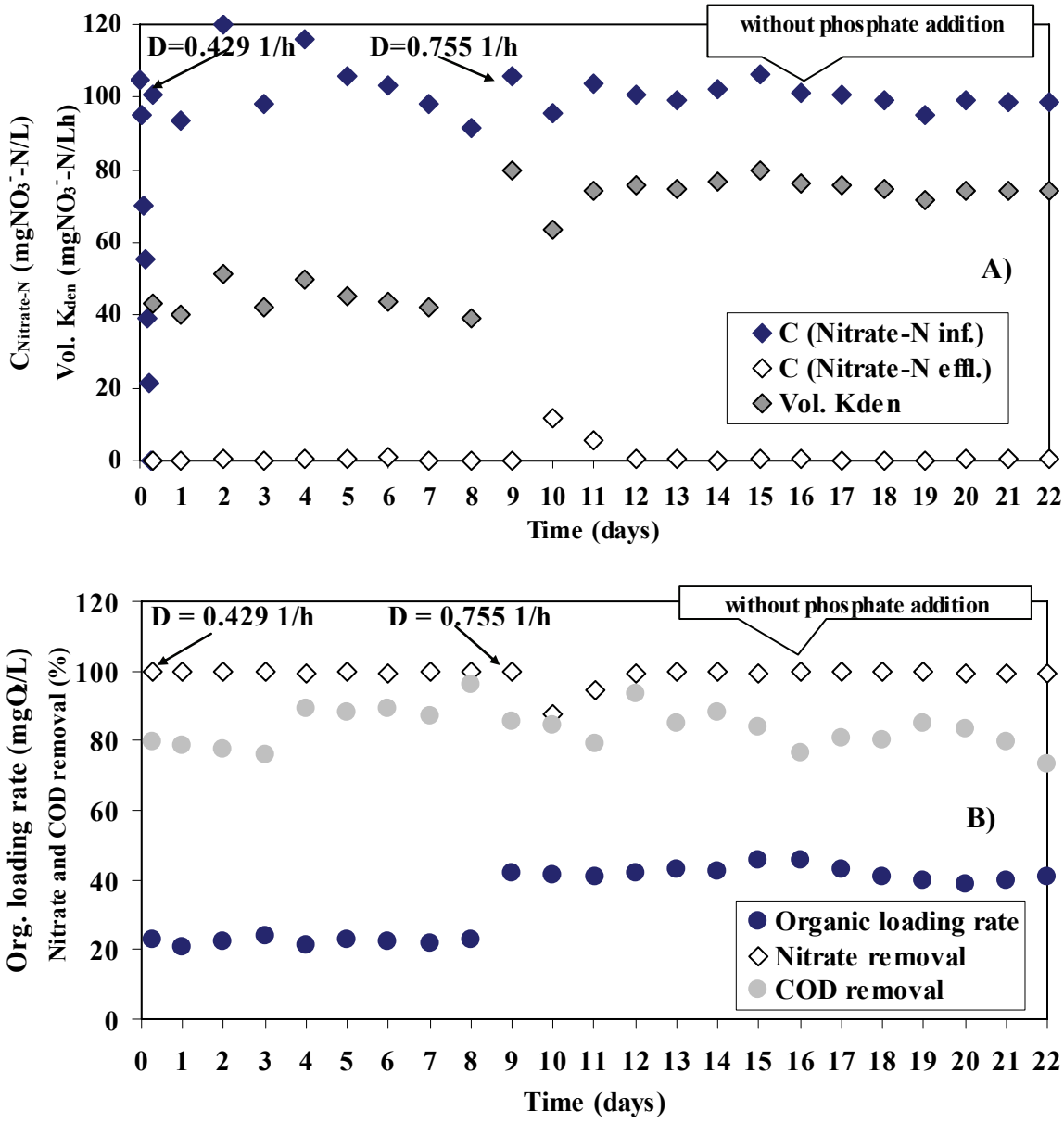


Figure 3. Time course of a continuous-flow denitrification: Influent, effluent nitrate-N and volumetric denitrification rates (A) and organic loading rates, nitrate and COD removal (B).

During the experiment the dissolved O_2 was regularly checked and the influent values of 6.2 – 7.5 mg O_2/L were lowered to the effluent values of 0.13±0.08 mg O_2/L. The temperature and pH were also monitored in the influent and effluent. Temperature values were always in the range of 21 – 26 °C and the influent pH values of 7.20 – 7.42 were increased to an average value of 7.56. The volumetric

denitrification rates were calculated and during the first 8 days they were in the range of 39.2 – 51.28 mg NO_3^--N/Lh and then it fluctuated within the range of 63.47 – 79.90 mg NO_3^--N/Lh with an average value of 74.37 mg NO_3^--N/Lh. The increase of dilution rates consequently increased nitrate loading rates and thus observed increase of the Vol. K_{den} was supported by the fact that the denitrification rates are dependent on the nitrate concentration. That was demonstrated by the presented results, which ranged between 2 – 74 mg NO_3^--N/Lh during the first set of tests and between 39.29 – 79.90 mg NO_3^--N/Lh during the second denitrification test (Fig. 3A). The obtained denitrification rates compare well with values obtained earlier [37], but since our values were somewhat higher, it could be assumed that the interaction of zeolite with the selected mixed culture was favorable for SW denitrification.

On day 16, the inlet SW solution was used as raw surface water (without addition of phosphate salts and sterilization) in order to determine the impact of phosphate addition. The average influent pH value of 7.28 was raised to the average effluent value of 8.55. These values were in some extent higher than observed in the effluent during the previous period, but as revealed from obtained results, nitrate and COD removal was still higher than 99.5% and 79% respectively (Fig. 3B). Finally, it was demonstrated that the denitrification with B-NPC in the continuous- flow stirred reactor could be effective even with raw surface water.

3. CONCLUSIONS

The denitrification with B-NPC in the continuous-flow stirred reactor was investigated at different dilution rates (0.027, 0.043, 0.095, 0.429 and 0.755 1/h) in order to achieve the optimal dilution rate and efficient nitrate removal from the SW. The efficient nitrate removal was determined and the obtained results, revealing that B-NPC in the presence of external organic carbon at CH_3OH/N mass ratio of 3:1 could effectively reduce 100 mg NO_3^--N/L present in the SW. Additionally, for effective nitrate removal, the process should be set up on a magnetic stirrer at 100 rpm and 20-25 °C under anoxic conditions. Throughout all tests, the nitrite accumulation was negligible and effluent nitrite was below 0.02 mg NO_2^--N/L. The results indicate that during continuous denitrification with the B-NPC, nitrate and COD removal exceeded 99% and 79% respectively. Even with the use of raw surface water, the process was stable and effective. Finally, the use of B-NPC was demonstrated as an efficient method for complete nitrate removal from the surface water.

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REFERENCES

[1] J.N.Galloway, J.D. Aber, J.W. Erisman, S.P. Seitzinger, R.W Howarth, E.B. Cowing, B.J. Cosby, The nitrogen cascade, Bioscience 53, (2003) 341–356.

[2] J.N. Galloway, A.R.Townsend, J.W. Erisman, M. Bekunda, Z.C. Cai, J.R. Freney, L.A.,Martinelli, S.P. Seitzinger, M.A. Sutton, Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320 (2008) 889–892.

[3] D.L. Dinnes, D.L. Karlen, D.B. Jaynes, T.C. Kaspar, J.L. Hatfield, T.S. Colvin, C.A. Cambardella, Nitrogen management strategies to reduce nitrate leaching in tile-drained Midwestern soils, Agron. J. 94 (2002) 153–171.

[4] D.B. Jaynes, T.C. Kaspar, T.B. Moorman, T.B. Parkin, In situ bioreactors and deep drain-pipe installation to reduce nitrate losses in artificially drained fields, J. Environ. Qual. 37 (2008) 429–436.

[5] R.H. Kadlec, Nitrogen farming for pollution control, J. Environ. Sci. Health Part A: Environ. Sci. Eng. 40 (2005) 1307–1330.

[6] J. Schick, P.Caullet, J-L. Paillaud, J. Patarin, C. Mangold-Callarec, Nitrate sorption from water on a Surfactant-Modified Zeolite. Fixed-bed column experiments, Microporous Mesopor. Mater. 142 (2011) 549–556.

[7] O.O. Nalcaci, N. Böke, B. Ovez, Potential of the bacterial strain Acidovorax avenae subsp. avenae LMG 17238 and macro algae Gracilaria verrucosa for denitrification, Desalination 274 (2011) 44–53.
[8] J. Schick, P.Caullet, J-L. Paillaud, J. Patarin, C. Mangold-Callarec, Batch-wise nitrate removal from water on a surfactant-modified zeolite, Microporous Mesopor. Mater.132 (2010) 395–400.
[9] P.J. Strong, B. McDonald, D.J. Gapes, Enhancing denitrification using a carbon supplement generated from the wet oxidation of waste activated sludge, Bioresour. Technol. 102 (2011) 5533–5540.
[10] J.A. Camargo, A. Alonso, Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment, Environ. Int. 32 (2006) 831–849.
[11] C. Glass, J. Silverstein, Denitrification of High-Nitrate, High-Salinity Wastewater, Water Res. 33 (1999) 223–229.
[12] World Health Organization, Health hazards from nitrate in drinking water, Environ Health 1, World Health Organisation, Copenhagen, 1985.
[13] M.S. Coyne, Biological denitrification, in: J.S. Schepers, W. Raun (Eds.), Nitrogen in Agricultural Systems, ASA-CSSSA-SSSA Agronomy Monography 49, Madison WI, 2008, pp. 197–249.
[14] M.O. Rivett, S.R. Buss, P.P. Morgan, J.W.N. Smith, C.D. Bemment, Nitrate attenuation in groundwater: a review of biogeochemical controlling processes, Water Res. 42 (2008) 4215–4232.
[15] S. Seitzinger, J.A. Harrison, J.K. Bohlke, A.F. Bouwman, R. Lowrance, B. Peterson, C. Tobias, G. Van Drecht, Denitrification across landscapes and waterscapes: a synthesis. Ecol. Appl. 16 (2006) 2064–2090.
[16] S. Oakley, A.J. Gold, A.J. Oczkowski, Nitrogen control through decentralized wastewater treatment: process performance and alternative management strategies. Ecol. Eng. 36 (2010) 1520–1531.
[17] M. Henze, M.C.M. van Loosdrecht, G.A. Ekama, Biological wastewater treatment: Principles, Modeling, and Design, Intl Water Assn Publishing, 2008.
[18] X. Li, G. Upadhyaya, W Yuen, J. Brown, E. Morgenroth, L. Raskin, Changes in the structure and function of microbial communities in drinking water treatment bioreactors upon addition of phosphorus, Appl. Environ. Microbiol. 76 (2010) 7473-7481.
[19] M. Tsezos, Adsorption by microbial biomass as a process for removal of ions from process or waste solutions, in: H.H. Eccles, S. Hunt (Eds.), Immobilization of ions by biosorption, Ellis Horwood Publication, Chichester, 1986, pp. 200–209.
[20] T. Parvanova-Mancheva, V. Beschkov, Microbial denitrification by immobilized bacteria *Pseudomonas denitrificans* stimulated by constant electric field, Biochem. Eng. J. 44 (2009) 208–213.
[21] S.L. Zala, J. Ayyer and A.J. Desai, Nitrate removal from the effluent of a fertilizer industry using a bioreactor packedwith immobilized cells of *Pseudomonas stutzeri* and *Comamonas testosteroni*, World J. Microbiol. Biotechnol. 20 (2004) 661–665.
[22] Z. Zhang, Z. Lei, X. Hea, Z. Zhang, Y. Yang, N. Sugiura, Nitrate removal by *Thiobacillus denitrificans* immobilized on poly(vinyl alcohol) carriers, J. Hazard. Mater. 163 (2009) 1090–1095.
[23] Y. Wang, X. Yang, H. Li, W. Tu, Immobilization of *Acidithiobacillus ferrooxidans* with complex of PVA and sodium alginate, Polym. Degrad. Stabil. 91 (2006) 2408–2414.
[24] B.Greene, G.W. Bedell, Algal gels or immobilized algae for metal recovery, in: I. Akatsuka (Ed.), An Introduction to Applied Phycology, SPB Academic Publishing, The Hague, 1990, pp. 137–149.
[25] A. Saeed and M. Iqbal, Immobilization of blue green microalgae on loofa sponge to biosorb cadmium in repeated shake flask batch and continuous flow fixed bed column reactor system, World J. Microbiol. Biotechnol. 22 (2006) 775–782.
[26] S.B. Wang, Y.L. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, Chem. Eng. J. 156 (2010) 11–24.
[27] Y.Zhan, J. Lin, Z. Zhu, Removal of nitrate from aqueous solution using cetylpyridinium bromide (CPB) modified zeolite as adsorbent, J. Hazard. Mater. 186 (2011) 1972–1978.
[28] H.Guan, E. Bestland, C. Zhu, H. Zhu, D.Albertsdottir, J. Hutson, C.T. Simmons, M. Ginic-Markovic, X. Tao, A.V. Ellis, Variation in performance of surfactant loading and resulting nitrate removal among four selected natural zeolites, J. Hazard. Mater. 183 (2010) 616–621.

[29] Z. Li, Use of surfactant-modified zeolite as fertilizer carriers to control nitrate release, Micropor. Mesopor. Mater. 61 (2003) 181–188.
[30] J.Hrenović, M. Rožić, L. Sekovanić, A. Anić-Vučinić, Interaction of surfactant-modified zeolites and phosphate accumulating bacteria, J. Hazard. Mater. 156 (2008) 576–582
[31] L. Foglar, N.Bolf, M. Lukić, Kinetic modelling of surface water biodenitrification, WSEAS Transaction on Environment and Development, 6 (5) (2010) 375–384.
[32] APHA, Standard Methods for the examination of water and wastewater. 17th ed. APHA/AWWA/Water Environment Federation, Washington DC, USA, 1989.
[33] K. Höll, Wasser, 6th ed. Valter deGruyter, Berlin, 1979.
[34] L. Foglar, L. Sipos, N. Bolf, Nitrate removal with bacterial cells attached to quartz sand and zeolite from salty wastewaters, World J. Microbiol. Biotechnol. 23 (2007). 1595-1603.
[35] H. Lemmer, A. Zaglauer, A. Neef, G. Metzner, Denitrification in a methanol fed fixed bed reactor. Part 1: Physico-chemical and biological characterization, Water Res. 31 (1997) 1897-1902.
[36] S-J. Park, C.G. Kim, T-I. Yoon, D.W. Kim, Evaluation of increased denitrification in an anoxic activated sludge using zeolite, Korean J. Chem. Eng. 20 (2003) 492-495.
[37] P. Kesserü, I. Kiss, Z. Bihari, B. Polyák, Biological denitrification in a continuous-flow pilot bioreactor containing immobilized *Pseudomonas butanovora* cells, Biores. Technol. 87 (2003) 75–80.

WORKING PRINCIPLE AND PRACTICAL APPLICATIONS OF ULTRASONIC LEVEL TRANSMITTERS IN WATER AND WASTE WATER SYSTEMS

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Abstract

In this paper basic principle of ultrasonic level transmitters as well as practical applications in water and waste water systems are described. Appropriate selection and appropriate usage of ultrasonic level transmitters can considerably enhance reliability of measurement systems in water and waste water plants, considerably decrease investment cost and enhance reliability and availability of technical systems. Understanding of basic working principles of ultrasonic level transmitters is essential for estimation of demands for installations and demands for electronic circuitry.

Descriptions of particular installations of ultrasonic level transmitters described in this text can be help in estimation of possibilities on particular places and help for managers, designers and maintenance personnel. Importance of watertight ultrasonic level transmitters is emphasized, as well as importance of user friendly installing procedures.

Keywords: *ultrasonic level transmitter, water tight level transmitters, level measurements*

1. INTRODUCTION

Level measurement of water is one of basic measurements in water and waste water systems. Information about level of water will turn on and turn off pumps and provide important information for SCADA systems. Reliability of level measuring system will depend on measuring principle used in particular application. Ultrasonic level measurement is one of most used level measurement systems. Appropriate selected and appropriate installed ultrasonic measuring system can provide years of reliable function. For appropriate selection and appropriate usage of ultrasonic transmitters it is necessary to analyze in details working principles.

2. ELABORATION

2.1. Ultrasonic Level Measurements

Ultrasonic level measurements are based on measuring of time from moment of transmission of signal to moment of detection of reflected signal (Fig. 1.).

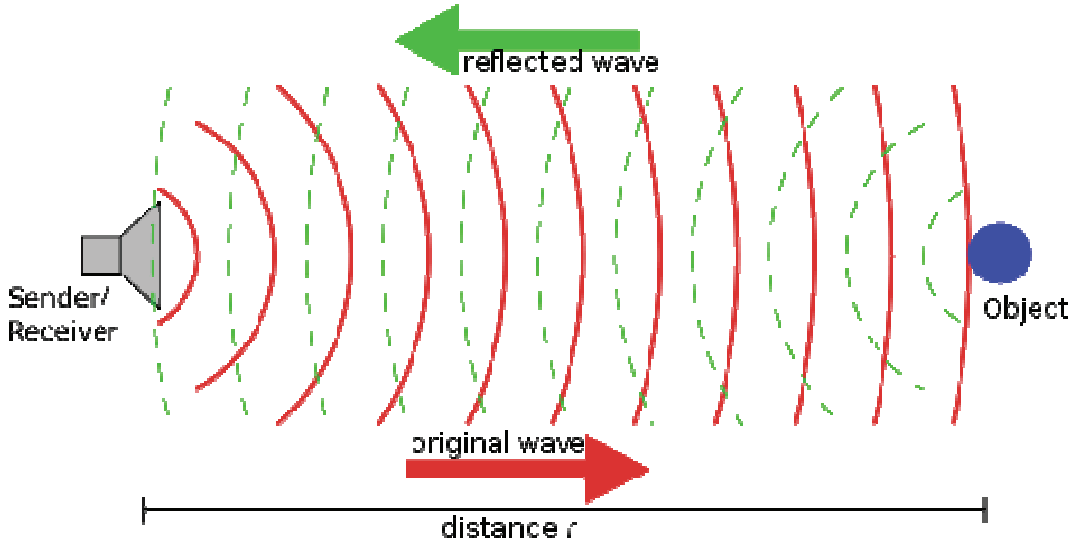


Figure 1. Measuring principle of ultrasonic level transmitters

Sensor transmits impulses and analyzes reflected signals (Fig. 2.). Complex software algorithms reject signals of noises from reflected signals and calculate distance. Reliability of measurements depends on quality of ultrasonic transmitter and in great deal on possibilities of software for reliable noise rejection.

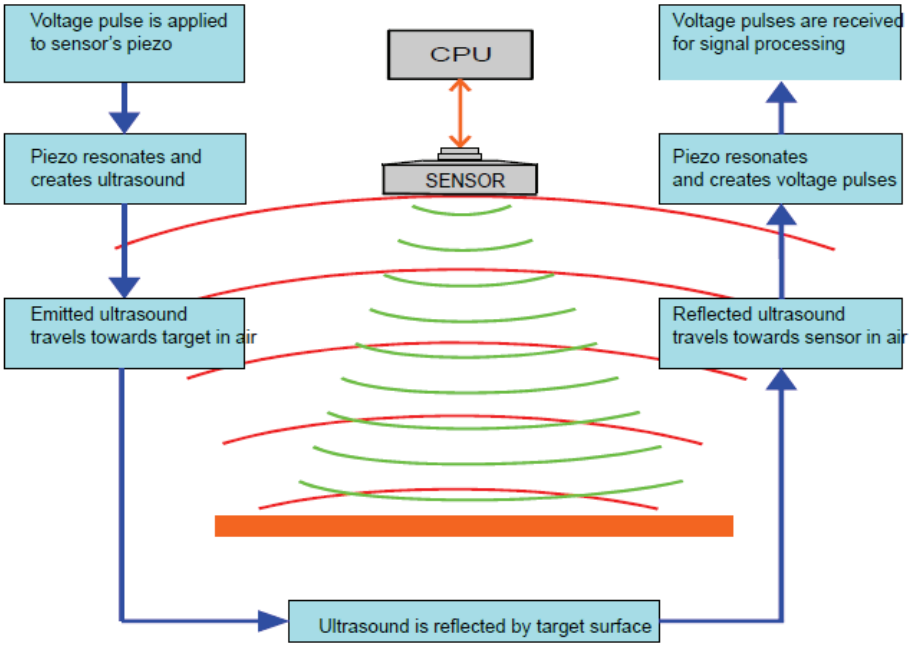


Figure 2. Working principle of ultrasonic transmitters

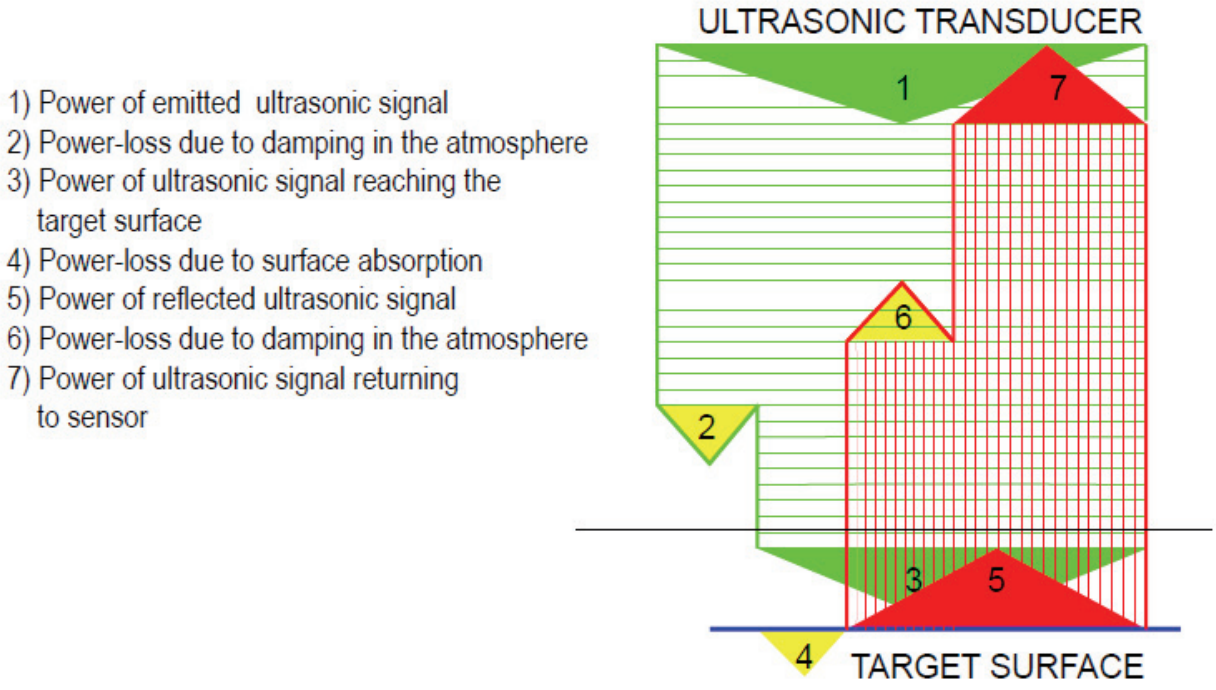


Figure 3. Energy lost during transmitting through air

On Fig. 3. losses of ultrasonic energy in air are described. Only one little part of energy is reflected back on ultrasonic transmitter. For reliable detection it is important that ultrasonic beam is narrow as possible (easy is spreading near obstructions, easy penetrate foams on surface of liquids, higher energy comes back to transmitter), and that surface of transducer is large (greater energy). Ultrasonic transmitter Easy TREK has very narrow ultrasonic beam what enable reliable operation (Fig. 4.)

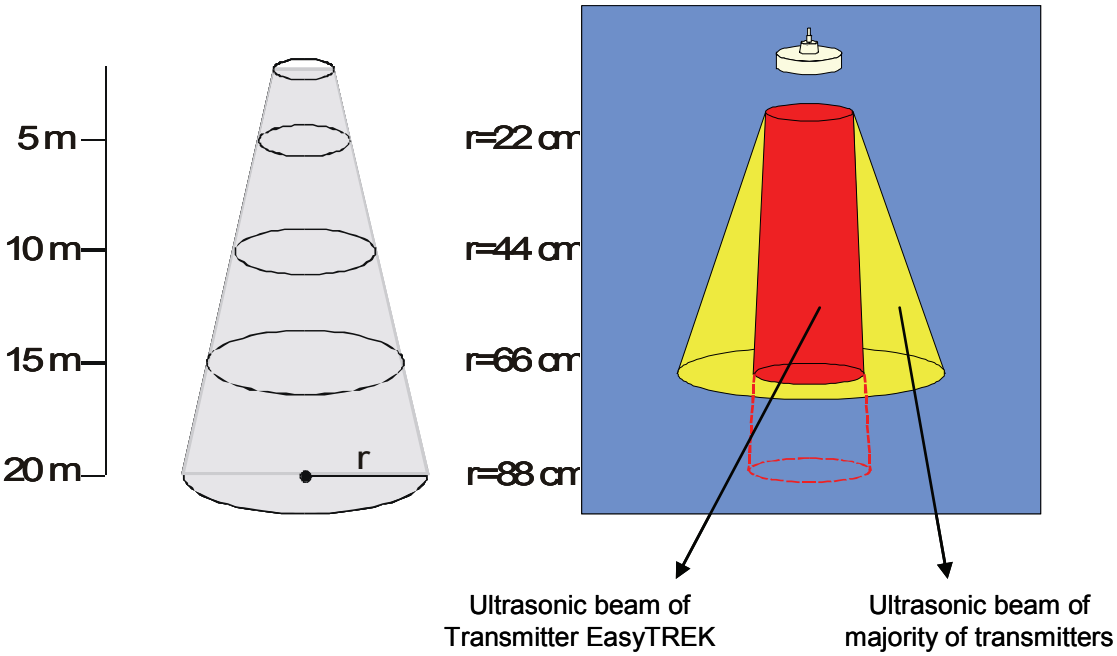


Figure 4. Ultrasonic beam of transmitter Easy TREK in comparison to majority of transmitters

Absorption in air depends on moisture, vapors, dust and in heavy environmental range of transmitter is restricted that means that reliable detection range is reduced. Due to that, for applications in heavy environments usage of long range transmitters is recommended (Fig. 5.).

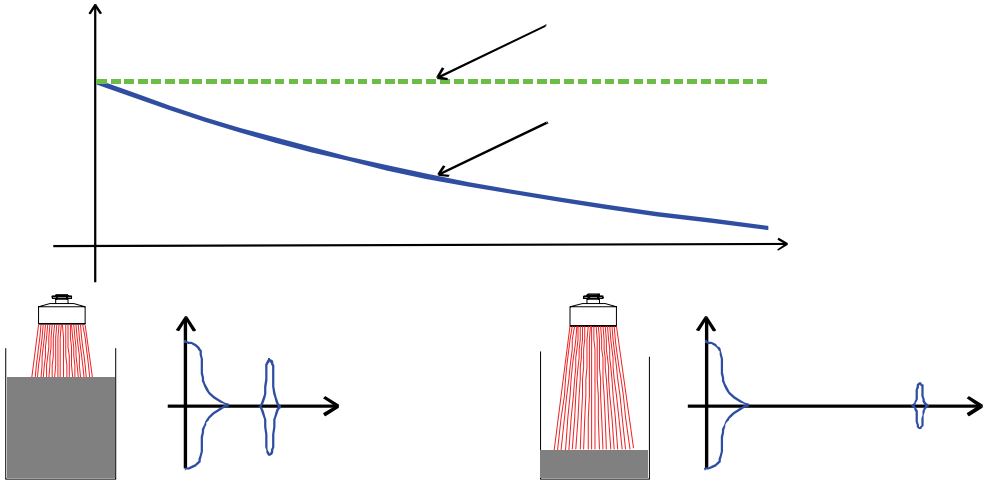


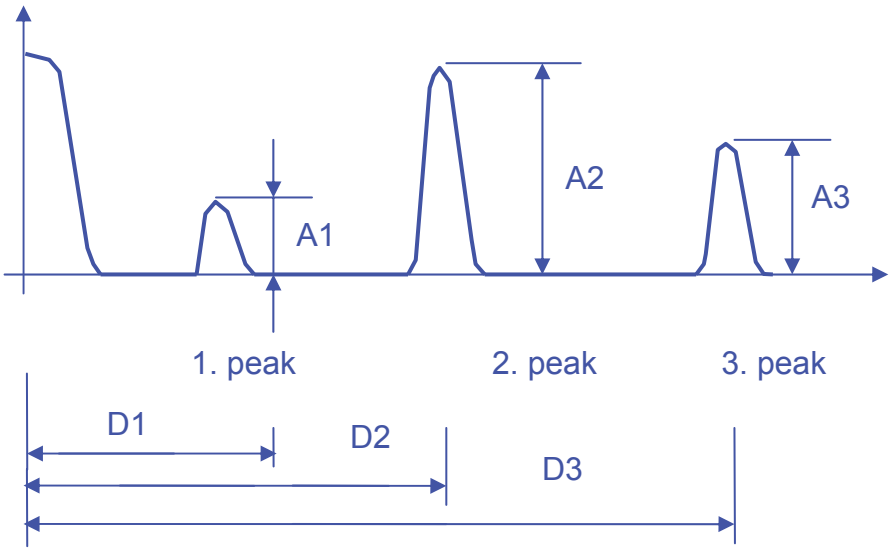
Figure 5. Reflected signal from higher distance has less energy and greater delay time.

2.2. Software

Softwares for data processing are divided in two groups: (i) softwares for reliable measurements and (ii) softwares for specific applications (flow calculation, volume calculation etc.)

2.2.1. Software for Reliable Measurement

Basic measuring principle is measuring of time from moment of transmission to the moment of detection of reflected ultrasonic impulse. But together with transmitted signals sensor will also detect other ultrasonic signals caused like effects of hits, explosions or other ultrasound sources. Simple measurements of time between transmission and reception in lot of cases is not enough reliable in industrial environments. One of software algorithms for signal processing is described in Fig. 6. After transmitting of impulses ultrasonic transducer waits for reflected signals. Software analyzes received signals, and store signals with the biggest amplitudes (can also be programmed to detect only first signal). Transmitter sends more impulses and process averiging on 16 (or 4) results.



Peak [i]	Distance Di [m]	Amplitude Ai [dB]
1	1.5	-33
2	3	-10
3	5.1	-22

Figure. 6. Signal processing of ultrasonic impulses

After 16 measurements when distance to reflection target is defined transmitter will set time window for reflection measurements – transmitter will process only signals which are placed in time window. On that way it is possible simply to reject high signals which are outside measuring window. On Fig. 7. signals from screws on tank and signals from surface of liquid are showed. Time window is defined and transmitter will process only signals inside time window. It is important to notice that signal of noises which are outside measuring time window will not have influence on measurement.

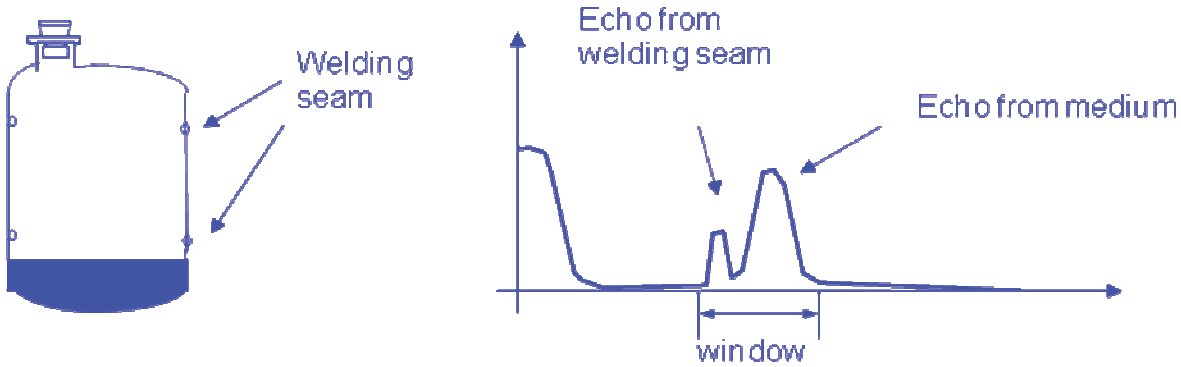


Figure 7. Signals received from welding seam and water surface

Ultrasonic transmitters can not measure distance closely in front of their surface because they have dead band (short zone in front of transmitter surface where detection is not possible). If on short distance in front of transmitter is wire or some other object strong reflected signals can be created and without additional programming of transducer it can be a problem. To avoid such situations modern ultrasonic transmitters have possibilities of programming (enhancing) of dead band, and in this way they can avoid possible problems.

2.3. Commercial Ultrasonic Transmitters

Commercial ultrasonic transmitters are produced with local display (that will enable on site reading of measuring results) or sealed watertight (IP 68) construction which is specially developed for usage in water and waste water applications.



Figure 8. Ultrasonic transmitters EchoTREK



Figure 9. Ultrasonic transmitters series EasyTREK

Ultrasonic transmitters have software for open channel flow measurements and can be reliable used in heavy industrial environments.



Figure 10. Open channel flow measurement



Figure 11. Application of ultrasonic transmitter EasyTREK in waste water pump station

Main applications of ultrasonic transmitter EasyTREK are pump stations. Because those transmitters are watertight and easy for installation they can provide years of reliable maintenance free operations.

3. CONCLUSIONS

Ultrasonic measurements of levels and flows on open channels can be reliable base of SCADA systems. Basic demands are appropriate selection of transmitters and appropriate installation. Angle of emitted ultrasonic beam and quality of software will play considerable role in reliability of measurements. For selecting of appropriate model it is very useful to contact experts for measuring equipment, people for installation and people for maintenance of systems and instruments.

LOADING DIFFERENCE OF RIVER WATER AND WASTEWATER DISCHARGE TO MAE KUANG RIVER

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Abstract

Management of water quality and preventing water resources from pollution is a very important aspect of water management. Particularly, control of the pollutants discharged to the river cannot be neglected. Loading of wastewater and river water should be considered as a high priority. In this work, qualities and flows of major wastewater discharged to Mae Kuang river, including water from this river, which is the main tributary of Ping river in upper northern Thailand, were determined in three seasons during December 2009 to December 2010.

The wastewater loading both from community and industrial sources showed the highest loadings of COD (278.26 kg d^{-1}) and BOD (61.79 kg d^{-1}) at the back side of the industrial estate (P3) in summer season. The loadings of SS (34.55 kg d^{-1}) and TKN (2.44 kg d^{-1}) were also highest in summer season, but P (1.11 kg d^{-1}) was highest in rainy season at the point near gymnasium (P4). Loadings of BOD (1 527 kg d^{-1}), TKN (1 050 kg d^{-1}), P (399 kg d^{-1}), and SS (8 838 kg d^{-1}) of Mae Kuang river in winter season were also highest at the bridge of Ban Sri Boonyuen (KU2). It was noted that river water loadings were very higher than wastewater loadings discharged to Mae Kuang river. The difference of these loadings was associated with the point sources and non-point sources of wastewater discharge to this river in the upstream area.

Keywords: *loading, wastewater, Mae Kuang river*

1. INTRODUCTION

Mae Kuang river is the main tributary of Ping river which is the major river in upper northern Thailand. It is an urban river flowing from north to south converging after passing through the central of Lamphun. Its total length spans 95 km, and supplied water to several areas [1]. This river is very important water source of citizens in Lamphun as it is main river used for agriculture, industry, as well as water supply. Particularly, there is a first regional industrial estate called "Northern Regional Industrial Estate" (NRIE) located near Mae Kuang river that used river as raw water source and receiving water [2]. In addition, there is extension of both factory and related services including the growth of various communities along the both side of Mae Kung river, especially near NRIE that closed to the central of city area. It is often to find river water use and untreated wastewater discharged to the river. Although there is wastewater treatment plants of NRIE and Lamphun municipality, Mae Kuang river water is still polluted. Especially, in dry season, it is almost no flow, and fishes died. According to the monitoring result in 2008 by ReO1, the water quality of this river was in the poor to poorer level [3].

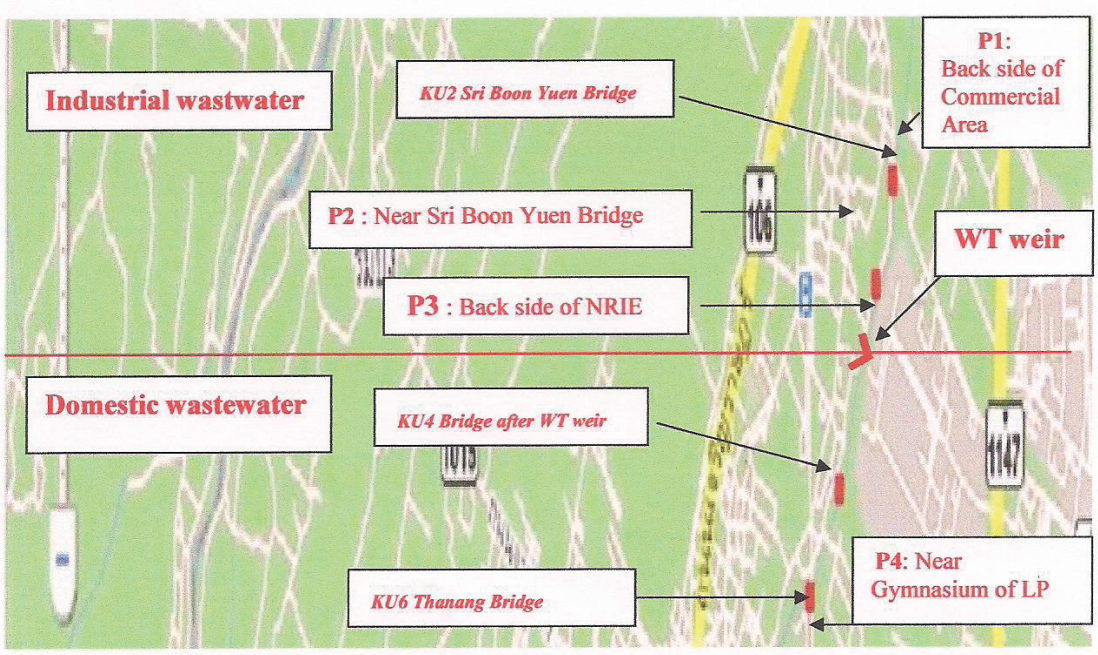
However, the studied on river water and wastewater loading is not yet appeared. Therefore, wastewater loading from various point sources along the sides of Mae Kuang was performed in 2009 to 2010. In this work, it focused on wastewater loading from point sources. It was also tried to find the difference between loading of river water and wastewater in order to obtain some point of water pollution control and management.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Study Area

The site selected for this study was the last part of Mae Kuang river that starts flowing from Chiang Mai (CM) - Lamphun (LP) highway road to NRIE and central of Lamphun until converging with Ping river at Pasang District in Lamphun. It was about 30 km long (Fig. 1).



Legend:
KU2 = Sri Boon Yuen Bridge; KU4 = Bridge after Ban Wang Tong (WT weir); KU6 = Tha Nang Bridge; P1 = Back side of Commercial area; P2 = Near Sri Boon Yuen Bridge; P3 = Back side of NRIE; P4 = Near Gymnasium of Lamphun (LP)

Figure 1. Study area and sampling points in Mae Kuang river

2.1.2. Samples and Period of Study

Based upon the source of wastewater generated and the relations among the sampling points along the river, 3 and 4 sampling points of river water and wastewater were collected in 3 seasons for 2 times in each season during December 2009 to December 2010.

2.1.3. Flow Measurement

2.1.3.1. Wastewater Flow

It is measured by the vessel vol. 10 l in the certain time of collection, and calculation by the following equation (1) [4]:

$$Q = V/T \quad (1)$$

where: Q = flow rate ($m^3\ d^{-1}$)
V = Volume of Vessel (l)
T = Time for collection (s)

2.1.3.2. *River Water Flow*

It was measured by using the floating material in the limited distance of material's movement (50 m), and calculation by the below equation (2) [5]:

$$Q = AV \quad (2)$$

$$V = S/T \quad (3)$$

where: Q = flow rate ($m^3\ d^{-1}$)
V = Average velocity of river water ($m\ min^{-1}$)
A = Cross-section area of the river (m^2)
S = Distance of material's movement (m)
T = Time for movement (m)

2.1.4. Related Parameters

2.1.4.1. Wastewater Parameter:

It consisted of Suspended Solid (SS), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Kajldahl Nitrogen (TKN), and Phosphorus (P)

2.1.4.2. River Water Parameter:

It was composed of Suspended Solid (SS), Biochemical Oxygen Demand (BOD), Total Kajldahl Nitrogen (TKN), and Phosphorus (P)

All parameters were analyzed by the Standard Method for the Examination of Water and Wastewater, 21st ed., APHA, AWWA, WPCF, 2005 [6].

2.1.5. Data Analysis

The simple statistics was used to analyze the result of flow and loadings; Mean ($\overline{X}$) and Standard Deviation (SD).

2.2. Theory and Calculation

2.2.1. Definition of Water Pollution

According to the Enhancement and Conservation of Thai National Environmental Quality Act, 1992, water pollution means the state of the water environment that has been effected, changed or contaminated by pollutants, resulting in deterioration of water quality [7].

2.2.2. Pollutant Source

The sources of wastewater could be classified into 2 major sources based upon the types of wastewater generated [7-8].

2.2.2.1. Point Source

It means any community, factory, building, structure, place of business or activity or any other thing from which water pollution is generated. In general, wastewater generated from point source is collected by a network of pipes or channels and conveyed to a single point of discharged into the receiving water; such as domestic and industrial wastewaters.

2.2.2.2. *Non-Point Source*

It means the wastewater generated from multiple discharged points; such as urban and agricultural wastewaters.

2.2.3. Type of Pollutant

The wide range of pollutants discharged to surface water from both point source and no-point source consists of oxygen-demanding material (BOD and COD), nutrients (N, and P), pathogens, suspended solid (SS), including endocrine-disrupting chemicals. Salts and toxic organic chemicals are in industrial wastewater and agricultural run off. Toxic metals are mostly in industrial wastewater and urban runoff [8].

2.2.4. Wastewater Flow

Usually, the components of wastewater from a community depend on the type of collection system used and include domestic wastewater, industrial wastewater, infiltration/inflow, and storm water. However, in this study, wastewater flows mostly mean wastewater generated from domestic and industrial sources.

2.2.5. Calculation of Pollutant Loading

There are 3 types of loading in this work as below [9]:

2.2.5.1. Organic Loading

It is considered in terms of BOD and COD loadings:

$$\textit{Organic loading} = \textit{Flow rate of wastewater } (m^3\ d^{-1}) \times \textit{[organic substance]}\ (kg\ d^{-1})$$

2.2.5.2. Inorganic/Nutrient Loading

It is considered in terms of TKN and P loadings:

$$\textit{Inorganic loading} = \textit{Flow rate of wastewater } (m^3\ d^{-1}) \times \textit{[inorganic substance]}\ (kg\ d^{-1})$$

2.2.5.3. Other loading

It is considered in terms of SS loading:

$$\textit{Suspended solid loading} = \textit{Flow rate of wastewater } (m^3\ d^{-1}) \times \textit{[SS]}\ (kg\ d^{-1})$$

2.3. Results and Discussion

2.3.1. Wastewater flow

Based upon the result of flow measurement of wastewater discharged to Mae Kuang river at different 4 sampling points (Table 1), it was found that the maximum of wastewater flow (770.65 $m^3\ d^{-1}$) came from the area near gymnasium of LP (P4) due to its location closed to the wastewater treatment (WWT) system of LP municipality. In addition, there was some untreated wastewater from the nearby communities discharged to Mae Kuang river. The minimum of wastewater flow (102.85 $m^3\ d^{-1}$) came from the commercial area (P1) that has its own WWT system before discharge to the water source. Thus, flow rate of wastewater depended on the related activities that wastewater was discharged into the river.

Table 1. Values of wastewater flow discharge to Mae Kuang river

Sampling point	Quantity of wastewater Flow (m^3 d^{-1})				
	Summer	Rainy	Winter	$\bar{x}$	SD
P1	65.80	35.62	207.13	102.85	91.56
P2	123.38	143.45	190.65	152.49	34.53
P3	421.30	184.61	1005.34	537.08	422.44
P4	540.55	269.23	1502.17	770.65	647.88

4.2 Wastewater loading

All wastewater loadings from point sources were shown in Table 2. The average values of organic loading in terms of COD and BOD were highest in summer season at the back side of NRIE (P3).

Table 2. Values of wastewater loading discharge to Mae Kuang river

Sampling point	SS Loading (kg d^{-1})			COD Loading (kg d^{-1})			BOD Loading (kg d^{-1})			TKN Loading (kg d^{-1})			P Loading (kg d^{-1})		
	S	R	W	S	R	W	S	R	W	S	R	W	S	R	W
P1	0.28	0.39	16.16	13.14	22.16	27.66	8.50	3.13	17.90	0.21	0.85	8.85	0.02	0.08	0.20
P2	0.15	1.89	13.15	43.59	21.31	18.04	24.12	12.76	9.80	0.76	2.21	8.49	0.23	0.63	0.24
P3	2.88	0.57	29.15	278.26	5.44	130.24	61.79	5.44	20.33	1.00	1.91	26.19	0.04	0.79	1.03
P4	0.62	3.04	34.55	184.74	22.09	129.47	49.81	24.80	20.11	2.44	3.39	41.56	0.71	1.11	1.07
$\bar{x}$	0.98	1.47	23.25	129.93	17.75	76.35	36.05	11.53	17.04	1.11	2.09	21.27	0.25	0.65	0.63
SD	1.28	1.24	10.24	123.96	8.22	61.91	24.18	9.75	4.95	0.95	1.05	15.85	0.32	0.43	0.48

Legend: S = Summer season; R = Rainy season; W = Winter season

As P3 is the area that both treated and untreated wastewater was discharged from NRIE and nearby communities. It was indicated that there was high concentration of organic substances polluted and oxygen demands were needed to be degraded these substances. Besides, the wastewater flow at P3 was also minimum in summer season (421.30 m^3 d^{-1}). This could be also the cause of accumulation of organic matter at this point. The average values of inorganic loading in terms of TKN and P were highest in winter season, and rainy season, respectively, near the gymnasium of LP (P4) due to high quantity and strong velocity of water current in these seasons. Moreover, P4 was the area that wastewater discharged to the river contained some excretion waste and detergent from washing as it mostly came from the domestic water use near the river. The average value of other loading in terms of SS was also highest in winter season at the point near the gymnasium of LP (P4). This was due to the maximum wastewater flow at this point, while concentration of SS was lowest (11.82 mg L^{-1}). Although the average concentration of SS at P1 was highest (31.03 mg L^{-1}), the average value of wastewater flow was lowest (102.85 m^3 d^{-1}). Therefore, the values of wastewater loading were dependent on both wastewater flow and concentration of pollutant substance.

4.3 River water flow

Usually, there is much river water in rainy season and velocity of water current is too strong to measure, and almost no flow in summer season due to a little water that could not be measured flow in Mae Kuang river. Winter season is the best time. Thus, river water flow was measured in winter season and adequate data was obtained by using 3 sampling points closed to 4 wastewater sampling points. It was found that KU2 where is upstream point was highest flow (387 462 m^3 d^{-1}). KU6 where is downstream point was lowest flow (190 080 m^3 d^{-1}). Moreover, there was a weir before KU4 that could reduce the rate of water flow and increase more organic substance at KU4 [10]. At KU4 that was between KU2 and KU6, water flow (218 118 m^3 d^{-1}) was less than KU2, but it was more than KU6.

4.4 River water loading

The value of organic loading in terms of BOD loading (1 527 kg d^{-1}) was highest at KU2. The value of inorganic loadings both TKN (1 050 kg d^{-1}) and P (399 kg d^{-1}) loadings were also highest at KU2. As

KU2 where there was crowded community area could be the source of organic and inorganic substances discharge to Mae Kuang river through various activities of the citizens in communities, such as restaurants, shops, and dormitories near the river side.

4.5 Loading Difference

The difference of loading between river water and wastewater discharged to Mae Kuang river could be compared clearly in winter season. This was due to the relationship between the sampling points (Fig. 1.) that was closed to each other; KU2 (community area) and P1 (commercial area), KU4 (community area) and P2-P3 (some community area and discharged point of NRIE), and KU6 (community area) and P4 (community area), as well as the adequate river water flow. It was found that river water loadings were higher than wastewater loadings discharged to Mae Kuang river (Table 3). It is implied that river water loadings came from both point sources and non-point sources at the upstream. While the upper river had much more activities from non-point sources, it should be included wastewater loading from these sources as well.

Table 3. Loading difference between river water and wastewater discharge to Mae Kuang river

Sampling point		SS Loading ($kg\ d^{-1}$)		BOD Loading ($kg\ d^{-1}$)		TKN Loading ($kg\ d^{-1}$)		P Loading ($kg\ d^{-1}$)	
		RW	WW	RW	WW	RW	WW	RW	WW
KU2	P1	28 838	0.39	1 527	3.13	1 050	0.85	399	0.08
KU4	P2	2 131	1.89	966	12.76	382	2.21	22	0.63
KU4	P3	2,131	29.15	966	5.44	382	1.91	22	0.79
KU6	P4	1 637	34.55	838	24.80	574	3.39	209	1.11

Legend: RW = River water; WW = Wastewater

In order to obtain the actual wastewater loading in Mae Kuang river, it is recommended to find an appropriate methodology for further study of the non-point source that discharge to the river. However, the implementation of proper action is needed to be done to preserve the river, for example, the strong enforcement for illegal action, and the enhancement of pre-treatment and treatment of wastewater before discharge to the river at the local level.

3. CONCLUSIONS

The highest loadings of COD (278.26 $kg\ d^{-1}$) and BOD (61.79 $kg\ d^{-1}$) were found at the back side of the industrial estate (P3) in summer season. The highest loadings of SS (34.55 $kg\ d^{-1}$) and TKN (2.44 $kg\ d^{-1}$), and P (1.11 $kg\ d^{-1}$) were also found at the point near gymnasium (P4) in summer season, and rainy season, respectively.

The highest loadings of BOD (1 527 $kg\ d^{-1}$), TKN (1 050 $kg\ d^{-1}$), P (399 $kg\ d^{-1}$), and SS (8 838 $kg\ d^{-1}$) of Mae Kuang river were found at the bridge of Ban Sri Boonyuen (KU2) in winter season.

The river water loadings were very higher than wastewater loadings discharged to Mae Kuang river. It is indicated that the downstream of Mae Kuang river was polluted by both point sources and non-point sources in the upstream area.

A proper action for pre-treatment and WWT system is recommended to implement at the local level with the strong enforcement.

Acknowledgements

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REFERENCES

[1] Department of Military Mapping, Map of Chiang Mai and Lamphun, 1985.

[2] K. Panyaping, The Impact of Industrial Development on Local Water Resource: A Case Study of Northern Regional Industrial Estate, Lamphun Province, RIT, Northern Campus, Chiang Mai, 1996.

[3] Office of the Regional Environment 1, Summary of State of Water Quality**,** Chiang Mai, 2008.
[4] Metcalf & Eddy, Wastewater Engineering, Treatment, Disposal, and Reuse, McGraw-Hill International Editions. 4th ed. Singapore, 2005.
[5] S. Phutakunchareon, Hydraulic. 5th ed., Library nine, Bangkok, 2002.
[6] APHA, AWWA, and WPCF, Standard Method for the Examination of Water and Wastewater, 21th ed., 2005.
[7] PCD, Laws and Standards on Pollution Control in Thailand, 4th ed., Ministry of Science, Technology and Environment, 1997.
[8] M.L. Davis, D.D. Cornwell, Introduction to Environmental Engineering, McGraw-Hill International Editions, Singapore, 2008.
[9] Metcalf & Eddy, Wastewater Engineering, Treatment, Disposal, and Reuse, McGraw-Hill International Editions. 3rd ed. Singapore, 1991.
[10] K. Panyaping, K. Ngeankumkong, Ban Wang Tong Weir and Utilization of Mae Kuang River and Effect to Water Quality, The Proceedings of 7th KU-KPS Conference, December 7-8, 2010.

ADSORPTION AND RECOVERY OF PERFLUORINATED SURFACTANTS FROM SYNTHETIC WASTEWATER USING FUNCTIONALIZED MESOPOROUS SILICATES

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Abstract

Perfluorinated surfactants (PFSs) appeared in the list of Persisted Organic Pollutants (POPs) due to their toxicity, extraordinary stability, and bioaccumulation. Hexagonal mesoporous silicate (HMS) can be modified by various methods, e.g., organic ligand modification, to enhance specific physico-chemical characteristics for Perfluorinated surfactants (PFSs) adsorption and recovery processes. Pristine HMS, 3-aminopropyltriethoxy and 3-mercaptopropyltrimethoxy functionalized HMSs were synthesized and characterized physico-chemical characteristics. Adsorption capacities of perfluorooctane sulfonate (PFOS) were investigated in batch adsorption experiments. Hydrophobic surfaces had higher PFOA adsorption capacities than hydrophilic surfaces. 3-aminopropyltriethoxy- grafted HMS gave higher adsorption capacity compared with other silicate adsorbents. Adsorption of both PFOS at had highest adsorption capacities at pH 7 (pH 5-9). Hydrogen bonding and electrostatic interaction might play the important role for PFCs adsorption on silicate adsorbents. The most effective ratio between ethanol and water for PFOS recovery was 5:5. Recovery efficiencies of PFOS on silicate surfaces were easier and stable nearly 100%.

Keywords: perfluorinated surfactant, mesoporous silicate, surface functional group, adsorption

1. INTRODUCTION

The environmentally persistent Perfluorinated Compounds (PFCs) has been found to accumulate and biomagnify through food webs all over the world. Because of PFCs are used in a variety of products such as surface protectants, fire-fighting foams to the production of Teflon, lubricants, and insecticides. These compounds are regarded as potential hazards to human health [1,2]. There are several technologies for degradation or removal of PFCs contaminated in environment such as photolysis, biodegradation processes, and Advanced Oxidation Processes (AOPs). However, in many cases, these methods have proven to be ineffective [3]. Hence, some physical technologies including adsorption process by adsorbed onto Granular Activated Carbon (GAC) was investigated [4]. They found that adsorption capacity of PFOS and PFOA onto GAC were detected at 230 mg g^{-1} and 57 mg g^{-1}, respectively. However, activated carbon is microporous material which has low removal efficiency and selectivity for some kinds of PCFs.

To solve these problem, Hexagonal mesoporous silicates (HMS) having been studied extensively in adsorption and catalytic fields because it has mesoscale pore and uniform surface functional groups. Silanol group on HMS surface is expected to have high affinity to sulfonyl groups in PFOS molecules. Moreover, effects of surface functional groups, crystalline structure, as well as pH on PFCs removal from aqueous phase by adsorption have not been studied. Hence, adsorption of PFCs on three different types of surface functional groups (3-aminopropyltriethoxysilane, 3-mercaptopropyltrimethoxysilane and silanol group) grafted onto Hexagonal Mesoporous Silicate (HMS) was investigated.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Adsorbate

In this study an anionic Perfluorinated Compounds (PFCs), Perfluorooctane sulfonate (PFOS), were chosen as representative compounds. PFOS with a purity of 40% will be purchased from Fluka Chemica (Switzerland).

2.1.2. Preparation of Adsorbents

2.1.2.1. Synthesis of HMS

A direct co-condensation method was performed for organic functionalization of mesoporous materials by using dodecylamine as a template and tetraethoxysilane (TEOS) as a silica precursor by mix 29.6 mol of water with 0.27 mol of dodecylamine and 9.09 mol of ethanol to form as organic template of HMS. Add 1.0 mol of tetraethoxysilane (TEOS) in the mixture and were then mixed under vigorous stirring. The reaction mixture was aged at an ambient temperature for 18 hours. The resulting mixture was filtered and air-dried on a glass plate. The product was calcinated in air under static condition at 650˚C for 4 hours to remove organic template [5].

2.1.2.2. Synthesis of HMS

Mix 50 mol of water with 0.25 mol of dodecylamine and 10.25 mol of ethanol to form as organic template of HMS. Add 1.0 mol of tetraethixysilane (TEOS) in the mixture and were then mixed under vigorous stirring for 30 min. Then 0.25 mol of 3-aminopropyltriethoxysilane or 3-mercaptopropyltrimethoxysilane was added in the mixture (A-HMS and M-HMS, respectively). The reaction mixture was vigorously stirred for 20 hours at ambient temperature and the resulting were filtered and air-dried on a glass plate for 24 hours. Residual organosilane and organic template were removed by solvent extraction for 72 hours with ethanol [6].

2.1.3. Physico-Chemical Characterization for Adsorbents

Powder X-ray diffraction (XRD) patterns of synthesized adsorbents were recorded on a powder diffractometer equipped with Cu K∞ radiation (Bruker AXS Model D8 Discover). BET specific surface area was calculated from nitrogen adsorption isotherms measured at 77 K by an ASAP 2020 micromeritic surface area and porosity analyzer. Pore diameter and mesopore volume were calculated by D-H method. Surface functional groups were investigated after drying at 105 °C for 4 hours by FT-IR spectrophotometer. Surface charges of all adsorbents were determined by acid-base titration with HCl and NaOH as in the methods previously describe [5]. Elemental analysis, the amount of nitrogen and sulfur in synthesized HMSs were measured by UV adsorption technique and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), respectively.

2.1.4. Adsorption Experiments

Adsorption kinetic was performed by varying the equilibrium contact time from 0 to 48 hours under batch condition at concentration of PFOS 100 mg L^{-1}, and the amount ratio of adsorbent to PFOS solution were set at 0.067 g: 200 mL. The PFOS adsorption isotherm was performed by varying initial PFOS concentration from 25, 50, 75, 100, 200, 300 mg L^{-1} under batch condition. Fixed initial pH solution at 7 and ionic strength at 0.01 M by phosphate buffer. For adsorption isotherm, the initial pH of solution was varied at pH 5, 7 and 9 and fixed ionic strength at 0.01 M by phosphate buffer. All of adsorption experiments, samples were shaken in shaking water bath at 25±2°C, 150 rpm. All experiments were conducted twice and the average value was adopted.

2.1.5. PFOS Recovery

Adsorbed PFOS on hydrophilic pristine HMS was extracted by varying the ethanol and MilliQ water ratios, while the temperature remained constant at 25 ˚C for 3 hours. The PFOS concentrations from the extractants were investigated by measuring the amounts of sulfur using ICP-AES.

2.1.6. PFOS determination

After the adsorption experiments, the mixture was filtrated by filter paper no.42. The control experiments indicated that the adsorption of PFOS on the membrane was negligible due to their high concentrations in solution. The concentration of PFOS was determined by using Total Organic Carbon (TOC) Analyzer (TOC-VCPH) which is determining the total organic carbon of surfactant. A 20 mL of sample was adding into glass vial for measured. The sample volume injected was 50 µL. The sorption amount was calculated according to the difference of PFOS concentrations before and after sorption.

2.3. Results and Discussion

2.3.1. Physico-Chemical Characterization

In this study, physico-chemical characteristics of synthesized HMSs were investigated. Obtained data were combined with adsorption experiment results for study relationships between physico-chemical characteristics (crystalline structure, surface characteristics, hydrophilicity, surface charges, etc.) and PFOS adsorption phenomenon. Fig. 1. presents the X-ray Powder Diffraction (XRD) pattern of synthesized HMSs According to the XRD pattern, synthesized pristine HMS (pure silica HMS) exhibited a strong sharp single diffraction peak corresponding to the (100) plane at 2θ = 2.22° or d-spacing = 4.01

nm and weak diffraction peak corresponding to the (200) plane at 2θ = 4.3° or d-spacing = 2.06 nm as an evidence of the hexagonal crystalline structure which is characteristic of HMS materials. XRD pattern of functionalized HMS (A-HMS and M-HMS) founded that crystalline structure was lost by co-condensation method compared with pristine HMS result.

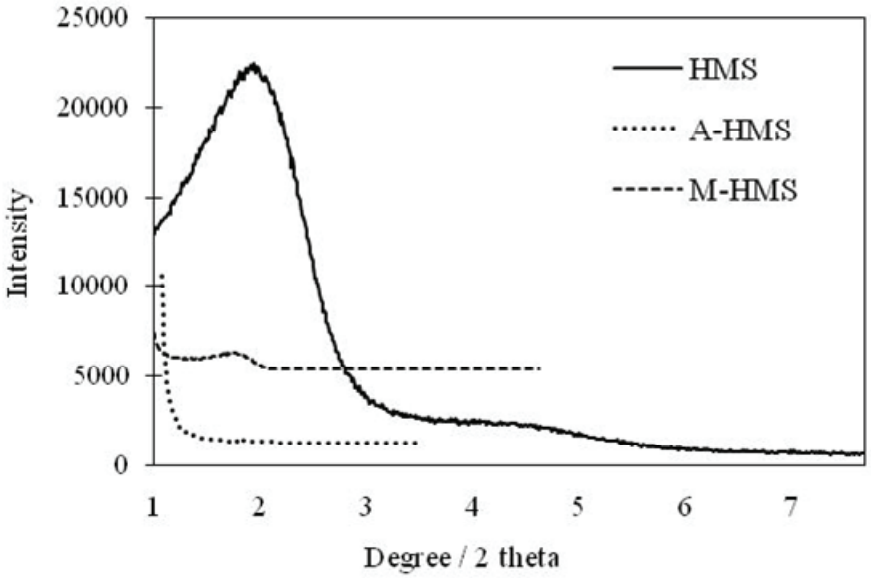


Figure 1. XRD Patterns of synthesized HMSs

Table 1. Physico-chemical characteristics of synthesized adsorbents (HMS, A-HMS and M-HMS)

Adsorbents	Pore diameter (nm)	BET Surface Area (m^2/g)	Pore volume (mm^3 g^{-1})	pH_{zpc}	Elemental (%N)	Elemental (%S)	Surface functional groups	Surface characteristic
HMS	2.60	712	773	4.0-6.00	-	-	Silanol	Hydrophilic
A-HMS	3.95	262	147	8.8	1.48	-	Amino, Silanol	Hydrophilic
M-HMS	2.48	912	433	3.97-6.14	-	9.92	Mercapto, Silanol	Hydrophobic

The BET surface areas, pore volumes, and pore size distributions of HMS, and functionalized HMSs were shown in Table 1. The results showed that specific surface areas of organosilane functionalized HMSs were decreased due to increasing of amino functional group. Obviously, amino-functional groups considerably affect the structure of mesoporous silicate which is indicative of decrease of BET surface area. On contrary, the specific surface area of M-HMS is larger than HMS indicating mercapto-functional groups do not affect disorder of mesostructure.

2.3.2. Adsorption Kinetic

Fig. 2 shows the adsorption kinetics of PFOS on the three adsorbents. The obtained results demonstrated that all the adsorption processes were time dependent. The adsorption of PFOS onto all adsorbents showed increase dramatically in first 30 minutes and reached equilibrium stage around 10 hours. To further understand the adsorption kinetics, the pseudo-first-order equation of Lagergren and the pseudo-second-order rate were evaluated base on the experimental data. These models have been successfully used in many adsorption processes over the whole time range, which can be expressed as follows [7]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_e and q_t are the amount of PFOS adsorbed on the adsorbents at equilibrium and time t (min); k_1 is Lagergren rate constant (min^{-1}); k_2 is the adsorption rate constant (($g\ mg^{-1}\ min^{-1}$).

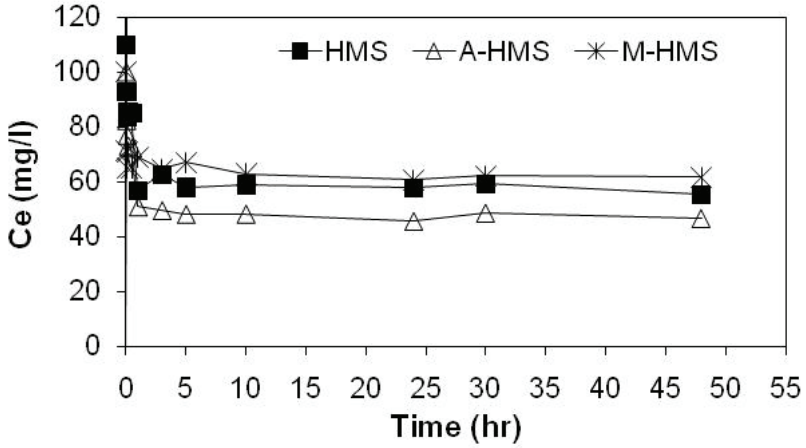


Figure 2. Adsorption kinetics of PFOS on synthesized HMSs at pH 7, IS 10 mM and 25 ˚C.

As shown in Table 2, the pseudo-second-order model fitted all the adsorption data well according to the relatively high correlation coefficients (R^2> 0.98), comparing with pseudo first order model.

Table 2. Kinetic parameters of PFOS adsorption onto HMS, A-HMS and M-HMS at pH 7.

Adsorbents	Pseudo First-order		Pseudo Second-order			
	R^2	k_1 (h^{-1})	R^2	k_2 (g mg^{-1} h^{-1})	Calculated q_e (mg g^{-1})	Experimental q_e (mg g^{-1})
HMS	0.3061	0.0691	0.9995	0.0043	41.10	43.46
A-HMS	0.3554	0.0967	0.9988	0.0003	157.41	159.25
M-HMS	0.6941	0.1105	0.9999	0.0004	115.27	114.63

2.3.3. Adsorption Isotherms

Fig. 3 illustrated adsorption isotherms of PFOS on pristine HMS, A-HMS and M-HMS at final pH solution in range of 6.5-7.0.

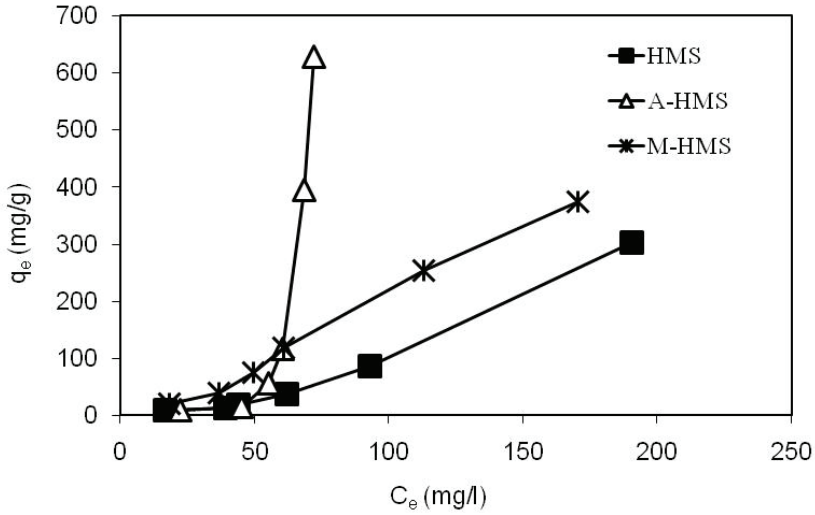


Figure 3. Adsorption isotherms of PFOS on synthesized HMSs at pH 7, IS 10 mM and 25 ˚C

The adsorption capacities of PFOS on A-HMS was highest followed with M-HMS and HMS, respectively. Adsorption of PFOS on A-HMS, which had both of high hydrophilicity and positively charged on surface comparing with silanol group on pristine HMS. On the contrary, hydrophobic interaction or van der Waals force might be the main interaction force for hydrophobic adsorbents (M-HMS). In this study, it found that effect of crystalline structure, surface area and pore volume of these synthesized HMSs did not affected adsorption of PFOS.

Two commonly used models, the Langmuir and Freundlich equations were adopted to describe the experimental data, which can be expressed respectively as:

$$q = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

$$q_e = K_f C_e^{1/n} \tag{4}$$

where q_e = equilibrium adsorption amount (mg g^{-1}), C_e represents the equilibrium concentration of adsorbate (mg L^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), b is a Langmuir coefficient related to the affinity between the sorbent and sorbate, k is Freundlich coefficient related to the affinity between the sorbent and sorbate, 1/n is Freundlich constants related to the concentration dependence. As shown in Table 3, the adsorption isotherms of PFOS on the three adsorbents can be fitted better by the Freundlich model than the Langmuir model with very high correlation coefficients ($R^2 > 0.98$). Hence, it might be indicated that adsorption phenomenon of PFOS on all adsorbents was multi-layer adsorption. According to the results of Freundlich fitting, all the isotherms are nonlinear as the values of 1/n. Nonlinearity may result from many causes such as the sorption site heterogeneity and sorbate–sorbate interactions [8]. Moreover, the sorbate–sorbate interactions such as electrostatic repulsion and hydrogen bonds may affect to the nonlinearity since the high concentrations of PFOS.

Table 3 Langmuir and Freundlich isotherms parameters of PFOS**.**

Adsorbents	Langmuir			Freundlich		
	q_m	K_L	R^2	K_f	$1/n$	R^2
HMS	7.9239	0.0064	0.9321	0.0663	1.4331	0.9926
A-HMS	18.975	0.0133	0.9910	6.984	3.5979	0.9966
M-HMS	172.414	0.0055	0.9828	0.410	1.3403	0.9922

2.3.4. Effect of pH

The effects of pH on the adsorption capacity of all adsorbents were investigated by varying pH of solution from 5, 7 and 9 controlled by phosphate buffer (Fig. 4.).

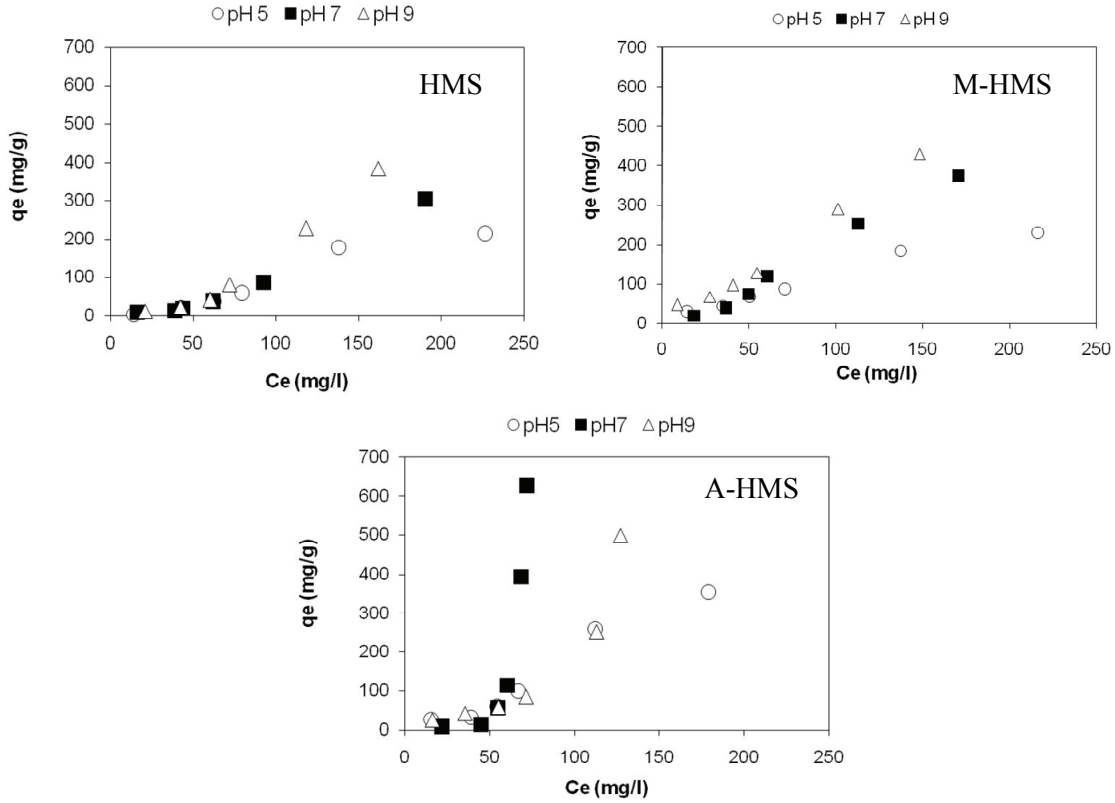


Figure 4. Effects of pH on adsorption of PFOS on synthesized HMSs

Increasing of positive charge on surface by decreasing of pH could enhance adsorption capacity of PFOS. However, it was found that at pH 9 adsorption capacities of PFOS adsorbed onto HMS and M-HMS were highest followed by pH 7 and 5, respectively. Hence, adsorption capacity of PFOS adsorbed onto these adsorbents was not affected by pH solution due to electrostatic interaction. For A-HMS, the obtained result showed consistent with surface charge of A-HMS caused by decreasing of pH solution. Moreover, at initial pH 5, adsorption capacity of HMS and M-HMS was lowest. It might be caused by electrostatic interaction between hydronium ion for water molecule and PFOS molecule which might interfere PFOS adsorption, especially at low pH solution.

2.3.5. PFOS recovery

From Table 4 recovery efficiency of PFOS from HMS increased when ratio between solvent and water was increased.

Table 4. Recovery ratio of PFOS for HMS

Solvent : Water	Recovery ratio % (100 mg/50 ml of mixture)
10:0	102
7:3	104
5:5	102
4:6	75
3:7	71.5
2:8	68.4
1:9	58.7

PFOS recovery efficiency of HMS was reached 100% when ratio of mixture was exceeded 5:5. Hydroxyl group of alcohol molecule is expected to play an important role in hydrogen bonding competition with HMS surface. Hydrogen bonding of hydrophilic part (sulfonyl functional group) of PFOS and silanol groups of HMS was suggested to be broken and replaced by alcohol molecule in the mixtures.

3. CONCLUSIONS

PFOS adsorption capacities adsorbed onto HMS and functionalized HMS at high level concentration were significantly affected by surface functional groups of adsorbents. 3-aminopropyltriethoxy-grafted HMS gave higher adsorption capacity compared with other silicate adsorbents. Adsorption of both PFOS at had highest adsorption capacities at pH 7 (pH 5-9). Hydrogen bonding and electrostatic interaction might play the important role for PFCs adsorption on silicate adsorbents. The most effective ratio between ethanol and water for PFOS recovery was 5:5. Recovery efficiencies of PFOS on silicate surfaces were easier and stable nearly 100%. Furthermore, crystalline structure might affect to PFOS adsorption capacities.

Acknowledgements

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REFERENCES

[1] N. Yamashita, G. Petrick , K. Kannan, S. Taniyasu, T. Gamo, Y. Horii, A global survey of perfluorinated acids in oceans, Mar. Pollut. Bull. 51 (2005) 658-668.

[2] K. Harada, A. Koizumi, K. Inoue, N. Saito, S. Kamiyama, S. Sasaki, T. Watanabe, T. Yoshinaga, The influence of time, sex and geographic factors on levels of perfluorooctane sulfonate and perfluorooctanoate in human serum over the last 25 years, J. Occup. Health. 46 (2004) 141-147.
[3] H. F. Schröder, R. J. W. Meesters, Stability of fluorinated surfactants in advanced oxidation processes - A follow up of degradation products using flow injection-mass spectrometry, liquid chromatography-mass spectrometry and liquid chromatography-multiple stage mass spectrometry. J. Chromatogr. A 1082 (1) (2005) 110-119.
[4] V. Ochoa-Herrera, R Sierra-Alvarez, Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. Chemosphere 70(10) (2008) 1588-93.
[5] P. Punyapalakul, S. Takizawa, Effect of Organic Grafting Modification of Hexagonal Mesoporous Silicate on Haloacetic Acid Removal, Environmental Engineering Forum 44 (2004) 247-256.
[6] P.T. Tanev, T.J. Pinnavaia, Mesoporous Silica Molecular Sieves Prepared by Ionic and Neutral Surfactant Templating: A Comparison of Physical Properties, Chem. Mater. 8 (1996) 2068-2079.
[7] Y.S. Ho, G. McKay, A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Process Saf. Environ. Protect. 76 (1998) 332–340.
[8] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char, Water Res. 35 (2001) 605–612.

PROCESS SIMULATION OF WATER WASH IN CO_2 ABSORPTION USING MONOETHANOLAMINE

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Abstract

In the research for a CO_2 removal process from exhaust gas, process simulation tools like Aspen Hysys and ProMax are used to evaluate absorption processes. This work continues the work with developing CO_2 removal processes from natural gas based power plants at Telemark University College. Implementation of water wash in the calculations is a challenge. The absorption and water wash columns have been simulated separately as well as combined by use of the process simulating tools Aspen Hysys and ProMax. The models that have been used to simulate absorber and water wash sections are Kent Eisenberg, Li-Mather, Wilson, NRTL and Electrolytic-NRTL. The MEA concentration in the decarbonated exhaust gas has been limited to 3 ppm through variation of column height, exhaust gas temperature, lean amine circulation rate and lean amine concentration. The Wilson model is better for water wash simulation in Aspen Hysys to calculate MEA concentration in the decarbonated exhaust gas. ProMax is a better simulation tool than Aspen Hysys to calculate MEA concentration in the decarbonated exhaust gas with either Kent Eisenberg or Electrolytic-NRTL model. In ProMax, the water wash column can be implemented using 1or 2 equilibrium stages with Kent Eisenberg or Li-Mather model. The most consistent way to simulate an absorption and water wash column is to use Aspen Hysys with Kent Eisenberg or Li-Mather model for the CO_2 absorption part and Wilson or NRTL model for the water wash part.

Keywords: *CO_2 absorption, Aspen Hysys, ProMax, monoethanolamine, process simulation*

1. INTRODUCTION

Implement the water washes and simulates it using a suitable simulation model is a challengeable work. This parametric study uses the Aspen Hysys software package (Aspen Hysys, 2006) to the process modelling based on aqueous MEA solution. In this work, water wash section simulates by changing several parameters. After the Aspen Hysys simulation, the ProMax simulation software is used to model the same absorption system. The ambition of this task is to identify the limitations and uncertainties of both Aspen Hysys and ProMax.

2. ELABORATION

2.1. Water Wash Section and Carbon Dioxide Absorption Section

An amine recovery apparatus including a carbon dioxide absorption section and two water washing sections (it is possible to achieve required target using only one water washing section) is described below in Fig. 1. The figure is based on information from the literature [1].

In the carbon dioxide absorption section the exhaust gas counter-currently is contacted with amine absorption liquid and produces decarbonated exhaust gas. The water washing sections bring the decarbonated exhaust gas into vapor-liquid contact with washing water and sequentially recover the amine compound accompanying the decarbonated exhaust gas. An explanation for the water washing section follows.

The combustion exhaust gas deprived of carbon dioxide (i.e. decarbonated exhaust gas) in the carbon dioxide absorption section of the carbon dioxide absorption tower travel through the demister 3 that is fixed just above the carbon dioxide absorption section and flows into the second stage of the water washing section. At this moment, the decarbonated exhaust gas carries some amine vapor. One reason is due to temperature rises in the decarbonated section. The reason for temperature rise is the exothermic reaction between carbon dioxide and the amine compound in the carbon dioxide absorption section. At this time, the decarbonated exhaust gas carrying water becomes a supply source for washing water in the

water washing section. The predicted temperature of the decarbonated exhaust gas flowing into the first-stage water washing section is about 50 to 80˚C.

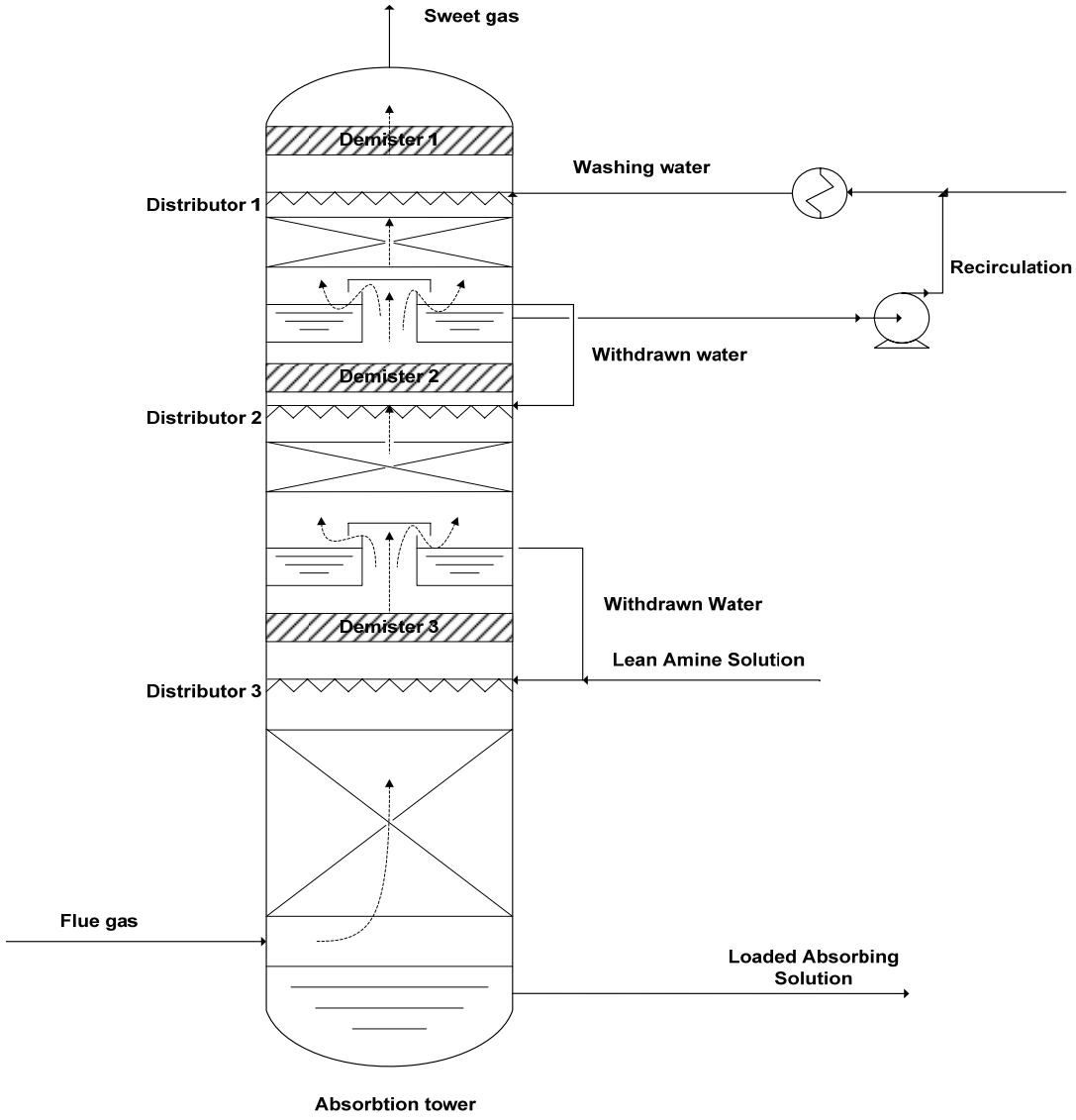


Figure 1. Amine recovery apparatus includes absorber and water washing section

The effluent of MEA (ppm) is not only dependent on equilibrium. But also vapour droplets will give MEA effluents. Because of this there will be a loss of the amine compound. The water droplets (absorbing solution) removed by the demister 3 flows downward and reserved at the bottom of the absorption tower. The excess water in the liquid reservoir in first stage is transported to the wash water line by a circulating pump. The circulating water and wash water is cooled by a heat exchanger and then supplied to the top of the first stage water washing section through distributor 1. The advantage of wash water cooling is to increase the absorption of CO_2. The reduced temperature reduces the equilibrium vapour pressure of amine and CO_2.

2.2. Models Available in Aspen Hysys and ProMax

The mostly used models for carbon dioxide absorption simulations in Aspen Hysys and ProMax can be categorized into four major models. Those are:

I. Kent and Eisenberg model
II. Li – Mather Electrolytic model
III. Wilson model
IV. Electrolytic NRTL model

2.3. Murphree Efficiency

The Murphree efficiency for stage number *n* is defined by:

$$E_M = \frac{(y - y_{n-1})}{(y^* - y_{n-1})} \tag{1}$$

where y is the mole fraction of CO_2 in the gas leaving stage, y_{n-1} is the mole fraction of CO_2 leaving the stage below, and y^* is the mole fraction CO_2 in equilibrium with the liquid leaving the stage [2]. This is illustrated in Fig. 2.

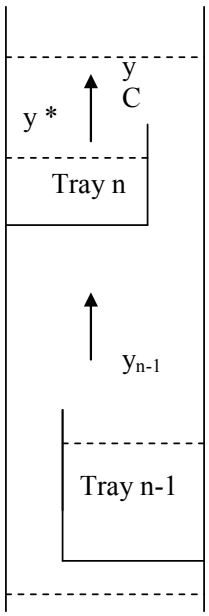


Figure 2. Definition of Murphree efficiency

2.3. Calculations

2.3.1. Aspen Hysys Implementations

The Aspen Hysys software has been used to calculate monoethanolamine concentration in the outlet decarbonated exhaust gas. These calculations are mainly implemented to analyze the behavior of the simulation models when those are applying to simulate the water wash section. The monoethanolamine concentration in the outlet decarbonated exhaust gas is calculated according to altering the column operating temperature, lean amine feeding flow rate for different column heights and lean amine feeding flow rate for different lean amine concentrations.

The water wash column which is having only 1 stage was separately simulated with varying the column operating temperature. The Wilson model was used as simulating model. Before treating from the wash water, the exhaust gas consisted of 350 ppm concentration MEA and rest completely nitrogen. The Murphree efficiency E_M is set at 70%. The wash liquid categorized into three different concentrations such as pure water, 0.5 M MEA and 1 M MEA. The temperatures of the two streams were altered from 30 to 60˚C along with column operating temperature. The exhaust gas molar flow and wash liquid mass flow are set at 85000 kmol h^{-1} and 10^5 kg h^{-1} respectively. After the simulations, variations of the MEA concentration in the decarbonated exhaust gas (sweet gas) with column operating temperature are plotted in the Fig. 3.

According to the Fig. 3., pure water does not contribute to increase the MEA concentration in the decarbonated exhaust gas with temperature increase. However 0.5 M and 1 M MEA solutions are having other behaviour than pure water. These two streams show that MEA concentration is increasing in the decarbonated exhaust gas with temperature rise. At 30 ˚C three streams gave MEA concentrations 0, 1 and 2 ppm respectively, and at 60 ˚C same streams gave MEA concentrations 1, 4 and 8 ppm respectively. In addition, the Nath and Bender [3] suggested that the activity coefficient must be laid in between 0.1-0.2 range for these temperatures.

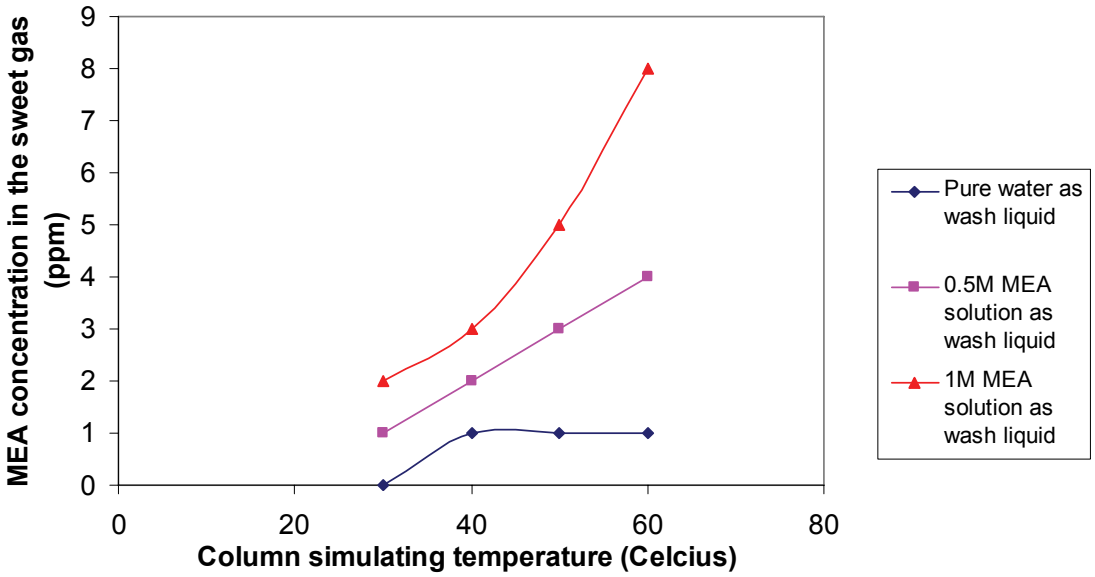


Figure 3. MEA concentration in decarbonated exhaust gas versus column operating temperature

The separate water wash column is having 2 stages and 6 stages are simulated separately without using amine property package. Wilson model is used as simulation model. The amine liquid which is fed to column as lean amine was set to 1M concentration. The column operating temperature and E_M is set at 60^0C and 70% respectively. The lean amine solution is fed to first stage in the column. The MEA concentration in the decarbonated exhaust gas is calculated by varying lean amine feeding flow rates for each height. According to the simulation results for 2 stages, the lowest MEA concentration in the decarbonated exhaust gas was 2.96 ppm. In fact, this concentration can be achieved by setting lean amine flow rate which is laid in the range 7×10^4 - 8×10^4 kg h^{-1}. The lean amine flow rate which is below or higher than this range always cause to increase the MEA concentration in the decarbonated exhaust gas than 3 ppm. According to the simulation results for 6 stages, the lowest MEA concentration in the decarbonated exhaust gas was 3 ppm at the 6×10^4 kg h^{-1} lean amine feeding flow rate. The lean amine feeding flow rates below or higher than above value couldn't achieve MEA concentration in the decarbonated exhaust gas below 3 ppm. However, the difference in between two different stages simulations is that, six stages column can achieve 3 ppm MEA concentration in the decarbonated exhaust gas relevant to low lean amine flow rate than 2 stages simulations.

The water wash column is simulated for three different lean amine concentrations, such as 0.03 M, 0.1 M and 1 M. Wilson model is used as simulation model. The solver and damping are selected as Modified HYSIM Inside-Out and Adaptive respectively. The simulations are conducted to two different column heights such as 6 and 7 stages. All simulations carried out at 60˚C temperature and 70% stage efficiency. The MEA concentration in the decarbonated exhaust gas is calculated according to varying the lean amine feeding flow rate for each above three concentrations. According to the simulation results for 6 stages, the lowest MEA concentrations in the decarbonated exhaust gas are 3, 0.5 and 0.3 ppm for 0.03 M, 0.1 M and 1 M lean amine concentrations respectively. The most significant thing is seen here that such MEA concentrations in decarbonated exhaust gas are appearing relevant to approximately between 6-7×10^4 kg h^{-1} lean amine feeding flow rate. According to the simulation results for 7 stages, the lowest MEA concentrations in the decarbonated exhaust gas are 0.07, 0.24 and 2.75 ppm for 0.03 M, 0.1 M and 1 M lean amine concentrations respectively. The most significant thing is seen here that such MEA concentrations in decarbonated exhaust gas are appearing relevant to approximately in between 4.7-5×10^4 kg h^{-1} lean amine feeding flow rate. The MEA concentration in decarbonated exhaust gas is remained lower value for the 7 stages than 6 stages for 0.03 M, 0.1 M and 1 M, respectively.

2.3.2. ProMax Implementations

The MEA concentrations variation in the decarbonated exhaust gas according to the number of absorber stages were calculated under conditions remained for every number of stages such as exhaust gas temperature 40 ˚C, lean amine circulation rate as 135000 kmol h^{-1} and Murphree efficiency E_M-25%. The exhaust gas contains H_2O, MEA, N_2 and CO_2 are set at 6.71%, 0%, 89.56% and 3.73% respectively. The Kent Eisenberg is used as simulation model. The numbers of stages were altered from 5 to 15. The

Fig. 4. explained the MEA concentration variations in the decarbonated exhaust gas according to the number of absorber stages.

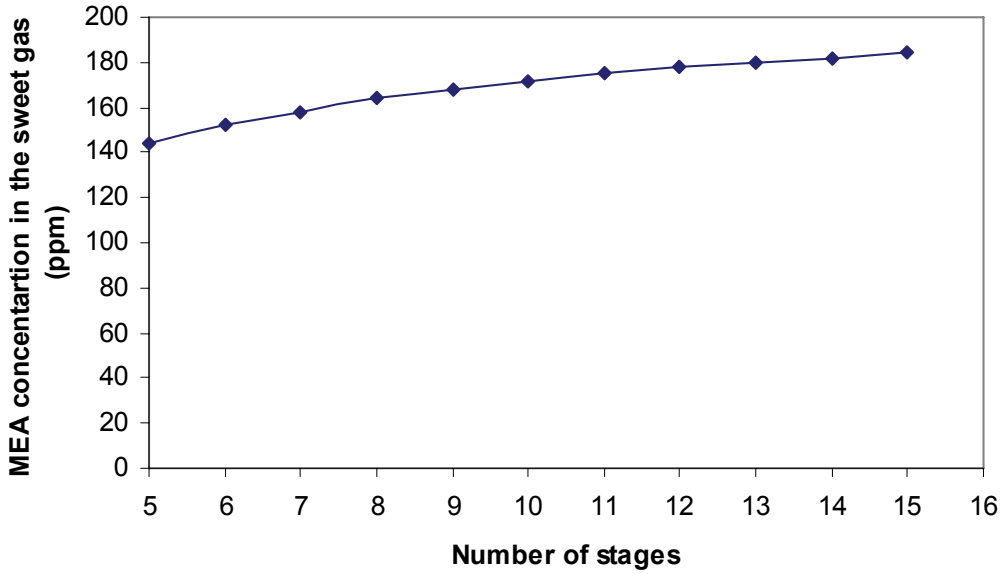


Figure 4. MEA concentration in the decarbonated exhaust gas versus number of stages

The water wash column is implemented in the top stages of the absorber column. However, simulations did not converge. Hence, the absorber column and water wash column were implemented separately. The number of stages is selected as 10 for the absorber column. The wash water stream flow rate is set at 90000 kg h^{-1}. Kent Eisenberg is used as simulation model. The MEA concentration in the outlet decarbonated exhaust gas is calculated according to altering the exhaust gas temperature. The calculated results are shown in the Fig. 5.

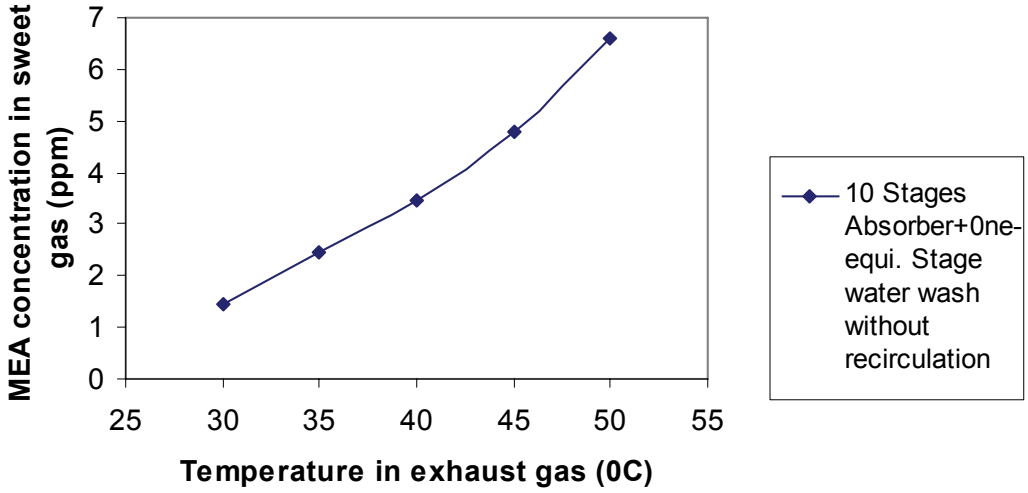


Figure 5. MEA concentration in the sweet gas versus temperature in the exhaust gas

In addition, 10 stages absorber with one-equilibrium stage water wash column was simulated without lean amine recirculation by using Electrolytic-NRTL model. Simulation conditions were remained as previous calculation. For in this case, the behavior of the MEA concentration in the decarbonated exhaust gas according to the temperature in the exhaust gas is remained similar to the Kent Eisenberg results. The details in the calculations are given in the Master Thesis report [4].

2.3.3. Models Comparing in Aspen Hysys

The MEA-Water vapour-liquid equilibrium mixture was simulated to compare the Kent Eisenberg, Li-Mather, Wilson and NRTL models with each other. All the simulations conducted at 40 ˚C temperature. The Table 1, 2, 3 and 4 are shown the calculations for Kent Eisenberg, Li-Mather, Wilson and NRTL models respectively.

Table 1. The Kent Eisenberg model

MEA concentration	Vapour phase mole fraction	Total pressure(Pa)	Partial pressure(Pa)	Activity coefficient(γ)
Pure MEA	1	164	164	
X_{MEA}=0.1	2.47×10^{-3}	6659	16.4	1.002
X_{MEA}=0.01	2.25×10^{-4}	7309	1.64	1.002

Table 2. The Li-Mather model

MEA concentration	Vapour phase mole fraction	Total pressure(Pa)	Partial pressure(Pa)	Activity coefficient(γ)
Pure MEA	1	164	164	
X_{MEA}=0.1	2.78×10^{-3}	6682	19	1.132
X_{MEA}=0.01	Outside range	-	-	-

Table 3. The Wilson model

MEA concentration	Vapour phase mole fraction	Total pressure(Pa)	Partial pressure(Pa)	Activity coefficient(γ)
Pure MEA	1	205	205	
X_{MEA}=0.1	1.29×10^{-3}	6472	8.3	0.407
X_{MEA}=0.01	6.93×10^{-5}	7308	0.51	0.247

Table 4. The NRTL model

MEA concentration	Vapour phase mole fraction	Total pressure(Pa)	Partial pressure(Pa)	Activity coefficient(γ)
Pure MEA	1	205	205	
X_{MEA}=0.1	1.17×10^{-3}	6490	7.6	0.370
X_{MEA}=0.01	6.46×10^{-5}	7308	0.47	0.230

2.4. Discussion

In Aspen Hysys, the absorption column along with water wash column has been simulated by altering the column operating temperature, lean amine feeding flow rate for different column heights and lean amine feeding flow rate for different lean amine concentrations. The simulation model was selected as Wilson model.

According to the Fig. 3, the exhaust gas temperature altered from 30 to 50 ˚C and which calculated MEA concentration in the decarbonated gas for three different lean amine concentrations. The calculated MEA concentrations are laid between 0 to 8 ppm. Then the water wash column height is changed to stages 2 and 6. In this each occasions lean amine feeding flow rate was altered while lean amine concentration remained at 1 M. The calculated MEA concentrations in the decarbonated exhaust gas are laid between 3 to 10 ppm. Finally, The MEA concentration in the decarbonated exhaust gas was calculated for 0.03, 0.1 and 1 M lean amine concentrations applying into the water wash column in two occasions such as 6 and 7 stages separately. The lean amine flow rate has altered here too to do the calculation. The calculated MEA concentrations have laid from 0.07 to 7 ppm. According to the above results, Wilson model realistically calculated the decarbonated exhaust gas MEA concentrations for water wash implementation in Aspen Hysys.

In ProMax, The absorber column has been simulated by altering the number of stages. According to the Fig. 4., the calculated MEA concentrations were laid in between 140 to 180 ppm. The simulated model was selected as Kent Eisenberg. The MEA concentrations in the decarbonated exhaust gas remained in realistic range.

Both Kent Eisenberg and Electrolytic-NRTL models were used to simulate 10 stages absorption column along with one-equilibrium stage water wash column in the condition of lean amine circulation rate-135000 kmol h^{-1} and E_M-25%. According to the Fig. 5., Kent Eisenberg equilibrium model calculated MEA concentrations in the decarbonated exhaust gas are laid in between 1 to 7 ppm for exhaust gas temperature variations. In addition to that, Electrolytic-NRTL model calculated MEA concentrations in the decarbonated exhaust gas are laid in between 1 to 10 ppm for exhaust gas temperature variations. Hence, these results proved that Both Kent Eisenberg and Electrolytic-NRTL models calculated the realistic results for MEA concentrations in the decarbonated exhaust gas by ProMax.

According to Tables 1 and 2, Kent Eisenberg and Li-Mather models have calculated the activity coefficient close to 1. This proves that Kent Eisenberg and Li-Mather models have conducted the calculation considering MEA-Water mixture as an ideal. Hence Kent Eisenberg and Li-Mather models are not realistic for MEA concentration calculations in Aspen Hysys. However, Table 3 and 4 show that Wilson model and NRTL models have calculated that the activity coefficient close to 0.25. This proves that both these two models are supposed to calculate MEA concentration more realistically in Aspen Hysys.

3. CONCLUSIONS

The absorption and water wash columns have been simulated separately as well as combined by use of the process simulating tools Aspen Hysys and ProMax. The models that have been used to simulate absorber and water wash sections are Kent Eisenberg, Li-Mather, Wilson, NRTL and Electrolytic-NRTL. The MEA concentration in the decarbonated exhaust gas has been limited to 3 ppm through variation of column height, exhaust gas temperature, lean amine circulation rate and lean amine concentration.

The Wilson model is better for water wash simulation in Aspen Hysys to calculate MEA concentration in the decarbonated exhaust gas. ProMax is a better simulation tool than Aspen Hysys to calculate MEA concentration in the decarbonated exhaust gas with either Kent Eisenberg or Electrolytic-NRTL model. These two models calculated the decarbonated exhaust gas MEA concentration within the range of 140 to 180 ppm in the absorber simulations. Those are more reasonable than the higher values (more than 300 ppm) calculated with Aspen Hysys. Aspen Hysys has shown better convergence characteristics for simulating all columns. Considering the water wash section, Wilson model might be a better selection to implement water wash column in Aspen Hysys. In ProMax, the water wash column can be implemented using 1or 2 equilibrium stages with Kent Eisenberg or Li-Mather model.

The most consistent way to simulate an absorption and water wash column is to use Aspen Hysys with Kent Eisenberg or Li-Mather model for the CO_2 absorption part and Wilson or NRTL model for the water wash part.

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REFERENCES

[1] T. Mimura , K. Ishida, Amine recovering apparatus and decarbonation apparatus having same, United States Patent, Mimura et al. (2008).
[2] Amines Property Package, page C-7.
[3] A. Nath, E. Bender, Isothermal vapour-Liquid equilibria of binary and ternary mixtures containing alcohol, alkanolamine, and water with a new static device. J. Chem. Eng. Data, (1983) 370-375.
[4] A.S.K Munasinghe, Master Thesis, Telemark University College, Porsgrunn, Norway (2009).

SOL-GEL PREPARATION, STRUCTURAL, TEXTURAL AND PERFORMANCE CHARACTERIZATION OF MIXED METAL OXIDE SORBENTS FOR HIGH TEMPERATURE GAS DESULFURIZATION

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Abstract

High temperature gas desulfurization (HTGD) is the main process for hydrogen sulfide removal from hot gases. Thus several metal oxide materials have been studied in an attempt to develop regenerable sorbents. Many metal oxides have been evaluated as regenerative sorbents and currently, $ZnO–TiO_2$ based sorbents appear to be leading for desulfurization. High temperature stable metal oxides such as Al_2O_3 can act as supports for strengthening the mechanical structure and prevent attrition or sintering of the sorbent during the regeneration process. In this work structural and textural modifications of $ZnO–TiO_2$ based sorbents by Al_2O_3 addition were studied. Five samples with composition $Zn_{(2-x)}Al_{2x}Ti_{(1-x)}O_4$, where x was 0, 0.25, 0.5, 0.75 and 1 were prepared. $ZnO–TiO_2–Al_2O_3$ type sorbents were prepared by sol-gel process followed by calcination at 500 °C for 2 h. The thermal evolution of obtained sorbents has been investigated using differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The crystallization products and structural properties were characterized using powder X-ray diffraction (XRD). The textural properties and pore size has been investigated using low temperature nitrogen adsorption. Nanocrystalline powders were produced at the low sintering temperature of 500 °C and the short sintering time of 2 h. Depending on the initial $ZnO:TiO_2:Al_2O_3$ molar ratio, zincite (ZnO), brookite (TiO_2) as well as gahnite ($ZnAl_2O_4$) solid solution were formed. The introduction of Al_2O_3 also induces textural modifications, causing changes in pore structure and the increase of specific surface area from 34 to 90 $m^2\ g^{-1}$. The sorbent sulfidation performance was tested using newly developed procedure comprising batch sulfidation process followed by XRD and TGA analysis and the results obtained are discussed on the basis of structural and textural properties. Sorbent with composition $Zn_{1.75}Al_{0.5}Ti_{0.75}O_4$ was found to possess the highest sulfidation reactivity, i.e. sulphur removal efficiency.

Keywords: *HTGD, desulfurization, sorbent, ZnO-Al_2O_3-TiO_2*

1. INTRODUCTION

Integrated gasification combined cycle (IGCC) system is one of the most promising power systems for producing electrical energy from coal due to the noticeable improvement in thermal efficiency that it can provide. This advanced power generating system involves the direct contact of hot coal-derived gases with turbine blades. In order to ensure high environmental requirements and the corrosion and abrasion protection of the turbines and related equipment, precleaning of the coal gas from pollutants, especially hydrogen sulphide, H_2S, is necessary. Economical as well as environmental aspects for advanced power generating systems mandate the high temperature gas desulfurization (HTGD) as the main process for the removal of the most abundant sulphur-containing compound in coal gas, hydrogen sulphide, which can react readily with the oxides of alkali earth and transition metals [1].

The development of metal oxide materials as a durable, chemically, mechanically and thermally stabile regenarable sorbents capable in supporting multiple desulfurization-regeneration cycles has been the goal of several studies. In vast number of metal oxides proposed, zinc-oxide based sorbents are being recognized as the one with best cost-benefit ratio and it are proven HTGD sorbents for removal of hydrogen sulphide. Despite zinc-oxide ensure efficient reduction of hydrogen sulphide ratio to the ppm level, it is unable to provide stable long term stable desulfurization-regeneration process. Namely desulfurization conditions promote reduction of Zn^{2+} to Zn, also, due to harsh temperature process conditions zinc is evaporating from the sorbent [2]. Another weakness of zinc oxide are insufficient mechanical properties yielding wearing during fluidization in the course of sulfidation-regeneration process [3,4].

In order to surpass those disadvantages combination of zinc oxide with other compounds was investigated [5-7]. Combination of ZnO with other metal oxide compounds were achieved in order to provide upgrade in ZnO based sorbents. TiO_2 and Al_2O_3 were emphasized as most useful to combine with. Combination with compounds like titanium oxide can provide thermal stability of the sorbent, i.e. can prevent the evaporation of the zinc [8]. On the other hand, by combination with Al_2O_3, which is proven as high temperature stable and durable material, mechanical wearing and attrition of the sorbent are to be minimized. Also the high temperature sintering process should be postponed, influencing in the pore structure which should lead to increase in specific surface. By the enlarged interaction interface a better desulfurization efficiency should be noticed [3,4].
The ability to provide efficient sorbent should not only be focused in optimizing of the chemical composition yet in proficient production technique. Vast number of sorbents are prepared by high temperature techniques which could annul the benefits achieved by chemical composition [9,10]. Therefore a technique which offers possibility to achieve sorbent synthesis at lower temperatures, the sol-gel technique, was applied [11].

In this work several combinations of the ZnO-Al_2O_3-TiO_2 based sorbent were synthesised by means of sol-gel process and investigated. Yielded sorbent performance was tested by newly developed high temperature and high pressure sulfidation process in batch reactor.

2. ELABORATION

2.1. Experimental

Materials used to prepare precursor gels were Aluminium sec butoxide (Asb, $Al(O^sBu)_3$, 97%, Acros organics, Belgium), Titanium n-butoxide (Tnb, $Ti(O^nBu)_4$, 98%, Alfa Aesar, Germany), Zinc nitrate hexahydrate ($Zn(NO_3)_2{\times}6H_2O$, 98%, Riedel-de Haën, Germany). Ethyl acetoacetate (Eaa, $C_6H_{10}O_3$, 99%, Fluka, Germany) was used as a complexing agent while Isopropyl alcohol (C_3H_7OH, 99%, Carlo Erba Reagents, Italy) was used as a solvent. All chemicals were used as received.

The appropriate amounts of Asb and Tnb were dissolved in Eaa and isopropyl alcohol solution independetly, also zinc nitrate hexahydrate was dissolved in isopropyl alcohol. The molar ratio of Asb and Tnb to Eaa was held 1/1 as it was previously experimentally proven to be optimal [12]. The mixtures were stirred 30 min. Then the Tnb solution was dropwise added to Asb solution and stirred for additional 30 min. After that the Zn nitrate solution was added in the same manner and the whole was stirred for 24 h at room temperature during which gelation occurred. The obtained samples were subsequently grinded to fine powders and stored. For the experiment five gels were prepared with compositions 0.500 ZnO x 0.500 Al_2O_3, 0.556 ZnO x 0.333 Al_2O_3 x 0.111 TiO_2, 0.600 ZnO x 0.200 Al_2O_3 x 0.200 TiO_2, 0.636 ZnO x 0.091 Al_2O_3 x 0.273 TiO_2 and 0.667 ZnO x 0.333 TiO_2, corresponding to the ternary diagram intersections as shown on Fig. 1. and denoted accordingly.

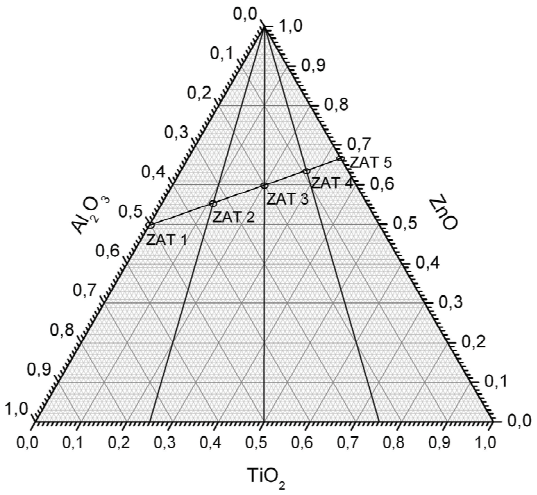


Figure 1. Starting molar composition and sample notation.

IR spectra of the samples were acquired using the Fourier transform infrared spectrometer Bruker Vertex 70 in ATR (attenuated total reflectance) mode. The samples were pressed on a diamond and the absorbance data were collected between 400 and 4000 cm^{-1} with spectral resolution of 1 cm^{-1} and 64 scans.

The crystal phases were identified by powder X-ray diffraction (XRD) using Shimadzu diffractometer XRD 6000 with CuKα radiation. Data were collected between 5 and 70° 2θ in a step scan mode with steps of 0.02° and scan speed of 2° 2θ min^{-1}.

The thermal behaviour of powder precursor was characterized with Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) using simultaneous DTA/TGA analyzer Netzsch STA 409. For the thermal analysis approximately 50 mg of material were placed in Pt crucibles and heated at a rate of 10 °$Cmin^{-1}$ to 1000 °C in a synthetic air flow of 30 cm^3min^{-1}, α-alumina was used as a reference.

Specific surface area of powders was determined by a Brunauer–Emmet–Teller (BET) N_2 gas adsorption-desorption isotherm obtained at 77 K on a Micromeritics ASAP-2000 equipment. Sample was previously degassed at 400 °C under a dynamic vacuum of $1.3* 10^{-2}$ Pa.

Sulfidation process was performed in a batch reactor. Approximately 250 mg of all samples ZAT 1 – 5 and reference ZnO sample were placed in separate crucibles in the reactor. Separately, FeS grains and 10% H_2SO_4 (Kipp's generator based setup) were prepared in order to produce H_2S. Reactor was heated at 200 °C for 2 hours.

The weight changes during regeneration process were monitored by Thermo-Gravimetric Analysis (TGA) using Perkin Elmer TGS-2 in Pt crucible and heated at a rate of 10 °$Cmin^{-1}$ to 1000 °C.

2.2. Results and Discussion

From the FTIR investigation of the gels the information about the chelation process can be obtained. Infra red spectra of the samples ZAT 1 – ZAT 5 dried gels are presented in Fig. 2. The assignments of FTIR spectra of Eaa based chelates is assigned as described in literature [13]. Eaa was added to the system in order to stabilize the rate of alkoxide hydrolysis. ß-ketoesters like Eaa resonate between keto and enol form (keto-enol tautomerism), in which the keto form is favoured in pure Eaa, while upon forming chelate with alkoxide enol form dominates. By monitoring the keto-enol equilibrium it is possible to have insight in the hydrolysis and condensation, i.e. in the sol-gel process.

IR spectra yield bands that are assigned to keto and enol form of Eaa. Eaa in both forms shows absorption frequencies from C-H stretching vibrations in region 2980-2850 cm^{-1}. Band at 2980 cm^{-1} results from the asymmetrical stretching mode in which two C-H bonds of the methyl group are extending, while the third one is contracting (ν_{as} CH_3). Band at 2870 cm^{-1} arises from symmetrical stretching (ν_s CH_3) in which all three C-H bonds extend and contract in phase. The asymmetrical stretching (ν_{as} CH_2) and symmetrical stretching (ν_s CH_2) occur at 2940 and 2850 cm^{-1}, respectively. Also bands at 1475 cm^{-1} (due to asymmetrical bending vibration involves out-of-phase bending of the C-H bonds, δ_{as} CH_3) and 1369 cm^{-1} (due to symmetrical bending vibration involves in phase bending of the C-H bonds, δ_s CH_3) were noticed. The CH_2 scissoring band in the spectrum occurs at 1470 cm^{-1}. The absorption frequencies from O-C-C stretching, -C-C-O stretching and C-C stretching occur at 1040 cm^{-1}, 1155 cm^{-1} and 1317 cm^{-1}, respectively.

Characteristic band for the keto form of Eaa occurs at 1753-1718 cm^{-1} due to the C=O stretching vibration of two carbonyl groups. Instead of bands of the keto form, in the spectrum of enolic form characteristic bands are observed at 1650 cm^{-1} due to hydrogen bonding between the ester C=O and the enolic hydroxyl group, as well as absorption frequencies of the alkene bond in conjugation with a carbonyl group at 1630 cm^{-1}. Eaa in chelate shows characteristic absorption bands at ~1610 cm^{-1} due to a C-O in enolic form bonded to Al, as well as absorption band at ~1525 cm-1 due to a C-C vibration of six membered ring of the complex. The major absorption bands due to a NO_3^- are located at 1305, 1445 and 1630 cm^{-1}, mostly overlapped with Eaa bands.

FTIR spectra presented in Fig. 2 confirm that Eaa, in all samples, i.e. for all Eaa/Asb/Tnb ratios, reacts with alkoxides and forms chelate. As can be seen, although the dominance of the enol form was observed, part of Eaa in dried samples is in keto form due to advanced hydrolysis process.

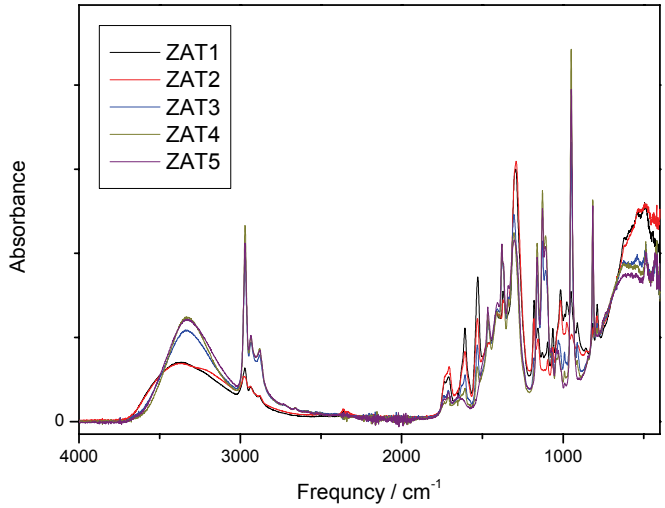


Figure 2. IR spectra of samples ZAT 1 – 5

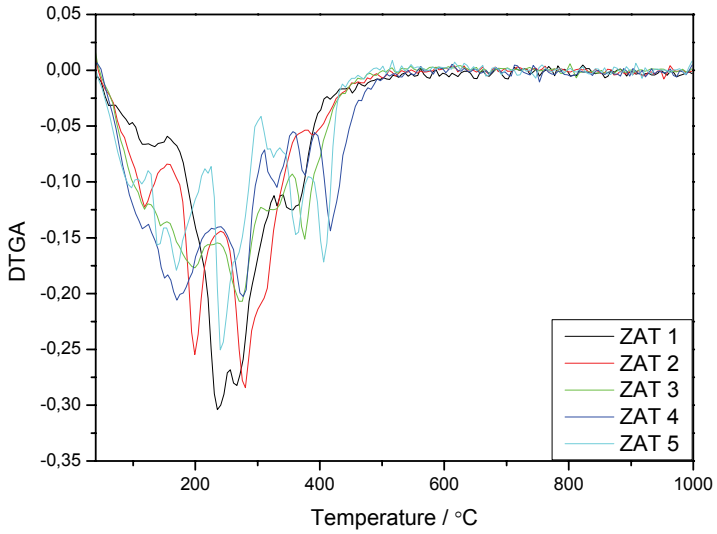


Figure 3. DTGA scans of all ZAT samples

The thermal behaviour of the all dried gels is characterized by multistep weight loss in the temperature range of 100-450 °C as shown by DTGA measurement on Fig. 3. In the higher temperature region the weight loss is constant at approximately 55 % mass loss for all samples (TGA scan, not shown on Fig. 3). DTA curves of all samples consist of series of endothermic and exothermic effects with various intensity and mutual superposition (not shown in Fig. 3) and correspond well to DTGA data in Fig. 3. In the temperature range up to 300 °C expected phenomena are related to the subsequent releases of adsorbed and chemisorbed water. Furthermore solvent degradation follows. At about 300 °C nitrates decompose [14]. At the temperatures above 300 °C effects occurring can be related to crystallization processes in system. Several crystal compositions are possible to occur, however to provide exact assignation of DTA effects structural investigations should have been performed at various temperatures. This was not the aim of this work; instead crystal composition was monitored after thermal treatment at the temperature of 500 °C and discussed in XRD section.

Samples were fired at as low as 500 °C for 2 hours in order to preserve high specific surfaces, as the temperature increase would cause increased sintering and therefore promote the reduction of the specific surface. All ZAT samples fired at 500 °C were subjected to XRD analysis in order to determinate phases present in the studied system (Fig. 4a). All scans exhibit crystalline phases. Chemical composition of the sample ZAT 1 was targeted to fit gahnite and gahnite is confirmed. ZAT 5 should fit to Zn_2TiO_4, as confirmed. Samples ZAT 2, 3 and 4 resemble to composition and phases chemically between the two

mentioned (zinc alumotitanate solid solutions). In samples ZAT 2-5 zincite, ZnO, has been noted, while in sample ZAT 5 brookite, TiO_2, crystallized.

To facilitate high efficiency of the sorbent it is essential to provide reaction interface as immense as possible during the whole cycle. To evaluate if the synthesis has been successful in terms of specific surface before and after sulfidation, BET measurements were performed. The determined specific surface areas are shown in Table 1. As can be seen, the greater alumina content brings about better texture properties.

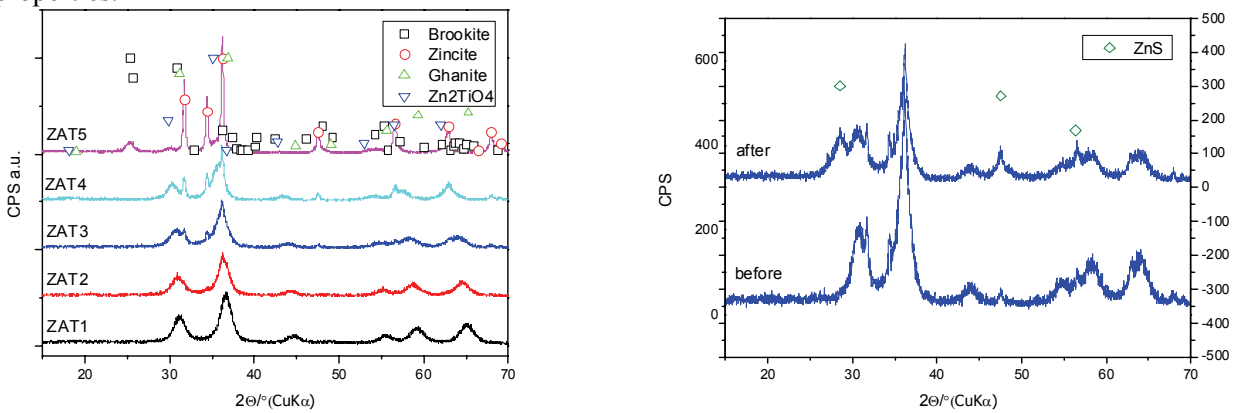


Figure 4. a) Diffractograms of samples ZAT 1 – 5 fired at 500 °C for 2 hours b) Comparison of diffractograms of sample ZAT 3 before and after sulfidation.

Table 1. BET specific surface of samples ZAT 1- 5

Sample	Specific surface area / m^2g^{-1}
ZAT 1	89.58
ZAT 2	88.98
ZAT 3	79.05
ZAT 4	67.74
ZAT 5	33.58

The conversion to ZnS has been investigated in a simulated sulfidation-regeneration process involving batch reactor for H_2S exposure as sulfidation and thermogravimetric method in synthetic air as regeneration process. After sulfidation process all samples were structurally analyzed by means of XRD analysis. The diffractograms of sample ZAT 3 before and after sulfidation are shown as example (Fig. 4b). All scans generally resemble very well to the diffractograms before sulfidation with one major difference; the occurrence of ZnS diffraction lines in all samples in various intensity. At the same time the intensity of zincite and spinel diffraction lines was reduced. Obviously, during the sulfidation process ZnO and spinel solid solution were partially converted to ZnS. Beside the establishment of phase composition in such manner the reliability of the batch method has been confirmed.

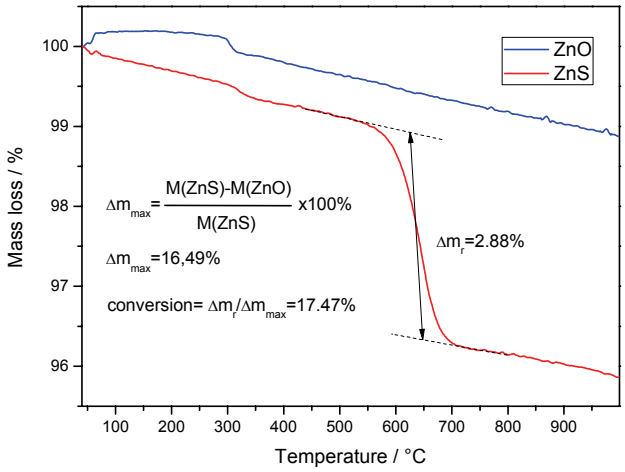


Figure 5. TGA regeneration of sulfidated ZnO reference sample

The amount of ZnS formed in the course of sulfidation process could be calculated from the mass loss in the course of regeneration process as shown in Fig. 5. The TGA curve of reference sample (pure zincite) was used to demonstrate the procedure. By assuming that all of the formed ZnS regenerates back to ZnO during the TGA measurement, the calculation of the sulfidation efficiency is enabled only from molar masses. For samples ZAT 1 - 5 the results are given in Table 2. As can be seen, best sulfidation efficiency exhibits sample ZAT 4 (composition $Zn_{1.75}Al_{0.5}Ti_{0.75}O_4$).

Table 2. Mass loss in the course of regeneration in TGA apparatus and calculated conversions.

Sample	Mass loss / %	Conversion / %
ZAT 1	3.97	24.08
ZAT 2	3.81	23.10
ZAT 3	4.11	24.92
ZAT 4	5.59	33.90
ZAT 5	3.95	23.95

For future work it would be interesting to correlate exactly the crystal species and appropriate amounts or ratios involved in the ZnO – ZnS – ZnO cycle. From quantitative XRD analysis it would be possible to calculate all conversions from exact crystal compositions. Furthermore the exact assignation in the course of thermal evolution could also lead to greater improvements in sorbent efficiency.

3. CONCLUSIONS

The novel zinc oxide based sorbents for high temperature gas desulfurization (HTGD) were prepared by sol-gel synthesis. FTIR analysis confirmed optimal synthesis parameters. When thermally treated at 500 °C samples yield several crystal phases: gahnite, zinc titanate, zinc alumotitanate, zincite and brookite, and show high specific surface areas.

A novel batch reactor for sulfidization of prepared sorbents was introduced. Monitoring of the ZnO – ZnS – ZnO cycle was enabled, revealing the efficiency of prepared sorbents. Sorbent with composition $Zn_{1.75}Al_{0.5}Ti_{0.75}O_4$ was found to possess the highest sulfidation reactivity, i.e. sulphur removal efficiency.

Acknowledgement

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REFERENCES

[1] T. Kyotani, H. Kawashima, A. Tomita, A. Palmer, and E. Furimsky, Removal of H_2S from hot gas in the presence of Cu-containing sorbents, Fuel 68 (1989) 74-79.

[2] W. Mojtahedi, J. Abbasian, H_2S removal from coal gas at elevated temperature and pressure in fluidized bed with zinc titanate sorbents. 1. Cyclic tests, Energy Fuels 9 (1995) 429-434.

[3] M. Dancila, I. Untea, V. Badilita, The Influence of Admixture of Al_2O_3 on the ZnO–TiO_2 Sorbent of Sulfurization–Regeneration trough Oxidation in Air at High Temperature, Revista de Chimie 58 (2007) 640–645.

[4] I. Untea, M. Dancila, E. Vasile, M. Belcu, Structural, morphological and textural modifications of ZnO-TiO_2 HTGD based sorbents induced by Al_2O_3 addition, thermal treatment and sulfurizing process, Pow. Teh. 191 (2009) 27-33.

[5] S.C. Christoforou, E.A. Efthimiadis, I.A. Vasalos, Sulfidation of mixed metal oxides in a fluidized-bed reactor, Ind. Eng. Chem. Res 34 (1995) 83–93.

[6] E. Garcia, C. Cilleruelo, J. Ibarra, M. Pineda, J.M. Palacios, Kinetic study of high temperature removal of H_2S by novel metal oxide sorbents, Ind. Eng. Chem. Res 36 (1997) 846–853.

[7] Y. Li, H. Guo, C. Li, S. Zhang, A study on the apparent kinetics of H_2S removal using a ZnO–MnO desulphurizer, Ind. Eng. Chem. Res 36 (1997) 3982–3987.

[8] M.C. Woods, S.K. Gangwal, K. Jothimurugesan, D.P. Harrison, Reaction between hydrogen sulphide and zinc oxide-titanium oxide sorbents. 1. Single-pellet kinetic studies, Ind. Eng. Chem. Res 29 (1990) 1160–1167.
[9] S.Y. Jung, S.J. Lee, J.J. Park, S.C. Lee, H.K. Jun, T.J. Lee, C.K. Ryu, J.C. Kim, The simultaneous removal of hydrogen sulphide and ammonia over zinc-based dry sorbent supported on alumina, Sep. Pur. Tech. 63 (2008) 297–302.
[10] R.B. Slimane, J. Abbasian, Regenerable mixed metal oxide sorbents for coal gas desulfurization at moderate temperatures, Adv. Env. Res. 4 (2000) 147-162.
[11] S. Kurajica, G. Mali, T. Gazivoda, J. Šipušić, V. Mandić, A spectroscopic study of calcium aluminate gels obtained from aluminium sec-butoxide chelated with ethyl acetoacetate in various ratios, J. Sol-Gel Sci. Tech, 50 (2009) 158-168.
[12] M.M. Haridas, N. Goyal, J.R. Bellare, Chemical synthesis of optical grade ceramic precursors: a spectrophotometric approach for analysis, Ceram. Intl. 24 (1998) 415-420
[13] R.M. Silverstein, F.X. Webster, Spectrometric Indetification of organic Compounds, 6th Ed., J. Willey & Sons Inc, New York, USA, 1998.
[14] S. Kurajica, V. Mandić, J. Šipušić, Thermal evolution of calcium aluminate gel, J. Cer. Sci. Tech. 2 (2011) 15-22.

RESEARCH ON WASTE REDUCTION TECHNOLOGIES IN EUROPE- AN ANALYSIS OF FP7-FUNDED PROJECTS AND NETWORKS

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Abstract

The main objective of this paper is to offer a profound overview of recent research trends and structures in European waste reduction research based on the 7th Framework Programme (FP7), the most important RTD programme in Europe. In order to analyse Europe-wide research efforts on waste reduction technologies we conducted a qualitative and quantitative analysis of 50 FP7-funded research projects to assess which approaches they take, which technologies they develop and which types of organisations play a leading role. We found that projects care for a multiplicity of environmental technologies concerning waste reduction. The most prominent research fields comprise: (1) the recovery of by-products and waste into biomass and other valuable products; (2) the development of technologies to rework manufacturing discarded products and therefore reduce the total use of raw materials; (3) the improvement of manufacturing technologies in order to cut down on industrial waste; and (4) the support of the development of recycling management processes. Research organisations from Germany play the most important role in waste research. 52% of all the participants are from the industry sector, which therefore plays an essential role. The three approaches show that FP7 supports the shift to a cradle-to-cradle society and is (at least partly) in line with the aims of the new Flagship Initiative "A Resource-Efficient Europe".

Keywords: *waste related research, waste hierarchy, waste technologies, research programme evaluation, resources efficiency, waste prevention*

1. INTRODUCTION

The global perspective concerning production and consumption is pointing to an alarming situation in terms of pollution and inability of management and storage of discarded products. A crucial issue is the worldwide effort from a "cradle-to-grave" way of thinking towards a more sustainable "from cradle-to-cradle" approach [1], the application of life-cycle thinking, reuse and recycling towards a "zero waste" society [2].

1.1. Policy Background

Two documents at EU level shape the policy background of this paper: the "Thematic Strategy on Waste Prevention and Recycling" under the 6th Environment Action Programme of the European Community 2002-2012 and the "Resource Efficiency Flagship Initiative" under the Europe 2020 Strategy. Based on the European Commission's Communication of the year 2005 the Thematic Strategy on Waste Prevention and Recycling [3] had been reviewed last year [4] and a new Communication was adopted by the Commission on January 19th 2011 [5]. The accompanying Staff Working Document [6] again highlights two key concepts which were already put in the focus of the Thematic Strategy a long time ago: the Waste Hierarchy and the Life Cycle Approach. In addition, the main challenges and recommendations for future actions in the area of Waste Management were described as (1) waste prevention transformation to a recycling society, (2) establishing markets for recycling products and secondary raw materials, (3) improving the effectiveness of recycling, (4) eliminating the difference in waste management between the European Member States, and (5) assessing the environmental impacts of recycling products and secondary raw materials. Summarising these issues one could identify a need to shift from treatment of waste (output orientation, cradle-to-grave approach) to resource management (input orientation, cradle-to-cradle approach). This shift is mirrored in the raise of importance of resource efficiency in European policies during the last decade. While in 2005 the EU Thematic Strategy on the Sustainable Use of Natural Resources [7] was a part of the 6th Environment Action Programme (and therefore just part of environmental policies), the issue became much more prominent as it became the Flagship Initiative "A resource-efficient Europe", one of the seven Flagship Initiatives [8] of the new

Europe 2020 strategy for smart, sustainable and inclusive growth (and therefore part of economic policies and competitiveness issues). It aims at a resource-efficient, low-carbon economy to achieve sustainable growth by improved productivity, cost savings and increased competitiveness. Therefore, research of new technologies is a key issue and the focus of our paper.

1.2. Research Background

As many different technologies, communities and markets are involved in waste reduction (e.g. waste to energy conversion, eco-design, dematerialization, industrial ecology), there is currently no overarching research agenda in this area – at least not on European level. On national level several strategies or programmes [9-12] and several leading researchers identified areas of future waste related research [13,14]:

- Research on the collection and treatment of the main waste streams such as household waste and industrial waste
- Research to improve waste collection and treatment processes, with a particular reference to anaerobic digestion, conversion of bio-waste into valuable products and improvement of the sorting system
- Research on materials coming out of recycling and reuse processes to test their usability for other production purposes and to assess their impacts on environment and health
- Research on reuse practices which are proficient from the point of view of both the company producing the material as a by-product and the company reusing it

In our study we wanted to analyse the most recent research trends in Europe and to assess which of the needs mentioned above are already taken up. We therefore identified and analysed research topics, projects and networks on life-cycle thinking, reuse and recycling in the 7th EU Framework Programme.

1.3. Scope and Focus of This Paper

The 7th Framework Programme (FP7) is the most important programme for research and technological development in Europe: with a total budget of more than 50 billion euros, a duration of seven years, a broad variety of themes and several thousands of research topics and projects, the programme is currently running from 2007 to 2013 and has a key role in terms of global competitiveness, economic growth and sustainable development of Europe. As FP7 allows conducting research on an international scale and therefore contributes to a European research area, it can be used as a main source to analyse which Europe-wide research projects are currently funded and on which issues they are focusing. Based on this analysis, we wanted to assess which networks and countries are in a leading position and which types of projects are currently carried out. In doing so, our analysis offers a profound overview of recent research trends and structures in European waste research and therefore serves as an important source for future R&D policies in the area of waste.

2. ELABORATION

2.1. Methodology

Assessing waste related research topics, projects and networks in FP7 is not easy, as none of the FP7 themes is targeted towards waste related research. To overcome these methodological challenges, we carried out our analysis in three subsequent steps.

(1) In a first step we used the FP7 monitoring system (www.FP7-4-SD.eu) [15], which we developed and maintained during the last years. It is based on the FP7 programme documents (i.e. annual work programmes containing more than 800 research topics every year) and links them to the operational objectives of the EU Sustainable Development Strategy. This allowed us to identify 35 research topics with expected positive impacts on two policy objectives:

- avoid generation of waste by applying the concept of life-cycle thinking
- avoid generation of waste by promoting reuse and recycling

(2) In a second step we carried out a qualitative and quantitative analysis based on the descriptions of 50 research projects which are linked to the topics we identified in the first step. Based on the project abstracts and (when available) a more detailed description of work packages we identify the typology of technology developed as well as the key waste streams involved and their provenience. In addition, we processed data on the total project budget and the EU funding. In doing so, we were distinguished between the different approaches of the Waste Hierarchy [6].

(3) In a third step we carried out a network analysis of partners and countries involved in the 50 projects identified in the previous step. In doing so we processed data on the project participants, their types of institution and their countries of provenience. This allowed us to identify the most important regions and collaboration structures in European waste research.

2.2. Results and Discussion

2.2.1. Research on Waste Technologies in the 7th EU Framework Programme for RTD

The 50 FP7-funded projects dealing with life-cycle thinking, reuse and recycling represent a total research budget of 340 million euros. The FP7-funding to the project budget is in total 229 million euros (in average 67% of the project budget). As the funded projects strongly depend on EU funding one can conclude that most of them would not exist without FP7. The average project duration is about three years (24 projects run between two and three years, 22 projects between three and four years and just 4 projects have a duration of less than two or more than four years). As already mentioned none of the FP7 themes is targeted specifically towards waste related research. Table 1 shows that waste related research projects can be found in several FP7 themes with rather different key indicators: while in the FP7 themes Energy and ICT rather large project with a total budget of about 12 million euros can be found, most of the projects funded in the other themes have a significantly lower budget.

Table 1. Analysis of waste related research projects by FP7 themes

FP7 theme	Number of projects	Number of participants	Average number of partners	Average project budget (mil €)	Average EC contribution (mil €)
Environment	13	199	15.3	4.6	3.4
Agriculture	8	110	13.7	5.5	4.0
Materials	12	173	14.4	7.7	5.2
Energy	8	113	14.0	12.0	7.6
ICT	2	26	13.0	12.7	7.7
Transport	7	93	13.2	3.4	2.4

2.2.2. Countries Leading and Involved in European Research on Waste Technologies

With 118 participations Germany is by far the most active country in FP7 waste related research, followed by Spain, Italy, the United Kingdom and France (all of them with more than 50 participations each). Another interesting result refers to the involvement of private-for-profit organisations which differs between the European member states: While in Germany, Italy, France, the Netherlands and Poland the number of participants from private-for-profit organisations is higher than 50% of the participations from the respective country, in all other countries research partners have a higher share. Partners from outside the EU play a minor role in waste related research: in total 629 participations in FP7 waste related research projects come from the 27 European member states, 35 come from non-EU European countries, 39 from Asia, 11 from Africa and not a single one from America. Several collaborative projects involving partners from African and Asian countries aim at establishing waste management systems in these countries.

2.2.3. Analysis on the Collaboration Patterns of FP7 Waste Related Research Organisations

In total, 572 organisations participate in the 50 FP7-funded projects dealing with waste-related research. The following analyses are based on publicly available data of research partners in FP7-funded projects (i.e. name of the institutions involved, their home countries and their involvements in different research projects). As the budget share of an institution in an individual project is not publicly available, we were not able to carry out an in-depth analysis of EC funding per partner. 84% of these organisations participate in just one research project, while 16% participate in several waste-related research projects. To analyse the structure and collaboration pattern we applied the method of Social Network Analysis (SNA). In our case SNA is based on the relational data of organisations which are engaged in the same collaborative project. By analysing these research collaborations, patterns of social ties among actors can be visualised and organisations can be identified which play a central role in the research network. Central players connect a large number of actors which are located more in the periphery of a network and therefore represent the backbone of network by ensuring participation and connectedness.

Furthermore, higher connectivity in a network facilitates the organisations' access to different knowledge pools and the flow of knowledge between various actors.
As Fig. 1. shows, a network has emerged among the organisations participating in FP7 waste related research (where the size of vertices indicates the degree of betweenness centrality, in other words the importance of the corresponding organisation for knowledge brokerage within the network). 562 out of 572 participating organisations are connected among each other via the different research projects, just 11 organisations (collaborating in the project "InfraGuidER" in the area of sustainable transport) form a separate component (see Fig. 1 upper right corner) which is currently not connected to the other research projects. The fact that almost all organisations involved in FP7 waste research are represented in one single component, implies a high level of connectivity which enables organisations to gain access (through high connectivity among actors) to a vast pool of knowledge.

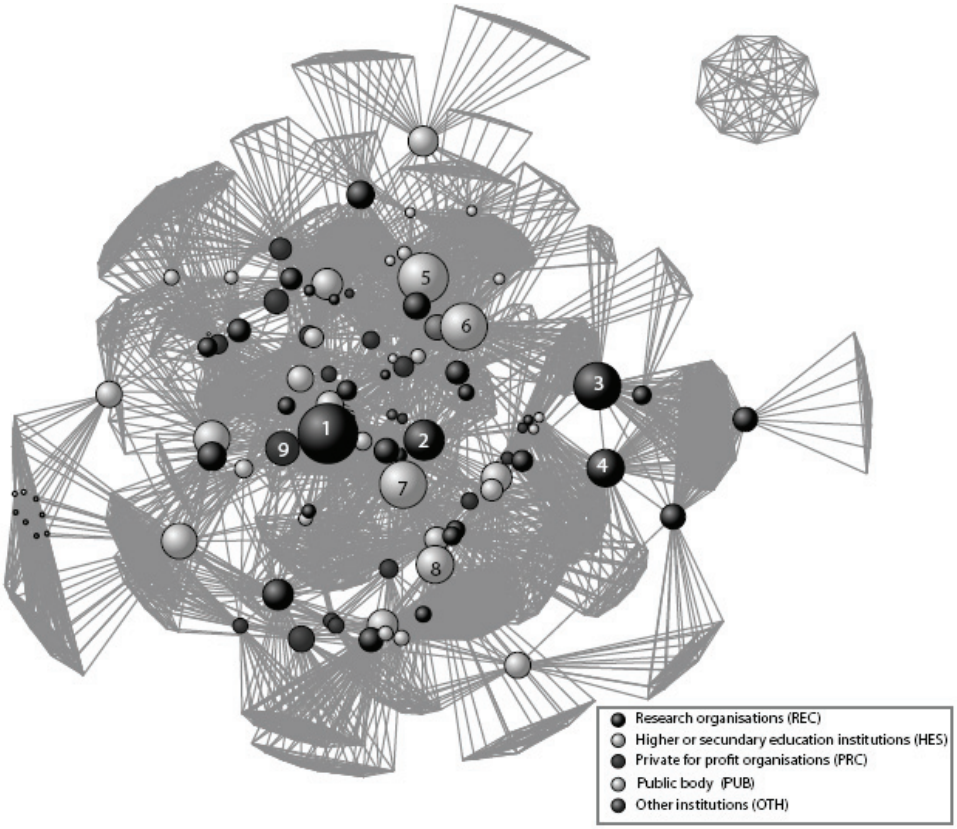


Figure 1. Social Network Analysis of FP7 waste related research

A more in-depth analysis of the FP7 waste network through the concept of betweenness centrality reveals the importance of organisations as knowledge brokers. The following organisations shown in Fig. 1. are core players regarding the knowledge flow within the network:

(1) Valtion Teknillinen Tutkimuskeskus (Research, DK)
(2) Fraunhofer-Gesellschaft (Research, DE)
(3) Agenzia Nazionale per le Nuove Tecnologie (Research, IT)
(4) Papiertechnische Stiftung (Research, DE)
(5) Rheinisch-Westfaelische Technische Hochschule Aachen (Research, DE)
(6) Danmarks Tekniske Universitet (University, DK)
(7) Universitaet Stuttgart (University, DE)
(8) University of Southampton (University, UK)
(9) Acciona Infrastruttura (private-for-profit organisation, ES)

Altogether these nine organisations maintain the highest number of collaborations, connect a large number of organisations and therefore enable the flow of information within network – in fact, they represent the backbone of the FP7 waste related research network. When further differentiating the various types of the organisations the dominating role of research partners compared to private-for-profit organisations is confirmed: research organisations (REC) form the most important group concerning

knowledge brokerage, followed by higher or secondary education institutions (HES), while private-for-profit organisations (PRC) only play a minor role in the flow of knowledge and connectivity among actors in the FP7 waste network.

2.2.4. Key Approaches in European Research on Waste Technologies

Whereas the previous chapters focused on structural information (budgets, organisations, countries), this chapter deals with the content of the 50 projects we assessed. As described in chapter 3 (methodology) we distinguished the different approaches according to the EU Waste Hierarchy and looked for common characteristics of the projects. Fig. 2. shows our results: 43.7% of the projects deal with waste prevention, 15.6% with reuse, 18.7% with recycling and 21.8% focus solely on recovery. As these projects just concern one approach, we called them "mono-research" to distinguish them from projects which follow two or more approaches at the same time (24%), which we call "multi-research". Further 12% deal with waste management issues which cannot be directly linked to one of the approaches mentioned in the waste hierarchy. Not a single project was found in the area of land filling.

As this analysis shows, there is a clear preference in FP7 for waste prevention research, followed by recycling, reuse and recovery related research. Therefore, we conclude that waste related research in FP7 supports the shift to a cradle-to-cradle society and is (at least partly) in line with the aims of the new Flagship Initiative "A Resource-Efficient Europe".

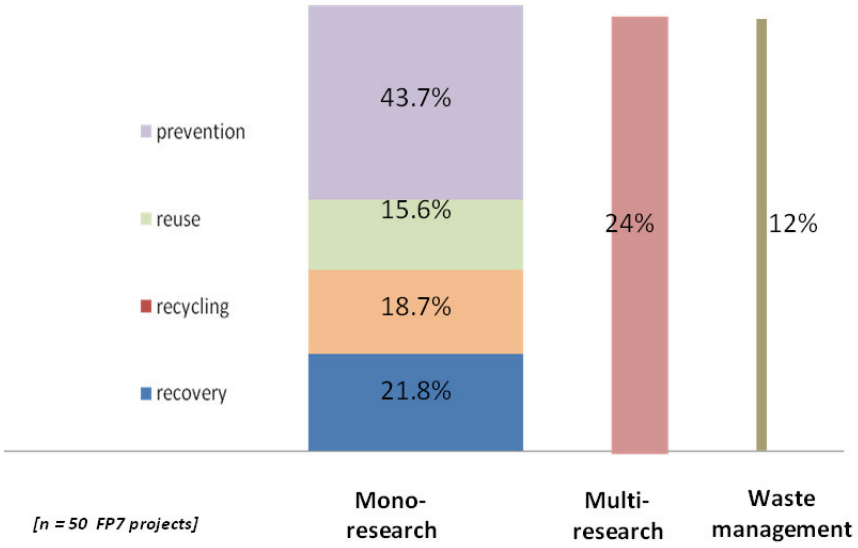


Figure 2. Analysis of FP7 waste related research projects by approach

2.2.4.1. Waste Prevention

Waste prevention is defined as *"...measures taken before a substance, material or product has become waste, that reduce: (a) the quantity of waste, including through the re-use of products or the extension of the life span of products; (b) the adverse impacts of the generated waste on the environment and human health; or (c) the content of harmful substances in materials and products (Article 4 of Directive 2008/98/EC")* [18].

Table 2. Examples of research projects in the area of waste prevention

Methodology Focus		Aspect of life cycle involved
Improvement of manufacturing processes	Elimination of cutting fluids Elimination of solid waste in the industry of aluminium Sustainable water use in industry	Product manufacturing
Development of new materials	Flexible paper for packaging; new fibre-based paper Perlite cells for construction	Product end of life (decrease of waste going to landfill)
Improvement of product life-time	Fuel cells for automotive	

The most prominent waste prevention related research concerns the improvement of production processes and machinery on industrial level, in order to reduce by-products and scraps generated during manufacturing. A minority of projects concerns the development of new materials whose features allow to reduce waste generated at the end of life of products or to increase product life. Projects therefore concern waste streams coming from industrial activities, mainly from thermal, mechanical and chemical process of metal, plastic, electronic parts and rinse water. The improvement of production systems is generally accompanied by the assessment of several environmental aspects like energy consumption, CO_2 emission analysis, life cycle assessment and impact on raw material usage.

2.2.4.2. Reuse

"Any operation by which products or components that are not waste are used again for the same purpose for which they were conceived." [19]. The most prominent field in this category is research on collection and conversion of waste and by-products into new valuable substances. The most interesting waste streams come from agricultural and industrial activities. We found a high representation of companies that use waste (e.g. as a source of energy or as a raw material) and a rather low representation of sectors which cause the waste.

Table 3. Examples of research projects in the area of reuse

Focus	Starting waste/by-product	Final Product
Collection and conversion of industrial waste and by products	• Animal, cereals by-products • Wood, paper mill and bark • Waste water	• Biologically valuable substances, food • Nano-materials • Polymers, polyurethane foam
Development of refillable/reusable packaging	-	
Collection and reuse of unused products from retailers	-	

2.2.4.3. Recycling

"Recycling: recovery operation by which waste materials are reprocessed into products, materials or substances whether for the original or other purposes. It does not include energy recovery and the reprocessing into materials that are to be used as fuels or for backfilling operations" [19]. Most prominent research fields embed at first the development of new materials for a multiplicity of purposes, especially concerning construction materials and packaging.

Table 4. Examples of research projects in the area of recycling

Focus	Subject of research	Technique (where specified)
Sorting techniques	Plastic, paper	Magnetic ultrasonic process sensors
Recycling management and process	Road materials, end-of-life vehicles, electrical and electronic equipment, tyres	Development of database and guidelines
Assure recyclability of new materials	Packaging, building materials, nanomaterials	Nanotechnology-based products development

An interesting branch concerns the development of recyclable nano-material-based products, usually accompanied by the necessity to test their environmental impact and effects on human health. Recycling management and processes affect also the development of database and guidelines, especially about dismantling and recovery of big units (ships, roads). The intent is to create a knowledge-exchange platform and databases. Within the cited fields, a minority of projects include the development of life-cycle assessment models. Most addressed waste streams come from household activities, industrial activities and dismantling of big units.

2.2.4.4. Recovery

"Recovery: any operation the principal result of which is waste serving a useful purpose by replacing other materials which would otherwise have been used to fulfil a particular function, or waste being prepared to fulfil that function, in the plant or in the wider economy" [19]. Recovery is completely oriented towards bio-energy production employing bio-waste. The most recurrent theme is the efficiency improvement of existing biomass conversion technology (like hydrolysis and anaerobic digestion). A relevant group of projects explores the possibility to operate power plants completely fed by biomasses coming just from waste (and not by dedicated crops). Research on renewable energy production focuses basically on biowaste coming from agricultural activities and municipal waste. The development of new technologies is expected to have positive impacts on raw material extraction, especially fossil fuel.

Table 5. Examples of research projects in the area of recovery

Focus	Technique (where specified)	Recovered by-product	Final product
Improvement / development of bio waste and by-products conversion techniques into biomass and energy Design, construction, implementation of power plants/ biorefinery operating by biomass	Hydrolysis ; thermodynamical conversion, pyrolisis fermentation and pelleting anaerobic digestion	Wood and ligneous biomass from forestry activity; animal by-products and residues; cereals and crops by-products, food waste; municipal bio waste	Bioethanol biofuel biogas energy, electricity and power other products
Creation of a network among stakeholders	-		

2.2.4.5. Multi-Research Projects

These projects introduce a complexity of themes at the same time. The most prominent research usually involves recycling related research combined with reuse related research, especially in the development of technologies to reprocess waste in different ways, followed by the combination of recycling and prevention, like the development of new recyclable materials explicitly intended to decrease waste going to landfill.

2.2.4.6. Waste Management

The essential objective of all provisions relating to waste management should be the protection of human health and the environment against harmful effects caused by the collection, transport, treatment, storage and tipping (DIRECTIVE 2006/12/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of April 5th 2006 (on waste) [19]. FP7 projects dealing with waste management basically concern urban waste streams. New waste management possibilities are analysed, assessing different urban development scenarios; among collaborations with African and Asian countries the most prominently developed field is meant to establish waste management systems in developing countries.

3. CONCLUSIONS

Our analysis of FP7 waste related research shows a plurality of thematic foci, methods and strategies. The main approaches are waste treatment, waste recovery into energy and valuable products and waste prevention (whereas not a single project dealt with waste disposal technologies). These results confirm that FP7 already supports the shift to a cradle-to-cradle society and is (at least partly) in line with the aims of the new Flagship Initiative "A resource-efficient Europe". Among the organisations participating in FP7 waste related research a network has already emerged. It is characterised by a high level of connectivity which enables organisations to gain access to a vast pool of knowledge. In this network nine organisations play a crucial role as they are involved in several projects and form the interfaces between them. For future actions a particular focus on these "lifelines" might facilitate the sustainability of the network. As eight of these organisations are research institutions and universities, their rationalities shape their role as knowledge brokers. Further integration of private-for-profit organisations as knowledge

brokers or the strengthening of their collaboration with the core organisations within the network could lead to an increased dissemination of waste technologies.

In this paper we presented results based on qualitative and quantitative desktop research. During the next months we will integrate newly-funded FP7 projects into our dataset and conduct a series of interviews with the co-ordinators of FP7 waste related projects to gain insights into networking mechanisms, to highlight the dissemination of waste technologies and to identify future research needs.

REFERENCES

[1] W. Mc Donough, M. Braungart, Cradle to cradle, North Point Press, 2002.
[2] S. El-Haggar, Sustainable Industrial Design and Waste Management-cradle to cradle for sustainable development, Burlington: Elsevier Academic Press, 2002.
[3] Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and The Committee of the Regions - Taking sustainable use of resources forward - A Thematic Strategy on the prevention and recycling of waste COM/2005/0666 final.
[4] Commission Staff Working Document Accompanying the Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions on the Thematic Strategy on the Prevention and Recycling of Waste, 2010, Brussels
[5] Report From The Commission To The European Parliament, The Council, The European Economic And Social Committee And The Committee Of The Regions on the Thematic Strategy on the Prevention and Recycling of Waste SEC(2011) 70 final (COM/2011/0013 final)
[6] Preparing For The Review Of The Thematic Strategy On The Prevention And Recycling Of Waste, Report from stakeholder event - 22 June 2010, Brussels
[7] Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions - Thematic Strategy on the sustainable use of natural resources {SEC(2005) 1683} {SEC(2005) 1684} (Com/2005/0670 Final)
[8] Communication From The Commission To The European Parliament, The Council, The European Economic And Social Committee And The Committee Of The Regions A resource-efficient Europe – Flagship initiative under the Europe 2020 Strategy, Brussels, 26.1.2011 COM(2011) 21.
[9] Defra's Evidence Investment Strategy: 2010-2013 and beyond, Annex 2: Defra Evidence Plan Summaries, 2011 Update, Page 37.
[10] G. Mininni, Il ruolo della ricerca nell'attuazione della disciplina sui rifiuti alla luce della nuova direttiva 2008/98, Proceeding of "La ricerca per la gestione dei rifiuti secondo gli standard europei" – CNR, Rome, 15 aprile 2009.
[11] A. Cavaliere, Gli obiettivi di supporto alla ricerca dell'Osservatorio Nazionale dei Rifiuti, Proceeding of "La ricerca per la gestione dei rifiuti secondo gli standard europei" – CNR, Rome, 15 aprile 2009.
[12] N. Lawlor, EU raw materials initiative: identifying issues and challenges, the need for foresights views, Workshop "Exploring Success Scenario for 2030", Brussels, 14 January 2011.
[13] V. Hampton, Managing our environment on three fronts, Research Trends, Scopus Issue 19-September 2010
[14] J. Kamalski, Research and practice in waste management, Research Trends, Scopus Issue 19-September 2010
[15] The FP7-4-SD website. [Online]. Available: www.FP7-4-SD.eu (2010)
[16] EPA, European Waste Catalogue and Hazardous Waste List 2002, Johnstown Castle Estate, County, Wexford, Ireland, 2002.
[17] "Testo Unico ambientale" Decreto Legislativo 3/4/2006 n. 152. Norme in materia ambientale (G.U. 14/4/2006 n. 88).
[18] Directive 2008/98/EC of the European Parliament and of the Council, Official Journal of the European Union, 22.11.2008.
[19] Directive 2006/12/EC of the European Parliament and of the Council, Official Journal of the European Union, 27.4.2006.

LIFE+ RECYCLING SYMPRAXIS PROJECT: AN ANALYSIS OF THE CURRENT SITUATION IN WASTE MANAGEMENT AND RECYCLING IN HALKIDIKI, A MASS TOURISM GREEK DESTINATION

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Abstract

This paper presents the results of the analysis of the current situation in waste management and recycling in Halkidiki a popular international mass tourism destination (a peninsula in the northwestern Aegean Sea). Results come from the implementation of LIFE+ project RECYCLING SYMPRAXIS (www.recyclingsympraxis.gr). The project started in 2009 and its core aim is to study, develop and implement pilot recycling schemes of various types of municipal solid waste through the collaboration of public and private sector and focusing on the touristic character of Halkidiki region. As part of the regional preparatory actions that took place in the first year of the project, a detailed field and literature survey was conducted as regards waste management and recycling of municipal non-hazardous solid waste in Halkidiki, with additional focus on four special types of waste (packaging, organic, electric/electronic equipment and construction and demolition). Several data were collected and evaluated: quantity, quality and time pattern of waste production (per each type abovementioned), existing waste management practices, available waste management infrastructure, equipment and logistic schemes, main obstacles and key incentives for participation in waste recycling schemes, level of motivation/commitment and level of environmental consciousness of Halkidiki population. Issues like the national and European legal framework and degree of implementation, existing policies and policy initiatives and the socio-economic framework (the role of regional or national institutions, waste management market operation, environmental NGOs etc.) were also taken into account and presented. The report constitutes the most complete and up-to-date SWOT analysis for the particular sector in the region The aforementioned detailed analysis of the current situation was used as a basis for the sound design of pilot schemes of the project that were implemented during the summers of 2010 and 2011.

Keywords: *municipal solid waste management, waste of electric and electronic equipment (WEEE), construction and demolition waste (CDW), Greece*

1. INTRODUCTION

According to EU sustainable - environmental policy waste generation should be prevented or reduced. Furthermore, what is generated should be recovered by means of re-use, recycling and other recovery actions, thus reducing disposal operations [1,2]. Up till now in Greece, waste management is left to be handled at the municipality level of administration and is not yet fully developed in comparison to other EU members [3]. Municipalities are responsible for the collection and transport of non-hazardous municipal waste. Each Region is responsible for its own planning and target setting through their perspective “Regional Plans for Solid Waste Management”. Responsibility for the implementation of the Regional Plans falls under each Region and the respective Management Bodies of Solid Waste of each Administrative Unit that are responsible for the temporary storage, reload, recovery and disposal and waste. At the same time the Greek State established several organizations and agencies for developing national recycling programmes which however face great challenges and do not always provide the services required. A general obligation of all those who produce waste for which exists legal framework for their alternative management, is to organize (private) or participate in (collective) Alternative Management Systems. The Alternative Management Systems are responsible for the collection, re-use and recovery of these waste streams. Participation in a collective Alternative Management System is accomplished by a monetary contribution and an annual fee. Today there are eleven certified collective systems and one individual private system for the alternative management of

waste in all over the country. However, in Greece according to Papachristou et al [3] from the total amount of MSW only 8% is recycled at the source and the majority us disposed without treatment.

Amidst the current economic downturn in Europe and in Greece specifically which has put public budgets under pressure as well as the lack of sources of revenues for local-regional authorities in order to cope, among other things, with contemporary demands of environmental protection there must be the question of implementing actions at a local level finding solutions towards sustainable development. In fact it has been documented [4] that authorities are looking for alternative solutions to reduction of costs with recycling posing as the most favored one. This paper draws on the implementation of the EU project "RECYCLING-SYMPRAXIS" LIFE07 ENV/GR/000265 in Halkidiki; a well known mass tourism destination in the Mediterranean, located in Northern Greece. The RECYCLING SYMPRAXIS LIFE+ Project (henceforth Project) started in January of 2009 and reaches its completion in December 2011. The aim of the project is the preparation and implementation (at pilot level) of waste prevention, recovery and recycling schemes driven by local, incentive-based Public Private Partnerships (PPP) of various types of Municipal Solid Waste (MSW). A consortium of nine partners; hence the name “SYMPRAXIS” which in Greek stands for synergy-cooperation-collaboration; both private (two well-known big hotels and one private owned consultant company, expert in the field of energy and recycling) and public stakeholders (Regional Administrative Body, the Tourist Development Institute, the Chamber of Halkidiki, three Municipalities all located in the coastal zone) was responsible for the actions of the project in the study area. The set of actions and working packages were distributed among the partners according to their expertise. The project was divided into two major steps: the stage of assessment, where valuable info was collected, evaluated and processed accordingly; and the stage of development and demonstration, where the project activities were designed, implemented, validated and improved.

In this paper we focus on the analysis of the current situation in waste management and recycling in Halkidiki. It should be pointed out that this was the first integrated effort to record and calculate not only quantitative but also qualitative data about waste management production in Halkidiki, as well as to focus on special types of recyclable waste such as Municipal Solid Waste (MSW), Packaging Waste (PW), Waste of Electric and Electronic Equipment (WEEE), Construction and Demolition Waste (CDW), and organic biodegradable waste (OBW).

2. ELABORATION

2.1. Study Area, Materials and Methods

Halkidiki is a peninsula of almost 3,000 km^2 and 80,000 permanent inhabitants [5] in northwestern Aegean Sea. Since the 1970s, the region has been experiencing major economic growth based mainly on seaside mass tourism. The area was selected as one facing environmental threats due to massive waste production by tourism activities, second-home development as well as agrifood (olive oil, olives, honey and wine) Small Medium Enterprises (SMEs). Halkidiki attracts week-end or day visitors from the urban dwellers of Thessaloniki and other cities in Northern Greece. In fact many of the residents of Thessaloniki own a second home cottage resort in Halkidiki. Tourists from all over Europe and the Balkan countries also come in the area especially in peak seasons. During 2010 there were more of 800,000 tourists staying in the officially registered accommodation establishments of Halkidiki. Out of them the majority (65%) were foreigners and the rest (35%) Greeks [6].

The study area and data collection and analysis covered the whole Prefecture of Halkidiki and not only the administrative borders of the coastal area Municipalities that participated in the project as partners (that is the Aristotetle, Sithonia and Kassandra Municipalities). This choice (to expand the study area beyond the limitations of the project) was mainly based upon the fact that a comprehensive display of the current situation would reveal the special characteristics of the region, as well as the interdependences and the spatial variations that occur within the region. The level of analysis detail/depth was determined to be the level of municipal administration- department (village).

In order to calculate the waste quantities generated in the area both a field research and literature review were conducted simultaneously. Secondary data was collected from available reports (both at a local, national and European level). All information collected was updated and enriched with new data based on the field research. The latter involved the collection of quantitative and qualitative data regarding the waste streams studied by means of questionnaires distributed and personal telephone or face-to-face interviews conducted. A feedback from the public (through open meetings) was also used as a tool [7]. Local actors that participated during the public meetings, more than 200 actors, satisfying the

highest possible representation were: local government level (Regional Authority of Central Macedonia, Regional Unit of Halkidiki-ex Prefecture of Halkidiki, Municipalities of Halkidiki, Association of Local Authorities of Greater Thessaloniki), Collective Alternative Systems, local waste management recycling companies, touristic enterprises (hotels, restaurants, taverns, snack-bars, camping and child holiday camps etc.), construction companies and building contractors, super markets.

To determine the MSW quantities produced, primary field data were collected from the three Sanitary Landfills (SL) that are in operation in Halkidiki region. For the Municipalities of Halkidiki that were not served by the abovementioned existing SL, as far as the final disposal of their municipal waste is concerned, an alternative indirect calculation method was used, based on data, assumptions and parameters of their existing logistic schemes of waste collection and thus production. The basic parameters used for this calculation was waste collection vehicles collection patterns and fullness and municipal solid waste mean density [8]. The time variability of municipal solid waste production was also studied.

For the quantification of PW produced, scarce primary data could be found for Halkidiki region, as up to now, no organized collection and recycling system for this waste stream exists. For the estimation of quantities produced, as well as for the presence of each separate material to the total packaging waste quantity, the assumption that packaging waste represents 20% w/w of MSW was used. The estimation of organic waste percent present in MSW was made similarly by using the appropriate qualitative model of the National Plan for the Management of Non-Hazardous Waste [9].

In order to calculate the quantities of CDW produced in Halkidiki, two methods were used and compared. The first one, using software USW MFC Application 2005/project KYPROS [10], produced a forecast algorithm of quantities of generated CDW in five years long term. Primary data such as annual number of construction and demolition licenses and annual total surface of new-build residencies in the region were used as input for the algorithm. The second method was based upon a general mathematical model (produced by the Environmental Science and Technology Unit of the Faculty of Chemical Engineering of the National Polytecnic University of Athens assessing separately the quantities of construction, demolition and excavation [11].

Primary data were collected from the only Greek Collective Alternative Management System of WEEE Appliances Recycling SA for the quantities of WEEE produced in Halkidiki, as the System has already developed collaboration with the majority of the Municipalities of Halkidiki, by being the final acceptor of WEEE collected in the region.

2.2. Results and Discussion

2.2.1. Current Situation in Waste Management and Recycling in Halkidiki

According to recent data (2000) MSW consisted of 47% organic, 20% paper, 8.5% plastic, 4.5% glass and 15.5% other [9]. Table 1 summarizes the basic information about current situation in waste management and recycling in Halkidiki, regarding the existing infrastructure for waste collection and disposal and the operation of recycling schemes. An important lack of waste management –collection, reload, temporary storage, sorting- infrastructure is observed. Two of the five municipalities of Halkidiki do not have a licensed sanitary landfill in their territory and therefore transfer the waste collected to the SL of the adjacent Municipalities, increasing significantly the relevant waste transport costs. Only two WRS have been constructed in Halkidiki region but they are not in full operation yet. As far as recycling is concerned, apart from recycling of WEEE with the cooperation of Appliances Recycling SA, there is complete absence of cooperation with the collective alternative management systems available.

According to the Regional Plan of Waste Management in place, the main quantitative goal for waste management was the processing of 300.000 tn of municipal solid waste in 2010 gradually increasing to 800,000 t of processed waste in 2020 by the means of promoting programmes of environmental education for prevention and elimination of waste generation by citizens and by the construction and operation of Material Recovering Facilities and Mechanical- Biological Processing Units. In Material Recovering Facilities (MRF) the sorting of packaging waste takes place. According to the Regional Plan of Waste management in place, 8 MRF are foreseen in order to cover the needs of the Region of Central Macedonia, none of them being located in Halkidiki region. This fact hinders dramatically the promotion of any packaging waste recycling scheme in Halkidiki. Therefore, the local authorities of Halkidiki are in negotiations with MEEC and HERRCO SA (the biggest certified collective system of alternative management of packaging waste) in order to manage the construction and operation of a central MRF in Halkidiki.

Table 1. Available infrastructure for municipal solid waste collection and final disposal in Municipalities of Halkidiki

		Municipality					Total Halkidiki
		Kassandra	Nea Propontida	Polygyros	Aristotetle	Sithonia	
Population	Winter	16,180	38,340	13,867	18,861	17,672	104,920
	Summer	170,000	93,000	33,500	54,700	103,000	454,200
Sanitary Landfills		Yes	Yes	Yes	No	No	0
Waste Reload Stations		No	No	No	1	1	2
Waste collection vehicles	Winter	7	20	5	11	12	55
	Summer	17	23	7	11	16	74
Waste collection personel	Winter	37	111	12	18	28	206
	Summer	143	193	24	30	64	454
Waste Recycling	Packinging	No	No	Yes (Polygyros)	Yes (Ierisos)	No	
	Oraganic	No	No	No	No	No	
	CDW	No	No	No	No	No	
	WEE	Yes	Yes	Yes	Yes	No	

Source*: Status report Life+ on Recycling and Waste Management in Halkidiki*

2.2.2. Municipal Solid Waste Production Quantities and Seasonality

Previous research in Greece [3] reveals that approximately 4.6 mil ton of MSW was generated with the two big urban cities (Athens and Thessaloniki) contributing to the 48% of these figures. Data about the quantities of municipal solid waste produced as well as the production seasonality pattern in the Municipalities of Halkidiki are presented in Table 2.

The greatest annual waste quantities produced were observed in the Municipality of Nea Propontida (29,920 t), followed by Municipalities of Kassandra (24,220 t) and Sithonia (20,995 t). The territories of Municipalities of Kassandra and Sithonia cover the majority of the coastal area of Halkidiki, centering therefore the main touristic development and infrastructure of the whole Prefecture (hotels, rent rooms, restaurants, camping areas, taverns etc.). On the other hand, Municipality of Nea Propontida is characterized by a large number of second homes/ cottages and a great number of weekend visitors, mainly due to its vicinity with the urban agglomeration of Thessaloniki. This can also be observed by the seasonal population variation of these three municipalities shown in Table 1, inducing the subsequent great seasonal waste production variations shown in Table 2 (+157% for Municipality of Kassandra, +76% for Municipality of Nea Propontida and +64% for Municipality of Sithonia) when compared to the rest Municipalities of the Prefecture. The remarkable increase of waste quantities produced in the summer touristic peak season impose additional difficulties and demands in the waste collection patterns the Municipalities need to apply.

Table 2. Municipal solid waste production quantities and seasonality in Halkidiki

Municipality	Municipal Solid Waste (t)		% variation	Annual MSW (t)	% of the total in Halkidiki
	Winter	Summer			
Aristotetle	4,480	5,085	+14	9,565	10
Kassandra	6,780	17,440	+157	24,220	26
Nea Propontida	10,600	18,620	+76	29,220	32
Sithonia	7,965	13,030	+64	20,995	23
Polygyros	4,600	3,375	-27	7,975	9
TOTAL	34,425	57,550		91,975	100

Source: *Status report Life+ on Recycling and Waste Management in Halkidiki*

2.2.3. Packaging Waste

Packaging waste is sorted in Material Recovery Facilities (MRFs) via a combination of mechanical and manual separation steps. The operations in MRFs include receiving of materials, pre-sorting and managing flows. MRFs accept fully co-mingled packaging waste or separate packaging waste streams, depending on the collection scheme used (single stream of packaging waste or separation at source and collection of more than one streams of packaging waste. In Table 4, the estimated quantities of packaging waste produced in Halkidiki as well as their production seasonality are presented. The total packaging waste quantities were calculated based on the assumptions that 20% w/w of municipal solid waste comprises of packaging waste. The qualitative analysis of packaging waste stream synthesis that is also presented in Table 4 is based on the relevant assumptions that follow in Table 3.

From data presented in Table 4, it can be concluded that packaging waste quantities increase by almost 1.5 time during the touristic peak summer season. The increase is directly proportional to the trend observed for MSW of the region.

Table 3. Packaging waste stream synthesis in Greece

Packaging waste category	% w/w present in packaging waste stream
Paper/ cardboard	42
Plastic	26
Glass	18
Metal	8
Wood-other	6
TOTAL	100

Source: [9]

Table 4.Packaging waste production quantities and seasonality in Halkidiki

		Aristotetle	Kassandra	Nea Propontida	Sithonia	Polygyros	Halkidiki total
Packaging solid waste (tn)	winter	896	1356	2120	1593	920	6885
	summer	1017	3488	3724	2606	675	11510
Paper	winter	376	570	890	669	386	2892
	summer	427	1465	1564	1095	284	4834
Plastic	winter	233	353	551	414	239	1790
	summer	264	907	968	678	176	2993
Glass	winter	161	244	382	287	166	1239
	summer	183	628	670	469	122	2072
Metal	winter	72	108	170	127	74	551
	summer	81	279	298	208	54	921

2.2.4. Organic Waste

The term “organic biodegradable waste” includes a variety of household waste such as kitchen and garden waste. The calculation of organic waste proportion in MSW quantities is extremely difficult as there are no reliable (time and quantity independent) data due to lack of a national program of analysis of the synthesis of municipal solid waste in Greece. In order to estimate organic waste quantities produced in Halkidiki region, the use of municipal waste synthesis simulation models were used. The synthesis simulation models used were developed by the Laboratory of Inorganic and Analytical Chemistry of School of Chemical Engineering of National Technical University of Athens as a result of a research program in 1990s. Several experimental measurements were conducted in order to determine the synthesis of municipal solid waste of various geographical units of Greece. Project team chose a

synthesis simulation model to apply to each Municipality of Halkidiki by comparing its geographical and socio-economic characteristics (geographical and spatial specific characteristics such as vicinity to urban center, agricultural character etc., specific characteristics of spatial distribution of touristic infrastructure, temporal distribution of the intensity of touristic flow, degree of development of the mass tourism model, degree of development of cottages or second homes) with those of the various geographical units that the synthesis simulation models were developed in the first place.

Approximately 50,000 tn of organic waste are produced annually in Halkidiki. The greatest quantities are observed in Municipalities with the most intense touristic character (Kassandra, Nea Propontida and Sithonia). It is estimated that the majority of organic waste produced originate from garden maintenance of hotels, cottages, municipal parks etc. as well as from food remains from restaurants, taverns and other food service enterprises.

Table 5. Organic waste production quantities estimation in Halkidiki

Municipality	Annual municipal solid waste (tn)	% w/w being organic waste	Organic waste quantities (t)
Aristotetle	9565	48.3	4620
Kassandra	24220	56.4	13660
Nea Propontida	29220	55.2	16129
Sithonia	20995	56.4	11841
Polygyros	7975	47	3748
TOTAL	91715		50000

Source: *Status report on Recycling and Waste Management in Halkidiki*

2.2.5. Construction and Demolition Waste

Construction and demolition waste is a generic term that involves a wide variety of materials that, according to their origin, can be divided into four main categories: debris from excavations, building construction and renovation activities, debris from road construction and maintenance activities, debris from building demolition activities and waste generated in building sites. Results from the calculations made based on software USW MFC Application 2005 and on a mathematical algorithm are presented in Table 6. Primary insert data used in the calculations (annual number of construction and demolition licenses and annual total surface of new-build residencies) were not available in such detail as Municipality level like the previously analyzed waste streams, so results are presented for the whole Prefecture of Halkidiki.

Table 6. CDW quantities estimation in Halkidiki- Comparison of two calculation methods

Year	Construction waste (tn)		Demolition waste (tn)		Excavation waste (tn)	
	Software	Algorithm	Software	Algorithm	Software	Algorithm
1997	24166.50	24195.80	411	6323.20	-	432978
2001	36781.90	36812.60	670.6	10316.80	-	547638
2004	38164.50	38187.20	649	9984	-	602238
2005	56120.40	56144.30	670.6	10316.80	-	785694
2006	36193.70	36219.30	1103.20	16972.80	-	537264
2007	31546.20	31565.50	1362.80	20966.40	-	559104
2008	28266.50	28284.20	735.5	11315.20	-	490308

2.2.6. Waste of Electric and Electronic Equipment

According to [11] electrical and electronic waste comprise of electric or electronic devices that have completed their life cycle and are discarded by their original owners and their end-of-life management and recycling is a critical issue as they are composed of ferrous metals, plastic, glass, aluminum and

copper, also containing some hazardous for human health and environmental substances such as PCBs, CFCs, heavy metals and radioactive substances

Table 7. WEEE production quantities estimation in Halkidiki (data from Appliances Recycling SA)

Municipality	WEEE quantities in 2009 (t)	WEEE quantities in 2010 (t)
Aristotetle	75	113
Kassandra	65	97
Nea Propontida	153	230
Sithonia	71	106
Polygyros	55	83
TOTAL	419	629

Source: *Status report Life+ on Recycling and Waste Management in Halkidiki*

3. CONCLUSIONS

Our study stems from the saying that "you cannot manage what you don't know". Hopefully this description of the current situation for the first time can provide the tool for effective decisions for waste management in the area. The description of the current situation leads to several points. The geographical and socioeconomic characteristics and particularities of the destination of Halkidiki reflect on waste generation patterns and pose a great risk to any possible private investment in waste management. In fact, the large number of small waste generation points with great geographical dispersion, the obsolete road system, the great seasonality in waste production and the lack of public infrastructure of temporary storage-sorting make any private investment at a local level not economically viable. All possible private stakeholders expressed the need for a big scale waste management plan that will cover the whole region of Halkidiki, in order to make up for the increased operational costs that will come up due to the abovementioned particularities. This is extremely difficult when also taking into account the following: a) lack of political consensus and collaboration between local authorities and great segmentation and confusion of authorities, especially nowadays due to the reforming that leads to b) lack of activities of the two collective packaging waste alternative management systems in Halkidiki so far c) severe global crisis of the recycled material market that makes risky the investments especially in the recycling of certain streams (i.e. printed paper), d) important lack of waste management –collection, reload, temporary storage, sorting- infrastructure of local municipalities (i.e. sanitary landfills), e) the very bad economic situation that characterizes almost all Greek municipalities including the municipalities-project partners having as a consequence important operation and organizational difficulties.

All Municipalities of the project are predominately tourism oriented and they present similar characteristics and problems. The intensity of tourism flows, high seasonality and the relevant peak in the volume of Solid Waste to be managed are the most common phenomena. The situation has become more complicated now after the major transformation in the administrative Charta on Greece. The reforming and merging of municipalities and responsibilities has changed all legislative frameworks making it more difficult for them to provide efficient services to the citizens or businesses alike. Furthermore the lack in the legislation for some types of waste (organic and construction-demolition waste) discourages any private initiative.

On the positive side, it has been remarked that citizens are increasingly being more interested in the idea of recycling, and more importantly they demand recycling services from all responsible authorities. Both the public sector and the collective packaging waste alternative management systems has until now been detrimental to the initiation of recycling schemes in Halkidiki, but given the increased pressure from the local population and the gradual operational improvement of the Municipalities (through Kallikratis) are variables that can improve the current status quo.

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REFERENCES

[1] A. Economopoulos, Technoeconomic aspects of alternative municipal solid wastes treatment methods, Waste Management. 30 (4) (2010) 707-715.
[2] European Commission, Green Paper on Integrated Product Policy, Brussels, 2001.
[3] E. Papachristou, H. Hadjianghelou, E. Darakas, K. Alivanis, A. Belou, D. Ioannidou, E. Paraskevopoulou, K. Poulios, A. Koukourikou, N. Kosmidou, K. Sortikos, Perspectives for integrated municipal solid waste management in Thessaloniki, Greece, Waste Management. 29 (3) (2009)1158-1162.
[4] R. Palatnik, O. Ayalon, M. Shechter, Household Demand for Waste Recycling Services, Environmental Management 35 (2005) 121-129.
[5] National Statistical Service of Greece (2010) http://www.statistics.gr/portal/page/portal/ESYE/PAGE-themes?p_param=A1302
[6] National Tourism Organization (2010)
[7] K. McComas, Public Meetings about Local Waste Management Problems: Comparing Participants to Nonparticipants, Environmental Management. 27 (1) (2001) 35-147.
[8] E. Vagli, Municipal solid waste management costs of 4th Administrative Unit of Prefecture of Halkidiki, Master Thesis, Hellenic Open University, 2009
[9] National Plan for the Management of Non-Hazardous Waste, Appendix II, Article 17, Greek Joint Ministerial Decision 50910/2727/2003. provided as Annex II to the Joint Ministerial Decision, section B.I, Skordilis, Current Data-Institutions-National Waste Management Planning, paper presented in Waste Management in Greece, Symposium http://www.lambadarioslaw.gr/publications/en/waste_management_greece.pdf.
[10] LIFE03/TCY/CY/000018, "Development of best management systems for high priority waste streams in Cyprus-KYPROS", www.uest.gr/kypros
[11] LIFE05/ENV/GR/000235, "Sustainable Construction in Public and Private Works through IPP Approach-SUSCON", http://www.uest.gr/suscon/Progress-Results/progress-results.html
[12] Ch. Achillas, Ch.Vlachokostas, N. Moussiopoulos, G. Banias G., Decision support system for the optimal location of electrical and electronic waste treatment plants: A case study in Greece, Waste Management. 30 (5) (2010) 870-879.

CURRENT STATUS AND DEVELOPMENT OF WASTE MANAGEMENT SYSTEM IN BIHAC REGION

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Abstract

Waste management system in Bihac region is the responsibility of municipalities. There is a public utility company in each municipality responsible for managing municipal waste. Currently, the system operates according to the formula one municipality - one utility company. Each of the utility companies has one landfill under the jurisdiction, except Cazin, Bosanska Krupa and Buzim that use a common landfill. Practice shows that the waste from certain urban and rural areas are collected and disposed at least once a week. Waste collection in municipalities is carried out through various types of bags, bins and containers. Each of the utility company, apart from vehicles for transport of waste, has the machinery for the treatment of waste in landfills. These are mainly bulldozers with the purpose of placing the covering material on the surface of the landfill. Equipment of all utility companies is relatively modest. Significant additional investment in the vehicles and unification of containers for collection of waste at source will be required for development of waste management system. Disposal of waste is carried out without the basic elements of a sanitary waste disposal. Therefore, municipal landfills have no system of drainage gas from landfills and treatment of leachate generated by landfilling waste, which certainly, endangering the environment and human health. It is necessary and possible to define a system of integrated waste management at the regional level, which will take into account the wide range of influential factors in the actual conditions of Bosnia and Herzegovina.

Keywords: *Regional waste management system, landfill, influential parameters, proposed model of integrated municipal waste management system*

1. INTRODUCTION

Increasing amounts and inadequate management of waste became global problem of mankind with tendency of more expressive jeopardizing of sustainable development of environment. In recent decades, the legislation of developed countries follow an intensive development of the concept of integrated waste management, with emphasis on reducing the amount of waste for landfilling. European Union's Waste Directives require from member states that primarily reduce generation of waste, then to recycle and purpose-built facilities with the most sophisticated technologies and application of the polluter pays principle, i.e. to cover the costs of waste management. With this treatment, the governments of Member States show not only responsibility towards the life in a healthy environment, but also point out the fact that any neglect of the environment will be paid at great cost.

Today, waste is considered one of the major environmental problems not only in Bosnia and Herzegovina, but also in the region. Drawing on the experience of neighboring countries, Bosnia and Herzegovina is making the important decision in which direction to go in choosing a final solution to the problem of waste management. The advantage in choosing a solution for Bosnia and Herzegovina is unbiasedness of earlier technologies on the one hand, and the possibility of quality monitoring and harmonizing the whole process with the European Union's legislation and directives, on the other side. Certainly, waste management is very important environmental issue, but it is also the economic activity. Selection of an inadequate and wrong concept of waste management, would certainly have had a very serious environmental and financial consequences which would be later a very difficult to change. Although, we are offered by variety of concepts and solutions, it is necessary by the overall knowledge of the current state, elementary facts, presence of the profession and lots of sincere willingness to bring primarily a political decision on waste management.

As according to the Constitution of Bosnia and Herzegovina, Entities are due to take care of environmental protection, all environmental regulations have been adopted on that level, i.e. on the level

of the Federation of Bosnia and Herzegovina, while no regulations exist on state level. In accordance with the Federal Law on Waste Management [1] and Solid Waste Management Strategy for Bosnia and Herzegovina [2] are defined activities on creation and organization the regional waste management system. The strategy has defined, among other things, the areas on which the regional sanitary landfills should be built. By this strategic document, the regional sanitary landfill in the Una-Sana Canton has been planned in the area of the Una-Sana Canton including Municipality of Drvar (so called Bihac region), which is situated in Canton no. 10.

2. ELABORATION

2.1. Current State of Waste Management in Bihac Region

2.1.1. Basic Data on Bihac Region

The Bihac region is situated in the north-west part of Bosnia and Herzegovina and covers the area of 4,714 km^2. The bigger part of the region belongs to the Una-Sana Canton whose administration center of the Una-Sana Canton is situated in Bihac. According to the administrative division Una-Sana Canton consists of the municipalities as follows: Bihac, Bosanska Krupa, Cazin, Bosanski Petrovac, Kljuc, Sanski Most, Velika Kladusa and Buzim. The waste management project area defined by the Biahac region covers all municipalities of the Una-Sana Caanton as well as Municipality Drvar that belongs to Canton no. 10.

According to the estimation of the population made by the Federal Bureau of Statistics as of December 31, 2005, about 300,621 inhabitants live on the territory of Bihac region, with the population density of 63.8 inh km^{-2}.

Table 1. The estimation of the population on the territory of the Una-Sana Canton as of Dec 31, 2005

Region	Number of inhabitants	Age		
		0-14	15-64	65+
Bihac	300,621	58,053	207,123	25,455

2.1.2. Waste Quantities

According to the data obtained by polling the public utility companies in the Bihac region [3] a total of 211,012 m^3 or 52,753 t of waste is produced on that region in a year. Out of that quantity some 60.4% makes a municipal waste – 127,444 m^3 or 31,861 t and 39.6% belongs to technological waste (waste from the service sector, industrial and medical waste) with 83,568 m^3 or 20,892 t.

The data on the waste quantities have been kept, in all companies, in the volume units. The only exception is the municipality of Sanski Most whose data are recorded in the mass units (tones). This magnitude has been, by 0.4 t m^{-3} conversion factor, presented in the Table 2 in the volumetric value.

Table 2. Total annual quantity of waste in the municipalities of Bihac region

Municipality	No. of Inhabitants	Estimation of portion of the collected waste (%)	Total annual quantity of waste (m^3)	Total per capita (m^3 per ihb)
Bihac	60,876	95	62,050	1,07
Bosanska Krupa	28,065	55	16,981	1,10
Bosanski Petrovac	8,020	75	24,485	4,07
Buzim	17,596	50	2,376	0,27
Cazin	61,673	80	20,058	0,40
Kljuc	19,966	75	9,312	0,62
Sanski Most	45,998	90	16,750	0,40
Velika Kladusa	46,741	70	18,000	0,55
Drvar	11,686	80	41,000	4,20
Overall	300,621		211,012	

2.1.3. Composition of Waste

The main characteristic of the Bihac region is that the waste is mostly composed of the municipal waste from the households and the waste from the service industry (catering and shops). There are no large industrial plants over the Bihac region territory and thus the quantities of the industrial waste are rather small. Therefore, in the table below, under category of industrial waste, there were considered, beside the waste from industrial plants, both the waste from the slaughterhouses and construction sites. The data on the waste from the slaughterhouses and construction sites are incomplete for all municipalities and therefore they have been assigned to a category of the common industrial waste. A survey of the waste types [3] has been given in the Table 3.

Table 3. Quantities by types of waste in the municipalities of Bihac region

Municipality	Municipal waste (m^3)	Services (m^3)	Industrial waste (m^3)	Medical waste (m^3)	Total annual quantity of waste (m^3)
Bihac	49,640	10,010	n/a	2,400	62,050
Bosanska Krupa	14,307	2,524	n/a	150	16,981
Bosanski Petrovac	9,855	1,055	12,775	800	24,485
Buzim	1,944	216	120	96	2,376
Cazin	14,208	3,552	1,962	336	20,058
Kljuc	4,455	1,113	3,552	192	9,312
Sanski Most	14,445	4,905	n/a	400	16,750
Velika Kladusa	11,340	4,680	1,260	720	18,000
Drvar	10,250	3,280	26,650	820	41,000
Total	**127,444**	**31,335**	**46,319**	**5,914**	**211,012**

2.1.4. Current Systems of the Waste Collection and Transport in Bihac Region

System of the waste management, in Bihac region, comes within competence of municipalities. There is, in each of municipalities of Bihac region, a public utility company in charge of managing the solid waste. The system is such that the competences of activities of the public utility companies are strictly within the borders of municipalities to which they belong. At the moment, the system is operating according the formula: one municipality – one public utility company. Each of these companies has one landfill within its competence, except municipalities of Cazin, Bosanska Krupa and Buzim that use joint landfill on the location of Mezdre-Vlaski do. Practice shows that the waste from certain urban and rural areas are collected and disposed at least once a week.

The system of the waste management is generally governed by the Law on Municipal Activities [4] on the level of the Una-Sana Canton. The Law regulates the communal activities of special social interest, the way of providing the special social interest, organization of performing the communal activities the way of their financing and other issues important for communal activities. On the basis of the aforementioned cantonal Law, the Decisions on municipal rules have been made in each of the municipalities. The Decisions have been made by the Municipal Council. The municipal order and its maintenance are regulated by them and special attention has been paid to specific features of particular municipalities. Among other communal activities the Decisions establish also the mechanisms of collection, removal and disposal of solid waste. The sorts of the municipal waste are defined by them as well.

Waste in municipalities is collected in different kinds of bags, dust bins, and containers. Public utility companies use 80-120 l bins, containers of 1.1000 l capacity and upwards, and containers with a capacity of 5-7 m3. Also, plastic bags are sometimes used for that purpose.

Each public utility company, besides waste transport vehicles, has its waste treatment machinery, mostly bulldozers for spreading covering material on landfill surface. Utility equipment in all companies is relatively modest. Establishment of a simple system requests significant additional investments into rolling pool and unification of waste collection on the spots.

2.1.5. Estimate of Impact of Landfills on Environment and Human Health

All the existing landfills on the Una-Sana Canton represent a serious problem regarding their impact on environment and human health. Almost all landfills on this territory have been inadequately designed

and constructed. Landfills are not equipped with facilities to protect waste from being scattered around or taken away, nor with devices for seepage water acceptance, recovery or treatment. Landfill Krivodol, used jointly by municipalities Bosanska

Krupa, Cazin and Buzim, is an exception. It is constructed according to sanitary standards, but its function for further usage, regarding its limited free volume for disposing waste, is disputable. Specific features of the terrain of the Bihac region area render more difficult provision of measures for protecting environment from solid landfills impact. In fact, karstic terrain prevailing in this Canton area creates conditions for spreading of possible pollutions by way of ground waters. Protection of springs, ground and surface waters in karstic terrain can be extremely difficult if water transport directions are not exactly defined and possibilities for their pollution are great. In general, it can be said that issues related to the protection of pollution penetrating from the existing solid landfills in the previous period were not solved adequately to their importance. In addition, the existing legal regulations are not easily applicable, because these regulations do not include specific provisions concerning landfills and conditions for their establishment and maintenance [5].

2.2. Integrated Waste Management System in Bosnia and Herzegovina

Bosnia and Herzegovina needs primarily to solve the quality of municipal waste management at municipal level, i.e. to strengthen the utility companies so that they can accept parts of an integrated system that applies exactly to their activity. This problem could be solved by the introduction of fees for each piece of packaging placed on the market. All manufacturers and traders who place any form of packaging on the market (plastic bags, glass bottles, PET, pallets, etc.) would be paying a fee of 0,01 KM (Convertible mark) for the record of packaging. This way the Environment Protection Fund of Federation of Bosnia and Herzegovina would receive about 2 million KM annually. This money would be, according to the Law on Environmental Protection [6], shared in the ratio of 30%:70% between the Federation of Bosnia and Herzegovina and the Cantons. The money would be used exclusively to strengthen the infrastructure of utility companies in charge for managing the municipal waste on the level of municipalities. Parallel with this system would be introduced integrated management system on a voluntary basis of association. For the companies that are not associated fees would be 0,02 KM. That would encourage the association, and also the responsibility over the waste put into circulation. Ministry would set targets, according to the number of inhabitants, in the amounts of collected waste for the organizations that would on selected area take care over the packing waste. For the difference between realized and unrealized targets in amounts of collected waste the "organization" pays per tons in the Environment Protection Fund. This system has a number of dilemmas that must be inter-sectoral adjusted and, as such, enforceable in one edition offered for adoption.

According to the Law on Waste Management in the Federation of Bosnia and Herzegovina [1], operational management of municipal waste is the responsibility of the cantons. Utility companies operate in accordance with special cantonal regulations and have a monopoly. Other companies cannot place their containers on public area that is under the supervision of the utility company. Federation of Bosnia and Herzegovina should choose a model that will be maximally decentralized, where Federal ministry will play the role of control in achieving the national target over the relevant cantonal ministries and the relevant inspection authorities.

In order to obtain adequate responses and the optimal solution, following questions are imposing:

- Is the organization through the Environmental Protection Fund the best solution?
- How much would be producers and retailers operative and efficient by using only the integrated system? Or would it work better through the Environmental Protection Fund?
- Would we have a problem by introducing an integrated system because of the complexity of governance structures in the field of environment?
- Whether we could expect and achieve higher percent of collection by introduction of deposit system, as motivation to individuals to deliver the waste to a specific location?

Overall consideration of these issues, analyzing the possible answers to these questions, with appropriate professional elaboration, however, as the most important and probably the best choice we need to predict the possibility of introducing a combined system. with this, combined system would be introduced appropriate fee for recording so called packaging products, which would be considerably less than the fee introduces by the deposit system, which would get the correct information on quantities, but at the same time would be established some type of integrated system which assign appropriate obligations to producers and traders.

2.3. Development of Integrated Waste Management System on Regional Level in Bosnia and Herzegovina

Taking into account the experience of member states and neighboring countries, and attempts of development of waste management systems on municipal level, as well as respecting the defining of influential factors that are imposed on the way of solving the future waste management system, briefly will be explained the most important elements of proposed model for development of waste management system on regional level.

Solid Waste Management Strategy for Bosnia and Herzegovina [2], made by support of European Union, defined sixteen (16) regional landfills (Regional centers for waste management). On the level of the Federation of Bosnia and Herzegovina has been adopted the whole set of environmental laws and regulations, that were mostly harmonized with the European Union Directives. Therefore, the most important preconditions for development and establishment of waste management system are fulfilled.

The main precondition for the below explained concept is the final decision on locality for future regional waste management center for Bihac.

2.3.1. Influencing Parameters

A large number of parameters influence integrated waste management system. These parameters could be classified into following categories:

- The parameters of waste generation (quantities of waste generation, composition of waste, number of municipalities under regional landfill, institutional and legal framework for collection, transport and landfilling of waste, development of current infrastructure, population of municipalities, habits of the population in terms of separate waste collection, social structure of population, standard of living, structure of economy: such as agriculture, urban areas, tourist areas etc.)
- The parameters of waste collection (with and without selection of usable waste centralized or decentralized collection of waste, existence of a recycling yards, transfer stations, green islands and similar facilities)
- Transport parameters (number of vehicles, types of vehicles, capacities of vehicles, equipment of the vehicles with presses and press containers, fuel consumption, type of fuel, distances, number and location of transfer stations)
- Parameters of usable waste (the potential for using secondary raw materials, energy production, cost of waste separation, prices of raw materials on the market, existence of customers and facilities that trade of secondary raw materials)
- The parameters of landfilling unusable waste (position and capacity of landfill, arrangement of the landfill, number and location of wild dumpsite, cost of waste disposal to landfill)
- The parameters of other categories of waste other than municipal (quantity and composition of other types of waste: industrial waste, medical waste, animal waste, hazardous waste, construction waste)
- Environmental parameters (emission of pollutants into the air, water and soil from landfill, vehicles and supporting infrastructure, composition and quantity of emissions, presence of other pollutants that are not directly related to waste management system, emission limit values prescribed by local law)

Based on the results of previous research on this subject, and based on practical experience of regional landfills in Bosnia and Herzegovina, the following influential parameters are selected to be used in creating a computer model for integrated municipal waste management system:

- Number of municipalities under regional landfill
- Quantity of waste generated by one municipality per year
- Distance from municipality to transfer station
- Distance from transfer station to regional landfill
- Transport costs per kilometer per ton of waste
- Labor costs of transfer station per ton of waste per year
- The degree of use of usable waste (recycling, incineration)
- Cost of landfilling of unused waste per ton of waste
- Cost of usage of usable waste per ton of waste
- Profit from usable waste per ton of waste

2.3.2. Description of Proposed Model of Integrated Municipal Waste Management System

Based on analysis of previous researches, model of integrated municipal waste management system is identified. For the purposes of this model it is necessary to define the objective function or criteria that will be used to select the most favorable combination of input parameters. On the other hand, it is also necessary to define the input data for this model, which could be divided in subsystems as follows:

- generation (quantities, composition, population, habits of the population)
- collection (with and without selection of usable waste, centralized or decentralized)
- transport (vehicle capacity, fuel consumption, distances, number and location of transfer stations with or without pressing of waste)
- usable waste (the potential for using secondary raw materials, energy production, cost of waste separation)
- landfilling (position and capacity of landfill)

Measurable input data should be provided for each of above stated subsystems, that could be obtained from the field (for example: the number and composition of the population, the capacity of the vehicle) or could be estimated on the basis of empirical data (fuel consumption per ton of waste per kilometer of distance, expected profit gained by the production of energy by incineration of waste).

Although, the existing similar models of integrated waste management include also some other parameters, such as the generation of production of pollutant substances or emissions into the environment, in this case, these parameters are not taken into account because it is beyond the scope of this research, and it is considered that the optimum ratio of the selected parameters will reduced these emissions to a minimum. In other words, if the number and location of transfer stations is chosen so that transport costs are the lowest, automatically the transport emissions are the lowest. Based on the above, we start from the following objective function, which implies that the waste is transported directly from each municipality to the regional landfill, without transfer stations:

$$\min(F) = \sum_{i=1}^{k} \left[Q_i \cdot L_i \cdot T_t + Q_i \cdot R \cdot (T_d + T_r - D_r) \right] \tag{1}$$

Where:

F	Objective function; Total costs (per year)
k	Number of municipalities under regional landfill
Q_i	Quantity of waste generated by municipality "i" in tons per year
L_i	Distance from municipality "i" to regional landfill in kilometers
T_t	Transport costs per kilometer per ton of waste
R	The degree of use of usable waste (recycling, incineration)
T_d	Cost of landfilling of unused waste per ton of waste
T_r	Cost of usage of usable waste per ton of waste
D_r	Profit from usable waste per ton of waste

The proposed objective function takes into account quantities of waste generated by individual municipality, the distance at which is transported, the cost of transportation, the cost of landfilling and recycling, minus the profit gained from re-use of usable waste. This function is presented in annual costs, and should have the minimum value for all possible combination of input parameters. By this function locality for regional landfill could be determinate if the transfer stations are not in use. On the basis of this function, location for regional landfill could be determined only if transfer stations are not in use.
If the transfer stations are in use, then the expression (4.1) is further complicated by:

$$\min(F) = \sum_{i=0}^{n} \left\{ \sum_{j=1}^{m} (Q_j \cdot L_{ij} \cdot T_t) + Q_i \cdot \left[(1 - R) \cdot L_i \cdot T_t + T_p + R \cdot (T_d + T_r - D_r) \right] \right\} \tag{2}$$

Where:

F	Objective function; Total costs (per year)
n	Number of transfer stations (it could have the value 0)
m	Number of municipalities under regional landfill
Q_j	Quantity of waste generated by municipality "j" in tons per year
Q_i	Quantity of waste processed by transfer station "i" in tons per year
L_{ij}	Distance from municipality "j" to transfer station "i" in kilometers
L_i	Distance from transfer station "i" to regional landfill in kilometers
T_t	Transport costs of 1 ton of waste per kilometer

T_p Labor costs of transfer station per ton of waste
R The degree of use of usable waste (recycling, incineration)
T_d Costs of landfilling of waste per ton
T_r Cost of usage of usable waste per ton
D_r Profit from usable waste per ton of waste

This function takes into account all parameters that are also presented in equation (1), and when it has the minimal value it provides an optimal balance between the number and location of transfer stations. equation (2) shows that quantity of waste which are transporting from transfer station to regional landfill depend on the degree of use of usable waste "R", because of that fact that all collected waste is not transported, but only the „unused“ part $Q_i \cdot (1-R)$. The quantities of waste processed by transfer stations are calculated as the sum of the amounts of waste collected from the municipalities that the transfer station covers.

There are three groups of input data when testing the objective function. The first group consists of fixed data, which will not often or not at all change over time. These data include geographical distances, the number of municipalities, population. In the second group of input data are those that are slightly changing or those on which change we do not have influence (fuel prices, transport costs per kilometer per ton of waste, costs of landfilling, costs of recycling). This group of input data could be called external input data, because their values could not be affected. In the third group are variable parameters that could be affected by the certain activities and changes in habits of the population (quantities of waste, the degree of use of usable waste, number and location of transfer stations). All these inputs are combined using the objective function, then the combination with the lowest total cost is selected among all combinations. For that purpose we can use an application in the form of MS Excel table with the input parameters. After entering the input parameters, combining are obtained the minimum value of objective function, i.e. the minimum total cost. As an example here is presented table with the costs.

Table 4. Costs

Description	Index	Value	Unit of measure
Labor costs of transfer station per ton of waste (annual)	Tp	25	KM/t
Transport costs of 1 ton of waste per kilometer	Tt	12.5	KM/km·t
Cost of usage of usable waste per ton (annual)	Tr	450	KM/t
Profit from usable waste per ton of waste (annual)	Dr	200	KM/t
Costs of landfilling of waste per ton (annual)	Td	50	KM/t
The degree of use of usable waste	R	0.3	-

The data in Table 4 were estimated from available data for the Una-Sana Canton, and based on experiences from the work of the regional landfill "Mošćanica" in Zenica. Labor costs of transfer stations per ton of waste on annual basis are 25 KM. These costs include all costs related the work of transfer stations. They are estimated based on data for transfer station in Visoko, Zenica-Doboj Canton. Transport costs of 1 ton of waste per kilometer highly depend on fuel prices, and according to prices from 2011, they amounted to about 12.5 KM per kilometer per ton of waste. These costs include costs of fuel consumption, vehicle maintenance, vehicle depreciation, and labor for loading, unloading and transport. Cost of usage of usable waste per ton is calculated for the case of manual separation of waste and is 450 KM per ton of waste per year. If 6 people work on selection of waste 8 months a year, the costs amount to 52.800 KM, during which time is processed about 117 tons of waste. This category of costs could be significantly reduced by introducing mechanization and automation of the process of separation of usable waste. Profit from usable waste per ton of waste is about 200 KM per ton of waste annually. Costs of landfilling of waste are about 50 KM per ton annually. This price includes all costs: energy, land use, machinery, manpower and other costs. The degree of use of usable waste is calculated based on available data for Bihac region for period of 2006-2008. To simplify the model, it is calculated the average level of use for all municipalities that gravitate to this regional landfill and received the degree of use of 30%, i.e. 0.3. In MS Excel spreadsheet, it is easy to determine which combination has the lowest cost. Furthermore, MS Excel spreadsheet or the objective function could be used for any group of input data, although these related to costs are the most important.

3. CONCLUSIONS

It is of special significance to identify the most influential parameters on the total cost of an integrated municipal waste management system in the actual conditions of Bosnia and Herzegovina. The proposed model, and mathematical expressions on which the model is based, can be used for fast calculation of the total cost of the integrated system, and which is also very important, they can easily be extended by introducing other influential parameters if it turns out that they could significantly affect the total cost of the system. The proposed model, implemented as a spreadsheet, was tested using data for the Bihac region. Input data was selected and their values were estimated or calculated based on realistic data from practice. The sensitivity of established model can be examined by changing the values of input parameters. Testing the model, by changing the values of parameters, has been shown that the most significant effect on the total cost of the integrated system has a transport, so that on this basis may be suggested the direction of further improvement of this system. However, the degree of use of usable waste has also significant influence on total costs, so that an increase in percentage of use of usable waste can significantly reduce overall system costs. The proposed model did not take into account all possible influential parameters, but the most important based on experience of few regional landfill in Bosnia and Herzegovina. This model could be improved by introducing the environmental parameters (emission of pollutants into the air, water and soil) or some other parameters which are not taken into account. Lack of the proposed model could represent the assumption of the average degree of use of usable materials. As results of testing the model have been shown the degree of use of usable waste was the second important influential parameter (right after the transport costs), so the model could be tested with the individual degree of use of usable waste for every municipality in Bihac region. It would, however, led to a substantial increase in the complexity of the model. The third disadvantage is reflected in the valuation of some input data, which are simply not available for the selected Bihac region, because the system has not yet been established. This lack has tried to overcome by using data from a similar regional landfill (regional landfill „Mošćanica“, Zenica), but it would definitely be checked with real data when the system for the Bihac region will be fully implemented.

REFERENCES

[1] Law on Waste Management, Official Gazette of the Federation of Bosnia and Herzegovina, issue 33/03, 2003
[2] State strategy of managing solid waste, EU PHARE, EA Technology Environment, Culham, Abingdon, Oxfordshire, 2000.
[3] Feasibility Study of Regional Sanitary Landfill “Grabez – Drenovo Tijesno”, Bihac Region, Bosna-S Oil Services Company, Sarajevo, 2007
[4] Law on Communal Activities, the Official Gazette of the Una-Sana Canton, the year IX, the issue 8
[5] Waste disposal dumps and their impact on surface and ground water resources, i.e. potable water springs – Una-Sana Canton Water Supply Programm, Una-Sana Programming Office, Bihac, 2000
[6] Law on Environmental Protection, Official Gazette of the Federation of Bosnia and Herzegovina, issue 33/03, 2003

QUANTIFICATION OF CONSTRUCTION AND DEMOLITION WASTE GENERATED IN SPANISH RAILWAY PROJECTS

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Abstract

Due to the increase in the amount of Construction and Demolition (C&D) waste generated during the last decade in Spain, the construction sector should assume the responsibility to reduce the harmful environmental and social impact it produces. To solve this situation researchers within the civil engineering sector have focused on the use of C&D waste as new building materials for road bases, sub-bases and firms. However, another research line to be considered, as has been developed in the building sector, is the estimation of C&D waste quantification to be generated in this type of works. In this sense, many authors have researched the way to optimize management including quantifying methods of C&D waste generation in building works.

The aim of this research study is to improve C&D waste management in Spanish railway construction works by estimating in advance the amount of C&D waste likely to be generated, according to the construction stages and the C&D waste category. This study has focused on collecting data from the reports and bill of quantities of railway works projects in order to obtain the waste generation rate. The results show that the mixed C&D waste not containing hazardous substances are the most generated ones in works of railway. On the other hand, the least generated C&D waste corresponds to packaging in general and metal waste. Results regarding construction stages show that the largest number of C&D waste is generated during the construction of the tunnels.

Keywords: *construction and demolition waste, waste management, quantification, railway construction works, waste categories*

1. INTRODUCTION

Presently in Spain, waste management is legally regulated by the Law on waste, established by the Ministry of Environment [1]. This law implied a new conception on waste policy, and stated a common normative for all types of waste, which has later been expanded with specific regulations for the different waste categories.

Although the latest ratios found for C&D waste generation in Spain are from 2008 (45 million tonnes), no recycling ratios have been found for that year. Instead, both ratios are defined for the period in which the 1st National Plan on C&D waste (I PNRCD in Spanish acronym) was in force [2]. In 2006, Spain generated roughly 47 million tons of C&D waste but only 13.60% of the C&D waste was recycled [3,4]. Regarding this issue, the aim of 60% reuse or recycle established by the I PNRCD was not fulfilled. The European Environment Agency (EEA) estimated that 65% on average of the waste was to be recycled in 2006 in the 27 European State members [4].

The definition of C&D waste both includes waste generated in building works and civil engineering. In this respect, the source of the data reported (Eurostat), does not distinguish between C&D waste generated in building works and civil engineering works. In 2008, the 2nd National Plan on C&D waste (II PNRCD in Spanish acronym) made a small distinction, claiming that civil works contracts exceeded building works [5].

To improve the situation, the European Parliament demands through the 2008/98 Directive on waste, the adoption by each EU Member of the necessary measures to ensure that by 2020, there is a 70% in weight increase in the recycling and other valorization operations of non-hazardous C&D waste, excluding the soil and stones not containing dangerous substances [6]. In particular, the Spanish

Government issued the 105/2008 Royal Decree (RD) [7] which regulates and establishes a legal frame for the production and management of C&D waste. Between the measures proposed in the RD, the C&D Waste Management Survey, drawn up by the C&D waste producer (the license holder), should be highlighted. This study should include, among other documents, an estimation of the quantity of the C&D waste to be generated on site, classified according to the European Waste Catalogue (EWC) [8]. Despite this, still the planning and carrying out of construction works are not influenced by environmental factors. There are no tools or methodological instruments that consider environmental aspects, not even in the regions where there is a C&D waste regulation (like in Catalonia and more recently in Madrid). In addition, today professionals continue to dump waste rather than recycling or reusing it (IIPNRCD).

This issue has promoted the development of new research projects towards the minimization of waste and the sustainability in the construction sector. During the last years research within the civil engineering sector have focused on the use of C&D waste as new building materials for bases, sub-bases and pavements, among which studies by Poon et al. [9], Aatheesan et al. [10], Courard et al. [11], and Kuo et al. [12] can be highlighted. In addition, there are other specific studies of C&D waste use in railway works, which include research works by Helsen et al. [13] about the recycling of Chromated Copper Arsenate treated wood waste from railway sleepers, Indraratna et al. [14] studies about recycled ballast, and Krezel et al. [15] works on the use of layered recycled aggregate concrete barriers as a means of lessening the noise from railway tracks.

Another research line to be considered is the estimation of the C&D waste quantification to be generated. Due to the requirement of estimating the quantification of the C&D waste generated in the C&D works present in the RD, many authors have researched to find an optimal management including both quantification and generation of C&D waste in building construction works.

Furthermore, Yuan [16] states that waste generation rates serve as valuable quantitative information for benchmarking different C&D waste management practices. Different practices however, still adopt different approaches to measure waste generation ratios, which leads to difficulties to the benchmark for measuring different C&D waste management performances. In this regard, further studies should be launched to enable the benchmark of different waste management performances using waste generation rates.

However, there are few studies that analyze the quantification of C&D waste generation in the civil engineering sector [17], but even less in railway construction works. Despite this, several studies quantifying C&D waste generation in building construction works in relation to the built area can be highlighted:

- Bossink and Brouwers in 1996 established preliminary estimations from a study of 184 house buildings developed in five different projects in Holland. They stated that according to the typology of the construction materials supplied on site, approximately 1% to 10% of them become waste [18]
- Mañà I Reixach *et al.,* (2000) developed the method used by the Construction Institute of Cataluña, obtaining the C&D waste generated per surface area for different constructive systems, considering three construction phases: structure, masonry and finishings [19]
- The study carried out by Chandrakanthi *et al.* in 2002 in Canada uses simulation models to establish the generation of waste in construction works regarding five categories, and based on the schedule of construction activities [20]
- Solís Guzmán *et al* in 2010 presented a model for C&D waste quantification and management in Spain based on budget data of building works. The model determines the total quantity of waste by categories and by project, estimating the volume in three different categories: demolitions, material loses during construction and packaging [21]
- Other researchers show results obtained through annual data, as can be the construction licenses. Hsiao *et al.* in 2002, for example, have used dynamic modeling for their analysis. Taking the built surface in accordance with the constructing permits issued up to 1999, for construction and demolition works in Taiwan, they estimated and planned the generation of concrete waste from 1981 to 2011 [22]
- The estimation method for construction, rehabilitation and demolition waste performed by Cochran *et al* in 2007 for the state of Florida is based on the National Methodology proposed by Franklin Associates for the U.S. Environmental Protection Agency (U.S. EPA) and the Industrial

Solid Waste Division. However, it uses estimation ranges which allow establishing differences in waste generation depending on the construction technique employed. Results are then broken up according to the nine categories of waste established [23]

- Kofoworola *et al.* in 2009, in Thailand, used this principle in a broader way. To the data obtained in Thailand form the construction permits issued, they apply factors of waste generation of 21.38 kg m^{-2} for residential construction works and of 18.99 kg m^{-2} for non-residential construction works [24]

In short, from the literature and documentation available, it can be concluded that there are many authors who have researched the management and development of the C&D waste in civil engineering works however, no previous studies have been found analyzing the quantification of C&D waste generation rates in railway works. Therefore, the aim of this research study is to improve C&D waste management in Spanish railway construction works by estimating in advance the amount of C&D waste likely to be generated, according to the construction stages and the C&D waste category.

2. ELABORATION

2.1. Methodology

The estimation of the C&D waste generated in railway works needs to be assessed regarding the characteristics of the project. In order to do so, the methodology followed in this article unfolds in four different phases:

- Selection of works
- Structure of the bill of quantities
- Data collection of the waste generated in the selected works, both for the totally of the work and for the different stages of the construction work

2.1.1. Selection of Works to be Studied

This research work focuses on railway infrastructure works in Spain. Therefore, a collection of real railway works carried out by Spanish construction company (Fomento Construcciones y Contratas), have been chosen. In general, the railway projects analyzed present the following characteristics: 17.113 km of railway road, 6 intersections and junctions, 17 cross drainage works, 9 underpasses, 1 overpass, 10.00 km of viaduct and 10.399 km of Tunnel.

2.1.2. Quantification Structure

This study has focused on collecting data from the reports and bill of quantities of the selected works projects. Due to the lack of homogeneity in the structure of the construction stages in the bill of quantities, the following guidelines were established to facilitate the comparison of the results:

- The bill of quantities should have a similar construction chapter structure in the different projects, where the elements of work were clearly identified
- The construction work chapters will contain the same units so that they comparisons of the results could be made
- Bill of quantities should provide a standardized classification of quantities so that they could be extrapolated to other projects of similar characteristics

Regarding these guidelines, the bills of quantities were divided into the following construction stages and sub-stages of work:

- Preliminary and explanation works
- Drainage: Longitudinal drainage and cross drainage works
- Structures: Underpasses; overpasses – footbridge and viaducts
- Junction: Linking paths
- Tunnel: Tunnel construction
- Temporary detours

2.1.3. Obtaining Data on Waste Generated

To quantify the weight and volume of C&D waste generated, the online available BEDEC database from the Catalonia Institute of Construction Technology (ITeC) has been used. This database gives environmental parameters for each sub-stage in the bill of quantities of the construction works. In this sense, values of the following environmental parameters for the analyzed works were available:

- Volumes in m^3, of waste generated and classified according to the EWC code
- Weights in kg, of waste generated and classified according to the EWC code

These environmental parameters have been identified not only for each of the sub-stages from the analyzed projects, but also by aggregation, for each chapter and for the whole railway construction work. Moreover, in this study, soil and stones not containing dangerous substances have been excluded (EWC code: 17 05 04) following the 2008/98/EC Directive of 19 November 2008 on waste which does not consider them as waste.

An example of how the data is obtained can be seen in Table 1 which shows a fragment from one of the analyzed chapters for the quantification of C&D waste generated in a viaduct construction.

Table 1. Example of quantification of C&D waste generated in the execution of a viaduct.

CHAPTER: VIADUCT							
WORK CHAPTER			ENVIRONMENTAL PARAMETERS				
			Waste per work chapter			Total waste	
Unit	Description	Quantity	Weight (kg)	Volume (m^3)	EWC Code	Weight (kg)	Volume (m^3)
SUB-CHAPTER: VIADUCT FOUNDATION							
m^3	Mass concrete for packings, levelling layers and cleaning.	152.82	25.00	$1x10^{-2}$	170101	$3.82x10^3$	1.53
m^3	Reinforced concrete in foundations, piles, screens, …	3,695.15	25.00	$1x10^{-2}$	170101	$9.24x10^4$	$3.70\ x10^1$
kg	Reinforcement steel bars.	643,477.45	0.05	$8.04x10^{-6}$	170405	$3.22x10^4$	5.17

2.2. Results and Discussion

The generated waste in railway works, according to the EWC code is identified as follows:

- 15 01 01 paper and cardboard packaging
- 15 01 02 plastic packaging
- 15 01 03 wooden packaging
- 15 01 10* packaging containing remains of or contaminated by dangerous substances
- 17 01 01 concrete
- 17 01 03 tiles and ceramics
- 17 02 01 wood
- 17 02 03 plastic
- 17 03 02 bituminous mixtures containing other than coal tar and tarred products
- 17 04 05 iron and steel
- 17 04 07 mixed metals
- 17 09 04 mixed construction and demolition wastes other than those containing dangerous substances

Once the total quantities, both in weight and in volume, have been obtained, results show that the mixed C&D waste not containing hazardous substances (EWC code: 17 09 04) are the most generated ones in railway construction works (Fig. 1.), representing 55% in weight and 85% in volume of the total. This is mainly due to the lack of C&D waste segregation onsite, despite the usual space available in railway construction works, to do so. This waste category is followed by the bituminous mixtures (EWC code: 17 03 02) that in turn, represent 7% in volume and 25% by weight.

On the other hand, plastic (EWC code: 15 01 02) and wood (EWC code: 15 01 03) packaging wastes and empty hazardous waste containers (EWC code: 15 01 10*) are generated in smaller proportions not even reaching 0.1% in weight and volume. Furthermore, waste categories such us 17 09 04 or 17 02 01, occupy huge volumes in the construction site related to their weight. In this sense, the use of mobile waste treatment plants for grinding and crushing or other measures could be considered.

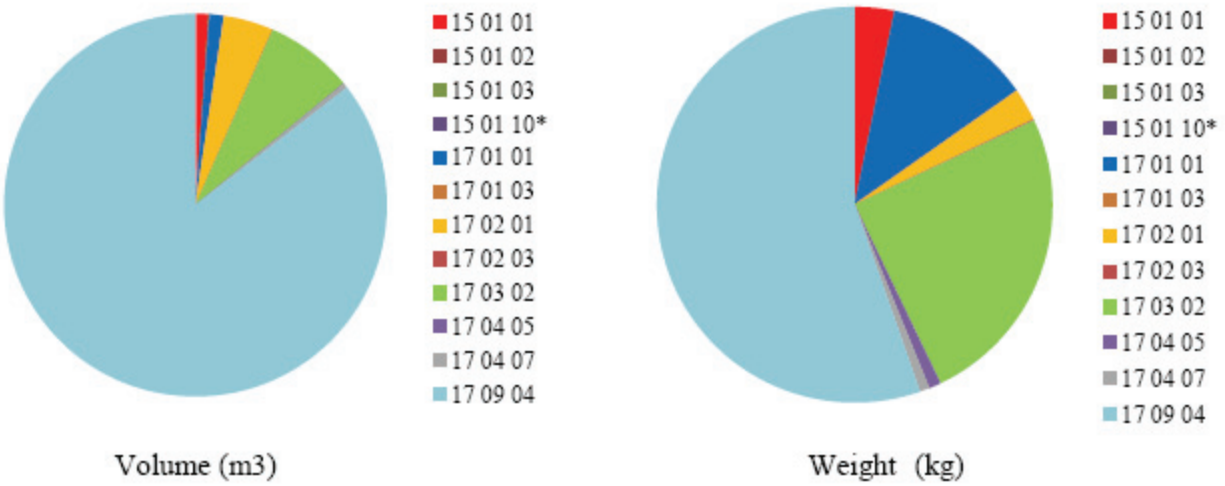


Figure 1. Percentage of C&D waste generated in volume (m^3) in rail works, according to the category

In addition, it is also important to consider when the waste will be generated, during the process of the railway construction. Therefore, the data obtained has been analyzed regarding the corresponding construction stages. Fig. 2. shows that the largest amount of C&D waste is generated during the tunnels construction–accounting for 59% of the total waste generated in volume and 46% by weight. This construction stage is followed by the preliminary and explanation works, which represents 37% in volume (m^3) of the total C&D waste generated, and 46% in weight (kg).

These two construction stages should be deeply analyzed by engineers during the design phase of a railway construction work in order to plan the appropriate management for each waste category to be generated.

On the other hand, the construction stages that generate less C&D waste correspond to drainage and temporary detours, not exceeding 7% both by weight and volume.

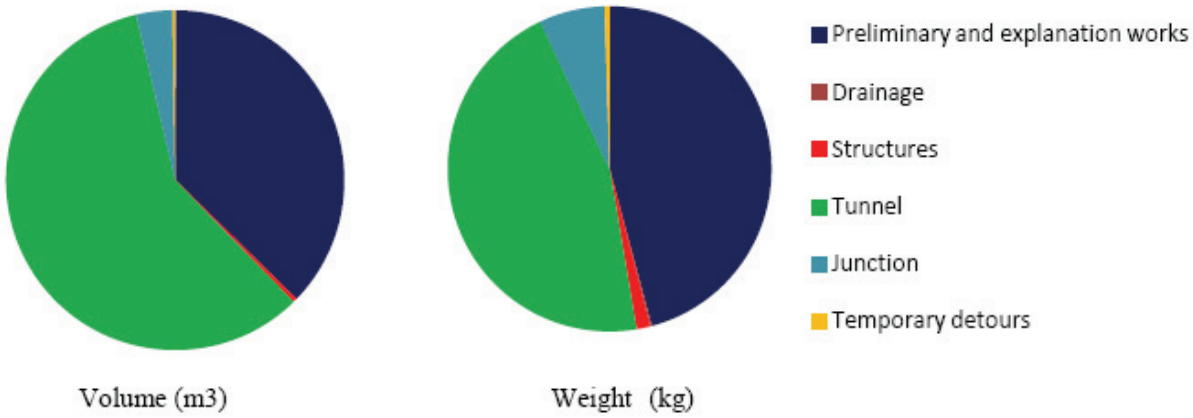


Figure 2. Percentage of C&D waste generated in weight (kg) and in volume (m^3) in railway construction works classified by construction stages

3. CONCLUSIONS

From the analysis performed in this study, the following conclusions can be drawn:

- The quantification tools for C&D waste generation presently being used in civil works are not detailed enough to answer to the increasing social pressure in relation to environmental concerns.
- The most generated C&D waste category in railway works corresponds to mixed C&D waste (EWC code: 17 09 04)
- In general, packaging wastes and empty hazardous waste containers are the less significant waste generated

- The construction of a tunnel in a railway becomes essential to quantify in advance the waste suitable to be generated during the works. Moreover, if construction agents focus their efforts in the waste generated in tunnels and preliminary explanation works, more than 90% of the total waste generated in railway works could be properly managed.

The implementation of these conclusions in railway construction projects will help in assigning an optimal and systematic management of the C&D waste produced, giving priority to treatments for reducing, reusing and recycling these wastes as opposed to a definite disposal, as well as anticipating good practices for their correct management throughout the construction process, as the RD 105/2008 states.

This study can help to improve existing waste management systems and assist the construction agents in developing the waste management plans according to the existing legislation, and therefore, contribute to achieve the quantitative targets set for this type of waste for 2015 in Spain.

Acknowledgement
The authors would like to thank Fomento Construcciones y Contratas (FCC) Company, especially the Department of Environment, for supplying the information about railway construction works performed by the company that was basic for this study. This research study has been concluded in the Framework of the CLEAM Project, partially funded by The Centre for the Development of Industrial Technology (CDTI) within the CENIT program. Its results are, consequently, exclusive property of the companies that carry out the Project and constitute the CLEAM CENIT, AIE.

REFERENCES

[1] Spanish Government. Ley 10/1998, de 21 de abril, de Residuos. BOE Num.96, 1998.
[2] Spanish Government. I Plan Nacional de Residuos de Construcción y Demolición 2001–2006, Ministry of the Environment, Madrid, Spain, 2001.
[3] Waste generation ratios for 2008 in the EU. Source Data: Eurostat. Last update: 16/11/2010
[4] European Environmental Agency. Working paper 'EU as a Recycling Society: Present recycling levels of Municipal Waste and Construction & Demolition Waste in the EU'. (2009)
[5] II Plan Nacional de Residuos de Construcción y Demolición 2008-2015 (II PNRCD). BOE Núm. 49, Anexo 6 Plan Nacional Integrado de Residuos (PNIR), 2009.
[6] European Directive 2008/98/CE of the European Parliament and of the Council, 2008.
[7] Spanish Government. Real Decreto 105/2008, de 1 de Febrero, por el que se Regula la Producción y Gestión de los Residuos de Construcción y Demolición (National Decree 105/2008, February 1, which Regulates the Production and Management of Construction and Demolition Waste). Ministry of the Presidency, Madrid, Spain, 2008.
[8] European Waste Catalogue. Commission Decision 2000/532/EC. Official Journal L 226.
[9] C.S. Poon, D.X. Chan, Feasible use of recycled concrete aggregates and crushed clay brick as unbound road sub-base. Construction and Building Materials. 20/8 (2006) 578-585
[10] T. Aatheesan, A. Arulrajah, J. Wilson, et al., Beneficial use of brick rubble as pavement sub-base material. In: 1st International Conference on Transportation Geotechnics, AUG 25-27 (2008) Nottingham, England. Proceedings of advances in transportation geotechnics. 695-699
[11] L. Courard, F. Michel and P. Delhez, Use of concrete road recycled aggregates for Roller Compacted Concrete. Construction and Building Materials. 24/3 (2010) 390-395
[12] M.F. Kuo, J.C. Du, D.H. Shen, Crushed waste concrete in stone mastic asphalt mixtures, Baltic Journal of Road and Bridge Engineering 5/3 (2010) 164-168.
[13] L. Helsen, E. Van den Bulck, J.S. Hery. Total recycling of CCA treated wood waste by low-temperature pyrolysis. Waste Management 18/6-8 (1998) 571-578.
[14] B. Indraratna, W. Salim, Deformation and degradation mechanics of recycled ballast stabilised with geosynthetics. Conference Information: 3rd International Symposium on Deformation Characteristics of Geomaterials, SEP, 2003 Lyon, France. Soils and Foundations 43/4 (2003) 35-46.
[15] Z.A. Krezel, K.J. McManus, G.E. Harding. The use of layered recycled aggregate concrete barriers in targeting urban noise. Conference Information: 3rd International Conference on Urban Regeneration and Sustainability, 2004 Siena, Italy. Sustainable City III: Urban Regeneration and Sustainability. Book Series: advances in architecture series 18 (2004) 673-682.

[16] H. Yuan, L. Shen, Trend of the research on construction and demolition waste management. Waste Management vol 31, 4, (2011) 670-679.
[17] Future Foundations. Towards zero waste for civil engineering. South West Regional Development Agency and DEFRA Business Resource Efficiency and Waste Programme. United Kingdom. Available at: www.southwestrda.org.uk . Last access: 23/09/2011.
[18] B.A.G. Bossink, H.J.H. Brouwers. Construction waste: quantification and source evaluation. Journal of Construction Engineering and Management ASCE 122, (1996) 55–60.
[19] F. Mañà i Reixach, J. Gonzàlez i Barroso, A. Sagrera i Cuscó, Dirección General de Medio Ambiente, Institut de Tecnología de la Construcció de Catalunya, Plan de Gestión de Residuos en las Obras de Construcción y Demolición, Programa Life. 2000.
[20] M. Chandrakanthi, P. Hettiarachi, B. Prado, J. Ruwanpura, Optimization of waste management for construction projects using simulation. Proceedings of the 2002 Winter Simulation Conference, San Diego, CA, (2002) 1771–1777.
[21] J. Solís-Guzmán, M. Marrero, M.V. Montes-Delgado, A. Ramírez-de-Arellano, A Spanish model for quantification and management of construction waste. Waste Management 29 (2009) 2542–2548
[22] T.Y. Hsiao, Y.T. Huang, Y.H. Yu, I.K. Wernick, Modeling materials flow of waste concrete from construction and demolition wastes in Taiwan. Resources Policy 28 (2002) 39–47
[23] K.M. Cochran, T.G. Townsend, D. Reinhart, H. Heck, Estimating construction and demolition debris generation using a materials flow analysis approach. Waste Management 30 (2010) 2247–2254
[24] O.F. Kofowoeola, S.H. Gheewala, Estimation of construction waste generation and management in Thailand, Waste Management 29 (2009) 731-738

A COMPARATIVE ANALYSIS OF UNIVERSITIES USING SUSTAINABILITY INDICATORS

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Abstract

Ranking of universities is a global phenomenon with several years of history, starting in 1983. The excellence of universities within the ranking tables is mostly assessed from two perspectives, research and teaching since these activities have been traditionally understood as two missions. On the other hand, universities play other important roles in the society: operating explicitly to serve it by education of future leaders, distribution of existing knowledge, development of innovations, and introduction of best available practices in sustainable development. This paper actualizes the model of multidimensional ranking, developed by the University of Maribor in 2008, integrating the sustainability performance in it. The model enables a comparison between universities regarding economic (research results and expenditure, highly cited researchers, etc.), social (graduation rate, foreign students' share, etc.) and environmental performances (environmental commitments, sustainability or environmentally oriented programmes, etc.). Based on the model, 15 top universities from ARWU and THES ranking tables each, published in 2010 were evaluated. The results were extended to the performances and trends of 7 selected universities from Croatia and Slovenia, enabling them to detect their strengths, weaknesses, opportunities, and threats in comparison with the world's best universities. Considerable changes have occurred in the 2011/2008 ranking, mostly due to universities' research (R), educational (E) or environmental (EN) orientation.

Keywords: *university ranking, research, education, environment, indicators, comparison*

1. INTRODUCTION

Over the course of the last three decades higher education ranking tables have emerged, offering information about the quality of higher education institutions. According to the Jesenšek [1] the purposes of ranking tables are: (1) evaluating a global entrance to the higher educational programmes, (2) evaluating a phenomenon of international higher education market, (3) introducing vehicle models for market push of universities at national levels (4) enhancing a healthy and positive competition for students, professors, and funding of universities.

The rankings began in 1983, when the U. S. News and World Report started to publish the annual issue of America's best colleges. This has resulted in the development and publication of more ranking tables from countries across the world. The ranking table of Canadian universities from the Maclean's magazine was first published in 1991. In 1992 the Princeton Review published its first annual Best Colleges' ranking of the 357 colleges. In 1999 the Center for higher education development introduced a ranking of German universities. Asiaweek published its rankings of Asia's best universities from 1997 to 2000 [2]. Moodie [2] claimed that the first important international rankings emerged in 2002, when the Swiss Centre for Science and Technology Studies published its Champions league of research institutions. Jiao Tong University, Institute of higher education in Shanghai published its academic ranking of world universities in 2003. In 2004 the Times Higher Education Supplement (THES) published its first university ranking [2]. Since 2004 also a Spanish ranking table of world universities, called Webometrics is published twice a year.

The designers and publishers of ranking tables try to objectively assess the universities excellence, but there exists a lot of criticism about the ranking methodologies. For example, Enserink [3] claims that vast differences between ranking methodologies exist, especially in the number and the nature of indicators, as well as the way the data are obtained, while Marginson [4] argues that ranking tables conceal a whole array of methodological problems and anomalies. There have been disagreements with the ranking methodologies, which led universities to hesitate in ranking participation. Hazelkorn [5]

argues that rankings sustain a single definition of quality at the time when universities have diversifying missions and visions. By focusing primarily on research and other dimensions, such as teaching and learning, environmental issues are neglected. In order to harmonize university rankings, an International Ranking Expert Group (IREG) has published Berlin principles on the ranking of higher education institutions. These principles focus on good practice for improving the rankings, emphasize the purposes and goals of rankings, design and weighting of indicators, processing of data, and presentation of results [6]. In our paper, a comparative analysis of universities using sustainability indicators, which cover all the three perspectives of sustainable development: (i) research, development, and investment (economic perspective), (ii) education and student services (social perspective), and (iii) the environmental perspective, has been carried out with an additional focus on the best universities in Slovenia, and Croatia.

2. ELABORATION

2.1. Overview of Ranking Tables

Analyses of ranking tables, including their publication process, frequency of issues as well as indicators have been carried out. Table 1 shows several differences between the ranking tables to exist. The differences are in:

- publication process – some ranking tables are published by newspapers and magazines (e.g. America's best Colleges), others by universities and institutes (e.g. Academic Ranking of World Universities, College Sustainability Report Card), or institutes together with the newspapers (e.g. CHE of University Ranking);
- frequency of issues – mostly they are published once or twice a year;
- range of the countries or regions that ranking tables cover.

Table 1. Six selected ranking tables

Country	Publisher	Ranking table	Range	Frequency
China	Shanghai Jiao Tong University, Institute of Higher Education	Academic Ranking of World Universities	international	annual
Germany	Centrum für Hochschulentwicklung, Deutcher Academischer Austausch Dienst, die Zeit	CHE of University Ranking	national and regional (German speaking universities)	annual
Spain	Laboratorio de Internet (CINDOC-CSIC)	Webometrics Ranking of World Universities	international	twice a year
UK	The Times Higher education Supplement	World University Rankings	international	annual
USA	U. S. News	America's Best Colleges	national/ regional	annual
USA	The Sustainable Endowments Institute	The College Sustainability Report Card	national/ regional	annual

All the ranking tables reviewed, except the CHE and the Sustainability Report Card, use a numerical structure to rank their universities. The German CHE ranking table provides a qualitative assessment in three groups (basic, intermediate and upper ones). Within these three groups, universities are listed according to the alphabetical order. The researchers at the CHE claim that group-based ranking prevents minor differences between universities from showing up as major differences in ranking [7]. On the other hand the Sustainability report card calculates grades based on the total number of points earned for the indicators within eight categories. The grades for the individual categories are A, B, C, D, and F. To receive an "A" in any category, a university needs to accumulate at least 70 percent of total available points for the indicators in that category [8].

Table 2 presents a more in-depth review of indicators or group of indicators used by the ranking tables selected. The analysis reveals some common indicators, traced out in most of the ranking tables reviewed. Such indicators deal with reputation, presented through scientific publications and citations. Other common indicators are financial means of a university, and student selection. Specific indicators, typical for only one ranking table can also be found. Such indicators are for example room rents, or

commuting possibilities identified in the CHE ranking table, number of pages recovered from four search engines Google, Yahoo, Live Search and Exalead from Webometric ranking table [9] or only environmentally oriented indicators, such as climate change and energy, food and recycling, etc. from the College sustainability report card [8]

Table 2. Indicators of selected ranking tables.

Ranking table	Number of indicator groups	Number of indicators	Indicators and their weights i
Academic Ranking of World Universities		6	1. Number of alumni who earned a Nobel Prize or Fields Medal (10 %) 2. Number of researchers who earned a Nobel Prize, and/or the Fields Medal (20 %) 3. Number of highly cited researchers (20 %) 4. Number of articles published in Nature, and Science (20 %) 5. Number of articles listed in *Science Citation Index Expanded* and *Social Science Citation Index* (20 %) 6. Per capita performance with respect to the size of an institution (10 %)
CHE	9 main groups	83	1. Students 2. Study output 3. International orientation 4. Research 5. Study and education 6. Equipment 7. Employment market 8. Overall opinion 9. Study environment and university
THES		13	1. Reputation survey – research (19,5 %) 2. Research income (5,25 %) 3. Paper per academic and research staff (4,5 %) 4. Public research income/total research income (0.75 %) 5. Reputational survey – teaching (15 %) 6. PhD awards per academic member (6 %) 7. Undergraduates admitted per academic member (4.5 %) 8. Income per academic member (2.25 %) 9. PhD and bachelors' awards (2.25) 10. Citation impact (normalized average citation per paper) (32,5 %) 11. Ratio of international to domestic staff (3 %) 12. Ratio of international to domestic students (2 %) 13. Research income from industry (per academic staff) (2,5 %).
Webo-metrics		4	1. Size (20 %) 2. Visibility (50 %) 3. Rich files (15 %) 4. Google Scholar (15 %)
U. S. News		7	1. Academic peer review (40 %) 2. Employer review (10 %) 3. Student-to-faculty ratio (20 %) 4. Citation per faculty member (20 %) 5. International faculty (5 %) 6. International students (5 %)
Sustaina-bility report card	9	48	1. Administration 2. Climate change and energy 3. Food and recycling 4. Green buildings 5. Students involvement 6. Transportation 7. Endowment transparency 8. Investment priorities 9. Shareholder engagement

2.2. Methods

The methodology, presented in Figure 1 has been followed in order to carry out a comparative analysis (for more detailed presentation of the methodology, see [9]).

Indicators covering various aspects (see Table 3) of university performance have been selected, based on the principle of objectivity and quantitative expression, grouped and judged according to their positive or negative impacts on the particular group (sub-index).

Finally, indicators have been weighted, using the analytic hierarchy process (AHP) and normalized in order to obtain the final ranking (index) or final rank (A), which is composed of sub-indices: research (B_1), educational (B_2) and environmental (B_3) ones, while the lower level consists of various individual indicators (C_i), Figure 2.

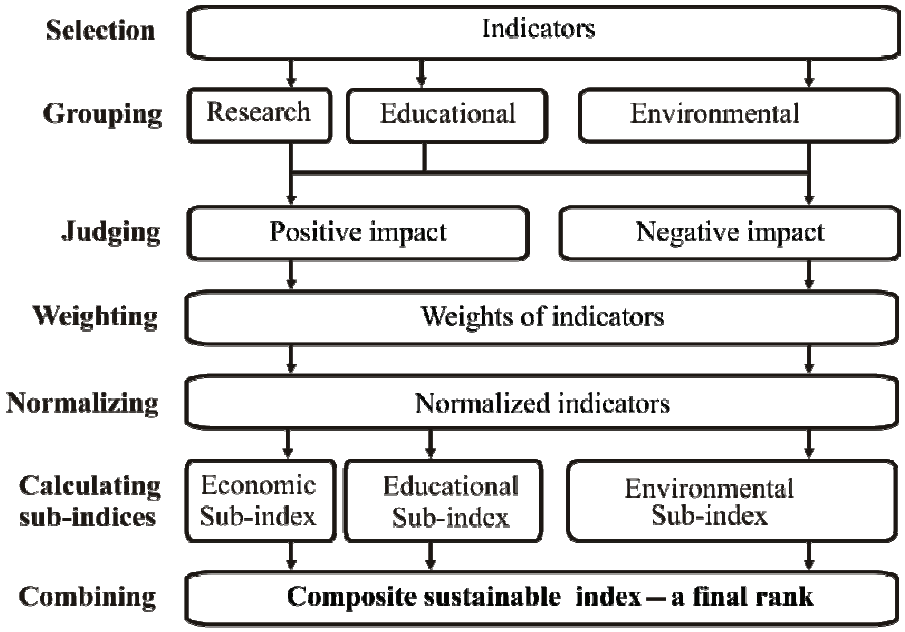


Figure 1. A methodology for determining the final ranks of universities [9]

Table 3. Sub-indices and indicators in our rating.

Research dimension (B_1)	Educational dimension (B_2)	Environmental dimension (B_3)
• Patents (C_1), expressed as number per staff. • Research expenditure (C_2) expressed in EUR per student on an annual basis. • Highly cited researchers (HiCi, C_3) expressed as a fraction of the top score citations in percentage. • H-index (C_4) quantifies both the actual scientific productivity and the apparent scientific impact of a scientist. H-index has been normalized by the number of academic staff. • SCI index (C_5) embraces the total number of articles indexed in Science Citation Index Expanded and Social Science Citation Index. • Annual expenses for computers and/or library per student (C_6).	• Student / academic staff ratio (C_7). • Graduation rate (C_8), an indicator determined by the fraction of students in a university attaining their educational goal. • Presence on the web (C_9) taken from data obtained by the Webometrics [14]. • Foreign students' rate (mobility) (C_{10}) shows the tendency of a university to internationalize.	• Voluntary environmental agreements or commitments (C_{11}) in order to obtain information about activities within community and global environments. • Sustainability oriented courses (C_{12}). • Sustainability oriented programmes (C_{13}). • Sustainability vision and mission (C_{14}). • Sustainability office, manager, council or consultant (C_{15}).

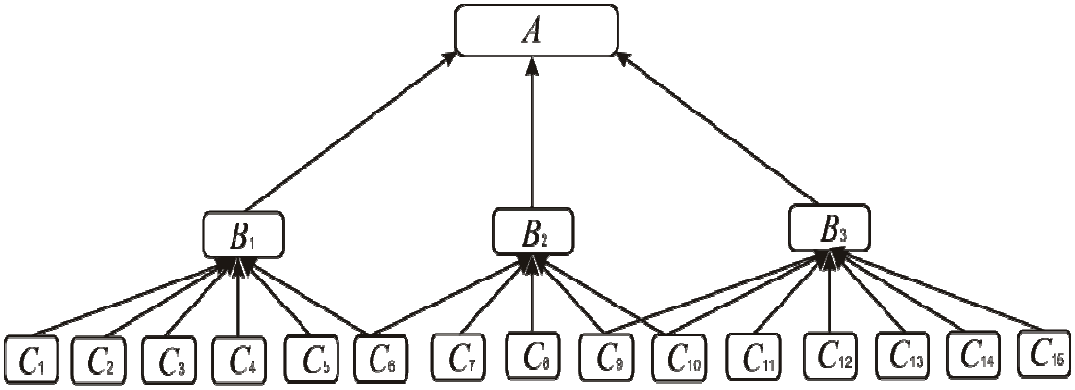


Figure 2. Hierarchical structure of the final index for university ranking.

2.3. Results

A sample of 15 common universities from ARWU 2010 and THES 2010 ranking tables, listed up to the 20th position were considered. 7 universities from Slovenia, and Croatia were added, in order to evaluate and compare their performance from the three perspectives of sustainability (research, educational, and environmental). The input data used was obtained in July 2011 from various ranking tables (e.g. ARWU, Webometrics, Web of Science, and Esp@cenet), or extracted from the Internet (e.g. graduation rates). Allowing for the fact that universities do not post data on the internet every year, the latest available data (during the research) was taken into consideration. The index (A), and thereby the final rank is problematic if data are unavailable for some of the individual indicators. OECD [10] argues that data unavailability is a common weakness regarding all sustainability efforts at present, regardless of the scale of publicity. Sub-indices (B_1, B_2, and B_3) were used to aggregate the values of each contributing group (research, educational, environmental), respectively (Table 4). The final rank A was calculated (Table 5).

Table 4. Sub-indices and their ranks in a new ranking table

UNIVERSITY	B_1	Rank	B_2	Rank	B_3	Rank
Harvard Univ	0.2801	4	0.2898	**1**	0.062	7
Univ of California, Berkeley	0.1734	13	0.1261	15	0.057	8
Stanford Univ	0.3203	3	0.2764	2	0.041	14
Massachusetts Inst of Tech (MIT)	0.3932	2	0.1910	10	0.047	11
University of Cambridge	0.1609	15	0.1784	13	0.041	13
California Institute of Technology	0.4243	**1**	0.1885	11	0.018	18
Princeton University	0.1845	10	0.2452	4	0.041	12
Columbia University	0.1909	9	0.2108	5	0.035	15
University of Chicago	0.1640	14	0.1954	7	0.089	2
University of Oxford	0.2185	7	0.2062	6	0.082	3
Yale University	0.2211	6	0.2644	3	0.068	6
Cornell University	0.1753	12	0.1944	8	0.117	**1**
Univ of California, Los Angeles	0.1824	11	0.1621	14	0.074	5
Univ of Pennsylvania	0.1940	8	0.1942	9	0.048	10
Johns Hopkins University	0.2768	5	0.1839	12	0.078	4
University of Ljubljana	0.0139	16	0.1007	16	0.027	16
University of Maribor	0.0041	18	0.0823	17	0.049	9
University of Zagreb	0.0135	17	0.0790	18	0.022	17
University of Rijeka	0.0006	19	0.0298	19	0.006	19
University of Split	0.0001	20	0.0141	20	0.003	20

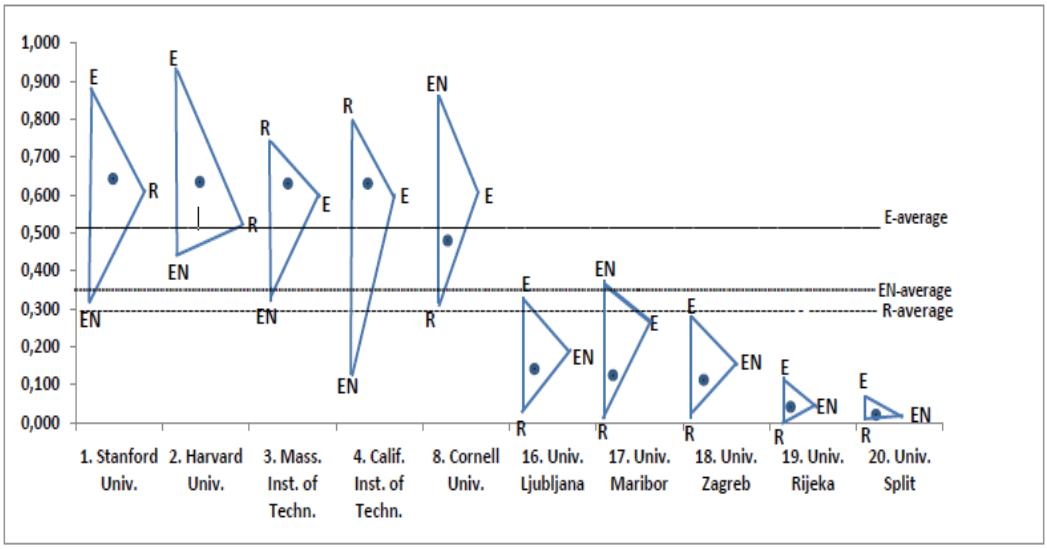
Some universities have been randomly chosen in order to present them on the graph, based on the "triangle method" [11]. The triangular diagram is produced when connecting the three dimensions of the universities together (Figure 3). Each angle shows research, educational, or environmental information about the university. Universities can be characterized by one of the three main groups with respect to their quality and characteristics:

- research universities, R, where the angle R is upwards;
- educational universities, where the angle E is the highest;
- environmentally-best universities, where the EN angle is dominating.

Table 5: A new ranking table of the selected universities.

RANK 2011 (2008)	*A*	UNIVERSITY
1 (2)	0.6376	Stanford
2 (1)	0.6317	Harvard
3 (3)	0.6308	Massachusetts Inst Technology
4 (7)	0.6304	California Inst Techn (Caltech)
5 (4)	0.5533	Yale Univ
6 (15)	0.5391	John Hopkins Univ
7 (17)	0.5065	Oxford Univ
8 (10)	0.4871	Cornell Univ
9 (6)	0.4712	Princeton University
10 (16)	0.4488	Chicago Univ
11 (13)	0.4365	Columbia Univ
12 (9)	0.4363	Univ Pennsylvania
13 (20)	0.4188	Univ California Los Angeles
14 (14)	0.3806	Cambridge Univ
15 (11)	0.3567	Univ California, Berkeley
16	0.1415	University of Ljubljana
17	0.1357	University of Maribor
18	0.1142	University of Zagreb
21*	0.0359	University of Rijeka
22*	0.0170	University of Split

*not all the data were available



Legend: • overall rank of a university R research performance E educational performance EN environmental performance

Figure 3. Triangular diagram: comprehensive comparison of randomly-selected universities

The overall comparison of the universities from excellent to very good and good is presented in Figure 3. The average for each of the three dimensions can be calculated, respectively. Thus, a deviation from the average practice can be observed. For example, Fig. 3 reveals that Stanford is an E-peak university, having also R above an average, but EN below it. Harvard is an E-peak university, even though its R and EN are above the 20-average. Fig. 3 also indicates that selected universities from Slovenia, and Croatia are E-peak universities, with research and environmental dimensions below the 20-average. However, the results show opportunities for universities, their room for improvement, and their place in comparison with other universities. In other words, it shows whether a specific university is in the forefront, or lagging behind, and what needs to be improved in order to achieve a better position.

3. CONCLUSIONS

The purpose of the raking presented here was to provide simplified information about the quality of universities in respect to the three various perspectives (research, educational, and environmental). This ranking enables quick realization of potential weaknesses or advantages regarding a particular university and its potential for improvement.

In our ranking table, the highest positions belong to American universities as in the ARWU and THES – they are listed at the first six places. This is not surprising, as the US allocates around 5,47 % of its GDP to research and development, and higher education, while Europe contributes only 3,12 % of its GDP for the purposes [12]. This is a consequence of the American Higher Education system. American universities mainly differ from the European ones with regard to the financial perspective. They are financed from both the public and private sectors, where financial means are also contributed by students, industries, and several foundations. Also, from the environmental sustainability perspective, American universities are in forefront and were the first to start approaches characterized by university management and constant curriculum changes [13].

A comparison with the ranking carried out in 2008 shows several changes, e.g. Caltech advanced from the 7th to the 4th position, John Hopkins University from the 15th to the 6th, Oxford from the 17th to the 7th, but also some regressions can be observed. Furthermore, changes have also occurred regarding the R, E, and EN orientations. In 2011 Harvard University and Stanford stayed E oriented, but R values are higher than EN, while in 2008 it was the opposite. In 2008 MIT was E oriented, but in 2011 it became R oriented with the E above EN, and also Cornell orientation has changed from E to EN.

The ranking in this paper was carried out in order to examine universities with regard to all the three important perspectives: research, educational, and environmental. The main aims were to better understand the development of universities and to provide an opportunity for determining “hot spots”, and their improvement options.

REFERENCES

[1] M. Jesenšek, Why the rankings are important? Katedra (Maribor) 1(4) (2006) 6–7. (in Slovene)

[2] G. Moodie, University rankings. Griffith University, 2005. Retrieved July 29, 2011 (http://www.griffith.edu.au/vc/staff/moodie/pdf/05atem3.pdf)

[3] M. Enserink, Who Ranks the University Rankers? Science 317 (2007) 1026–1028.

[4] S. Marginson, Global University Rankings: Implications in General and for Australia, J. Higher Educ. Pol. Manage. 29 (2) (2007) 131–142.

[5] E. Hazelkorn, The problem with university rankings. Science and Innovation Policy. (2009). Retrieved August 11, 2011 (http://www.scidev.net/en/science-and-innovation- policy/knowledge-economy/opinions/the-problem-with-university-rankings.html)

[6] J. Merisotis, J. Sadlak, International Partnership Issues Groundbreaking Principles on Ranking of Higher Education Institutions. UNESCO-CEPES, The Institute for Higher Education Policy, 2006.

[7] CHE Ranking. Retrieved April 22, 2006 (http://www.che-ranking.de/cms/?getObject=2&getLang=de)

[8] College Sustainability Report Card (2011). Retrieved August 10, 2010 (http://www.greenreportcard.org/)

[9] R. Lukman, D. Krajnc, P. Glavič, University ranking using research, educational and environmental indicators, Journal of Cleaner Production, 18(7) (2010) 619-628.

[10] OECD — Organization for Economic Co-operation and Development, 2002. An Update of the OECD Composite Leading Indicators. Short-term Economic Statistics Division, Statistics Directorate/OECD.
[11] L. Xiang-mei, T. Min Mand Chuan-Feng. The functional assessment of agricultural ecosystems in Hubei Province, China. Ecol. Model. 187 (2005) 352–360.
[12] Eurostat 2011, Education and training, http://epp.eurostat.ec.europa.eu, accessed August 30, 2011
[13] P. Glavič, Sustainability Engineering Education, Clean Technol. Environ. Policy 8 (2006) 24–30.
[14] Webometrics (2011). Retrieved July 25, 2011 (http://www.webometrics.info/)

INTEGRATED APPROACH OF KNOWLEDGE, ENVIRONMENT AND SOCIETY BASED PERFORMANCE EVALUATION

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Abstract

Continuous measurement and evaluation of corporate performance is necessary, it can be the key of success. In these days measuring and evaluating processes are promoted by different management tools and methods, which are known from the field of performance management. As the intellectual capital became the most important recourse of the information era, companies should change the system of traditional performance evaluation and find new methods. But the environmental and social capitals also have become important factors, so the performance evaluation of these capitals is also needed to be improved. Aim of this paper is to introduce the definition and evaluation of the key, success factors, which are the intellectual (knowledge), environmental and social capital. After the introduction common characteristics can be visual which are base for a common, integrated evaluation by the help of indicators. Main aim and goal of this paper is the scaling of the model of the integrated approach of knowledge, environment and society based (micro)economy in the field of performance evaluation. The paper also aimed to concentrate for environmental performance evaluation in connection with Hungarian tendering operations, because sustainable activities are requirements in the processes of EU's and Hungary's tenders (applications) too.

Keywords: *performance evaluation, intellectual capital, corporate social responsibility, environmental performance evaluation, integrated evaluation*

1. INTRODUCTION

Continuous development in the market and in business competition adds up to different changes in the life of business organizations. In this paper three of these mentionable changes will be introduced and examined. The first one is the change in the main resource of organizations in information era – so the intellectual capital has became the key resource of the organization –, the second one is the impact of sustainable development's concept – so the nature, the environment is also a value for the organizations, and have to be watchful with the status of nature –, and the last one – is in connection with sustainable development too – is the impact of the corporate social responsibility's concept – so the organizations have a responsibility on their stakeholders, which responsibility also makes a success for corporations. These changes have resulted the need of changes in the performance evaluation of these capitals, so the evaluation methods, concepts have to be improved. Improved methods and concepts are new, up-to-date solutions for organizations, so have to find the help for them, the incentives for the usage of these tools. However the help is starting at the definition and the recognition of these capitals, because most of the organizations cannot recognize these different changes, and the importance of these changes.

2. ELABORATION

2.1. The Factors of Success and the Existing Evaluating Methods – Theory

First of all it is necessary to introduce the three changes in life of business organizations and the meaning of these changes, and then the connecting activities – the evaluation – also will be introduced.

2.1.1. Intellectual Capital

In the industrial era, in the competition the technology and the mass production were important. But from the second part of the XX century there is a new competition, the competition of information era. The new age means the management of the intellectual, immaterial capital, because these are the main resources of the age [1]. Defining the concept of intellectual capital is not an easy work. Lev [2] uses the next expressions like synonyms: intangibles, knowledge assets and intellectual capital; and defines them like a demand which is in connection with profit in the future and which has not get monetary body and

physical appearance too [2, 3]. Edvinsson [4] defines the intellectual capital like the occupancy of the next abilities: knowledge, experience of employees, technology, consumer relationship and professional abilities. These facts give competitive edge in the market for the corporation [3,4]. About Stewart it is a totality of useful knowledge, which contains the organizational processes, technologies, abilities of employees, information about consumers, suppliers and stakeholders. Brooking says it is a totality of immaterial capital, which makes the organization workable and valuable. The most suit definition for the authors comes from Tóth, who writes that the immaterial capital is an asset, which is not-subjected. One part of this capital can be visual in the balance sheet, between the intangible stocks, but the other part completes these intangible assets. This part cannot be visual in the balance sheet, thanks for the special, different property [3].

As the main resources changed, the evaluation also should be changed, because these new values can't be measurable by the traditional financial methods. The financial model which is only for the industrial value measures the past events, and doesn't measure the ability of the investment to future value-maker resources [1].

According to professors of Cranfield School of Management the traditional financial system cannot show to the managers and investors that how the intellectual capital can produce value in the future. So, this is why should be special interest of intellectual capital's evaluation, and the information about the future opportunities will be the result from this evaluation [5].

According to Gyökér and Finna there are two ways for correct evaluation of these new, up-to-date methods: the first one is the improvement of the traditional bookkeeping and financial system, and the second one tries to find this invisible value by examining the quality factors of it [6]. Sveiby prepares four categories of the methods: direct methods, methods based on market value, methods of return on assets and the scorecards [7]. Most known methods of the evaluation are the scorecard methods, which measure the performance from different aspect. Indicators are defined in scorecards, but it is hard to find the best indicators, because these should be measureable, enough, easy to define, cost-effective and be able to measure the performance time to time.

2.1.2. Environmental Capital

According to Kapusy [8], the organization, the company is able to work on long run with success if ambient society and environment (like resources) also be on long run, so it means that the resources and the market (consumers) also have to be viable. Therefore the responsibility for the future generations is a part of the responsibility of owners. Concept of sustainable development –which meets the needs of the present without compromising the ability of future generations to meet their own needs – and the pillars – environmental, social and economic – confirm the importance of the environmental and social points in the competitiveness.

As the organizations are part of a bigger system – which is the natural and societal systems – there should be a strong relationship between these systems. This relationship influences the success of the organization. Natural environment is one of these bigger systems, so the organization can't emerge the environmental aspects of its' activities. The authors use the claim has proved by literature reviews and own, earlier works, that the environmental, natural capital are also key, success factors of organizations, like the intellectual capital.

If there is a key, success capital, organizations should evaluate the use of this capital. According to a research, which was made in 2009 and 2010, most of the asked companies use the tools of sustainability management because of the need from society and demand of the market. The most used sustainability methods are the quality and environmental management systems, employee suggestion systems, environmental audits, and risk analysis. Even so it is real important to mention that according to the research less than half of the companies measure the effects of environmental or social activities on corporate success [9], although there are many methods and tools for environmental performance evaluation.

The environmental performance evaluation (EPE) is an essential tool for decision makers to support the decisions in issue of environment. It is necessary to use the EPE, because as was it mentioned and confirmed the environment is a critical, success factor for organizations. The EPE is the measurable result of the management in point of environmental aspects. It is an internal, continuous management process and tool, which uses environmental indicators to make a comparison between the present and past environmental performance (EP) and the criterions of the environmental performance [10].

There are many tools and methods for EPE, but the main point is the use of indicators. These are the first, real methods of the evaluation. Organizations have to define enough and measurable indicators,

which should reflect the operation and the volume of the corporation, and complexion and intensity of the possible environmental impacts [10]. The EPE also helps the recognition, implementation and check of the opportunities which have strategic importance.

2.1.3. Social Capital

As it was before mentioned according to Kapusy not just the environment can influence the long run success of the organization than the society also has an influence, namely that what kind of relationship is between the corporation and society, so what kind of corporate social responsibility (CSR) the organization has, or rather what kind of relationship is with the stakeholders. There is a new interpretation of the CSR where the stakeholder point of view should be focused (company stakeholder responsibility) instead of the social point of view (corporate social responsibility). In this concept the claims and interests of stakeholders should be in the centre of the strategy and of the processes of the company. This concept has come from Freeman et al. [11]. There is a question, that why organizations should deal with the society and stakeholders, why they should thinking about CSR like a success factor. The answer is the evidence from different researches, which was made by the authors, so Hungarian and international literature was examined. According to experts there is a strong relation between the corporate social responsibility (CSR) and the financial performance of the corporation, in addition CSR also can help to achieve the competitiveness for a long run. There is a symbiotic where the corporation and social organizations help each other reciprocally to achieve their aims, goals [11-13].

However there is a question that how the results of CSR activities appear in the measuring and evaluating processes, tools and methods, so how the CSR activity can be measured and evaluated. Reviewing the Hungarian and international literature – like a secondary research – authors have found existing methods and tools for evaluation of CSR. Existing CSR evaluating methods are the CSR Self-Assessment Handbook and the ISO 26000 Standard.

CSR Self-assessment Handbook (improved by the UNDP) gives practical help for organizations, because according to the EU, the promotion of CSR reflects the need to defend common values and increase the sense of solidarity and cohesion in Europe [14]. For evaluation and measurement the handbook uses 25 questions in the questionnaire. The questions are grouped under five overall categories: Governance, Environment, Labour, Community Relations, and Business Environment. This method uses questions for preparing indicators, which questions should be scored, and at final it can be evaluated that how many points has for CSR performance from the total 100 points.

In 2005 was formed the work-group, to work out the international standard, which introduces the main guidelines of social responsibility and which is usable for non-experts too. 2010 was the publishing date of the standard, which is the ISO 26000:2010(E) Guidance on social responsibility. It is providing guidance does not contain requirements but may contain recommendations and it is not a management system standard, so it can't be certified. It defines the principles of social responsibility, the two fundamental practices of social responsibility, the core subjects, the way of integration throughout on organization and examples of voluntary initiatives and tools [15]. About the performance of CSR and about the evaluation there is some information in the standard, in the Clause 7, which is the Guidance on integrating social responsibility throughout an organization. The Chapter 7.7 examines the activities which reviewing and improving an organization's actions and practices related to social responsibility. This chapter introduces the necessity of the reviewing and monitoring activities: "it is important to monitor ongoing performance on the activities related to core subjects and relevant issues" [15]. There is also information about the usable tools, because the standard says that there are "many different methods for monitoring performance on social responsibility: reviews at appropriate intervals; benchmarking; obtaining feedback from stakeholders; comparing; indicators" [15]. The standard offers the use of indicators, because with these the measurement and evaluation is easy. However there is a comment that indicators "relatively straightforward to use, they may not be sufficient for all aspects of social responsibility" because we can't measure it in simple way. "As social responsibility is based on values, application of principles of social responsibility and attitudes, monitoring can involve more subjective approaches such as interviewing, observing and other techniques for evaluating behavior and commitments" [15]. After the measurement and evaluation there is a part in connection with the improvement of the evaluation, because "should consider ways in which it could improve its performance on social responsibility" [15].

2.2. Environmental Performance Evaluation in Hungarian Practice – Practice

According to the ruling of European Commission and Hungarian Government every project has to be achieved so that these can help the sustainable development, the protection of the environment and the improvement of status of the environment. Aim of the "Handbook for Validation of Sustainable Development in case of applications in Project called Új Széchenyi Terv" is to introduce the meaning and aspects of sustainable development for the applicant and to help validating the sustainable aspect during the implementation of the project. The applicant has to choose between different sustainable aspects and has to implement and prove the implementation of that. There are examinations of 60 aspects, which like indicators are in the handbook. Most of these indicators are in connection with environmental aspects of the organization, but there are aspects of social point of view. It is important to mention that with these mentioned indicators in the handbook, organizations can evaluate and follow the environmental performance (for example indicator of used energy resources; of waste management methods; of environmental education programs), but there is an exact indicator in connection with EPE: Indicator No. 3/d is in connection with the implementation of the regular environmental performance evaluation method. All of the indicators are well defined, understandable and there are defined units which also help in the usage of these indicators [16].

One of the offered tools in the handbook is the preparation of Sustainability Plans, Indicator No. 2, which means the environmental and social planning of the organization, definition of objectives, programs and indicators which can measure the performance of these programs. Authors have an experience preparing of these Plans, as in 2010 there were three Plans prepared by authors for three different Hungarian public administrative institutions. These Plans are also able to measure and evaluate the environmental and sometimes the social performance of organizations. During the preparation of these documents expert has to start with an environmental audit to get to know the environmental status and main characteristics of organizations in connection with environmental and social point of view. Then together with the representatives of the organization experts offer objectives for the organizations which are in connection with the environmental and social faults and main impacts. After the common discussion a set of achievable objectives will be defined and expert offer indicators, which measure the present environmental and social status of the organization and can measure the achievement of these objectives, so the performance. These prepared Plans will be implemented documents in the organization, which means that all of the employees have to know it and adopt it.

We can summarize that the handbook (and tools in the handbook) is a good initiative for use of performance evaluation in case of social and environmental capital and also good guideline for organization into the introduction of performance evaluation.

2.3. Common characteristics and Integrated Evaluation – Result and Discussion

Like results authors used the experiences from literature review and experiences from the practice to examine the main characteristics of the factors of the success and of the evaluations and make a model, which is based on these main, common characteristics of these capitals.

2.3.1. Common Characteristics of Capitals

The importance of intellectual, environmental and social capitals in these days is a fact. Just to prove this fact there is a short summary about the characteristics of capitals, resources which make the organizations successful. According to Gyökér [17] resources make competiveness for corporations if these are valuable, rare, can't be copied and can't be replaced. Examining the three important capitals, like success factors, we can find the next facts:

All of the examined capitals are valuable, because:

- The intellectual capital – knowledge, the relationship, the organizational culture and structure – ensures the utilization of opportunities.
- There are many advantages for organization which are come from the protection of the environmental capital. So the liveable environment is valuable.
- The livable society is valuable. They are not only consumers and stakeholders; they can be partners in actions.

All of the examined capitals are rare, because:

- The human knowledge, relationships are properties of person.
- The environmental capital is limited (finite). There are no limitless natural resources and there is no limitless receiver, occlusive capacities.

- The livable society is unique in space.

All of the examined capitals can't be copied, because:

- However intellectual capital is compliable with learning, improvement, but it never will be the same.
- The environmental behavior, actions (e.g.: use of standards) are organization-specific.
- The society is given, they are unique and specific.

All of the examined capitals can't be replaced, because:

- The knowledge, the relationship, the information can't be fungible with physical or monetary resources.
- It is an interesting question, because the mainstream is the replacement with alternative resources. But it can't be fungible with monetary resources.
- It can't be fungible with physical or monetary resources.

2.3.2. Common Characteristics of Evaluation

Collecting and introducing the main characteristics of the three success factors and the performance evaluation of the success factors, capitals (intellectual, environmental and social capital) in these days it is able to find common specifics, which are common problems, failures and common solutions in case of these capitals. Making general claims is hard in case of specific things but it is possible in this case without weakening these specialties. In the next three points we can summarize these common, general characteristics of these special capitals in micro level:

- The problem with the traditional evaluation is common in all cases, because the general system of accounting cannot visualize the value of these capitals – in the methods, tools and results of general accounting knowledge, environmental and social value of the corporation are hidden, these methods cannot show the real value of the organization.
- The use of indicators in case of evaluation are also common characteristics, mostly all of the performance evaluating methods are based on indicators – most of the new, up-to-date methods of evaluation of performance (it was mentioned in case of intellectual capital) based on scorecards, so based on indicators.

In all cases there is a need for evaluation because these are the key, success factors of today's organizations; organizations should evaluate these capitals, because these can make competitiveness in a long run for the organization – and research show that these capitals generally are not evaluated, are not measured on corporate success.

2.3.3. Integrated Evaluation

The common characteristics make the authors defining models and opportunities for common, integrated evaluation of these capitals. It is important that in the theoretical way we explain the steps/characteristics of the common evaluation and in this article only the brief summary of the integrated evaluation is shown.

The next model (Fig. 1.) shows the system of the integrating evaluation which was made by the authors and was leaned on the different national and international literature reviewing and primer modeling. For the integrated evaluation it is necessary to collect all of the relevant, suitable indicators which are created by the different methods. It is not enough to use for evaluation only the indicators of traditional performance evaluation, accounting, it is necessary to collect the measuring and evaluating indicators of new success factors, so the indicators of intellectual capital, environmental and social capital too. It is necessary to evaluate these together, in the same time, because the organization has to account with the value of these capitals too in the age of knowledge, environment and society based economy. At the bottom of the figure there are 'smaller' integrations, which are examples between the integrated evaluations of new success factors, which are sometimes yet existing methods. One of these is the GRI – Global Reporting Initiatives – which offers different indicators for measuring and evaluating the sustainability of the organization. It contains economic, social and environmental indicators too, so there is a suggestion in the system for the usage of Performance Indicators, which give comparable information on the economic, environmental, and social performance of the organization. The second one is the BSC – Balanced Scorecard – which is the most known method for evaluate intellectual capital. This method is also based on indicators which are defined in different aspects. The Balanced Scorecard brakes down the strategy into exact objectives and indicators, and manage them, evaluating the performance according to four different perspectives: traditional financial perspective, perspectives of customers, internal business processes, learning and growth [1]. BSC is a complex performance

evaluating system, so it is able to join the different fields of corporate performance, in this way the BSC it is good to measure the environmental activities and activities in connection with social or stakeholder responsibility too. For example Harangozó suggests the implementation of environmental, social aspect to the scorecard system, and call it Sustainability Balanced Scorecard (SBSC) [18].

As the use of indicators was a common characteristic, a suitable set of indicators can help for organizations in evaluating and monitoring, reviewing in an integrated level. There are many tools to help for organizations in evaluation. These tools are available for different type of organizations – as was it mentioned before for example in case of ISO 26000 – and many of these are existing methods, so the integration of these methods is also usable for different types of organizations in practice.

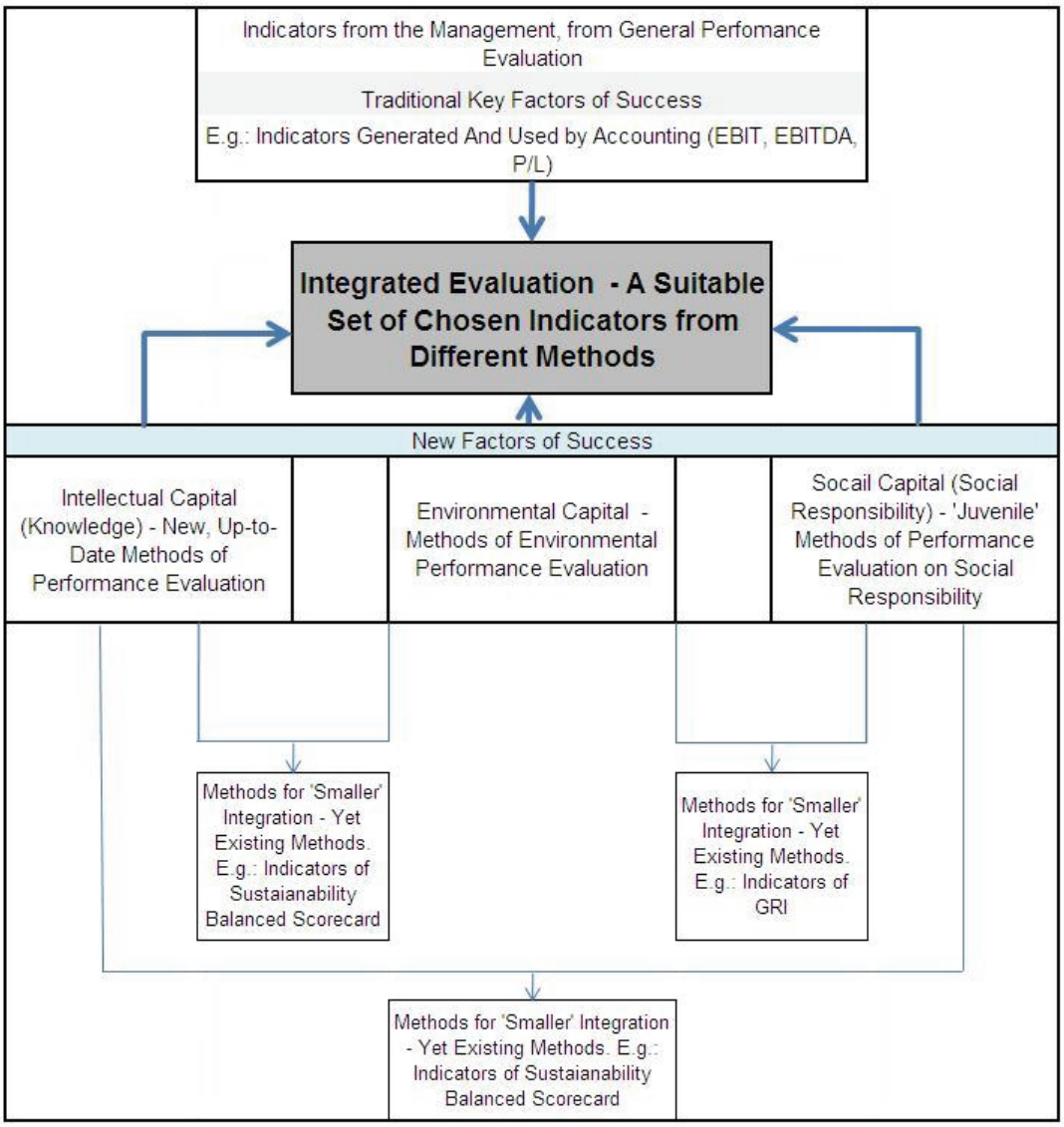


Figure 1. Model/Logic of Integrated Performance Evaluation

3. CONCLUSIONS

Today's organization has to realize the new factors of the success, which are the intellectual, environmental and social capitals. These capitals reach all of the characteristics which define the success factors of the organization. After this realization organizations has to realize the importance of evaluation of these capitals and has to implement the methods of performance evaluation. Many of the examined researches – like literature review – show that organizations have yet realized the importance of the mentioned capitals, but don't use any of the evaluating methods. Integrated evaluation can be a solution for these organizations, because with the integration all of the present success factors are evaluated, examined, measured and reviewed.

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REFERENCES

[1] R.S. Kaplan, D.P. Norton, Balanced Scorecard, KJK, Budapest, 2000.
[2] B. Lev, Improvement of competitiveness thanks to intellectual goods, in Hungarian language: Az immateriális javakban rejlő versenyelőny fokozása, Harvard Business Manager; Hungarian edition, December (2004) old
[3] Zs.E. Tóth, Examination of measuring opportunities of intellectual capital based on models of self-evaluation, in Hungarian language: Az intellektuális tőke mérési lehetőségeinek vizsgálata önértékelési modellek alapján, PhD-work, BME Central Library, 2008.
[4] L. Edvinsson, Developing intellectual capital at Skandia, Long Range Planning, 30 (3) (1997) 366-373.
[5] J. Mouritsen, P.N. Bukh, B. Marr, Reporting on intellectual capital: why, what and how? 2004. (www.som.cranfield.ac.uk)
[6] I. Gyökér, H. Finna, Performance management, in Hungarian language: Teljesítménymenedzsment, Educational material, 2007. (www.mvt.bme.hu)
[7] K.E. Sveiby, Methods for Measuring Intangible Assets. 2001, 2007. (www.sveiby.com)
[8] P. Kapusy, Relationship between sustainable development and corporations, in Hungarian language: A fenntartható fejlődés és a vállalatok kapcsolata, Minőség és Megbízhatóság, 1 (2007) 23-24.
[9] S.E. Windolph, D. Harms, 'Corporate Sustainability Barometer' – How do Companies in Germany Implement Sustainability Management?, Newsletter, Centre for Sustainability Management, 01/2010, (2010) 4-5.
[10] K. Kósi, L. Valkó, Environmental Management, in Hungarian language: Környezetmenedzsment, Typotex, Budapest, 2006.
[11] J. Szlávik, H. Csáfor, M. Csete, N. Csigéné Nagypál, M. Füle, T. Pálvölgyi, Corporate Social Responsibility, in Hungarian language: A vállalatok társadalmi felelősségvállalása. CompLex Kiadó Jogi és Üzleti Tartalomszolgáltató Kft., Budapest, 2009.
[12] E.M. Porter, M.R. Kramer, The Competitive Advantage of Corporate Philantrophy. Harward Business Review, 12 (2002) 56-58.
[13] A. Chikán, Corporate competitiveness and social responsibility, in Hungarian language: Vállalati versenyképesség és társadalmi felelősség, Harvard Business Review Hungarian edition, 11 (2008) 6-13.
[15] ISO 26000:2010(E) Guidance on social responsibility, The Standard is Available on the Budapest University of Technology and Economics, Department of Environmental Economics.
[14] UNDP, CSR Self-assessment Handbook for companies, United NAtions Development Programme, (http://www.undp.lt/uploads/201008/handbook_1draft_final.pdf)
[16] NFÜ – Hungarian Development Agency, Handbook for Validation of Sustainable Development in case of applications in Project called Új Széchenyi Terv, in Hungarian language: Útmutató a fenntartható fejlődés érvényesítéséhez az Új Széchényi Terv keretében kiírt pályázatokhoz, (www.nfu.hu/download/.../21_melleklet_fenntarthato_fejlodes_utmutato.pdf)
[17] I. Gyökér, The immaterial capital of the corporation – uncounted value, in Hungarian language: A vállalat szellemi tőkéje – számolatlan vagyon, Harvard Business Manager; Hungarian edition, December (2004)
[18] G. Harangozó, Methods of the environmental performance evaluation, In Hungarian language: A környezeti teljesítményértékelés módszerei, Vezetéstudomány, 39/2 (2008) 46

TRAINING METHODS FOR PURCHASING OFFICERS TO FACILITATE GREEN PROCUREMENT IN HUNGARY

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Abstract

This paper is addressing symposium topic "Education for Sustainable Development" and is focusing on the methods of training procurement officers to facilitate the use of green procurement.

Green procurement is a tool that is to be used to reach sustainable consumption patterns, further innovation and give a market to eco-technologies. Green procurement means that procurers take environmental issues into account when buying goods or services.

No matter if we speak of a private company or a public institution the success of implementing green procurement usually has the same factors. The main barriers -mentioned in the topic related literature - and based on our experiences with local authorities and companies applying green procurement are the followings: lack of knowledge and know-how, perception of financial burden, lack of management/political support and engagement.

From these barriers the training and awareness raising will be highlighted because while developing a green procurement toolkit specially designed for Hungary many question have arisen in connection with engaging adults for sustainable consumption. This paper's aim is to answer these questions and further develop the solutions to be a part of the Hungarian green procurement toolkit.

Keywords: *green procurement, adult education, green procurement toolkit, Hungary*

1. INTRODUCTION

The European Union spends the 17% of it's GDP on public procurement [5]. This financial power should definitely support environmental goals. For this reason the European Commission is committed to the implementation of green public procurement (GPP) in each Member State.

GPP means that contracting authorities and entities take environmental considerations into account when tendering for products and services.

The aim of GPP is to reduce the impact of procurement on the environment (CO2 emissions, toxic material, amount of waste etc) and human health. The possible benefits of GPP are wide spreading. First of all- with the implementation of GPP -public authorities can set example for the competing sector and the households. It is also true that if public authorities take environmental issues seriously in their everyday practice it is easier for them to expect an environmental friendlier act from the public sector too. GPP can also be a tool for raising environmental awareness. Its economic benefits are also considerable. By requiring more and more environmental related criteria in the call for tenders, contracting authorities can influence the market by raising the demand for environmental friendly goods and services. That can increase the competition and reduce the prices in the field of environmental technologies. This aspect is commonly said to be the most important advantage, although influencing the market of "green" goods is rather a long term perspective. Another long term benefit of GPP is that it drives innovation.

The efficient use of GPP can lead to major changes at the contracting authorities too. Administrations can use the occasion of implementing GPP for making internal procedures more efficient by reconsidering the general process of procurement. And the most important and commonly doubted benefit of green public procurement is that it often leads to savings. The competitiveness of green products is based on quality and innovation. For this reason the products and services that are meeting the criteria for greening are the ones that use the most recently released technologies which can have advantages like energy saving. These products' whole life cycle costs are proved to be less than the average products'. In addition to these hereby sketched advantages a political aspect can also be added: a

visible focus on greening the procurement will likely result a positive judgment of the government in charge.

Private procurers, like companies or citizens are not restricted by strict administrative requirements and of course the limitations for spending the taxpayers' money are not valid for them. So of course the regulations described in the next chapter don't affect them, but the criteria setting section and the other technical specifications are very useful. Nowadays it is becoming more and more important for companies in the competing sector to stand out from the crowd of others. So in connection with CSR or simply environmental awareness it is worth taking actions for environmental protection. The products and services that meet the "green" criteria are usually top quality and represent the latest technical trends. This means that there is a major saving potential in their use. Together the positive public judgment and the financial savings can result better position in the market, a competitive edge. Green procurement is an obvious tool, because it is one the most active and most demonstrative ways of environmental protection.

The concept of green procurement can be used in a wide range of product groups, but it should be admitted that some groups are more suitable for "greening" than the others. For example research, advertising and auditing services rarely contain environmental aspects, but for furniture and IT there is a great possibility to set requirements.

In the Take-5 Study [2], which was finished for the European Commission in May 2006 they reported on the current state of GPP in Europe. They highlighted seven Member States that use GPP very effectively. They are called the "green-7" (Austria, Denmark, Finland, Germany, Netherlands, Sweden and the UK) Based on this study a list of product groups was collected.

Table 1. Product groups that are the most suitable for "greening"

Product groups that are the most suitable for "greening"	
• Cleaning products and services	• Construction works
• Horticultural services	• Construction products (including heating/cooling /lighting appliances)
• Medical devices – pharmaceuticals	• Furniture and other manufactured goods
• (Electrical) machinery - communication equipment	• Paper, printed matter, printing services
• Energy	• Transport and communication services
• Sewage- and refuse-disposal services	• Chemical products, rubber, plastic
• Sanitation and environmental services	• Food products and beverages, Restaurant services
• Transport equipment	• Architectural, construction, installation and related consultancy services
• Office machinery (computers/monitors/ printers/ copiers)	

Source: Green Public Procurement in Europe, Bouwer M et al 2006 [2]

2. ELABORATION

2.1. Green Procurement Toolkit

2.1.1 The Means of Development

In Table 2. we would like to show the main barriers -mentioned in the topic related literature -and based on our experiences with local authorities and companies applying green procurement in Germany and would like to present our methods to provide solutions for these problems.

Table 2. Barriers of green procurement and recommended solutions

Barrier	Recommended Solution (toolkit)	Flexibility
Lack of technical knowledge	Performance criteria collection	fixed
Perception of financial burden	Calculation tool	
Lack of management/political support/engagement	Awareness, training, motivation, handbook	flexible
Market barriers	Policy, communication	

Source: own compilation

The green procurement toolkit is specially designed for Hungary, and it is suitable for the use of public authorities and private companies as well. The toolkit is meant to be easy-to-use and understand so that green procurement would not result a lot of extra paperwork and new tasks for the officers. The new practice needs careful implementation and user friendliness because the procurement officers' commitment is crucial to the success of green procurement systems.
The toolkit has fixed and flexible parts. Flexibility is one of the success factors, since integrating the green criteria into the procurement of different organizations (in size and type as well) calls for the personalization. The fixed parts are the performance sheets and the calculation tool. The flexible parts are in connection with the actual implementation, the green procurement policy and handbook of the organization and above all the training methods. In the next parts a brief description of the fixed parts (2.1.2.) and a more detailed analysis of the flexible parts (2.2.) will be presented.

2.1.2. Fixed Parts of the Toolkit

2.1.2.1. Performance Sheets

Setting the environmental criteria sometimes causes major difficulties to the procurement officers, especially because usually they are jurists or at least they are not experts in the fields of technology and sciences. This problem can be solved with the strong cooperation of environmental experts and procurers, so we are developing a so called performance criteria collection which contains the technical specification of environmental friendly product alternatives for the following product groups:

Energy consuming products

- IT, household, vehicles…

Material consuming products

- Paper, textiles, detergents…

Services

- Cleaning, gardening, construction.

The product groups were chosen based on the most suitable products for "greening" and on the suspected needs of a public authority or a company. The criteria is based on ISO type I eco labels and the EcoDesign Directives of the EU. Standards are useful in public procurement specifications as they are clear, non-discriminatory and developed on a consensus basis. For certain products and services several national eco-labeling criteria and the EU Flower criteria were applied. These labels take into account the main environmental impact of products and services, are compatible with market principles, and allow products to be easily identified. The eco-label criteria are established on the basis of scientific information and through wide stakeholder consultation and be accessible to all interested parties.

The performance criteria for each product consist of four categories. These are: energy consumption, lifetime, noise emission and other environmental criteria. The performance criteria collection has two basic versions. One of them is the simplified procedure and the other is the comprehensive procedure. The simplified procedure contains basic minimum criteria (inserted in the technical specification of the call for tenders), according to the EU EcoDesign Directives. These criteria must be fulfilled by the product or it gets excluded from the procurement process. The comprehensive procedure means that there are more criteria based on Eco-label criteria. These are more difficult to fulfill, and at this point the innovation driver function of green procurement starts working. The criteria are target criteria and points can be awarded for the better performance (maximum for meeting all the requirements) It is up to the procurers to decide which category has greater importance for them, so they can set the maximum points of the award criteria of energy consumption, lifetime, noise emission and other environmental criteria. These four maximum points should add up to 100, because this value is used in the evaluation process (to be described by the calculation tool).

2.1.2.2. Calculation Tool

To calculate the costs and to evaluate the tenders we developed a calculation tool that compares the different products. The comparison is based on energy cost, maintenance costs, the cost of purchasing, and the scores (points) reached by the environmental target criteria. The results give a clear overview of all the costs of the product for the next years of use. This is important since higher initial investments and tight budgets are often the first problem by buying green, although it is proved that GPP does not cause major cost increase for the public authorities. This is proved by several studies, but the most recent ones are conducted by McKinsey for Germany and PricewaterhouseCoopers for the "green7" countries. Both of them highlight that despite of the possibly higher procurement costs the products and services cost less for the public authorities in their life cycle.

By the evaluation process the relevant technical data of the product (e.g. annual energy consumption, size, useful lifetime), the purchasing price (including the additional costs, e.g. transfer), the annual maintenance costs, and the annual energy costs should be added into the calculation tool. The result will give a life cycle cost for the useful lifetime of the product. This case we do not define the life cycle of the product according to the classical "cradle to cradle" definition due to practical reasons. At this point of our workflow, the calculation tools are ready for the energy consuming products. In case of these products the difference between the purchasing costs and the energy costs should be highlighted, to promote energy saving products. For this reason and because it is quite expensive to carry out a LCA for all product groups in this exceptional case we consider the simplification of the life cycle definition acceptable. This point of the calculation needs further development in the future.

In case of simplified procedure the ranking of the products is based on the life-cycle costs. The best economic offer is the product that's life cycle cost is the lowest.

In case of comprehensive procedure additional data should be added to the before described calculation tool. These are the points achieved by the target criteria and the weighting share of the life cycle costs and environmental criteria. European legislation recommends that the maximum weighting share of environmental criteria should be 45%, so that still the cost effectiveness is dominant in case of spending public money, public procurement. If the calculation tool is used by a private company there is a possibility to give different shares too, depending on the preferences in their purchasing policy.

The combination of the scores for LCC and environmental criteria results in a "best economic offer" row of the calculation tool.

To sum up the possibly higher purchasing costs are compensated by the lower operating costs, but still some benefits of sustainable procurement cannot be expressed in monetary terms.

Despite of the above mentioned financial savings political commitment is necessary to defend long-term and non-financial benefits.

2.2. Awareness, Training, Motivation, Handbook

Senior public sector officials often have low awareness of the importance of GPP and sustainability issues. Without a strong strategic focus and an organizational policy that promotes GPP (with time and money) the integration level of environmental aspects will remain low. Not even a high level of commitment to national targets is always a guarantee of success. Often there is a low level of understanding of the concept, which creates an *'implementation gap'*, the conflict between policy and practice. Even a high level commitment via policies and targets can become weaker if it reaches the purchasing officials. At this stage, sustainability issues are often lost and "best value" is easily translated into "cheapest is the best". The "best value" approach is not an alternative to an environmentally sustainable procurement, but one element of comprehensive procedure.

How could this resistance to change on political and executive level be tackled? How much training is needed to raise awareness? Could this be done within the organization or should help form outside be provided? The success of the green procurement toolkit depends on personal commitment and the know-how of the procurement officers. For this reason we put special emphasis on the training methods for the officers when designing the kick off training for them, which would provide an opportunity to transform the use of the toolkit into a competence of the procurers and develop it into an everyday routine. We took into consideration the fact that adult education is a complex, unique and yet very important field of education. By planning the most important question were:

Who is the training for? Pre-analysis of the target group is essential, in terms of previous education, current duties, and personal interests. This information can be gathered in form of questionnaires or consultation with the officers' superiors to get the participant's perspectives about what topics to cover and in order to provide projects that reflect their personal interests. We think that this is an important part since adults as learners are very goal and relevancy oriented. They need the practical knowledge that they can combine with their life experiences and knowledge and that is applicable to their work or other responsibilities to be of value to them.

Why? (goals) The goals of the training and the benefits for the participants should be made clear at the beginning. Usually adult learners have several motivation factors, but in this case two of them are the most important. One of them is the social welfare factor, which- according to Lieb helps to improve ability to serve mankind, prepare service to the community and improve ability to participate in community work [7]. This can be connected to the environmental aspects, the topic of sustainable development and taking responsibility for the next generations' welfare. On the other hand there is the

other factor which is more materialistic: external expectations. In this case learning is done to comply with instructions from someone else, to fulfill the expectations or recommendations of someone with formal authority [7]. Speaking of green procurement training the need for learning new skills, and the need to learn in order to comply with the organization's directives will probably be stronger.

What to teach? Because of the above mentioned facts, the quality and quantity of the lessons should be carefully chosen. The emphasis should be laid on the special procurement needs of the organization, tailor made to the duties of the participants. Although the general green procurement basics and the information on the toolkit should not be exchanged to any other topic of the participants' interest.

How? The teaching method should be chosen according to the target group and the quality and quantity of the teaching material. The analysis of techniques used in adult education generally divides the strategies in three broad categories: teacher oriented techniques, interactive techniques and independent techniques. We decided to use all three types of techniques in the different stages of the training. The training consists of an introduction part that contains the theory, history and the basics of green procurement. At this stage we would use the teacher oriented techniques: lectures and questioning. Lectures are useful when the subject-matter of study requires specific information, the learning community is large and the place of learning allows it. It is the case in the introduction part of green procurement. This part should be planned in terms of length and placement and should have a structured outline, including an introduction, a body and a conclusion. Questioning techniques are a powerful way of increasing student participation. For this reason this technique is used at the end of the first introduction part of green procurement training. The trainer plans the questions according to a higher or lower level of response. They could ask for summarizing, understanding, encouraging critical thinking, enhancing problem-solving ability or stimulating creativity. Following the theoretical first part the participants will be asked to fill in a test to check what the group has learnt. The second part of the training consists of the introduction to the performance sheets, calculators and general use of the toolkit with case studies. This part definitely calls for the participants' involvement, so the interactive techniques would be used. Case studies are extensively used in medicine and legal professions, and they refer to real life problems narrated with a story telling quality and challenges participants to find recommendations and solutions to the problems. They are mainly used in teaching knowledge, values and attitudes [7]. After several case studies the participants get to work in groups on simulated procurement cases. The sessions end with "homework", a case provided online to the participants that should be solved individually. The feedbacks on the course form both sides, from the participant and from the trainer as well should be individually addressed using online communication, but keeping the possibility of personal consultation as well.

As a final occasion of the training the participants and their trainer develop a tailor made green procurement handbook for the organization. With this cooperation the participants can develop something new, use what they learnt and make sure that their knowledge will be used in their everyday routines.

Some help from outside the organization- for example: seminars, experience exchange, result publication can help keeping the concept going as well.

Sometimes personal barriers can cause problems in the implementation phase: the lack of employees' awareness of environmental problems, and protesting against new solutions can make the newly trained procurement officers' work difficult. To avoid the above mentioned problem training material are to be developed that help raising awareness, and reaching engagement of all colleagues within the organization. A general awareness raising, educational session for all stuff of the organization in form of a basic, obligatory e-learning solution can be a useful information source followed by the possibility of individual learning.

2.3. Follow up and Communication

For measuring the success and the level of use of the green procurement toolkit a follow up of the works done by the procurers should be done after a half year period. This follow up should consist of an information-collecting and consultation session. Yearly audits are also recommended, to keep the concept going and help further development.

As the final point of green procurement is communication. On one hand green procurement relies on innovative standards, so it can be difficult to find suppliers able to provide the necessary products or services. Market research and the widespread communication of the intentions and about implementation of green procurement is indispensable. As a result of communication in advance suppliers can prepare

such products that meet the criteria. This can be done by an initial green purchasing policy in which the organization describes the chosen product groups, to be used standards and the level of requirements towards the suppliers, the public, and their own staff as well. On the other hand communication is crucial to reach all benefits of green procurement: to set example, to influence the market by raising the demand for environmental friendly goods and services, to increase the competition and reduce the prices in the field of environmental technologies.

3. CONCLUSIONS

The article's aim was to highlight the main barriers of green procurement and show a method, a toolkit, which would provide a solution for these problems. The fixed parts of the toolkit were presented (the performance sheets and the calculation tool) along with the flexible parts like procurement policy, handbook and first of all the training methods. Learning how to buy green and energy efficient products and learning how to decide whether a product environmental friendly is or not, creates more awareness among people and helps giving the expression "sustainable consumption" a meaning.

All in all the following factors are necessary to bridge the implementation- gap in the case of green procurement: (1) assuring commitment of the participants-highlighting their personal interests, (2) common participation, efforts, know-how –trainings (3) feedback-visibility of achievements.

In addition to these it is essential for organizations to realize that there is a direct correlation between performance and socially and environmentally responsible consumption patterns.

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REFERENCES

[1] A. Benedek, Tanulás a harmadik évezredben, A "digitális" pedagógia szerepe; HEFOP 3.5.1.„Korszerű felnőttkepzesi modszerek kidolgozasa es alkalmazasa", Tanar-tovabbkepzesi konferenciak 2007. Budapest–Siofok–Hajduszoboszlo, Nemzeti Szakkepzesi es Felnőttkepzesi Intezet, (www.nive.hu)

[2] M. Bouwer, M. Jonk, T. Berman, R. Bersani, H. Lusser, V. Nappa, A. Nissinen, K. Parikka, P. Szuppinger, C. Viganò, Green Public Procurement in Europe 2006 – Conclusions and recommendations. 2006. Virage Milieu & Management bv, Korte Spaarne 31, 2011 AJ Haarlem, the Netherlands. (http://europa.eu.int/comm/environment/gpp)

[3] Buy Smart- Green Procurement for Smart Purchasing, Project funded by Intelligent Energy Europe, (www.buy-smart.info)

[4] K. Szilágyi, A képzéshez tartozó szolágltatások és fejlesztési irányai; HEFOP 3.5.1.„Korszerű felnőttkepzesi modszerek kidolgozasa es alkalmazasa", Tanar-tovabbkepzesi konferenciak 2007. Budapest–Siofok–Hajduszoboszlo, Nemzeti Szakkepzesi es Felnőttkepzesi Intezet, (www.nive.hu)

[5] Official website of the European Union on Green Public Procurement, (http://ec.europa.eu/environment/gpp/index_en.htm)

[6] Potenziale der öffentlichen Beschaffung für Ökologische Industriepolitik und Klimaschutz, Potenziale der öffentlichen Beschaffung für Ökologische Industriepolitik und Klimaschutz 2008. november, (www.bmu.de)

[7] Principles of Adult Learning, Stephen Lieb ,Senior Technical Writer and Planner, Arizona Department of Health Services and part-time Instructor, South Mountain Community College from VISION, Fall 1991.

[8] M. K. Smith, The Encyclopedia of Informal Education. 2003. (http://www.infed.org/biblio/b-explrn.htm)

[9] Social and Economic Impact of GPP in Hungary, A zöld közbeszerzési eljárás bevezetésével kapcsolatos gazdasági-társadalmi hatáselemzés, Magyar Környezetgazdaságtani Központ, 2009.

[10] The value of green - Collection of statistical information on Green Public Procurement in the EU, Report on data collection results by PricewaterhouseCoopers, Significant and Ecofys. 2009. (www.thevalueofgreen.com)

A "SMALL, GREEN AND COMPETITIVE ECONOMY" CROATIA'S ROAD TO THE EU

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Abstract

Environmental issues are becoming an increasingly important element of the economic and business environment. Stopping climate change, biodiversity conservation, energy security and efficiency, improved quality of living and working environment are challenges, have recently gained the status of the imperative, with direct implications on the economy. In the business context, this trend is manifested in two ways: as a threat and as an opportunity. On the one hand, the introduction of increasingly demanding environmental standards and goals results with environmentally unacceptable business behaviour which is uncompetitive and unsustainable. On the other hand, a successfully restructured business becomes more resource and market efficient, as well as competitive, while a new kind of demand and rapidly growing new markets create new business opportunities. Current considerable investments in environmental infrastructure in Croatia and the adoption of environmental standards in the business community certainly represent an investment for the future, encourage entrepreneurship, increase foreign competitiveness of Croatian firms and create new jobs.

This paper presents the basic findings of the analysis of small and medium enterprises in Croatia in terms of the impact of their activities on the environment and nature. It also provides some recommendations for the development of small and green entrepreneurship as an important factor contributing to the competitiveness of the Croatian economy in the European Union.

Keywords: *green entrepreneurship, SMEs, competitiveness, environmental protection*

1. INTRODUCTION

Economic growth is currently still necessary, even though it is no longer sufficient. Sustainable – green and social entrepreneurship is the engine of positive, systemic change that will alter what we do, how we do it and why it matters [1]. In the framework of the current economic crisis, supporting entrepreneurial small and medium enterprises (SME's) as a stepping stone to renewed and sustainable growth is the smart choice. SME's are drivers of innovation, job creation and growth [2]. This is supported by an increasing number of scientific studies and papers on the topic of sustainable entrepreneurship and green SME's, in particular as the new driving force for development and innovation and a key competitiveness factor [3]. Croatian strategies and action plans are on the track of new sustainable economic development needs. They all perceive the future through green glasses: our economic growth will be sustainable (Sustainable Development Strategy, 2009), the environment will be protected (National Environment Strategy, 2002; Energy Development Strategy, 2009), high social standards will be applied, equal opportunities will be provided for the disabled, children, women, elderly (Joint Memorandum on Social Inclusion of the Republic of Croatia, 2010). Most of this is supposed to be achieved between 2013 and 2020. The fact is that SME's are the backbone of the EU economy, and they have often been cited as the engine of economic growth. In the Republic of Croatia the business data on SME's do not show major deviations from EU countries. The question is whether SME's are aware that they are a crucial factor for promoting green development and whether they are ready to take over these new challenges. Namely, in the final strategic document related to SME's - "Plan for Encouraging Small and Medium Sized Enterprises 2008-2012"[4] their environmental and social dimensions as well as their contribution to the development of green economy in Croatia are not clear. Further, recent research of corporate social responsibility (CSR) indicates a more declarative SME's determination to protect and preserve the environment than the concrete understanding of environmental orientation as a competitive advantage in the international environment. Recognizing the significance and importance of SME's in supporting sustainable development, green economy and social entrepreneurship, the EU has implemented extensive research and launched programs that support green entrepreneurship and innovation. One of best known programs is "Clean, small, competitive," which has since 2007 systematically encouraged entrepreneurs to use green technology, socially responsible behavior and

investment in eco-innovations. The European experience and recommendations are a good starting point for Croatian SME's in achieving their important role in promoting green entrepreneurship and implementing sustainable development in Croatia.

2. ELABORATION

2.1. Methodology

The literature review was identified through online search using the Publish or Perish (PoP) tool, followed by the ISI Web of knowledge. Furthermore, the following bases were searched: Academic Search Premier, Google Scholar, Science Direct and Soc INDEX. Studies and papers of authors in Croatia were examined using the academic base CROSBI.

In addition to these databases, the entire web was searched, i.e. the so-called "deep web" through a detailed analysis of relevant institutions and strategic documents, particularly those in Croatia which are directly related to SME's, environmental policy and green entrepreneurship as a competitiveness factor of the Croatian economy in the European Union.

The terms used in the search focused on the term "green SME's" and its variations (including, for example, sustainable entrepreneurship and green entrepreneurship). Further, terms such as EU environmental policies, environmental strategies, laws and regulations were searched. Journal articles, working papers, conference papers and book chapters were included in the survey, in addition to key development strategies, global and national strategic documents, relevant EC guidelines and communication notes. The terms were searched both in Croatian and in English.

The literature was analyzed with particular attention given to green SME's competitiveness and sustainability envisioned in the surveyed papers. Additionally, the analysis of strategic documents in Croatia was confirmed, on the basis of which further support to making SME's green would be implemented and all available databases and analysis that cover SME's behavior in regard to environmental protection and management were analyzed. The available data on the index of corporate social responsibility (CSR) and of the National Competitiveness Council were also used. However, a separate analysis of SME's related to these issues was not performed. This presents our research challenge.

Based on the analysis of the conditions and results of the study, the recommendations for Croatia were prepared according to additional research on the improvement of these issues; for entrepreneurs themselves how to become green and why it is important to them in the context of competitiveness in the European market; and for development decision makers and for public policies in Croatia to help them by providing arguments and suggesting measures to be undertaken. The recommendations are fully in line with the recent European development initiatives and strategic documents.

2.2. Theoretical Framework

In the past few years there has been an increasing interest in making businesses green, and particularly the SME's. According to the EC, SME's are enterprises that either employ less than 250 workers or have an annual turnover of 50 million euro or less [5].

The study of green entrepreneurship is a topic that is rapidly developing in the past few years, and the results show that SME's are still operating on a level of making existing jobs green through investments in technological processes that reduce environmental pollution and not through initiatives to develop new innovative business opportunities and develop comparative advantages through the sale of green products and services. The first research on these new green business solutions and their use, aiming not only to improve the environment but also related to new business perspectives, appeared in the 1970s [6], and by the end of the 1990s the new concept called "ecopreneur" was developed, which included SME's and entrepreneurs who pursued their businesses based on the green development concept [7]. It is the fact today that there are no alternatives to sustainable development, and sustainability and green entrepreneurship are key drivers of innovation [8].

The road from the implementation of legal regulations related to environmental issues by reducing the emissions in the environment through the introduction of environmentally friendly technologies and business processes to creating green entrepreneurship and new green businesses is simple and short. Recent studies show that SME's which initiate such a process usually go through five key stages [8]. In the first step SME's change to green practices under pressures of law and doing business according to legislative procedures. Most laws contain precise environmental standards and norms which should be

followed by the entrepreneur in its operations and that often means that the polluter should take over the costs of environmental pollution. The second step includes the development of sustainable value chains, i.e. entrepreneurs become proactive towards environmental issues, mostly through the reduction of non renewable resources and energy efficiency measures. The third step includes the design of green and sustainable products and services and the use of eco-friendly SME policies as a part of the firm's image on the market. This step is considered as a great step forward, and today a growing number of consumers prefer eco-friendly offerings. The promotion of cooperation with green NGOs is an added value to SME's in contributing to its green image on the market. Developing new green business models is the following, fourth step in implementing sustainability. We are not dealing here just with the rethinking of the customers' values perception of the company but rather with the creation of new fields for business activities, e.g. waste management, new technologies for reduction of carbon dioxide, international partnership for water, etc. Significant incentives for the achievement of breakthroughs in business shows that the market related to waste management was about 14 billon USD in 2009, which is about 40% more that in 2007. The final, fifth step in achieving green sustainable practice is the creation of the next – practice platform, which motivates entrepreneurs to leave their physical, material framework and to extend their services, products and processes beyond the single market through internet by using digital technology with the aim of decreasing the environmental costs and reusing the energy efficiency.

Unfortunately, there is no systematic research on green entrepreneurship opportunities in Croatia. The existing papers mainly relate to the implementation of EU environmental directives in the Croatian legislation and the obligations, standards and measures to be fulfilled by entrepreneurs regarding environmental policy and laws [9], as well as the benefits of using green technologies that save energy and resources in daily business [10]. However, in recent years, some aspects of the attitudes of entrepreneurs and SME's regarding environmental protection are included in surveys of entrepreneurs [11] and analyzed in the scope of the report on regional competitiveness [12,1], through the analysis of the index of socially responsible behavior [13,1] and the research on innovation in entrepreneurship [14].

2.3. Results and Discussion

Green SME's and sustainable entrepreneurship provides numerous possibilities that can successfully identify the development of new opportunities - products and services, provide improvements to the efficiency through value chains sustainability, enable new business methods of marketing and the reconfiguration of existing business models as new practice platforms [15]. They cover up to 99% of all businesses, employ over 100 million people, make approximately 57% of the total newly realized values and provide a significant contribution to entrepreneurship and innovation. Based on EU experience, SME's are still, on average, significantly less engaged in the environment, which manifests itself primarily as an average poor knowledge of and compliance with environmental legislation. There is a small proportion of companies which have introduced the environmental management system and the prevailing belief is that their business processes do not require the systematic pursuit "irrespective of their size and intensity" of environmental aspects. As the result, most SME's assume that they meet all environmental legislation and became conscious of possible non-compatibilities only when they are explicitly warned by some form of control and supervision. The EU, in parallel with environmentally demanding "rules of the game", has launched various programs for supporting the economy aiming at painless and successful transition into a new era of sustainable green economy [16], for example, the EU program "Small, clean and competitive" initiated by the European Commission in 2007 with a goal of assisting SME's with a number of recommendations for the successful realization of the described challenges of global economic and green ecologic crisis of growth and development. The program includes joint measures to promote compliance/alignment of SME's operations with environmental legislation, improving environmental efficiency (energy and resource) of SME's, through the introduction of environmental management systems and other appropriate tools, as well as the promotion of eco-innovation, exploring the possibilities of so-called green activities such as waste management or water supply and sewer systems. In considering further development and guidance to entrepreneurship, the EU emphasized the importance of green SME's since they have the potential to become a major driving force in the overall transition to a more sustainable European future. Almost all new initiatives in the EU, related to encouraging entrepreneurship and SME's, agree that in market-based economy entrepreneurs play a critical role in the adoption of green business practices by demonstrating the economic, social as well as long term financial benefits that come crisis imposed a lot of challenges in Croatia. The fact is that in Croatia, in spite of ambitious forecasts of economic growth and development, and all elaborated

strategic documents, measures and activities, economic activity has fallen over the past two years. Real gross domestic product (GDP) declined by 5.8% in 2009 and 1.4% in 2010 [18]. A modest recovery of 1% is expected in 2011, mainly driven by external demand. The average number of unemployed persons rose by 14.9% in 2010, compared to 2009. Administrative unemployment rate in March 2011 was 19.3%. The current account deficit has declined considerably over the period 2008-2010, from 9.2% of GDP in 2008 to 1.9 in 2010 (5.5% in 2009). However, there is a large entrepreneurial potential since, similar to the EU, SME's in Croatia account for 99.6% of all registered businesses, employing 66.6% of the total employed population and achieving 51.6% share in total revenues. Therefore, a substantial part of the responsibility for sustainable growth and greening of Croatian economy lies on small businesses [19]. It seems that the worst of the recession is over, but Croatia is yet to see signs of a sustained economic recovery. The Economic Recovery Program [20] identifies that investment in green technologies and renewable energy can contribute to increasing economic activity and employment and support technological development. Green, sustained economic recovery requires addressing long-standing structural problems such as high wages (compared to regional peers), rigid labour markets, generous social benefits and high business costs. Recent research [21] shows that only the construction of waste management centers, investment in water supply and drainage and air purifiers, which are to be implemented according to Heavy Environmental Directives of the EU assumed in 2009 in Croatian legislation, will cost about 10 billion Euros over the next fifteen years. Moreover, interventions of the Government foreseen by the Croatian Economic Recovery Plan include investments that reduce carbon emissions and pollution, enhance energy and resource efficiency and prevent the loss of biodiversity and ecosystem losses. There are also a number of sectoral strategies and development plans, for example, for agriculture, tourism and transport, indicating that a part of the sustainability and environmental acceptability of the proposed goals and measures have appropriate environmental costs. It is disappointing that the existing key strategic documents for the promotion of SME's do not contain measures for greening entrepreneurship nor do they observe small green economy as a comparative advantage of the Croatian economy on the European market.

In Croatia there are no systematic studies of the greening of our SME’s and there is no awareness that greening is an important direction towards increasing competitiveness. For example, the report on the Croatian Regional Competitiveness Index 2010 [12,2] states that to achieve regional development large scale infrastructure projects in environmental protection are expected to be financed, and the total amount of waste, used waste, investments and current expenditure for environmental protection are monitored through the analysis of public sector and infrastructure. It does not seem that eco-entrepreneurship is recognized as a potential for competitiveness, nor do the recommendations indicate that the forthcoming investments in the implementation of Heavy Environmental Directives in Croatia, which will mostly (hopefully) be financed from the European funds, present an excellent opportunity for eco-entrepreneurs and the "greening" of the Croatian paradigm. Comparing the situation in Croatia with theoretical remodeling of the five steps that SME's need to pass in greening their operations, future investments could introduce Croatian entrepreneurs and SME's at level 4 and enable the sustainable development of the Croatian economy. There is little time and Croatia is still at the early stage of greening its economy. Not only analysts, but also entrepreneurs and SME’s are not familiar with the concept of eco-entrepreneurship or green entrepreneurship. According to recent research of the index of corporate social responsibility [13,2], less than 50% of SME’s integrate environmental concern in their daily operations, monitor influences of business on the environment, 25% include environmental criteria in the selection of suppliers, but nobody pointed out green business as their business niche.

Based on European experience, some of the concrete measures to promote environmental improvements in SME’s, which could be easily and without major costs implemented in Croatia, are the development of business associations for the promotion of green entrepreneurs, intervention of large companies in greening SME’s through supply chains, as well as the improvement of the environmental performance of an entire sector through a value chain approach considering all the activities that a good or service requires from its conception to its end [22].

Some other means are more policy oriented and affect public commitment to encourage investments in green economies, such as specific public-funded programs and facilities. Concrete activities which might be undertaken for the development of small and green entrepreneurship as an essential factor of competitiveness of the Croatian economy in the European Union are:

- Improving the content and implementation of existing regulations to reduce harmful and useless administrative redundancy and release resources that can be used to improve environmental

compliance. It is a general permanent measure focusing on environmental legislation and a superficial insight into the condition [23] reveals that this area has plenty of room for improvement. It could certainly be further improved by clarifying the structure of legal requirements, reducing the redundancy in the questionnaire on pollution and the quantity of emissions from entrepreneurial activities, reviewing procedures for issuing licenses, more intense use of IC technology, the introduction of experience and suggestions of SME's and inspection services on the possibilities to reduce complexity and improve the efficiency of regulation, and finally, instigating permanent exchange of experience, as well as the identification and dissemination of good practice.

- Ensuring available and appropriate Environmental Management System Scheme (EMS) for SME's. Voluntary introduction of environmental management systems (EMS) has proved its usefulness and superiority of the multiple regulatory systems that rely only on the prescribed standards and inspection of the environment and business, i.e. business success. It would be opportune that often complex EMS schemes are adapted to SME's, with a surplus of discarded rigid administrative procedures, and retain a substance that ensures the effectiveness and credibility. It is necessary to organize information campaigns, promote awareness and education about the benefits of the EMS focused on SME's as well as to support the introduction of EMS into a regional and/or sectoral clusters bound to supply chains, which reduces the individual cost of deployment and generates additional positive effects (the contribution of business networking, wide spreading of innovations, etc.)
- Providing targeted financial assistance and establishing a multi-year program of financial support for sustainable, green production in SME's. Lack of financial resources is a very common obstacle in rising environmental and resource efficiency of SME's business services by introducing the best available technology, investing in research and development of eco-innovation, etc. The whole range of EU funds - including *Life+, JEREMIE, CIP, and European regional development, cohesion and social funds* - have provided funds for the financing of projects to improve the environmental performance of SME's (including most of the activities recommended by the program "Small, clean and competitive".

For efficient implementation of the recommendations for greening the Croatian economy it is important to stress some basic limitations and challenges that are unique to all European countries and will surely find its application also in Croatia:

- To motivate SME's to become engaged in green challenges and European programs. They are generally not motivated by concern for environmental quality, but most often by the announced certain possibility of reducing production costs by improving energy and resource efficiency and/or a certain possibility of establishing business contacts with attractive business partners.
- To achieve program efficiency the most appropriate action is at the regional level, since it is "close to the field" to be regionally specific and to work with real SME's networks, and sufficiently "high" to have the necessary expertise, personnel and financial capacity for their implementation. The national level is appropriate for the implementation of some less specific and targeted activities common to all regions, including the possible consolidation of those raising the cost effectiveness of the program.
- To establish trust, encourage changes in behavior and finally achieve something, it takes time. Short programs are often "too short" and several short programs more often create confusion and fatigue than synergy and cumulativeness. On the other hand, it is not good that the programs are too long and comprehensive as they become sluggish and poorly focused.
- To implement the majority of described types of help to SME's in order to improve their environmental performance, public funding is required (at least initially, even in cases where it certainly achieves a quick return on investment through realized higher efficiency, productivity and market competitiveness).
- To introduce a strong marketing and communications component for greening of SME's is very important.
- To build on existing "networks" and current so-called "*gate-keepers*" (NGOs, etc.) increases the response and the intensity of involvement.
- To start the program of "SME's network" that includes big companies and production chains is stimulating because it has additional non-environmental attractiveness for SME's (engagement in manufacturing and supply chains). This is particularly true in particular for clusters, as a form of networking that has proven to encourage competitiveness and innovation.

3. CONCLUSIONS

Environmental sustainability requires the integration of the principles of sustainable development into policies and programs, reversing the loss of environmental resources, as well as reducing biodiversity loss. The road towards green economy implies the implementation of the Millennium Development Goals.

The Road map towards implementing Millennium Development Goals identified the actions to create and maintain green sustainable economies and strengthen green SME's had to be made by the support of international organizations, financial institutions, governments, local authorities, academic community and civil society organization.

The EU has emphasized the strength of SME's in greening its economy through a number of activities in this direction, and one of the programs from which Croatia can certainly learn is "Small, clean and competitive".

The economy is deteriorating in Croatia and a large part is represented by SME's which record losses to total net income from year to year, so they are the right address for quick changes.

Despite the recent development strategies and sectoral policy documents that are green in theory, the practice of environmental sustainability and green entrepreneurship, as a component of green economy in Croatia, has not been ensured so far. Croatian SME's are starting their green and sustainable image – the adaptation of legislation in regard to 3000 directives which Croatia took over from the EU is itself a big challenge. Therefore, there is a long way to go to the new green business paradigms; not only declaratively, but it is also insufficiently based on recent strategic documents, and there are no clear measures and activities.

Based on the scarce analytical background of CSR index and the regional national council, it is possible to conduct provisional conclusions on the barriers to increasing "environmental performance" of SME's in Croatia: lack of awareness and knowledge about environmental issues, effects and risks, and lack of strategic and policy documents which through specific objectives and measures encourage the greening of SME's. Furthermore, the level of knowledge as to the potential benefits of qualitative considerations and environmental management is very low, mostly due to inadequate availability of relevant environmental information, tools and training. Certainly, no less important is the fact that financial, personnel and professional resources for dealing with environmental issues are limited and short-term business planning with a purpose "living from today to tomorrow" still prevails.

Some of the concrete measures to promote environmental improvements in SME's are business associations, intervention of large companies in greening SME's through supply chains, and improvement of the environmental performance of an entire sector through a value chain approach. Some other means are more policy oriented and affect public commitment to encourage investments in green economies, such as specific public-funded programs and facilities. In doing so, the experiences of European countries indicate the need to reduce harmful and useless administrative redundancy and release resources that can be used to improve environmental compliance, ensuring available and more adapted schemes to SME's of Environmental Management System (EMS), establishment of a multi-year program of financial support for sustainable production in SME's, providing locally available environmental expert support to SME's, improving communication and providing targeted information.

Finally, in the implementation of previous recommendations it is important to make sure that the motivation of SME's, in participating in the programs, is generally not motivated by the concern for the environment, but, rather, by the reduction of production costs; the most appropriate effective measures are operating at the regional level; it takes time to encourage changes in behavior, public financing, marketing and communications support as well as their integration into the thematic green clusters.

REFERENCES

[1] H. Neck, C. Brush, E. Allen, The landscape of social entrepreneurship, Business Horizons 52 (2009) 13-19.

[2] The Declaration of Bilbao on "Fostering eco-innovation in SMEs" (2010), Available at: http://ec.europa.eu/environment/ecoinnovation2010/1st_forum/pdf/declaration.pdf

[3] D.S. Levinsohn, E. Brundin, Beyond "shades of green" – opportunities for a renewed conceptualization of entrepreneurial sustainability in SMEs: a literature review, the 56th Annual ICSB Conference, Sweden, (2011).

(http://www.icsb2011.org/download/18.62efe22412f41132d41800012014/189.pdf)
[4] Ministarstvo gospodarstva, rada i poduzetništva RH. Program poticanja malog i srednjeg poduzetništva 2008. – 2012. Zagreb: Vlada RH, 2008. (http://www.mingorp.hr/default.aspx?id=1618)
[5] SMEs and the Environment in the European Union / prepared by Danish technological Institute and PLANET S.A., Greece. European Commission, DG Enterprise and Industry, (2010). (http://ec.europa.eu/enterprise/policies/sme/business-environment/files/main)
[6] J.K. Hall, G.A. Daneke, M. J. Lenox, Sustainable development and entrepreneurship: Past contributions and future directions, J. of Busines Venturing. 25 (2010) 439-448
[7] M. Schaper, The Essence of Ecopreneurship, Greener Management International. 38 (2002) 25-30.
[8] R. Nidumolu, C.K. Prahalad, M.R. Rangaswani, Why sustainability is now the key driver of innovations, Harvard Business Review. 9 (2009) 57-61.
[9] Zaštita okoliša - Minivodič za poslovnu zajednicu. Zagreb: Ministarstvo gospodarstva, rada i poduzetništva, 2009. (http://eobrazovanje.mingorp.hr/UserDocsImages/minivodic_zastita%20okolisa.pdf)
[10] Z. Zeman, M. Geiger, Marija, Think green, act green - new business ethic, sustainability and responsibility for life, in: P.Ćosić, S. Dolinšek, G. Đukić,G. Barić, (Eds.), Management of Technology - Step to Sustainable Production - Conference Proceedings, Fakultet strojarstva i brodogradnje Zagreb, Fakultet managementa Kopar, Zagreb - Kopar, 2009, 445-449.
[11] S. Kalambura, D. Kalambura, Zelene tehnologije i održivi razvoj, in: VeljkoĐukić (Ed.), Zbornik radova ICASUS, Održivi razvoj i očuvanje biodiverziteta, Panevropski univerzitet "APEIRON", Banja Luka, 2011, pp. 241-247.
[12] M. Alpezaet et al., Regionalni indeks konkurentnosti Hrvatske 2010. Zagreb: UNDP i Nacionalno vijeće za konkurentnost, 2010. Available at : www.konkurentnost.hr/lgs.axd?t=16&id=312
[13] N. Miošić, M. Škrabalo. Komparativni pregled nalaza Indeksa DOP –a 2008. – 2010, Gospodarstvo i održivost. 26 (2011) 12-15.
[14] Hrvatski kvocjent inovativnosti 2011, Sense Consulting i veleučilišta VERN. (http://www.inovativnost.hr/Rezultati)
[15] P.D. Reynolds, D. Storey, P. Westhead, Cross- national comparisons of the variation in new firm formation rates, Regional Studies, The Journal of the regional Studies Association 4 (1994) 443-456.
[16] W. De Backer, Resource scarcity will define the 21st century, Europe s World J. 18 (2011) 66-67.
[17] Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions Rio+20: towards the green economy and better governance. European Commission.(2011). (http://ec.europa.eu/environment/nature/biodiversity/comm2006/pdf/2020/1_EN_ACT_part1_v7%5B1%5D.pdf)
[18] A.M. Boromisa, True Colour of Croatian Economy: Blue, Green, Rose...?, in: 2011 South East Europe Management Forum: South East Europe and the European Union, Looking ahead, Lj. Jurčić, D. Djurićin, M. Mlinarević, Ž. Primorac, D. Purg, I. Teodorivić (Eds.). Hrvatsko društvo ekonomista, Zagreb, 2011, pp. 91-116.
[19] D. Kovačić, Poslovanje malog poduzetništva u 2009. i 2010. godini, Zagreb: FINA, (2010). (http://portal.wlw.hr/Uploads/1461/1/3/5413/5419/FINA_1.pdf)
[20] Vlada Republike Hrvatske, Program gospodarskog oporavka, (2010). (www.vlada.hr/en/content/.../Program%20gospodarskog%20oporavka.pdf)
[21] AM. Boromisa, A. Pavičić-Kaselj, S. Tišma, Analysis of environmental financing through various development strategies - recommendations for environmental protection financing system, ESEE 2009, in: A. Perpar (Ed.), 8th International Conference of the European Society for Ecological Economics, Transformation, Innovation and Adaptation for Sustainability, 29th June-2nd July, Ljubljanja, Slovenia, Biotechnical Faculty - University of Ljubljana and European Society of Ecological Economics, Ljubljana, 2009, pp. 1-24

CALCIUM SULPHOALUMINATE ECO-CEMENT FROM INDUSTRIAL WASTE

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Abstract

The manufacture of portland cement (PC) consumes huge amount of energy and has a significant CO_2 emission. Calcium sulfoaluminate cement (CSAC) is a promising alternative binder to PC due to: a) lower limestone requirement in CSAC; b) about 200 K lower sintering temperature for CSAC than for PC; and c) much easier grinding of the fired CSAC. Each of these arguments considerably reduces energy consumption and CO_2 emission from cement manufacture.

In this paper, the potential benefits offered by CSAC production from industrial wastes or by-products already present in Republic of Croatia had been addressed. A variety of industrial wastes, namely phosphogypsum (PG), coal bottom ash (BA) and electric arc furnace slag (EAFS), were used as raw materials to provide additional environmental advantages in production of CSAC. Mass fraction of Klein's compound (the principal hydraulic mineral) in the prepared CSAC was determined by quantitative X-ray powder diffraction. In conclusion, CSAC production offers an alternative and feasible way of industrial waste minimization.

Keywords: *calcium sulfoaluminate special cement, X-ray powder diffraction, waste minimisation, phosphogypsum, electric arc furnace slag, coal bottom ash*

1. INTRODUCTION

Man-made CO_2 emissions and extensive use of natural resources pose a serious threat to the future sustainable development and also trigger climatic change. Cement industry accounts for up to 7% of CO_2 emissions due to the large global production of cement (2 billion tones per year) and also due to the high temperatures involved in production along with large quantity of calcareous materials needed per tone of cement produced. However, the cement industry has a large potential of reuse of vast quantities of various industrial wastes and by-products that can be incorporated, in certain amount, as raw material or added during the final grinding of clinker. Calcium sulphoaluminate cement (CSAC) had been recognized as the so called "low energy cement" due to the much lower energy consumption for its production and is therefore extensively investigated in recent years [1]. At same mixing water to cement ratios and achieved degrees of hydration the obtained porosity of cement pastes made from CSAC is considerably lower than that of ordinary PC. This is because of the higher stoichiometric requirement of the chemically bound water in the hydration products formed by hydration reactions of CSAC, especially in that of the AFt type [1] hydration products. About million tons of CSAC type cements are produced annually in China [2], where special cement standards were issued. To manufacture CSAC clinker, an appropriate starting raw mixture need to be burnt at maximum temperatures 1200-1300°C. The reuse of such waste raw materials, principally phosphogypsum, reduces both the temperature and the time of the firing process (e.g. [3]). On a large scale manufacture, the firing process can be performed in conventional rotary kilns used for PC manufacture [4]. Kleinite ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ i.e. C_4A_3s in shortened cement mineralogy notation, Table 1) is the principal mineral phase responsible for the early strength development during cement hydration. Depending on the proportion of the individual mineral phases in the clinker and the content of calcium sulphate, CSAC may perform as non-expansive high early strength cements, or as expansive cements. This depends on the time of formation of ettringite: before (no expansion) or after (expansion) the development of the rigid skeletal structure. To prevent expansion, the ettringite must be formed in the absence of free CaO [1]. However, a limited amount of CaO is desirable in order to enable rapid strength development and a high early strength. The optimal C_4A_3s content in non-expansive CSAC is between 30 – 40% [3]. In the presence of the iron minerals in the raw mixture, a considerable amount of iron may form solid solution of the type $C_4A_{(3-x)}F_xs$ where x

may be up to 0.15 [5]. The ferrite phase ($C_2(A,F)$) exhibits a higher reactivity than in ordinary PC, contributing to both the early strength development and long term strength of the CASC. This higher reactivity is most likely due to its formation at lower firing temperature [5]. The C_2F starts to be formed at about 1100 °C and at higher temperatures it incorporates alumina, which finally attains a composition of C_6AF_2. To obtain the kleinite (C_4A_3s) and to avoid its decomposition as well as decomposition of $CaSO_4$ at higher temperatures, the firing temperature in the manufacture of CSAC must not exceed 1300°C (especially if reusing the waste as raw materials). Belite (C_2S) is usually present in its β modification, but also sometimes in α form. Belite has only very small contribution to early strength development, but is mainly responsible for the ultimate strength of the CASC. Ternesite (C_5S_2s, also called sulfospurrite) can be formed as an intermediate phase, from about 900 °C [3] and decomposes above 1200-1280 °C to C_2S and $CaSO_4$.

In this work, the potential benefits offered by CSAC production from industrial waste materials already present in Republic of Croatia had been addressed. The main raw material components are: waste phosphogypsum form mineral fertilizer production, electric arc furnace slag (EAFS) form steel production and bottom ash from coal fired electric energy production plant. The quantity of bauxite and limestone are added to the raw mix in order to correct bulk chemical and mineralogical composition to obtain useful properties of the final CSAC cement. Mineralogical composition of samples was investigated by XRD powder diffraction.

2. ELABORATION

2.1. CASC *vs.* PC: Assessment of Energy Saving and CO_2 Emission

CSAC can lay claim to being a very attractive ‘‘high-performance’’ cement mainly due to following reasons [1]: a) the low energy and low CO_2 emission associated with its production; b) its ability to form cements, mortars and concretes with high early and final strengths; c) shrinkage compensating abilities; d) its excellent durability, especially in saline marine environments, and the protection it affords to embedded steel (as well as excellent resistance to alkali-silica reaction [1]). Whereas OPC is normally interground with a few weight percent of $CaSO_4$ (or Cs in cement notation, Table 1), CSAC is typically interground with 16–25% of $CaSO_4$.

Next, the energy requirement and environmental impact of CASC and PC production is quantitatively compared. The energy balances and CO_2 emissions depend on the efficiency of the kiln and fuel. Indications of these balances are shown in Tables 2-4, regarding firing process, grinding process and CO_2 emission. For the purpose of such comparison we consider a standard grade PC product (CEM II/B-M(S-V) 42,5N) with 15 mas. % of supplementary addition (granulated blast furnace slag and fly ash). On account of the low $CaCO_3$ content, relative to OPC, CO_2 emissions are markedly reduced in CSAC clinkers. Further economical benefits of CASC over PC in specific fuel (per kilogram of cement produced) and CO_2 release results from the high level of gypsum addition, 15–25%, typically made to the clinker, as well as the low energy requirements for grinding the clinker. The influence on the energy requirement for the firing in kiln was divided in two segments (Table 2): (i) the influence of the firing temperature, and (ii) the influence of the amount of raw material. Literature values were used for firing temperature and amount of raw material [1] for both types of cements. Enthalpy of the formation of the CSAC clinker is much lower than that of ordinary PC and even of belitic clinkers. Firstly, this is mainly because the thermal losses are reduced due to a lower firing temperature required (1200 - 1300 °C instead of 1450 °C). Secondly, energy saving for firing is also due to the lower overall CaO content to be produced in CSAC, and because the fraction of the CaO is formed from $CaSO_4$ instead of $CaCO_3$. A potential problem in industrial manufacture may be the partial thermal decomposition of $CaSO_4$ during firing the raw material, which may call for an appropriate technology to control the SO_3 emission. However, the emission of CO_2 and NO_x is significantly reduced [6]. The energy requirement for the grinding process of the CSAC clinker is much lower than that of typical ordinary PC clinker (Table 3). The values in Table 3 show energy savings assessment in grinding process of raw materials (before sintering) as well as cement clinker (after sintering). According to the known stoichiometric amount of the raw materials that needs to be grinded the savings in energy is estimated to be about 28 %, while the overall savings is estimated to be about 33 %.

Table 4 presents the ecological and economical benefits of CASC over PC regarding the CO_2 emission. The basic fee for CO_2 emission in Croatia was taken to be 14 - 18kn/t CO_2. Reaction of $CaCO_3$ decomposition ($CaCO_3 \rightarrow CaO + CO_2$) forms 44 mas. % of CO_2. The emission of CO_2 per t of cement is

calculated according to the amount of the $CaCO_3$ raw material needed for the production of cement. For PC this emission amounts 0.374 t CO_2 / t cem. (0.85 $CaCO_3$ / t cem. · 0.44), while for CSAC the savings is 0.242 t CO_2 / t cement (Table 4). Beside the CO_2 emission from $CaCO_3$, there is also a significant emission resulting form fuel combustion. According to Cement data book by W.H. Duda, value for energy requirement for 1 t of cement and amount of CO_2 emission in kg / GJ the estimation of emission from fuel combustion is calculated (e.g. for CSAC 2.48 GJ / t cem. · 90 kg CO_2 / GJ = 223 kg / t cem). The waste management savings assessment is given in Table 5.

Table 1. Cement mineralogy notation

Oxides	CaO	Al_2O_3	SiO_2	SO_3	Fe_2O_3	H_2O	MgO	TiO_2
Symbol	C	A	S	s	F	H	M	T

Table 2. Firing process: ecological and economical benefits of CASC over PC

SINTERING	CSAC	PC (CEM II)	Savings in regard to the PC
Temperature	1200 °C Lower heat loss	1450 °C (3.1 GJ/t cem)	~15 % (0.5 GJ/t cem)
Amount	0.3 t $CaCO_3$ / t cement	0.85 t $CaCO_3$ / t cement	0.55 t $CaCO_3$ / t cement => 0.6 GJ/t*
	1.25 t raw / t cement	1.6 t raw / t cement	0.35 t raw / t cement
	Total saving		> 1.1 GJ/t cem

*considering 60% of energy for $CaCO_3$ decomposition (1.78 GJ/t $CaCO_3$) for conversion to per t of cement

Table 3. Grinding process: economical benefits of CASC over PC

GRINDING	CSAC	PC (CEM II)	Savings in regard to the PC, %
raw materials for sintering	0,3 t $CaCO_3$ / t cement bauxite 10 %	0,85 t $CaCO_3$ / t cement (16 kWh / t cem.)	~ 28*
of cement klinker	sintered = low energy requirement ~ 40 % less than for PC	partly melted = huge energy requirement (36 kWh/ t cem.)	~ 40
	Total saving		~ 33

*economical benefit for the same specific energy requirement (per 1t cement) for grinding due to lower mass of raw materials for production of 1t of cement.

Table 4. CO_2 emission: ecological and economical benefits of CASC over PC

CO_2 EMISSION	CSAC	PC (CEM II)	Savings in regard to the PC, %
Raw material ($CaCO_3$)	0.3 t $CaCO_3$ / t cement 0.132 t CO_2 / t cement	0.85 t $CaCO_3$ / t cement 0.374 t CO_2 / t cement	0.242 t CO_2 /t cement
FUEL	(2.48 GJ/t cem.) 90 kg CO_2 /GJ 223 kg CO_2 / t cem.	(3.1 GJ/t cem.) 90 kg CO_2 /GJ 279 kg CO_2 / t cement	20 %
	Total saving		42.5 %

Table 5. Waste management: savings assessment.

CSAC	PC (CEM II)	Savings in regard to the PC, %
bottom ash ~ 12 % EAFS ~ 30 % phosphogypsum ~ 15 % (35 kn/t waste) 14.7 kn/t cement	ash + EAFS = 10 % (35 kn/t waste) 3.5 kn/t cement	11.2 kn / t cem.

Table 6. Chemical composition of used raw materials (in mass %).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	TiO_2	$Na_2O + K_2O$	SO_3
EAFS	11	2	30	33	13	6	-	-	-
coal bottom ash	54	23	7	5	-	-	-	-	-
bauxite	3.5	57	22.5	1	0.5	-	2.5	< 1	-
phosphogypsum	-	-	-	-	-	-	-	-	79

Table 7. Experimental plan: mass fraction of raw materials and chemical composition used for the preparation of CSAC.

CSAC Sample	J	1c	A	3b	4
Raw mixture (mass %)					
limestone	25.00	25.00	25.00	25.00	31.25
phosphogypsum	30.00	20.00	25.00	25.00	12.5
bauxite	8.00	23.00	8.00	13.00	10.00
bottom ash	18.00	0.00	22.00	10.00	12.50
EAFS	19.00	32.00	20.00	27.00	33.75
Chemical composition (mass %)					
CaO	31.59	38.75	32.27	36.09	45.17
Al_2O_3	11.58	17.31	12.69	12.96	11.74
SiO_2	15.42	5.45	18.19	11.16	13.73
$CaSO_4$	30.23	19.89	25.02	24.97	12.54
Fe_2O_3	11.17	18.60	11.83	14.82	16.82

Table 8. Results of the QXRD analysis.

Sample	3b	J	1c	A	4
w(Ye'elimite), %	32.0	28.1	27.1	31.3	29.2

2.2. Experimental

To formulate the clinkers, three industrial by-products were used as raw materials:

- electric arc furnace slag (EAFS), *Plomin Power Plant II* (Plomin, Croatia);
- coal bottom ash (BA), *Sisak Ironworks d.d.* (Sisak, Croatia);
- phosphogypsum (PG), *Petrokemija d.d.* – Kutina (Kutina, Croatia);

Their chemical oxide composition is shown in Table 6. To correct the bulk chemical and mineralogical composition two additional raw materials were employed:

- bauxite, *CALUCEM* cement plant (Pula, Croatia);
- limestone, p.a. Kemika Zagreb.

Raw materials were milled in a ring agate mortar and sieved below 125 μm. They were than wet homogenized in planetary mill (FRITSCH, Pulverisette 5, α-alumina pot and grinding balls), according to desired proportions (weighted on analytical balance, homogenised for 5 min at 250 rpm with addition of demineralised water, and then fired (sintered) in porcelain pots at 1200 °C for 1 h (above 1250°C occurred partial melting) in an air atmosphere electric furnace (Nabertherm) with a heating rate of 10 K/min and natural cooling rate of the furnace). CSAC clinker samples were milled in a ring agate mortar (very easily, i.e. with low energy requirement) and sieved below 125 μm. Mineralogical composition of samples was investigated by XRD powder diffraction. Shimadzu XRD 6000 (Japan) diffractometer with a CuKa radiation (30 kV, 30 mA) was used.

We employed the quantitative X-ray diffraction (QXRD) by using the adiabatic principle with auto flushing [7-9] as a proven suitable method for quantifying the minerals in cement. In such method the relationship between the intensity of the characteristic X-ray reflection I_i is directly proportional to the weight fraction of the component by the factor k_i which contains the mass absorption coefficient of the total sample. Experimentally determined k_i values hold only for the detecting system and for no other. Reasonable standard materials for such a study are rutile (TiO_2) [10] or corundum (Al_2O_3) [9]. The rutile used in this study had a narrow particle size distribution around approximately 0.4 μm, which would reduce microabsorption effect. XRD analysis of chosen standard rutile showed no traces of anatase. In this work, C_4A_3s in prepared sample is quantified based on the Chung method. The k_i values were determined by mixing of pure phase and standard mineral rutile (TiO_2) in a 50:50 weigh ratio. For the syntheses of C_4A_3s, precipitated calcite ($CaCO_3$ analytical grade purity, Kemika), anhydrite (analytical grade purity, Kemika) and gibbsite ($Al(OH)_3$, Sigma-Aldrich) have been wet homogenized in planetary mill (FRITSCH, Pulverisette 5, α-alumina pot and grinding balls) in the required stoichiometric mole proportion, dried at 105 °C and fired at 1150 °C, for 4 h in an air atmosphere electric furnace. Cement samples were milled in a ring agate mortar and sieved below 40 μm to maximize the number of particles analyzed, to improve powder homogeneity and packing characteristics, and to minimize microabsorption-related problems. Each sample prepared for QXRD was mixed with 10 mass % of rutile, followed by grinding and homogenization in an agate mortar under acetone. Appropriate corrections for peak overlap were meticulously applied by inference to the (measured) intensities of the pattern due to the pure phases. Measurement uncertainty of the QXRD analysis is evaluated to be ± 2 % (with 95 % confidence level).

2.3. Results and Discussion

The CSAC sample clinkers were formulated attempting to obtain different contents of cement mineral phases (Table 7). Five series of CSAC clinkers were synthesized. The chemical oxide composition is calculated from the known chemical oxide composition of each raw material (Table 6) and their proportions (Table 7) in the raw mixture. For this calculation a computer program was written for the setting in the Matlab (CaO is increased by the MgO content multiplied by the stoichiometric factor of 1.4). By using the mixture experimental design we aim to achieve the different cement clinker formulations and then emphasize the differences between derived cements. The main drawback is the difficulty to estimate the correct amount of each phase after clinkering in such complex systems. Moreover, the thermal behavior of distinct formulations might diverge and differential kinetics might alter the theoretical predictions on the phase development. The raw materials were sintered in porcelain pots at 1200 °C for 1 h. At 1250 °C occurred the partial melting of the material.

2.3.1 XRD Analysis of Employed Industrial Waste

The composition of EAFS is based on component compositions of the type $CaO\text{-}SiO_2$, CaO-FeO, $CaO\text{-}SiO_2\text{-}MnO$, $CaO\text{-}Al_2O_3$, $CaO\text{-}FeO\text{-}SiO_2$ and $CaO\text{-}SiO_2\text{-}FeO\text{-}MgO$ [11, 12] (Table 6). X-ray diffraction analysis, shown in Fig. 1., indicated the following principally represented minerals in investigated EAFS: F (Fe), C_2F, C_4AF, wustite (FeO), magnetite (Fe_3O_4), mayenite ($C_{12}A_7$), and C_2S. Fig. 2. shows the X-ray diffraction analysis of the coal bottom ash (Plomin) used for preparation of the CSAC. It can be seen that a significant portion of the ash sample is amorphous (glassy), while the crystalline phases identified are *α*-quartz and mullite, which is in accordance with the chemical composition (SiO_2 i Al_2O_3 make 75-80% of the ash) shown in Table 6.

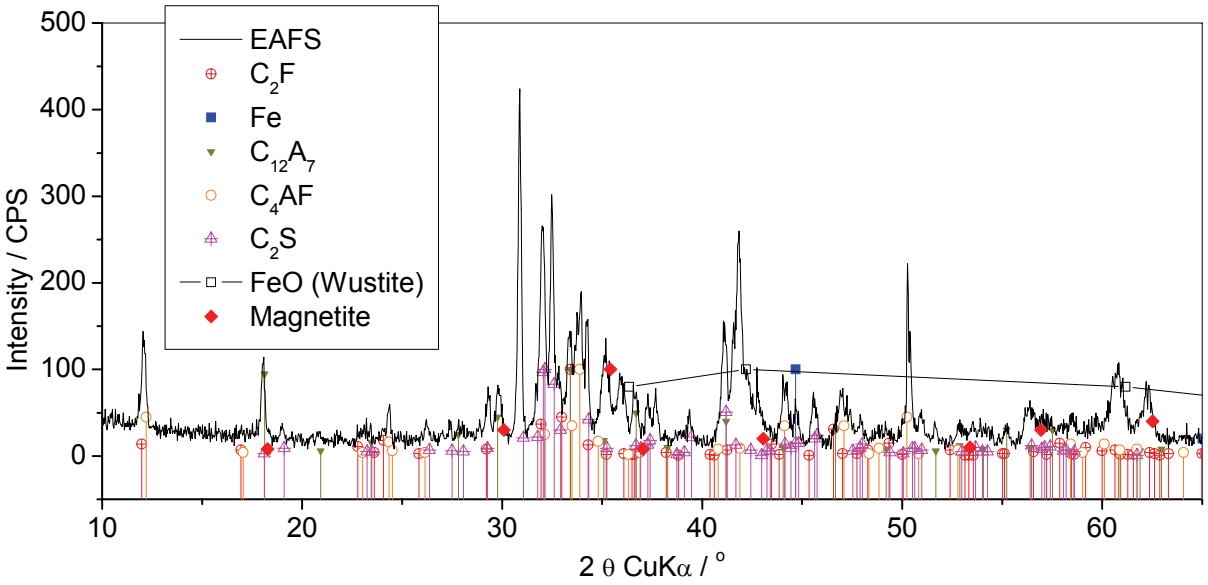


Figure 1. X-ray diffraction analysis of electric arc furnace slag (EAFS, Sisak).

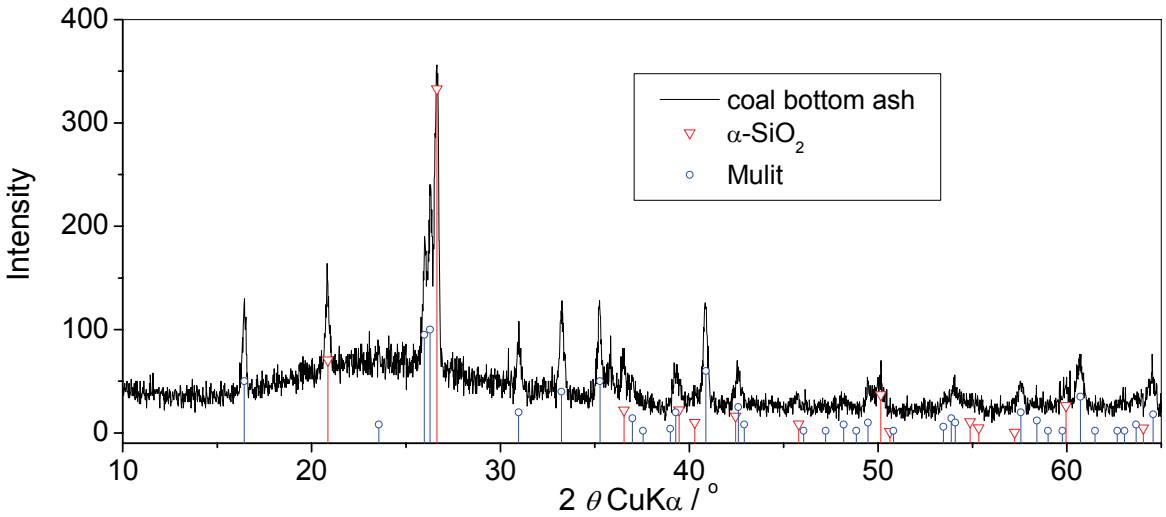


Figure 2. X-ray diffraction analysis of coal bottom ash (Plomin).

2.3.2 Phase Formation

Figs. 3. and 4. present X-ray diffraction analysis of the obtained CSAC sample clinkers from the raw mixture with the chemical composition shown in Table 7. The main mineral phases identified are: Kleinite (C_4A_3s, also called Klein's compound or Ye'elimite), anhydrite ($CaSO_4$), Ternesite (C_5S_2s, also called sulfospurite), ferrite phase (C_4AF, or more precisely $C_2(A,F)$ with varying amount of Al), magnetite (Fe_3O_4). It is worth noting that hematite (Fe_2O_3) at higher temperatures (in air) is in an equilibrium with magnetite (Fe_3O_4). The magnetic behaviour, observed upon testing with a magnet, may be ascribed to the presence of magnetite (Fe_3O_4). The indentified phases are present in distinct relative amounts, depending on the formulations. Ternesite (C_5S_2s, also called sulfospurrite) is formed as an intermediate phase, and is expected to decompose above 1200-1280 °C to C_2S and $CaSO_4$. As the samples fired at 1250 °C were partially melted and hard to separate from the porcelain pots, further mineralogical analysis at temepratures higher than 1200°C were not performed. From the results presented in the Figs. 3. and 4. it can be concluded that the presence of ferrite phase excludes the formation of ternesite, and vice versa.

Mass fraction of Klein's compound in the prepared CSAC as determined by quantitative X-ray powder diffraction (Fig. 4.) was shown to be in the range 27 to 32 mass %, Table 8. As the optimal C_4A_3s content in non-expansive CSAC is between 30 – 40% [1, 3] one can conclude that CSAC production offers an alternative and feasible way of the investigated industrial waste minimization.

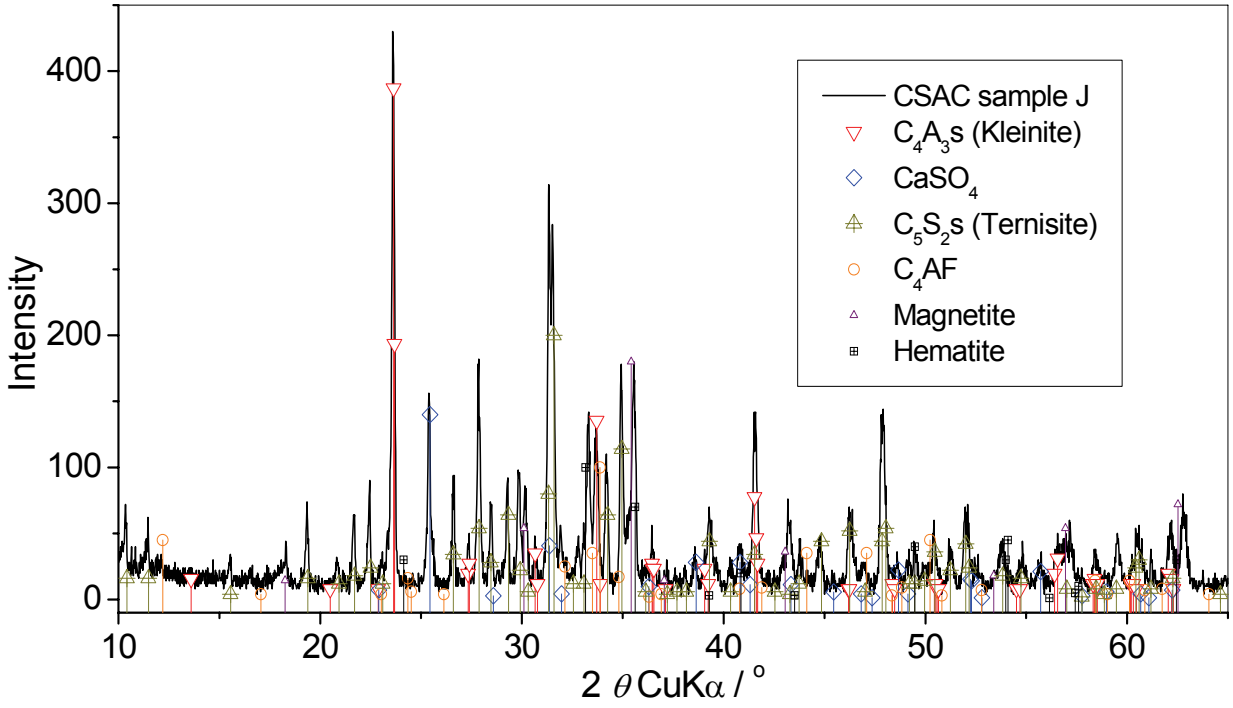


Figure 3. X-ray diffraction analysis of CSAC sample J.

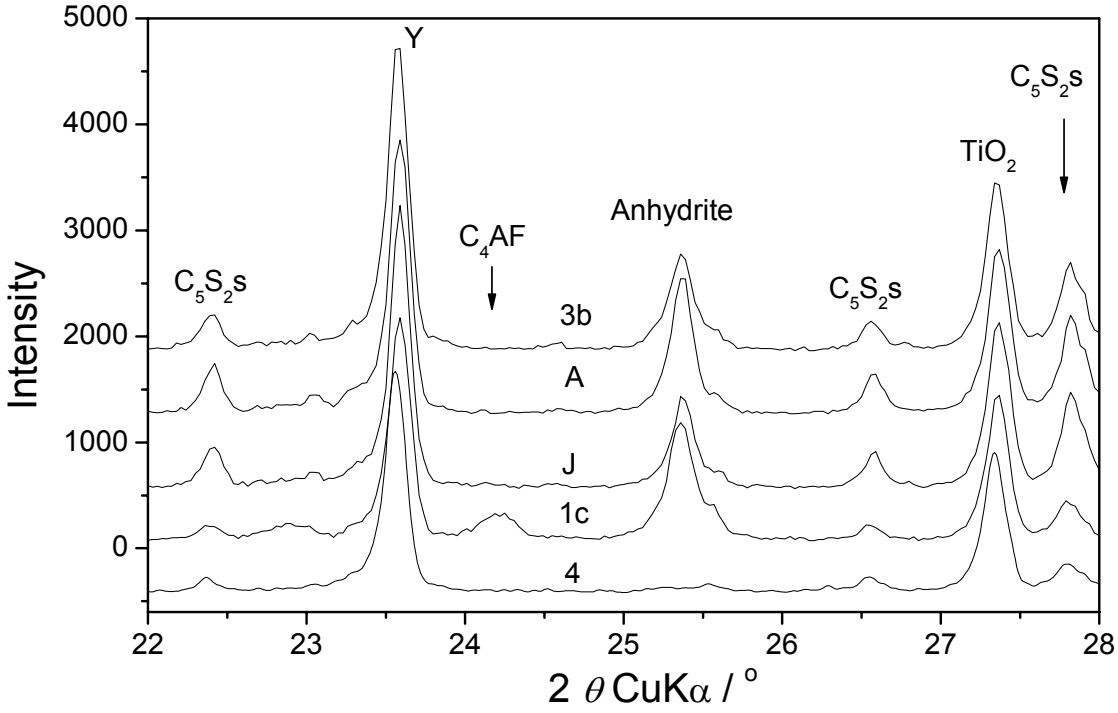


Figure 4. Quantitative X-ray diffraction analysis of prepared CSAC cement samples, (Y – C_4A_3s)

3. CONCLUSIONS

CSAC materials are a potentially very attractive high-performance eco-cement. The potential benefits offered by CSAC production from industrial wastes or by-products already present in Republic of Croatia had been addressed. A variety of industrial wastes, namely phosphogypsum (PG), coal bottom ash (BA) and electric arc furnace slag (EAFS) were used as raw materials to provide additional environmental advantages in production of CSAC. Five series of CSAC clinkers were synthesized attempting to obtain different contents of cement mineral phases. Mass fraction of Klein's compound in

the prepared CSAC as determined by quantitative X-ray powder diffraction was in the range 27 to 32 mass %. In conclusion, CSAC production offers an alternative and feasible way of industrial waste minimization.

Acknowledgment
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REFERENCES

[1] I. Odler, Special Inorganic Cements, E&FN Spon, New York, 2000.
[2] L. Zhang, M. Su, and Y. Wang, Developement of the use of sulfo- and feroaluminate cements in China, Adv. Cem. Res. 11 (1999) 15-21.
[3] J. Beretka, B. de Vito, L. Santoro, N. Sherman, G.L. Valenti, Hydraulic behaviour of calcium sulfoaluminate-based cements derived from industrial process waste, Cem. Concr. Res. 23 (1993) 1205-1214.
[4] G. A. Mudbhatkal, P.S. Parmeswaran, A.S. Heble, B.V.B. Pai, A.K. Chatterjee, Non-alitic cement from calcium sulfoaluminate clinker – optimization for high strength and low temperature applications, Proceedings of 8th International Conference on Cement Chemistry, Rio de Janerio, Brasil, 1986, Vol. 4, pp. 364-370.
[5] J. H. Sharp, C. D. Lawrence, R. Yang, Calcium sulfoaluminate cements – low-energy cements, special cements or what?, Adv. Cem. Res. 11 (1999) 3-13.
[6] Y. Takuma, T. Shirasaka, M. Kanaya, K. Kobayashi, Shun-ichiro Uchida, Effect of reducing the emission of CO_2 and the characteristics of clinker in the system C_2S-C_4A_3S-C_4AF-Cs, J. Cer. Society of Japan vol. 102, no. 1, (1994) 1115-1121.
[7] A. Bezjak, X-ray-Quantitative Analysis of Multiphase Systems. Croatica Chemica Acta 33 (1961) 197-200.
[8] F. H. Chung, Quantitative interpretation of X-ray diffraction patterns of mixtures. II. Adiabatic principle of X-ray diffraction analysis of mixtures, Journal of Applied Crystalography 7 (1974) 526-531.
[9] H. G. Midgley, Quantitative Determination of Phases in High Alumina Cement Clinkers by X-ray Diffraction, Cem. Concr. Res. 6 (1976) 217-224.
[10] B. M. Mohamed, J.H. Sharp, Kinetics and mechanisms of formation of tricalcium-aluminate $Ca_3Al_2O_6$, Thermochimica Acta 388 (2002) 105-114.
[11] M. Cioroi, L. Nistor, Recycling Possibilities of Metallurgical Slag, The Annals of "Dunarea De Jos" University of Galati. Fascicle IX. Metallurgy and Materials Science 1 (2007) 78-82.
[12] T. Sofilić, A. Mladenović, U. Sofilić, Characterization of the EAF steel slag as aggregate for use in road construction, Chemical engineering transactions 19 (2010) 117-123.

DESIGN OF LOW-ENERGY DISTRICT HEATING SYSTEM FOR A SETTLEMENT WITH LOW-ENERGY BUILDINGS

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Abstract

With the integration of new low-energy buildings the traditional district heating (DH) systems with high operating temperatures will have significantly higher heat loss according to the heat supplied to the district. The relatively higher heat loss could be reduced with low operating temperatures of 55 °C and 25 °C in supply and return line of DH network, respectively with a convenient control of in-house installations (substations). Traditional DH pipe dimensioning methods were based on size searching algorithm in which lowest possible pipe diameter was defined according to the limit of max velocity and/or max pressure gradient. Since traditional dimensioning methods cause over-dimensioned network, special attention has to be given to lower the dimensions and as a consequence heat loss from the DH network further. In this investigation pipe dimensioning method of low-energy DH system was developed with an optimization method in the objective of minimizing heat loss from the network while pressure drop values were kept as the constraints through the DH network. In the dimensioning method also descending pipe dimensions were formed in the branched type DH network by taking into account simultaneity of heat load, according to the cumulative consumer load, on each pipe segment separately. According to the traditional dimensioning method, 14% reduction in the heat loss was achieved with the developed optimization method. The resultant pipe dimensions were evaluated via hydraulic and thermal simulation software Termis with simultaneity factor based randomly generated heat demand scenarios for peak winter situation. The simulation results were re-sampled with bootstrapping method and confidence interval of the reliability of the DH system was presented as a result.

Keywords: *low-energy, district heating, pipe dimensioning, simultaneity factor, optimization method*

1. INTRODUCTION

The integration of new low-energy buildings and the low-energy renovation of existing buildings, as a consequence of the efforts to reduce the energy consumption in European buildings, increase the percentage of heat loss from the piping network of a traditional District Heating (DH) system [1-4]. Olsen et al. [5] accentuated that a low-energy DH system operating at very low temperatures, 55 °C in the case of supply and 25 °C of return, can satisfy the heating demand of consumers through an adequate control of the substations [6]. Also, special attention needs to be directed at dimensioning of the DH piping network to prevent over-dimensioned network and high heat loss from the network, which are inevitable consequences of traditional dimensioning methods [7,8]. Descending pipe dimensions were formed in the branched type DH network by taking into account simultaneity of heat consumption, as a function of consumer load, applied on each pipe segment separately [9]. Three pipe dimensioning methods, two of them based on maximum pressure gradient criteria and the other one based on optimization, were compared in terms of heat loss from the DH network [10-14]. The optimal pipe dimensions were evaluated by means of the commercial software Termis with input of randomly generated heat demand data based on simultaneity factor [11,15]. The reliability of the DH network with optimal pipe dimensions was evaluated by use of the hydraulic and thermal simulation software Termis in terms of maximum static pressure obtained through the DH network.

2. ELABORATION

2.1. Methods

In this paper, calculations were carried out separately on each of the pipe segments of which the DH network consisted, as shown at Figure 1.

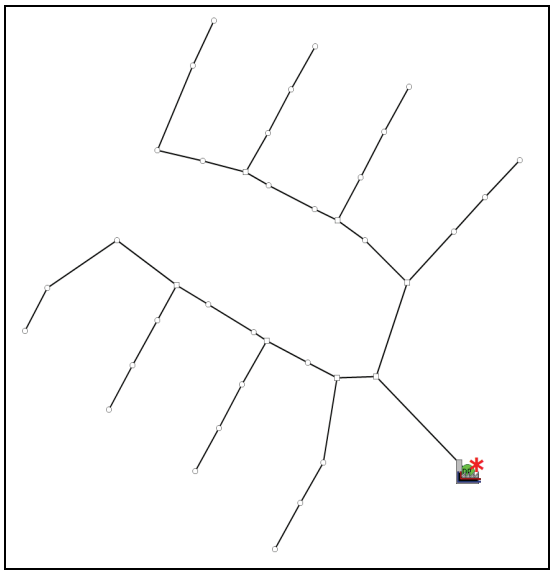


Figure 1. Branched DH piping network as a layout for Trekroner area

2.1.1. Estimation of Heat Load

In this paper, a suburban area of Trekroner (in Roskilde Municipality, Denmark) consisting of 165 low-energy houses with peak heat demand of 2.9 kW for Space Heating (SH) and 3 kW for Domestic Hot Water (DHW) with the use of a substation having a 120 litre buffer tank (more information can be reached at [16-19]), unique for each individual consumer, was studied. A branched type DH piping network was proposed there with total length of 1.2 km trench, excluding end-user connections to the houses. Each consumer in the DH network is not expected to consume heat at full demand level or at exactly the same time, which is the basic idea behind the use of simultaneity factor [9]. Hence special attention was directed at including simultaneity factor at each pipe segment separately as a function of the cumulative number of consumers to which heat is supplied by the pipe segment in question. The heat loads at the pipe segments, including the simultaneity factor as a function of consumer load on them, were calculated in terms of space heating and domestic hot water by use of, respectively, Eq. (1) and Eq. (2) [16,18-20].

$$\dot{Q}_{SHL}(N_i) = \left[0.62 + \frac{0.38}{CC(N_i)}\right] \times CC(N_i) \times \dot{Q}_{SHD} \quad (1)$$

$$\dot{Q}_{DHWL}(N_i) = 1.19 \times CC(N_i) + 1.5 \times CC(N_i)^{0.5} + 0.3 \quad (2)$$

where $CC(N_i)$ is the cumulative consumer number at the node N_i, $\dot{Q}_{SHD}$ is the individual heat demand for each consumer while $\dot{Q}_{SHL}(N_i)$ and $\dot{Q}_{DHWL}(N_i)$ are the heat load for, respectively, space heating and domestic hot water at the node N_i.

2.1.2. Calculations

The pressure drop was calculated by use of the Darcy-Weisbach equation with consideration of the temperature and the flow condition of the heat carrier medium in different pipe segments while the friction coefficient, used in the equation, was calculated by use of Clamond algorithm [21,22].

Heat loss from the DH network was calculated according to the linear temperature dependent thermal coefficient based on the temperatures of the heat carrier medium and ground, distinctively at supply and return lines [3,23,24].

2.1.3. Dimensioning Methods

The heat load defined in chapter 0 was used as an input data for each of the dimensioning methods, given below. Although great reduction was achieved through the lowered heat loads at the pipe segments by including simultaneity factor at each of them, it is still essential to define a proper pipe dimensioning method with special attention given to pressure drop throughout the DH network.

2.1.3.1. Method 1 - The Maximum Pressure Gradient in the Limit of Critical Route

The maximum pressure gradient method in the limit of critical route has been widely used in traditional dimensioning methods. In this method, a critical route is defined with consideration given to the highest pressure drop occurring through the routes, and a maximum pressure gradient value is calculated according to this critical route, which is later used as the maximum limit while dimensioning

the rest of the pipe segments in each route at the DH network [10]. In this study critical route was set as the longest route of the DH network. In a fundamental manner, a pump which is dimensioned according to the critical route can also satisfy the lower pressure drops occurring in other routes at a closed loop system [10,21]. The following pipe dimensioning methods, Methods 2 and 3, were proposed according to this fundamental in order to prevent unused potential of head lift supplied by the pump, and as a consequence inevitable over-dimensions resulted by use of Method 1.

2.1.3.2. Method 2 – The Maximum Pressure Gradient in the Limit of Multi-Route

This method is developed on the basis of Method 1. Unlike the limit definition in Method 1, this method allows different maximum pressure gradient limits defined distinctly per each individual route of which the DH network consisted. Each pipe segment thus is dimensioned in the limit of the maximum pressure gradient of the route to which it belonged.

2.1.3.3. Method 3 – The Optimization Method

The excessive unused pressure drop potential, obtained as a result of Method 2, showed that the piping network of DH was still over-dimensioned. On the basis of fundamental, the pump defined for the DH network can satisfy the pressure drop of each route evenly, an optimization method was developed in which the pipe dimensions are reduced until each individual pressure drop through the routes reaches to the maximum allowable pressure drop, with the aim of lowering the heat loss from the DH network. The dimensions of the piping network were determined with simultaneous consideration of objective function - minimizing heat loss from the DH network - and constraint functions - utilization of pressure drops along the routes as much as possible - by means of "Optimization Tool" of the commercial software Matlab with "Active Set" algorithm.

2.1.4. Evaluation of the Pipe Dimensions

The hydraulic and thermal simulation software Termis, in its basic assumption, is based on mass continuity in all of the pipe segments, linked within each other at the DH network. Therefore determination of the heat demands of the nodes, in accordance to the fundamental of the mass continuity, was needed for the evaluation of the optimal pipe dimensions, resulted by use of Method 3, in the commercial software Termis. Several scenarios, representing the peak situation of winter months, were generated as input data for the Termis software by means of randomly generated heat demand data based on use of the simultaneity factors, included in each pipe segment. The results of Termis simulations, such as the maximum static pressure in the DH network and the minimum pressure difference for the consumers, were evaluated in comparison to the design limits defined for them. The purpose of the evaluation was to be sure of the reliability of the dimensions in terms of sufficient pressure drop obtained across the substations of the consumers and maximum static pressure occurring through the whole network, not violating the design limit. The confidence interval for the maximum static pressure was determined by means of the bootstrap method, which increases the reliability of the confidence interval by means of re-sampling the simulation results [25].

2.2. Results and Discussion

Design parameters, given at Table 1, were used as input data to dimension the piping network of the DH system. Maximum allowable pressure drop was calculated as 8 bar for all of the routes of the DH network as a whole for supply and return line per each route. Twin pipes were chosen to be used in pipe selection because of their advantages of lower heat loss and construction cost.

Table 1. Design parameters as input data to dimension the piping network of the DH system

Design Parameters	Set Value	Unit	Description
Supply Temperature	55	ºC	Set on the supply line at the heat source
Return Temperature	25	ºC	Set on the return line at all of the substations
Ground Temperature	2	ºC	Set for the whole DH network
Maximum Static Pressure	10	bar	Set for the whole DH network
Holding Pressure	1.5	bar	Set on the return line at the heat source
Minimum Pressure Difference	0.5	bar	Set for all of the substations

2.2.1. Dimensioning Methods

Figure 2 shows the pressure drop values obtained along the various routes as the results of the three different dimensioning methods in question. The maximum allowable pressure drop was calculated as 1,617 (Pa m^{-1}) for the critical route, defined for Route 8 in Method 1 while as 4,651; 3,520; 2,563; 2,141; 4,643; 3,388; 2,491 and; 1,617 (Pa m^{-1}) for the routes, in order, in Method 2. Both methods resulted in residual unused pressure drop along the routes, which is the main reason for over-dimensioned piping network. Method 3 resulted in pressure drop values obtained as much close to the maximum allowable pressure drop, allowing smaller dimensions for all of the pipe segments at the DH network, as seen at Figure 3. Method 3, due to the optimization algorithm it uses, exceptionally tended to increase the dimensions of the main pipe lines, which hereby allowed further reduction of the dimensions for the street pipe lines. The reduction in heat loss was observed as 2% and 14% by use of, respectively, Method 2 and Method 3 in comparison to Method 1. Although maximum velocity criteria was not considered at Method 3, maximum velocity was reached as 2.4 m s^{-1} through the whole DH network, located at the edge of the street lines.

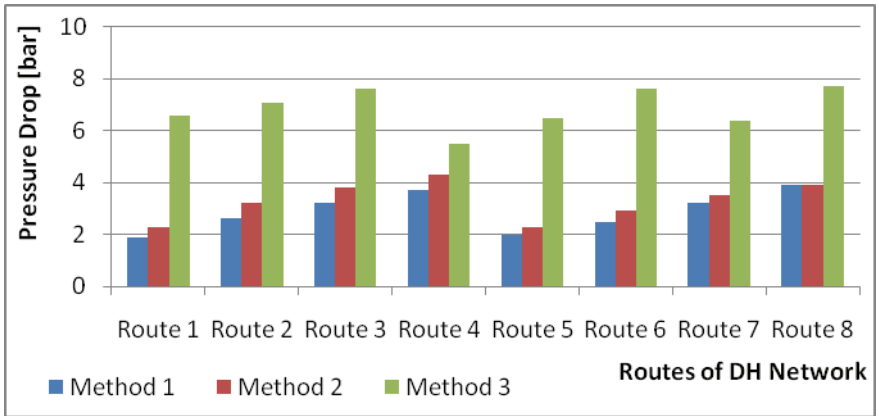


Figure 2. Pressure drop values obtained through the routes as the results of dimensioning methods in question

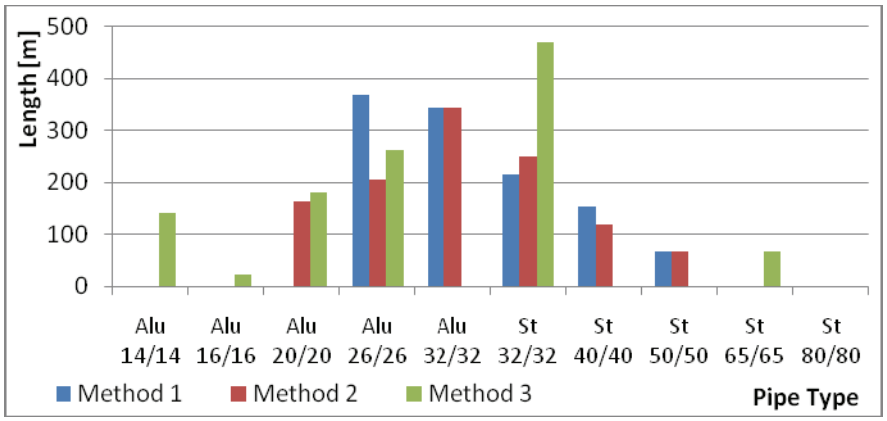


Figure 3. Length of the pipes as a result of dimensioning methods in question (Alu refers to AluFlex Twin Pipe, St refers to Steel Twin Pipe [26]).

2.2.2. Evaluation of Pipe Dimensions

The DH Termis model was simulated hundred times with different individual heat demand patterns, of which the scenarios consisted. The 95% confidence interval of the maximum static pressure, obtained at the DH network, was founded as 1010 ± 3.1 kPa and, after re-sampling the resultant values 50,000 times with bootstrap method, as 1007.5 ± 0.015 kPa. From the confidence interval, it can be seen that the max static pressure values are satisfactory although they are slightly higher than the design limit of static pressure of 10 bar since peak winter conditions occur very seldom, and the pipe segment where observed maximum static pressure was dimensioned with Steel Twin Pipe as a result of Method 3, which has a design limit of maximum operating pressure of 25 bar. Simulation results of the Termis model, with focus given on maximum static pressure, velocity of the flow and pressure difference at substations were shown at Figure 4.

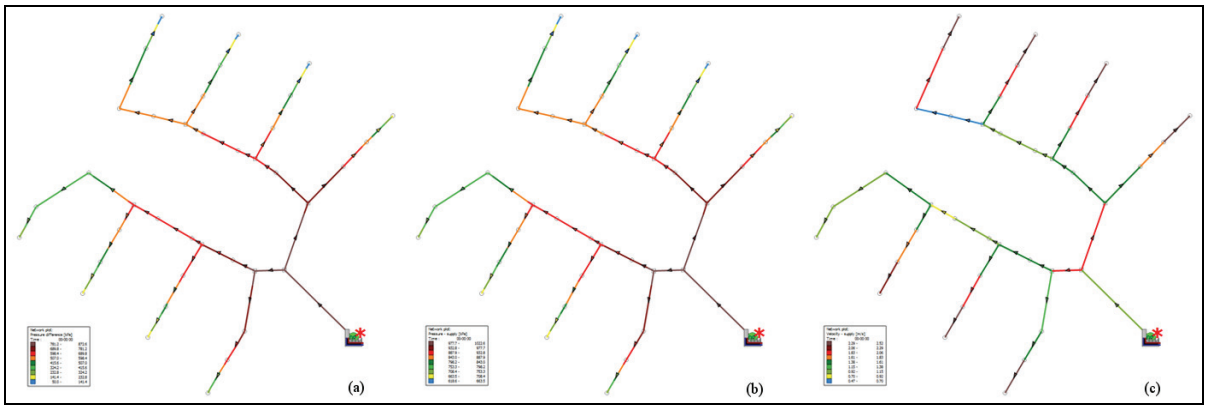


Figure 4. Termis simulation results in respect to (a) Pressure difference (kPa), (b) Static pressure obtained at supply pipe line (kPa) and, (c) Velocity of flow obtained at supply pipe line (m s^{-1})

3. CONCLUSIONS

Traditional dimensioning methods can result in over-dimensioned and as a consequence low energy efficient, DH piping network. Thus in this paper a new pipe-dimensioning method was proposed with consideration given to the aim of reducing heat loss from the DH network while utilizing the head lift provided by the pump as much as possible throughout the whole routes. Special attention was also given to the determination of the heat load by taking into consideration of simultaneity factor at each specific pipe segment, as a function of the consumer number to which each pipe segment supplies heat.

The reliability of the optimal piping network was evaluated by means of simulations which were carried out at the commercial software Termis with the input of heat demand scenarios which were randomly generated by taking into account of the simultaneity factor in each pipe segment. The simulation results proved the validity of the optimization method proposed with 14% reduction in heat loss from the DH network.

REFERENCES

[1] H. Lund, B.V. Mathiesen, Energy system analysis of 100% renewable energy systems—The case of Denmark in years 2030 and 2050, Energy. 34 (5) (2009) 524-531.

[2] U. Persson, S. Werner, Heat distribution and the future competitiveness of district heating, Applied Energy. 88 (3) (2011) 568-576.

[3] A. Dalla Rosa, H. Li, S. Svendsen, Steady state heat losses in pre-insulated pipes for low-energy district heating, The 12th International Symposium on District Heating and Cooling. (2010) 83.

[4] K. Çomaklı, B. Yüksel, Ö. Çomaklı, Evaluation of energy and exergy losses in district heating network, Applied Thermal Engineering. 24 (7) (2004) 1009-1017.

[5] P.K. Olsen, H. Lambertsen, R. Hummelshøj, B. Bøhm, C.H. Christiansen, S. Svendsen, et al., A new low-temperature district heating system for low-energy buildings, The 11th International Symposium on District Heating and Cooling. (2008).

[6] O. Paulsen, J. Fan, S. Furbo, J.E. Thorsen, Consumer Unit for Low Energy District Heating Net, The 11th International Symposium on District Heating and Cooling. (2008) 1-8.

[7] J. Overgaard, S. Knudsen, District heating networks - choosing the right pipe dimensions, DBDH. 1 (1) (2006) 1-2.

[8] M. Rämä, K. Sipilä, Challanges on low heat density district heating network design, The 12th International Symposium on District Heating and Cooling. (2010) 69-72.

[9] W. Winter, T. Haslauer, I. Obernberger, Simultaneity surveys in district heating networks: Results and project experience [Untersuchungen zur Gleich-zeitigkeit in Nahwärmenetzen : Ergebnisse und Projekterfahrungen] [In German], Euroheat&Power. 30 (2001) 42-47.

[10] C. González, B. Macarulla, D. Sallán, Recursive design of pressurized branched irrigation networks, Journal of Irrigation and Drainage Engineering. In Press, Corrected Proof (2010).

[11] A. Benonysson, B. Bøhm, H.F. Ravn, Operational optimization in a district heating system, Energy Conversion and Management. 36 (5) (1995) 297-314.

[12] N. Yildirim, M. Toksoy, G. Gokcen, Piping network design of geothermal district heating systems: Case study for a university campus, Energy. 35 (8) (2010) 3256-3262.
[13] A. Bejan, G. Tsatsaronis, M. Moran, Thermoeconomic optimization, Thermal Design & Optimization, John Wiley & Sons, Inc, New York, 1996, pp. 463-510.
[14] D. Dobersek, D. Goricanec, Optimisation of tree path pipe network with nonlinear optimisation method, Applied Thermal Engineering. 29 (8-9) (2009) 1584-1591.
[15] I. Gabrielaitiene, B. Bøhm, B. Sunden, Modelling temperature dynamics of a district heating system in Naestved, Denmark—A case study, Energy Conversion and Management. 48 (1) (2007) 78-86.
[16] J.E. Thorsen, C.H. Christiansen, M. Brand, P.K. Olesen, C.T. Larsen, Experiences on low-temperature district heating in Lystrup - Denmark, International Conference on District Energy. (in press).
[17] J.E. Thorsen, H. Kristjansson, Cost considerations on storage tank versus heat exchanger for hot water preparation, 1-10.
[18] M. Brand, A. Dalla Rosa, S. Svendsen, Performance of low temperature district heating systems for low energy houses, International Energy Agency Energy Conversation in Buildings and Community Systems Annex 49. (2010) 174-183.
[19] M. Brand, J.E. Thorsen, S. Svendsen, C.H. Christiansen, A direct heat exchanger unit used for domestic hot water supply in a single-family house supplied by low energy district heating , Proceedings of 12th International Symposium on District Heating and Cooling, (2010), 60-68
[20] J. Worm, H. Jørgensen, J.E. Thorsen, J. Bennetsen, C.T. Larsen, O. Juhl, et al., Demonstration of low energy district heating system for low energy building in ringgårdens Afd. 34 in Lystrup [Demonstration af lavenergifjernvarme til lavenergibyggeri i boligforeningen ringgårdens afd. 34 i Lystrup] [in Danish], in press (2011).
[21] R.L. Sanks, Pumping station design, Elsevier Gulf, United States of America, 1998.
[22] D. Clamond, Efficient resolution of the Colebrook equation, Industrial & Engineering Chemistry Research. 48 (7) (2009) 3665-3671.
[23] A. Dalla Rosa, H. Li, S. Svendsen, Method for optimal design of pipes for low-energy district heating, with focus on heat losses, Energy. In Press, Corrected Proof (2011) 1-9.
[24] H. Li, A. Dalla Rosa, S. Svendsen, Design of low temperature district heating network with supply water recirculation, The 12th International Symposium on District Heating and Cooling. (2010) 73-80.
[25] B. Efron, R. Tibshirani, Bootstrap methods for standard errors, confidence intervals, and other measures of statistical accuracy, Statistical Science. 1 (1) (1986) pp. 54-75.
[26] The twinpipes - Logstor product catalog, 2011 (03/2011) (2009) 58.

EFFICIENCY ENHANCEMENT OF ORGANIC-INORGANIC SOLAR CELLS USING ZnO NANO-RODS SHAPE CONTROLLED WITH CONCENTRATION OF PRECURSORS

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Abstract

Zinc Oxide is actively investigated for hybrid organic inorganic device applications. The interface greatly influences the electronic properties of these devices. Molecular surface modification of ZnO is being investigated for its potential to control the alignment of energy levels, charge transfer, as well as, interfacial chemical characteristic influence device fabrication.

In this study, the influences of buffer layers on the performance of hybrid solar cells that are fabricated with an active layer blend of poly (3-hexylthiophene) (P3HT) and [6, 6]-phenyl-C61-buytyric acid methylester (PCBM). The ZnO thin films were used as an electron transport layer in solar cells to improve the photovoltaic performances. We fabricated ITO glass on PET substrate, consist of Au/MoO_3/PCBM:P3HT/ZnO/ITO. Solar cell in which the ZnO nanorods were controlled ZnO nanorods arrays under concentration of precursors. We conclude that the differences observed in the two types of device predominantly arise from changes in interfacial dipoles, and intermediate materials processing can be critical to solar cell performance.

Keywords: *ZnO nanorods, organic-inorganic solar cell, concentration of precursors, electron transport layer*

1. INTRODUCTION

Organic solar cells have attracted significant attention due to the great potential for large-area [1–4], light-weight, flexible [5–7], and low-cost devices [8]. However, organic materials have the small excitons diffusion length and low carrier mobility. This causes the organic solar cells to reduce the efficiency. An approach to reduce the problem is to insert a buffer layer between the metal and active layers as a path for photo-generated carriers to collect at the electrode. To solve the three problems, we investigate the way of changing the nature of charge collection by using a more air- stable high work function electrode as the back contact to collect holes [9,10] while using metal oxide nanostructures at the ITO to select and collect electrons [11-14]. It integrates the advantages of the two materials: solution process ability, high hole mobility and photosensitivity of polymers, and high electron mobility of inorganic semiconductors [15,16].

The zinc oxide (ZnO), among metal oxide semiconductor films, is a n-type direct band gap semiconductor with a large exciton biding energy of 60meV and Eg of 3.37eV at room temperature [17,18]. The large exciton binding energy facilitates low-threshold stimulated emission in ZnO via excitonic recombination, which is a more efficient radiative process than an electron-hole plasma process. Efficient lasing action through excitonic recombination at room temperature has been reported in both ZnO thin films and nanostructures [19-21]. In addition, significant efforts for realization of high-sensitivity nanoscale chemical sensors using ZnO nanostructures have been made [22-24].

Many attempts have thus been made to prepare ZnO nanorods, including metal organic chemical vapor deposition, ratio frequency, sputtering, chemical spray phyrolysis pulsed laser deposition, successive ion layer adsorption and recation, sol-gel and chemical bath deposition.

During the past several years, various methods have been developed for the synthesis of oriented arrays of ZnO nanorods and nanowires, including vapor–liquid–solid (VLS) [25], metal–organic chemical vapor deposition (MOCVD) [26], template-assisted [27], and solution method [28].

In this paper, we used the sol–gel method to study the thickness of ZnO nanorods in solar cells. We studied attempts to investigate the effects of precursor concentration to growth ZnO nanorods on the solar cells and the thickness effect of ZnO nanorods were explored and optimized for the solar cells. We

described the wet chemical method of ZnO nanorods arrays under concentration of precursors. We tried to study suitable ZnO nanorods growth condition to apply to organic-inorganic hybrid solar cell. We demonstrate that the concentration of precursors have influence on the morphology and optical properties, growth density and its distribution of the arrayed ZnO nanorods can be effectively controlled by using suitable conditions.

2. ELABORATION

2.1. Experimental Procedure

The substrate used in our experiment included indium tin oxide (ITO) glass and ITO PES. In our experimental processes, a substrate was coated with a droplet of 0.01M zinc acetate dehydrate[$Zn(CH_3COO)_2 \cdot 6H_2O$] aqueous solution, and blown N^2 gas and then annealed at 100□ for 10min. This coating step is repeated 5 times to get high seed density. Then the precursor solutions were prepared by mixing zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] with hexamethylentetramine while keeping their volume ratio at 1 : 1.

ZnO nanorods were grown in 250 mL of 0.025 M, 0.075 M aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ and HMT in beaker on hot plate and heated 95˚C. After washing several times with de-ionized water and drying at 100˚C on hot plate. Then, a blend of P3HT:PCBM (1 : 1 by weight) was deposited on the fullerene interlayer by spin-coating a 1.5 wt% chlorobenzene solution in air. The thickness of the photo active layer is about 300 nm. Finally, gold film (~150nm) as deposited on top of the photo active layer. Solar cells were measured under illumination at 1000W/m^2 (Air mass 1.5 illumination).

2.2. Results and Discussion

Fig. 1. is the FE-SEM photograph which observed the ZnO nanorod surface and section morphology to two concentration of precursors. While concentration of precursors increases, nanorod diameters increased a little. ZnO nanorod having comparatively uniform size was grown by the density of low 0.025 M and 0.075 M.

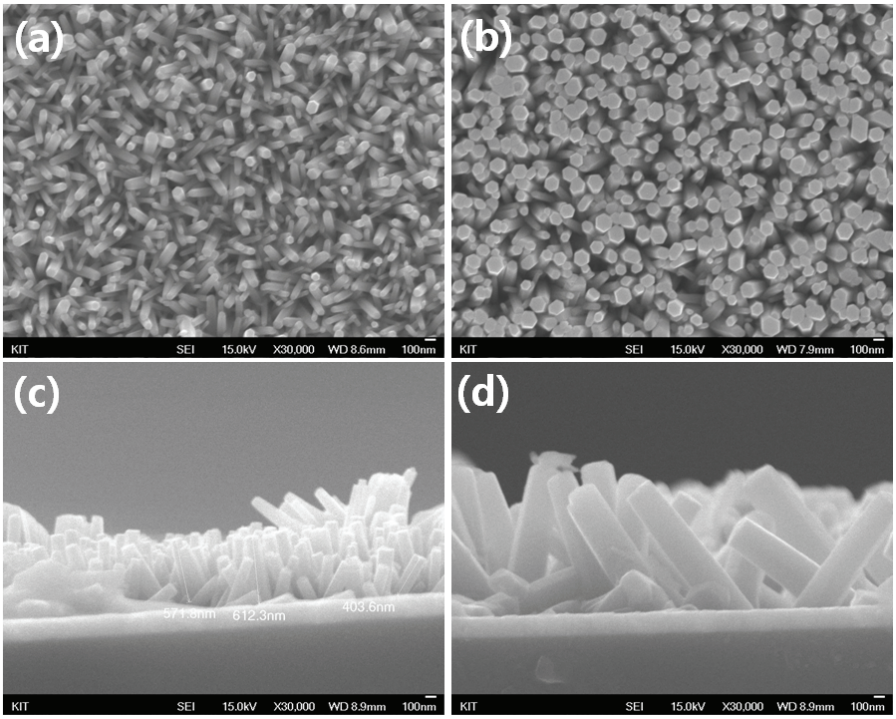


Figure 1. SEM images of ZnO nanorod grown on ITO glass with different concentration of precursors ((a) 0.025 M top side, (b) 0.075 M top side, (c) 0.025 M cross-section, (d) 0.075 M cross-section)

For such a reason, Vayssieres [29] reported the formation of ZnO microrods on unmodified substrates and found that the width of ZnO rods can be reduced from 1–2 mm to100–200 nm by lowering the overall concentration of the reactant while keeping the ratio of Zn^{2+} to amine constant at 1:1 [28]. Since the substrates used in our work were premodified with ZnO nanoparticles and the nanoparticles

have a great influence on the diameter of the ZnO rods, it is necessary to investigate the effects of precursor concentration on the size of ZnO nanorods grown on modified substrates.

The crystalline structure of the nanorod was characterized by X-ray diffraction with Cu kα radiation. The surface morphology and cross-sectional images of the nanorods were studied by field emission scanning electron microscopy. The optical absorbance of the nanorod was recorded by an ultraviolet-visible spectroscopy. The resistivity, hall mobility were verified by hall measurement. It is characterization on the crystallographic properties of the nanorods was performed by XRD. The ZnO nanorod growth on ITO glass shows reflection, indicating their high orientation with c-axis vertical to the substrate surface. (Fig. 2.)

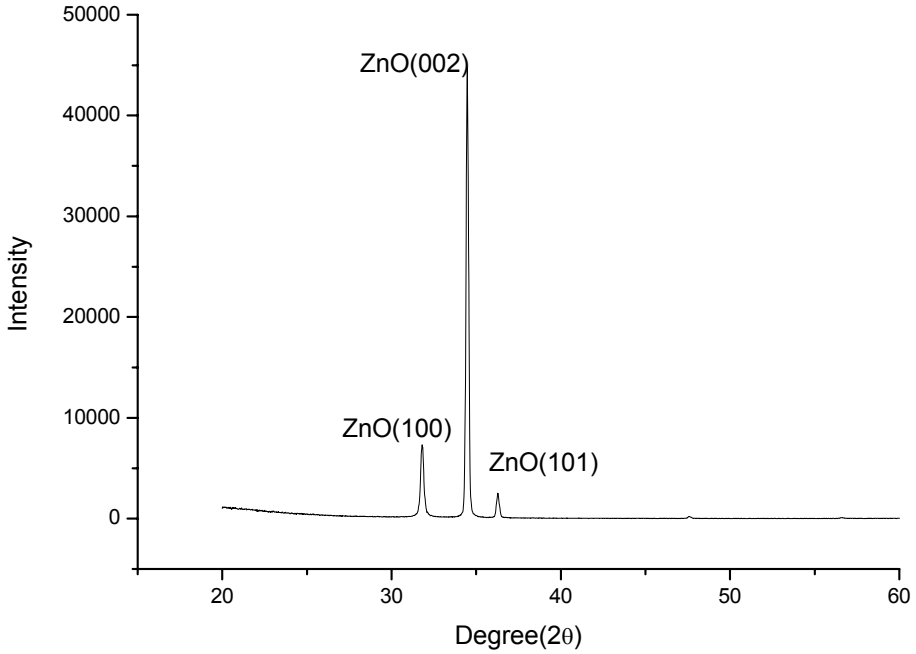


Fig. 2. XRD result of the ZnO nanorod growth on ITO glass

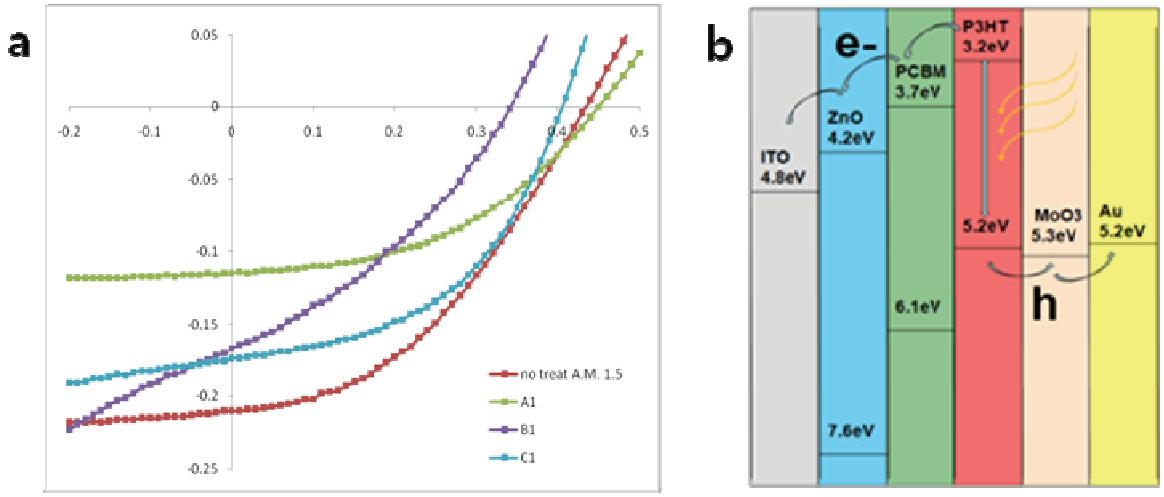


Figure 3. (a) The current–voltage characteristics of the solar cell under 100mW cm^{-2} AM 1.5G irradiation (A1, B1 and C1 represent the hybrid solar cells under different precursor concentration: 0.025 M, 0.075 M, 0.1 M, respectively). (b) Energy band diagram for P3HT:PCBM/ZnO nanorod arrays hybrid solar cells

This study attempts to investigate the effects of precursor concentration to growth ZnO nanorods on the hybrid solar cells. The J–V characteristics of the solar cell are plotted together in Fig. 3(a) for comparison. The energy band diagram for the device with a structure of ITO/ZnO nanorod arrays

P3HT:PCBM/MoO_3/Au is shown in Fig. 3(b). The 3 types of precursor concentration to growth ZnO nanorods of A1, B1, C1 were absorbed the better surface, but there is no promotion of solar cell property.

3. CONCLUSIONS

In this paper, we studied the effect of nanorod diameter controlled the concentration of precursors at the polymer/ZnO nanorod hybrid solar cell. Surface morphologies and optical qualities of ZnO nanorods that were prepared by the sol–gel method were investigated and optimized for inorganic–organic solar cell structures. We found the nanorod diameter and deposited transparent ZnO nanorods using the sol–gel method. The ZnO buffer layer influenced *J*sc of the organic-inorganic solar cells due to the combined factors of electron mobility. The 3 types of hydrogen treatment of A1, B1, C1 were absorbed the better surface, but there is no promotion of solar cell property.

REFERENCES

[1] F. C. Krebs, H. Spanggard, T. Kjær, M. Biancardo, J. Alstrup, Large area plastic solar cell modules, Mater. Sci. Eng. B138 (2007) 106–111.
[2] C. Lungenschmied, G. Dennler, H. Neugebauer, S. N. Sariciftci, M. Glatthaar, T. Meyer, A. Meyer, Flexible, long- lived, large-area, organic solar cells, Sol. Energy Mater. Sol. Cells 91 (2007) 379–384.
[3] M. Niggemann, B. Zimmermann, J. Haschke, M. Glatthaar, A. Gombert, Organic solar cell modules for specific applications—from energy autonomous systems to large area photovoltaics, Thin Solid Films 516 (2008) 7181–7187.
[4] R. Tipnis, J. Bernkopf, S. Jia, J. Krieg, S. Li, M. Storch, D. Laird, Large- area organic photovoltaic module— fabrication and performance, Sol. Energy Mater. Sol. Cells 93 (2009) 442–446.
[5] L. Blankenburg, K. Schultheis, H. Schache, S. Sensfuss, M. Schrodner, Reel-to- reel wet coating as an efficient up- scaling technique for the production of bulk-heterojunction polymer solar cells,Sol. Energy Mater. Sol. Cells 93 (2009)476–483.
[6] F. C. Krebs, Polymer solar cell modules prepared using roll-to-roll methods: knife- over- edge coating, slot-die coating and screen printing, Sol. Energy Mater. Sol. Cells 93 (2009) 465–475.
[7] F. C. Krebs, S. A. Gevorgyan, J. Alstrup, Aroll- to- roll process to flexible polymer solar cells: model studies, manufacture and operational stability studies, J. Mater. Chem. 19 (2009) 5442–5451.
[8] F. C. Krebs, M. Jørgensen, K. Norrman, O. Hagemann, J. Alstrup, T. D. Nielsen, J. Fyenbo, K. Larsen, J. Kristensen, A complete process for production of flexible large area polymer solar cells entirely using screen printing— first public demonstration, Sol. Energy Mater. Sol. Cells 93 (2009) 422–441.
[9] F. C. Krebs, Air stable polymer photovoltaics based on a process free from vacuum steps and fullerenes, Sol. Energy Mater. Sol. Cells 92 (2008) 715–726.
[10] F. C. Krebs, Y. Thomann, R. Thomann, J. W. Andreasen, A simple nanostructured polymer/ZnO hybrid solar cell- preparation and operation in air, Nanotechnology 19 (42) (2008) 424013.
[11] K. Takanezawa, K. Tajima, K. Hashimoto, Efficiency enhancement of polymer photovoltaic devices hybridized with ZnO nanorod arrays by the introduction of a vanadium oxide buffer layer, Appl. Phys. Lett. 93 (2008) 063308.
[12] B. Y. Yu, A. Tsai, S. P. Tsai, K. T. Wong, Y. Yang, C. W. Chu, J. J. Shyue, Efficient inverted solar cells using TiO2 nanotube arrays, Nanotechnology 19 (25) (2008) 255202.
[13] C.-Y.Chou, J.-S.Huang, C.-H.Wu, C.-Y.Lee, C.-F.Lin, Lengthening the polymer solidification time to improve the performance of polymer/ZnO nanorod hybrid solar cells, Sol. Energy Mater. Sol. Cells 93 (2009) 1608–1612.
[14] J.-S.Huang, C.-Y.Chou, M.-Y.Liu, K.-H.Tsai, W.-H.Lin, C.-F.Lin, Solution- processed vanadium oxide as an anode interlayer for inverted polymer solar cells hybridized with ZnO nanorods, Org. Electron. 10 (2009) 1060–1065.
[15] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, Hybrid nanorod-polymer solar cells, Science 295 (2002) 2425–2427.
[16] S. Gunes, N.S. Sariciftci, Hybrid solar cells, Inorg. Chim.Acta 361 (2008) 581–588.
[17] K. Hummer, Interband Magnetoreflection of ZnO, Phys. Stat. Sol. B 56, (1973) 249-260.

[18] A. Mang, K. Reimann, St. Ruhenacke, Band gaps, crystal-field splitting, spin-orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure, Solid State Commun. 94, (1995) 251-254.
[19] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, M. Y. Shen, T. Goto, Optically pumped lasing of ZnO at room temperature, Appl. Phys. Lett. 73, (1998) 1038.
[20] A. Ohtomo, K. Tamura, M. Kawasaki, T. Makino, Y.Segawa, Z. K. Tang, G. K. L. Wong, Y. Matsumoto, H. Koinuma, Room-temperature stimulated emission of excitons in ZnO/(Mg, Zn)O superlattices, Appl. Phys. Lett. 77, (2000) 2204.
[21] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H.Kind, E. Weber, R. Russo, P. Yang, Room-Temperature Ultraviolet Nanowire Nanolasers, Science 292, (2001) 1897-1899.
[22] Q. H. Li, Q. Wan, Y. X. Liang, T. H. Wang, Electronic transport through individual ZnO nanowires, Appl.Phys. Lett. 84, (2004) 4556.
[23] Z. Fan, D. Wang, P. Chang, W. Tseng, J. G. Lu, ZnO nanowire field-effect transistor and oxygen sensing property, Appl. Phys. Lett. 85, (2004) 5923.
[24] P. Feng, Q. Wan, T. H. Wang, Contact-controlled sensing properties of flowerlike ZnO nanostructures, Appl. Phys. Lett. 87, (2005) 213111.
[25] M.H. Huang, Y.Y. Wu, H. Feick, N. Tran, E. Weber, P.D. Yang, Catalytic Growth of Zinc Oxide Nanowires by Vapor Transport, Adv. Mater. 13 (2001) 113–116.
[26] K.S. Kim, H.W. Kim, Synthesis of ZnO nanorod on bare Si substrate using metal organic chemical vapor deposition, Phys. B: Condens. Matter 328 (2003) 368–371.
[27] Y. Li, G.W.Meng, L.D. Zhang, F. Phillipp, Ordered semiconductor ZnO nanowire arrays and their photoluminescence properties, Appl. Phys. Lett. 76 (2000) 2011–2013.
[28] L. Vayssieres, Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions, Adv. Mater. 15 (2003) 464–466.

DEVELOPMENT OF RADIATION COOLING PANEL FOR ENERGY CONSERVATION

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Abstract

The aim of this study was to examine the effectiveness of a radiant cooling panel coated with natural nephrite to improve radiation efficiency. First, radiant capability such as radiant temperature, panel surface temperature, and flowing water temperature were measured in the old type of radiant cooling panel (O panel) and radiant cooling panel coated with natural nephrite (N panel). The N panel showed a distribution of the lower temperature radiant compared with the O panel and improved energy conservation. Next, eight healthy male students participated in the experiment to assess the differences of thermal comfort and thermal sensation between an N panel and an air conditioner. They felt thermal comfort even in a warm thermal state rather than the neutral thermal sensation in N panel, and thermal comfort tolerance was larger in N panel than in air conditioning.

Keywords: *radiant cooling panel, thermal comfort, thermal sensation, skin temperature, energy conservation*

1. INTRODUCTION

Because summer air conditioning exerts a major influence on electric power demand, many studies have focused on the utilization of radiant cooling as an alternative to conventional air conditioning. It is widely believed that radiant cooling systems could significantly reduce electric power consumption. Radiant cooling is also believed to hold promise as a means of reducing the occurrence of air-conditioning syndrome and local cooling, which are often encountered with conventional cooling by air conditioners due to exposure to cold airstreams, and as a means of increasing overall thermal comfort levels [1]. Research on radiant cooling has typically focused on its utilization in ceiling and wall panel installations, and many studies have investigated the energy savings and comfort levels of radiant cooling relative to conventional air conditioning. In radiant cooling installations, however, the effectiveness of the panels is substantially reduced by surface condensation and the distance from the cooling target, and radiation efficiency as a performance characteristic has generally been low. A further drawback of these types of installations is the lack of flexibility for targeting specific areas or individuals in the dwelling, in contrast to the adjustable targeting of conventional air conditioners [2,3].

Therefore, in the present study, we focused on the possibility of increasing the efficiency of radiant cooling systems by applying a coating produced from natural jade ore. To facilitate positioning within the room, we fabricated a mobile radiant cooling system using a coated panel and evaluated its effectiveness in experimental trials to determine its radiation efficiency and the comfort levels experienced by volunteer subjects.

2. ELABORATION

2.1. Overview of Study

Two sets of experimental trials were performed to evaluate the proposed mobile radiant cooling system using a jade-ore-based coating on the radiant panel surface. We first performed an experimental comparison of the spatial domain of the radiant energy effect of panels with and without the jade-ore-based coating. We then conducted experimental trials with volunteer subjects to investigate the level of comfort provided by the proposed radiant cooling unit using the coated panel relative to that provided by a conventional air conditioner.

2.2. Radiant Effect Experiments

2.2.1. Experimental Method

As shown schematically in Fig. 1., a radiant panel (85 × 85 × 3 cm) formed from a Galvalume sheet was placed in a room with 35 radiant temperature measurement points arrayed in front of the panel at

distances up to 100 cm. The measurements were made with transducers (INNOVA, MM0036) of a PMV Data Logger (INNOVA, 1221). The air temperature was measured with an indoor thermometer (Espec, RSW-20S) located 50 cm in front of the radiant panel center and 0.6 m above the floor. A circulation system was fabricated to supply cooling water to the panel at a temperature setting of 6.2°C, and the air temperature was maintained with an air conditioner (Daikin, S28-KMV) set at 25°C throughout the experiments. The surface temperature in the central part of the radiant panel was measured with a thermocouple (CENTER, 309DL).

The only factor that varied between the two sets of trials was the radiant panel employed. In one set, a panel with a coating made from natural jade ore (panel N) was used as the radiant surface. In the other set, an uncoated panel (panel O) was used.

2.2.2. Experimental Results and Discussion

Fig. 2. shows the temperature distributions near panel N and panel O, respectively. The radiant temperature values in the measurement space with no radiant panel were found to be almost identical to the air temperature in the room. As the mean air temperature in the room during the experiments was 25.25°C, it may therefore be concluded that those regions showing temperatures of less than 25°C in these two figures represent the domains of the cooling effect of the panels. The cooling domain of panel N extended at least 100 cm in front of the panel surface , while the cooling domain of panel O extended only 40 cm at its maximum point. The minimum radiant temperature observed with panel N was 22.1°C, which was 2.7°C lower than the minimum observed with panel O, 24.8°C. The greater effectiveness of panel N could also be observed from the mean temperature over the measurement region, which was 1.6°C lower with panel N than with panel O.

The surface temperature of panel N was found to be 15.5°C, 1.8°C higher than the surface of panel O (13.7°C). This difference is attributable to differences in radiation efficiency, surface conformation, and other properties of the coating on panel N. These results, and the substantially lower radiant temperatures observed in the measurement region with panel N than with panel O, indicate a high thermal radiation effect of panel N.

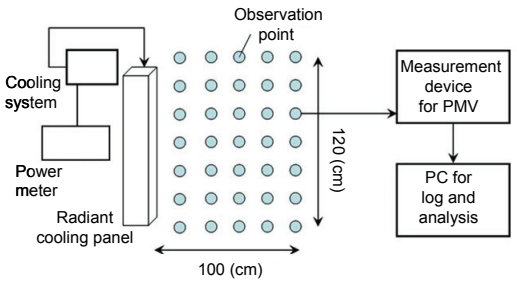


Figure 1 Experimental layout

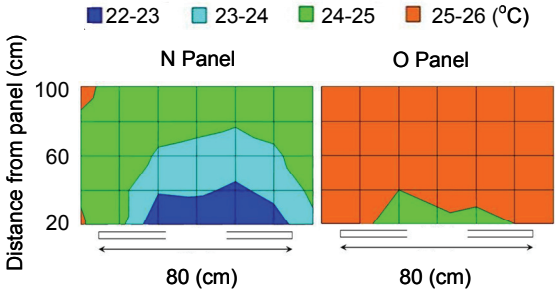


Figure 2 Temperature distributions near panels

2.3. Comfort Level Trials

2.3.1. Experimental Materials and Procedure

In light of the findings in the radiant effect experiments, we fabricated a mobile radiant cooling unit incorporating a radiant panel (80 × 150 × 2 cm) formed from a Galvalume sheet, which has a surface coating produced from natural jade ore, together with an internal cooling water circulation system. To investigate the comfort level that could be attained with this unit, we performed comfort level trials in which we compared the effectiveness of the radiant cooling unit with that of a conventional air conditioner. The trials were performed at the Environmental Laboratory Building at the Hino Campus of Tokyo Metropolitan University during the months of September and October on days with similar outdoor temperatures. The cooling systems compared were the proposed mobile radiant cooling system and a conventional air conditioner (Daikin, S28-KMV). The volunteer test subjects were eight male university students (age, 24.3 ± 1.7 years). All subjects were dressed identically in a t-shirt, short pants, and underwear. The clothing quantity was equivalent to 0.33 clo.

Fig. 3 shows the schedule for each trial, which consisted of a radiant cooling session and an air conditioner cooling session, both on the same day. The thermal histories of all subjects were equalized by having each subject remain seated for 20 min prior to the beginning of each session in an anteroom set to a temperature of 28°C. The subject was then immediately moved from the anteroom to the

Environmental Laboratory Building, and a 60-min exposure trial was conducted in which the subject's physiological and psychological responses were recorded.

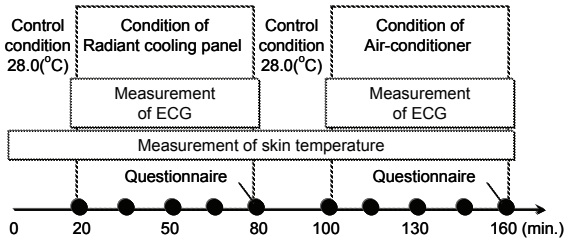


Figure 3 Schedule for each trial

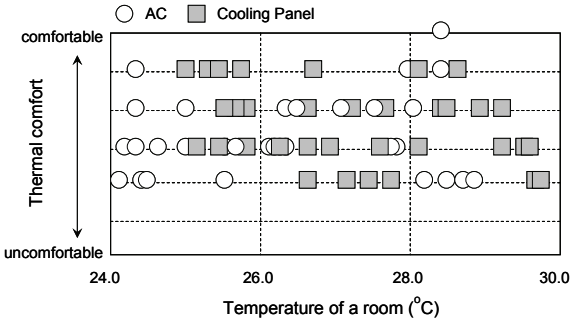


Figure 4 Comfort levels reported by all subjects

2.3.2. Evaluation Indices

2.3.2.1. Thermal Environment Conditions

Indoor thermometers (Espec, RSW-20S) were placed in the center of the room at 0.1, 0.6, and 1.1 m above the floor, and temperature and humidity were measured at 5-min intervals. The operative temperature at 0.6 m above the floor was measured at 1-sec intervals with the transducers (INNOVA, MM0060) of the PMV Data Logger (INNOVA, 1221).

The air conditioner setting was adjusted as necessary during the radiant cooling sessions to maintain a uniform thermal environment during the cooling sessions, based on the time-series variation found in the operative temperature during the radiant cooling experiments.

2.3.2.2. Physiological Indicator

Skin surface temperature was measured and recorded as the physiological indicator. The sensors of a temperature logger (Gram, LT-8A) were taped directly to the skin at eight points: forehead, forearm, back of hand (dorsum manus), abdomen, thigh, lower leg, instep (dorsum pedis), and fingertip. The mean skin surface temperature was computed by the Hardy-DuBois 7-point method [4].

2.3.2.3. Psychological Response

The ISO-10551 seven-point scale was used to measure psychological response. The subjects reported comfort level, total thermal sensation, local thermal sensations (head, arm and leg), and other aspects at 15-min intervals throughout each exposure session, including at the start and end.

2.3.3. Experimental Results and Discussion

2.3.3.1. Indoor Temperature and Skin Surface Temperature to Comfort Level

Fig. 4. shows the comfort levels reported by all subjects for all of the room temperatures in the radiant cooling and air conditioner trials. As indicated by the figure, at room temperatures of 26°C or below, a large proportion of subjects reported that the radiant cooling was more comfortable than the air conditioning. At room temperatures of 26°C or higher, most subjects rated their level of comfort as 0 or higher in both the radiant cooling and air conditioner cooling trials; thus, there did not appear to be much difference in comfort levels between the two cooling methods. These results indicate that, in environments with temperatures of 30°C or lower, the proposed radiant cooling system can provide the same level of comfort as air conditioning.

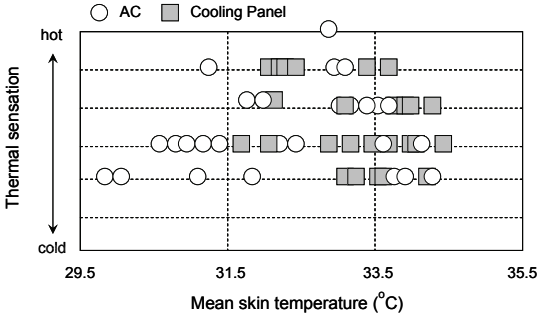


Figure 5 Lower skin surface temperatures

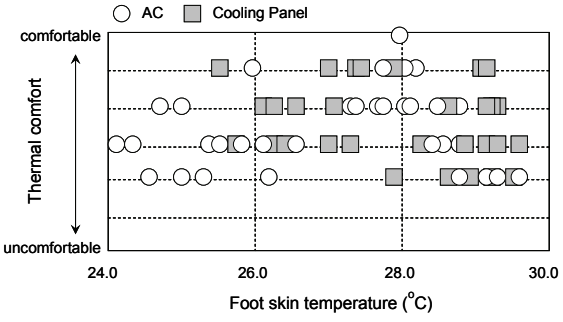


Figure 6 Dorsum pedis temperature

As shown in Fig. 5., the distribution of reported comfort levels shifted substantially toward the region of lower skin surface temperatures during the air conditioner cooling sessions compared to the radiant cooling sessions. Presumably, this was a result of the contraction of peripheral blood vessels in the hands and feet due to airstreams from the air conditioner; the consequent lowering of skin surface temperature contributed to the sense of discomfort reported by most subjects. With the radiant cooling system, in contrast, the decrease in skin surface temperature was substantially smaller, even though the radiant cooling panel was not far from the subjects [5].

2.3.3.2. Skin Surface Temperature and Total Thermal Sensation in a Given Room Temperature Range

Fig. 6. shows the thermal sensation reported by subjects plotted according to dorsum pedis temperature at room temperatures of 24 to 26°C. During the air conditioner cooling sessions, a larger proportion of subjects exhibited substantial lowering in dorsum pedis skin surface temperature and reported a feeling of coldness in the room for temperatures 26°C and below as compared to radiant cooling. This is presumably the reason that a larger proportion of subjects reported a sensation of comfort during radiant cooling than during air conditioner cooling for room temperatures of 26°C and below. In a previous study performed in the summer [6] it was possible to obtain a neutral thermal sensation and a sensation of comfort with differences between mean skin surface temperature and local skin surface temperature of 2.3°C or below and 2.7°C or below, respectively. Together with the present finding that the difference between mean skin surface temperature and dorsum pedis skin surface temperature was 3.55°C with air conditioner cooling but only 1.61°C with the proposed radiant cooling system, these results clearly show that the proposed system is more effective for achieving a neutral thermal environment than air conditioning.

3. CONCLUSIONS

The following two conclusions can be drawn from the results of this study. (i) The application of a high-radiant coating made from natural jade ore to the radiant cooling panel substantially enlarged the domain of the radiant cooling effect of the panel. (ii) Skin surface temperature measurements and thermal sensation reports showed that the proposed radiant cooling system can provide the same degree of comfort as an air conditioner at room temperatures of up to 30°C.

REFERENCES

[1] H. Senuma, H. Takeda, Journal of Environmental Engineering (Transactions of AIJ), 623 (2008) 31-38.
[2] T. Itoigawa, H. Hayama, M. Enai, K. Kikuta, H. Yamagishi, Journal of Environmental Engineering (Transactions of AIJ), 614 (2007) 79-86.
[3] D. Song, T. Kim, S. Song, S. Hwang, S.B. Leigh, Performance evaluation of a radiant floor cooling system integrated with dehumidified ventilation, Applied Thermal Engineering 28 (2008) 1299-1311.
[4] J.D.Hardy, E.F. DuBois, The technic of measuring radiation and convection. J. Nutr, 15 (1938) 461-475.
[5] N.Pellerin, A. Deschuyteneer, V. Candas, Local thermal unpleasantness and discomfort prediction in the vicinity of theroneutrality. Eur J Appl Physiol, 92 (2004) 717-720.
[6] T.Sakoi, K. Tsuzuki, S. Kato, R. Ooka, D. Song, S. Zhu, Thermal comfort, skin temperature distribution, and sensible heat loss distribution in the sitting posture in various asymmetric radiant fields. Building and Environment, 42 (2007) 3984-3999.

ISOLATION OF SULFUR-OXIDIZING BACTERIA WITH POTENTIAL APPLICATION IN SULFUR-COMPOUNDS POLLUTED ENVIRONMENTS

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Abstract

Among the pollutants of importance at world level, sulfur compounds have great relevance due to the adverse environmental impact on ecosystems and human health. A variety of industries emit these compounds to the atmosphere in different forms, and then technologies must be implemented to eliminate or reduce them. The present work proposes to obtain and characterize microbial consortia with sulfur-oxidizing activity, with the intention of integrating new proposals of biological processes related to the sulfur removal. From sulfur-environments located in Tlaxcala, Michoacán, Chiapas and the State of Mexico, samples were collected. A total of 75 microbial cultures with sulfur-tolerance capacity were obtained, finding bacteria Gram (-), Gram (+) spore forming, filamentous fungi, yeasts and actinomycetes. From these, 54 isolates were screened for their ability to oxidize sulfur. Results showed that three microbial cultures, coded as AZCT-M125-5, AZCT-M125-6 and AZCT-M125-7, had the highest sulfur-oxidizing activity. All consortia were able to oxidize elemental sulfur at concentrations from 1 to 9% causing a pH decrease to less than 1; they were able to grow over a wide range of pH (3 to 7) during their lithoautotrophic growth. Microbial cultures were identified as *Acidithiobacillus sp* by means of its 16S rRNA gen.

Keywords: *sulfur-oxidizing, chemoorganotrophic, chemolithotrophic, acidophilic, neutrophilic*

1. INTRODUCTION

Among the most common pollutants in environment, sulfur compounds are important because they cause adverse environmental impact in nature. Their release into the environment is associated with acid rain, corrosion phenomena, odor and damage to health [1]. To reduce or eliminate definitively the damage caused by these contaminants, physical and chemical processes have been implemented however most of them are expensive, so other alternative solutions must be searched to face this problem. The use or application of sulfur-oxidizing bacteria could be a possible alternative since they have the ability to oxidize inorganic sulfur compounds such as hydrogen sulfide, sulfite, sulfur, thiosulfate and several polithionates [2]. During the microbial oxidation of these compounds, microorganisms can work at acid, neutral or alkaline pHs being classified as acidophilic, neutrophilic and alkalophilic sulfur-oxidizing microorganisms [3,4]. In the case of sulfur-oxidizing prokaryotes it can found members of Archaea and Bacteria domain, obligate or facultative chemolithotrophic aerobic organisms or phototrophic anaerobic organisms [5]. Examples of these previous mentioned organisms are *Thiobacillus, Acidithiobacillus, Beggiatoa, Thiothrix, Thermothix, Thiovolum, Acidianus, Sulfolobus, Bacillus, Thioalcalimicrobium, Thioalkalivibrio* [6-9].

In the case of sulfur-oxidizing eukaryotic microorganisms, filamentous fungi predominate. They can use organic compounds as carbon and energy sources [10]. The fact to get microorganisms from natural sources allows obtaining pure or mixed well-adapted cultures to these compounds, characteristics that could have important biotechnological application to those activities related to sulfur compounds pollution such as wastewaters or hazardous wastes. The aim of the present work was to isolate sulfur-oxidizing microorganisms that came from natural or artificial sulfur-containing samples and afterwards evaluate the effect of sulfur concentration and pH on their ability to oxidize sulfur in liquid media.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Microorganisms and Culture Media

Acidithiobacillus ferrooxidans ATCC 53987, *Acidithiobacillus thiooxidans* ATCC 55020, *Sulfobacillus disulfidooxidans* ATCC 51911 and *Acidithiobacillus thiooxidans* ATCC 8085 were used as reference strains to oxidize sulfur. Different media were used for the isolation and enrichment cultures of sulfur-oxidizing bacteria: media ATCC 125 (g L^{-1}), $(NH_4)_2SO_4$, 2; $MgSO_4 \times 7H_2O$, 0.5; $CaCl_2$, 0.25; KH_2PO_4, 3; $FeSO_4$, 5 mg, sulfur 1%, pH was adjusted to 3 with sulfuric acid. Starkey media, is composed of the following salts ((g L^{-1})): $(NH_4)_2SO_4$, 3; $Na_2SO_4 10H_2O$, 3.2; KCl, 0.1; KH_2PO_4, 0.05; $MgSO_4 \times 7H_2O$, 0.5, $Ca(NO_3)_2$, 0.01. This medium also consists of trace elements (mg L^{-1}): $FeCl_3 \times 6H_20$, 11; $CuSO_4 \times 5H_2O$, 0.5; HBO_3, 2; $MnSO_4 \times H_2O$; $Na_2MoO_4 \times 2H_2O$, 0.8; $CoCl_2 \times 6H_2O$, 0.6; $ZnSO_4 \times 7H_2O$, 0.9 [11], elemental sulfur was added at 1% (w/v) as energy source. The basal media was adjusted to pH 2.5 with sulfuric acid [12]**.** Solid and liquid modified Starkey media was composed (g L^{-1}): KH_2PO_4, 3; $(NH_4)_2SO_4$, 0.2; $MgSO_4 \times 7H_2O$, 0.5; $CaCl_2 \times 2H_2O$, 0.3 and $FeSO_4 \times 7H_2O$, 0.1. This media was supplemented with 30 ppb of molybdenum [13] and 1% (w/v) of elemental sulfur. The basal medium was adjusted to pH 3 with sulfuric acid [2, 13]; Starkey thiosulfate media, instead of elemental sulfur (1%), sodium thiosulfate was added at 5 g L^{-1}. Solid media was prepared by adding agar-agar at 18 g L^{-1} [2, 14]. To obtain heterotrophic sulfur oxidizing microorganisms, dextrose (5 g/L) was added to the Starkey media [14]. The solid and liquid thiosulfate mineral media (MMT) was composed (g L^{-1}): NH_4Cl, 0.1 g, KH_2PO_4, 0.05; $MgSO_4 \times 7H_2O$, 0.02; $NaS_2O_3 \times 5H_2O$, 0.4 and 1 g of yeast extract, the pH was adjusted to 3 with sulfuric acid [15]. The media 9K, is composed (g L^{-1}): KH_2PO_4, 0.4; $CaCl_2 \times 2H_2O$; $MgSO_4 \times 7H_2O$, 0.4; $(NH_4)_2SO_4$, 0.4; $FeSO_4 \times 7H_2O$, 33.3. The basal media was adjusted to pH 1.5-2 with sulfuric acid [16-18].

2.1.2. Microorganisms Source

Both liquid and solid samples were collected from environmental or artificial sites with high sulfur-content. Samples came from Chiapas, Tlaxcala, Michoacán and Mexico State. Samples were collected in sterile plastic vials, stored at room temperature and transported to laboratory for analysis. In the case of solid samples previous to use, these were crushed and ground in a mortar to reduce particle size and homogenized. Liquid samples were used directly without any treatment.

2.1.3. Isolation in Solid and Liquid Media

For the isolation of sulfur-oxidizing microorganisms, enrichment culture was performed using 5 g of solid or 5 mL of liquid sample, placed in 125 mL Erlenmeyer flasks containing 30 mL of Starkey media containing sulfur at 1%, Starkey thiosulfate media, MMT media, ATCC 125 media, 9K media and MSM media. Inoculated flasks were incubated at 30 ºC, 140 rpm for 7 days or until turbidity development, which was related to microbial growth. Plates were incubated at 30 ºC during 7 days. Those flasks that showed turbidity, series of decimal dilutions were prepared from 10^{-2} to 10^{-4} and each dilution (aliquot of 0.1 mL) was spread on plates containing Starkey-sulfur solid media, Starkey thiosulfate media, mineral thiosulfate media and ATCC media by the dispersion method.

Petri dishes were then incubated at 30°C until observation of microbial growth [12]. The perfectly isolated colonies were selected based on a different colonial morphology and then were plated in previous mentioned media to obtain pure cultures. A bright-field microscope was used for observation of colonies purity by means of Gram staining and microculture for filamentous fungi. Based on microbial growth Starkey modified mineral media was selected for future studies.

2.1.4. Evaluation of Sulfur-Oxidizing Ability and Microbial Growth

Inocula of ATCC strains and interesting microbial cultures (54 pure and mixed cultures) were prepared in 50 mL antibiotic-type bottles containing 10 mL of Starkey modified mineral media, the inoculated cultures were left for 6 days for adequate growth, then inoculum of 10% was transferred to fresh media to test their sulfur-oxidizing ability in batch culture, using 125 mL Erlenmeyer flasks containing 30 mL of modified Starkey media (elemental sulfur at 1%). Flasks were incubated at 30ºC, 140 rpm during 7 days. After this period, sulfur oxidation was evaluated determining the SO_4^{2-} concentration in supernatant according the NMX-k-436-1977 method. The production of sulfuric acid was evaluated by pH measurement. Microbial growth was evaluated by Bradford method [19].

2.1.5. Effect of Sulfur Concentration

Experimental sets were prepared to determine the maximum sulfur concentration that can be oxidized by microorganisms in 125 mL Erlenmeyer flasks containing 30 mL of Starkey modified media (pH 3),

and different sulfur concentrations (1,3,4,5,7 and 9% w/v), an inoculum of 10% of selected microorganisms was used in each experimentation (AZCT-M125-5, AZCT-M125-6, AZCT-M125-7 and *Acidithiobacillus ferrooxidans* ATCC 53987). Erlenmeyer flaks were incubated at 30°C and 140 rpm during 7 days. Control flasks with media containing different sulfur concentrations but without inocula were included. After this period, the microbial oxidation of elemental sulfur was evaluated by the production of SO_4^{2-} in supernatant. Also, pH was determined at the final of experiments.

2.1.6. Effect of pH on Microbial Oxidation of Elemental Sulfur

An inoculum was prepared as it was mentioned previously then, 125 mL Erlenmeyer flasks containing 30 mL of Starkey modified media added with sulfur at 1%. Experimental sets were prepared as follows, Starkey modified mineral media was adjusted to different pH (3, 4, 5, 6 and 7), inoculated (10%) and incubated at 30 °C, 140 rpm during 7 days. Microbial cultures coded as AZCT-M125-5, AZCT-M125-6, AZCT-M125-7 and *Acidithiobacillus ferrooxidans* ATCC 53987 were used in the experiments. Controls with Starkey media at different pHs but not inoculated were also included. The oxidation of elemental sulfur was evaluated by means of SO_4^{2-} production after the incubation period.

2.1.7. Amplification and Sequencing of 16SrRNA Gen

The biomass of 30 mL of microbial cultures were harvested by centrifugation at 4000 rpm for 5 min, the cellular package was washed with 1 mL of sterile and deionized water and centrifuged at 4000 rpm for 5 min. Cell lysis was performed by chemical breakdown using 10 mM of Tris-HCl pH 8.0, 1 mM EDTA, 10 mM NaCl, SDS at 1% and mechanically with glass beads (0.5 g). Later, the mixture was vortexed 8 pulses of 3 sec and left to stand in ice for periods of 30 sec. Then 200 µL of a phenol-chloroform-isoamyl alcohol solution in a ratio of 25:24:1 was added. It was vortexed with 200 µL of TE buffer, the resulting mixture was centrifuged at 14000 rpm for 5 min. The supernatant was recovered in a microtube, which was added with 1 mL of absolute ethanol and mixed by inversion. The above mixture was then cooled for 20 min at -20 ºC, then centrifuged at 14000 rpm for 5 min. The ethanol was removed and washing was performed with 1 mL of ethanol at 70%. The DNA sample was dried in a laminar flow hood at room temperature.

DNA sample was suspended in 50 µL of sterile and deionized water. The presence and quality of DNA was determined by chromatographic separation on agarose gel at 1% [22]. By means of PCR a 1540 bp (base pairs) fragment was amplified, corresponding to the 16S rRNA of the consortia members under study, using universal primers 8 (right: gcg gat ccg cgg ccg ctg cag agt ttg atc ctg gct cag) and 1492 (reverse ggc tcg agc ggc cgc ccg ggt tac ctt gtt acg act t) previously recommended [23]. A thermal cycler TC-3000 (Techne) was used. Every 50 µL contain 2 µL of dNTP (10 mM), 5 µL 10X buffer solution, 6 µL $MgCl_2$ (50 mM), 2 µL of each primer (10 pM), 2 µL of DNA sample (50-100 ng), 1 µL Taq polymerase (5 U) and sufficient purified water to complete the final volume. DNA amplification was carried under the following conditions, initial denaturalization at 94 °C for 5 min; 30 cycles of 92 °C for 1 min, 55 °C for 1 min, and 72 °C for 1 min. 16S rRNA of all samples were purified using commercial reagent kit QIAquick gel extraction kit, Qiagen. The sequencing of the purified PCR products was performed with an automated sequencer ABI PRISM 310 Genetic Analyzer PE (Applied Biosystems) at LANGEBIO-Irapuato.

2.2. Results and Discussion

2.2.1. Isolation of Sulfur-Oxidizing Microorganisms

As a result of the isolations in solid and liquid media, 75 isolates were obtained between pure and mixed cultures; microbial diversity was composed by bacteria, actinomycetes, yeasts and filamentous fungi. The predominant microbial group were Gram (–) small bacilli, Gram (+) non-spore forming, and spore forming bacilli and finally actinomycetes with and without mycelia fragmentation. Respect to the resulting microbial groups, it has been reported species belonging to the genera *Thiobacillus, Thiomicrospira* and *Thiosphaera,* and other species such as *Paracoccus, Xanthobacter, Alcaligenes* and *Pseudomonas* which have a chemolithotrophic growth in presence of inorganic sulfur [9], also species related to the genera *Acidithiobacillus*, *Sulfobacillus, Bacillus* and Archaea such as *Ferroplasma* [6-8] and actinomycetes such as *Streptomyces* [24]. In the case of sulfur-oxidizing eukaryotic organisms, most of the isolates corresponded to yeasts with variable size and form. Some genera of yeasts such as *Debaryomyces, Saccharomyces* and *Rhodotorula* have been reported as sulfur-oxidizing microorganisms [10]. In the case of filamentous fungi, some of them were identified as *Aspergillus sp, Aspergillus niger, Penicillium sp, Geotrichum sp, Alternaria sp, Rhizopus sp* and *Mucor.* For the isolation of this group, in the culture media was added dextrose at 0.5% since they are considered chemoorganotrophs. Some

reports mention the ability to oxidize inorganic sulfur compounds by some fungi such as *Alternaria, Aureobasidium, Penicillium* and *Fusarium solani* [10].

2.2.2. Oxidation of Sulfur Compounds by Isolates

Among the 75 isolates, 54 isolates (those able to grow in media added with sulfur) were evaluated by their ability to oxidize elemental sulfur to sulfates. Filamentous fungi were spread in the Starkey modified media added with elemental sulfur 1% and dextrose at 0.5%, the values of produced sulfates by this microbial group were low, in the order of 4 to 11 mg L^{-1} (data not shown). In the case of bacteria, all grew autotrophically using the elemental sulfur as energy source; seven of them were those that showed the higher levels of sulfates in supernatant, final product of the sulfur oxidation. Fig. 1. shows the 7 isolates which were coded as AZCT-M125-1, AZCT-M125-2, AZCT-M125-5, AZCT-M125-6, AZCT-M125-7, AZCT-M125-9 and AZCT-M125-13 which sulfates values were in the order of 190 to 380 mg/L, that is, they showed the best ability to oxidize sulfur since there is a direct correlation between oxidized sulfur and produced sulfates [25]**,** these results were similar to those obtained for the strain *Acidithiobacillus thiooxidans* ATCC 55020 which sulfate production was around 330 mg L^{-1}. Strains *Acidithiobacillus ferrooxidans* ATCC 53987 and *Acidithiobacillus thiooxidans* ATCC 8085 presented a sulfate production lower than 53 mg L^{-1}. Regarding to pH, the isolates provoked a decrease in pH values reaching values lower than 1.6 due to the production of sulfuric acid.

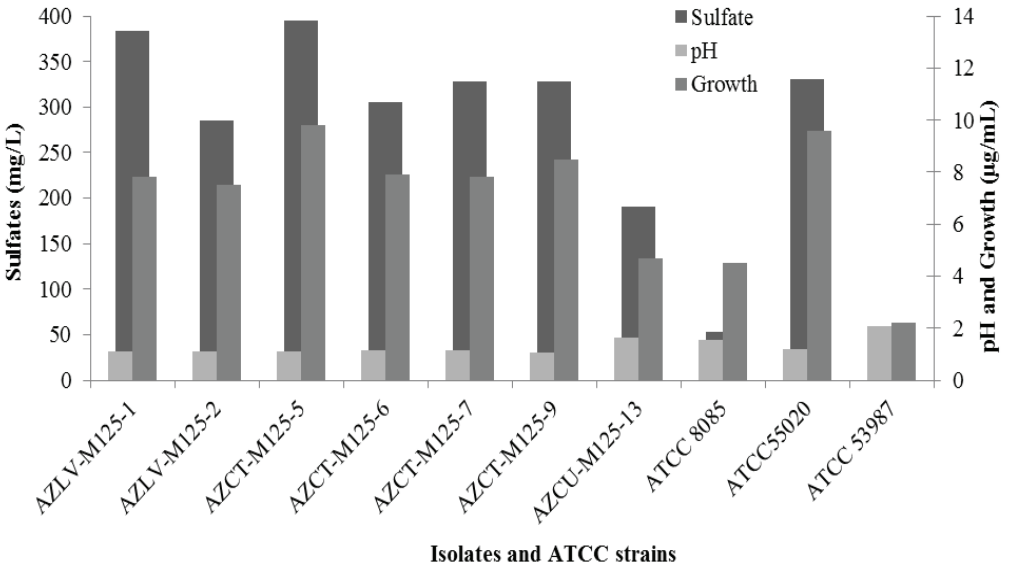


Figure 1. Production of sulfates, pH and microbial growth (protein) by the best sulfur-oxidizing isolates after 7 days of incubation at 30 °C, 140 rpm in modified Starkey media plus elemental sulfur 1%.

2.2.3. Evaluation of the Microbial Sulfur Oxidizing Ability at Different Sulfur Concentrations

Among the best seven sulfur-oxidizing isolates and reference strains assayed, the isolates coded as AZCT-M125-5, AZCT-M125-6 and AZCT-M125-7 showed the highest sulfate production and also they were able to decrease the pH at higher extent. Fig. 2. shows the values of produced sulfates by these isolates, founding a maximum sulfate production of 885 mg L^{-1} for the isolate AZCT-M125-5 at a sulfur concentration of 7%. Isolates AZCT-M125-6 and AZCT-M125-7 were able to produce sulfates at an extent of 687 and 470 mg L^{-1} respectively at a sulfur concentration of 9%. For reference strains, only *Acidithiobacillus ferrooxidans* ATCC 53987 showed a sulfate production of 200 ml L^{-1} at a sulfur concentration of 5%. All studied isolates were able to produce four or five times more sulfate than *Acidithiobacillus ferrooxidans* ATCC 53987.

According with data, the isolate AZCT-M125-5 showed higher levels of sulfur transformation or sulfur oxidation, which corresponded to 2.5 to 3 g at concentrations of 4 to 9%, that is, a sulfur transformation to sulfates of 60%. Regarding pH, it can be observed (Fig. 3.) that at higher sulfur concentrations major decreases in pH, where lower values corresponded to 0.6.

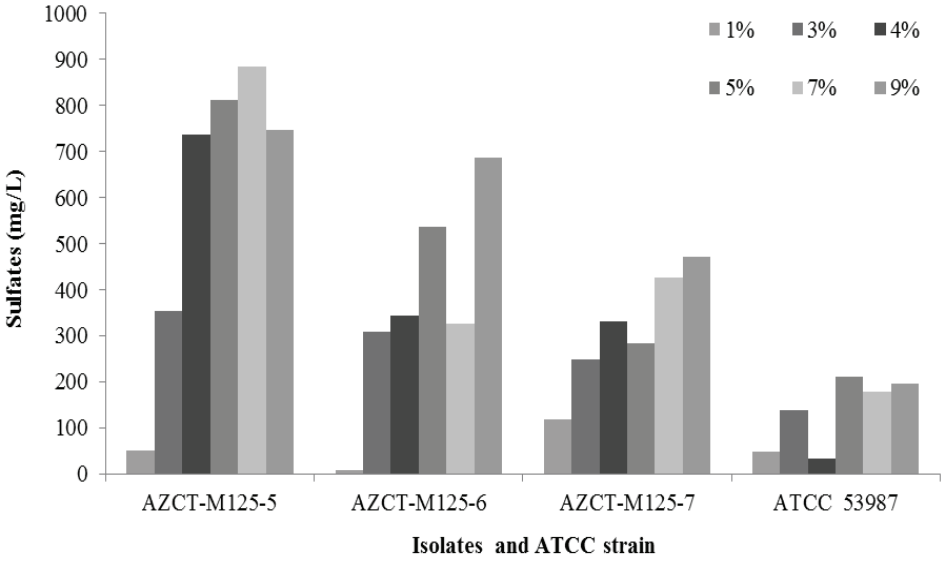


Figure 2. Production of sulfates at different sulfur concentrations by isolates after 7 days of incubation at 30 °C, 140 rpm in modified Starkey media plus elemental sulfur 1%.

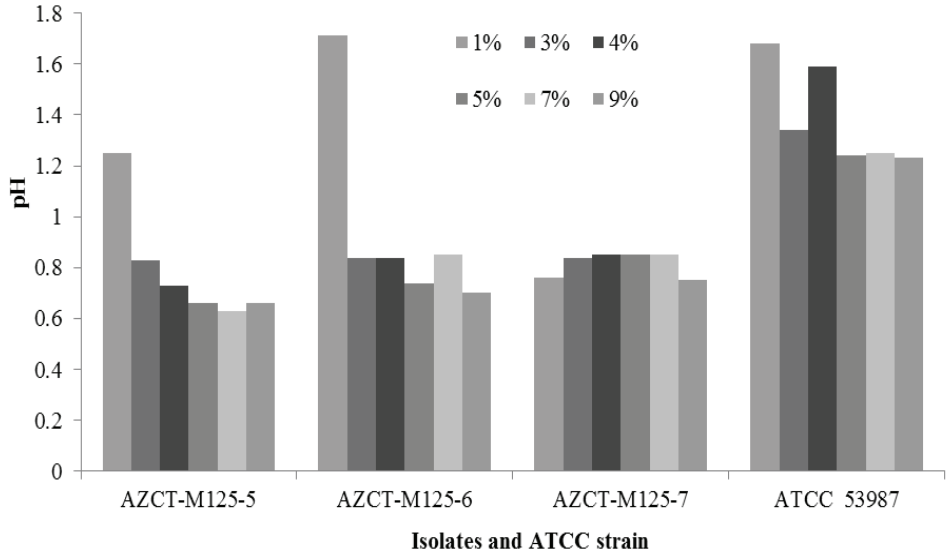


Figure 3. Changes in pH during the evaluation of sulfate production at different sulfur concentrations by isolates after 7 days of incubation at 30°C, 140 rpm in modified Starkey media plus elemental sulfur 1%.

To oxidize sulfur, first of all, bacteria are adsorbed to the insoluble sulfur particles, which increment the oxidation rate and acidification by sulfur-oxidizing bacteria. It has been reported that at concentrations of 0.5 to 5 g L^{-1} the elemental sulfur increases the oxidation rate, reduce pH and produce sulfates [26], however these reported concentrations are lower than those assayed in our study. Isolates in this study can grow perfectly at higher sulfur concentrations such as 9%.

2.2.4. Effect of pH on Microbial Sulfur Oxidation

To know the influence of pH in the elemental sulfur microbial oxidation, different pH values and the best sulfur oxidizing microorganisms were evaluated in Starkey modified media. In the Fig. 4. it is showed that all microorganisms were able to produce sulfates, as a result of oxidation of elemental sulfur, then producing sulfuric acid. However each isolate presented a different behavior respect to pH. The isolate AZCT-M125-5 showed a higher sulfate production at pH 7, reaching a production of 280 mg L^{-1} of sulfates, the isolate AZCT-M125-6 produced 180 mg L^{-1} at pH 4 and the isolate AZCT-M125-7 at pH 6 had a production of 190 mg L^{-1}. For the case of acidophilic sulfur-oxidizing bacteria it has been observed a good growth at pH within 2.5 to 6.5 [15, 16] with an optimum pH 4 for sulfur oxidation [3], however

some acidophilic strains can grow at values lower than pH 3 [16]**.** Based on this behavior, sulfur-oxidizing bacteria in this study can be classified as acidophilic, neutrophilic and alcalophilic sulfur-oxidizing [3, 4]. Then, isolates coded as AZCT-M125-6 and AZCT-M125-7 can be classified as acidophilic sulfur-oxidizing, and the isolate AZCT-M125-5 as neutrophilic sulfur-oxidizing. Last strain can be also used in the biodegradation of cement biodegradation such as *Halothiobacillus neapolitanus* and *Thiomonas intermedia* [27]. In the case of acidophilic sulfur-oxidizing, they can be used in the leaching of heavy metals such as copper, nickel, cobalt, zinc and molybdenum [12, 28-30], in the desulfurization of charcoal [3] or the sulfur elimination from polluted samples.

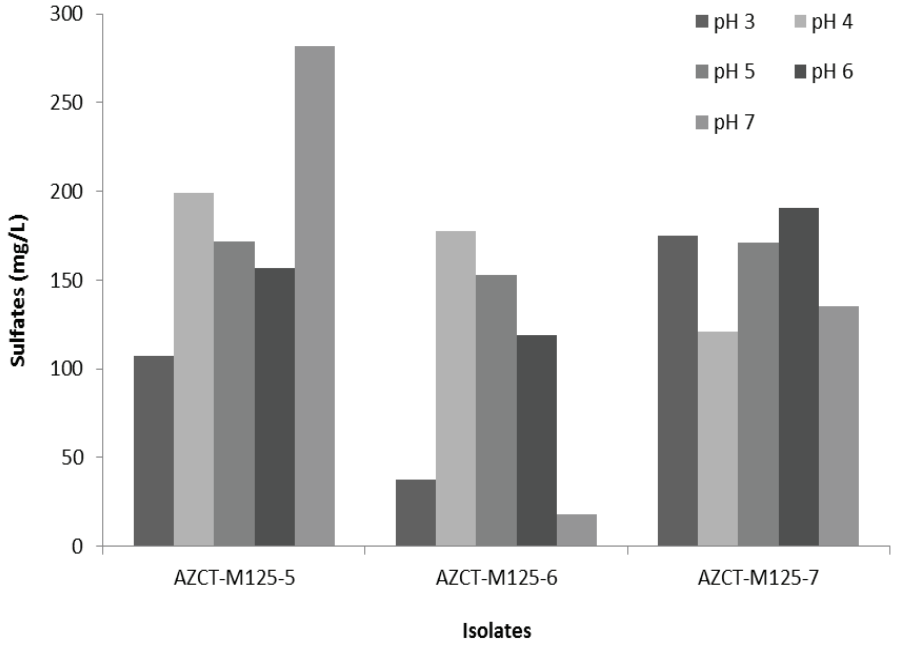


Figure 4. Effect of pH on the sulfate production by isolates after 7 days of incubation at 30 °C, 140 rpm in modified Starkey media plus elemental sulfur.

2.2.5. Analysis of the 16S rRNA Gen Sequence and Microbial Culture Identification

The resulting sequences of the cultures coded as AZCT-M125-5, AZCT-M125-6 and AZCT-M125-7 were manually edited with the FinchTV program version 1.4.0 (Geospiza 2004-2006) and afterwards were submitted to a search of similar sequences in the GenBank by means of the BLASTN program version 2.2.3 [31] in the web page of NCBI (http://www.ncbi.nlm.nih.gov/). From the provided information of sequences, it was possible to taxonomically locate the cultures as follows: AZCT-M125-5 and AZCT-M125-6 as *Acidithiobacillus* sp and AZCT-M125-7 as *Acidithiobacillus thiooxidans.* The microbial culture coded as AZCT-M125-5 had a 96% of identity with the genus *Acidithiobacillus* while AZCT-M125-6 had a 99% of identity with the species *Acidithiobacillus thiooxidans* and *Acidithiobacillus caldus*. Finally the culture coded as AZCT-M125-7 had a high degree of identity (99%) with *Acidithiobacillus thiooxidans.*

3. CONCLUSIONS

Two acidophilic and one neutrophilic sulfur-oxidizing bacteria were isolated from natural and artificial environmental samples. Microbial cultures coded as AZCT-M125-5, AZCT-M125-6 and AZCT M125-7 belong to genus *Acidithiobacillus.* These microorganisms were able to grow chemolithotrophically and oxidize elemental sulfur at concentration within 1 to 9%, and pHs of 3 to 7.

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REFERENCES

[1] S. McEldowney S, D. Hardman, S. Waite, *Pollution: Ecology and Biotreatment*. Logman Sci. & Tech., Singapure. (1993) 193-230.

[2] Y. Konishi, S. Asai S, N. Yoshida, Growth Kinetics of *Thiobacillus thiooxidans* on the Surface of Elemental Sulfur. Appl. Environ. Microbiol. 61 (1995). 3617-3622.

[3] J.T. Pronk, R. Meulenberg, W. Hazeu, P. Bos, J. G. Kuenen, Oxidation of reduced inorganic sulphur compounds by acidophilic thiobacilli. Microbiol. Rev. 75 (1990) 293-306

[4] D. Y. Sorokin, J. G. Kuenen, Haloalkaliphilic sulfur-oxidizing bacteria in soda lakes. FEMS Microbiol. Rev. 29 (2005) 685–702.

[5] C.G Friedrich, D. Rother, F. Bardischewsky, A. Quentmeier, J. Fischer, Oxidation of Reduced Inorganic Sulfur Compounds by Bacteria: Emergence of a Common Mechanism?. Appl. Environ. Microbiol. 67 (2001) 2873-2882.

[6] S. Dufresne, J. Bousquet, M. Boissinot, R. Guay, *Sulfobacillus disulfidooxidans* sp. nov., a New Acidophilic, Disulfide-Oxidizing, Gram-Positive, Spore-Forming Bacterium. Int. J. Syst. Bacteriol. 46(1996) 1056-1064.

[7] O. Naoko, G. Mariekie, K. B. Hallberg, D. B. Johnson, Enumeration and Characterization of Acidophilic Microorganisms Isolated from a Pilot Plant Stirred-Tank Bioleaching Operation. Appl. Environ. Microbiol. 69 (2003) 936-1943.

[8] G. I. Karavaiko, T. I. Bogdanova, T. P. Tourova, T. F. Kondrat'eva, I. A. Tsaplina, M. A. Egorova, E. N. Krasil'nikova, L. M. Zakharchuk, Reclassification of '*Sulfobacillus thermosulfidooxidans* subsp. *thermotolerans*' strain K1 as *Alicyclobacillus tolerans* sp. nov. and *Sulfobacillus disulfidooxidans* Dufresne et al. 1996 as *Alicyclobacillus disulfidooxidans* comb. nov., and emended description of the genus *Alicyclobacillus*. Int J Syst Evol Microbiol. 55 (2005) 941–947.

[9] R. Vidyalakshmi, R. Paranthaman and R. Bhakyaraj. Sulphur Oxidizing Bacteria and Pulse Nutrition - A Review. World J. Agricultural Sci. (2009) 270-278.

[10] X. S. Li, T. Sato, Y. Ooiwa, A. Kusumi, J. D. Gu, Y. Katayama, Oxidation of Elemental Sulfur by *Fusarium solani* Strain THIF01 Harboring *Endobacterium Bradyrhizobium* sp. Microb Ecol. 60 (2010) 96–104.

[11] M. Dopson, E. B. Lindström. Potential Role of *Thiobacillus caldus* in Arsenopyrite Bioleaching. Appl. Environ. Microbiol. 65 (1999) 36-40.

[12] Q. G. Zhou, F. Bo, Z. H. Bo, L. Xi, G. Jian, L. F. Fei, C. X. Hua, Isolation of a strain of *Acidithiobacillus caldus* and its role in bioleaching of chalcopyrite. World J. Microbiol. Biotechnol. 23 (2005) 217–1225.

[13] S. Takakuwa, T. Nishiwaki, K. Hosoda, N. Tominaga, H. Iwasaki, Promoting effect of molybdate on the growth of a sulfur-oxidizing bacterium, *Thiobacillus thiooxidans*. J. Gen. Appl. Microbiol, 23 (1977) 163-173.

[14] R. Vidyalakshmi, R. Sridar, Isolation and characterization of sulphur oxidizing bacteria. J. Culture Collections. 5 (2007) 73-772.

[15] H. Ohba, N. Owa, Isolation and identification of sulfur-oxidizing bacteria from the buried layer containing reduced sulfur compound of a paddy field on Sado Island in Niigata Prefecture. Bull. Facul. Agric. Niigata Univ. 58 (2005) 55-61.

[16] R. Jamshid, A. Azimi, M. H. Ardabili, B. Nasernejad, M. Arabnezhad, M. J. Hajipour, Isolation and Characterization Two Novel Indigenous Acidophilic Species Involved Copper Extraction (Bioleaching) from the Aliabad Copper Mine in Iran. Int. J. Chem. Engineer. Res., 5 (2009) 143–154.

[17] C. L. Corrales, C. L. Sánchez L, S. P. Cortes, S. A. León, S. V. Quintero, Z. J Díaz,. Estudios piloto de aislamiento y fenotipificación de bacterias que participan en los procesos de biolixiviación en zonas mineras del departamento de boyaca. NOVA-Publicación Científica, 4 (2006) 57-63.

[18] H.W. Ryu, Y. K. Chang, S. D. Kim, Microbial coal desulfuration in an airlift bioreactor by sulfur-oxiding bacterium *Thiobacillus ferrooxidans*. Fuel Process. Technol. 36 (1993) 267-275.

[19] M. Bradford, A Rapid and Sensitive Method for the Quantitation of Microgram Quantities of Protein Utilizing the Principle of Protein-Dye Binding. Anal. Biochem. 72 (1976) 248 254.

[20] D. Gevertz, J. A. Telang, G. Voordouw, E. J. Jenneman, Isolation and Characterization of Strains CVO and FWKO B, Two Novel Nitrate-Reducing, Sulfide-Oxidizing Bacteria Isolated from Oil Field Brine. Appl. and Environ. Microbiol. 66 (2000) 2491-2501.
[21] Y. K. Fujimura, H. Kuraishi, Characterization of *Thiobacillus novellus* and its thiosulfate oxidation. J. Gen. Appl. Microbiol. 26 (1980) 357-367.
[22] R. Sambrook, *Molecular cloning a laboratory manual* (3a Edición ed.). China: Cold Spring Harbor laboratory press. (2001).
[23] D. Relman, Universal bacterial 16S rDNA amplification and sequencing. In D. Persing, T. Smith, C. Tenover, T. White, *Diagnostic molecular microbiology: principles and applications* (pp. 489-496). NY: American Society of Microbiology, 1993.
[24] S. Yagi, S. Kitai, T. Kimura, Oxidation of Elemental Sulfur to Thiosulfate by *Streptomyces*. Appl. Microbiol. 22 (1971) 157-159.
[25] R.D. Tyagi, J.F. Blais, L. Deschenes, P. Lafrance, J. P. Villeneuve, Comparison of microbial sulfuric acid production in sewage sludge from added sulfur and thiosulfate. J. Environ. Qual. 23 (1994) 1065-1070.
[26] S. Y. Chen, J.G. Lin, Bioleaching of heavy metals from contaminated sediment by indigenous sulfur-oxidizing bacteria in an air-lift bioreactor: effects of sulfur concentration. Water Res. 38 (2004) 3205–3214.
[27] O. Aviam, B. N. Gabi, Y. Zeiri, Accelerated Biodegradation of Cement by Sulfur-Oxidizing Bacteria as a Bioassay for Evaluating Immobilization of Low-Level Radioactive Waste. Appl. Environ. Microbiol. 70 (2004) 6031-6036.
[28] L. C. Chan, X. Y. Gu, J. W. C. Wong, Comparison of bioleaching of heavy metals from sewage sludge using iron- and sulfur-oxidizing bacteria. Adv. Environ. Res. 7 (2003) 603–607.
[29] T. Sugio, M. Wakabayashi, T. Kanao, F. Takeuchi, Isolation and Characterization of *Acidithiobacillus ferrooxidans* Strain D3-2 Active in Copper Bioleaching from a Copper Mine in Chile. Biosci. Biotechnol. Biochem. 72 (2008) 998–1004.
[30] B. Fu, H. Zhou, K. Zhang, G. Qiu, Bioleaching of chalcopyrite by pure and mixed cultures of *Acidithiobacillus* spp. and *Leptospirillum ferriphilum*. Internat. Biodet. Biodeg. 62 (2008) 109-115.
[31] S. Altschul, T. Madden, A. Schäffer, J. Zhang, Z. Zhang, W. Miller, *et al* Gapped BLAST and PSI-BLAST: a new generation of protein database search programs. Nucleic Acids Res. 25 (1997) 3389-3402.

APPLICATION OF FOUNDRY WASTE FOR ADSORPTION OF HEXAVALENT CHROMIUM

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Abstract

It is well known if the amount of heavy metals in liquid waste is higher than allowed, there is a potential danger for the health of humans and other living organisms. They can also cause different troubles in technological processes. That is why monitoring and controlling the content of heavy metals in liquid waste of industrial system is very important.

Furthermore, foundries also have great difficulties with the disposal of waste material which contain harmful substances. Safe disposal of waste material and dangerous substances is the task equally important as maintaining the quality and profit. The aim must be to reduce the amount of waste through regeneration or some other applications.

The purpose of this paper is to examine adsorption of Cr (VI) ions from water solution on the non-toxic foundry waste material. The result showed that foundry waste material can be used for adsorbing of Cr (VI) ions.

Keywords: *foundry waste, Cr (VI) ions, adsorption*

1. INTRODUCTION

Chromium and its compounds are toxic metals introduced into natural water from a variety of industrial wastes. They cause severe environmental and public health problems. The major sources are from leather tanning, textile dyeing, electroplating, and metal finishing industries. The hexavalent form of chromium is considered to be a group "A" human carcinogen because of its mutagenic and carcinogenic properties. It leads to liver damage, pulmonary congestion, edema, and causes skin irritation, resulting in ulcer formation [1].

In Croatia, the max limit for the discharge of Cr (VI) into inland surface water and public drainage system is 0.1 mg L^{-1} [2]. A wide range of physical and chemical processes are available for the removal of Cr (VI) from waste water, such as electro-chemical precipitation, ultra-filtration, ion exchange, electro-dialysis, reverse osmosis, chemical precipitation, and adsorption [3-5]. The major drawbacks with these processes are high cost, toxic sludge generation or incomplete metal removal [6]. Comparison of all techniques shows that more economically favorable alternative for the removal of metals from aqueous solutions. Activated carbons are widely used because of their high adsorption abilities for a large number of heavy metal ions. However, the price of activated carbon is relatively high, which limits their usage. This has led many researchers to search for low cost adsorbents such as anode dust, electric furnace slag and steel shot and biosorbents [7-10]. In this study, waste mould sand, a byproduct of the gray iron foundry, was used as a low-cost adsorbent for treating wastewater contaminated with Cr (VI) ions. Thus, re-using foundry waste mould sand as adsorbents is attractive in terms of sustainable development, and also allows the foundry industry to accrue savings through reduced disposal cost [11].

2. ELABORATION

2.1. Materials and Methods

Used waste mould sand is a non-toxic waste material from the gray iron foundry. For analysis, a representative sample of waste mould sand was obtained by a quartering technique. It was dried at 105 °C for 4 hours. The chemical composition of the sample was determined by atomic absorption spectroscopy. A series of Erlenmeyer's flasks containing 1 g waste mould sand in 50 mL solution of Cr (VI) ions with different initial concentration (50-500 mg Ll^{-1}) were sealed until equilibrium was obtained. Then the adsorbent was removed by filtration. The concentration of Cr (VI) ions was determined by atomic adsorption spectrometer. Temperature of Cr (VI) solutions was 293, 303 and 313 °C.

The adsorption isotherm was tested in accordance with the following models:

Freundlich model: $$\ln q_e = \ln K_F + 1/n \ln c_e \quad (1)$$

Langmuir model: $$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot c_e} + \frac{1}{q_m} \quad (2)$$

Eadie-Hoffstee model: $$q_e = q_m - \frac{q_e}{K_E c_e} \quad (3)$$

Temkin model: $$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln c_e \quad (4)$$

where q_e is equilibrium concentration of Cr (VI) ions on adsorbent (mg g^{-1}), c_e is the equilibrium concentration of Cr (VI) ions in solution (mg L^{-1}), q_m is the adsorption capacity (mg g^{-1}), T is temperature (K), R is universal gas constant (J $mol^{-1}K^{-1}$), K_F, K_L, K_E, K_T, b_T are adsorption constants. The free energy of an adsorption, considering the adsorption equilibrium constant K_L is given by the following equation:

$$\Delta G° = -RT \ln K_L \quad (5)$$

Other thermodynamic parameters were calculated using the following equation:

$$\ln K_L = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (6)$$

$\Delta G°$ is standard free energy change (J mol^{-1}), $\Delta H°$ is enthalpy change (kJ mol^{-1}), $\Delta S°$ is entropy change (J $mol^{-1}K^{-1}$), K_L is Langmuir constant (L mg^{-1}).

Mineralogical composition and information about the chemistry of the surface were investigated by means of X-ray diffraction analysis, XRD, and Fourier transformation infrared, FTIR, spectroscopy. XRD analysis was performed on instrument using Cu Kα radiation, operated at 40 kV and 30 mA. Diffraction measurement was conducted within the 2θ range of 5–75° with 0.04° step and in 1 s/step. The FTIR spectra were recorded on instrument equipped with an attenuated total reflection (ATR) accessory with a diamond crystal. Each spectrum from 4000 to 400 cm^{-1} was averaged over 16 scans at 4 cm^{-1} resolution.

2.2. Results and Discussion

Table 1 present chemical composition of examined waste mould sand. Mineralogical composition of the waste mould sand was determined using the X-ray diffraction method (XRD method). Fig. 1. shows the result of the diffraction analysis.

Table 1. Chemical and mineralogical composition of waste mould sand

Composition	SiO_2	Fe	Al_2O_3	Ca	C	Mg	Cr	Mn
wt. %	96.1	2.57	0.85	0.31	0.12	0.03	0.009	0.008

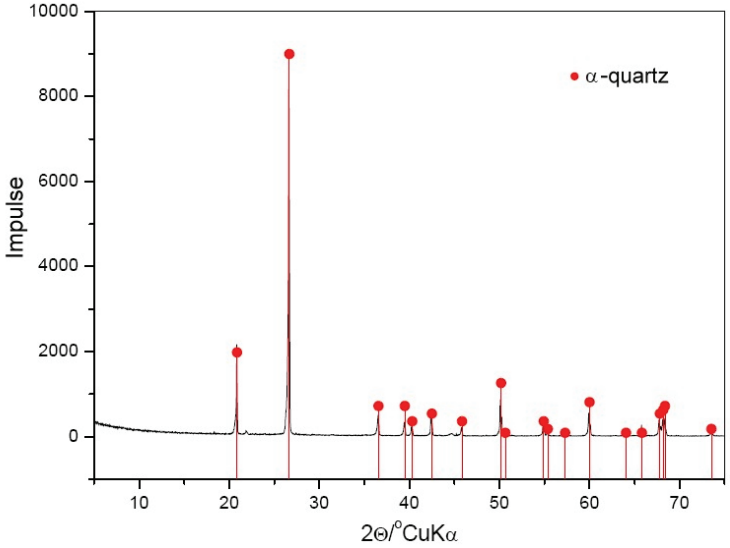


Figure 1. XRD analysis of waste mould sand

Used waste mould sand is mixture of silica sand, clay binder and organic carbon source (typically coal dust) that are used to make moulds for gray iron casting. As a reactive medium, the coal dust provides organic carbon for adsorption, and the iron particles act as a reducing agent.

2.2.1. Adsorption isotherms

Fig. 2. shows experimental results of Cr (VI) ions adsorption on waste mould sand at three different temperatures, at 293, 303 and 313 K.

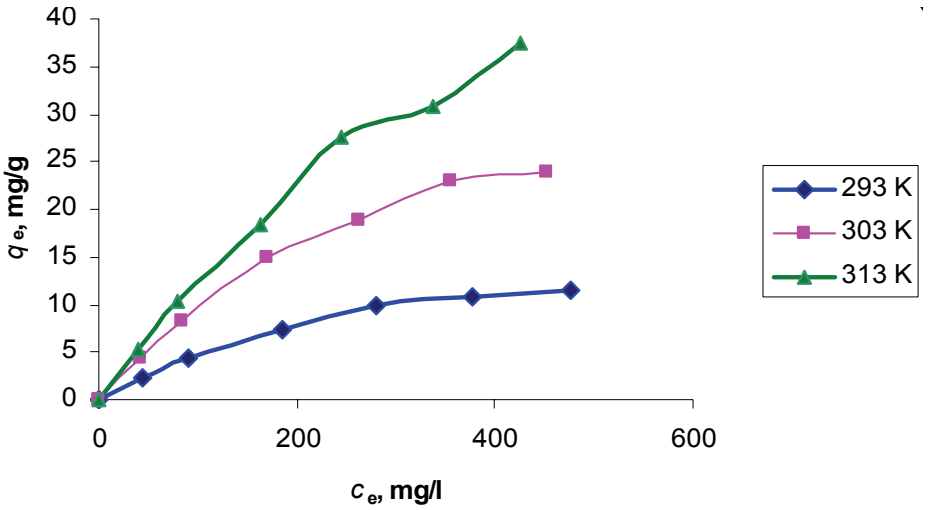


Figure 2. Adsorption isotherms for system Cr (VI) / waste mould sand at 293, 303 and 313 K

It can be seen that the adsorption of Cr (VI) ions increases with increasing temperature. The obtained adsorption capacity for Cr (VI) ions is a good indicator of waste mould sand potential for use in aqueous adsorption systems. This phenomenon probably comes from the reasons that the increase in temperature result in increases the mobility of chromium ions in aqueous solution and a better ability to bind these ions on the surface of the waste molding sand.

Fig. 3. shows FTIR analysis of waste mould sand before and after Cr (VI) adsorption.

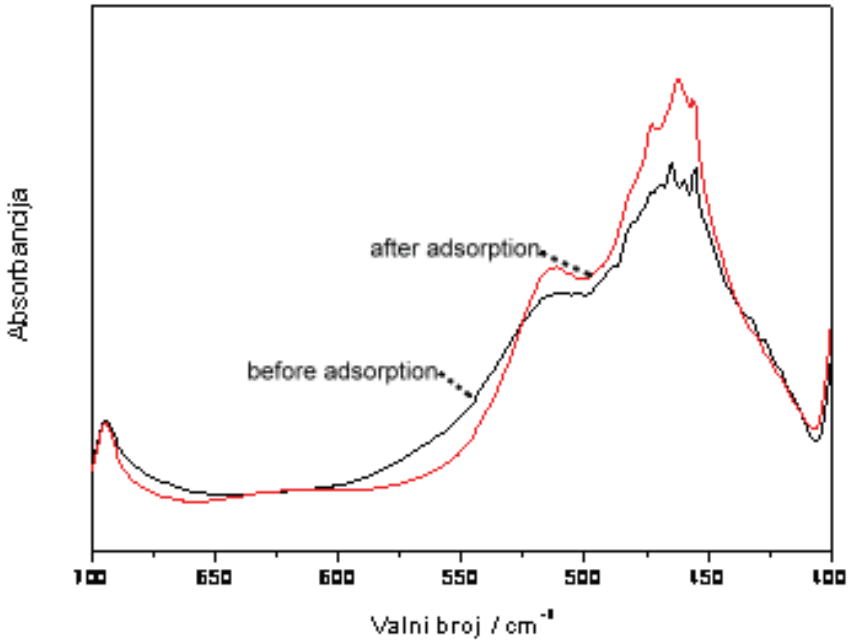


Figure 3. FTIR analysis of waste mould sand before and after adsorption of Cr (VI) ions

FTIR analysis provides information on the chemistry of the surface of the tested samples. The characteristic bands which are used for identification of Cr_2O_3 phase are in the 650-300 cm^{-1} [12,13]. Figure 3 shows visible peaks at 625 and 475 cm^{-1} compared to the original sample, which confirmed that

there was a binding Cr (VI) ions on the waste mold sand. These data are also a good indicator of waste mould sand potential for use in aqueous adsorption system.

For understanding and interpreting the binding of toxic metals on the adsorbent it is necessary to carry out the equilibrium analysis to determine the parameters which significantly affect the balance of individual adsorption processes. In this paper, Langmuir, Freundlich, Eadie-Hoffstee and Temkin model were used for analysis of equilibrium binding of Cr (VI) ions on waste mould sand. Figs. 4.-7. show the adsorption isotherms.

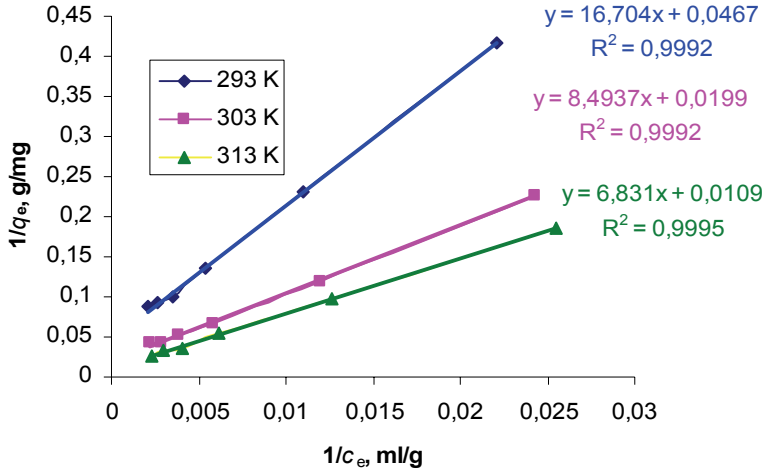


Figure 4. Langmuir isotherms for system Cr (VI) / waste mould sand at 293, 303 and 313 K

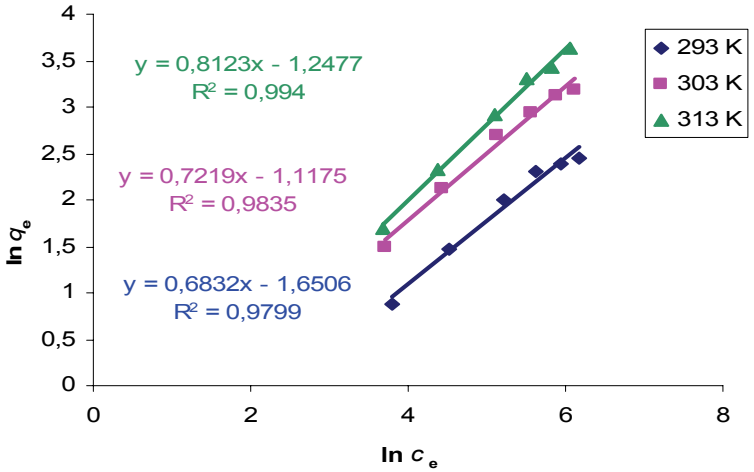


Figure 5. Freundlich isotherms for system Cr (VI) / waste mould sand at 293, 303 and 313 K

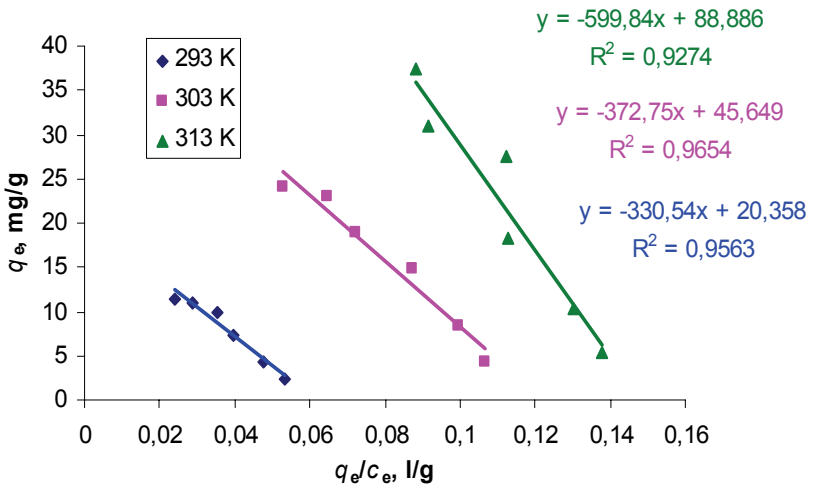


Figure 6. Eadie-Hoffstee isotherms for system Cr (VI) / waste mould sand at 293, 303 and 313 K

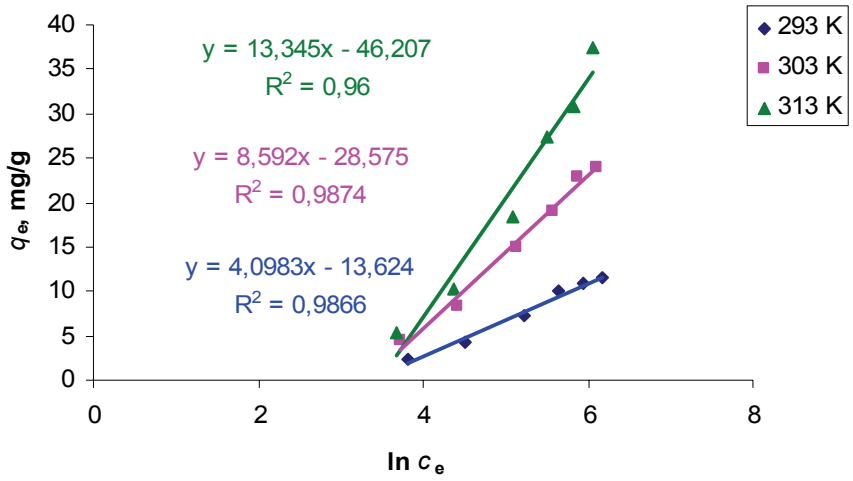


Figure 7. Temkin isotherms for system Cr (VI) / waste mould sand at 293, 303 and 313 K

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. In the Langmuir theory the basic assumption is that adsorption takes place at specific homogeneous sites within the adsorbent. Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbens-adsorbate interactions and adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [14]. The Eadie-Hofstee isotherm considers the variation in affinity constants and overlying resistance of the unstirred water layer at different sites [15].
The values of parameters for all isotherms are given in Table 2.

Table 2. The values of parameters for isotherms

	Langmuir isotherm			Freundlich isotherm			Eadie-Hoffstee isotherm			Temkin isotherm		
T, K	K_L	q_m	r^2	K_F	$1/n$	r^2	K_E	q_m	r^2	K_T	b_T	r^2
293	0.008	21.413	0.9992	0.1919	0.683	0.9799	-0.0030	20.358	0.9563	0.127	-5.44	0.8635
303	0.0023	50.251	0.9992	0.3271	0.722	0.9835	-0.0027	45.649	0.9654	0.0004	-2.94	0.8473
313	0.0015	91.743	0.9995	0.2871	0.812	0.9940	-0.0017	88.886	0.9274	0.205×10^{-6}	-2.12	0.7774

Comparison of correlation coefficients shows that the Langmuir and Freundlich isotherm fits better to the experimental data than other isotherms.

The mono-component Langmuir constant q_m, is the monolayer saturation at equilibrium. The other mono-component Langmuir constant, K_L, corresponds to the concentration and indicates the affinity for the binding of Cr (VI) ions on waste mould sand. A small K_L value indicates a low affinity. K_F and $1/n$, the mono-component Freundlich constants, are indicators of adsorption capacity and adsorption intensity, respectively. The higher value of $1/n$, the higher will be the slope expressed by $1/n$ and thus higher the affinity. As the value of 1/n close to zero, the system is less heterogeneous. The data obtained in this study (Table 2) indicated that the waste mould sand represents homogenous surface. Temkin and Eadie-Hoffstee isotherms have lower correlation coefficients and are not recommended for describing the adsorption process of Cr (VI) ions on the waste mould sand.

2.2.2. Thermodynamic study

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, $\Delta G°$, is an indicator of chemical reaction spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if $\Delta G°$ has a negative value. The values of thermodynamic parameters calculated form equations 5 and 6 for adsorption of Cr (VI) ions on waste mould sand are given in Table 3.

Table 3. Thermodynamic parameters of adsorption of Cr (VI) ions on waste mould sand

T (K)	$-\Delta G°$ (J mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (JmolK)
293	6.82081	67.459	184.596
303	57.9403		
313	41.6365		

The negative values of $\Delta G°$ (Table 3) show that the adsorption is highly favorable and spontaneous. A negative value of $\Delta H°$ implies that the adsorption phenomenon is exothermic. A positive value of $\Delta S°$ reflects the affinity of the adsorbent towards the adsorbate. In addition, positive value of ΔS suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The adsorbed ions, which are displaced by the adsorbate, gain more translational entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of thermodynamics randomness in the system [16].

3. CONCLUSIONS

- Obtained results show that waste mould sand was effective adsorbent for removal of Cr (VI) ions from aqueous solutions.
- The adsorption of Cr (VI) ions increased with increasing temperature.
- The equilibrium data were analyzed using Langmuir, Freundlich, Eadie-Hoffstee and Temkin isotherms, and the Langmuire and Freundlich isotherm model showed a better agreement with the equilibrium data.
- The negative values of $\Delta G°$ show that the adsorption is highly favorable and spontaneous. A negative value of $\Delta H°$ implies that the adsorption phenomenon is exothermic.

REFERENCES

[1] G. F. Nordberg, B. A. Fowler, M. Nordberg, L. Friberg, Handbook of toxicology of metals, European Environment Agency, Copenhagen, 2005.
[2] Narodne novine: Pravilnik o graničnim vrijednostima pokazatelja opasnih i drugih tvari u otpadnim vodama, NN 94/2008.
[3] S. Arivolis, M. Hema, M. Karuppaiah, S. Saravanan Adsorption of chromium ion by acid activated low cost carbon-kinetic, mechanistic, thermodynamic and equilibrium studies, E-Journal of Chemistry. 5 (2008) 820-831
[4] M. Trgo, J. Perić, N. Vukojević Medvidović**,** The effect of demulsifier and Dewatering agent on separation of phases from oily water, Holist. Appro. Environ. 1(2011), 3-11
[5] N. Tazrouti, M. Amrani, Chromium (VI) adsorption onto activated Kraft lignin produced from Alfa grass (Sipta tenacissima). BioResources. 4(3) (2009) 740-746.
[6] A. A. Attia, S. A. Khedr, S. A. Elkholy, Adsorption of chromium ion (VI) by acid activated carbon, Braz. J. Chem. Eng. 27 (2010) 183-193.
[7] A. Štrkalj, A. Rađenović, J. Malina, Primjena čelične sačme za uklanjanje Cr (Vi) iona iz vodenih otopina, Proceedings of 10th International foundry Conference, Advanced Foundry Materials and Technologies, F. Unkić (ed.), Metalurški fakultet, Opatija 2010.
[8] D. Kučić, S. Miljanić, M. Rožić, Sorption of methylene blue onto orange and lemon peel, Holist. Appro. Environ. 1 (2011) 3-11.
[9] A. Štrkalj, A. Rađenović, J. Malina, Use of waste anode dust for sorption of Ni (II) from aqueous solution, Can. Metall. Q. 50 (2011) 3-9.
[10] L. Ćurković, M. Trgo, A. Rastovčan-Mioč, N. Vukojević-Medvidović, Removal of Cu and Pb ions from aqueous solutions by electric furnace slag: Kinetic and thermodynamic aspects, Indian journal of Chemical Technology 16 (2009) 84-88.
[11] T. Lee, C. H. Benson, G. R. Eykholt Waste green sands as reactive media for groundwater contaminated with trichloroethylene (TCE). J. Hazard. Mater. B109 (2004) 25–36.

[12] W. Nakbanpote, B. A. Goodmanb, P. Thiravetyan, Copper adsorption on rice husk derived materials studied by EPR and FTIR, Colloids Surf., A. 304 (2007) 7-13.
[13] I. I. Salame, T. J. Bandosz, Surface Chemistry of Activated Carbons: Combining the results of Temperature-Programed Desorption, Boehm, and Potentiometric Titrations, J. Colloid Interface Sci. 240 (2001) 252-258.
[14] I. D. Mall, V. C. Srivastava, N. K. Agarwal, Adsorptive removal of Auramine-O: Kinetic and equilibrium study, J. Haz. Mater. 143 (2007) 386–395.
[15] A. B. R. Thomson, Limitations of the Eadie-Hofstee plot to estimate kinetic parameters of intestinal transport in the presence of an unstirred water layer, J. Membr. Biol. 47 (1979) 39-57.
[16] D. M. Ruthven, Principes of adsorption & adsorption processes, John Willey and Sons, Inc. Canada, 1984.

REMOVAL OF GLUCOCORTICOSTEROIDS AND ANESTHETICS FROM WATER WITH RO/NF MEMBRANES

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Abstract

This study addresses the removal of glucocorticosteroids and anesthetics at relatively low concentrations onto nanofiltration/reverse osmosis (RO/NF) membranes in a long-term operation. Four surrogate compounds in binary and mixture solutions (dexamethasone, hydrocortisone, lidocaine and procaine) and six NF/RO membranes (XLE, SWC, LFC, CPA, NF270 and NF90) were tested under cross-flow conditions. Hydrocortisone and dexamethasone are members of the glucocorticoid class of steroid hormones while lidocaine and procaine are anesthetic drugs. These compounds are considered as the emerging contaminants which should be subject of the removal from the potable water. Feed solutions were prepared by spiking the appropriate amount of stock solution into Milli-Q water and treated in RO/NF laboratory set-up. The RO/NF experiments were of the long-run type to test physicochemical interaction between solute, solvent and a membrane and to get accurate rejection of selected compounds. The analyses of pharmaceuticals were performed using a high performance liquid chromatography with diode array detector (HPLC-DAD) on C18 and CN modified stationary phase. Tested membranes showed almost complete removal of selected compounds and saturation of the membrane system was accomplished.

Keywords: *reverse osmosis; nanofiltration; rejection; glucocorticosteroid; anesthetic*

1. INTRODUCTION

Over the past few years, pharmaceuticals are considered as an emerging environmental problem due to their continuous input and persistence to the aquatic ecosystem even at low concentrations [1,2]. In these last years, the use of antibiotics in veterinary and human medicine was widespread (annual consumption of 100 000-200 000 tons) and consequently, the possibility of water contamination with such compounds increased [3]. They have been detected worldwide in environmental matrices, indicating their ineffective removal from water and wastewater using conventional treatment methods [1,4].

Dexamethasone (DEXA) and hydrocortisone (HYDRO) are synthetic members of the glucocorticoid class of steroid hormones. Dexamethasone is used to treat many inflammatory and autoimmune conditions, such as rheumatoid arthritis, while hydrocortisone is released in response to stress and a low level of blood glucocorticoids. Hydrocortisones primary functions are to increase blood sugar through gluconeogenesis, suppress the immune system and aid in fat, protein and carbohydrate metabolism.

Lidocaine (LIDO), an amide synthesized from cocaine, is one of the most extensively used local anesthetics and peripheral analgesic, which is effective to reduce pain. Second anesthetic investigated in this study was procaine (PROCA) which is a local anesthetic drug of the amino ester group. It is used primarily to reduce the pain of intramuscular injection of penicillin, and it was also used in dentistry.

Membrane treatment technologies reverse osmosis and nanofiltration (RO and NF) are recognized for the successful removal of various pharmaceuticals from water [5-8]. According to the authors' knowledge, no articles on removal of HYDRO, DEXA, LIDO and PROCA were published, except our previous paper [9] for removal of DEXA. In this paper removal of DEXA in Milli-Q water with NF/RO membranes (XLE, LFC–1, NF90, NF270, NF and HL) was higher than 99.2%. Therefore, the aim of this work was the removal of glucocorticosteroids (HYDRO and DEXA) and anesthetics (LIDO and PROCA) with RO/NF membranes in a long-term operation.

2. ELABORATION

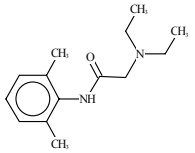
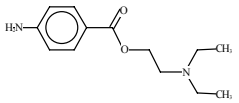
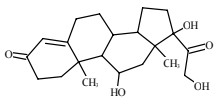
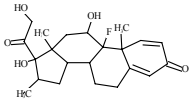
2.1. Materials and Methods

2.1.2. Chemicals

Two glucocorticosteroids (HYDRO and DEXA) and two anesthetics (LIDO and PROCA) were selected as micropollutants for study their removal with RO/NF membrane treatment. All drugs were provided by Veterina, Kalinovica, Croatia. The purities of all drugs were ≥ 97%, as determined by supplier. The chemical structures of the pharmaceutical substances and their physico-chemical properties according to increase of molecular weight (MW) are presented in Table 1. These compounds represent a hydrophilic group (with little approach to hydrophobic for LIDO and PROCA) of micropollutants and are different in size and solubility which can influence to membrane rejection. Order of testing compounds was with decrease of MW.

Two series of solutions, binary solutions of individual standards and a mixture, were prepared in Milli-Q water. Concentration of all drugs in solutions was around 20 mg L^{-1}.

Table 1. The chemical structure and physico-chemical properties of selected pharmaceuticals

Pharmaceutical	Molecular structure	CAS number	MW (g mol^{-1})	Log K_{OW}[a]
Lidocain [C_{14} H_{22} N_2 O_1]		000137-58-6	234.34	2.44
Procain [C_{13} H_{20} N_2 O_2]		000059-46-1	236.32	2.14
Hydrocortisone [C_{21} H_{30} O_5]		000050-23-7	362.47	1.61
Dexamethasone [C_{22} H_{29} F_1 O_5]		000050-02-2	392.47	1.83

[a] Obtained from EPI SUITE™ v4.10

2.1.2. Membranes

The commercially available RO and NF membranes examined in this experiment included the XLE (Dow/FilmTec, Midland MI), LFC–1, CPA3 and SWC1 (Hydranautics, Oceanside, CA) polyamide RO membranes, and NF90 and NF270 (Dow/FilmTec) polyamide NF membranes. All membranes were stored in dark cold place (refrigerator).

Removal of glucocorticosteroids and anesthetics were tested in laboratory set-up (described in details in [9]) in long-term operation (24 h) at working pressure of 10 bar and cross-flow velocity 500 mL min^{-1}. First, the preserved membranes were washed with demineralized water without pressure and then pressurized at 15 bar for 3 h. Nominal characteristics of membranes were checked by testing solution sodium chloride (NaCl) and calcium chloride ($CaCl_2$). Samples of pharmaceuticals were taken at the beginning of experiment and after 24 h of treatment. Membranes were cleaned after each compound. Cleaning was performed with organic cleaning agent (1.5%) at the temperature around 35 °C.

2.1.3. Chemical analysis

The concentrations of inorganic salts (c_{feed}=300 mg L^{-1}) were determined by the conductometer (Instruments Lab 960 SCHOTT, Germany).

The analyses of glucocorticosteroids and anesthetics were performed using a Varian ProStar 500 (Walnut Creek, CA, USA) HPLC system consisting of a ProStar 410 autosampler, ProStar 230 tertiary pump system, ProStar 330 diode array detector, and thermostatted column compartment. The column temperature was set to 20 °C and injection volume was 30 μL. C18 Synergy Fusion 150 mm×4.6 mm, particle size 4 μm column (Phenomenex) was used to separate DEXA and HYDRO, and Luna CN 100 mm×4.6 mm, particle size 3 μm column (Phenomenex) was used to separate PROCA and LIDO. The mobile phase used in the chromatographic separation consisted of a binary mixture of solvents A (0.01 % formic acid in water) and B (0.01 % formic acid in acetonitrile). Simultaneous mobile phase gradient program was used: the elution started with 2.5 min linear gradient from 100% A to 8% B, followed by 3.5 min linear gradient to 10% B, 5 min linear gradient to 30% B, 4 min linear gradient to 60% B and finally 3 min linear gradient to 95% B which was maintained for 10 min and then 0.1 min linear gradient back to 100% of A. Flow rate was 0.5 mL/min. The separation was monitored at absorbance wavelength of 245 nm for DEXA and HYDRO, for PROCA at 300 nm and for LIDO at 210 nm. Limit of detections (LOD) for DEXA, HYDRO, PROCA and LIDO were 0.012 mg L^{-1}, 0.012 mg L^{-1},0.050 mg L^{-1} and 0.050 mg L^{-1}, respectively.

2.2. Results and Discussion

2.2.1. Membrane Characteristics

Nominal characteristics of membranes were checked with two typical inorganic salts, sodium and calcium chloride and their initial rejection factors are displayed in Table 2. The highest values for NaCl were for RO membranes (XLE, SWC1, LFC–1). For CPA3 rejection factor for sodium chloride was only 76.02% and it is assume that this was experimental error, or relatively ‘’bad’’ sample of membrane since the manufacturers guarantees 99.7% [10]. For RO membranes values for NaCl and $CaCl_2$ show small difference indicating that the basic separation mechanism is the size exclusion while the relatively larger differences between rejection factor of monovalent and divalent salts in case of NF270 membrane indicate the strong repelling action of NF membranes on divalent ions, confirming the presence of a noticeable electrical charge on these membranes.

Also Table 2 presents rejection factors of NaCl after treatment of DEXA with cleaning (1.5% organic agent) and after all solutions with cleaning (1.5% organic agent). Very small increase of rejection confirms that membranes weren’t permanently fouled. Rejection factors of $CaCl_2$ at the beginning and the end are the same for all membranes except for NF270 and CPA3. Rejection of 14.83% of $CaCl_2$ at the end for NF270 is very small and there is no explanation for this because it was made after the NaCl at the end which is highest (28.57%) of all NaCl measurements.

Table 2. Rejection factors of NaCl (initial, after DEXA with cleaning and after mixture with cleaning) and $CaCl_2$ (initial and after mixture with cleaning)

		Rejection / %					
		XLE	SWC1	LFC–1	NF270	CPA3	NF90
NaCl	Initial	92.44	98.64	91.06	20.53	76.02	83.40
	Middle[a]	97.59	98.77	96.10	22.50	94.39	94.46
	End[b]	97.39	98.35	97.55	28.57	94.03	94.79
$CaCl_2$	Initial	96.07	98.74	96.38	43.33	83.21	96.29
	End[b]	96.79	98.15	96.34	14.83	88.33	96.40

[a] after DEXA and cleaning
[b] after mixture and cleaning

2.2.2. Removal of Glucocorticosteroids and Anesthetics

Feed concentrations at the beginning of experiment and the end of treatment for binary and mixture solutions are presented in Table 3. These show that difference between beginning and the end were in the range 0.3-1.1 mg L^{-1}. All solutions were covered with aluminum foil to prevent degradation but concentrations of LIDO, HYDRO and DEXA are lower than 20 mg L^{-1} and the reason could be degradation of the investigated compounds [11]. The main goal of this work was removal of compounds stated before and not searching for degradation products.

Table 3. Feed concentrations at the beginning and the end of treatment for binary and mixture solution.

			LIDO	PROCA	HYDRO	DEXA
Binary	0 h	c (mg L^{-1})	14.8	20.2	13.5	16.5
	24 h	c (mg L^{-1})	15.2	20.9	13.1	15.8
Mixture	0 h	c (mg L^{-1})	14.0	19.2	13.9	13.4
	24 h	c (mg L^{-1})	14.4	20.3	14.6	13.7

Rejection factors and concentrations of selected compounds in binary solutions at the beginning and the end of the treatment are presented in Table 4.

Table 4. Rejection, R with standard deviation (S.D.) and concentration, c of selected compounds in binary solution at the beginning (0 h) and the end of treatment (24 h)

			LIDO	PROCA	HYDRO	DEXA
XLE	0 h	R (%)	98.38 ± 0.04	99.61 ± 0.04	99.28 ± 0.03	99.26 ± 0.03
		c (mg L^{-1})	0.237	0.080	0.097	0.122
	24 h	R (%)	98.35 ± 0.09	95.99 ± 0.07	98.83 ± 0.03	99.64 ± 0.06
		c (mg L^{-1})	0.255	0.836	0.154	0.056
SWC1	0 h	R (%)	>99.99	>99.99	99.61 ± 0.05	99.98 ± 0.02
		c (mg L^{-1})	0.103	<LOD	<LOD	<LOD
	24 h	R (%)	98.60 ± 0.02	97.56 ± 0.03	99.69 ± 0.18	99.60 ± 0.06
		c (mg L^{-1})	0.216	0.510	0.054	0.063
LFC–1	0 h	R (%)	>99.99	>99.99	99.61 ± 0.05	99.81 ± 0.02
		c (mg L^{-1})	<LOD	<LOD	0.052	0.031
	24 h	R (%)	>99.99	99.44 ± 0.07	99.69 ± 0.18	99.80 ± 0.03
		c (mg L^{-1})	<LOD	0.117	0.040	0.032
NF270	0 h	R (%)	60.77 ± 0.41	69.12 ± 0.42	94.80 ± 0.10	99.10 ± 0.04
		c (mg L^{-1})	5.719	6.238	0.702	0.148
	24 h	R (%)	61.65 ± 1.19	43.21 ± 0.41	95.75 ± 0.00	99.13 ± 0.10
		c (mg L^{-1})	5.919	11.856	0.557	0.138
CPA3	0 h	R (%)	98.79 ± 0.21	99.59 ± 0.06	95.83 ± 0.06	98.19 ± 0.12
		c (mg L^{-1})	0.177	0.082	0.562	0.299
	24 h	R (%)	77.19 ± 0.11	91.64 ± 0.23	94.47 ± 0.03	97.15 ± 0.13
		c (mg L^{-1})	3.521	2.406	0.726	0.449
NF90	0 h	R (%)	99.32 ± 0.07	99.32 ± 0.00	99.37 ± 0.04	99.59 ± 0.02
		c (mg L^{-1})	0.099	0.138	0.085	0.068
	24 h	R (%)	99.18 ± 0.04	98.77 ± 0.06	99.37 ± 0.03	99.66 ± 0.03
		c (mg L^{-1})	0.126	0.258	0.083	0.054

At the beginning the highest rejections were for RO membranes, i.e. all investigated compounds were removed almost completely. This can be explained with size exclusion mechanism due to large MW (> 234 g mol^{-1}) of the compounds and low molecular weight cut off (MWCO) of the RO membranes (100 Da) [12]. Also pore sizes of reverse osmosis membranes are less than 1 nm [9,13]. The same behavior showed tight NF90 nanofiltration membrane because this membrane has similar porous structure to RO membrane. Second tight NF270 membrane had rejection 60.77% and 69.12% for smaller compounds (LIDO and PROCA) and due to size exclusion mechanism rejection increased with increase of MW. Experiments were performed in a long-term operation (24 h) to get accurate rejection of selected compound. Kimura et al. [14] showed that steady-state was accomplished after 6 hours. Due to

accomplishing steady-state second sampling was after 24 h. Rejection factors for HYDRO and DEXA after 24 h were very similar to rejection on the beginning for almost all membranes. Similar rejections and concentrations of the compounds in permeate are proof that the main mechanism was size exclusion and confirms that hydrophilic compounds do not adsorb to the membrane polymetric matrix (membrane selective layer or ''skin'') [15]. LIDO and PROCA have logK_{OW} 2.44 and 2.14, respectively which means that they have small hydrophobic characteristics. After 24 h rejection of LIDO with SWC1 and CPA3 membranes and PROCA with XLE, SWC1, NF270, CPA3 and NF90 membranes were lower (1-26%) compared to rejection at the beginning. These results show that the rejection was smaller probable because of adsorption of LIDO and PROCA to NF/RO polymeric matrix. This is in an agreement with [15]; they concluded that the removal of some hydrophobic compounds can be actually lower than that predicted based solely on a steric hindrance transport model. Namely hydrophobic compounds can adsorb to NF/RO membranes and then diffuse through the dense polymeric matrix, resulting in considerable transport of these compounds across the ultra-thin active layer. Confirmation that these compounds diffuse through polymeric matrix was significantly higher concentrations (≥96%) after 24 h.

In mixture solution (Table 5) NF/RO membranes almost completely removed all investigated compounds. In the case of RO and tight NF90 membranes, no significant difference between rejection in binary and mixture solutions is observed because these membranes provides excellent rejection (> 95%) but for nanofiltration NF270 membrane were higher.

Table 5. Rejection, *R* with standard deviation (S.D.) and concentration, *c* of selected compounds in mixture solution at the beginning (0 h) and the end of treatment (24 h)

			LIDO	PROCA	HYDRO	DEXA
	0 h	*R* (%)	98.89 ± 0.06	99.38 ± 0.02	99.02 ± 0.09	99.47 ± 0.09
XLE		*c* (mg L^{-1})	0.158	0.118	0.135	0.071
	24 h	*R* (%)	98.98 ± 0.27	97.83 ± 0.02	99.08 ± 0.02	99.60 ± 0.03
		c (mg L^{-1})	0.150	0.441	0.135	0.054
	0 h	*R* (%)	>99.99	>99.99	>99.99	>99.99
SWC1		*c* (mg L^{-1})	<LOD	<LOD	<LOD	0.017
	24 h	*R* (%)	98.51 ± 0.29	97.45 ± 0.07	99.60 ± 0.02	99.81 ± 0.03
		c (mg L^{-1})	0.219	0.519	0.059	0.026
	0 h	*R* (%)	>99.99	>99.99	99.74 ± 0.02	>99.99
LFC–1		*c* (mg L^{-1})	<LOD	<LOD	0.035	<LOD
	24 h	*R* (%)	99.76 ± 0.02	99.43 ± 0.03	99.69 ± 0.02	>99.99
		c (mg L^{-1})	<LOD	0.116	0.045	<LOD
	0 h	*R* (%)	87.84 ± 2.09	57.80 ± 0.21	93.79 ± 0.04	96.68 ± 0.07
NF270		*c* (mg L^{-1})	1.728	8.095	0.860	0.447
	24 h	*R* (%)	91.82 ± 0.97	70.08 ± 0.03	96.69 ± 0.02	97.61 ±0.10
		c (mg L^{-1})	1.203	6.081	0.486	0.328
	0 h	*R* (%)	99.18 ± 0.02	99.71 ± 0.04	97.98 ± 0.11	98.73 ± 0.01
CPA3		*c* (mg L^{-1})	0.116	0.055	0.280	0.171
	24 h	*R* (%)	93.18 ± 0.15	90.81 ± 0.06	95.20 ± 0.02	97.22 ± 0.18
		c (mg L^{-1})	1.003	1.867	0.704	0.382
	0 h	*R* (%)	99.42 ± 0.02	99.58 ± 0.04	99.40 ± 0.03	99.78 ± 0.00
NF90		*c* (mg L^{-1})	0.082	0.081	0.083	0.028
	24 h	*R* (%)	99.53 ± 0.06	99.22 ± 0.02	99.68 ± 0.00	99.71 ± 0.06
		c (mg L^{-1})	0.069	0.159	0.047	0.040

Also for removal of LIDO with CPA3 membrane rejection was higher than in binary solution. This proves the positive synergy (an effect arising between two or more compounds that produces an effect greater than that of their individual effects) concerning the rejection effectiveness. The next important goal of this study will be working in long-term operation but sampling every 2 h. This will help in understanding the rejection mechanism and adsorption of organic compounds onto NF/RO membranes.

3. CONCLUSIONS

Initial rejection of two typical inorganic salts (NaCl and $CaCl_2$) was > 83% for RO and tight NF90 membranes while for nanofiltration NF270 was 20.53%. Rejections of NaCl and $CaCl_2$ confirmed size exclusion as a basic mechanism for RO membranes and additional electric charge for nanofiltration membranes. The obtained rejection of NaCl and $CaCl_2$ presented stability of tested membranes. Therefore membranes weren't permanently fouled due to insignificant differences in rejection of salts. An excellent removal (> 95%) of all investigated compounds was achieved with RO and nanofiltration NF90 membrane and the main rejection mechanism was size exclusion. Only nanofiltration NF270 membrane had rejection of LIDO and PROCA 60.77% and 69.12%, respectively and in mixture additional synergistic effect had influence on rejection. Rejection factors for HYDRO and DEXA after 24 h were very similar to initial and confirms that hydrophilic compounds do not adsorb to skin of polymeric membranes. LIDO and HYDRO, compound with little higher $\log K_{OW}$, i.e. weak hydrophobic characteristic, had lower rejections (1-26%) after 24 h treatment compared to initial values and probable were adsorbed on polymeric matrix.

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REFERENCES

[1] C.M. Coetsier, S. Spinelli, L. Lin, B. Roig, E. Touraud, Discharge of pharmaceutical priducts (PPs) through a conventional biological sewage treatment plant: MECs vs PECs?, Environ. Int. 35 (2009) 787-792.
[2] P.H. Roberts, K.V. Thomas, The occurence of selected pharmaceuticals in wastewater effluent and surface waters of the lower Tyne catchment, Sci. Total Environ. 356 (2006) 143-153.
[3] W-H. Xu, G. Zhang, S-C. Zou, X-D. Li, Y-C. Liu, Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry, Environ. Pollut. 145 (2007) 672-679.
[4] M. Huerta-Fontela, M.T. Galceran, F. Ventura, Occurence and removal of pharmaceuticals and hormones through drinking water treatment, Water Res. 45 (2011) 1432-1442.
[5] Y. Yoon, P. Westerhoff, S.A. Snyder, E.C. Wert, J. Yoon, Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes, Desalination 202 (2007) 16-23.
[6] V. Yangali-Quintanilla, S.K. Maeng, T. Fujioka, M. Kennedy, G. Amy, Proposing nanofiltration as acceptable barrier for organic contaminants in water reuse, J. Memb. Sci. 362 (2010) 334-345.
[7] J.H. Al-Rifai, H. Khabbaz, A.I. Schäfer, Removal of pharmaceuticals and endocrine disrupting compounds in a water recycling process using reverse osmosis, Sep. Purif. Techn. 77 (2011) 60-67.
[8] S. Gur-Reznik, I. Koren-Menashe, L. Heller-Grossman, O. Rufel, C.G. Dosoretz, Influence of seasonal and operating conditions on the rejection of pharmaceutical active compounds by RO and NF membranes, Desalination 277 (2011) 250-256.
[9] D. Dolar, A. Vuković, D. Ašperger, K. Košutić, Effect of water matrices on removal of veterinary pharmaceuticals by nanofiltration and reverse osmosis membranes, J. Environ. Sci. 23(8) (2011) 1299-1307.
[10] http://www.lenntech.com/Data-sheets/CPA3-8040.pdf (accessed 02.09.2011.)

[11] P.Calza, E. Pelizzetti, M. Brussino, C. Biocchi, Ion trap tandem mass spectrometry study of dexamethasone transformation products on light activated TiO_2 surface, J. Am. Soc. Mass Spectrom. 12 (2001) 1286-1295.
[12] P. Xu, J.E. Drewes, T-U. Kim, C. Bellona, G. Amy, Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications, J. Membr. Sci. 279 (2006) 165-175.
[13] K. Košutić, D. Dolar, B. Kunst, On experimental parameters characterizing the reverse osmosis and (nanofiltration membranes' active layer, J. Membr. Sci. 282 (2006) 109-114.
[14] K. Kimura, G. Amy, J.E. Drewes, T. Heberer, T-U. Kim, Y. Watanabe, Rejection of organic micropollutants (disinfection by-products, endocrine disrupting compounds, and pharmaceutically active compounds) by NF/RO membranes, J. Membr. Sci. 227 (2003) 113-121.
[15] A.A. Alturki, N. Tadkaew, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse application, J. Membr. Sci. 365 (2010) 206-215.

DESIGN OF THE FIXED BED COLUMN FOR LEAD REMOVAL ON NATURAL ZEOLITE BASED ON BATCH STUDIES

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Abstract

This paper presents the prediction of breakthrough curves for the fixed bed column based on batch studies. Batch studies of lead removal on natural zeolite clinoptilolite have been performed. The obtained experimental data have been tested according to the Langmuir and Freundlich isotherms, and their parameters have been calculated. These parameters and the Mass Transfer Model have been used to predict theoretical breakthrough curves. Theoretical breakthrough curves have been compared with the experimental ones and a good agreement has been observed. This indicates that the Mass Transfer Model is applicable for prediction of breakthrough curves from batch studies. The overall mass transfer coefficient has been calculated from column experiments. This value allows for calculation of the height of the mass transfer zone as a very important parameter necessary for the column design.

Keywords: *lead, natural zeolite, column modeling, Mass Transfer Model*

1. INTRODUCTION

The column system has been getting increased attention in removal of different solutes on adsorbents due to its simplicity, ease of operation and handling, low costs and minimum sludge production. For design of fixed bed column, mostly are used models such as Bohart-Adams, Thomas, Wolborska, etc. which are based on column experimental data. The Mass Transfer Model uses the experimental data from batch studies and provides the necessary data for the column design. This procedure can be performed in a shorter time compared to the procedure carried out in a column [1-4]. For that reason, in this study, the Mass Transfer Model is used for prediction of theoretical breakthrough curves for lead removal on zeolite, based on data obtained from batch isotherm studies. The overall mass transfer coefficient and the height of the mass transfer zone have been evaluated for different zeolite particle sizes and initial lead concentrations.

1.1. Theoretical Background - Application of the Mass Transfer Model to Obtain Theoretical Breakthrough Curves

The results obtained from the batch experiment allow prediction of the theoretical breakthrough curve. This procedure consists of the following steps [1-4]:

Step 1. Testing the experimental data from the batch experiment against the Langmuir and Freundlich isotherm and calculating Langmuir and Freundlich parameters.

The general form of Langmuir and Freundlich isotherms can be written as follows [5]:

$$q_e = (b \cdot q_T \cdot \gamma_e)/(1 + b \cdot \gamma_e) \quad (1)$$

$$q_e = K_F \cdot \gamma_e^{1/n} \quad (2)$$

where: q_e - the equilibrium amount of the solute on the adsorbent, mg g^{-1}; q_T - the total amount of the solute required to create a monomolecular layer on the surface of particles of the adsorbent, mg g^{-1}; γ_e- the equilibrium concentration of the solute in the solution, mg L^{-1}; b – a factor which depends on the type of the adsorbent, L mg^{-1}; K_F and n - Freundlich constants characteristic of the system.

Step 2. Construction of the *operating line*. The operating line can be constructed by considering the material balance over the column. Namely, the amount of the solute on the adsorbent can be expressed as:

$$q = \gamma/\gamma_0 \cdot (q_e - q_r) + q_r \quad (3)$$

where: q - the amount of the solute on the adsorbent, mg g^{-1}; γ- the concentration of the solute in the solution, mg L^{-1}; γ_o – the initial solute concentration in the solution, mg L^{-1}; q_e – the value of q in

equilibrium with the initial solute concentration γ_o, mg g^{-1}; q_r – the residual amount of the solute on the adsorbent after regeneration, mg g^{-1}.
Assuming the fresh adsorbent is being used, $q_r = 0$, Equation (3) becomes:

$$q = \gamma / \gamma_o \cdot q_e . \tag{4}$$

In the column experiment, the equilibrium is reached at $\gamma_o = \gamma_e$ Thus, when $\gamma = \gamma_e$, q equals q_e, and the coordinates [γ_e, q_e] represent the first point of the operating line, while the second point is the origin, as shown in Fig. 1. The value of q_e is calculated by inserting the value of the initial solute concentration into the Langmuir or Freundlich isotherm, which was obtained by analyzing the results from the batch experiment in the previous step.

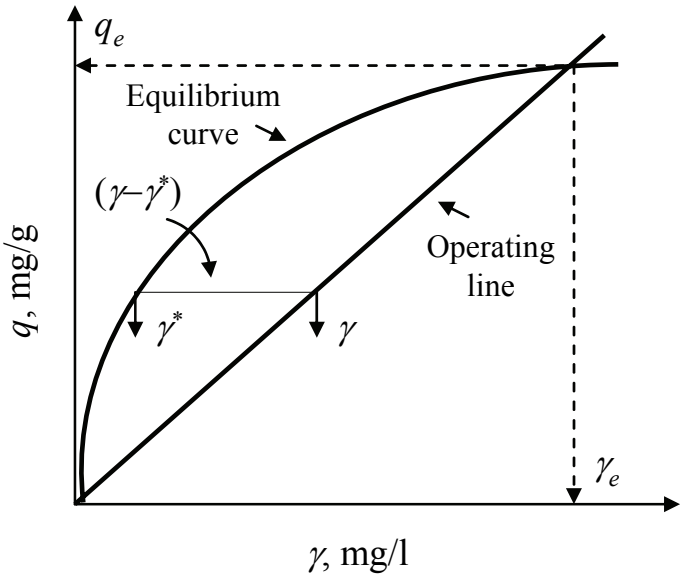


Figure 1. Construction of the operating line and the equilibrium curve.

Step 3. The *Equilibrium curve* is obtained by calculating the value γ^* from Langmuir and Freundlich isotherm equations, in the range from 0 to q_e. Thus, for each ordinate q, the two values of the abscissa are obtained: the first for the equilibrium curve (γ^*), the second for the operating line (γ).
Step 4. The mass transfer rate of the solute from the solution through the column at different bed depths, *dh*, is given by the following equation:

$$G_W dc = Ka \cdot (\gamma - \gamma^*) dh \tag{5}$$

where: G_W – the mass flux of the solution in kg min^{-1} m^{-2}; Ka – the overall mass transfer coefficient which includes resistance to diffusion through the film and diffusion through pores in kg min^{-1} m^{-3}; γ^*- the equilibrium concentration of the solute in the solution corresponding to the adsorbed concentration q in mg L^{-1}.
Expression (γ - γ^*) is the driving force of sorption, and it is equal to the distance between the operating line and the equilibrium curve for any value of q. By integrating the above expression in the range from γ_B to γ_E, where γ_B is the concentration of the solute at the breakthrough point, and γ_E is the concentration of the solute at the exhaustion point, the expression for the height of the mass transfer zone is obtained:

$$h_Z = (G_W / K_a) \int_{\gamma_B}^{\gamma_E} d\gamma / (\gamma - \gamma^*) \tag{6}$$

where h_z is the height of the mass transfer zone in m.
Any value of h lower than h_z corresponds to concentration γ, so that the h value can be calculated from the equation (6) in the range from γ_B to γ.

$$h = (G_W / K_a) \int_{\gamma_B}^{\gamma} d\gamma / (\gamma - \gamma^*) \tag{7}$$

By dividing Equations (7) and (6), the following is obtained:

$$h / h_Z = \int_{\gamma_B}^{\gamma} d\gamma / (\gamma - \gamma^*) / \int_{\gamma_B}^{\gamma_E} d\gamma / (\gamma - \gamma^*) = (V - V_B) / (V_E - V_B) \tag{8}$$

where: V_B - volume of the solution up to the breakthrough point, in L; V_E - volume of the solution up to the exhaustion point, in L; V - volume of the solution between V_B and V_E in L.
Step 5. Graphical plotting of γ/γ_o vs. $(V-V_B)/(V_E-V_B)$ represents the theoretical breakthrough curve.

2. ELABORATION

2.1 Experimental

2.1.1. Zeolite sample

Natural sample - The natural zeolite sample containing ≈ 80 % of clinoptilolite originated from the Vranjska Banja (Serbia) deposit. The sample was crushed and sieved to particle sizes of 0.6-0.8 mm and 0.1-0.5 mm, then rinsed in doubly distilled water and dried at 60 ˚C.
Pretreated zeolite sample – The natural zeolite sample was pretreated with a 2 mol L^{-1} NaCl solution, with stirring in the incubator shaker at a speed of 230-250 rpm for five days at 37 °C. After equilibration, the solution was filtered and the precipitate rinsed until the negative reaction to chloride. After drying at 60°C, the sample was stored in a desiccator.

2.1.2. Solutions

Solutions of different initial lead concentrations were prepared by dissolving appropriate amounts of $Pb(NO_3)_2$ in ultrapure water, without adjusting the initial pH values. The exact lead concentration was determined by complexometric titration in an acid medium, using a highly selective indicator, methyl thymol blue [6]. The solution for regeneration was prepared by dissolving $NaNO_3$ in ultrapure water.

2.1.3. Batch Experiment

Examinations in the system of zeolite-lead aqueous solution were carried out at 25°C and at a constant mixing rate of 230-250 rpm. 0.5 g pre-treated zeolite samples of both zeolite particle sizes have been equilibrated with 50 ml of the lead solution with different initial concentrations in the range from 118.5 - 1700.5 mg L^{-1}, during 3 days. Afterwards, the suspension was filtered through the vacuum filtration apparatus and the lead concentration in the filtrate was determined.

2.1.4. Column Experiment

The experiments were performed using two glass columns with the inner diameter of 12 mm and the height of 500 mm. One column was filled with the zeolite particle size of 0.6 - 0.8, and the other with the zeolite particle size of 0.1-0.5 mm. The fixed zeolite bed depth in both columns was 115 mm, which corresponds to the bed volume of 13 cm^3. The porosity of the fixed bed filled with zeolite particle sizes of 0.6 - 0.8 and 0.1-0.5 mm, was 0.693 and 0.659, respectively.

Service cycles were performed by passing lead solutions with different initial lead concentrations in the range of 212.5 - 520.5 mg L^{-1}, through the fixed zeolite bed using the down-flow mode at the constant flow rate of 1 mL min^{-1}. At selected time intervals the lead concentration in the effluent was determined. The process was stopped when the Pb concentration in the effluent became equal to the initial. After each service cycle, the regeneration was performed with the solution of $NaNO_3$, with the concentration of 15 g L^{-1}. Our previous papers have presented the experimental results with breakthrough and regeneration curves [7].

2.2. Results and Discussion

2.2.1. Calculation of the Theoretical Breakthrough Curve from Batch Experiments

Experimental data obtained from batch experiments were tested according to the Langmuir (equation 1) and Freundlich isotherms (equation 2). From the linear graphical dependence of isotherms, the parameters of Langmuir and Freundlich isotherm have been calculated and shown in Table 1.

Table 1. Parameters of Langmuir and Freundlich isotherms

Zeolite particle size, mm	Langmuir			Freundlich		
	b (L mg^{-1})	q_T (mg g^{-1})	R^2	K_F	n	R^2
0.6-0.8	0.061	147.06	0.935	99.86	18.215	0.942
0.1-0.5	0.084	147.06	0.933	105.99	21.186	0.969

The operating line and the equilibrium curve have been constructed according to the previously described *steps 2 and 3*. Fig. 2. shows the operating lines and equilibrium curves based on the Freundlich isotherm for different initial lead concentrations and zeolite particle sizes.

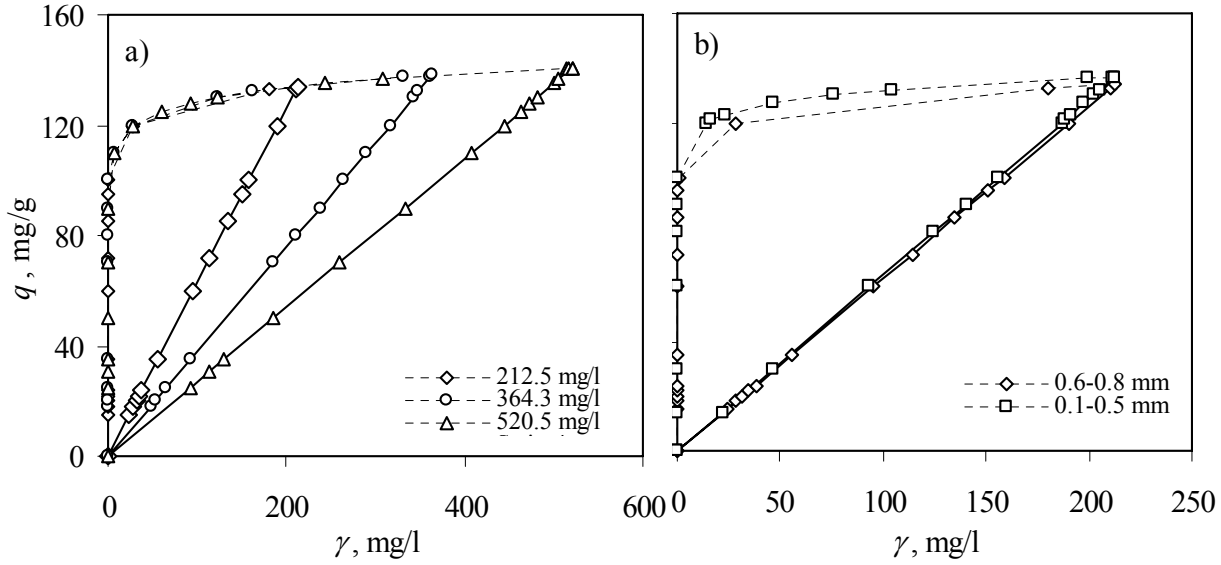


Figure 2. Equilibrium curves (the dashed line with empty symbols) and the operating line (full line) for determination of the breakthrough curve of lead removal by fixed bed of zeolite for: a) different initial concentrations and the particle size 0.6-0.8 mm, b) two different particle sizes of zeolite and the initial lead concentration of 212.5 mg L^{-1}.

Fig. 3. shows a graphical dependence of $1/(\gamma - \gamma^*)$ vs. concentration. The graphical integration of the area under each curve yielded the value of integrals $\int_{\gamma_B}^{\gamma_E} d\gamma/(\gamma - \gamma^*)$, and the term $(V\text{-}V_B)/(V_E\text{-}V_B)$ has been calculated. Plots of γ/γ_o vs. $(V\text{-}V_B)/(V_E\text{-}V_B)$ represent the theoretical breakthrough curves, shown in Fig. 4.

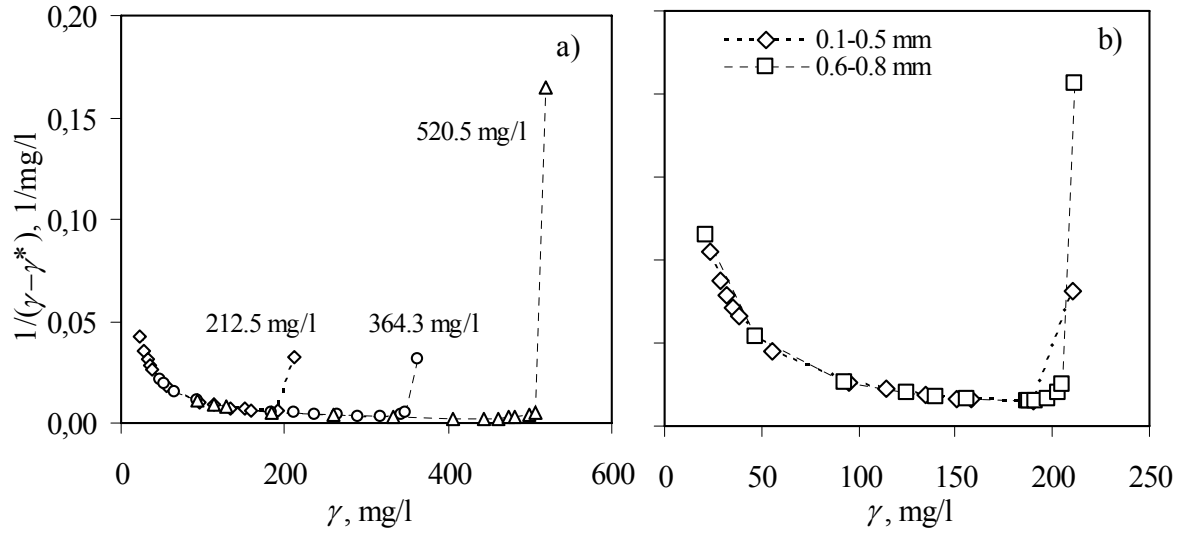


Figure 3. Dependence of $1/(\gamma - \gamma^*)$ vs. concentration for: a) different initial concentrations and the particle size of 0.6-0.8 mm, b) two different particle sizes of zeolite and the initial lead concentration of 212.5 mg L^{-1}

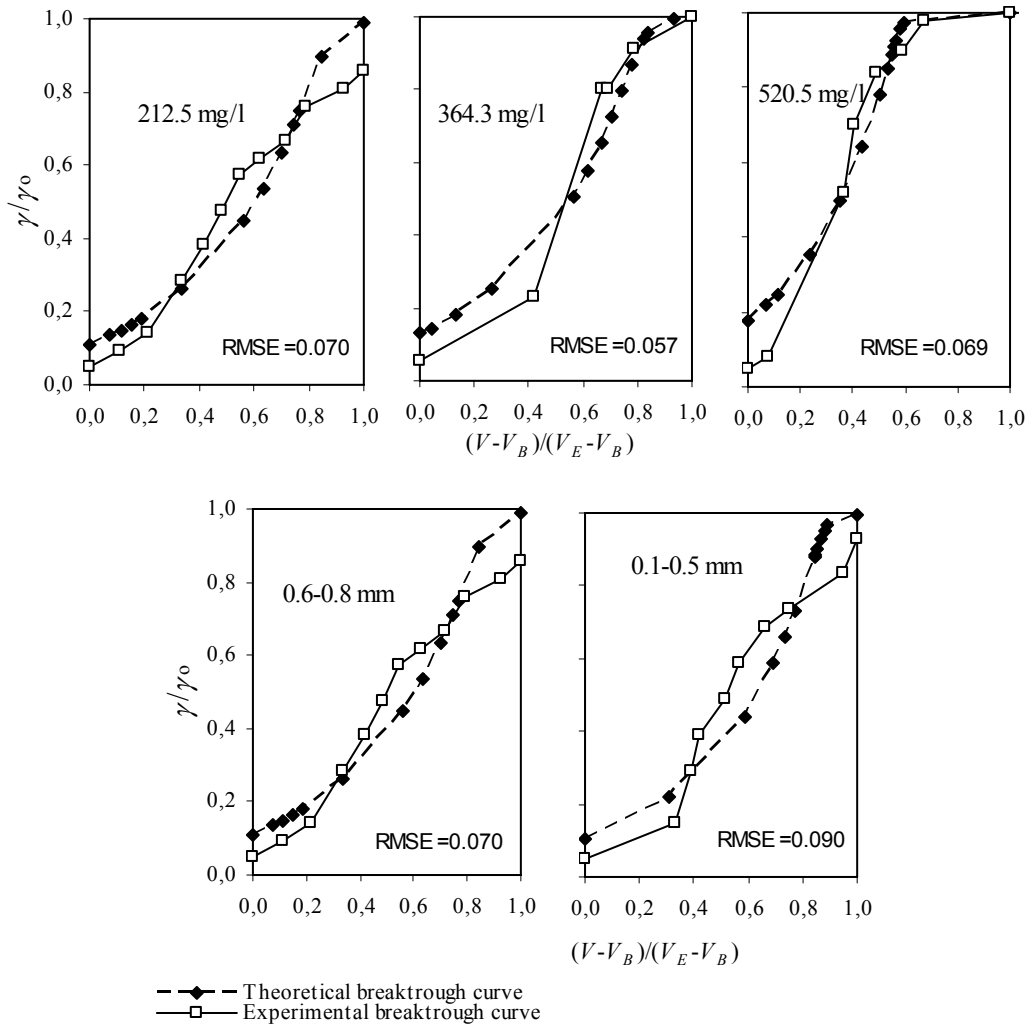


Figure 4. Comparison of theoretical breakthrough curves obtained from the Freundlich isotherm with the experimentally obtained breakthrough curves for different initial lead concentrations and the two zeolite particle sizes.

Calculated values of root mean square error (RMSE) presented on Figure 4 indicate that the theoretical breakthrough curves from the Freundlich isotherm equations are in good agreement with the experimentally obtained curves of lead removal from the aqueous solution on a fixed bed of zeolite. Similar results have been obtained for the Langmuir isotherm. This indicates that the parameters of Langmuir and Freundlich isotherms obtained from batch experiments and the design approach based on the Mass Transfer Model are suitable for prediction of column experiments.

2.2.2. Calculation of the Height of the Mass Transfer Zone

The height of the mass transfer zone is a very important parameter necessary for column design. From expression (6), and with known values of G_w and Ka, the height of the mass transfer zone h_Z can be calculated. However, there are great difficulties in evaluation the overall mass transfer coefficient, Ka. With the assumption that film diffusion controls mass transfer in the column, a graphical dependency of γ/γ_o vs. $1+\ln(\gamma/\gamma_o)$ is suggested, in which the following equation is valid [8]:

$$1+\ln(\gamma/\gamma_o) = N \cdot (\tau-1) \tag{9}$$

where: τ - dimensionless time, (-); N - number of mass transfer units, (-).

The value of τ can be calculated as:

$$\tau = t_B / t_E \tag{10}$$

where: t_B - time at the breakthrough point, min; t_E – time at the exhaustion point, min.

The ratio of t_B/t_E is proportional to the total capacity of the fixed bed. From the graphical dependence of γ/γ_o vs. $1 + \ln(\gamma/\gamma_o)$, the value $1+\ln(\gamma/\gamma_o)$ is evaluated at point where $\gamma/\gamma_o \sim 0.05$, which is shown in Fig. 5.

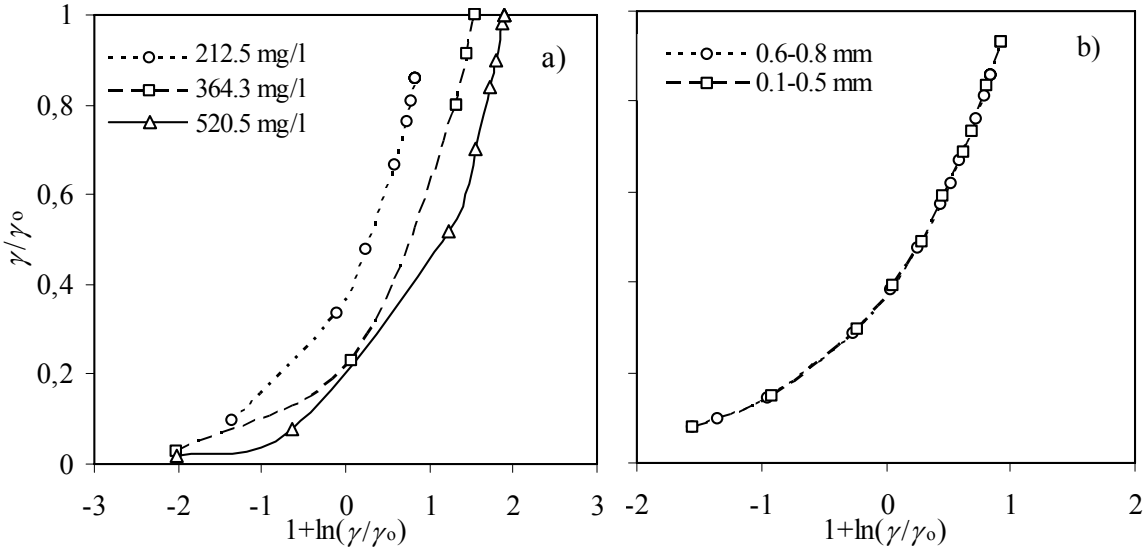


Figure 5. Plots of γ/γ_o vs. $1+\ln(\gamma/\gamma_o)$ for: a) different initial concentrations and the zeolite particle size of 0.6-0.8 mm, b) two different particle sizes and the initial lead concentration of 212.5 mg L^{-1}.

As $1+\ln(\gamma/\gamma_o) = N\cdot(\tau-1)$ and for known values of τ, the values of N are calculated and shown in Table 3.

The overall mass transfer coefficient, *Ka* is given by the following equation:

$$Ka = (N\cdot G_W)/H \tag{11}$$

where *H* is the fixed bed depth in the column in m.

The mass flux of the solution in the column is calculated from the following relation:

$$G_W = (Q\cdot\rho)/(A\cdot\varepsilon) \tag{12}$$

where: Q – the flow of the solution through the column in m^3 min^{-1}; A – the cross-sectional area of the column in m^2; ρ - density of water at 25 °C (ρ = 997.13 kg m^{-3}); ε - fixed bed porosity (-).

Table 3 shows the calculated values of *Ka* for different initial lead concentrations and zeolite particle sizes. From the known value of *Ka*, the height of mass transfer zone h_Z, can be calculated according to Equation (6). Table 3 also compares the results for the experimentally obtained h_Z with the value of h_Z calculated according to the Mass Transfer Model.

Table 3. Calculation of the overall mass transfer coefficient *Ka* and the height of the mass transfer zone h_z.

	τ	N	G_w	*Ka*	Langmuir $\int_{\gamma_B}^{\gamma_E}\frac{d\gamma}{(\gamma-\gamma^*)}$	h_z calc.	Freundlich $\int_{\gamma_B}^{\gamma_E}\frac{d\gamma}{(\gamma-\gamma^*)}$	h_z calc.	h_z exp.
Initial lead concentration (mg L-1)									
212.5	0.858	10.54	12.73	1166	2.775	3.03	2.528	2.76	2.84
364.3	0.807	10.46	12.73	1158	2.768	3.04	2.355	2.59	2.24
520.5	0.785	9.41	12.73	1042	3.284	4.01	2.997	3.66	2.44
Particle zeolite size (mm)									
0.6-0.8	0.858	10.54	12.73	1166	2.775	3.03	2.528	2.76	2.84
0.1-0.5	0.760	8.43	11.41	1012	2.581	2.91	2.716	3.06	2.52

Note: τ - dimensionless time, (-); N - number of mass transfer units, (-); G_W - mass flux of solution in kg min^{-1} m^{-2}) *Ka* - overall mass transfer coefficient, kg min^{-1} m^{-3}; h_z - height of mass transfer zone, cm.

It can be observed that the calculated values of *Ka* are independent of concentration, and have similar values for both sizes of zeolite particles. The experimentally obtained values of h_Z show a very good agreement with the values of h_Z calculated according to the Mass Transfer Model, indicating the validity of calculated *Ka* values.

The Mass Transfer Model allows for obtaining the necessary data for column design based on batch experiments. This is very important because batch experiments can be performed in a shorter time and with lower costs compared to tests carried out in a column, which other models usually require.

3. CONCLUSIONS

This paper describes the design approach based on a batch experiment. The Mass Transfer Model has been applied to experimental data of the batch experiment, in order to predict the theoretical breakthrough curve for lead removal onto the fixed bed of zeolite. A good agreement between experimental and theoretical breakthrough curves indicates that the Mass Transfer Model is applicable for prediction of breakthrough curves from batch experiments.

The overall mass transfer coefficient has been evaluated for different zeolite particle sizes and initial lead concentrations. This value allows for calculation of the height of the mass transfer zone as a very important parameter necessary for column design.

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REFERENCES

[1] L.D. Benefield, J.F. Judkins, B.L. Weand, Process chemistry for water and wastewater treatment: Prentice-Hall, Inc., New Jersey, 1982.
[2] S. Ayoob, A.K. Gupta, P.B. Bhakat, Analysis of breakthrough developments and modeling of fixed bed adsorption system for As(V) removal from water by modified calcined bauxite (MCB), Sep. Purif. Technol. 52 (2007) 430-438.
[3] A. Adak, A. Pal, Removal of phenol from aquatic environment by SDS-modified alumina: Batch and fixed bed studies, Sep. Purif. Technol. 50 (2006) 256-262.
[4] U. Kumar, M. Bandyopadhyay, Fixed bed column study for Cd(II) removal from wastewater using treated rice husk, J. Hazard. Mater. B129 (2006) 253-259.
[5] J. Perić, M. Trgo, N. Vukojević Medvidović, Removal of zinc, copper and lead by natural zeolite - a comparison of adsorption isotherms, Water Res. 38 (2004) 1893-1899.
[6] Complexometric Assay Methods with Triplex, E. Merck (Ed.), Darmstadt, 1982, pp.55.
[7] N. Vukojević Medvidović, J. Perić, M. Trgo, Column performance of lead removal from aqueous solutions by fixed bed of natural zeolite-clinoptilolite, Sep. Purif. Technol. 49 (2006) 237-244.
[8] I.C.C. Mantovaneli, E.C. Ferretti, M.R. Simoes, C. Ferreira da Silva, The effect of temperature and flow rate on the clarification of the aqueous stevia-extract in a fixed bed column with zeolites, Braz. J. Chem. Eng. 21 (2004) 449-458.

EFFICIENCY OF BIOLOGICAL LEACHATE TREATMENT FROM TOBACCO WASTE

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Abstract

In this study an aerobic treatment of leachate from tobacco waste using activated sludge under batch conditions was carried out. In experiments, pH value, dissolved oxygen, chemical oxygen demand (COD), and suspended solids have been monitored. Leachate treatment was conducted with different initial concentrations of leachate from 500 to 5000 mg dm^{-3} and initial concentrations of activated sludge from 1.84 to 6.62 g dm^{-3} during 96 hours. Leachate treatment efficiency was 80.0 – 99.8 % for Experiment A, 88.0 – 91.5 % for Experiment B, 87.0 – 92.0 % for Experiment C, 84.0 – 96.0 % for Experiment D, and 81.0 – 95.0 % for Experiment E in respect to initial COD concentrations.

Keywords: *biological treatment, leachate, tobacco waste*

1. INTRODUCTION

Concern about environmental protection has increased over the years from a global viewpoint. During cigarette manufacturing large quantities of tobacco waste are produced annually and its disposal is a serious ecological problem. Treatment of tobacco waste represents a major problem because of high concentrations of toxic compounds [1-3].

Leachate is a complex wastewater with considerable variation in both quality and quantity. Leachate consists of many different organic and inorganic compounds that may be either dissolved or suspended and which are biodegradable and non-biodegradable. Increasingly stringent environmental regulations require the processing of waste and wastewater before disposal or release into the environment. The removal of organic material based on chemical oxygen demand (COD), biochemical oxygen demand (BOD) and BOD/COD ratio from leachate is the usual prerequisite before discharging the leachates into natural waters. The knowledge of these specific parameters may help to select suitable treatment processes for the lowering of organic matter present in leachate [4-6].

During many years, conventional biological treatments and physical-chemical methods have been considered as the most appropriate technologies for manipulation and management of high strength effluents like landfill leachate. Due to its reliability and simplicity, biological treatment is commonly used for leachate treatment. In recent years, biological processes have been considered to be a cost-effective and environmentally sustainable alternative for the treatment of such wastewaters. Aerobic biological processes based on suspended-growth biomass, such as aerated lagoons, conventional activated sludge processes and sequencing batch reactors (SBR) have been widely studied and adopted. SBR technology has become an attractive option for tobacco wastewater treatment. Activated sludge is a process for biodegrading organic contaminants in wastewater using a mixed population of microorganisms at relatively high concentration in an aerobic environment, which can degrade organics compounds to carbon dioxide and sludge under aerobic conditions [7-9].

The aim of this work was to study the efficiency of biodegradation of organic pollutants of leachate from tobacco waste under batch conditions.

2. ELABORATION

2.1. Experimental

Batch biodegradation experiments were conducted in 500 cm^3 conical flasks using 250 cm^3 of diluted leachate and inoculated with 15.0 g, 12.5 g, 11.3 g, 7.5 g, and 3.8 g of the centrifuged activated sludge for experiments A-E, respectively. Samples were taken every 24 h for determination of chemical oxygen demand (COD), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MVLSS), pH value and dissolved oxygen (DO). At the beginning of the experiment COD and

biochemical oxygen demand (BOD_5) of original leachate medium were measured. All experiments were performed at 25±2°C and were maintained in aerobic conditions agitated on a rotary shaker at 160 rpm for 96 hours.

The activated sludge sample was taken from the Wastewater Treatment Plant in Zagreb, ZOV, Croatia. The sludge sample from WWTP was collected from aeration tank, centrifuged (Sigma 3K15, Germany) at 5,411 ×g for 10 min and 0 °C. Experiments were performed under different activated sludge concentration levels, X_0, in the range of 1.84-6.62 g dm^{-3} (MLSS).

The leachate used in the research was prepared from solid sample of the tobacco waste, Hrvatski duhani d.d., Virovitica, Croatia according to European standard of EN 12457-4:2002 [10]. The starting concentration of prepared leachate was around 34430 mg dm^{-3} COD, and value of BOD_5 was of approximately 18572 mg dm^{-3}. For the set of experiments, the leachate sample was diluted to initial concentrations, S_0, of 500, 1000, 1500, 3000, and 5000 mg dm^{-3} (COD), and marked as S_1 – S_5, respectively.

MLSS and MVLSS were determined gravimetrically, and BOD, COD measured according to APHA standards [11]. DO and pH values were measured with an oxygen meter and pH meter (WTW Multi 340i, Germany). All determinations were averages of duplicate samples.

The morphology of the activated sludge was investigated by light microscopy. Sludge samples were collected from the bioreactor and monitored under a light microscope (Olympus BX50, Olympus Optical Co. Ltd., Japan, with Olympus DP 10 camera). A drop of mixed liquor was carefully deposited on a glass slide and covered with a cover slip before being observed through the microscope.

2.2. Results and Discussion

One of the principle aims of present day wastewater treatment is the removal of organic carbon (COD) from wastewaters. COD and biochemical oxygen demand (BOD_5) are two of the most common generic indices used to assess aquatic organic pollution. BOD_5 is often used to evaluate the biodegradable fraction, and COD the total organic pollution load of waters contaminated by reductive pollutants. The biodegradability criterion for wastewater is the ratio of BOD/COD, which was about 0.54 in the leachate medium. The relatively higher values of ratio indicate pollution of the leachate by biodegradable matter. Biological processes have been shown to be very effective in removing organic matter from leachates when the BOD/COD ratio has a high value (>0.5) [5,12,13].

Table 1. Experimental results in the aerobic biodegradation process.

Exp. #	MLSS (mg dm^{-3})	MLVSS/MLSS	pH (-)	DO (mg dm^{-3})
A	6.62±0.02	0.716 ± 0.02	7.75 ± 0.10	3.24 ± 0.76
B	5.04±0.04	0.620 ± 0.03	7.79 ± 0.08	3.42 ± 0.81
C	4.06±0.04	0.654 ± 0.02	8.04 ± 0.24	5.21 ± 0.84
D	3.11±0.01	0.689 ± 0.04	8.14 ± 0.22	4.38 ± 1.31
E	1.84±0.06	0.687 ± 0.03	8.17 ± 0.27	5.36 ± 1.00

Experimental results in the aerobic biodegradation process are shown in Tabel 1. In a biological treatment process, sludge concentration is an important factor to ensure biological treatment ability. The mixed liquor suspended solids (MLSS) were used to characterize the biological mass in the activated sludge. The initial MLSS concentration in experiments was 6.62–1.84 g dm^{-3} for Exp. A - E, respectively. Tabel 1 shows the ratio of MLVSS/MLSS changes in the bioreactor over the experimental period. This value was in the range 0.620–0.716, almost constant over the whole experimental period. That indicated no obvious accumulation of inorganic matter in the bioreactor [14].

The important environmental factor that affects to activity of microorganisms in activated sludge is pH value. The optimum pH value for biological process of wastewater treatment is in the range 6.0 - 9.0, therefore it is an optimum range of the most economic purification processes [15-17]. Tabel 1 shows that pH values for conducted experiments varied only slightly and ranged in optimal limits of 7.75 to 8.17. There has been an increase in pH values in all experiments, A through E. The increase in pH value was most probably caused by oxidative effect of biodegradation process [5].

In aerobic bioprocesses, available dissolved oxygen for the growth and maintenance of microorganisms is often the most critical parameter which limits the effectiveness of the process. Therefore the control of DO plays an important role in the process of biodegradation. The concentration of DO in bioreactor affects on the behaviour and activity of microorganisms living in the activated sludge. Some authors suggest that concentration of DO should be in the range of 0.5 to 5.0 mg O_2 dm^{-3} [18]. The values that are within the concentration gradient of 0.5 to 5.0 mg O_2 dm^{-3} are considered sufficiently high to supply enough oxygen to microorganisms for biodegradation.

For series of conducted experiments, designated from A to E, concentrations of dissolved oxygen were in the range 3.24 – 5.36 mg dm^{-3}. We can see that values for Exp. C and Exp. E slightly deviated from optimal values but not significantly, so they did not affect the quality of the sludge and the efficiency of biodegradation. Therefore, we can say that all obtained values correspond to values proposed in the literature for the aerobic biodegradation of wastewater.

The biokinetic parameters were calculated using the concentration range of 500 - 5000 mg dm^{-3} for Exp. A and Exp. D, during the experimental period of 96 hours. The most important is the cell metabolism synthesis phase (parameter $Y_{x/s}$) with production of new cells (MLVSS). The food-to-microorganism ratio (F/M) is controlled by the rate of activated sludge wasting [13].

Table 2. Mean values of biokinetic parameters in the aerobic biodegradation process.

S_0 (mg dm^{-3})	Exp. A		Exp. D	
	$Y_{x/s}$ (mg mg^{-1})	F/M (mg mg^{-1} h^{-1})	$Y_{x/s}$ (mg mg^{-1})	F/M (mg mg^{-1} h^{-1})
500	0.326±0.06	0.003±0.01	0.401±0.06	0.004±0.01
1000	0.334±0.05	0.007±0.01	0.385±0.08	0.011±0.01
1500	0.351±0.07	0.010±0.02	0.378±0.04	0.019±0.03
3000	0.360±0.07	0.018±0.04	0.403±0.03	0.031±0.06
5000	0.347±0.06	0.021±0.07	0.396±0.03	0.042±0.08

Results obtained from batch biodegradation experiments A and D are shown in Tabel 2. Growth yield is defined as increase in biomass which results from the utilization of amount of substrate. The growth yield coefficient, $Y_{X/S}$, is defined as the ratio of maximum mass of cells formed to the mass of substrate utilized. The overall biomass yield Y, at time t_{end} is $Y_{X/S} = MLVSS_{max} - MLVSS_0 / COD_0 - COD_{max}$ where $MLVSS_0$ and $MLVSS_{max}$ are biomass concentration at the start of the experiment and maximum biomass concentration reached throughout the experiments. Similarly, COD_0 and COD_{min} are corresponding substrate concentrations [19]. Mean values of $Y_{X/S}$ varied between 0.326-0.347 g MLVSS (g COD)$^{-1}$ and 0.401 -0.396 g MLVSS (g COD)$^{-1}$ from 500 to 5000 mg dm^{-3} in experiment A and D, respectively. For the conventional activated sludge process for treating wastewater, growth yield is normally in the range 0.25–0.4 g MLVSS (g COD)$^{-1}$[14].

The food to microorganism (F/M) ratio tells us something about growth and cell condition. In biological wastewater treatment process, F/M is calculated through dividing the amount of treated organic material per unit time by the amount of microorganisms [20]. As can be seen from Table 2, in this study the values of F/M ratio increased by increasing initial concentration of substrate from 0.003 to 0.021 g COD (g MLVSS)$^{-1}$ h^{-1} for Exp. A and 0.004 to 0.042 g COD (g MLVSS)$^{-1}$ h^{-1} for Exp. D. In experiment A value of F/M ratio was lower than in experiment D. Low F/M ratio equals little substrate per unit biomass, which leads to competition among microorganisms and results in reduction of the net sludge production. This is in accordance with the maintenance which demands that biomass growth slows down with decreasing nutrient supply [19].

The biological component of the activated sludge system is comprised of microorganisms. A light microscope was used to examine the microorganism population of the activated sludge system. The diversity of the microbial community in activated sludge is very large. Protozoa are a useful biological indicator of the condition of the activated sludge. The hallmark of a well-operated, stable activated-sludge system is the existence of large numbers of highly evolved protozoa in the biological mass [13,21]. The results of microscopic examination are shown in Fig. 1.

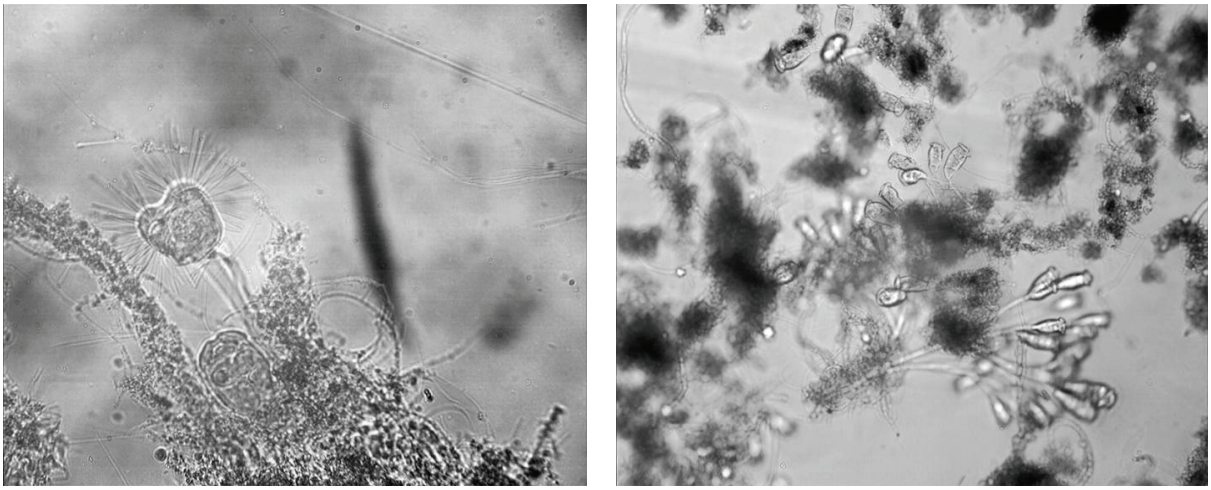


Figure 1. Microphotographs of protozoa from the batch reactor in the aerobic biodegradation process.

These microscopic images show some species of Protozoa which were present over the course of the experiment. Presence of protozoa populations provides evaluation of sludge quality and biodegradation ability. Protozoa are significant predators of bacteria which play a key role in the degradation processes. Therefore we can say that the presence of protozoa in activated sludge indicates a good quality of activated sludge, as well as the good performance of the process of biodegradation [17,22].

Biological treatment methods are extensively applied for the treatment of different type of wastewater and leachate. Conventional activated sludge process is suboptimal for tobacco wastewater treatment. The main purpose of this process is a removal of organic pollution from wastewater by microorganisms that are in activated sludge. The organic pollution of the leachate is expressed as COD which represents the amount of oxygen consumed by the organic compounds and inorganic matter which were oxidized in water by microorganisms [5,23,24].

Table 3. Efficiency of biodegradation of the leachate expressed as COD removal

Exp. #	COD removal (%)				
	S_1	S_2	S_3	S_4	S_5
A	80.0 ± 0.16	99.8 ± 0.32	89.3 ± 0.67	90.8 ± 1.40	90.4 ± 2.67
B	87.8 ± 0.10	91.5 ± 0.13	91.1 ± 0.38	91.3 ± 1.13	91.3 ± 3.47
C	87.0 ± 0.13	90.9 ± 0.20	91.8 ± 0.43	91.5 ± 1.15	90.6 ± 3.67
D	83.8 ± 0.23	91.7 ± 0.65	90.0 ± 0.76	93.4 ± 2.13	95.9 ±3.98
E	81.0 ± 0.16	89.5 ± 0.44	87.3 ± 0.54	93.3 ± 1.85	95.1 ± 4.78

After the biological treatment, the efficiency of COD removal was approximately 80 – 99%, as shown in Table 3, considering all the experiments. The highest COD removal (99.8 %) was obtained with 6 g dm^{-3} of activated sludge concentration (Exp. A). These values are very similar to other values proposed in the literature for an aerobic biodegradation of tobacco wastewater [23].

3. CONCLUSIONS

The obtained results have shown efficiency of biodegradation of organic pollutants of leachate from tobacco waste under batch conditions. The ratio of MLVSS/MLSS was in the range 0.620–0.716. These values show that biomass maintained throughout the experiments. The pH values and DO were about 7.96 and between 3.24 to 5.36 g dm^{-3}. Values of pH and DO were in the optimal range for biodegradation processes. Mean value of $Y_{X/S}$ was approximately 0.368 g MLVSS (g COD)$^{-1}$. The F/M ratio was between 0.003 and 0.042 g COD (g MLSS) $^{-1}$ d^{-1}. In all conducted experiments efficiency of COD removal was high and ranged from 80.0 to 99.9%.

Nomenclature

COD	chemical oxygen demand	mg dm^{-3}
COD_0	initial substrate concentration	mg dm^{-3}
COD_{min}	minimum substrate concentration	mg dm^{-3}
DO	dissolved oxygen concentration	mg dm^{-3}
F/M	food to microorganism ratio	g g^{-1} d^{-1}
MLSS	mixed liquor suspended solids	g dm^{-3}
MLVSS	mixed liquor volatile suspended solids	g dm^{-3}
$MLVSS_0$	initial biomass concentration	g dm^{-3}
$MLVSS_{max}$	maximum biomass concentration	g dm^{-3}
$Y_{X/S}$	growth yield coefficient	g g^{-1}
$S_{0/i}$	initial substrate concentration	mg dm^{-3}

REFERENCES

[1] I.J. Buerge, M. Kahle, H.R. Buser, M.D. Muller, T. Poiger, Nicotine derivatives in wastewater and surface waters: application as chemical markers for domestic wastewater. Environ. Sci. Technol. 42 (2008), 6354–6360.

[2] M. Wang, G. Yang, H. Mina, Z. Lv, X. Jiab, Bioaugmentation with the nicotine-degrading bacterium *Pseudomonas* sp. HF-1 in a sequencing batch reactor treating tobacco wastewater: Degradation study and analysis of its mechanisms Water Res. 43 (2009) 4187–4196.

[3] F. Briški, Z. Gomzi, N. Horgas, M.Vuković, Aerobic composting of tobacco solid waste. Acta Chim. Slov., 50 (2003) 715-729.

[4] K.Y. Foo, B.H. Hameed, An overview of landfill leachate treatment via activated carbon adsorption process, J. Hazard. Mater. 171 (2009) 54–56.

[5] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: Review and opportunity, J. Hazard. Mater. 150 (2008), 468–493.

[6] M.C. Tomei, M.C. Annesini, S.Bussoletti, 4-Nitrophenol biodegradation in a sequencing batch reactor: kinetic study and effect of filling time. Water Res. 38 (2004), 375–384.

[7] E. Celis, P. Elefsiniotis, N. Singhal, Biodegradation of agricultural herbicides in sequencing batch reactors under aerobic and anaerobic conditions. Water Res. 42 (2008) 3218–3224.

[8] B. Bae, E. Jung,Y. Kim, H. Shin, Treatment of landfill leachate using activated sludge process and electron-beam radiation, Water Res. 33 (1999) 2669–2673.

[9] J. Dollerer, P.A. Wilderer, Biological treatment of leachates from hazardous waste landfills using SBBR technology. Water Sci. Technol. 34 (1996) 437–453.

[10] EN 12457-4:2002, Characterization of waste - Leaching; Compliance test for leaching of granular waste materials and sludges - Part 4: One-stage batch test at a liquid to solids ratio of 10 l/kg for materials with particle size below 10 (without or with size reduction), European Committee for Standardization.

[11] APHA (1998). Standard methods for examination of water and wastewater, 20th Edition. APHA, Washington DC, USA.

[12] L.K. Wang, N.C. Pereira, Y.-T. Hung, Biological treatment processes, Humana Press, New York, 2009, pp. 207-278.

[13] G. Bitton, Wastewater Microbiology, John Wiley & Sons, New York, 1994.

[14] X. Huang, P. Gui, Y. Qian, Effect of sludge retention time on microbial behaviour in a submerged membrane bioreactor, Process Biochem. 36 (2001) 1001–1006.

[15] W. Wesley Eckenfelder, Industrial Water Pollution Controll, 3rd edition, McGraw – Hill Environ. Engineering Series, New York, 2000. str. 109, 124, 186, 417, 462.

[16] S. Zheng, Y. Zhang, T. Tong, C. Cui, J. Sun, Dominance of yeast in activated sludge under acidic pH and high organic loading, Biochemical Engineering Journal 52 (2010) 282-288.

[17] S.F. Yang, X.Y. Li, H.Q. Yu, Formation and characterisation of fungal and bacterial granules under different feeding alkalinity and pH conditions, Process Biochemistry. 43 (2008) 8–14.

[18] B. Holenda, E. Domokos, A. Redey, J. Fazakas, Dissolved oxygen control of the activated sludge wastewater treatment process using model predictive control, Computer and Chemical Engeineering 32 (2008) 1270-1278.

[19] E. Sahinkaya, F.B. Dilek, Biodegradation of 4-chlorophenol byacclimated and unacclimated activated sludge-Evaluation of biokinetic coefficients, Environ. Res. 99 (2005) 243-252.
[20] S.-H. Yoon,. Important operational parameters of membrane bioreactor-sludge disintegration (MBR-SD) system for zero excess sludge production, Water Res. 37(2003) 1921–1931.
[21] C.A. Papadimitriou, A. Papatheodoulou, V. Takavakoglou, A. Zdragas, P. Samaras, G.P. Sakellaropoulos, M. Lazaridou, G. Zalidis, Investigation of protozoa as indicators of wastewater treatment efficiency in constructed wetlands, Desalination. 250 (2010) 378-382.
[22] M. Vuković, F. Briški, M. Matošić, I. Mijatović, Analysis of the activated sludge process in an MBR under starvation conditions, Chem. Eng. Technol. 29 (2006) 357-363.
[23] M. Wang, G. Yang, H. Min, Z. Lv, X. Jia, Bioaugmentation with the nicotine-degrading bacterium Pseudomonas sp. HF-1 in a sequencing batch reactor treating tobacco wastewater: Degradation study and analysis of its mechanisms, Water research. 43 (2009) 4187-4196.
[24] F. Kargi, Y. Pamukoglu, Aerobic biological treatment of pre-treated landfill leachate by fed-batch operation. Enzyme Microb. Tech. 33 (2003) 588-595.

DEGRADATION OF LEACHATE FROM TOBACCO DUST BY ACTIVATED SLUDGE PROCESS

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Abstract

Treatment of tobacco dust represents an important problem because of high concentrations of organic compounds, expressed as COD concentration. This research investigated an aerobic biodegradation of leachate from tobacco dust with high concentrations of COD. Experiments were conducted by activated sludge process in batch conditions with different initial concentrations of leachate and different initial concentrations of activated sludge (3.0, 6.0 g dm^{-3}) during 7 hours. Experiments were called Exp. 1 and Exp. 2 with respect to initial concentrations of activated sludge. Values of COD removal efficiency varied from 54.9 to 71.3 % for Exp. 1 and from 59.0 to 77.7 % for Exp. 2. Biokinetic analysis was conducted according to the Monod model. This model gives very good fits to experimental data, accompanied by a high correlation coefficient (R^2).

Keywords: *tobacco waste, leachate, aerobic biodegradation, kinetic study*

1. INTRODUCTION

Increasingly affluent lifestyles, continuing industrial and commercial growth in many countries around the world in the past decade has been accompanied by rapid increases in both the municipal and industrial solid waste. The classification of industrial wastes of organic origin includes tobacco wastes, which are generated during different processes of the tobacco and cigarette production cycle [1,2].

Tobacco waste and dust appear in different steps of tobacco processing after harvest as well as in the course of manufacturing of some tobacco products such as cigarettes. The consequence of increase manufacture of tobacco products is raising level of various tobacco wastes. These waste products are resold, recirculated, compacted, or put in landfills.[3,4]. The biggest problem concerning these wastes is the presence of toxic compounds. Investigations carried out showed that the most important sources of these toxic contaminants are nicotine, flavouring chemicals containing glycogen and alcohol, absorbable organic halogens (AOX), and pesticides from tobacco leaves [5]. The nicotine contains high concentration of toxic compounds, and the powdery structure which cannot be recycled. Nicotine is highly soluble in water; therefore the toxic compound, nicotine can be transferred from the solid phase to an aqueous solution through efficient percolation. It may also be leached from the wastes and may permeate into ground waters and surface waters [1,2,6,7].

The main characteristic of tobacco solid wastes and leachate, beside their toxicity is their low moisture content. Due to of this problem it is desirable to apply biological or thermal process during the treatment of these wastes. Biological treatment is flexible, reliable, and high cost-effectiveness, which is commonly used for treatment of tobacco solid wastes and leachate.

This study aims to investigate the aerobic biodegradation of organic pollutants of leachate from tobacco dust in batch bioreactor, and evaluate biokinetic parameters using the Monod model.

2. ELABORATION

2.1. Experimental

The activated sludge sample was taken from the Wastewater Treatment Plant in Zagreb, ZOV, Croatia. The sludge sample from WWTP is collected from aeration tank, centrifuged (Sigma 3K15, Germany) at 5,411 ×g for 10 min and 0 °C. Initial concentrations of activated sludge were 3.0 and 6.0 g dm^{-3}. The leachate used in the research was prepared from tobacco dust, Hrvatski duhani d.d., Virovitica according to European standard of EN 12457-4:2002 [8]. The leachate sample that was obtained from the tobacco waste contained high COD, 40000 mg dm^{-3}. For the set of experiments, the leachate sample was diluted to initial concentrations of 500, 1000, 1500, 3000, 5000 mg dm^{-3}.

Batch biodegradation experiments were conducted in 500 cm^3 conical flasks using 250 cm^3 of diluted leachate and inoculated with 7.5 g (Exp. 1) and 15 g (Exp. 2) of the centrifuged activated sludge. Samples were taken every hour for determination of chemical oxygen demand (COD), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MVLSS), pH value and dissolved oxygen (DO), and for microscopic investigation. All experiments were performed at 25±2°C and were maintained in aerobic conditions agitated on a rotary shaker at 160 rpm for 7 hours.

Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MVLSS) were determined gravimetrically and the chemical oxygen demand (COD) was determined by means of the dichromate method using Standard Methods (APHA, 1998). Dissolved oxygen (DO) and pH values were measured with an oxygen meter and pH meter (WTW Multi 340i, Germany). All determinations were averages of duplicate samples.

The morphology of the activated sludge was investigated by light microscopy. Samples of activated sludge were monitored under a light microscope (Olympus BX50, Olympus Optical Co. Ltd., Japan, with Olympus DP 10 camera). A drop of mixed liquor was carefully deposited on a glass slide and covered with a cover slip before being observed through the microscope.

2.2. Results and Discussion

2.2.1. Pollutant removal performances

Legal regulation dictates that wastewater and leachate must be treated before it can be discharged. Activated sludge process has been widely applied to treat wastewater and leachate due to its advantages including low running cost and high degradation efficiency [1].

Chemical oxygen demand (COD) value is used to evaluate the organic strength of leachate. A biodegradation was conducted for leachate originated from tobacco waste. This leachate sample contained very high COD, 40000 mg dm^{-3}. Therefore it was diluted to initial concentrations of 500, 1000, 1500, 3000, 5000 mg dm^{-3} marked by from S1 to S5, respectively. The total removal reached in every experiment is calculated and shown in Fig.1.

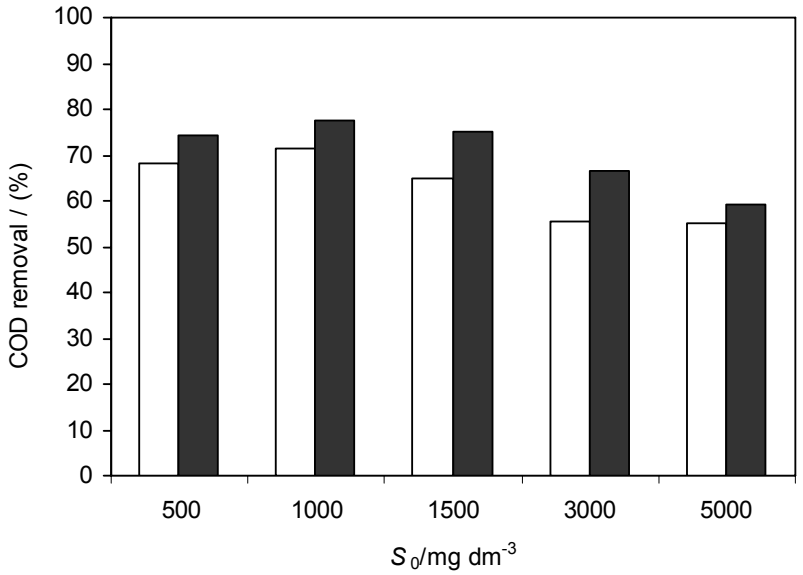


Figure 1. Efficiency of biodegradation of leachate from tobacco dust at different starting concentrations of substrate for Exp. 1 (□) and Exp. 2 (■).

For the series varying initial substrate concentration, values of COD concentration decreased continuously with reaction time. Values of COD removal efficiency varied from 54.9 to 71.3 % for Exp. 1 and from 59.0 to 77.7 % for Exp. 2. These results demonstrated that the leachate was biologically treatable. Results show that efficiency is the best for leachate with initial concentration of 1000 mg dm^{-3}. In this case COD was reduced to 71.3 % for Exp. 1 and 77.7 % for Exp. 2. It can be explained that the ratio of biomass and substrate was optimal and suitable, what enables the production of a quality effluent with a high value of performance degradation. We can see that efficiency of biodegradation was gradually decreased for samples with highest initial concentration for Exp. 1 and Exp. 2, respectively. It

can be explained by the fact that ratio of biomass and substrate was not optimal. Therefore, there is possibility that an inappropriate ratio biomass and substrate causes inhibition of substrate degradation at higher initial concentration of leachate.

2.2.2. Response of the control variables

In biological treatment process, use of activated sludge is an effective way of treating leachate with high concentrations of organic compounds. In a biological treatment process, sludge concentration is an important factor to ensure biological treatment ability. A sufficient sludge concentration will ensure good performance in pollutant removal and better effluent quality [9]. The mixed liquor suspended solids (MLSS) present a mixture of activated sludge and suspend solids from leachate. It should be noted that the MLSS consists of organic and inorganic matter, as well as microorganisms, and other inert suspended matter. Therefore, the MLSS is an indirect measure of total biomass [10]. Initial MLSS concentrations were 3.11 and 6.0 g dm^{-3} for conducted experiments marked as Exp. 1 and Exp. 2, respectively.

For both experiments during 7 hours concentration of MLSS was lightly and gradually increased. By increase of initial concentrations of substrate from S1 to S5, values of MLSS increased up to 26.13 % for Exp. 1. In the Exp. 2, values of concentrations of MLSS show significantly smaller increase with respect to starting concentrations of 6.0 g $dm^{-3}$and increased up by only 6.98 %.

The mixed liquor volatile suspended solid (MLVSS) represents the amount of organic or volatile suspended solids in sample of MLSS. This volatile portion is used as a measure or indication of the presence of microorganisms. The presence of microorganisms plays important role in the process of biodegradation. Therefore, the ratio of MLVSS/MLSS can be used to determine whether there are enough microorganisms present to digest the sludge and biodegradation. Variations in ratio of MLVSS/MLSS indicate a change in amount of biomass share

Table 1. Results of the control variables obtained in the Exp. 1.

Exp. 1	MLVSS/MLSS	pH	DO, mg dm^{-3}
S1	0.714 ± 0.03	8.15 ± 0.16	5.91 ± 1.08
S2	0.716 ± 0.02	7.99 ± 0.12	4.36 ± 1.16
S3	0.719 ± 0.02	7.94 ± 0.10	3.62 ± 0.92
S4	0.726 ± 0.02	7.85 ± 0.10	1.60 ± 0.90
S5	0.732 ± 0.03	7l.76 ± 0.13	0.57 ± 0.25

Table 2. Results of the control variables obtained in the Exp. 2.

Exp. 2	MLVSS/MLSS	pH	DO, mg dm^{-3}
S1	0.717 ± 0.02	7.92 ± 0.19	4.27 ± 1.30
S2	0.719 ± 0.01	7.89 ± 0.19	3.88 ± 1.22
S3	0.723 ± 0.01	7.85 ± 0.18	2.88 ± 1.34
S4	0.748 ± 0.02	7.77 ± 0.21	1.05 ± 1.01
S5	0.725 ± 0.03	7.69 ± 0.24	0.31 ± 0.02

Table 1. and 2. show that the values obtained for ratio of MLVSS/MLSS were almost constant and range in limits from 0.714 to 0.732 for Exp. 1 and from 0.717 to 0.725 for Exp. 2. These results show that there were no significant changes in the amount of viable sludge. The environmental factor that influences rates and limits microbial growth and thus the process of biodegradation is the pH value. The pH value lightly decreased by increasing initial concentration of leachate and ranged in optimal limits (7.76 – 8.15) and (7.69 – 7.92) for Exp. 1 and Exp. 2, respectively. These values correspond to the biological activity of sludge [12].

In aerobic bioprocesses, the control of the dissolved oxygen level plays an important role. The dissolved oxygen concentration in the activated sludge process should be sufficiently high to supply enough oxygen to microorganisms in the sludge in order for the organic matter to be degraded by them

[11]. Average values of DO concentration (Tab.1. and Tab.2.) decreased by increasing initial concentration of leachate. We can see that values of the average concentration of dissolved oxygen are significantly low at higher concentration of leachate in both conducted experiments. It is due to the fact that at higher initial concentration of leachate a lot more oxygen is necessary for substrate degradation [13].

2.2.3. Biokinetic analysis

Microbial degradation is generally defined as the biologically catalyzed reduction in chemical complexity. In the natural environment, conditions for biodegradation are very complex and the rate and extent of biodegradation depend on the chemical, physical and biological factors that may be different for different ecosystems. Although microbial processes are very complex, individual process incidences or groups of these incidences can be represented by model [12].

Most analyses with regards to biokinetic in wastewater treatment processes were done on the assumption that the reaction follows Monod kinetics or first-order reactions. This model defines the functional dependence of the specific growth rate and biomass concentration [12, 13], equation (1):

$$\mu = \mu_{\max} \cdot S / (K_s + S) \tag{1}$$

where in μ (h^{-1}) is the specific growth rate, μ_{max} (h^{-1}) is maximum specific growth rate, S (mg COD dm^{-3}) is the limiting substrate concentration and K_s (mg dm^{-3}) is substrate saturation constant (i.e. substrate concentration at half μ_{max}).

Microbial growth occurs as a consequence of the process of biodegradation by removing substrates as described by equations (2) and (3)

$$r_x = X_v / dt = \mu X_v \tag{2}$$

$$r_s = dS / dt = q_s X_v \tag{3}$$

where r_s (mg COD dm^{-3} h^{-1}) is substrate degradation rate, r_x (mg MLVSS dm^{-3} h^{-1}) is biomass growth rate, X_v (mg MLVSS dm^{-3}) is biomass concentration, q_s (mg COD (mg MLVSS)$^{-1}$ h^{-1}) is specific substrate degradation rate and t (h) is time.

The concentration of the substrate is usually reduced by growth of microorganisms, therefore r_s (mg COD dm^{-3} h^{-1}) is well described by equation (4):

$$r_s = \mu_{\max} X_v S / Y(K_s + S) \tag{4}$$

where Y (mg MLVSS (mg COD)$^{-1}$) is overall yield coefficient.

Real biomass yield per substrate, $Y_{x/s}$, and specific substrate degradation rate, q_s can be calculated directly from experimental data from the following equations (5) and (6):

$$Y_{x/s} = (X_v - X_{v0}) / (S_0 - S_i) \tag{5}$$

$$q_s = ((S_0 - S_i) / (t_0 - t_i)) / (X_v - X_{v0}) \tag{6}$$

According to this procedure, Tables 3. and Tables 4. show values of kinetic results in the aerobic degradation process and biokinetic parameters evaluated by kinetic model. Model parameters were estimated by non-linear regression analysis using least - squares method implemented in MS Excel software. Numerical values of model parameters were obtained by fitting the model to experimental data using MS Solver software. The optimization method was conducted according to GRG2 (Generalized Reduced Gradient) which is integral part of MS Solver software. Differential equations of the model are solved numerically by Runge Kutta 4 algorithm. A set of optimal parameters of the model were used for the process simulations. The residual error was defined as the sum of squares of the differences between the experimental and calculated data.

Tab 3. shows the values obtained for parameters ($Y_{x/s}$ and q_s) in the experiment according to Eq. (5) and Eq. (6). The growth yield coefficient, $Y_{x/s}$, is defined as increase in biomass which results from the utilization of amount of substrate. Mean values obtained for growth yield coefficient $Y_{x/s}$ (mg MLVSS (mg COD)$^{-1}$) are in the range from 0.355 to 0.393 mg mg^{-1} and from 0.189 to 0.242 mg mg^{-1} in conducted experiments marked as Exp. 1 and Exp. 2. These values show good match with expected values for the activated sludge process. Data obtained for specific substrate degradation rates, q_s (mg COD (mg

MLVSS)$^{-1}$ h^{-1}) are very close with other values proposed in the literature for the aerobic biodegradation of different wastewater [14].

Table 3. Mean values of kinetic results in the aerobic degradation process.

S_0 (mg dm^{-3})	Exp. 1		Exp. 2	
	$Y_{x/s}$ (mg mg^{-1})	q_s (mg mg^{-1} h^{-1})	$Y_{x/s}$ (mg mg^{-1})	q_s (mg mg^{-1} h^{-1})
500	0.355±0.12	0.027±0.04	0.189±0.06	0.022±0.02
1000	0.369±0.07	0.074±0.06	0.193±0.06	0.048±0.04
1500	0.391±0.04	0.094±0.07	0.213±0.08	0.065±0.06
3000	0.389±0.02	0.144±0.04	0.235±0.10	0.106±0.10
5000	0.393±0.07	0.217±0.09	0.242±0.09	0.120±0.20

Table 4. Biokinetic parameters.

Biokinetic parameters	Exp. 1	Exp. 2
μ_{max} (h^{-1})	0.088	0.052
K_s (mg dm^{-3})	4241	3168
Y (mg mg^{-1})	0.400	0.257

Applying a non-linear regression analysis to the experimental results were estimated biokinetic parameters according to Eq. (4). Tab. 4. shows the values of obtained results. Comparison of model and experimental results are shown Fig. 2. and Fig. 3. for Exp. 1 and Exp. 2. A good arrangement of the experimental points around a straight line confirms the agreement with the proposed model.

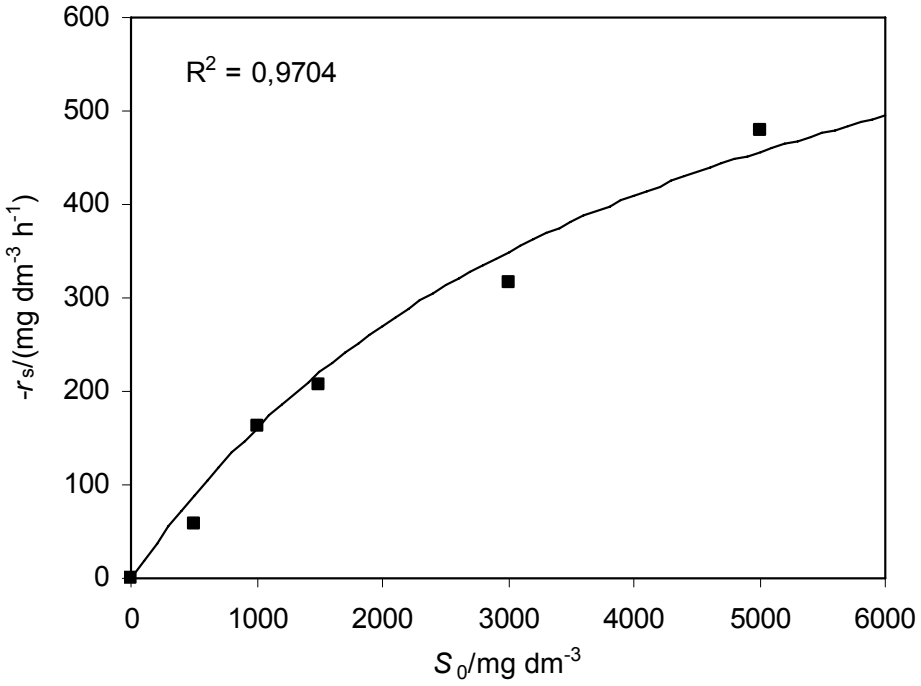


Figure 2. Influence of initial COD on substrate degradation rate for Exp. 1, (■) experimental data, and (—) model.

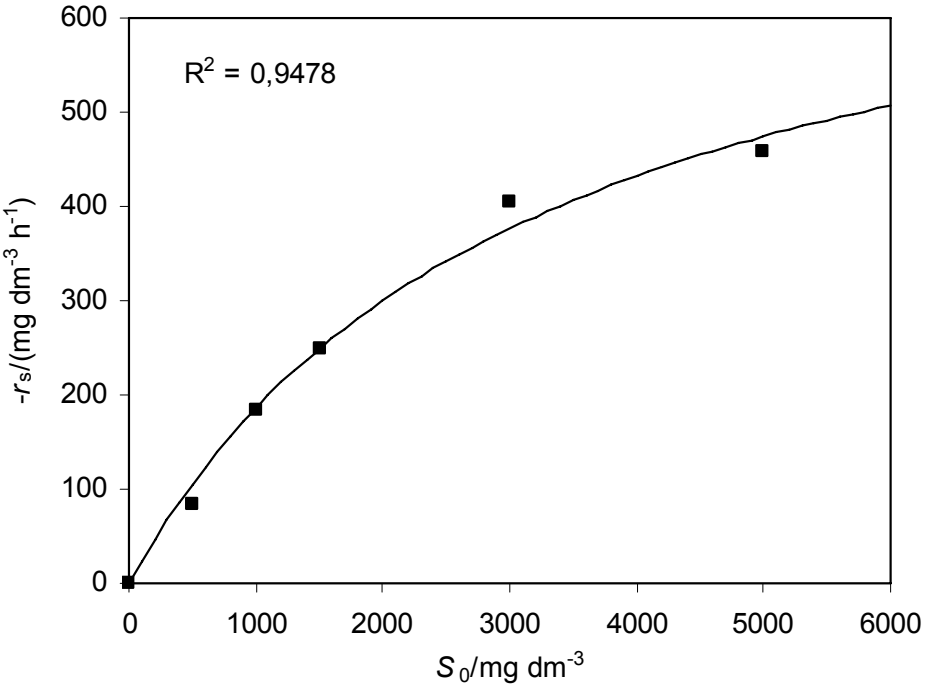


Figure 3. Influence of initial COD on substrate degradation rate for Exp. 2, (■) experimental data, and (—) model.

Fig.2. shows fit of calculated values obtained from model and experimental results for Exp. 1. As can be seen substrate degradation rate, r_s (mg COD dm^{-3} h^{-1}), is increased when initial substrate concentration also increases, as could be expected.

Also, Fig. 3. show fit of calculated values obtained from model and experimental results for Exp. 2. We can see that Exp. 1 shows insignificantly better match to experimental data than Exp. 2. These results demonstrated that the applied Monod model describes well the dynamics of the process accompanied by a high regression coefficient (R^2 = 0.9704 for Exp. 1, and R^2 = 0.9704 for Exp. 2)

2.2.4. Microscopical Examination

MLSS were regularly monitored to adjust the sludge concentration to a preset level. In order to describe the morphology of the activated sludge, microscopic investigation was conducted. The morphological properties of sludge were characterized by flocs [15, 16]. Flocs present in water play an important part in all issues related to water quality and treatment. Small sludge flocs can provide a favourable environment for enhancement of mass transfer, thus enabling the system to show a higher organic removal rate [16].

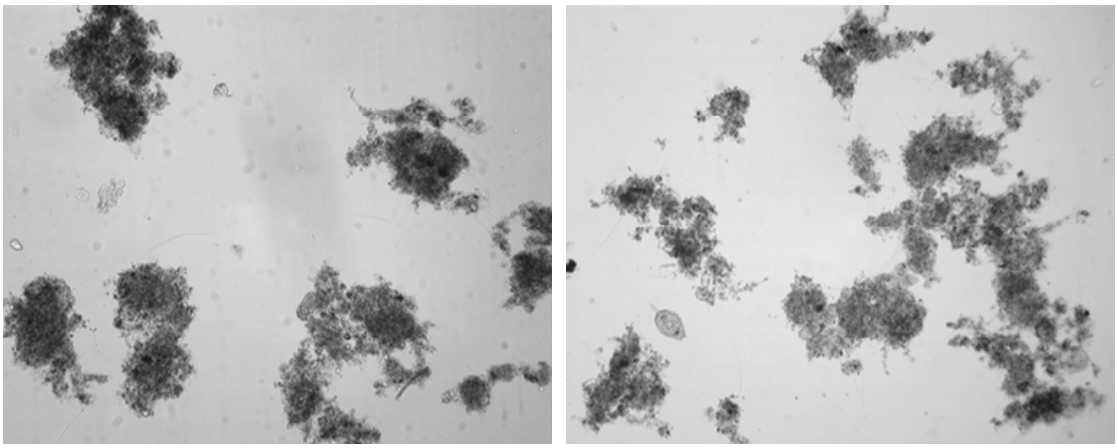


Fig.4. Microphotographs of activated sludge flocs in batch conditions for Exp. 1 and Exp. 2, respectively: left- at the start of the experiment and right- at the end of the experiment (100× magnification)

The results of microscopically examination are shown in Fig. 4.These figures show form of the flocs at the beginning and at the end of the process. The flocs at the beginning of the process shown in Fig.4.-left are characterized by regular formed flocs which enables producing a high quality effluent. We can see, also that flocs at the beginning of the process were significantly more compact than flocs at the end of the process. This can be explained by the fact that microorganisms at the end of process were not sufficiently supplied by substrate which is necessary for growth and maintenance of flocs.

3. CONCLUSIONS

The obtained results have shown biodegradability of leachate from tobacco dust. The values of COD removal efficiency varied from 54.9 to 71.3 % for Exp. 1 and from 59.0 to 77.7 % for Exp. 2. The ratio of MLVSS/MLSS and pH value were almost constant and ranged in optimal limits during the whole experimental period for Exp. 1 and Exp. 2, respectively. These results correspond to biological activity of activated sludge. Average values of DO concentrations decreased by increasing initial concentrations from 5.91 to 0.57mg dm^{-3} and from 4.27 to 0.31 mg dm^{-3} for Exp. 1 and Exp. 2, respectively. Obtained results show that microorganisms consumed most oxygen to oxidize most of available organic matter, and that the maximum oxygen consumption was in experiments with higher concentrations of substrate. The application of Monod model describes well the reaction kinetics for conducted experiments. Good fits to experimental data and high regression coefficient (R^2) pointed out that biological treatment of leachate from tobacco dust was successfully conducted.

Nomenclature

COD	chemical oxygen demand	mg dm^{-3}
DO	dissolved oxygen concentration	mg dm^{-3}
K_s	substrate saturation constant	mg dm^{-3}
MLSS	mixed liquor suspended solids	g dm^{-3}
MLVSS	mixed liquor volatile suspended solids	g dm^{-3}
q_s	specific substrate degradation rate	mg mg^{-1} h^{-1}
r_s	substrate degradation rate	mg dm^{-3} h^{-1}
r_x	biomass growth rate	g dm^{-3} h^{-1}
S	substrate concentration	mg dm^{-3}
t	time	h
X_v	biomass concentration	mg dm^{-3}
Y	overall yield coefficient	mg mg^{-1}
$Y_{x/s}$	growth yield coefficient	g g^{-1}
μ	specific growth rate of biomass	h^{-1}
μ_{max}	maximum specific growth rate of biomass	h^{-1}

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REFERENCES

[1] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: Review and opportunity, J. Hazard. Mater. 150 (2008) 468-493

[2] A. Piotrowska-Cyplik, A. Olejnik, Z. Cyplik, J. Dach, Z. Czarnecki, The kinetics of nicotine degradation, enzyme activities and genotoxic potential in the characterization of tobacco waste composting, Bioresour. Technol. 100 (2009) 5037-5044.

[3] T.E. Novotny, F. Zhao, Consumption and production waste: another externality of tobacco use, Tobacco Control, 8 (1999) 75–80.

[4] US National Industrial Pollution Control Council, The tobacco industry and pollution, sub-council report. WashingtonDC, US Government Printing Office (Publication No 483-135/6.), 1972.

[5] D.T. Sponza, Toxicity studies in a tobacco industry biological treatment plant, Water Air Soil Poll. 134 (2002) 137-154.
[6] H.Z. Tang, S.N. Wang, L.Y. Ma, X.Z. Meng, Z.X. Deng, D.K. Zhang, C.Q. Ma, P. Xu, A novel gene encoding 6-hydroxy-3-succinoylpyridine hydroxylase in nicotine degradation by *Pseudomonas putida* strain S16., Appl. Environ. Microbiol. 74 (2008) 1567-1574.
[7] S.N. Wang, Z. Liu, H.Z. Tang, J. Meng, P. Xu, C.Q. Ma, Green' route to 6-hydroxy-3 succinoyl-pyridine from (S)-nicotine of tobacco waste by whole cells of *Pseudomonas* sp., Environ. Sci. Technol. 39 (2005) 6877-6880.
[8] EN 12457-4:2002, Characterization of waste - Leaching; Compliance test for leaching of granular waste materials and sludges - Part 4: One-stage batch test at a liquid to solids ratio of 10 l/kg for materials with particle size below 10 (without or with size reduction), European Committee for Standardization.
[9] X. Huang, P. Gui, & Y. Qian, Effect of sludge retention time on microbial behaviour in a submerged membrane bioreactor, Process Biochem. 36 (2001) 1001–1006.
[10] M. Vuković, F. Briški, M. Matošić, I. Mijatović, Analysis of the activated sludge process in an MBR under starvation conditions, Chem. Eng. Technol. 29 (2006) 357-363..
[11] B. Holenda, E. Domokos, A. Rédey, J. Fazakas, Dissolved oxygen control of the activated sludge wastewater treatment process using model predictive control, Comput. Chem. Eng. 32 (2008) 1270–1278.
[12] G. Bitton, Wastewater Microbiology. John Wiley & Sons. New York. 1994.
[13] T.J. Casey, Unit Treatment Processes in Water and Waste Engineering. John Wiley & Sons. New York. 1996.
[14] J. Beltran, T. Gonzalez, J. Garcia, Kinetics of the biodegradation of green table olive wastewaters by aerobic and anaerobic treatments, J. Hazard. Mater. 154 (2008) 839-548
[15] E. Liwarska-Bizukojc & M. Bizukojc, Digital image analysis to estimate the influence of sodium dodecyl sulphate on activated sludge flocs, Process Biochem. 40 (2005) 2067–2072..
[16] J. Wu, X. Jiang & A. Wheatley, Characterizing activated sludge process effluent by particle size distribution, respirometry and modelling, Desalination. 249 (2009) 969-975.

THE EFFCIENCY OF PILOT-SCALE CONSTRUCTED WETLAND FOR THE TREATMENT OF LEACHATE WATER

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Abstract

Constructed wetland is the system which simulates a natural regime and can treat wastewater with the support of different physical, chemical and biological processes. In this work, the efficiency of pilot-scale subsurface constructed wetland for the treatment of leachate water has been assessed on the basis of the following parameters: iron, chromium, phosphates and total organic carbon (TOC) content as well as chemical oxygen demand (COD) and coloration. In order to increase the efficiency, the leachate water has been recirculated in the constructed wetland system. The results obtained has shown the increase of the efficiency for the removal of iron and TOC values, while at the same time, recirculation did not show any significant impact on the chromium removal. On the other hand, decrease of COD value and color removal was observed in the first 10 days of recirculation, while phosphate concentration increased.
Keywords: *leachate water, constructed wetland, pilot-scale, wastewater treatment*

1. INTRODUCTION

Disposal of untreated waste on numerous local landfills without reaching necessary environmental standards is still the most wide used approach of the waste management in Croatia and abroad [1]. Unfortunately, the majority of those landfills have not been equipped with the appropriate systems for preventing hazardous emissions in the environment such as leachate water and gases treatment which have been formed in enormous amount at landfills, especially in early stages of waste stabilization. Disposal landfills operate as huge microbial and chemical reactors and the complete stabilization of disposal waste have been achieved after very long periods. For particular pollutants this period could exceed a couple of decades [2]. For the observing of possible long-term environmental impacts it is most important to know and constantly monitor all the parameters of soil and air pollution and particularly leachate water quality. According to the current legislative leachate water have to be collected efficiently and treated adequately. Constructed wetland systems offer a solution for the treatment of such water. Constructed wetland has been designed as the system which takes the advantage of many processes occurring in natural systems (wetland), but within controlled process parameters [3]. Low energy efficiency, susceptibility to flow variations, possibility of construction on the site whereas pollution is generated, simple and cheap construction presents just several of advantages of constructed wetland. One of constructed wetland disadvantages is requirement for relatively large area for the treatment of even not-heavily loaded wastewater.

Leachate water is a wastewater occurring by leaching of storm water through the layer of waste placed on a landfill. Due to anaerobic conditions and long retaining period characterized for landfills, leachate water contains high concentrations of organic and nutrient compounds, pathogens and heavy metals which can cause pollution of local environment and ground water, if not treated properly. Wastewater purification technology based on the principles of constructed wetland system is around 40 years old but has been in the focus of interest for the last 10 years. At the moment a couple of thousands of constructed wetland has been operating in the world. The possibility of constructed wetland application in Croatia has been studied on a pilot-scale basis (Hrvatske vode) for water region of Sava river [4]. On the locations where it is possible to assure sufficient area, constructed wetlands present an attractive alternative for the treatment of leachate water. By the employment of constructed wetland system it is possible to transfer typical pollutants from wastewater into harmless byproducts or basic nutrients which can be used by microorganisms for their growth and development [5]. Constructed wetland is designed and constituted on the principles of natural wetland system outside of natural habitat

in order to purify wastewater circulating in controlled conditions. Constructed wetland is consisted of an aqueous media, substrate and the plant with the role of the treatment of the dot or diffuse source of water pollution. In this type of system, water is treated by the combination of physical, chemical and biological processes. The process involves precipitation and filtration of suspended compounds, assimilation of nutrients in plants and chemical reactions [6]. In general, constructed wetlands can be divided in two basic types:

- free water surface systems
- subsurface flow systems.

Free water surface constructed wetland considers the system whereas aqueous medium is passing through under the atmospheric conditions [7]. Those systems have been found efficient for the removal of total nitrogen and less efficient for the removal of total phosphorus. In surface flow constructed wetland system wastewater is passing through granulated media (substrate), without contact with atmosphere. This type of constructed wetland is commonly used in secondary treatment of wastewater and can efficiently remove biological oxygen demand (BOD_5) value and total suspended solids (TOS). On the other hand, surface flow constructed wetland system have been found less efficient for the removal of nitrogen and phosphorus. The lower efficiency of nitrogen removal has been connected with the lack of oxygen within the system and phosphorus removal with physico-chemical and hydrological properties of the substrate since phosphorus is mainly adsorbed or precipitated within the system [8].

The most used aquatic plants in constructed wetland systems are macrophytes which occur naturally along the coastal areas of lakes and swamps, *i.e.* helophytes. The species *Phragmites australis* and subspecies *Carex, Scirpus* and *Typha* belong in this group. The most important role of macrophytes in wastewater is the physical one. Macrophytes stabilize the area of constructed wetland, they assure good conditions for physical filtration, protect from freezing during winter times, adsorb nutrients and enable formation of the large surface for microorganism growth [9]. Microorganisms have been found the most important factors in the process of wastewater purification since they use organic compound as nutrient and energy sources transforming it to biomass and energy at the same time [10].

Advantages and disadvantages of constructed wetland systems have been shown in Table 1.

Table 1. Advantages and disadvantages of constructed wetland systems

Advantages	**Disadvantages**
• Low construction and operating costs	• Larger requirements for the space
• The ability of work with small capacities and production of the less amounts of the sludge [11]	• Slow process of wastewater treatment due to the low flow rates
• Low energy requirements [12]	• Higher sensitivity in anaerobic conditions
• Possibility of on-site construction	• Weed control (during vegetation period)
• Simple and cheap implementation with minimal requirements for control and maintenance	• Requirement of the mechanical equipment on the slope area
• Insensible on the flow rates variations, expected lifetime 20 – 30 years, acceptable landscape fit in	• Limited removal of pathogens [13]

Directive on landfill of waste 99/31/EC [14] obligates EU member countries on collecting and treatment of leachate water from landfills. Treatment of this type of wastewaters requires aerobic system or transportation to the place of treatment which is often very demanding and expensive, especially for the landfills intended for shutting down. Therefore, it is necessary to treat leachate wastewater on the place of generation with minimal costs and constructed wetland systems have been offered as a solution [15].

In this study, the efficiency of constructed wetland was monitored in three weeks period. The scope of the work was to determine the hypothesis that for some environmental parameters it is possible to achieve increase of constructed wetland efficiency after implementation of recirculation approach.

2. ELABORATION

2.1. Experimental

In controlled laboratory conditions the possibilities of wastewater purification in pilot-scale constructed wetland based on subsurface flow system have been studied. Constructed wetland consisted of a tank for wastewater of 5 L volume, two connected linear basins, carrying container of 5 L volume and three fluorescent lamps (Fig. 1.).

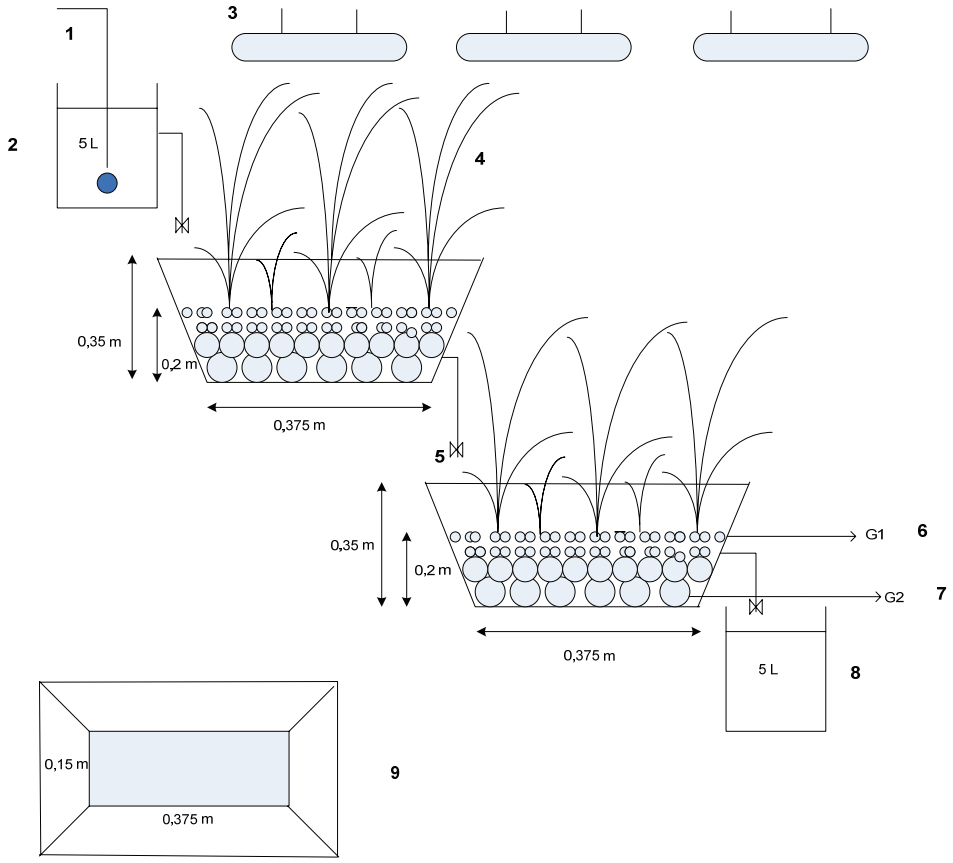


Figure 1. Schematic diagram of constructed wetland (1. aeration pump, 2. a tank, 3. fluorescent lamps, 4. cane, 5. rubber pipes with valves for the flow maintenance, 6. granulation substrate of 4-8 mm, 7. granulation substrate of 16-32 mm, 8. carrying tank, 9. a basin; top view)

The tank was 0.15 m wide, 0.375 m long and 0.35 m high with 0.8 m height of the fill. Each basin has been loaded with 4-32 mm of substrate with 0.35 of porosity coefficient and planted with 4 – 6 plants of cane (*Phragmites australis*). The basins were joined by rubber pipe equipped with the valve for the wastewater flow maintenance. Rubber pipe with the valve were also connected with the tank from where the treated water has been transferred to the carrying tank. The flow of water was enforced by gravitation. Recirculation was assured manually and aeration with the pump. The lamps as a light source for the plants were run 10 hours per day during three weeks period.

Three weeks before the time of loading constructed wetland with leachate water, the plants have been laid in together with addition of nutrients for the growth enhancement. The flow of leachate water was maintained at 0.00125 m^3 day^{-1}. Due to such low flow rate and small radius of rubber pipe it varied from 0.0002 – 0.0014 m^3 day^{-1}. On the tenth day of the process recirculation was introduced in order to achieve the better treatment efficiency. The leachate water treatment process was divided in the three phases. The first phase lasted three days. In that period the leachate water started to pass through the constructed wetland system where the tap water was loaded previously. In the second phase which took

10 days, the leachate water was spread throughout the whole constructed wetland system and the treatment has started. The third phase included recirculation procedure.

Wastewater that was purified in such constructed system presented leachate water form Jakuševac landfill, Zagreb, Croatia. Original sample was diluted with the tap water in 1 : 1 ratio. The following parameters of wastewater have been determined during operation of the system: iron, chromium, phosphates and total organic carbon (TOC) content as well as chemical oxygen demand (COD) and coloration. The values of initial parameters have been shown with Table 2.

Table 2. The values of initial parameters

Parameter	Input value
Iron [mg L^{-1}]	2.42
Chromium [mg L^{-1}]	1.16
Phosphates [mg L^{-1}]	2.71
Total organic carbon [mg L^{-1}]	223
Chemical oxygen demand [mg L^{-1}]	437
Coloration (NTU)	808

2.1.1. Determination of Iron and Chromium

Concentration of iron and chromium in the samples of leachate water was determined by molecular absorption spectroscopy in the ultraviolet (UV) and visible (VIS). Determination of iron is based on reactions of formation of complex species between the ions of metal or inorganic or organic ligand or on the absorption of electromagnetic irradiation of an ion (anion). Iron in the form of ferric ion reacts in the acidic environment with thiocyanate ion forming reddish complex with the maximum of absorption at λ_{max} = 480 nm. Determination of chromium is based on the reaction of chromium (VI) ion with diphenylcarbazide in the acidic environment forming the complex of an intensive coloration with the maximum of absorption at λ_{max} = 545 nm. Absorption was measured by using spectrophotometer MA 9535 – SPEKOL 210, Iskra, Kranj.

2.1.2. Determination of Total Organic Carbon Content (TOC)

Total organic carbon content was determined by using Shimadzu TOC –V_{WS} Total Organic Carbon Analyzer.

2.1.3. Determination of Color, Chemical Oxygen Demand (COD) and Phosphates

Coloration, COD and phosphates were determined by using spectrophotometer HACH DR/2500. In order to determine coloration extent the sample was filtrated and absorption was measured in the range of wavelengths λ = 455 – 465 nm. Concentration of COD was determined according the method number 8000 from HACH catalogue at the wavelength λ = 620 nm. Concentration of phosphates was determined by using a method number 8048 from HACH catalogue. After sample dilution (1 : 10) and filtration a reagent was added and phosphate concentration was measured at λ = 420 nm by spectrophotometer.

2.2. Results and Discussion

2.2.1. The Efficiency of Iron and Chromium Removal

The results of iron and chromium removal efficiencies from leachate water in a studied subsurface flow constructed wetland system have been shown in Fig. 2. It can be seen that in the first phase of treatment which took three days, concentrations of iron and chromium varied due to different distribution inside the constructed wetland. In the second phase, which took seven days, constructed wetland system adopted on the leachate water and removal of iron and chromium has been more significant. Third phase included recirculation of leachate water in the system which was performed in order to increase the efficiency of chromium removal. Iron concentration decreased from the initial one of 2.420 mg L^{-1} up to 0.483 mg L^{-1} after 20 days of treatment in a subsurface flow constructed wetland system. From the Fig. 2., it can be also seen that chromium concentration decreased from initial one of 1.160 mg L^{-1} up to 0.6 mg L^{-1} in the third phase. Relatively less efficient removal of chromium in comparison with iron removal could impose that recirculation process employment had the lower impact for the removal of chromium.

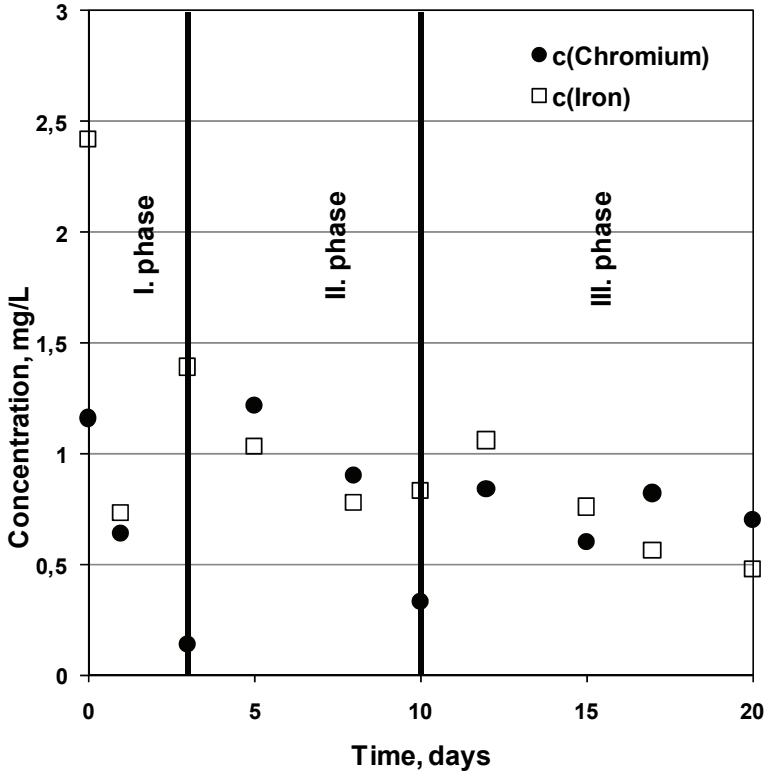


Figure 2. Iron and chromium removal *vs.* time

2.2.2. The Efficiency of Phosphates Removal

The results of phosphates removal efficiency from leachate water in a studied subsurface flow constructed wetland system have been shown in Fig. 3.

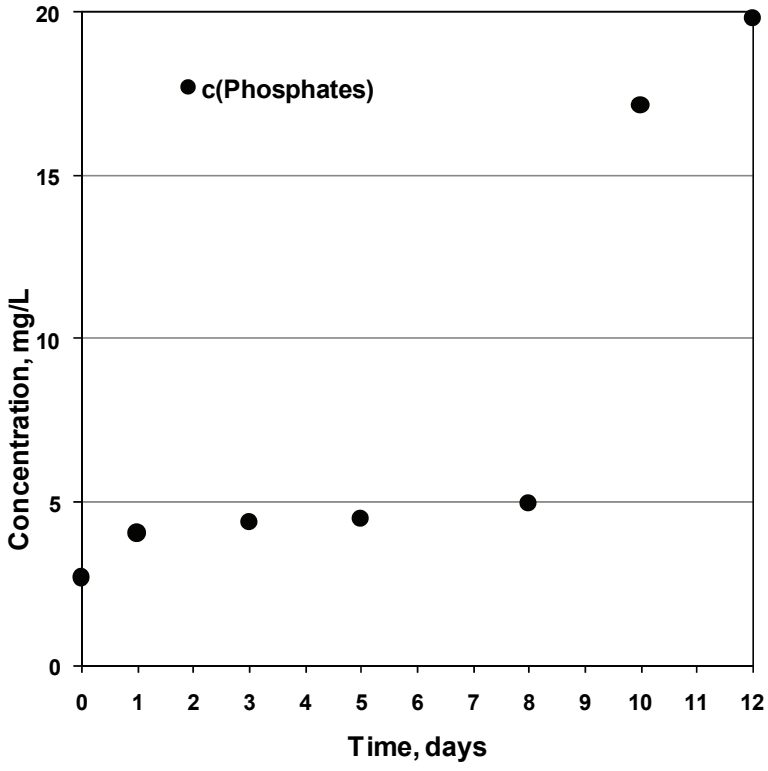


Figure 3. Phosphates removal *vs.* time

It can be seen that initial concentration of phosphates from initial one of 2.710 mg L^{-1} increased up to 19.840 mg L^{-1} after 12 days of treatment in the constructed wetland system. Inefficient removal of phosphates by constructed wetland system could be explained with the possibility of it's leaching from the sediment in particular conditions [16]. Namely, phosphorus has been primarily removed by ion exchange of phosphate with water or hydroxide on the surface of iron or aluminum hydroxide. Substrate that has been used in a subsurface constructed wetland, usually do not contain a sufficient amount of iron, aluminum or calcium which makes phosphorus removal inefficient in general [17].

2.2.3. The Efficiency of TOC and COD Removal

The results of TOC and COD removal efficiencies from leachate water in a studied subsurface flow constructed wetland system have been shown in Fig. 4. Regarding total organic carbon content, a continual decrease of TOC value can be observed, except in the third phase of the treatment which is characterized with slight oscillations of TOC vales. A maximal measured value in this phase was found to be 237.4 mg L^{-1}. In the second phase microorganisms adopted in constructed wetland which resulted with increase of it's biomass. It can be assumed that increase of TOC from initial 223 mg L^{-1} up to 237.4 mg L^{-1} occurred due to the formation of microorganism's metabolites. Due to the lack of technical support COD concentration *vs.* time was monitored just in the first and second phase of the treatment. It can be assumed that COD value decrease was the consequence of conducting of physical processes (sedimentation and filtration) and have been less influenced by the appearance of biological processes [18].

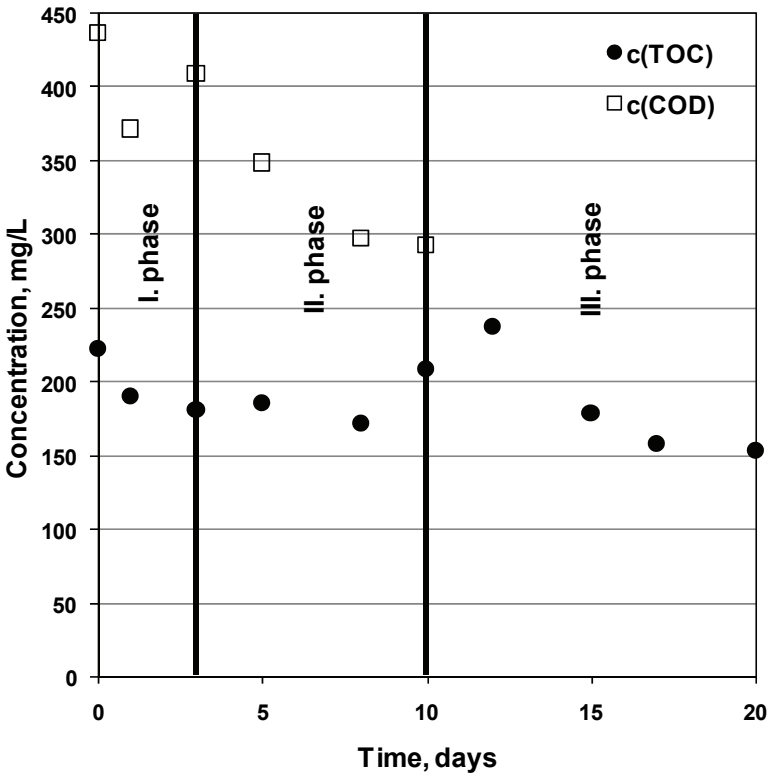


Figure 4. TOC and COD concentrations *vs.* time

2.2.4. The Efficiency of Color Removal

The results of color removal efficiency from leachate water in a studied subsurface flow constructed wetland system have been shown in Fig. 5. It can be seen that the extent of color removal efficiency was almost the same in the all three phases (around 55 %). Moreover, the results show that recirculation did not have any impact on the color removal. Coloration of the leachate water was found to be dark yellow towards brownish, while it was pale yellow on the exit of the constructed wetland.

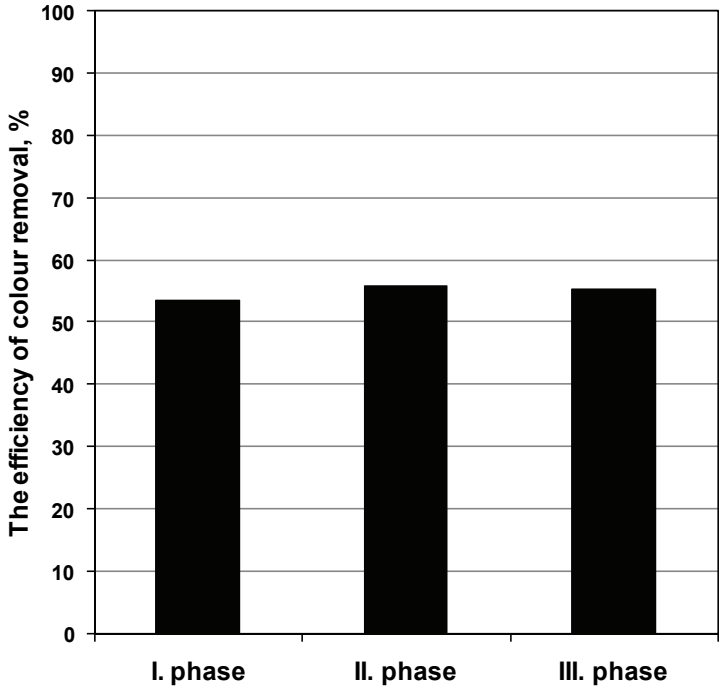


Figure 5. The efficiency of color removal

3. CONCLUSIONS

In this work an application of subsurface constructed wetland system was applied for the treatment of leachate water during the three weeks period. The efficiency of the process was estimated on the basis of iron, chromium, phosphates, TOC, COD and color removal. Iron concentration decreased for 80 % and chromium concentration for 48.3 %. The concentration of phosphates increased for more than seven times in comparison with the initial concentration. Total organic carbon content decreased for 31.3 % after 20 days of treatment in constructed wetland. The extent of coloration of the treated leachate water remained almost unchanged. The obtained results impose that studied surface constructed wetland systems have a significant potential as a technology of choice for the treatment of leachate water regarding heavy metals and TOC removal.

REFERENCES

[1] R. Stegmann, Concepts of waste landfilling, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), Proceedings of the 5th international landfill Symposium, Sardinia, 1995, pp. 2-12.

[2] H. Belevi, P. Baccini, Long-term leachate emissions from municipal solid waste, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), Landfilling of waste: leachate, Elsevier Applied Science, London, 1992, pp. 431-440.

[3] L. Vymazal, Constructed wetlands for wastewater treatment, Ecol. Eng. 25 (2005) 475-477.

[4] http://slobodnalika.com/novosti/4236_biolosko+prociscavanje+otpadnih+voda++biljni+uredaji+za+prociscavanje+otpadnih+voda.html, 08.09.2011.

[5] R.H. Kadlec, R.L. Knight, Treatment Wetlands, Lewis Publisher, Boca Raton, Florida, 1996.

[6] J. Mulqueen, M. Rodgers, G. O' Leary, G. Carty, Wastewater treatment manuals – treatment systems for single houses, Environmental Protection Agency – EPA, Wexford, Ireland, 2000.

[7] E. Tousingnant, Guidance Manual for the Design, Construction and Operations of Constructed Wetlands for Rural Applications in Ontario, Stantec Consulting Ltd., Ontario, Canada, 1999.

[8] C. Vohla, R. Alas, K Nurk, S. Baatz, U. Mander, Dynamics of phosphorus, nitrogen and carbon removal in a horizontal subsurface flow constructed wetland, Sci. Total Environ., 380 (2007) 66-74.

[9] J. Vymazal, Removal of BOD_5 in constructed wetlands with horizontal sub-surface flow: Czech experience, Water Sci. Technol., 40 (1999) 133-138.

[10] D. Vrhovšek, V. Kukanja, T. Bulc, Constructed wetlands (CW) for industrial wastewater treatment, Water Res., 10 (1996) 2287-2292.
[11] P. Molle, A. Lienard, A. Grasmick, A. Iwema, Effect of reeds and feeding operations on hydraulic behavior of vertical flow constructed wetlands under hydraulic overloads, Water Res., 40 (2006) 606-612.
[12] A.K.C. Chung, Y. Wu, N.F.Y. Tam, M.H. Wong, Nitrogen and phosphate mass balance in a sub-surface flow constructed wetland for treating municipal wastewater, Eco. Eng., 32 (2008) 81-89.
[13] A. Ghermandi, D. Bixio, P. Traverso, I. Cersosimo, C. Thoeye, The Removal of Patoghens in Constructed Wetlands and it's Implications for Water Reuse, in: S. Eduardo, C. Carla, C. Bruno, G. Ana Rita, B. Catarina (Eds.), The Eye, MAOTDR, Lisabon, Portugal, 2006, pp. 281-304.
[14] Council Directive 1999/31/EC on the landfill of waste, http://ec.europa.eu/environment/waste/landfill_index.htm, 08.09.2011.
[15] V. Sawaittayothin, C. Polprasert, Nitrogen mass balance and microbial analysis of constructed wetlands treating municipal landfill leachate, Bioresource Technol., 98 (2007) 565-570.
[16] K-Y. Song, K-D. Zoh, H. Kang, Release of phosphate in a wetland by changes in hydrological regime, Sci. Total Environ., 380 (2007) 13-18.
[17] J. Vymazal, Eco. Eng., Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment, 25 (2005) 478-490.
[18] M.P. Ciria, M.L. Solano, P. Soriano, Role of Macrophyte Typha latifolia in a Constructed Wetland for Wastewater Treatment and Assessment of its Potential as a Biomass Fuel, Biosyst. Eng., 92 (2005) 535-544.

ELECTROCHEMICAL TREATMENT OF LANDFILL LEACHATE

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Abstract

The aim of this research was development of appropriate procedure for the treatment of landfill leachate taken from the Piškornica, Mraclinska Dubrava and Viševac sanitary landfills. Due to the complex nature of the effluent a combined treatment approach was applied. The pretreatment step included simultaneous treatment with calcium oxide and electrocoagulation/electrooxidation by stainless steel electrode set. The main treatment included electrocoagulation/electrooxidation using the set of stainless steel, iron and aluminum electrodes. Pretreatment allows the destruction of the humic and fulvic acids and optimization of pH values for the formation of reactive oxidative species, as well as the transformation of NH_4-N into volatile NH_3-N. This pretreatment allows the softening of the water and 100% removal of the bacteria, between 90 and 96% removal of color, turbidity and suspended solids, approximately 65% removal of NH_3-N and more than 98% removal of fluorides, phosphates and heavy metals, while the hardly biodegradable organic matter decomposes into more easily degradable carboxylic acids. In the presence of added calcium oxide and electrochemically generated coagulant the removal of the fluorides, phosphates and heavy metals occur trough the formation of poorly soluble fluorapatite, hydroxyl apatite, and various hydroxides. During the main treatment electrochemically generated reactive oxidative species carried out rapid decomposition of the organic matter and ammonia, resulting in the removal of COD up to 98%, color and turbidity up to 99% and ammonia up to 97%. Following the electrochemical treatment the suspension was passed through an electromagnet in order to speed the separation of the sludge from the treated water. Applied treatment approach resulted in clear, colorless and odorless effluent with the values of all measured parameters significantly lower compared to the upper permissible limit for discharge into the environment.

Keywords: *landfill leachate, CaO, electrocoagulation/electrooxidation/electroreduction, stainless steel/iron/aluminum anode*

1. INTRODUCTION

Landfill leachate was formed by the complex physico-chemical and biochemical transformations of the solid waste deposited at the sanitary landfill as well as by the percolation of atmospheric water thorough the waste body of the sanitary landfill. It is characterized by dark color, unpleasant odor, high conductivity, high concentration of organic bio-refractory compounds and ammonia as well as increased to high concentration of heavy metals [1, 2]. Due to the complex nature and low biodegradability of the effluent a combined treatment approach should be applied.

The possibilities for landfill leachate treatment were summarized in the work of Renou et al., [3]. Among them biological methods based on either aerobic or anaerobic processes, membrane technologies (reverse osmosis, ultrafiltration, nanofiltration), physico-chemical methods (flotation, chemical precipitation, coagulation/flocculation, adsorption, stripping, chemical oxidation), advanced oxidation processes and various electrochemical treatment approaches were used most commonly. Among electrochemical methods electrochemical oxidation is one of the most widely used for the treatment of landfill leachate [4]. An important advantage of this method is the possibility of direct oxidation of the heavily degradable organic matter into CO_2 and water. Promising results in the treatment of landfill leachate were also achieved by electrocoagulation using Al and Fe anodes [5, 6]. A combined treatment approach of the landfill leachate taken from Piškornica landfill using advanced oxidation, electrochemical methods and microwaves resulted in the removal efficiency of color, turbidity,

suspended solids, ammonia, COD and iron for 98.43%, 99.48%, 98.96%, 98.80%, 94.17% and 98.56%, respectively [2].

Piškornica landfill is situated in Koprivnički Ivanec municipality, 9 km north of Koprivnica city and 2.5 km of Puštakovec village [1, 2]. The municipal as well as industrial waste was deposited since 1982. Mraclinska Dubrava landfill is located about 7.5 kilometers south of the center of Velika Gorica and 1650 m south of the village Mraclin. The waste was disposed at the landfill since 1976. Viševac municipal waste landfill is located in the municipality Viškovo, about 10 km southwest of Rijeka. The landfill is located in a karst area, 4 kilometers from the coastline at an altitude of 300 meters. Viševac sinkhole is used for the disposal of municipal waste since 1964.

Until 2005 at all three landfills the waste material was loaded directly on the ground without preliminary foundation of the basic leak proof layer, without daily cover of the deposited waste and without leachate collection and treatment. The recovery work at all three landfills started in 2005 with the aim to isolate all deposited waste material from the environment. The bottom leak proof layer was made of geofoil and clay material with the final soil cover. Following the reconstruction of the landfill, landfill gases are controlled while the landfill leachate is collected by the pipe network into lagoons.

The first attempt of the treatment of landfill leachate from the Piškornica landfill was done by Orescanin et al., [1]. A combined treatment with calcium oxide followed by ferric chloride and finally by clinoptilolite resulted in the removal efficiencies of color, turbidity, suspended solids, ammonia, COD, Fe and Zn for 96.09%, 98.55%, 98.26%, 81.60%, 81.00%, 98.12% and 93.97%, respectively. It was concluded that calcium oxide should be used as a pretreatment step prior to the final electrochemical treatment (electrooxidation, electrocoagulation) or membrane techniques.

2. ELABORATION

2.1. Experimental

2.1.1. Sampling and Sample Handling

For the treatment experiments 100 L of landfill leachate was collected from lagoon of each sanitary landfill. In order to obtain homogeneous sample the effluent was combined into a single tank and mixed for 10 minutes (600 rpm) before analysis or each treatment experiment.

2.1.2. Treatment Methods

For each experiment 20 L of the wastewater was pumped into reaction vessel equipped with stainless steel electrode set and subjected to pre-treatment with optimum dose of calcium oxide (Lika lime factroy, Ličko Lešće, Croatia). For the leachate from Piškornica landfill 25 g/L of CaO was used while in the case of Viševac and Mraclinska Dubrava, 10 g/L was applied. The suspension was mixed by air bubbles supplied by diffuser placed at the bottom of the reaction vessel. After an hour of the pretreatment the suspension was decanted into sedimentation tank and allowed to settle for additional 30 minutes. Pretreated effluent was pumped into electrochemical reactor and subjected to electrooxidation/electrocoagulation using stainless steel electrode set (I=12A; U=6V; reaction time 90 minutes) followed by electroreduction/electrocoagulation using the set of iron electrodes (I=12A; U=6V; reaction time 15 minutes) and finally by electrocoagulation using aluminum electrode set (I=12A; U=6V; reaction time 15 minutes). Each electrode set contained of ten, quadratic, one millimeter thick plates (75 x 250 mm) in the parallel arrangement, separated by electro insulator [2]. The distance between plates was 10 mm. Following the treatment by aluminum electrode set the suspension was subjected to slow mixing with air bubbles for additional 30 minutes in order to complete coagulation/flocculation, while additional 30 minutes was needed for flock's settlement. All conducted experiments were done in triplicate. In all cases RSD was less than 10%.

2.1.3. Sample Preparation and Analysis of Heavy Metals

For the analysis of heavy metals in the samples of the original and purified landfill leachate the samples were pretreated as follows: 100 mL of the leachate was evaporated to dryness and treated with concentrated nitric acid/hydrogen peroxide (30% wt.) at 80^0C, evaporated to dryness and treated again until white deposit was formed which was finally dissolved in 0.5M HNO_3. After complete dissolution, the samples were diluted to 100 mL with double distilled water [1]. The samples of the landfill leachate before/after treatment after the digestion procedure described above were preconcentrated by ammonium-pyrolidinedithiocarbamate (APDC) (Merck, Schuchardt, Germany) and prepared as thin target using a Millipore micro filtration system. The prepared targets were air-dried, protected with a thin

mylar foil (2 μm) and analyzed by X-ray spectrometer [1, 2]. The X-ray spectrometer consisted of the X-ray tube (''Oxford instruments'') with Mo anode (high voltage: 40 kV; current: 900 μA; cooling medium: Air). The detection of characteristic X-ray radiation from the sample was conducted with Si drift detector - model SXD15C-150-500 (Canberra, Meriden, USA) (surface: 15mm^2; FWHM for 5.9 keV ^{55}Fe: 145 eV; Window: 13 μm Be; cooling: thermo-electrical (peltier)). For the signal processing DSA 2000 (Canberra) was used. The spectral data were collected by Genie-2000 software (Canberra) while for the spectrum deconvolution and quantitative analysis WinAxil software package (Canberra) was used. In order to obtain a good counting statistic, collecting time was 10000 s. The calibration model for the qualitative and quantitative analysis was created on the basis of the measurements of the standard solutions (Merck) having the concentration range from 10 to 200 μg/L, prepared and measured in the same way as unknown samples.

2.1.4. Determination of Other Parameters

Color was determined according to 8025 APHA platinum-cobalt standard method (adopted from Standard Methods for the Examination of Water and Wastewater) using HACH DR890 colorimeter (Hach Company, Loveland, Colorado, USA). For accuracy and performance check a 500 platinum-cobalt unit's color standard solution (Cole-Parmer, USA) was used. Turbidity was determined by 8237 absorptometric method using HACH DR890 colorimeter. For accuracy and performance check 4000 NTU Formazin stock solution (Cole-Parmer, USA) was used. Suspended solids were determined by 8006 photometric method using HACH DR890 colorimeter. Chemical oxygen demand (COD) was determined by reactor digestion method using HACH DR890 colorimeter. For sample digestion DRB 200 reactor (Hach Company) was used. NH_4^+ was determined by 8155 salicylate method using HACH DR890 colorimeter. For accuracy and performance check 10 mg/L standard solution (Hach Company, Loveland, Colorado, USA) was used. Estimated detection limit was 0.02 mg/L NH_4^+ and standard deviation ±0.02 mg/L. Fluorides were determined by the 10225 SPADNS 2 method using SPADNS 2 reagent solution using HACH DR890 colorimeter. For accuracy and performance check 0.1 mg/L standard solution (Cole-Parmer) was used. Estimated detection limit was 0.05 mg/L F^- and standard deviation ±0.035 mg/L. pH value, electrical conductivity (EC) and total dissolved solids (TDS) were determined by PHT-027 – water quality multiparameter monitor (Kelilong Electron, Fuan Fujian, China). For calibration purpose Cole-Parmer standard solutions were used.

2.2. Results and Discussion

2.2.1. Piškornica Landfill

The values of physico-chemical parameters in the landfill leachate from the Piškornica landfill prior/after the treatment were presented in Table 1. It was stable leachate with slightly alkaline reaction and dark brown to black color (caused by the presence of high molecular weight humic substances), high turbidity and suspended solids. The parameters COD and phosphates increased more than four times and five times respectively over upper permissible limit [7] while ammonia 42 times exceeded that limit. Generally, the concentrations of heavy metals were low and only iron slightly exceeded permissible limit. Due to the complex composition and low biodegradability of the leachate a combined treatment was applied.

Following the pretreatment with CaO and electrocoagulation/electrooxidation by stainless steel electrode set, 94.93% of color, 98.19% of turbidity and 97.22% of suspended solids was removed from the leachate (Table 1; Fig. 1). Addition of CaO resulted with increased pH value over 12 and consequently transformation of NH_4^+ into volatile NH_3 form which could be removed from the leachate more easily. Over 70% of ammonia was stripped from the treated effluent after an hour of the pretreatment. Moreover, the optimization of pH value allowed the formation of the reactive oxidative species that carried out rapid decomposition of the organic matter which resulted in the removal of COD for more than 60%. Removal of phosphates (98.72%) and fluorides (97.87%) was most probably achieved by the formation of the stable compounds like hydroxyl apatite and flour apatite and heavy metals by the formation of their hydroxides. Following the main electrochemical treatment the removal efficiency of color, turbidity, suspended solids, COD, ammonia and phosphates was over 99% while in the case of heavy metals the removal efficiency ranged from 95.52% to 100%. The removal of higher molecular weight substances and heavy metals was most probably achieved by the coagulation with electrochemically generated $Fe^{2+}/Fe^{3+}/Al^{3+}$ ions while the removal of lower molecular weight substances and ammonia was mostly achieved by indirect anodic oxidation with chlorine/hypochlorite generated *in*

situ from the chloride ions already present in the leachate. Following the combined treatment all measured parameters in the final effluent were in accordance with regulated values (Table 1).

Table 1. Physical and chemical parameters determined in the landfill leachate from Piškornica landfill prior/after the treatment together with the upper permissible limit for wastewater suitable for discharge into natural recipient. *Regulations on limit values of the emission of wastewaters (OG No. 87/10) [7]

Parameter	Untreated	Treated		UPL*
		Pretreatment	Final electrochemical treatment	
Color (PtCo)	**5600**	284	18	without
Turbidity (NTU)	**1550**	28	4	without
SS (mg/L)	**576**	16	4	35
pH	7.33	12.65	8.74	6.5-9
EC (mS/cm)	2.93	3.55	3.17	-
TDS (mg/L)	2050	2490	2210	-
COD (mg/L)	**617**	241	36	125
NH_4-N (mg/L)	**420**	125	1.5	10
PO_4-P (mg/L)	**5.79**	0.074	0.006	1
F^- (mg/L)	0.94	0.02	0.02	10
Fe (mg/L)	**2.017**	0.078	0.029	2
Zn (mg/L)	0.63	0.23	0.06	2
Cr (mg/L)	0.016	n.d.	n.d.	0.5
Ni (mg/L)	0.023	n.d.	n.d.	0.5
Cu (mg/L)	0.067	0.008	0.003	0.5
Pb (mg/L)	0.003	n.d.	n.d.	0.5

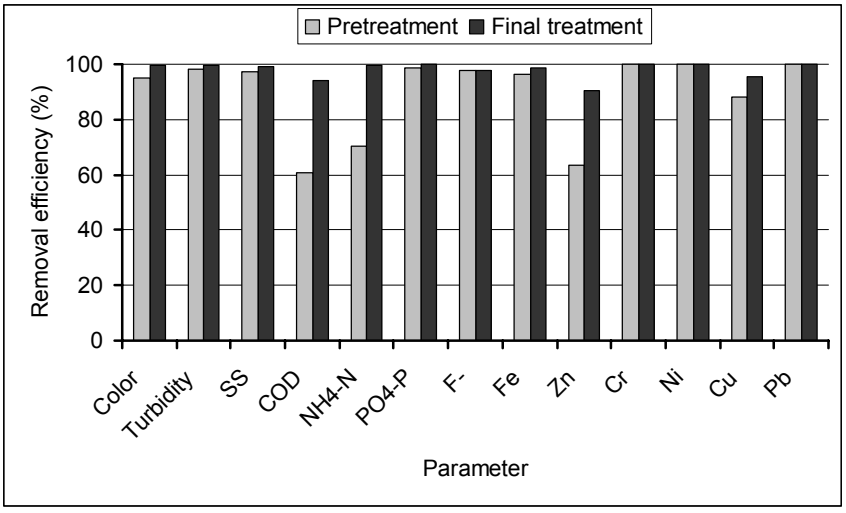


Figure 1. Removal efficiency of the parameters from the landfill leachate from Piškornica landfill following the combined treatment with CaO and electrochemical methods

2.2.2. Mraclinska Dubrava Landfill

The values of physico-chemical parameters in the landfill leachate from the Mraclinska Dubrava landfill prior/after the treatments were presented in Table 2. Compared to the regulated values [7] the parameters (Table 2) color, turbidity, suspended solids, organic matter (COD), ammonia, iron and chromium exceeded the upper permissible limit. Following an hour of the pretreatment over 95% of color and turbidity and almost 92% of suspended solids was removed from the leachate (Fig 2) while the removal efficiency of COD, ammonia, iron and chromium was 66.55%, 56.25%, 98.72% and 94.70%, respectively.

Table 2. Physical and chemical parameters determined in the landfill leachate from Mraclinska Dubrava landfill prior/after the treatment together with the upper permissible limit for wastewater suitable for discharge into natural recipient. *Regulations on limit values of the emission of wastewaters (OG No. 87/10) [7].

Parameter	Untreated	Treated		UPL*
		Pretreatment	Final electrochemical treatment	
Color (PtCo)	3960	171	48	without
Turbidity (NTU)	250	12	4	without
SS (mg/L)	171	14	5	35
pH	7.47	11.88	8.88	6.5-9
EC (mS/cm)	4.92	8.56	3.12	-
TDS (mg/L)	3400	5930	2170	-
COD (mg/L)	580	194	80	125
NH_4-N (mg/L)	200	87.5	0.75	10
PO_4-P (mg/L)	0.79	0.25	0	1
F^- (mg/L)	0.97	0.39	0.27	10
Fe (mg/L)	3.356	0.043	0.044	2
Zn (mg/L)	0.472	0.025	0.014	2
Cr (mg/L)	1.037	0.055	0.019	0.5
Ni (mg/L)	0.263	0.017	0.013	0.5
Cu (mg/L)	0.124	0.019	0.006	0.5
Pb (mg/L)	0.008	0.001	0.001	0.5

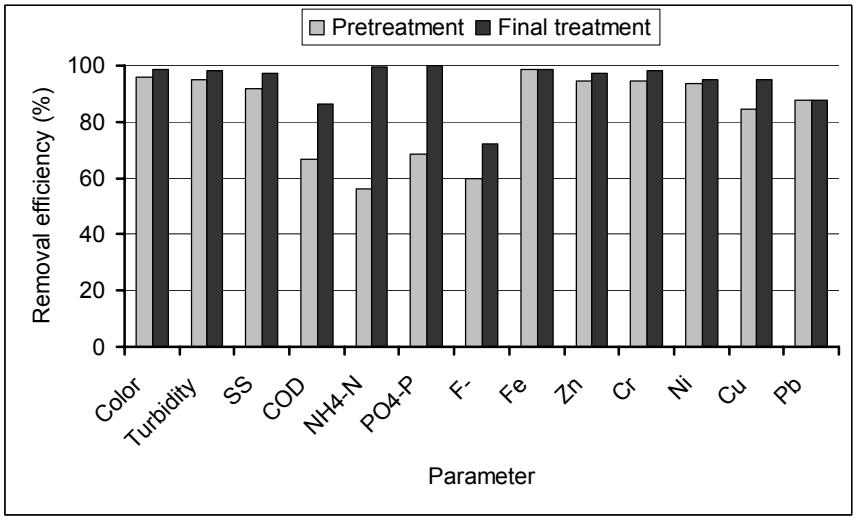


Figure 2. Removal efficiency of the parameters from the landfill leachate from Mraclinska Dubrava landfill following the combined treatment with CaO and electrochemical methods

Following the final electrochemical treatment all measured parameters in the final effluent were in accordance with regulated values (Table 2) with the removal efficiency of color, turbidity, suspended solids, COD, ammonia, phosphates, fluorides, iron, zinc, chromium, nickel, copper and lead reaching the following values: 98.79%, 98.40%, 97.08%, 86.21%, 99.63%, 100%, 72.16%, 98.69%, 97.03%, 98.17%, 95.06%, 95.16% and 87.50%, respectively. In the case of heavy metals and nutrients, the removal efficiency increased with increasing initial concentration.

2.2.3. Viševac landfill

The values of physico-chemical parameters in the landfill leachate from the Viševac landfill prior/after the treatment were presented in Table 3. Compared to the regulated values the parameters (Table 3) color, turbidity, suspended solids, COD and ammonia exceeded the upper permissible limit [7]. Following an hour of the pretreatment with CaO/stainless steel electrode set removal efficiency of these five parameters reached the following values: 95.04%, 97.69%, 93.33%, 65.76% and 76.67%, respectively (Fig 3). Following the final electrochemical treatment all measured parameters in the final effluent were significantly lower compared to upper permissible limit (Table 3) with the removal efficiency of color, turbidity, suspended solids, COD, ammonia, phosphates, fluorides, iron, zinc, chromium, nickel, copper and lead reaching the following values: 99.53%, 98.46%, 97.78%, 74.92%, 99.65%, 100%, 97.73%, 98.86%, 99.20%, 78.42%, 89.80%, 92.00% and 90.83%, respectively.

Table 3. Physical and chemical parameters determined in the landfill leachate from Viševac landfill prior/after the treatment together with the upper permissible limit for wastewater suitable for discharge into natural recipient. *Regulations on limit values of the emission of wastewaters (OG No. 87/10) [7].

Parameter	Untreated	Treated		UPL*
		Pretreatment	Final electrochemical treatment	
Color (PtCo)	**1270**	63	6	without
Turbidity (NTU)	**130**	3	2	without
SS (mg/L)	**90**	6	2	35
pH	8.18	12.02	8.84	6.5-9
EC (mS/cm)	2.38	4.17	2.98	-
TDS (mg/L)	1660	2940	2090	-
COD (mg/L)	**295**	101	74	125
NH_4-N (mg/L)	**150**	35	0.52	10
PO_4-P (mg/L)	0.53	0.10	0	1
F^- (mg/L)	0.44	0.12	0.01	10
Fe (mg/L)	1.476	0.029	0.017	2
Zn (mg/L)	0.631	0.052	0.005	2
Cr (mg/L)	0.038	0.011	0.008	0.5
Ni (mg/L)	0.049	0.012	0.005	0.5
Cu (mg/L)	0.034	0.018	0.003	0.5
Pb (mg/L)	0.048	0.007	0.004	0.5

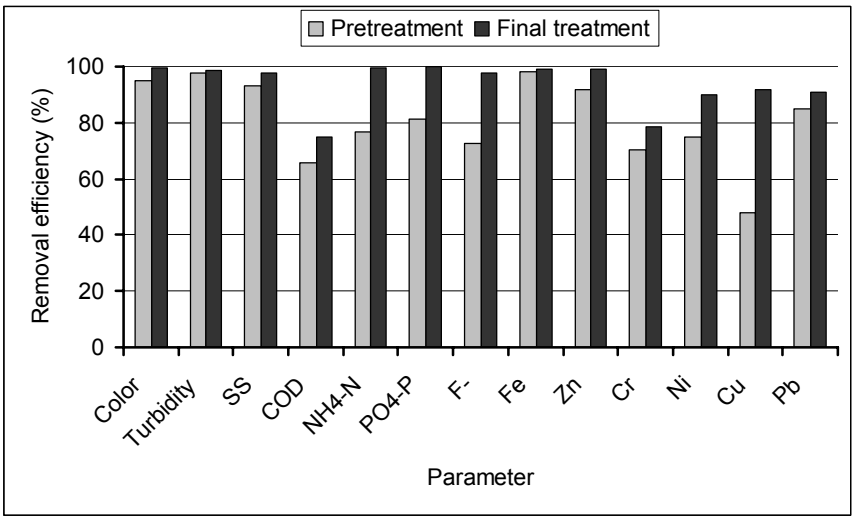


Figure 3. Removal efficiency of the parameters from the landfill leachate from Viševac landfill following the combined treatment with CaO and electrochemical methods

3. CONCLUSIONS

From the presented results it could be concluded that the pretreatment with CaO/stainless steel electrodes allows the destruction of high molecular weight humic and fulvic substances and their removal by coagulation/flocculation with electrochemically generated Fe^{2+}/Fe^{3+} flocs as well as by the destruction of organic substances with electrochemically generated reactive oxidative species resulting with the removal of color from 94.93% to 95.68%, turbidity from 95.20% to 98.19% and COD from 60.94% to 66.55%. Increase of pH value to over 11 following the addition of CaO caused the transformation of NH_4-N into volatile NH_3-N and its removal from the leachate from 56.25% to 76.67%. During the main treatment electrochemically generated reactive oxidative species carried out rapid decomposition of the organic matter and ammonia, resulting in the removal of COD from 74.92% to 94.17%, color from 98.79% to 99.68%, turbidity from 98.40% to 99.31% and ammonia from 99.63% to 99.65%. Slightly better results for the removal efficiency of color, turbidity and suspended solids were obtained in the case of Piškornica landfill compared with the other two landfills, while the COD removal efficiency decreases in the following order: Piškornica >Mraclinska Dubrava >Viševac. This could be related to the age of the landfill, which increases in the same order. Consequently, with the increasing age of the landfill the degree of degradability of the organic matter highly reduces. Applied treatment approach resulted in clear, colorless and odorless effluent with the values of all measured parameters in the leachate from all three landfills significantly lower compared to the upper permissible limit for discharge into the environment.

REFERENCES

[1] V. Orescanin, D. Ruk, R. Kollar, Lovrencic I. Mikelic, K. Nad, N.Mikulic, A combined treatment of landfill leachate using calcium oxide, ferric chloride and clinoptilolite, J. Environ. Sci. Health, Part A. 46 (2011) 323-328.

[2] V. Orescanin, R. Kollar, D. Ruk, K. Nad, Characterization and electrochemical treatment of landfill leachate, J. Environ. Sci. Health, Part A. 2011, *In press*.

[3] S. Renou, J.G. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: Review and opportunity, J. Hazard. Mat. 150 (2008) 468-493.

[4] Y. Deng, D.J. Englehardt, Electrochemical oxidation for landfill leachate treatment, Waste Manage. 27 (2007) 380–388.

[5] C.T. Tsai, S.T. Lin, Y.C. Shue, P.L. Su, Electrolysis of soluble organic matter in leachate from landfills, Water Res. 17 (1997) 773–778.

[6] S. Veli, T. Öztürk, A. Dimoglo, Treatment of municipal solid wastes leachate by means of chemical and electro-coagulation, Sep. Purif. Technol. 61 (2008) 82-88.

[7] Regulations on limit values of the emission of wastewaters (OG No. 87/10).

INFLUENCE OF MICROWAVE AND ULTRASONIC IRRADIATION ON ZEOLITE MATERIAL CATION-EXCHANGE PROPERTIES

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Abstract

In this work, preliminary investigations of waste mud immobilization study in a mud-zeolite ceramic bricks are presented. In order to improve the cation exchange properties of examined clinoptilolite samples (Donje Jesenje pit, Croatia, Europe), influence of microwave and ultrasonic irradiation treatment on its exchange abilities was examined. The presented results indicate the positive influence of ultrasonic irradiation, while at the same time microwave irradiation demonstrated negative effect. For examine the zeolite's cation-exchange properties, one of the most frequently used methods, the cobalt(III)-hexamine method was applied.

Keywords: *cation exchange properties, zeolite, microwave irradiation, ultrasonic irradiation*

1. INTRODUCTION

Zeolites are microporous alumosilicate minerals that are commonly used as a commercial adsorbens. The therm zeolite (from the Greek lenguage; word *zeo* means babble, and *lithos* stone) is introduced by Swedish scientist Axel Fredrik Cronstedt [1]. During the heating of zeolite he observed that mineral is babbling. This babbling effect is connected with boiling of the liquid water generally contained in zeolite pores. Till the end of 2010, 194 unique zeolite frameworks have been identified, and over 40 of them are naturally occurring zeolite frameworks (so called *natural zeolites*) [2]. Regardless, only several natural zeolites exist in substantial quantities in sedimentary layers, namely: analcime, chabazite, mordenite, erionite, heulandites, phillipsite, and especially clinoptilolite, which attract strong commercial interest as the world most abundant zeolite mineral.

Zeolites are among the most important inorganic cation exchangers [4]. The aluminosilicate structure is negatively charged and attracts cations that come to reside inside the pores and channels.

Cation exchange properties of zeolite are usually defined by the amount of exchangeable cations in the mineral, and are usually expressed in milliequivalents per gram of mineral.

The transfer of ions from a solution to zeolite and reverse is determined by electro-neutrality of zeolite structure, regulating the concentration of ions in both phases and the selectivity. The zeolite cation-selectivity is a function of cations electrostatic interactions with negatively charged cation-exchange sites on the zeolite skeleton and the interactions among the cations and solvent molecules (water). Zeolites with higher Si/Al ratio, prefer larger, more weakly hydrated cations such as Cs^+, K^+, Rb^+, and selectivity is more dependent on a difference between the enthalpy of hydration of two cations, than the difference in their electrostatic interactions with zeolite skeleton. In contrast, zeolites with lower Si/Al ratio have a tendency toward more mobile, smaller cations, such as Li^+ and Na^+. In this case, the selectivity is more controlled by cation-skeleton interactions, than interactions between cations and water. In case of divalent cations, zeolites, regardless of their composition, preferred cations of large diameter.

2. ELABORATION

2.1. Experimental

2.1.1. Reagents and Solutions

Zeolite samples used in this work were clinoptilolite samples supplied from Vranjska Banja, Serbia. For examination of clinoptilolite's cation exchange properties cobalt(III)-hexamine chloride (99%, Acros Organics, New Jersey, USA) was used. All solutions used in experiments were prepared by using deionized water (18 MΩ, Millipore, Billerica, USA).

2.1.2. Pretreatment of Zeolites

1000 grams of natural zeolite clinoptilolite was air dried in oven at 105 °C for 48 hours. After drying, the zeolite was crushed in a planetary ball mill (Pulverisette 6, Fritsch), and then sieved to particle size 0.25-0.60 millimeters. The sifted zeolite (approximately 1.1 g each, weighed on a technical scale) were processed by microwaves (MARS-X, CEM Corporation, USA) and ultrasonic waves (Bandelin SONOREX Digital 10 P Ultrasonic bath, Sigma-Aldrich, St. Louis, USA). The variable parameters were power of microwave oven (0, 150, 300, and 600 W), microwave treatment duration (0, 5, 10, and 20 min), power of ultrasonic bath (0, 240, 600, and 1200 W), ultrasonic-wave treatment duration (0, 5, 10, 20 and 40 min). According to *full-factorial design* methodology [5] this provided 130 differently pretreated zeolite samples.

2.1.3. Calibration diagram

An appropriate amount of $[Co(NH_3)_6]Cl_{3(s)}$ was dried in oven at 105 °C for 1 hour. After drying, the weighed mass of 4.2575 g of salt was dissolved in deionized water and quantitatively transferred into a 100 mL flask. Flask was supplemented to the mark with deionised water, and the basic standard solution (BSS) with cobalt complex concentration of 166.67 mM was obtained. Working standard solutions (WSS) were prepared by diluting BSS by factor of 10. Solutions for calibration line were prepared in values of 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25, 50, 75, 100 and 150% of the WSS concentration.

For cobalt(III)-hexamine solutions, absorbance maximum in range from 200-700 nm was determined (Lambda 35 UV-Vis Spectrometer, Perkin Elmer, Waltham, USA). All further measurements were performed at maximal absorption wavelength.

2.1.4. *Examing the Zeolite's Cation-Exchange Properties*

Among numerous methods for determination of cation exchange capacity of soils and sediments, the cobalt-hexamine method [6][7] is quite frequently used.

To examine the exchange properties of pretreated zeolite samples, 1.0000 g of each sample was placed in a 50 mL plastic container. After the addition of 40 mL WSS solution, the containers were placed in a shaker at 200 rpm and 30 °C for 2 hours. Finally, solutions are filtered through 0.2 μm filter, and analyzed by UV/Vis spectrophotometer at wavelength related to maximal absorbance.

2.3. Results and Discussion

For examination of zeolite's cation-exchange properties, the cobalt-hexamine method was used. The scanning of cobalt-hexamine spectra in range 200-700 nm indicated absorption maximum at 475.3 nm.

The obtained results are presented as 3D plots where mass of the adsorbed cobalt per gram of treated zeolite sample is set in relation with treatment durations. The plots are presented for each combination of microwave oven and ultrasonic bath powers.

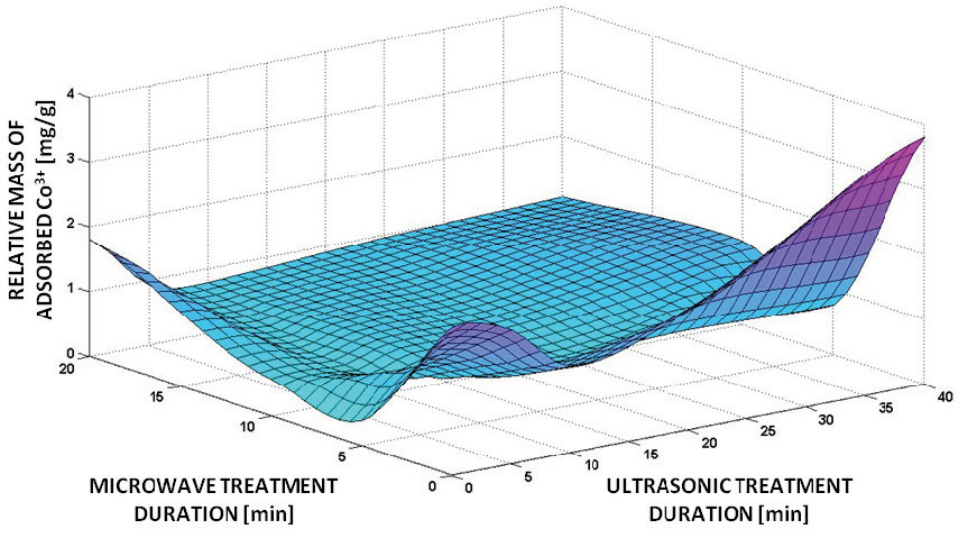


Figure 1. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 150 W and ultrasonic waves at 240 W.

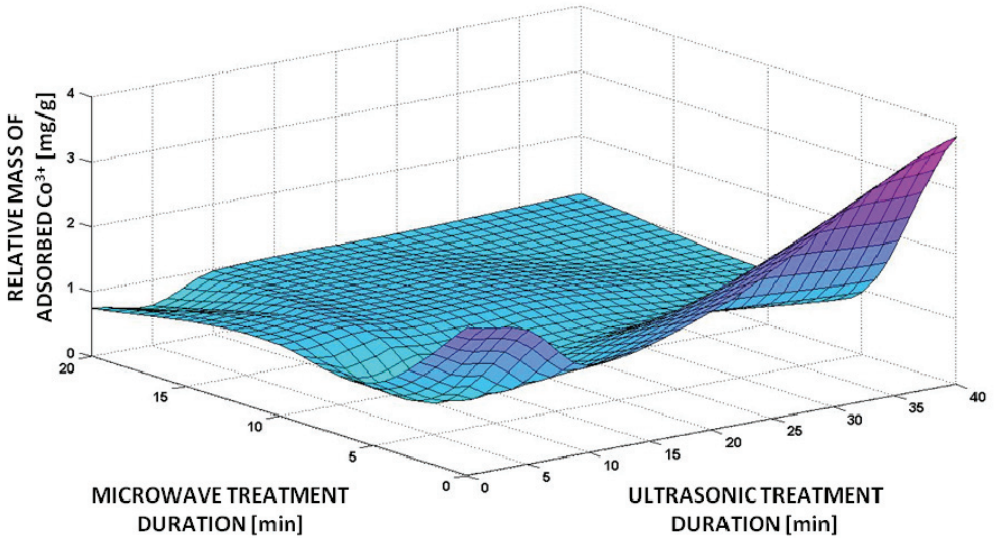


Figure 2. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 300 W and ultrasonic waves at 240 W.

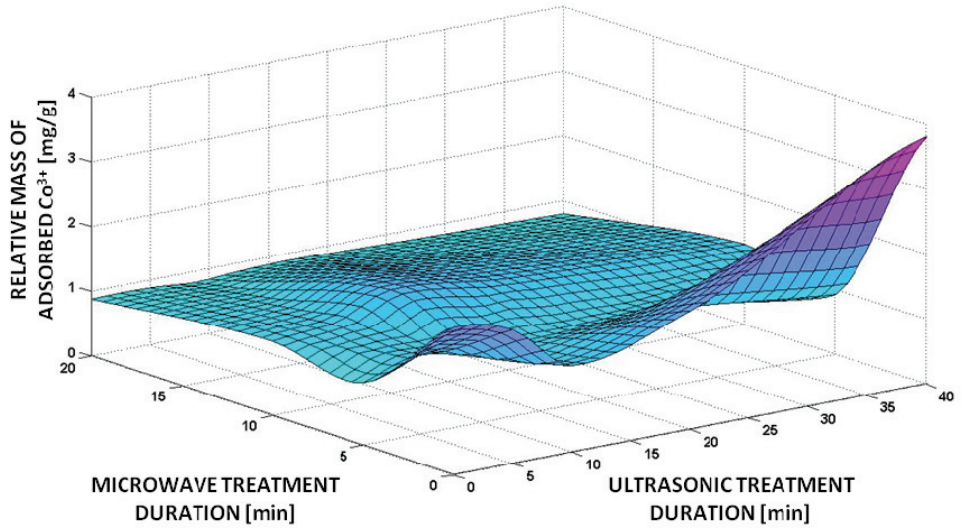


Figure 3. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 600 W and ultrasonic waves at 240 W.

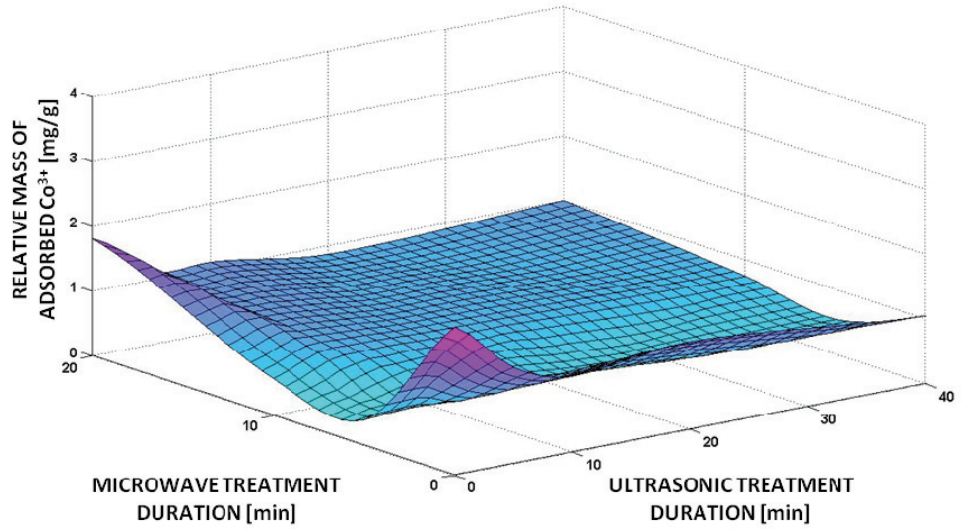


Figure 4. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 150 W and ultrasonic waves at 600 W.

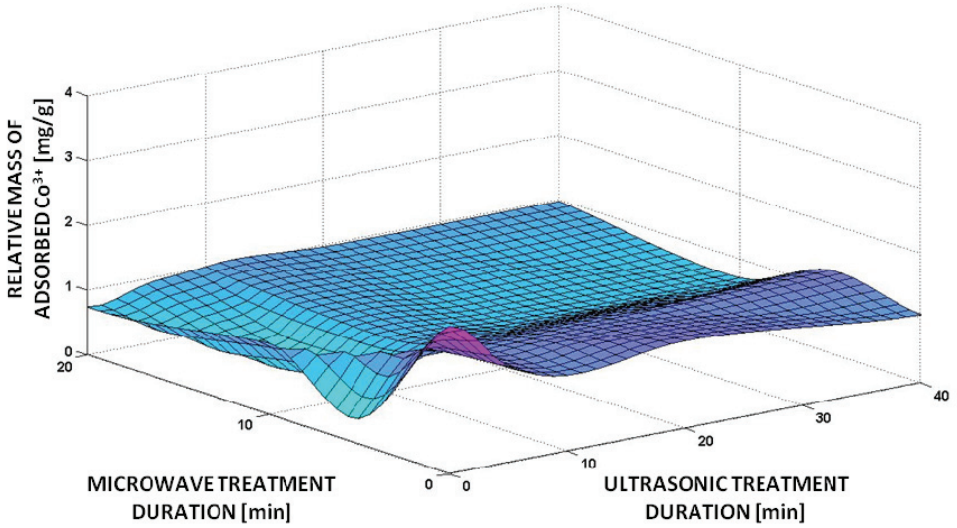


Figure 5. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 300 W and ultrasonic waves at 600 W.

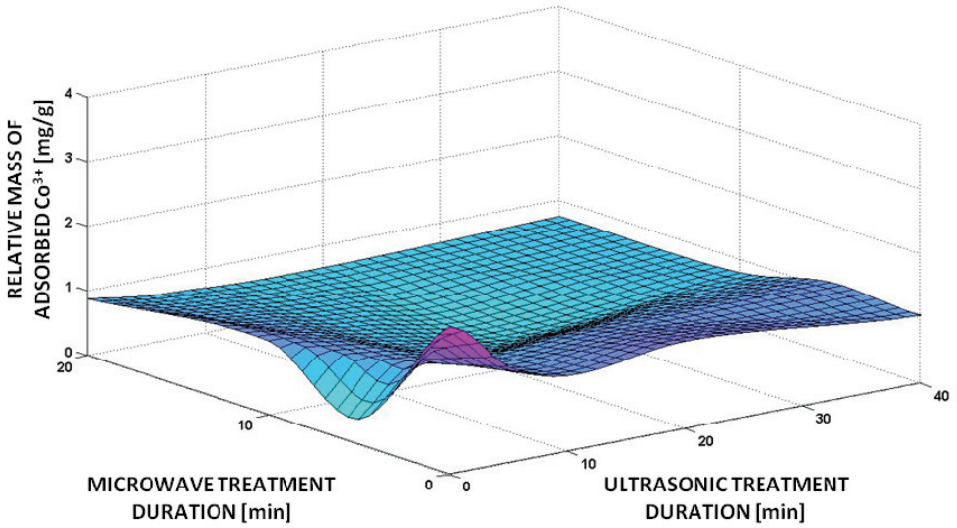


Figure 6. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 600 W and ultrasonic waves at 600 W.

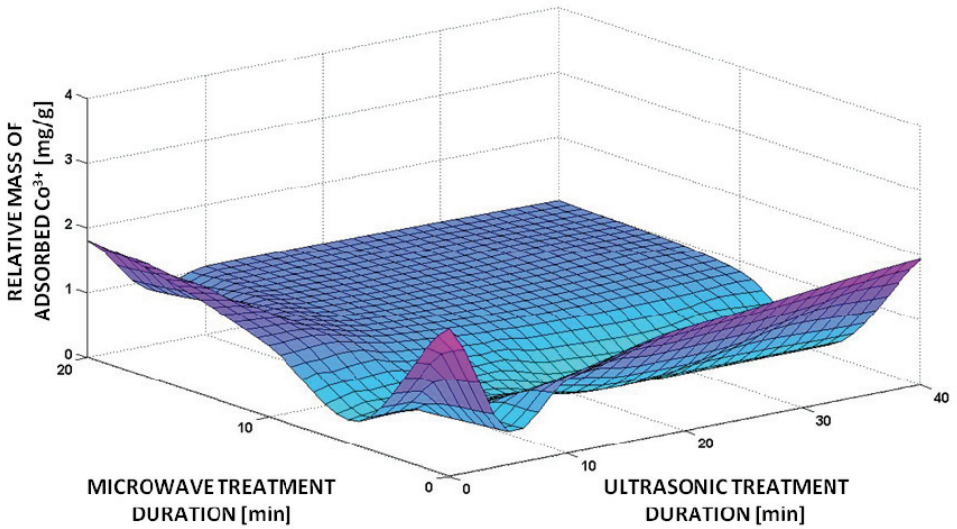


Figure 7. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 150 W and ultrasonic waves at 1200 W.

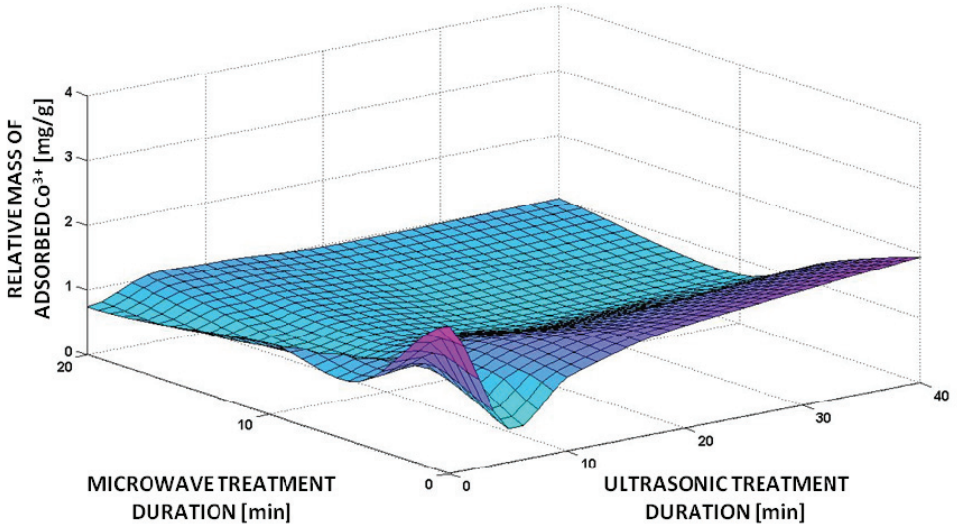


Figure 8. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 300 W and ultrasonic waves at 1200 W.

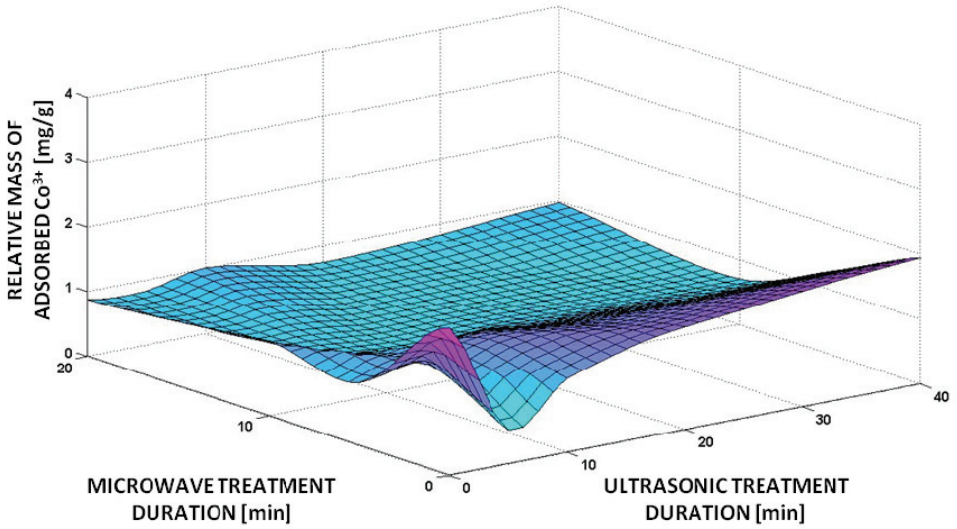


Figure 9. Mass of adsorbed cobalt per gram of zeolite sample in dependence of treatment duration. Sample is treated by microwaves at 600 W and ultrasonic waves at 1200 W.

Figs. 1., 4. and 7. show an increase in mass of the adsorbed cobalt with increasing of microwave treatment duration. In other cases this trend is slightly expressed or no noticeable at all. Figs. 1.-3. and 7.-9. indicate the increase in mass of the adsorbed cobalt with ultrasonic treatment duration, which is not noticeable at other figures (Figs. 4.-6.). Among these easy perceptions, presented results also bring out several quite interesting annotations that should be considered for further research. The amount of cobalt adsorbed by non-treated zeolite is higher than any obtained by microwave treated zeolite samples. At the same time, the best adsorption results are obtained if the samples are treated only ultrasonically. The possible reason for such behavior could be destructive influence of microwaves on zeolite skeleton, and thereupon plugging of zeolite pores. Such scenario should be confirmed by structural analysis, but it would undoubtedly cause the reduction of adsorption active surface, and therefore decrement of adsorbed amount of cobalt. Opposite to microwaves, much less destructive approach such as usage of ultrasonic waves can contribute the increasing of cation exchange abilities. Though, it is important to notice that excessive ultrasonic treatment can have negative effect on cation adsorption, since the better results are obtained while bath was working at 240 W, than in cases at 600 or 1200 W. Therefore, in general, the best adsorption result of 3.8022 mg Co per gram of zeolite is obtained when the mineral sample is treated only ultrasonically at 240 W in duration of 40 minutes.

3. CONCLUSIONS

In this work the clinoptilolite samples were treated by micro and ultrasonic waves. Although both treatments are similar in nature, the intensity of their waves is significantly different and therefore they do not have similar effects. While reasonable ultrasonic treatment can provide the increasing of cation exchange ability, the excessive treatments have slight or even no noticeable effect. Opposite to ultrasonic treatment, microwaves decreasing the cobalt adsorption, and their application proved to be unjustifiable.

The best adsorption characteristics are obtained for zeolite sample treated only ultrasonically at 240 W in duration of 40 minutes.

REFERENCES

[1] C. Colella, A.F. Gualtieri, Cronstedt's zeolite, Micropor. Mesopor. Mat. 105 (2007) 213–221.

[2] J.A.C. Lobo, Heterogeneous asymmetric epoxidation of cis-ethyl cinnamte over Jacobsen's catalyst immobilized in inorganic porous materials, PhD thesis, University of Technology of Aachen, Department of Chemical Technology and Heterogeneous Catalysis, Aachen, Germany, 2005.

[3] www.iza-structure.org/databases/

[4] F. Aydın, A. Kuleyin, The Effect of Modification and Initial Concentration on Ammonia Removal from Leachate by Zeolite, WASET, 78 (2011) 293-296.

[5] S.N. Deming, S.L. Morgan: Experimental Design, a Chemometric Approach, 2nd ed., Elsevier, Amsterdam, 1993.

[6] P. Renault, P. Cazevieille, J. Verdier, J. Lahlah, C. Clara, F. Favre, Variations in the cation exchange capacity of a ferralsol supplied with vinasse, under changing aeration conditions: Comparison between CEC measuring methods, Geoderma 154 (2009) 101–110.

[7] D. Aran, A. Maul, J.F. Masfaraud, A spectrophotometric measurement of soil cation exchange capacity based on cobaltihexamine chloride absorbance, C. R. Geoscience 340 (2008) 865–871.

INFLUENCE OF ULTRASONIC AND MICROWAVE IRRADIATION ON CATION EXCHANGE PROPETRIES OF CLAY MATERIAL

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Abstract

This paper presents preliminary investigations of waste mud immobilization study in a mud-clay ceramic. Although one of the most popular physical methods of structure modification is thermal treatment, some other irradiation treatments could possibly provide good results. In this work, the effect of microwave and ultrasonic irradiation on cation exchange properties of clay material was investigated. In order to improve these properties, influence of microwave and ultrasonic irradiation treatment on clay exchange abilities was examined. For all experiments the clay-raw from pit Dren, in the vicinity of town Vinkovci, (Croatia, Europe) was used, and maximal amount of exchanged cations was determine using cobalt(III)-hexamine method. The obtained results were presented and extensively discussed.
Keywords: *cation exchange, clay, microwave irradiation, ultrasonic irradiation*

1. INTRODUCTION

In nowadays the significance of waste management extremely grows, due mostly to highly expressed public environmental awareness, and consequently the numerous new environmental legislations. Extremely popular approach for immobilization of numerous hazardous substances is solidification in cement, or as a rather new approach, the immobilization in ceramic or glass.

The basic component of “traditional” ceramic is clay [1]. Clay is a natural aluminum silicate, a mineralogical sediment created by degradation (mechanical, chemical or organic) of diverse magmatic and silicate rocks [2]. Along with aluminosilicate minerals (kaolinite, montmorillonite, illite, nontronite…) some other additives such as: quartz, iron hydroxide, carbonate, orthoclase, humus, and coal [3,4] can be found. Specific properties of all clay minerals are derived from their chemical composition, layered structure and particle size. Due to them, clay is very versatile materials and hundreds of millions of tons find applications not only in ceramics and building materials, paper coatings an fillings, drilling muds, foundry moulds, pharmaceuticals, but also as adsorbents, catalysts or catalyst supports, ion exchangers… [5-11].

The most importan clay characteristic for metal waste removal is ion-exchange. In the ion-exchange process, the major factor is clay's specific surface, i.e. the availability of the active sites to exchangeable ions. Consequently, any change in clay structure could increase or decrease the exchange abilities. The intention of this work was to make such structural changes by microwave and/or ultrasonic treatments, and to monitor the advantages or disadvantages of such approach on cation exchange abilities of clay material.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Materials and Reagents

The examined clay samples were supplied from clay-pit Dren near town Vinkovci, Croatia. Determination abilities of heavy-metal exchange were tested on cobalt ions. For that purpose cobalt(III)-hexamine chloride (99%, Acros Organics, New Jersey, USA) was used. Deionized water (18 MΩ, Millipore, Billerica, USA) was used for preparation of all solutions.

2.1.2. Pretreatment of Clay

1000 g of clay-raw was dried in the oven at 105 °C for 48 hours. After drying, the clay was crushed in a planetary ball mill (Pulverisette 6, Fritsch), then sieved to particle size 0.25-0.60 μm. Experimental

variables were power of microwave oven (0, 150, 300, and 600 W), microwave treatment duration (0, 5, 10, and 20 min), power of ultrasonic bath (0, 240, 600, and 1200 W) and ultrasonic-wave treatment duration (0, 5, 10, 20 and 40 min). Designing the experiment according to *full-factorial methodology* [12], 130 samples of sieved clay, aproximately 1.1 g each, were treated differently by microwaves (MARS-X, CEM Corporation, USA) and ultrasonic waves (Bandelin SONOREX Digital 10 P Ultrasonic bath, Sigma-Aldrich, St. Louis, USA).

2.1.3. Determination of Cation Exchange Abilities of Clay Samples

The exchange of heavy-metals on clay material was tested using cobalt(III)-hexamine method [13-14]. Primary, the calibration diagram for cobalt complex was made. In order to obtain basic standard solution (BSS), 4.2575 g of dried $[Co(NH_3)_6]Cl_3$ salt (at 105 °C for 1 hour) was dissolved in deionized water, quantitatively transferred into a 100 mL flask and supplemented with deionized water to the mark. Working standard solutions (WSS) were obtained by diluting the BSS by factor 10. Solutions for calibration line were prepared in values of 0.1, 0.25, 0.5, 1, 2.5, 5, 10, 25, 50, 75, 100, and 150% of the WSS concentration. Absorbance spectrum for $[Co(NH_3)_6]^{3+}$ was recorded in range 200-700 nm on UV/Vis spectrophotometer (Lambda 35 UV-Vis Spectrometer, Perkin Elmer, Waltham, USA) and maximal absorption wavelength was determined (Fig. 1).

To examine the cation exchange abilities of tested clay mineral, 1.0000 g of each sample (pretreated clay) was set in contact with 40 mL of WSS solution in thermostatic shaker at 200 rpm and 30 °C for 2 hours. Finally, solutions are filtered through 0.2 μm filter, and analyzed by UV/Vis spectrophotometer at maximal adsorption wavelength (475.3 nm, Fig. 1).

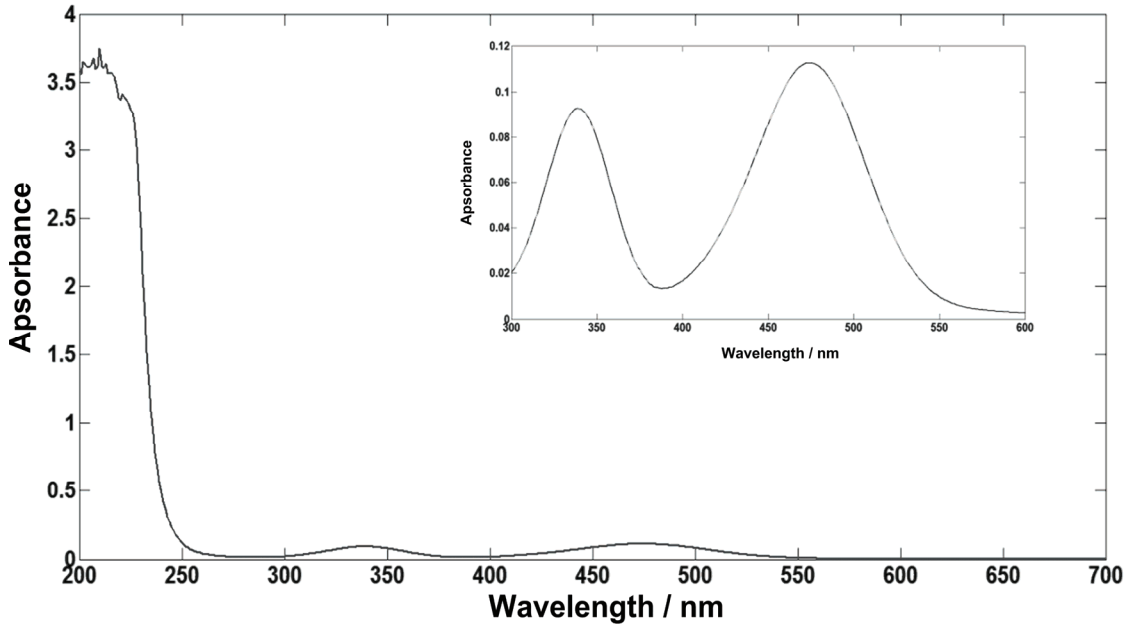


Figure 1. Absorbance spectrum of cobalt(III)-hexamine complexes in range 200-700 nm.

2.2. Results and Discussion

The influence of microwave and ultrasonic irradiation on adsorption properties of clay material was examined in this work. Since the clay is a natural ion-exchanger, and metals in solution exist in ion form, the basic presumption was that major mechanism in metal adsorption on clay material is ion-exchange. The results of adsorbed cobalt on differently treated clay samples are shown at Figure 2.

On presented response surfaces several local extremes are noticeable. Speaking in terms of duration times of ultrasonic and microwave treatment these points are: {10, 0}, {40, 10}, and {0, 20}. The first and third coordinate presents local minima, while the second one is local maxima. It is difficult to explain the existence of these extremes (especially the case of local minima) without detail structural analysis. Nevertheless, the influence of increasing power of microwave oven and ultrasonic bath on these extremes is very noticeable. Increasing power of ultrasonic bath leads to reduction of local extreme no. 1. The same situation is with extremes no. 2 and 3 when speaking about power increase of microwave oven. It appears that growing microwave treatment duration leads to easy increment of adsorbed cobalt, until some final adsorption value. This increment is reached much earlier when microwave oven is set on

higher power (sleeked response surface). It is important to point that mentioned final value is lower than the value obtained in local extreme no. 2.

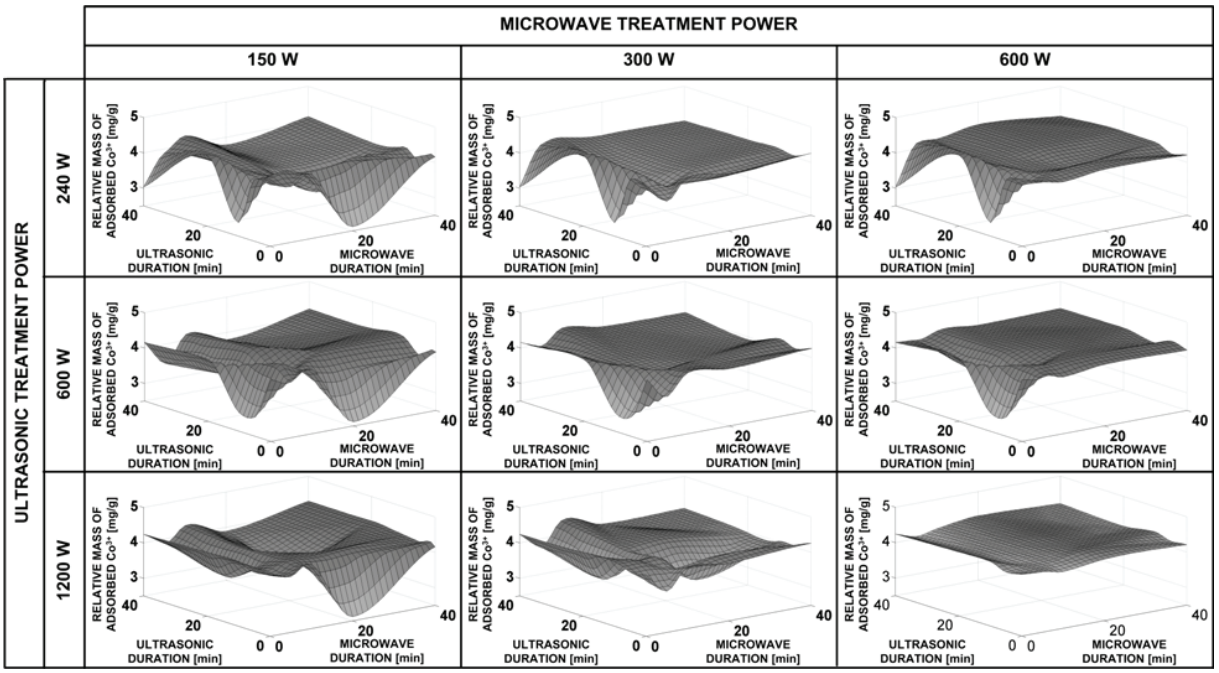


Figure 2. Mass of the adsorbed cobalt per gram of clay material related with microwave and ultrasonic treatment duration. The charts are presented for different powers of microwave oven (150, 300, and 600 W) and ultrasonic bath (240, 600, and 1200 W).

Therefore, an excessive microwave treatment should be avoided, and the heavy-metal removal from water should be performed on clay samples treated 40 minutes ultrasonically at 1200 W, and 10 minutes by microwaves at 150 W (conditions of local extreme no. 2).

3. CONCLUSIONS

The aim of this study was to examine the adsorption abilities of natural clay sample for heavy metals. The tested metal was cobalt. The examined clay samples were differently treated by microwaves and ultrasonic waves, and their adsorption abilities for cobalt cation were tested.

The best results were obtained on clay samples treated 40 minutes ultrasonically at 1200 W, and 10 minutes by microwaves at 150 W.

REFERENCES

[1] P. Bormas, Ceramics are More than Clay Alone, Cambridge International Science Publishing, Cambridge, 2004.
[2] R. Zlatunić, Nastanak gline, Tehnologija i mineralogija keramike, Histria archaeologica, 36 (2005) 61-114.
[3] M. Tajder, M. Herak, Petrografija i geologija, Školska knjiga, Zagreb, 1966.
[4] J. Tišljar, Sedimentne stijene, Školska knjiga, Zagreb, 1994.
[5] R.E. Grim, Clay Mineralogy, 2nd ed., McGraw-Hill, New York, 1968.
[6] H. Van Olphen, J.J. Fripiat, Data Handbook for Clay Minerals and Other Non-metallic Materials, Pergamon, Oxford, UK, 1979.
[7] E. Nemecz, Clay Minerals, Akadémiai Kiado, Budapest, Hungary, 1981.
[8] L. Fodwen, R.A. Barrer, P.B. Tinker, Clay Minerals: their Structure, Behaviour and Use, The Royal Society, London, UK, 1984.
[9] W.T. Reichle, Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite), Solid State Ionics, 22 (1986) 135-141.

[10] A.C.D. Newman, Chemistry of Clays and Clay Minerals, Mineralogical Society Monograph No 6, Longmans, Essex, UK, 1987.
[11] F. Cavani, F. Trifirò, A. Vaccari, Hydrotalcite-type anionic clays: Preparation, properties and applications, Catal. Today, 11 (1991) 173-301.
[12] S.N. Deming, S.L. Morgan: Experimental Design, a Chemometric Approach, 2nd ed., Elsevier, Amsterdam, 1993.
[13] P. Renault, P. Cazevieille, J. Verdier, J. Lahlah, C. Clara, F. Favre, Variations in the cation exchange capacity of a ferralsol supplied with vinasse, under changing aeration conditions: Comparison between CEC measuring methods, Geoderma 154 (2009) 101–110.
[14] D. Aran, A. Maul, J.F. Masfaraud, A spectrophotometric measurement of soil cation exchange capacity based on cobaltihexamine chloride absorbance, C. R. Geoscience 340 (2008) 865–871.

CHEMICAL RECYCLING OF POSTCONSUMER POLY (ETHYLENE-TEREPHTALATE) BOTTLES

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Abstract

Poly(ethylene-terephthalate), PET, waste bottles was chemically recycled by glycolysis process. The glycolysis reaction was carried out at three temperatures 170, 180 and 190 °C in different time intervals (1, 3, 6 hours) with a weight ratio of ethylene glycol (EG) to PET 1:18 and the zinc acetate as a transesterification catalyst. The glycolysis reaction leads to formation of bis(2-hydroxyethyl)terephthalate (BHET) monomer and various types of PET oligomers. Depolymerization products were further characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). From the results it can be seen that remaining PET products i.e. oligomers are thermally very stable and they are suitable to obtain other polymers.

Keywords: *bis(2-hydroxyethyl)terephthalate; chemical recycling; glycolysis; poly(ethylene-terephthalate)*

1. INTRODUCTION

The development of new technologies and the better understanding of it will increase consumption of the recycled PET contributing to the increase of aggregated value and consequently reducing the environmental impact. Poly (ethylene-terephthalate) (PET), a semi-crystalline thermoplastic polyester that is extensively used in diverse applications like textiles, high strength fibers, photographic films, disposable soft-drink bottles and others. The PET package is simply discarded by the consumer and becomes part of the waste stream as post consumer waste and is known as post consumer PET. The excellent properties of PET needed for its many applications are also responsible for the difficult degradation of PET and an accumulation of polymer waste, which in turn creates serious environmental problems connected to littering and illegal landfilling or incineration. Chemical decomposition of PET and conversion into reusable chemical products is one of the important recycling strategies for this material. Chemical recycling processes for PET are divided as follows: glycolysis, methanolysis, hydrolysis and other processes such as aminolysis or ammonolysis [1-5]. Glycolysis of recycled PET can lead to the production of BHET monomer which has been widely used in the production of unsaturated polyesters and rigid or flexible polyurethanes. The thermal properties of obtained glycolysis products (BHET monomer and oligomers) were investigated in the present study.

2. ELABORATION

2.1. Experimental

2.1.1. Materials

Post-consumer PET bottles were cleaned, dried and cut to square chips with cryogenic rotary cutter (Retsch SM 2000) to the particle size of 3 mm x 3 mm. Samples were first conditioned with an aqueous diluted sodium hydroxide solution (2% wt) for 30 min to remove any surface impurities and subsequently washed with water and dried in an oven at 80 °C to eliminate moisture. Ethylene glycol (EG), which was used as a solvent for glycolysis (Merk, Darmstadt), sodium hydrate (Kemika, Zagreb) and zinc acetate (Kemika, Zagreb) were of analytical reagent grade. Reaction of PET waste chips and EG (molar ratio of PET/EG was 1:18) was catalyzed with a 1 mass % of zinc acetate and reaction was carried out at three temperatures (170, 180 and 190 °C) and different times (1, 3 and 6 hours). The reactor and the mixture of EG and the catalyst were preheated to the selected temperature prior to the addition of the PET scraps in order to minimize the time required to reach the reaction temperature.

2.1.2. Characterization

The solid fraction of degraded PET by glycolysis (BHET monomer and oligomers) was characterized by DSC and TGA. DSC was performed on a MettlerToledo DSC 823^e T instrument (sample size about 10 mg) under a nitrogen stream with a standard heating/cooling rate of 10 °C/min in the temperature range of 25-280 °C. The melting (Tm) and crystallization temperature (Tc) of the BHET monomer and obtained PET oligomers were determined as the onset temperatures. The thermal properties of the PET glycolysis products were investigated in the temperature range of 25-550 °C using an instrument TA Instruments Q500. Experiment was carried out in a nitrogen flow rate of 100 ml/min at heating rate of 5 °/min.

2.2. Results and Discussion

2.2.1. DSC analysis

DSC thermograms of PET glycolysis products (oligomers) are presented in Figure 1. The analysis of the thermograms indicates presence of various types of oligomers, Figs. 1a)-1c) and monomer BHET, Fig. 1d).

Oligomers that are formed during the depolymerization, consist of various number of the repeating monomer units *n*, that can be in interval of *n* = 2-20. Generally, it is known that experimentally obtained melting endotherms of oligomers can give an idea of their structure and detect the side reaction products [6-8]. For example, there are PET oligomers with specific structure as H(GA)OH, $H(GA)_2OH$, $H(GA)_3OH$ and $H(GA)_2$-G-H with molecular masses in the range of 210-595 gmol^{-1}. In quoted structures the mark A stands for $–OCC_6H_4CO-$ and G for $–OCH_2CH_2O-$. From the endotherms at Figs. 1a) and 1b) it can be observed that melting temperatures are in interval from 249-254 °C of PET products obtained after glycolysis. These results denoted that the formed PET oligomers have complex structure HO-A-$(GA)_4$ OH and HO-A-$(GA)_5$OH and molecular masses between 935 and 1127 gmol^{-1} [8].

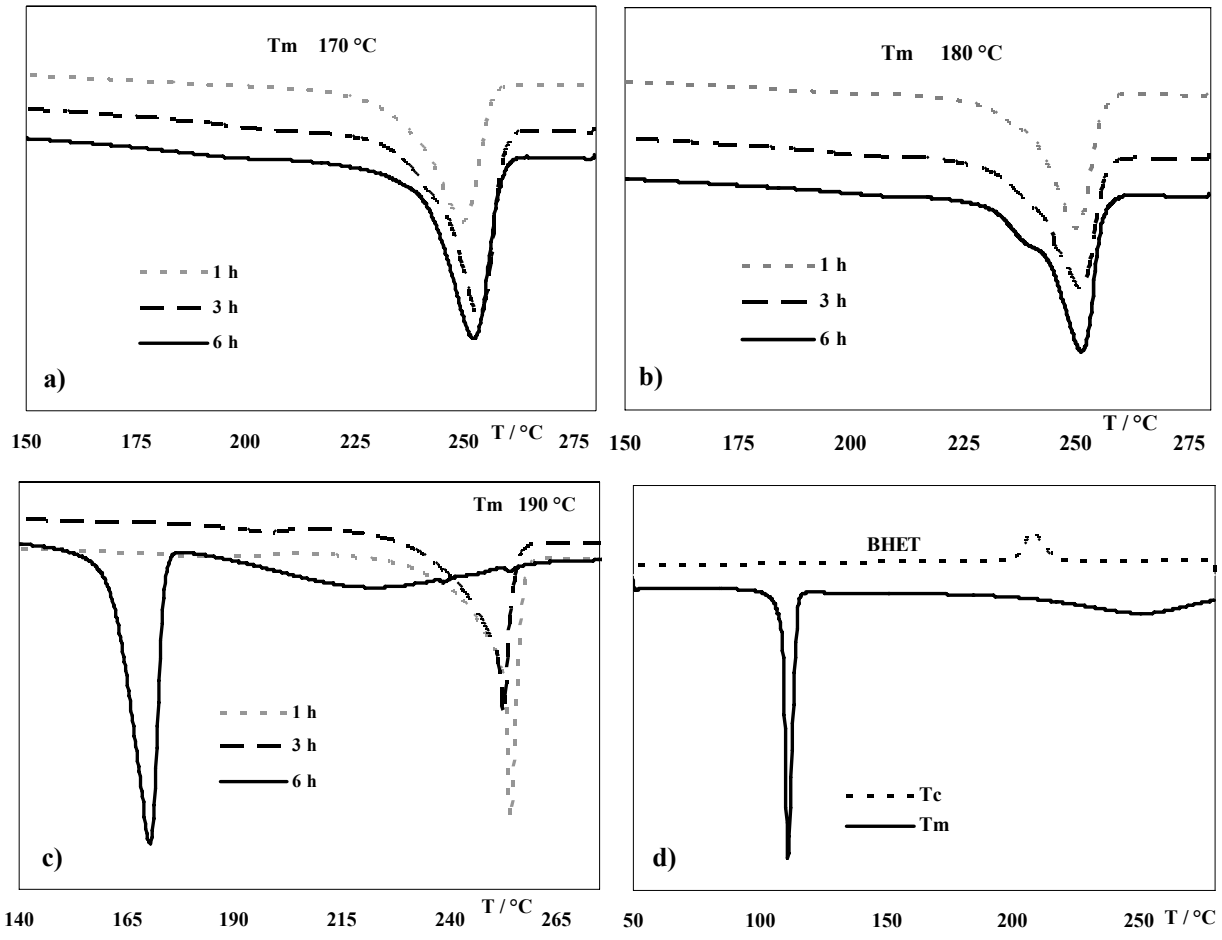


Figure 1. Melting temperatures (T_m) of PET oligomers recorded after 1, 3 and 6 h at a) 170 °C, b) 180 °C, c) 190 °C and d) melting and crystallization (T_c) temperatures of extracted monomer BHET

Slight differences of values of melting temperature (Tm) and crystallization temperature (Tc) indicate presence of other structured oligomers. This is particularly evident due to new peaks at Fig 1b) indicating formation of oligomers of lower molecular masses and with various chain ends. Additionally, it can be seen that extended depolymerization time leads to polycondensation reaction if we consider the results of Tm and Tc at 170 °C. DSC thermogram of the sample glycolysed 6 hours at 190 °C, Fig. 1c), consists of two endothermic melting peaks: the first peak centered at 170 °C is considered as the melting point of dimer BHET [9, 10]. The second maximum is detected around 225 °C and it is quite broad and can be related to the presence of low content of a mixture of oligomers. Thermogram in Fig. 1d), show a reasonably sharp endothermic peak at 110 °C and peak at 207°C of crystallization temperature, which agrees with the melting and crystallization point of monomer BHET reported in the literatures and this is confirmation that neat monomer BHET was obtained from the solid phase [11-13].

2.2.2. TG analysis

The solid fraction of PET products was also studied using TG analysis. The thermograms of PET products are reported in Figs. 2(a), 2(b), and 2(c), while for BHET monomer in Fig.3.

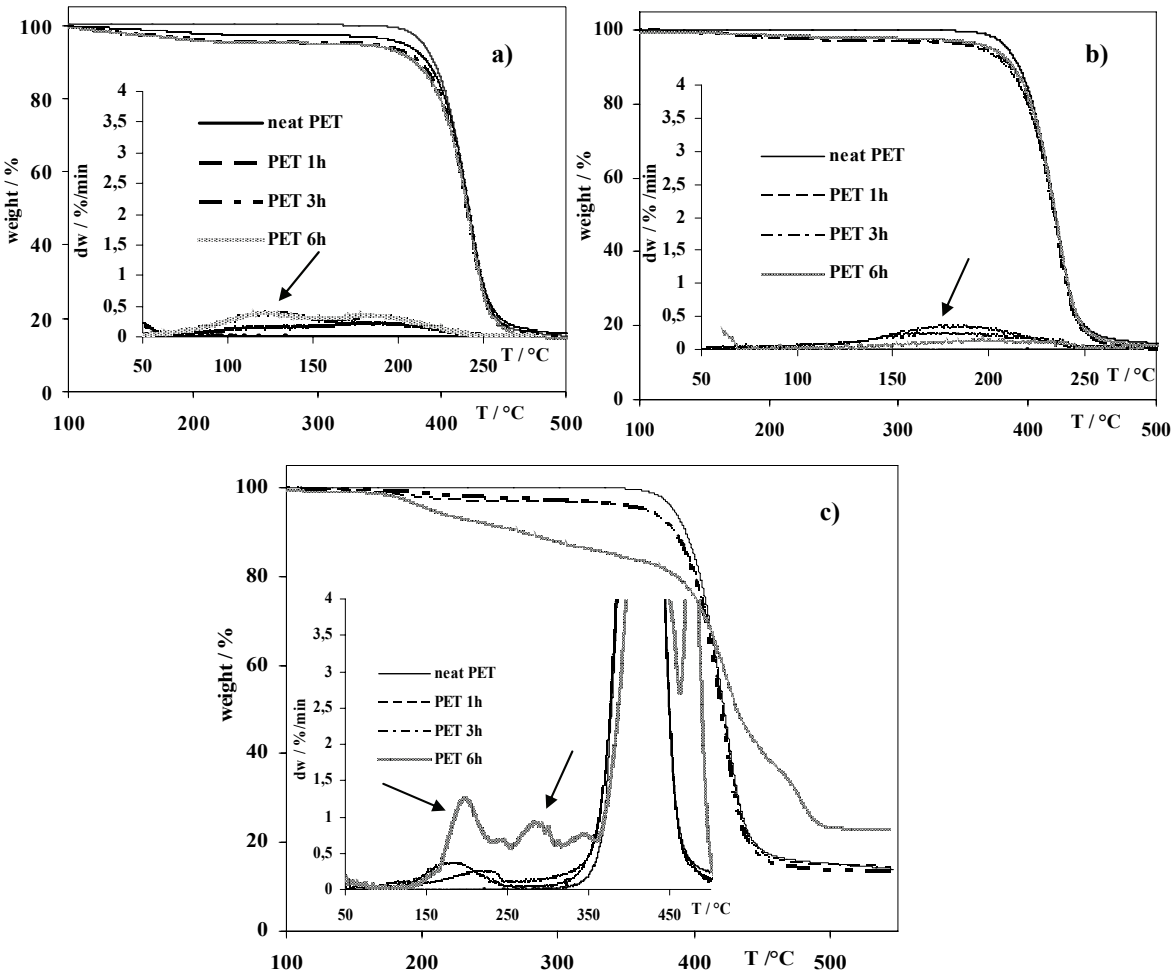


Figure 2. Thermograms of neat PET and of glycolysis products recorded after 1, 3 and 6 h at: a) 170 °C, b) 180 °C, c) 190 °C. Inset: corresponding DTG curves

It was assumed that various oligomer structures should show different thermal behavior. Comparison of the TG traces obtained under nitrogen flow for the polymers glycolysed at 170 and 180 °C, Figs. 2a) and 2b), reveals almost none differences in the mass-loss behavior in contrast to samples exposed to depolymerization reaction for 6 hours and at 190 °C, Fig. 2c). Samples of PET that were glycolysed 1, 3 and 6 hours at 170 and 180 °C as well as these at 190 °C for 1 and 3 h undergoes one step of mass-loss stretching between 180 and 480 °C and losing 85 % of its initial mass. Slight mass-loss were observed in the beginning of the thermal degradation between 145 and 280 °C, which is evident as a new maximum decomposition rate temperatures from the all DTG curves at Fig. 2). This 5 % of initial mass of PET

samples represents thermal degradation of newly formed oligomers of lower molecular masses showing different thermal behavior than polymer chain. It is assumed that solid residues of 15 % consist of oligomers of high molecular masses due to their higher thermal stability, which is equal to those of the neat PET polymer. On the contrary, PET that was glycolysed 6 hours at 190 °C sees 20 % of its initial mass evolved in the first and the second step starting at 200 °C and 300 °C, before undergoing the third and the fourth mass-loss step, starting at about 300 °C and at around 460 °C, Fig. 2c). The first mass-loss step can be attributed to the evolution of oligomers of low-molar mass and other species like benzoic acid, vinyl benzoate chain-ends, and other various degradation products [14]. In Fig.3. is presented the thermogram of the extracted monomer BHET and it can be clearly seen the two-step of degradation of monomer where in the first step decomposed 37 mass % of monomer at 237 °C and the residue of monomer decomposed in the second stage at 422 °C [15].

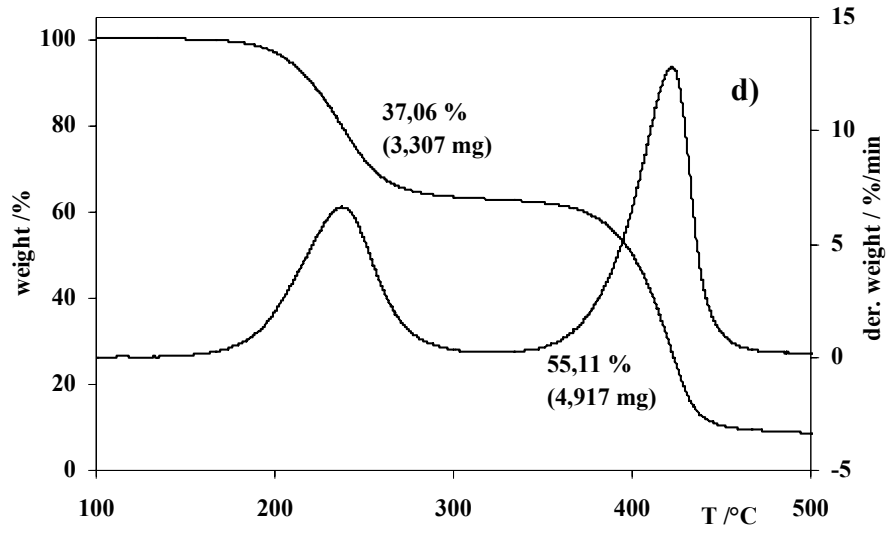


Figure 3. Thermogram of extracted BHET monomer.

3. CONCLUSIONS

Glycolysis reaction with ethylene glycol was employed to decompose PET and from the result obtained after chemical recycling it can be concluded that high concentration of PET oligomers of high molecular mass is formed at lower temperatures (170 and 180 °C). PET products obtained by glycolysis are thermally stable as the neat PET polymer. DSC endotherms show slight changes in melting and crystallization temperatures indicating presence of oligomers of lower molecular masses. Presence of monomer and dimer BHET is confirmed by both thermal methods due to thermal degradation in two-steps by TGA and by melting peak at 170 °C obtained by DSC.

REFERENCES

[1] F. Pardal, G. Tersac, Comparative reactivity of glycols in PET glycolysis, Polym. Degrad. Stab. 91 (2006) 2567-2578.

[2] N.D. Pingale, S.R. Shukla, Microwave assisted ecofriendly recycling of poly (ethylene terephthalate) bottle waste, Euro. Polym. J. 44 (2008) 4151-4156.

[3] G. Güçlü, T. Yalçınyuva, S. Özgümü, M. Orbay, Simultaneous glycolysis and hydrolysis of polyethylene terephthalate and characterization of products by differential scanning calorimetry, Polymer. 44 (2003) 7609-7616.

[4] V. Sinha, M.R. Patel, J.V. Patel, Pet Waste Management by Chemical Recycling: A Review, J. Polym. Environ. 18 (2010) 8-25.

[5] G.P. Karayannidis, D.S. Achilias, Chemical Recycling of Poly(ethylene terephthalate), Macromol. Mater. Eng. 292 (2007) 128-146.

[6] G. Güçlü, A. Kaşgöz, S. Özbudak, S. Özgümüş, M. Orbay, Glycolysis of poly(ethylene terephthalate) wastes in xylene, J. Appl. Polym. Sci. 69 (1998) 2311-2319.

[7] J.W. Chen, L.W. Chen, The Glycolysis of Poly (ethylene terephthalate), J. Appl. Polym. Sci. 73 (1999) 35-40.
[8] E.L. Ringwald, E.L. Lawton, Physical properties of poly (oxyethyl-oxyterephtaloyl) (poly(ethylene terephtalate)), in: J. Brandrup, E.H. Immergut, W. McDowell (Eds.), Polymer Handbook, Wiley, New York, 1975, p. 71.
[9] S. Baliga, W.T. Wong, Depolymerization of poly(ethylene-terephthalate) recycled from post-consumer soft-drink bottles, J. Polym. Sci. Polym. Chem. 27 (1989) 2071-2082.
[10] C.Y. Kao, W.H. Cheng, B.Z. Wan, Investigation of catalytic glycolysis of polyethylene terephthalate by differential scanning calorimetry, Thermochi. Acta. 292 (1997) 95-104.
[11] M. Ghaemy, K. Mossaddegh, Depolymerisation of poly(ethylene terephthalate) fibre wastes using ethylene glycol, Polym. Degrad. Stab. 90 (2005) 570-576.
[12] S.R. Shukla, K.S. Kulkarni, Depolymerization of poly (ethylene terephthalate) waste, J. Appl. Polym. Sci. 85 (2002) 1765-1770.
[13] A. Krzan, Microwave irradiation as an energy source in poly(ethylene terephthalate) solvolysis, J.Appl. Polym. Sci. 69 (1998) 1115-1118.
[14] H.A. Lecomte, J.J. Liggat, Degradation mechanism of diethylene glycol units in a terephthalate polymer, Polym. Degrad. Stab. 91 (2006) 681-689.
[15] C. Chen, C.Y. Chen, Y. Lo, C. Mao, W. Liao, Studies of glycolysis of poly(ethyleneterephthalate) recycled from postconsumer soft-drink bottles. I. Influences of glycolysis conditions, J. Appl. Polym. Sci. 80 (2001) 943–948.

STEEL SLAG RADIOACTIVITY AS A SIGNIFICANT FACTOR FOR ITS USE IN CONSTRUCTION INDUSTRY

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Abstract

In the present study, the activity concentrations of ^{226}Ra, ^{232}Th, ^{40}K in steel slags generated during the production of low carbon steel in the CMC Sisak Steel Mill has been investigated using gamma spectroscopy technique and mathematical models. The radionuclide activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, activities index (I1, I2, I3) and radium equivalent concentrations (Ra_{eq}) of steel slags were determined in order to assess the radiological hazards from steel slags due to the their utilization as raw materials in building industry. The measured activities concentrations of ^{226}Ra, ^{232}Th, ^{40}K in electric arc furnace slag and ladle furnace slag are significantly lower than the maximum Croatian allowed limit so investigated slags, in terms of the radionuclides present, may be applied as raw materials and/or additives in the construction industry. Activities index (I1, I2, I3) calculated on the basis of measured radionuclide activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were less than 1, i.e. it shows that neither of the examined slags samples exceeds values recommended by the Nuclear Safety Authority (STUK) Guide ST 12.2 and Croatian Ordinance.

Keywords: *steel slag, ladle slag, radioactivity, utilization, construction industry*

1. INTRODUCTION

Materials generated as by-products or waste from industrial processes can be used in the building industry in various ways. Recent studies showed that applications of industrial by-products as nontraditional material have been considered in building industry [1-5]. In the last three decades there has been a growing tendency to use industrial by-products throughout the world. With the increase of environmental awareness, devastation of landfill areas and due to ever increasing costs, industrial by-products or waste utilization have become an attractive alternative to disposal. Recent studies [1-4] show that applications of industrial by-products or non-hazardous waste have been considered in the construction industry. Incorporation of such materials in building material can be seen as a factor of preservation of natural non-renewable sources of mineral aggregates, as well as simultaneous undesirable effects on the environment of all activities connected with the exploitation and transport from the origin point to the installation point. These factors impress upon us the need to understand the environmental and economic aspects of using natural mineral raw materials in relation to alternative sources – industrial waste materials – which can contribute to the sustainable development in the construction industry. Although steel slag (electric arc furnace slag, EAFS and ladle furnace slag, LFS) has been classified as non-hazardous waste, and is possible to be disposed without danger to the environment, this is rarely applied. The permanent disposal of steel slag is expensive and requires a vast area, and the valuable ingredients of steel slag are lost forever. Therefore, it is indispensable to consider the electric arc furnace slag as a by-product and not as metallurgic waste, but to examine it in detail and, apply it as a valuable raw material in other industries. Through environmental awareness and the concept of sustainable development, extensive research and development has removed slag from industrial waste and turned it into modern industrial product which is effectively and profitably used for many industrial purposes, especially in numerous building applications [6,7]. Over the past 100 years, slag (EAFS and LFS) has been used for many industrial purposes, especially as raw material in cement production, landfill cover material, and construction and agricultural applications. Steel slag can also be used in the lower layers of the pavement structure as granular base, in sub base and even in embankments. Steelmaking slag is being successfully used as a high quality mineral aggregate for the construction industry and therefore promoted as “sustainable” building materials substituting natural raw materials. The steel slags are in

many features similar to building materials like crushed stone, sand, cement etc. that are extracted from natural raw materials and sometimes exceed them regarding their physical-mechanical properties.

It is important to be familiar with the technical significance of the secondary application of steel slag, and with its possible environmental effects. Its application as building material reduces the quantity of landfills, but some steel slag might contain increased concentrations of substances harmful to human health or the environment. Radionuclides, highly hazardous elements, are the least researched of all pollutants emitted from the metallurgical processes. Steel making, as well as many other non-nuclear industries, can generate by-products or waste in which the concentration of naturally occurring radioactive material is enhanced additionally. Steel slag containing enhanced activities of naturally radionuclides can be used as secondary raw material in building industry, causing a significant impact onto the environment. The problem of natural radioactivity is completely excluded from regulations dealing with the environmental protection in general, and hazards caused by radiation originating from naturally radioactive materials is rarely taken into consideration when the treatment or utilization of industrial by-products or waste is planned. Because no one knows whether allowed limits of risk have been exceeded or not, the problem of regulatory control does not exist and very often this implies that there is no risk evaluation and no need for control. Consequently, very often even highly serious radiation risk can be out of radiation protection control system. The importance of radiation risk caused by natural radioactivity has been underlined in the Council Directive 96/29 EURATOM as one of basic safety standards [8] for the protection of workers' and the general public's health against the danger arising from ionizing radiation. In the Council Directive 96/29, among other things, it is clearly stated that: *a* - work activities involving operations with, and storage of, materials, not usually regarded as radioactive but which contain naturally occurring radionuclides, causing a significant increase in the exposure of workers and, where appropriate, members of the public and *b* - work activities which lead to the production of residues not usually regarded as radioactive but which contain naturally occurring radionuclides, causing a significant increase in the exposure of members of the public and, where appropriate, workers. All building materials derived from rock and soil contain naturally occurring radioactive material (NORM), mainly natural radionuclides of uranium (^{238}U) and thorium (^{232}Th) series, and the radioactive isotope of potassium (^{40}K). In the uranium series, the decay chain segment starting from radium ^{226}Ra is radiologically the most important and, therefore, reference is often made to radium instead of uranium. In natural raw materials for cement, concrete, bricks, mortar and other building material, activity concentrations of ^{40}K, ^{226}Ra, ^{232}Th, ^{238}U vary considerably, depending on both the nature and the origin of the compounds. Generally, natural building materials reflect the geology of their site of origin, and the average activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the Earth's crust are about 40, 40 and 400 Bqkg^{-1} respectively [5]. Nowadays, due to a relatively high share of steel slag as raw material in the total amount of building material produced throughout the world, activity concentrations of radionuclides are becoming increasingly important. This industrial by-product can represent a polluting radioactive source when used as addition in building materials, thus determining a supplementary radiation hazard towards the natural radioactivity background, which cannot be neglected. In this manner, the presence of natural isotope was determined in the steel slag with the purpose of its characterization as a type of steel making process. Special attention has been paid to investigating the possibilities of it being used in building material industry (road construction, paving, cement industry, concrete production, etc.). In the present study, the radium equivalent concentrations were calculated from the obtained activity concentrations of ^{40}K, ^{226}Ra, ^{232}Th of investigated samples. Indoors dose rate for investigated concrete is calculated, after which obtained values were used to calculate annual effective doses (D_E).

2. ELABORATION

2.1. Experimental

Two kinds of slag are produced during production of steel in CMC Sisak d.o.o.: Electric Arc Furnace Slag (EAFS), and Ladle Furnace Slag (LFS). Electric arc furnace is used only for preparation of molten steel from steel scrap charge. After being tapped from the electric arc furnace (EAF), the molten steel is transferred to the ladle furnace (LF) for further refinement, i.e. removal of additional impurities still contained within the steel, Fig 1. Ladle furnace basic slag is produced in the final stages of steelmaking process, which is generally known as the secondary metallurgy process. Capacity of both EAF and LF amounts to 60 tons of steel.

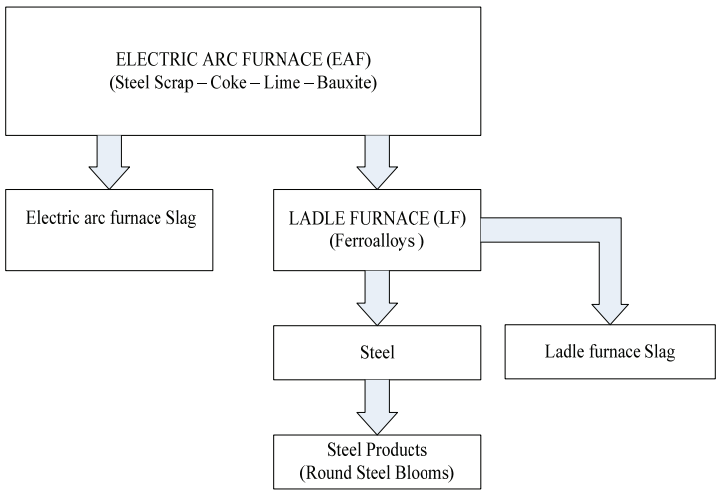


Figure 1. Electric arc furnace steel making process

Testing has been conducted on EAFS and LFS generated during the production of low carbon steel by electric arc furnace process in the Steel Mill of CMC Sisak in the period from September 2010 to April 2011. Both of them have been analyzed by γ-spectrometry in order to determine the presence of radionuclides and their activity in steel slag samples.

2.1.1. Sampling

Liquid slag was, after being poured out of the electric arc furnace, cooled with water, after which it was subjected to the following procedures: grinding, magnetic separation in order to remove leftover particles of the cooled steel melt, fragmentation and sieving. Liquid ladle furnace slag was, after being poured out of the ladle furnace, cooled with air, after which it was subjected to grinding, fragmentation and sieving.Samples of materials used in the electric arc furnace steel making process i.e. graphite electrodes, refractory blocks, ferroalloys, bauxite, fluorite, lime, coke, carburite, (about 5 kg each) were crushed in a ring mill to grain size below 1 mm, homogenised, and then quartered to the quantity of 1.00 kg. They were dried at 378 K for 24 hours, transferred to glass bottles with ground cap, and marked.

2.1.2. Quantitative determination

All of the samples were dried, homogenized and transferred to standard counting vessels of 125 cm^3 and weighed. The loaded vessels were sealed and stored for at least 4 weeks to allow the in-growth of gaseous ^{222}Rn (3.8 day half-life), and its short-lived decay products to equilibrate with the long-lived ^{226}Ra precursor in the sample.The samples were counted at the end of the in-growth period. The activities of ^{40}K, ^{226}Ra, ^{232}Th, were determined by γ-ray spectrometry, using a low background hyper pure germanium semiconductor detector system coupled to 8192-channel CANBERRA analyzer. Broad type of detector was used, with characteristics as follows: active diameter 70mm, active area 3800 mm^2, thickness 30 mm, window thickness 0,5 mm, window material – carbon epoxy, bias voltage 4500 V, energy resolution (FWHM) at 59,5 keV of 554 eV (FWTM 1032 eV) FWHM at 1332,5 keV of 2053 eV (FWTM 4106). Detector system was calibrated using gamma mixed standards supplied by Eckert & Ziegler (Analytics USA). Depending on sample mass and activity, spectra were recorded for times ranging 80,000-200,000 seconds, and analyzed using the GENIE 2K CANBERRA software. Activities of ^{226}Ra were calculated from the 609.4 keV-peak of its ^{214}Bi progeny. Activities of ^{232}Th were calculated over ^{228}Ra from the 911.1 keV-peak of its ^{228}Ac progeny. Activities of ^{40}K were calculated from the 1460.7 keV-peak. Efficiency of the system was regularly checked during inter-comparison runs. Precision and accuracy of the system were checked additionally by simultaneous measurement of IAEA Reference Materials (International Atomic Energy Agency) as Laboratory is accredited by Croatian Accreditation Agency for gamma-spectrometric measurements (HRN EN ISO/IEC 17025:2007). It should be mentioned that efficiency was calculated as function of energy and geometry at the base of experimental data.Limit of detection (LD) was determined according to L. Currie relation for aired observation and zero blank [9]. From LD, a lower limit of detection (LLD) was estimated at the base of known efficiency, counting time, energy intensity and sample mass. Measured uncertainty, multiplied by coverage factor k = 2, was calculated as sum of net peak area uncertainty, efficiency uncertainty and background fluctuation uncertainty.

2.2. Results and Discussion

During the steel making process, naturally and artificial occurring radionuclides may be concentrated to a radiologically relevant level. EAFS and LFS may also contain radionuclides originating from steel scrap, ferroalloys and other materials used in the steel making process. Very often steel scrap used in the EAF process can become contaminated with radionuclides arising from different origins. Some of the main origins are the demolition or decommissioning of industrial facilities which used to process raw materials and still contain naturally occurring radionuclides, the decommissioning of nuclear installations and other facilities, loss of sealed radioactive sources, demolition of equipment in which radioactive sources have been used, etc. If such steel slags are used as raw material for the production of building material, the final product will also contain this radionuclide, depending on the physical-chemical properties of the radionuclide and thermodynamic conditions in electric arc or ladle furnace during melting and refinement processes. The obtained results of activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in examined slags intended for utilization in building industry are presented in Tables 1 and 2. Although artificially occurring radionuclides (^{90}Sr, ^{241}Am, ^{241}Cm) may be concentrated and remain in the slag during steelmaking, their presence has not been determined by measuring and in this study artificial radionuclides have not been taken into account.

Table 1. Results of γ-spectrometric analysis of the EAF slag samples

EAF slag	Activity concentration (Bqkg^{-1})		
	^{40}K	^{232}Th	^{226}Ra
EAFS 1	62.9 ± 12.1	15.1 ± 2.8	21.4 ± 2.8
EAFS 2	57.0 ± 11.3	13.3 ± 2.6	19.5 ± 2.5
EAFS 3	54.6 ± 11.3	15.4 ± 2.9	20.8 ± 2.7
EAFS 4	50.3 ± 10.5	14.5 ± 2.8	18.0 ± 2.4
EAFS 5	58.5 ± 11.5	14.5 ± 2.9	20.4 ± 2.6
EAFS 6	52.5 ± 10.8	13.5 ± 2.6	19.1 ± 2.5
EAFS 7	49.1 ± 9.3	13.2 ± 2.4	15.2 ± 2.0

Table 1 shows results of measured activity concentrations with measurement of uncertainty of radionuclides in EAF slag. In line with expectations, the EAFS samples contain natural isotopes ^{40}K, ^{226}Ra, and ^{232}Th. The measured values regarding presence of individual isotopes and their activities were as follows: ^{40}K from 49.1 ± 9.3Bqkg^{-1} (EAFS 7) to 62.9 ± 12.1Bqkg^{-1} (EAFS 1); ^{232}Th from 13.2 ± 2.4Bqkg^{-1} (EAFS 7) to 15.4 ± 2.9Bqkg^{-1} (EAFS 3) and ^{226}Ra from 15.2 ± 2.0Bqkg^{-1} (EAFS 7) to 21.4 ± 2.8Bqkg^{-1} (EAFS 1).

Table 2. Results of γ-spectrometric analysis of the LF slag samples

LF slag	Activity concentration (Bqkg^{-1})		
	^{40}K	^{232}Th	^{226}Ra
LFS 1	<15.1	3.48 ± 1.7	30.1 ± 3.7
LFS 2	18.6 ± 10.8	3.95 ± 1.7	29.0 ± 3.6
LFS 3	<13.7	6.06 ± 2.2	28.4 ± 3.5
LFS 4	<13.5	6.03 ± 1.9	24.6 ± 3.1
LFS 5	<15.6	3.78 ± 1.7	22.8 ± 3.1
LFS 6	<15.6	12.2 ± 2.8	26.4 ± 3.4
LFS 7	17.3 ± 10.3	11.1 ± 3.1	35.2 ± 4.5

Table 2 shows results of measured activity concentration with measurement of uncertainty of radionuclides in LFS and the measured values regarding presence of individual isotopes and their activities were as follows: ^{40}K from <13.5 Bqkg^{-1} (sample LFS 4) to 18.6Bqkg^{-1} (LFS 2); ^{232}Th from 3.48Bqkg^{-1} (LFS 1) to 12.2Bqkg^{-1} (LFS 6) and ^{226}Ra from 22.8Bqkg^{-1} (LFS 5) to 35.2Bqkg^{-1} (LFS 7). The obtained results were consistent with the results of activity equivalent concentrations of the same radionuclides in the same materials from an earlier study carried out by other authors [10]. S. Brown [10] studied the radiochemical characteristics of EAFS from steelmaking in Australia and the results for ^{226}Ra, ^{232}Th and ^{40}K are given in Table 3.

Table 3. Results of γ-spectrometric analysis of the Australian steel slags [10]

Slag	Activity concentration ($Bqkg^{-1}$)		
	^{40}K	^{232}Th	^{226}Ra
EAFS	<30	3-6	8-12
LFS	<40	6-12	11-25

In order to attempt to determine the source isotope in investigated steel slags, the materials of natural origin used for the production of steel melt were tested for the presence of radionuclides. The analysis included the mineral materials added into the electric arc furnace as non-metal additives (ferroalloys, bauxite, fluorite, lime and coke), graphite electrodes, carburite and used refractory material. Obtained results are shown in Table 4.

Table 4. Results of γ-spectrometric analysis of non-metal additives used in the EAF process

Material	Activity concentration ($Bqkg^{-1}$)		
	^{40}K	^{232}Th	^{226}Ra
FeSiMn	<5.93	<0.767	0.89±0.5
FeCr	<6.57	<0.85	<0.9
NitroVan	<11.7	2.7±1.6	4.5±1.3
Bauxite	34.2± 7.2	58.9±6.3	59.6±1.9
Fluorite	10±2.0	118.5±7.5	123.8±2.3
Lime	<22.9	<3.25	16.4±3.4
Coke	70.2±24.7	20.8±7.29	40.5±6.4
Graphite electrode	46.4± 8.7	2.5±0.6	2.5±0.5
Carburite	190.5±27.8	14.5±4.30	39.7±5.1
Refractory material Magne Hearth820	<8.71	<1.13	5.59±1.2
Refractory material C-MAG C220	13.7±8.6	2.37±1.4	7.20±1.6

The measured values regarding the presence of individual isotopes and their activities, presented in Table 4, showed very low values or values less then lower limit of detection. One recently published European Commission document [5] provides guidance for setting controls on the radioactivity of building materials in European countries. This document is the first comprehensive act which sets the principles of radiological protection principles concerning the natural radioactivity of building materials, which makes it relevant for newly produced building materials, but not intended to be applied to existing buildings. Because steel slag can be used for many industrial purposes, especially as raw material in building applications, it is essential to fulfil the very often prescribed values of Croatian maximum limit radioactivity of building material [11], which should not exceed the following concentration of activities: 300 $Bqkg^{-1}$ for ^{226}Ra, 200 $Bqkg^{-1}$ for ^{232}Th and 3000 $Bqkg^{-1}$ for ^{40}K. From the radiological point of view, the maximum value of the activity index (I1) for house building material must be as follows:

$$I1 = (C_{Ra}/300) + (C_{Th}/200) + (C_K/3000);\ I1 \leq 1 \quad (1)$$

where C_{Ra}, C_{Th} and C_K are the concentrations of appropriate radionuclides in $Bqkg^{-1}$. If the activity index I1 is 1 or less than 1, the steel slag can be used in bulk amounts as building material, as far as radioactivity is concerned, without restriction.

When steel slag is added into material that will be used for road construction, according to the Finnish Radiation and Nuclear Safety Authority (STUK) Guide ST 12.2 [12], the activity index for materials used in road, street and related building (I2) must be as follows:

$$I2 = (C_{Ra}/700) + (C_{Th}/500) + (C_K/8000);\ I2 \leq 1 \quad (2)$$

where: C_{Ra}, C_{Th} and C_K are the concentrations of appropriate radionuclides in $Bqkg^{-1}$. If the activity index I2 is 1 or less than 1, the steel slag can be used as building material in road construction, as far as radioactivity is concerned, without restriction.

According to the Finnish model [12], the activity index for materials used in landfill and landscaping is (I3) must be as follows:

$$I3 = (C_{Ra}/2000) + (C_{Th}/1500) + (C_K/20000);\ I3 \leq 1 \quad (3)$$

where: C_{Ra}, C_{Th} and C_K are the concentrations of appropriate radionuclides in Bqkg^{-1}. If the activity index I3 is 1 or less than 1, the steel slag can be used as landfill cover material, as far as radioactivity is concerned, without restriction.

Table 5. Index values of activities concentrations in the steel slags

Slag	Activity concentration (Bqkg^{-1})			Activity Indeks (Bqkg^{-1})		
	^{40}K	^{232}Th	^{226}Ra	I1	I2	I3
EAFS 1	62.9 ± 12.1	15.1 ± 2.8	21.4 ± 2.8	0.17	0.07	0.02
EAFS 2	57.0 ± 11.3	13.3 ± 2.6	19.5 ± 2.5	0.15	0.06	0.02
EAFS 3	54.6 ± 11.3	15.4 ± 2.9	20.8 ± 2.7	0.16	0.07	0.02
EAFS 4	50.3 ± 10.5	14.5 ± 2.8	18.0 ± 2.4	0.15	0.06	0.02
EAFS 5	58.5 ± 11.5	14.5 ± 2.9	20.4 ± 2.6	0.16	0.07	0.02
EAFS 6	52.5 ± 10.8	13.5 ± 2.6	19.1 ± 2.5	0.15	0.06	0.02
EAFS 7	49.1 ± 9.3	13.2 ± 2.4	15.2 ± 2.0	0.13	0.05	0.02
LFS 1	<15.1	3.48 ± 1.7	30.1 ± 3.7	<0.12	<0.05	<0.02
LFS 2	18.6 ± 10.8	3.95 ± 1.7	29.0 ± 3.6	0.12	0.05	0.02
LFS 3	<13.7	6.06 ± 2.2	28.4 ± 3.5	<0.13	<0.05	<0.02
LFS 4	<13.5	6.03 ± 1.9	24.6 ± 3.1	<0.12	<0.05	<0.02
LFS 5	<15.6	3.78 ± 1.7	22.8 ± 3.1	<0.10	<0.04	<0.01
LFS 6	<15.6	12.2 ± 2.8	26.4 ± 3.4	<0.15	<0.06	<0.02
LFS 7	17.3 ± 10.3	11.1 ± 3.1	35.2 ± 4.5	0.18	0.07	0.02
Allowed value (House building)	3000	200	300	≤ 1.00	-	-
Allowed value (Road construction)	8000	500	700	-	≤ 1.00	-
Allowed value (Landfill & Landscaping)	20000	1500	2000	-	-	≤ 1.00

Table 6. Activity index and maximum allowed or recommended concentrations in building materials in some European countries and Israel [12-14]

Country	Activity Indeks (Bqkg^{-1})
Finland	
Residential building	$(C_{Ra}/300) + (C_{Th}/200) + (C_K/3000) < 1$
Roads, streets /populated areas	$(C_{Ra}/700) + (C_{Th}/500) + (C_K/8000) + (C_{Cs}/2000) < 1$
Landfilling/Landscaping	$(C_{Ra}/2000) + (C_{Th}/1500) + (C_K/20000) + (C_{Cs}/5000) < 1$
Handling of ash	$(C_{Ra}/4000) + (C_{Th}/3000) + (C_K/50000) + (C_{Cs}/10000) < 1$
Latvia	
Residential building	$(C_{Ra} + C_{Th})/170<1$; $C_K<1500$ Bqkg^{-1}
Industrial building	$(C_{Ra} + C_{Th})/250<1$; $C_K<2000$ Bqkg^{-1}
Roads/populated areas	$(C_{Ra} + C_{Th})/300<1$; $C_K<2500$ Bqkg^{-1}
Lithuania	
All building material	$(C_{Ra}/300) + (C_{Th}/200) + (C_K/3000) < 1$
Streets, roads, etc.	$(C_{Ra}/700) + (C_{Th}/500) + (C_K/8000) + (C_{Cs}/2000) < 1$
Landscaping	$(C_{Ra}/2000) + (C_{Th}/1500) + (C_K/20000) + (C_{Cs}/5000) < 1$
Norway	$(C_{Ra}/300) + (C_{Th}/200) + (C_K/3000) < 1$; $C_{Ra}<200$ Bqkg^{-1}
Poland	$0.0027C_{Ra} + 0.0043C_{Th} + 0.00027C_K < 1$; $C_{Ra}<185$ Bqkg^{-1}
Slovenia	$(C_{Ra}/300) + (C_{Th}/200) + (C_K/3000)< 1$
Israel	$(C_{Ra}/150) + (C_{Th}/185) + (C_K/3500) < 1$

Table 5 presents the calculated values of activities concentrations (I1, I2, I3) in the specimens of analyzed steel slags. From the data listed in Table 5 we reach the conclusion that the analyzed steel slags, from the radiation point of view, can be used as raw material in numerous building applications, especially for house building, road construction, landfill covering and landscaping. Most of the European

countries apply their controls based on the upper end of the dose scale (1.0 $mSva^{-1}$). However, some of them apply the strictest criteria based on the lower end of the dose scale (0.3 $mSva^{-1}$). At the same time many European and other countries, which have similar regulations, apply more liberal dose criteria. European and non-European countries with reference levels for radionuclides in building materials apply activity index or maximum allowed/recommended concentrations, Table 6. The activity index is calculated on the basis of the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K. Artificial radionuclides are sometimes taken into consideration [12,13] as well (Lithuania and Finland).

In order to compare specific activities of materials containing different amounts of ^{226}Ra, ^{232}Th and ^{40}K, numerous authors [15,16] have applied an index called the radium equivalent concentration Ra_{eq}. to ensure the uniformity in the distribution of natural radionuclides ^{226}Ra, ^{232}Th and ^{40}K, equation (4):

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (4)$$

where C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, respectively, in $Bqkg^{-1}$.

It was assumed that 370 $Bqkg^{-1}$ of ^{226}Ra, 259 $Bqkg^{-1}$ of ^{232}Th and 4810 $Bqkg^{-1}$ of ^{40}K produce the same gamma-ray dose rate. The maximum dose Ra_{eq} in building materials must be less than 370 $Bqkg^{-1}$ for safe use, i.e., to keep the external dose below 1.5 $mSvy^{-1}$.

From the measured activity concentrations values of ^{226}Ra, ^{232}Th and ^{40}K of investigated steel slags, the radium equivalent concentrations were computed and the results are presented in Table 7.

Table 7. The radium equivalent concentration in steel slags

Slag	Activity concentration ($Bqkg^{-1}$)			Ra_{eq} ($Bqkg^{-1}$)	
	^{40}K	^{232}Th	^{226}Ra	This study	S. Braun [10]
EAFS 1	62.9 ± 12.1	15.1 ± 2.8	21.4 ± 2.8	47.84	
EAFS 2	57.0 ± 11.3	13.3 ± 2.6	19.5 ± 2.5	42.91	
EAFS 3	54.6 ± 11.3	15.4 ± 2.9	20.8 ± 2.7	47.03	
EAFS 4	50.3 ± 10.5	14.5 ± 2.8	18.0 ± 2.4	42.61	15-25
EAFS 5	58.5 ± 11.5	14.5 ± 2.9	20.4 ± 2.6	45.64	
EAFS 6	52.5 ± 10.8	13.5 ± 2.6	19.1 ± 2.5	42.45	
EAFS 7	49.1 ± 9.3	13.2 ± 2.4	15.2 ± 2.0	37.86	
LFS 1	<15.1	3.48 ± 1.7	30.1 ± 3.7	<36.24	
LFS 2	18.6 ± 10.8	3.95 ± 1.7	29.0 ± 3.6	36.08	
LFS 3	<13.7	6.06 ± 2.2	28.4 ± 3.5	<38.12	
LFS 4	<13.5	6.03 ± 1.9	24.6 ± 3.1	<34.26	20-40
LFS 5	<15.6	3.78 ± 1.7	22.8 ± 3.1	<29.41	
LFS 6	<15.6	12.2 ± 2.8	26.4 ± 3.4	<45.02	
LFS 7	17.3 ± 10.3	11.1 ± 3.1	35.2 ± 4.5	52.41	

Table 7 presents results of radium equivalent concentrations in steel slags. The obtained calculated values of radium equivalent concentrations for EAF slag were from 37.86 Bq kg^{-1} (EAFS 7) to 47.84Bq kg^{-1} (EAFS 1). The calculated values of Ra_{eq} for LF slag were from <29.41Bq kg^{-1} (LFS 5) to 52.41Bq kg^{-1} (LFS 7). The obtained results of Ra_{eq} for investigated EAF steel slags were consistent but higher than radium equivalent concentrations in the same kind of steel slags from an earlier study carried out by an another author [10]. The obtained results of Ra_{eq} for investigated LF steel slags were consistent with radium equivalent concentrations in the same kind of steel slags from the earlier study carried out by the same author.

3. CONCLUSIONS

Radiological significance of steel slag samples generated during the production of low carbon steel in the Steel Mill of CMC Sisak has been investigated using gamma spectroscopy technique and mathematical models. The radionuclide activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K, activities index (I1, I2, I3) and radium equivalent concentrations (Ra_{eq}) of EAFS and LFS were determined to assess the radiological hazards from steel slags. Results show that ^{40}K has the largest activity concentration in EAFS and its activity concentration ranges from 49.1 to 62.9$Bqkg^{-1}$. The obtained values of ^{226}Ra and ^{232}Th activity concentrations were from 15.2 to 21.4$Bqkg^{-1}$ and 13.2 to 15.4$Bqkg^{-1}$, respectively.

Radionuclide activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in LFS show similar values for all radionuclides ranges, as follows: ^{40}K from <13.7 to 18.6Bqkg^{-1}; ^{232}Th from 3.48 to 12.2Bqkg^{-1} and ^{226}Ra from 22.8 to 35.2Bqkg^{-1}. Activities index (I1, I2, I3) calculated on the basis of measured radionuclide activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K were less than 1, i.e. it shows that neither of the examined samples exceeds values recommended by the Nuclear Safety Authority (STUK) Guide ST 12.2 and Croatian Ordinance. Results of calculated Radium equivalent concentrations (Ra_{eq}) of ^{226}Ra, ^{232}Th and ^{40}K for investigated slags are in line with the results for the same by-product presented by other authors. The Ra_{eq} value for EAFS (37.86-47.84 Bq kg^{-1}) as well as for LFS (<29.41-52.41Bq kg^{-1}) were determined as lower than the recommended maximum level of radium equivalent of 370 Bq kg^{-1} for building raw materials and products. The measured and calculated values all of considered parameters of naturally occurring radionuclides in examined slags are significantly lower than the maximum values recommended by the Nuclear Safety Authority (STUK) Guide ST 12.2 as well as Croatian Ordinance allowed limit, so steel slags, in terms of the radionuclides present, may be applied as aggregates in the production of various building materials as concrete aggregate and as a cement ingredients, aggregates in road construction, roofing material, landfill cover material, landscape aggregate, etc.

REFERENCES

[1] N. Almeida, F. Branco, J.R. Santos, Recycling of stone slurry in industrial activities: Application to concrete mixtures. Build. Environ. 42 (2) (2007) 810-819.

[2] S. Badur, R. Chaudhary, Utilization of hazardous wastes and by-products as a green concrete material through S/S process: A review. Rev. Adv. Mater. Sci. 17(1-2) (2008)42-61.

[3] L. Jaillon, C.S. Poon, Y.H. Chiang, Quantifying the waste reduction potential of using prefabrication in building construction in Hong Kong. Waste Manage 29 (1) (2009)309-320.

[4] S.B. Park, Y.I. Jang, J. Lee, B.J. Lee, An experimental study on the hazard assessment and mechanical properties of porous concrete utilizing coal bottom ash coarse aggregate in Korea. J.Hazard.Mater.166 (1) (2009)348-355.

[5] EUROPEAN COMMISSION, Radiological Protection Principles Concerning the Natural Radioactivity of Building Materials, Radiation Protection 112, European Commission, Directorate-General, Environment, Nuclear Safety and Civil Protection, 1999, p.11

[6] J.M. Manso, M. Losañez, J.A. Polanco, J.J. Gonzalez, Ladle furnace slag in construction. J Mat In Civ Engrg 17(5) (2005) 513–518

[7] M. Dziarmagowski, Possibilities of converter slag utilization. Arch. Metall Mater 50(3) (2005) 769-782.

[8] EUROPEAN COMMISSION, Council Directive 96/29/EURATOM of 13 May 1996 laying down basic safety standards for the protection of the health of workers and the general public against the dangers from ionizing radiation, Off. J. Eur. Communities, L159 (1996), 1-114, (http://www.ec.europa.eu/energy/nuclear/radioprotection/doc/legislation/9629_en.pdf)

[9] L.A. Currie, Limits for Qualitative Detection and Quantitative Determination: Application to Radiochemistry, Anal. Chem. 40, 3(1968)586-593.

[10] S. Braun, Assessment of Naturally Occurring Radionuclides in Australian Iron and Steel Slags, ANSTO Minerals Technical Memorandum: AM_TM_2010_08_20, (2010) 7-10.

[11] Ordinance on the conditions, methods and terms as well, for systematically research and monitoring of types and activities of radioactive substances in air, soil, see, rivers, lakes, underground waters, solid and liquid rainfalls, drinking water, food and stuff of commonly usage and housing and business rooms as well. Official Gazette No. 60/2008 (in Croatian).

[12] Radiation and Nuclear Safety Authority (STUK)-GUIDE ST 12.2 2005. The radioactivity of building materials and ash, Helsinki 2005, ISSN 0789-4554, (http://www.finlex.fi/pdf/normit/23857-ST12-2e.pdf.)

[13] K. Kovler, Radiation of Building materials. (http://tx.technion.ac.il/~cvrkost/Krina/sld001.htm)

[14] Uredba o mejnih dozah, radioaktivni kontaminaciji in intervencijskih nivojih, Uradni list RS št. 49/2004 (in Slovenian).

[15] J. Beretka, P.J Mathwew, Natural Radioactivity of Austrian Building Materials, Industrial Waste and By-Products, Health Phys. 48 (1985) 87-95.

[16] T. Mondal, D. Sengupta, A. Mandal, Natural radioactivity of ash and coal in major thermal power plants of West Bengal, India, Current Science, 91, 10(2006) 1387-1393.

BIODEGRADATION OF NICOTINE FOR DETOXIFICATION OF TOBACCO WASTE

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Abstract

Tobacco industries produce large quantities of solid and liquid wastes. These wastes pose an important environmental problem, as some main components are harmful and toxic. They contain a high concentration of nicotine and total organic carbon. Furthermore, tobacco solid waste cannot be disposed in a landfill under European Union Regulation because nicotine is a toxic and harmful compound. The aim of this work was to identify the nicotine degrading microorganisms after successful nicotine removal by composting process. The experiment was carried out in a closed reactor (24 dm^3) under adiabatic conditions at an airflow rate of 0.4 $dm^3 \cdot min^{-1} \cdot kg^{-1}$ of volatile solids during 19 days. The detoxification process during the composting was monitored by observing the nicotine concentration and changes in the total number of microorganisms of the reactor samples. Nicotine concentration was measured using high performance liquid chromatography (HPLC). Nicotine degrading bacteria were isolated from agar plates and identified using API 20 NE set. After 19 days, the raw compost was almost free of nicotine. From the raw compost were isolated and identified two bacterial species *Pseudomonas aeruginosa* and *Chryseomonas luteola*. To test that isolated bacteria are the true nicotine degraders another set of experiments were carried out using the tobacco leachate. The leachate was prepared by mixing tobacco waste and tap water and filtered for batch experiments. Isolated bacteria exhibited considerably strong pollution elimination abilities, with 100% nicotine degradation and between 75 and 80% chemical oxygen demand (COD) removal within 28 h and 75 h, depending on initial nicotine concentration and the COD concentration in tobacco leachate.

Keywords: *nicotine, biodegradation, tobacco waste, Pseudomonas aeruginosa, Chryseomonas luteola*

1. INTRODUCTION

Management of agro-industrial wastes represent an important problem in many countries. The solid or semi-solid wastes are produced in large quantities in a short period. Organic fractions of these wastes have an important role in environmental pollution and they must be adequately disposed [1-5]. Tobacco plant residues and liquid mass, which are generated during several processes of cigarette manufacturing, are treated as an agro-industrial waste as well. Tobacco waste contains considerable amount of organic matter and nicotine, which is toxic and hazardous compound [6]. Nicotine being water-soluble compound may be leached from the tobacco wastes during improper storage and migrate in the surrounding environment and enter in to the ground water. Therefore, composting of tobacco waste may be one of the best choices among the available processes to prevent environmental pollution [6-8]. During this process, different microbial species transform organic fraction of solid waste and the remaining organic substances are converted to a humus-like product. Usually, nicotine is not readily degradable and is toxic to the most groups of microorganisms. In spite of it, several authors [9-12] reported that bacteria such as *Pseudomonas* sp., *Ochrobactrum intermedium* and *Rhodococcus* sp, are capable to degrade that compound. Therefore, if these bacterial genera are present in material during composting process, nicotine biodegradation also may occur and then simultaneous detoxification of tobacco waste is possible.

The aim of the present work was to study the detoxification of tobacco solid waste by composting in thermally insulated reactor under the forced aeration. The study objectives were: (a) to monitor nicotine biodegradation during composting, (b) to isolate and identify nicotine-degrading microorganisms and (c) to verify that isolated cultures are a truly nicotine degraders.

2. ELABORATION

2.1. Experimental

2.1.1. Reactor System and Experimental Run

Composting was carried out in a closed reactor (24 dm^3) at an airflow rate of 0.4 $dm^3 \cdot min^{-1} \cdot kg^{-1}$ of volatile solids. Tobacco solid waste from TDR d.d. Rovinj, Croatia, with initial moisture content of 60% was used as a composting material for this experiment. The temperature at the inlet and at the outlet of the reactor was monitored by thermocouples connected to the data logger during 19 days. Reactor was placed on scale and composting samples were taken from reactor for physical-chemical and microbiological analysis at predefined time.

2.1.2. Isolation and Identification of Nicotine Degrading Bacteria

The predominating separated bacterial colonies present on the solid plates, after counting the number of (CFU) in composting samples, were transferred on to the solid plates containing 1.0 g dm^{-3} nicotine and inorganic salt medium and incubated at 30°C for 48 h. Two purified isolates with a high capacity for nicotine degrading were named strain B-1 and B-2. Cell morphology of the isolated strains were observed by a light microscope (Olympus B 201, Japan) after Gram staining [13]. The cell physiological characteristics were determined according to the Manual of Determinative Bacteriology [14]. Biochemical characteristics of isolated strains were determined by the API 20 NE system (bioMerieux, France).

2.1.3. Nicotine Degradation and COD Removal by Bacterial Biomass in the Batch Experiments

The leachate used in this study was prepared as follows: tobacco dust (Hrvatski duhani d.d. Virovitica, Croatia) and tap water were mixed at a ratio of 1:100 (g dm^{-3}) according to European standard EN 12457-4:2002 [15]. As presented in Table 2.1. the resultant leachate was diluted and contained initial nicotine concentration between 0.14 g dm^{-3} and 0.91 g dm^{-3}, and COD concentration from 5.000 mg dm^{-3} to 27.175 mg dm^{-3}.

Table 1. Prepared dilutions of leachate

No. of experiment	Dilution of leachate (%)	Initial COD (mg dm^{-3})
Experiment 1	100 - original	27.175
Experiment 2	75	20.381
Experiment 3	50	13.587
Experiment 4	25	6.793
Experiment 5	17	5.000

Each Erlenmeyer flask with 100 cm^3 of previously prepared leachate was inoculated with 0.218 g dm^{-3} of biomass (bacterial suspension of culture B-1 and B-2 in ratio 1:1), and incubated at 30° C on a rotary shaker at 150 rpm. Samples taken at predefined times were analysed for nicotine and the COD concentration. All experiments were performed in duplicate.

2.1.4. Analytical Methods

The nicotine concentration in all solid and liquid samples were analysed using HPLC 1.22 SPI, Shimadzu, Japan [16]. Leachate samples were analysed for the COD concentration in accordance with standard methods [17]. Viable plate count was determined by decimal dilution method and the results expressed as a colony forming units (CFU) of mesophilic and thermophilic bacteria per gram of dry matter. Petri dishes were incubated at 37°C and 50°C during 48 h.

2.2. Results and Discussion

2.2.1. Biodegradation of Nicotine during Composting Process

For the efficiency of composting of the tobacco solid waste and nicotine biodegradation in a reactor system, it is necessary to know, among the others, the behaviour of microbial flora and its diversity. Microbial succession during composting is known to be rapid, it might take 1-2 days, and temperature in reactor may reach more than 50° C due to the evolved reaction heat. Therefore, composting of selected waste was closely monitored during 19 days.

Changes in the number of bacteria and nicotine concentration during the composting of tobacco waste are presented in Fig. 1. and temperature changes in the reactor in Fig. 2. At the start of the experiment, the number of mesophilic and thermophilic bacteria were 4.7×10^8 per gram of substrate, after 3 days their number was 2.7×10^9 and reaching the maximum on the day nine and being 3.9×10^9 (Fig. 1.). On the contrary, in the first 14 days, nicotine degradation was slow but afterward biodegradation became fast and at the end of the experiment conversion of nicotine reached 89,8%.

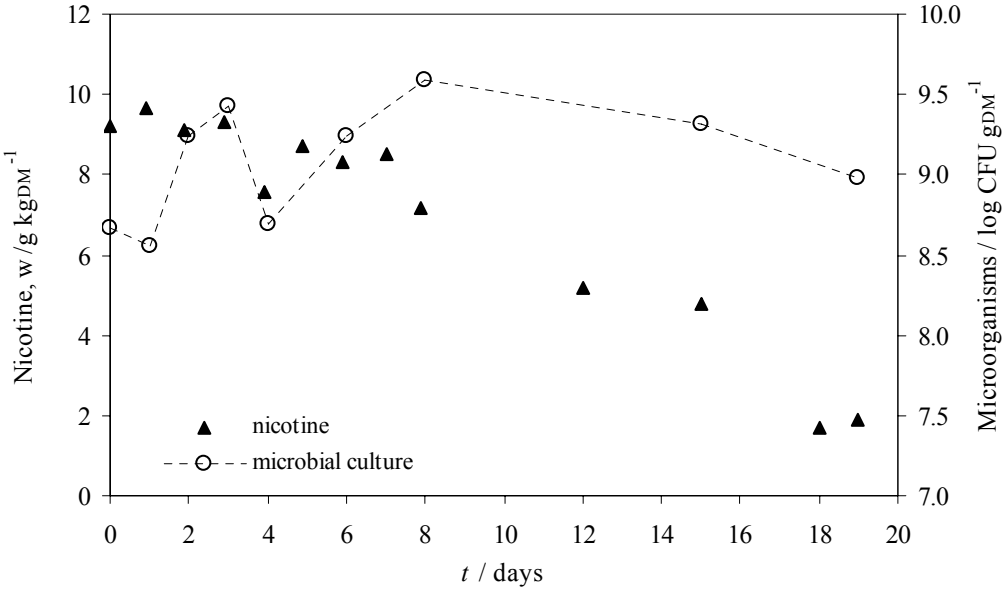


Figure 1. Growth of microorganisms and nicotine biodegradation during 19 days of composting

It is known that mesophilic and thermophilic microorganisms play a key role in the substrate biodegradation but for the nicotine degradation, mesophilic bacteria are responsible [9, 10]. Thus, after 14 days when the temperature in composting mass started to drop (Fig. 2.) further activity of mesophilic bacteria intensified nicotine biodegradation.

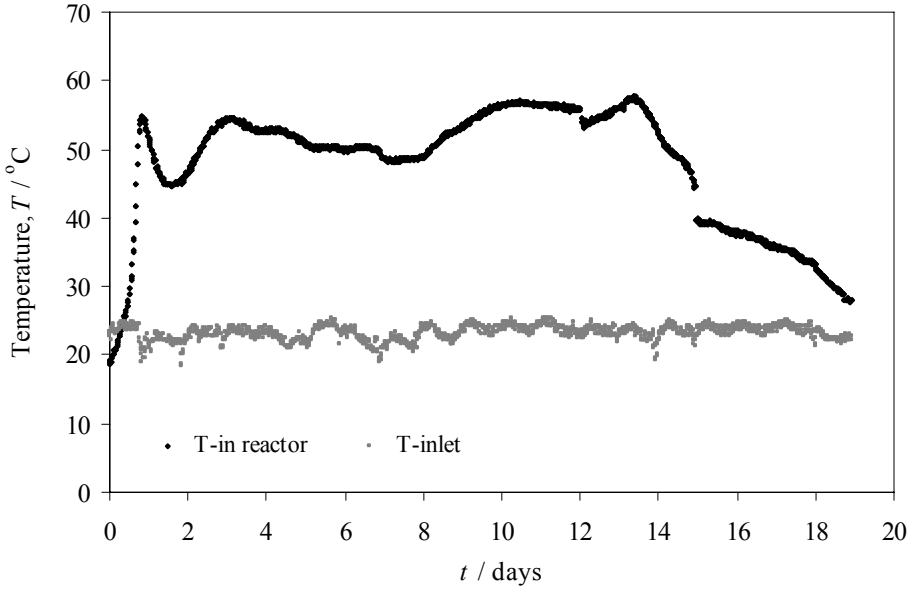


Figure 2. Measured temperature variation with time during 19 days of composting

2.2.2. Isolation and Identification of Nicotine–Degrading Bacteria

During composting, the number of bacteria was regularly checked by the pour plate method. Prevailing and well-separated mesophilic bacterial colonies were picked up and inoculated on the new plates repeatedly, until a pure culture was obtained (Fig. 3.).

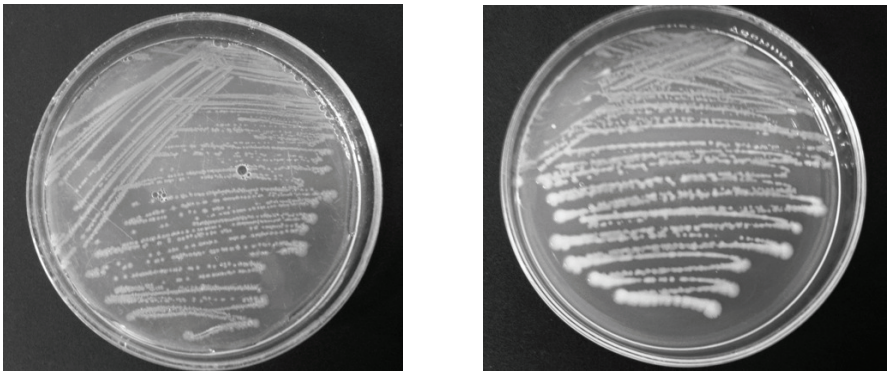


Figure 3. Morphological appearance of isolated bacterial colonies of *P. aeruginosa* (left) and *C. luteola* (right)

Microscopic examination of bacterial cells stained by Gram method showed that both isolated cultures, B-1 and B-2, were gram-negative rods. Identification of those cultures was carried out by API 20 NE system and it was found out that isolate B-1 is *Pseudomonas aeruginosa* and isolate B-2 is *Chryseomonas luteola* (Fig. 3.).

2.2.3. Biodegradation of Nicotine

To verify that the two isolated cultures are a truly nicotine degraders the set of five experiments was carried out using tobacco leachate. Biodegradation of nicotine in tobacco leachate and growth of bacterial biomass (*P. aeruginosa* and *C. luteola*) are presented in Figs. 4. and 5.

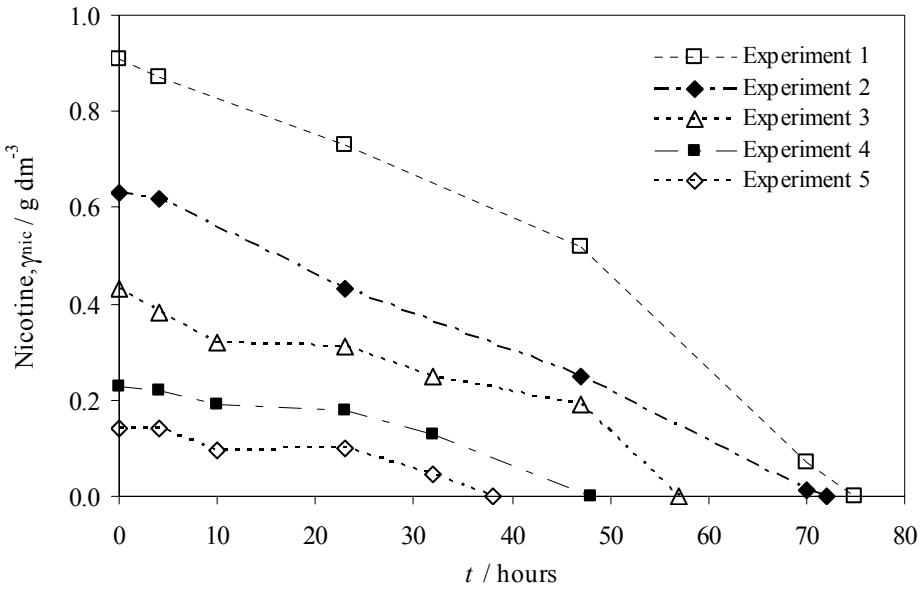


Figure 4. Effect of initial nicotine concentration on the nicotine biodegradation

Depending on the initial nicotine concentration degradation lasted from 38 h to 75 h (Fig. 4.). It can be seen that in the first 20 h in all experiments nicotine biodegradation was relatively slow. Afterward, nicotine concentration rapidly decreased and was completely degraded what is in agreement with literature [10]. The most rapid growth of bacterial biomass was during the first 20 h and after that in the experiments 3, 4 and 5 stationary phase of growth appeared. At the same time, between the late exponential phase and at the beginning of stationary phase of cell growth, the rapid nicotine degradation started (Figs. 4. and 5). In the experiments 1 and 2, stationary phase of the bacterial growth was reached 50 hours later. It was due to the simultaneous biodegradation of nicotine and other organic matter present in the leachate, as the initial COD concentrations in these experiments were 27.175 and 20.381 mg dm^{-3}, respectively. At the end of all experiments, COD removal was in the range of 75-80.5%.

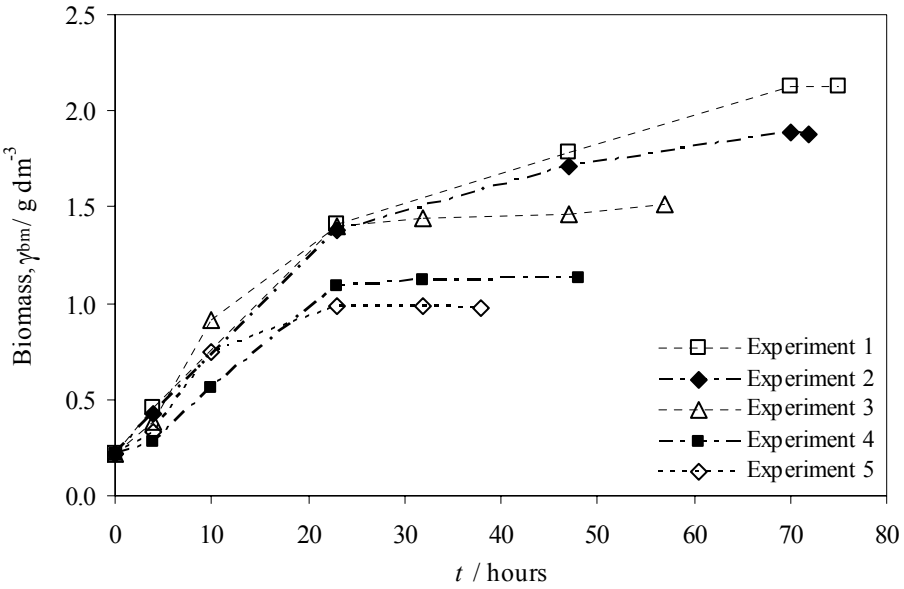


Figure 5. Effect of initial nicotine concentration on biomass growth

Furthermore, it was evident that initial nicotine concentrations used in these experiments were not toxic to the isolated *P. aeruginosa* and *C. luteola*, although the biodegradation rates depended on the initial concentration of nicotine [18].

3. CONCLUSIONS

During the 19 days of composting of tobacco solid waste 89.8% of nicotine was biodegraded. The rapid nicotine degradation started after 14 days, when the temperature in the composting mass started to decrease.

Two mesophilic nicotine-degrading bacterial species *Pseudomonas aeruginosa* and *Chryseomonas luteola* were isolated from the composting mass.

Applying bacterial biomass of *P. aeruginosa* and *C. luteola* in the batch experiments with the initial nicotine concentrations in leachate 0.14 - 0.91 g dm^{-3}, 100% of nicotine and 75 - 80% of COD removal were obtained within 28 h and 75 h.

Acknowledgement
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REFERENCES

[1] J.W.C. Wong, K.F. Mak, N.W. Chan, A. Lam, M. Fang, L.X. Zhou, Q.T. Wu, X.D. Liao, Co-composting of soybean residues and leaves in Hong Kong, Biores. Technol. 76 (2001) 99-106.
[2] R. Kulcu, Q. Yaldiz, Determination of aeration rate and kinetics of composting some agricultural wastes, Biores. Technol. 93 (2004) 49-57.
[3] M.L. Cayuela, M.A. Sanchez-Monedero, A. Roig, Evaluation of two different aeration systems for compsting two-phase olive mill wastes, Proc. Biochem. 41 (2006) 616-623.
[4] V. Sanchez-Arias, F.J. Fernandez, J. Villasenor, L. Rodriguez, Enhancing the co-composting of olive mill wastes and sewage sludge by the addition of and industrial waste, Biores. Technol. 99 (2008) 6346-6355.
[5] L.T. Fontenelle, S.C. Corgie, L.P. Walker, Integrating mixed bacterial population dynamics into modeling energy transport during initial stages of the aerobic composting of a switchgrass mixture, Biores. Technol. 102 (2011) 5162-5168.

[6] A. Piotrowska-Cyplik, A. Olejnik, P. Cyplik, J. Dach, Z. Czarnecki, The kinetic of nicotine degradation, enzyme activities and genotoxic potential in the characterization of tobacco waste composting, Biores. Technol. 100 (2009) 5037-5044.
[7] F. Briški, Z. Gomzi, N. Horgas, M. Vuković, Aerobic composting of tobacco solid waste, Acta Chim. Slov. 50 (2003) 715-729.
[8] N. Bolf, N. Kopčić, F. Briški, Z. Gomzi, Software sensors for monitoring of solid waste composting, Chem. Pap. 61 (2008) 98-102.
[9] A. Ruan, H. Min, X. Peng, Z. Huang, Isolation and characterization of *Pseudomonas* sp. strain HF-1, capable of degrading nicotine, Res. Microbiol. 156 (2005) 700–706.
[10] M Wang, G. Yang, H. Min, Z. Lu, X. Jia, Bioaugmentation with the nicotine-degrading bacterium *Pseudomonas* sp. HF-1 in a sequencing batch reactor treating tobacco wastewater: Degradation study and analysis of its mechanisms, Wat. Res. 43 (2009) 4187-4196.
[11] Y.J. Yuan, Z.X. Lu, N. Wu, L.J. Huang, F.X. Lu, X.M. Bie, Isolation and preliminary characterization of a novel nicotine-degrading bacterium, *Ochrobactrum intermedium* DN2, Int. Biodeter. Biodegr. 56 (2005) 45–50.
[12] X.-W. Gong , Jin-Kui Yang, Y.-Qi.Dua, J.-Y. Dong, W.Zhe, L Wang, Q.-H. Li, K.-Q. Zhang, Isolation and characterization of *Rhodococcus* sp. Y22 and its potential application to tobacco processing, Res. Microbiol. 160 (2009) 200-204.
[13] L. M. Prescott, J. P. Harley, D. A. Klein, *Microbiology*, WCB Publishers, Chichester, 1996.
[14] J.G. Holt, N.R. Krieg, P.H.A. Sneath, J-T. Staley, S.T. Williams, Bergey's Manual of Determinative Bacteriology, 9th Ed., William&Wilkins, Baltimore, 1994.
[15] EN 12457-4:2002, Characterization of waste - Leaching; Compliance test for leaching of granular waste materials and sludges - Part 4: One-stage batch test at a liquid to solids ratio of 10 l/kg for materials with particle size below 10 (without or with size reduction), European Committee for Standardization.
[16] K.R. Tambwekar, R,B. Kakariya, S. Garg, A validated high performance liquid chromatographic method for analysis of nicotine in pure form and from formulations, J. Pharm. Biomed. Anal. 32 (2003) 441-450.
[17] APHA, AWWA, WEF, Standard Methods for Water and Wastewater Examination, 20th ed. American Public Health Association, Washington, DC., 1998.
[18] Y.J. Yuan, Z.X. Lu, L.J. Huang, F.X. Lu, X.M. Bie, Y.Q. Teng, Q. Lin, Biodegradation of nicotine from tobacco waste extract by *Ochrobactrum intermedium* DN2, J. Ind. Microbiol. Biotechnol. 34 (2007) 567–570.

MULTI-CRITERIA DECISION ANALYSIS IN STRATEGIC PLANNING OF WASTE MANAGEMENT

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Abstract

Multi-Criteria Decision Analysis (MCDA) or Multi-Criteria Decision Making (MCDM) is a discipline aimed at supporting decision makers faced with making numerous and sometimes conflicting evaluations. MCDA aims at highlighting these conflicts and deriving a way to come to a compromise in a transparent process. In this study, MCDA was used to attain a systematic approach to strategic planning of waste management, *i.e.* selection of a site for waste management centre (WMC). Ecological, spatial and social criteria involved the following: population density of the area in the neighborhood of potential locations, population density along the roads intended for transport of waste to the landfill site, impact of construction works on the environment, impact on the previous intention of the area, natural characteristics of the location (geological, seismic, hydrogeological…), biological and environmental characteristics of the location and surrounding area, gases and noise emissions and their distribution in the surrounding area under atmospheric conditions. Criteria have been considered and evaluated whereas "1" was taken as the lowest mark and "5" as the highest for every potential location on the basis of available data. MCDA was applied for the comparison of potential landfill sites, on the basis of their overall environmental impact. As a measure for evaluation of the importance of particular criteria in the process of evaluating WMC locations, weight factors were determined. Score calculation was performed by criteria application for each of the considered locations.

Keywords: *multi-criteria decision analysis, waste management, strategic planning, decision making*

1. INTRODUCTION

Waste management has been found as one of the most significant environmental issues in the modern world. It is an important part of urban infrastructure and presents either technical issue as well as a highly political one [1]. Development and implementation of waste management system in affordable and effective way is becoming increasingly complex since it requires a systematic strategic planning approach in order to achieve sustainable urbanization and development of modern societies. Therefore, waste management needs to be considered as an integrated system implementing principles of engineering, hydrology, economy, regional spatial and physical planning as well as health and sociologic aspects that affect public opinion [2]. The use of mathematical modeling for planning waste management systems has been very common [3 – 5]. Used models were usually waste allocation and treatment models seeking to optimize a system consisting either of a set of locations for a chosen type of treatment facility, or a set of facilities coupled to limited set of locations [6]. MCDM uses a variety of methods and tools as a part of a decision making process. The multi-criteria approach assists decision-makers to learn about the problem and possible alternative courses of action addressed from different points of view.

In recent years, municipal solid waste management in Republic of Croatia has been evolving from the decentralized disposal of untreated waste on numerous local landfills without reaching necessary environmental standards, towards centralized waste management approach covering the needs for solving waste management problems on a county level. WMC approach was adopted by Croatian government within national Plan of waste management [7].

The goal of this work was to demonstrate a potential for enhancing strategic design approach for achieving an effective waste management system on a case study of a single region in a particular County in Republic of Croatia.

2. ELABORATION

2.1. Theory

Multi-criteria decision analysis (MCDA) is a numerical multi-criteria decision making (MCDM) process used for comparison of alternatives on a comparable scale. The main principle in MCDA is that any viable solution has to reflect a compromise between criteria. General approach in MCDA, after possible alternative solutions have been identified includes:

- Determination of reasonably independent criteria used for evaluating alternative solutions;
- Defining criteria weights that describe the relative importance of criteria between themselves. Relative importance of the criteria is usually given by a set of weights which are standardized to a sum equal to one:

  $W^T = (w_1, w_2, \ldots, w_n); \sum_{i=1}^{n} w_i = 1$

  where n equals the number of attributes, T equals the traverse form of a set and W^T is a set of weights with n attributes.
- Evaluate the performance of each selected alternative with respect to selected criteria
- Convert the evaluations to a numerical score, thus obtaining ranking of the considered alternatives

Advantages and disadvantages of multi-criteria decision analysis are [8]:

- Advantages:
  - Allows a systematic approach to evaluate policy options and helps understanding the problem;
  - A mixture of quantitative and qualitative information can be incorporated. MCDA goes beyond the evaluation of purely economic consequences and allows non-economic criteria to be assessed on an equal basis;
  - Preferences of the various stakeholder groups with conflicting objectives can be taken into account;
  - Multi-criteria techniques offer a level of flexibility and inclusiveness that purely economic based models tend to lack;
  - These methods do not produce the "best" solution, but a set of preferred solutions or a general ranking of all solutions. Solving such a multi-criteria problem is therefore a compromise and depends on the circumstances in which the decision aiding process is taking place.
- Disadvantages:
  - There is a need for personal judgment and experience in making the decisions;
  - Some of the multi-criteria techniques are very cumbersome and unwieldy;
  - The allocation of weights to each criterion is subjective. Changing the weights could lead to a different result;
  - By this category of models waste prevention, waste minimization or product design for the environment, which would eliminate the production of materials that cannot be reused, recycled or naturally biodegraded are generally not considered.

2.2. Results and Discussion

On the basis of preliminary research, 7 potential microlocations have been determined and evaluated as potential locations for WMC where municipal waste could be disposed. These locations have been already recognized as potential landfills. Preliminary study included analysis and assessment of ecological, spatial and social impacts on the environment for each of the potential locations with the comparison of the project costs. Due to the possible environmental impacts during construction, operation and after run-out (life-cycle assessment), the criteria have been determined and used for comparison and identification of differences between locations. Criteria included parameters which have been considered and evaluated correspondingly ("1" is the lowest mark and "5" the highest), for each of the locations, on the basis of the existing data:

- population density of the area in the surrounding of the potential location;
- population density along the roads intended for transportation of waste;
- projects required on the field and landscape transformation;

- impact on the original purpose of the area;
- natural characteristics of the site (geologic, seismic, hydrogeology etc.);
- biological and ecological characteristics of the site and the surrounding area (three specific criteria);
- gas and noise emissions and their distribution in the environment under the different meteorological conditions.

For the comparison of locations on the basis of their overall environmental impact, a multi-criteria analysis was applied. Weight factors were determined as a measure for the assessment of relative importance between criteria in the comparison process. Calculation of the overall score for each location was performed by summing the results of particular assessments. Applied weight factors have been agreed by the working group appointed for this particular study, taking into account knowledge and experience of the working group members, previous studies in the field, as well as point of views of previous working groups about mutual importance of particular criteria.

For the preliminary environmental impact assessment studies, available data without additional measurements were used. The results for location comparison according to environmental impact group criteria are shown in Table 1.

Table 1. Comparison of potential locations according to environmental criteria

Environmental, spatial and social criteria for the assessment										
Potential location	Population density	The impact of waste transportation	Spatial interventions required for construction	Utilization and allocation of the area	Geological criteria	Phytocenology	Zoocenology	Biocenosis	Meteorological criteria	Total mark
A	3	2	2	4	4	3	3	3	3	3.05
B	4	4	3	4	4	3	3	3	4	3.70
C	4	3	4	4	2	3	3	3	3	3.25
D	4	3	2	4	2	2	2	2	4	2.95
E	3	3	3	3	2	3	3	3	3	2.85
F	2	4	2	4	2	2	2	2	3	2.70
G	4	4	3	4	4	3	3	3	3	3.60
	15 %	15 %	10%	15 %	15 %	5 %	5 %	10 %	10 %	100 %
Weight factors										

Assessment of the potential locations has been made on the basis of approximate costs *i.e.* investment costs for WMC construction and operating costs (operational and maintenance costs). Locations C and D have not been included in the further analysis due to their geographical position and space limitation (insufficient space availability for expansion).

Table 2. Comparison of potential locations according to the framework project costs for the 15 years period

Potential location	Construction costs of WMC and transfer stations (kn)	Operating costs of the system (kn)	Annual overall costs (kn)
A	18.044.000,00	21.825.042.00	39.869.042.00
B	18.044.000,00	21.818.861.00	39.862.861.00
E	18.044.000,00	21.171.306.00	39.215.306.00
F	18.044.000,00	21.389.634.00	39.433.634.00
G	18.044.000,00	21.703.457.00	39.747.457.00

Individual and overall costs as parameters of relative technical and economic feasibility for the 15 years period have been shown in Table 2. It can be seen that the construction costs for WMCs and transfer stations are the same for all the 5 studied locations. It was estimated that the lowest operating costs would be for location E, as well as the annual overall costs due to the lowest waste transportation costs.

Table 3. presents the comparison of locations including environmental and economic criteria whereas environmental criteria have been evaluated with weight factor 0.9 and 0.1 for the economic criteria. It can be seen that location G was marked with the highest grade and ranked at the first place.

Table 3. Comparison of potential locations according to environmental and ecological criteria

	A	B	E	F	G
Environmental criteria	3.05	3.70	2.85	2.70	3.60
Weight factor	0.90	0.90	0.90	0.90	0.90
Economic criteria	1.00	2.00	5.00	4.00	5.00
Weight factor	0.10	0.10	0.10	0.10	0.10
Overall mark	2.85	3.53	3.07	2.83	3.74
Ranking	4	2	3	5	1

3. CONCLUSIONS

Within this study, an analysis based on available data as well as data obtained by field research has been performed in order to rank the preference of 7 potential locations for implementation of WMC in particular County in Republic of Croatia. Study included physical and regional aspects, available areas, potential conflicts on the location, possibilities for traffic connection (traffic roads of the high priority at the first place), economic and environmental aspects with the emphasis on the important elements for realization of WMC: seismic activity, water resource management (existing and predicted), flooding, hydrogeological and geotechnical aspects as well as impact on air quality and ecological network. Field research was focused on geological, hydrogeological and geotechnical aspects. Their results, together with the results of previous researches, have been used for the evaluation of the availability of the location regarding the issues of County's WMC placement and water protection. On the basis of MCDA results, location G was found to be as the best potential location for construction of WMC.

REFERENCES

[1] V. Kum, A. Sharp, N. Harnpornchai, Improving the Solid Waste Management in Phnom Pehn City: A Strategic Approach, Waste Manage. 25 (2005) 101-109.
[2] S. Tedeschi, P. Maifredi, M. Piccazzo, Manual for Municipal Solid Waste Management in Mediterranean Countries. Priority Actions Programme, Center for Regional Activities, Split, 1991.
[3] K.D. Barlishen, B.W. Baetz, Development of a Decision Support System for Municipal Solid Waste Management Systems Planning, Waste Manage. Res. 14 (1996) 71-86.
[4] M. Fabbrcino, An Integrated Programme for Municipal Solid Waste Management, Waste Manage. Res. 19 (2001) 368-379.
[5] N.M. Abou, M. El-Fadel, G. Ayoub, M. El-Taha, F. Al-Awar, An Optimization Model for Regional Integrated Solid Waste Management I. Model Formulation, Waste Manage. Res. 20 (2002) 37-45.
[6] M. Maimone, An Application of Multi-Criteria Evaluation in Assessing Municipal Solid Waste Treatment and Disposal Systems, Waste Manage. Res. 3 (1985) 217-231.
[7] Waste management plan in Republic of Croatia for the period from 2007. – 2015., Official Gazette 85/07
[8] A.J. Morrisey, J. Browne, Waste Management Models and their Application their Application to Sustainable Waste Management, Waste Manage. 24 (2004) 297-308.

EFFECT OF INTERMITTENT STIRRING ON COMPOSTING PERFORMANCE IN TWO DIFFERENT TYPES OF REACTORS

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Abstract

A pilot-scale composting of tobacco waste was conducted in two thermally insulated, forcefully aerated reactors to determine the effect of intermittent stirring on the composting performance. The first two experiments were carried out in a 240 dm^3 packed bed reactor at airflow rate of 0.65 $dm^3\ min^{-1}\ kg_{VSinitial}^{-1}$; the first experiment was carried out without stirring (PBR_{NS}); during the second experiment reactor was periodically opened and the substrate was manually stirred (PBR_S). The third experiment was conducted in a 200 dm^3 horizontal reactor with stirrers (HR_S) at airflow rate of 0.38 $dm^3 min^{-1} kg_{VSinitial}^{-1}$. Substrate was automatically agitated every 24 hours for 1 minute with the stirring rate of 6.3 rpm.
During the composting in PBR_{NS} there was a significant temperature distribution over the bed height. At the end of the processes in PBR_{NS}, PBR_S and HR_S conversions of the volatile matter were 50.6% (at 38. day), 53.0% (at 28. day) and 51.1% (at 29. day), respectively, showing that stirring increases the degradation rate. Obtained temperature profiles and calculated reaction enthalpies showed that in PBR_S there was a significant heat loss caused by periodic stirring of the composting mass while the reactor was opened. For that reason, although similar conversions of volatile matter obtained in PBRs and HRs, horizontal reactor with stirrers is recommended. Furthermore, process in HR_S is easier to handle and consumption of electricity for stirring could be partly compensate with lower aeration rate.
Keywords: *composting, stirring, horizontal reactor, packed bed reactor*

1. INTRODUCTION

Composting has become increasingly popular in the past decade as a biological treatment process of organic solid wastes and it is acceptable solution to reduce the volume of bulky solid waste and to stabilize waste material in the form of compost [1]. The solid wastes, which originate from the food processing and agricultural industries, are suitable substrates for composting [2-4]. Successful composting requires meticulous attention to key parameters, e.g. moisture content (*MC*), air supply, temperature, *pH* and carbon to nitrogen ratio (*C/N*) of the composting material [1,3,5,6]. Among other factors, *MC* has been referred to as the critical design and operating factor to optimize compost systems, because decomposition of organic matter depends on the presence of moisture to support microbial activity [7]. Optimum moisture requirements for successful composting of a wide variety of organic wastes range from 25 to 80% and the range should be determined for the specific waste material [8].
Organic fraction of solid waste can be composted either in nonreactor system or reactor system [9]. The advantages of the in-vessel composting or reactor systems are in more controllable composting performance and prevention of air pollutants and odor emissions [10-12]. There are many types of composting reactors with regard to geometry of the reactor, aeration mode, and agitation [9,13]. Agitation or stirring of the composting bed provides enhanced oxygen supply to microbial community and the homogeneity of the composting mass. Stirring also prevents the substrate particles to agglomerate which hamper channeling in the composting bed and increase disposable area of the substrate for the microbial activity [13]. Those phenomena are highly effective on composting performance when composting powdery substrates consisted of small particles, what is the case in this work.

The aim of the work was to investigate composting of tobacco solid waste in two types of pilot-scale thermally insulated reactors. The study objectives were: (a) to define substrate and process parameters for effective composting, (b) to determine the heat of reaction ($-\Delta Hr$) and the degradation rate of substrate volatile solids (VS) and (c) to define efficiency of stirring on composting process.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Composting Material

For the composting tests, tobacco solid waste generated in the tobacco production in Virovitica, Croatia, was used as a composting substrate. The tobacco waste product consisted of very fine, powdery residues where about 70 % of particles were smaller than 1 mm. The average initial moisture content (*MC*) of the raw material was about 8 %.

2.1.1.1. Determining the Optimum Moisture Content

Concept of free air space (*FAS*), adopted from soil science, was used to establish the relation between moisture content (*MC*) and physical structure of the composting materials. *FAS* (%), porosity (*P*, %) and *MC* (%) are related through the following equation [6]:

$$FAS = P(1 - MC/100) \tag{1}$$

To obtain optimum composting, 20-35% FAS is required [6].

The method used to investigate optimum *MC* of the compostable material is reported in the work of Madejon et al. [8]. The measurements were carried out in a glass tube of 0.4 dm^3. Tube was filled with samples of waste mixture with different *MC*; the water was slowly added to completely fill the free air space, shaking slightly to avoid the formation of air bubbles. The difference between the final and initial weight was considered as the volume of pores. Values of *P* were calculated for a series of samples with different *MC*. Three measurements were performed for each initial *MC*. The values of *FAS* were calculated applying the equation (1).

2.1.2. Pilot-scale Reactors

Composting was conducted in two specially designed thermally insulated, forcefully aerated reactors. The moisture content of the substrate was set to about 60 % by adding the water and the substrate was put into reactors from the top which could be easily opened. Three experiments were carried out; two in the vertical packed bed reactor (without stirring (PBR_{NS}) and with intermittent stirring (PBR_S)) and one in horizontal reactor with stirrers (HR_S). During composting in all experiments, continuous upward aeration was provided by an air blower. To ensure permanent air humidity at the reactors inlet, prior to entering the reactor air was saturated with moist by passing through humidification tank. After leaving the reactor, the hot spent air cooled down naturally and the condensate collected into the graduated cylinder (Fig. 1.).

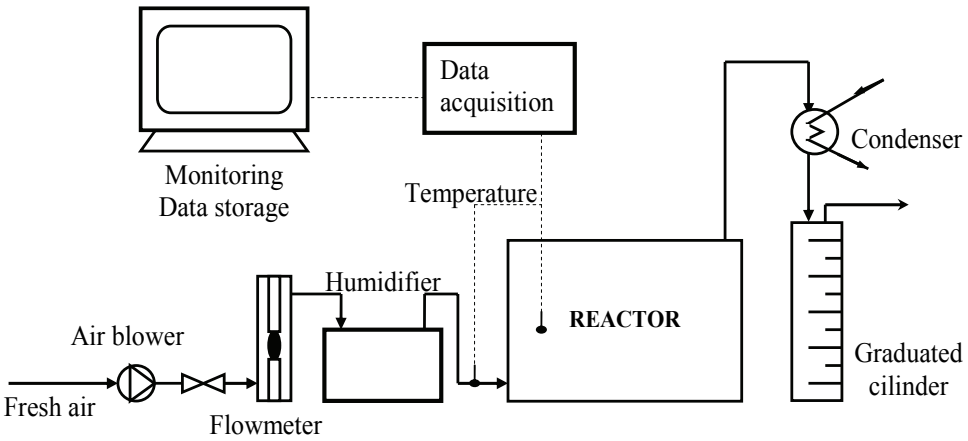


Figure 1. Schematic diagram of the composting process

2.1.2.1. Packed-bed Reactor (PBR).

Reactor (Fig. 2.) was made of PVC with a working volume of 240 dm^3 (L×W×H = 540×500×890 mm). The waste material was placed into reactor on the perforated plate. Temperature was periodically measured with digital temperature probe at the reactor inlet and inside the reactor at five different heights: 200, 350, 500, 650 and 800 mm, respectively, starting from the bottom. Two experiments were carried out with initial mass of the wet substrate of 120.0 kg at airflow rate of 0.65 $dm^3 min^{-1} kg_{VSinitial}^{-1}$.

The first experiment was conducted without stirring (PBR_{NS}); during the second experiment reactor was periodically opened and the substrate was manually stirred (PBR_S).

2.1.2.2. Horizontal Reactor with Stirrer (HR_S).

Horizontal stirred-drum reactor (Fig. 2.) had a total working volume of 200 dm^3 with inner diameter of 494 mm. Stirrer with 12 paddles was mounted on a central axis powered by an electromotor on the side of the reactor. Reactor was filled from the top with 74.0 kg of wet substrate and the experiment was carried out at airflow rate of 0.38 $dm^3 min^{-1}$ $kg_{VSinitial}^{-1}$. RTD probes for continuous temperature monitoring were placed at the reactors inlet and inside the reactor next to the central axis of the stirrer. Substrate was automatically agitated every 24 hours for 1 minute with the stirring rate of 6.3 min^{-1}.

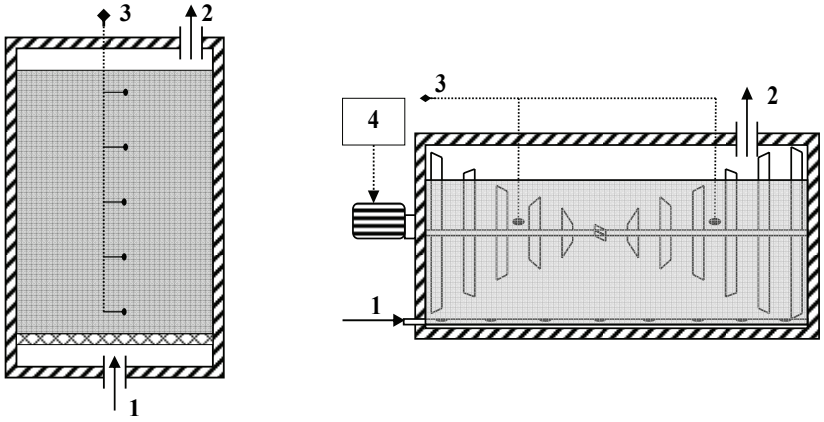


Figure. 2. Schemes of packed bed reactor-PBR (left) and horizontal reactor with stirrer-HR_S (right); (1-air inlet; 2-spent air outlet; 3-temperature probes; 4-electromotor)

2.1.3. Physical-Chemical Monitoring and Analyses

Temperatures at different positions were monitored by means of the temperature probes. Airflow rate was regulated by airflow-meter with a regulation valve. At the beginning and at the end of the process mass of the substrate/composting mass was determined and samples were taken in order to analyze most relevant physical-chemical parameters (pH-value, moisture content and dry matter, volatile solids content). All analyses were carried out in duplicate and according to the Austrian standard methods (OENORM S 2023) for analysis of compost [14], which is widely used in Europe.

2.2. Theory and Calculation

The reaction enthalpy ($-\Delta H_r$) was calculated from experimental results by measuring the temperature of the composting mass during the reaction. The value of $-\Delta H_r$ was calculated using the following equation (2):

$$(-\Delta H_r) = \frac{\rho_Z Q_V}{m_{VS0}(1-w_{VS})} \int_0^t \left[c_{pz}(T - T_{in}) + h_{w(T)}(H_{S(T)} - H_{S0}) \right] \cdot dt \qquad (2)$$

where m_{VS0} is initial mass of volatile solids, T and T_{in} are temperatures of the substrate and of the air at reactor's inlet, $h_{w(T)}$ is the heat of vaporization and $H_{S(T)}$ and H_{S0} are saturated humidities at reactor and ambient temperature.

Equation (2) was assigned to a mathematical model developed using the kinetic model [6] and mass and energy balances and was reported in previous work [15]. Reactors were modeled as a continuous stirred tank reactor (CSTR) and several assumptions were used in developing the model: biodegradation of the substrate was slow compared to oxygen transfer through the boundary gas layer; oxygen concentration in the substrate bed was constant; airflow rate during composting was constant. It was also assumed that the process had been carried out under adiabatic conditions and that the released heat was proportional to the progress of biodegradation.

2.3. Results and Discussion

2.3.1. Optimization of Initial Moisture Content

Obtained values of moisture content (*MC*) and free air space (*FAS*) were linearly correlated with high coefficient of determination (R^2 = 0.9976) and linear regression equation was $MC = -1.2311 \cdot FAS +$

90.987. Finally, knowing the optimal *FAS* range, optimal *MC* of the given substrate was calculated to be between 47.9 and 66.4 %.

2.3.2. Temperature and the Reaction Enthalpy

Composting of tobacco waste was carried out in packed bed reactor and in a horizontal reactor with stirrers. Temperature of the composting mass in the reactors was continuously monitored as an indicator of the extent of the reaction. Temperature curves obtained in the experiments are shown in Figs. 3-5.
During the process conducted in packed bed reactor without stirring (PBR_{NS}) temperature maximum was reached at day 2 and thermophilic phase in the middle of the reactor lasted to day 28. (Fig. 3). After the day 5 there was a significant temperature distribution over the bed height. The temperature measured at the top and at the bottom of the reactor (200 and 800 mm from the bottom) was about 40 °C while in the middle of reactor was between 50 and 57°C. Temperature distribution indicated that the reaction rate was not the same in all segments of the reactor.

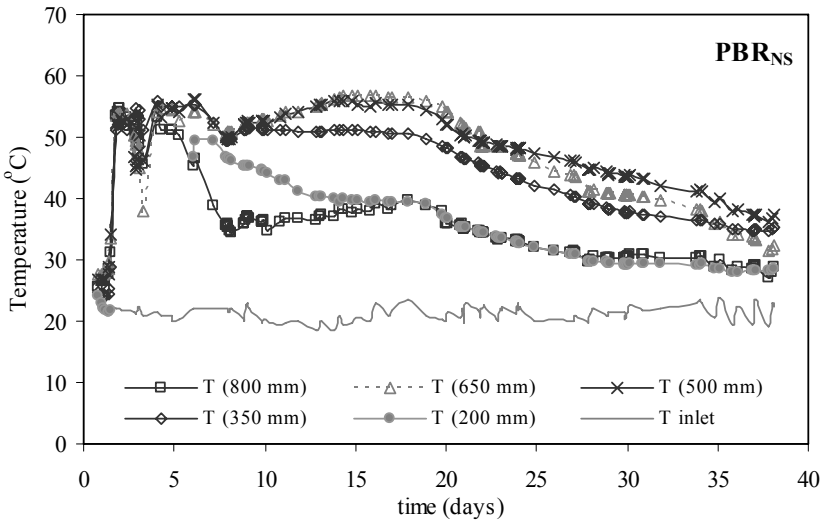


Figure 3. Temperature profiles during 38 days of composting in packed bed reactor without stirring (PBR_{NS}).

In the second experiment composting was carried out in packed bed reactor where the substrate was manually stirred (PBR_S) twice a week. Obtained temperature values were similar to those obtained in PBR_{NS} but the temperature distribution was less distinctive (Fig. 4.). Nevertheless, temperatures measured at the lowest point were considerably lower than other values. It was due to inability of complete manual stirring of the substrate bottom layer.

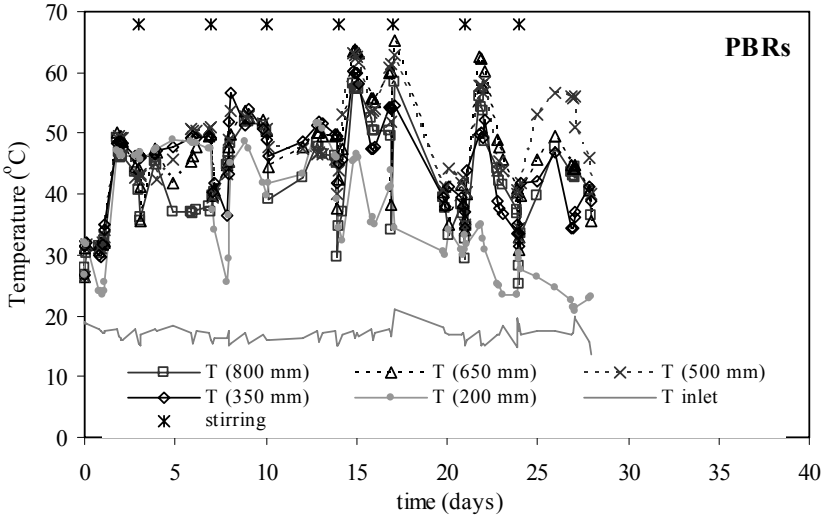


Figure 4. Temperature profiles during composting in packed bed reactor with stirring (PBR_S)

Temperature profiles in Fig. 4. also showed a rapid increase in temperature after stirring period. In fact, stirring provided breakdown of the agglomerates and increased the available area of the substrate particles for further degradation. Rapid temperature decrease in the moment of stirring was a consequence of stirring of the composting mass while the reactor was opened.

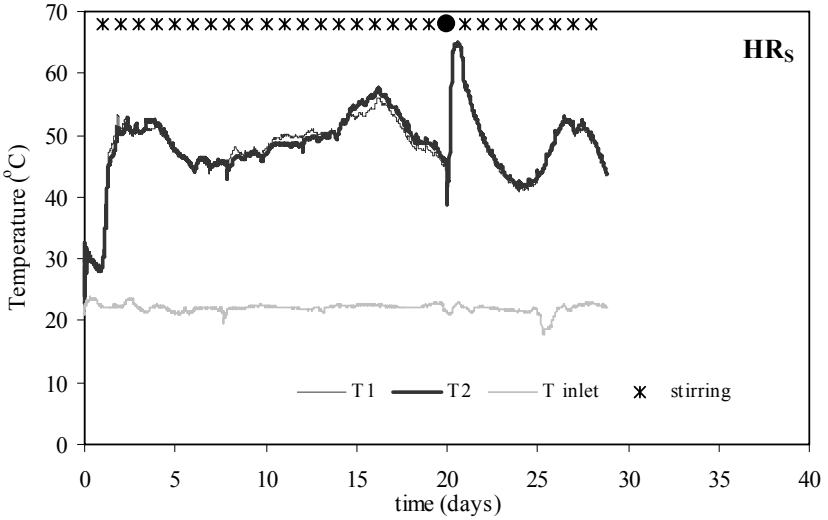


Figure 5. Temperature profiles during composting in horizontal reactor with stirrer (HR_S); ● marks overall mixing during 10 minutes.

During the experiment in the horizontal reactor (HR_S) stirring was conducted automatically once a day for 1 minute. Unlike the PBR_S, the horizontal reactor was closed during the whole process and rapid increase in temperature after stirring was not observed (Fig. 5.). Exception was the overall mechanical and manual stirring for the 10 minutes at the day 19. Namely, that action was done to remove thin layer of the composting material captured between the paddles and the reactor wall as well as to explore substrate "potential" for further degradation. After overall mixing, the temperature in the composting bed was increased to 64 °C. That effect indicated that some modification of the stirrer should be done and that the stirring intervals should be precisely investigated in further work.

The reaction enthalpy ($-\Delta H_r$) was calculated from the equation (2) using experimentally obtained temperature values of the composting mass. Calculated values ($-\Delta H_r$) and necessary data for the calculation are given in Table 1.

Table 1. Dimensions and characteristics of process and calculated reaction enthalpy ($-\Delta H_r$)

Experiment	PBR_{NS}	PBR_S	HR_S
Initial mass of volatile matter, m_{VS0} (kg)	41.5	41.5	23.5
Air flow rate, Q_V ($dm^3\ min^{-1}\ kg_{VS}^{-1}$)	0.65	0.65	0.38
Heat capacity of air, c_{pz} ($kJ\ kg^{-1}K^{-1}$)	1.01	1.01	1.01
Air density, ρ_z ($kg\ m^{-3}$)	1.3	1.3	1.3
Inlet air temperature (°C)	21.0 ± 2.0	19.5 ± 2.0	21.5 ± 1.5
Reaction enthalpy($-\Delta H_r$) ($kJ\ kg_{VSinitial}^{-1}$)	5538	4675	5179

The obtained values of reaction enthalpy ($-\Delta H_r$) for the selected substrate were similar to those in the literature [6,15]. Calculated reaction enthalpy for the PBR_S showed that there was a significant heat loss caused by periodic stirring of the composting mass while the reactor was opened. It should be noticed that the reaction enthalpy in packed bed reactors was calculated using the temperature measured at the middle of the reactors height. Higher temperatures at the middle of the reactor in PBR_{NS} and longer composting period (38 days) were the reason for the highest ($-\Delta H_r$) value.

2.3.3.. Mass Loss and Degradation of the Substrate

The substrate at the beginning and the product at the end of composting were weighted and samples were analyzed to determine: moisture content, pH-value and volatile solids content. At the end of the process in PBR_{NS}, PBR_S and HR_S conversions of the volatile matter were 50.6% (at 38. day), 53.0% (at 28. day) and 51.1% (at 29. day), respectively (Table 2). The obtained values of the conversions as well as the duration of the composting process showed that stirring increases the degradation rate. Final moisture content was the lowest in PBR_S. That confirms the fact of heat and water loss by evaporation due to opening the reactor, which is not the case in HR_S. Stirring of the bed in HR_S while the reactor was closed maintained the *MC* during the process at satisfied level [16].

Table 2. Physical-chemical properties of the substrate and the product of the composting processes

Experiment	PBR_{NS}		PBR_S		HR_S	
	Initial	Final	Initial	Final	Initial	Final
Mass of wet substrate, m (kg)	120.0	77.0	120.0	53.9	74.0	49.1
Moisture content, MC (%)	59.7	65.5	59.6	52.4	60.4	59.4
pH-value	5.6	7.2	5.3	8.9	6.1	9.4
Volatile solids content, VS (%)	85.8	77.1	85.2	75.9	80.0	63.0
Conversion of VS, X_{VS}(%)		50.6		53.0		51.1

Physical and organoleptic characteristics of the end product in HR_S (Fig. 6(B)) gave it a typical compost appearance (black color with white spots, smell of humid earth, among others). At the end of the process in the PBR_{NS} the top of the material was good in appearance (Fig 6(A)); structurally adequate and overgrown by actinomycetes what indicated the proper moisture and good oxygen supply in higher regions of the reactor. In spite of it, after removing the composting product from the reactor, dry and not degraded as well as moist and smelly zones were observed in the rest of the material. In addition, shrinkage of the material in PBR_{NS} was observed what probably facilitated pass of air between edges of material and the reactor wall (Fig. 6(A)) and limited oxygen supply to the composting bulk [13,17].

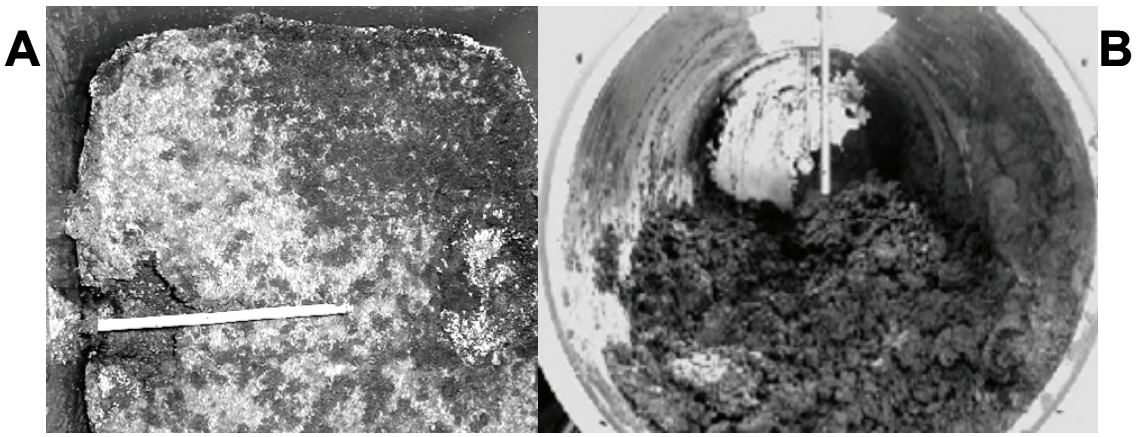


Figure 6. Photographs of a composting mass at the end of the process:
(A) in packed bed reactor without stirring (PBR_{NS}, photography taken from the top);
(B) in horizontal reactor (photography taken from the side, after removing the stirrer)

3. CONCLUSIONS

The optimum moisture content (MC) for efficient composting of the tobacco waste was estimated by a simple method and calculated to be between 47.9 and 66.4 %.

During composting in PBR_{NS} there was a significant temperature distribution over the bed height. At the end of the process channeling and shrinkage of the material was observed.

At the end of the processes conducted in PBR_S (28th day) and in HR_S (29th day) 53.0% and 51.1% of volatile solids were degraded, respectively. Obtained temperature profiles and calculated reaction enthalpies showed that in packed bed with stirring (PBR_S) was a significant heat loss caused by periodic stirring of the composting mass while the reactor was opened. For that reason, although similar conversions of volatile matter were obtained in PBRs and HRs, horizontal reactor with stirrers could be recommended.

Due to breakdown of the agglomerates and minimizing possibility of channeling, stirring of the composting bed during the process contributes to better oxygen supply and thus enables higher degradation rate.

Nomenclature

c_{pz} - specific heat capacity of air, kJ kg^{-1} K^{-1}
FAS – free air space of the material, vol. %
$h_{w(T)}$ - heat of vaporization of water at reactor temperature, kJ kg^{-1}
$H_{S(T)}$ - saturated humidity at reactor temp., kg kg^{-1} H_{S0} - saturated humidity at ambient temp., kg kg^{-1}
m - mass of the substrate, kg
m_{VS0} – initial mass of volatile solids
MC – moisture content of the material, %
P - porosity of the material, vol. %
Q_v - airflow volume, m^3 h^{-1}
t - time, day
T - temperature in reactor, °C
T_{in} - temperature of air at the reactor inlet,°C
w_{VS} - mass fraction of volatile solids, kg_{VS} kg $_{VSinitial}^{-1}$
ΔHr - reaction enthalpy, kJ $kg_{VSinitial}^{-1}$
ρ_z - air density, kg m^{-3}

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REFERENCES

[1] A.J. Biddlestone, K.R. Gray, Aerobic processing of solid organic wastes for the production of a peat alternative, Process Biochem. 26 (1991) 275-279.
[2] M.J. Díaz, E. Madejón, F. López, R. López, F. Cabrera, Composting of vinasse and cotton gin waste by using two different systems, Resour., Conserv. Recycling 34 (2002) 235-248.
[3] M.P. Bernal, M.A. SaÂnchez-Monedero, A.R. C. Paredes, Carbon mineralization from organic wastes at different composting stages during their incubation with soil, Agric., Ecosyst. Environ. 69 (1998) 175-189.
[4] M.J. Diaz, E. Madejón, F. López, R. López, F. Cabrera, Optimization of the rate vinasse/grape marc for co-composting process, Process Biochem. 37 (2002) 1143-1150.
[5] M. Iranzo, J.V. Canizares, L. Roca-Perez, I. Sainz-Pardo, S. Mormeneo, R. Boluda, Characteristics of rice straw and sewage sludge as composting materials in Valencia (Spain), Bioresource Technol. 95 (2004) 107-112.
[6] R.T. Haug, The practical handbook of compost engineering, Lewis, Boca Raton, 1993.
[7] T.L. Richard, H.V.M. Hamelers, A. Veeken, T. Silva, Moisture Relationships in Composting Processes, Compost Sci. Util. 10 (2002) 286-302.
[8] E. Madejon, M.J. Dıaz, R. Lopez, F. Cabrera, New approaches to establish optimum moisture content for compostable materials, Bioresource Technol. 85 (2002) 73-78.
[9] L.F. Diaz, M. deBertoldi, W. Bidlingmaier, (Eds.) Compost science and technology, Elsevier, Amsterdam, 2007., pp 67-87.
[10] Q.H. Bari, A. Koenig, T. Guihe, Kinetic analysis of forced aeration composting - I. Reaction rates and temperature, Waste Manage. Res. 18 (2000) 303-312.
[11] J. Peigné, P. Girardin, Environmental Impacts of Farm-Scale Composting Practices, Water Air Soil Poll. 153 (2003) 45-68.
[12] M.T.I. Cabaraban, M.V. Khire, E.C. Alocilja, Aerobic in-vessel composting versus bioreactor landfilling using life cycle inventory models, Clean. Techn. Environ. Policy 10 (2008) 39-52.

[13] D.A. Mitchell, N. Krieger, M. Berovič, Solid-state fermentation bioreactors-Fundamentals of design and operation, Springer-Verlag, Berlin Heidelberg, 2006.
[14] Austrian standard S 2023, Analytical Methods and Quality Control for Waste Compost, Austrian Standardization Institute, Viena, 1986.
[15] A.E. Ghaly, F. Alkoaik, A. Snow, Thermal balance of invessel composting of tomato plant residues, Can. Biosyst. Eng. 48 (2006) 6.1-6.11.
[16] J. Cegarra, J.A. Alburquerque, J. Gonzálvez, G. Tortosa, D. Chaw, Effects of the forced ventilation on composting of a solid olive-mill by-product ("alperujo") managed by mechanical turning, Waste Manage. 26 (2006) 1377-1383.
[17] P.D. Schloss, B. Chaves, L.P. Walker, The use of the analysis of variance to assess the influence of mixing during composting, Process Biochem. 35 (2000) 675-684 .

DETERMINATION OF AMMONIA AND CARBON DIOXIDE IN EXHAUST GASES DURING COMPOSTING OF TOBACCO WASTE IN A CLOSED REACTOR

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Abstract

Solid waste accumulated during the processing of tobacco for cigarette manufacture mostly contains tobacco particles and flavouring agents. The main characteristic of that waste is a lower than optimal C/N ratio and a high content of nicotine as a toxic substance. Tobacco waste is classified as agro-industrial waste and as such can be decomposed by composting. Ammonia is one of the main compounds responsible for generation of offensive odours, and atmospheric pollution when composting organic wastes with high nitrogen content.

The objective of this work was to determine amount of ammonia and carbon dioxide in the exhaust gases during composting of tobacco waste. Composting process was carried out with forced aeration (0.66 L min^{-1} kg_{VS0}^{-1}) in column reactor (10 L) under adiabatic conditions during 26 days. During the process, temperature changes in the reactor, pH value, C/N ratio and mesophilic and thermophilic microorganisms in the mixed microbial culture were closely monitored while evolved CO_2 and NH_3 were analyzed periodically. Ammonia was measured both in the condensate and in 4 % boric acid trap while CO_2 was trapped in 1 M NaOH.

It was found that emission of carbon dioxide depended on temperature while emission of ammonia mainly depended on pH value in composting mass. The most of carbon dioxide was evolved in the first several days of composting process due to the highest activity of microorganisms. At the end of the process total CO_2 evolved (per kilogram of initial volatile solids) was 302.0 g kg_{VS0}^{-1}. No significant amount of ammonia was detected until day fifteen. Total NH_3 evolved during 26 days of composting was 2.972 g kg_{VS0}^{-1} and it was found that condensate contained approximately 80% of that amount.

Keywords: *composting, tobacco waste, adiabatic closed reactor, ammonia and carbon dioxide emissions*

1. INTRODUCTION

Industrial wastes include solid or liquid mass and contain considerable amounts of organic matter. Classification of industrial wastes of organic origin includes tobacco wastes, which are generated during different processes of the tobacco and cigarette production cycle. These wastes frequently contain residues of tobacco leaves [1].

Composting is an environmentally friendly and effective technology to treat or manage organic wastes. It is a biological treatment in which aerobic mesophilic and thermophilic microorganisms transform the biodegradable organic matter into CO_2, H_2O and a stable organic matter-compost [2]. Carbon dioxide is identified as a biogenic gas, because CO_2 is a measure of microbial respiration and ammonia is generated as product of microbial transformation of organic nitrogen [3].

Composting the toxic tobacco waste would minimise waste and the compost could be useful for agricultural purposes. However, mismanagement of the composting process results in emission of harmful gases and corresponding environmental problems. [4]. Two major polluting gasses during tobacco composting are carbon dioxide (CO_2) and ammonia (NH_3). CO_2 is a greenhouse gas with the largest impact on climate changes, while ammonia is one of the main compounds responsible for generation of offensive odours and atmospheric pollution when composting organic waste with high nitrogen content [5].

The aim of this work was to determine the evolution of ammonia and carbon dioxide in the exhaust gases during composting of tobacco waste in a laboratory–scale column reactor.

2. ELABORATION

2.1. Materials and methods

2.1.1. Tobacco Waste

Tobacco waste, which is used in the composting experiments, was obtained from Cigarette Company in Croatia. Table 1 presents the main characteristics of the initial composting mixture.

Table 1. Characteristics of the initial tobacco waste

Parameter	
Moisture (%)	65
Dry matter (%)	35
Volatile matter (%)	78,43
N-Kjeldhal (% dry matter)	1,96
C/N ratio	21
pH-value	6,5

2.1.2. Composting Experiments

The composting experiment of tobacco waste was conducted in a closed thermally insulated column reactor with effective volume of 10 L. The reactor was operated at an airflow rate of 0.66 L min^{-1} kg^{-1} $_{volatile\ solids\ (VS)}$ and the temperature was monitored by thermocouples connected to the data logger during the 26 days of composting period. Condensate and exhaust air were collected in volumetric flasks, ammonia was trapped in boric acid solution and carbon dioxide in sodium hydroxide solution. All experiments were performed in duplicate.

2.1.3. Analytical Methods

Composting samples, taken periodically from reactor, were tested for pH, moisture, volatile solid contents, carbon and nitrogen (C/N) ratio and microbial diversity. The moisture content and volatile solids in the composting mass were determined gravimetrically, pH-value was measured with pH meter and the total nitrogen content using Kjeldahl method [6].

Ammonium from the exhaust gas was absorbed into 4% boric acid [7] and carbon dioxide in 1 M sodium hydroxide. The graduated cylinder was used for measuring daily production of condensate. In condensate pH-value and presence of ammonium was checked regularly. The growth of both mesophilic and thermophilic bacteria and fungi were determined. The incubation time was 24-48 h for mesophilic and thermophilic bacteria and 72 h for mesophilic and thermophilic fungi. The temperature was 37°C and 28°C for mesophilic bacteria and fungi and 50°C for thermophilic bacteria and fungi. The results were expressed as CFU per 1 g of dry matter [8].

2.2. Results and Discussion

2.2.1. Temperature Profile and Growth of Microorganisms

Temperature is one of the most important parameters for maintaining the efficiency of composting process. Biological activity is an indicator of biodegradation of organic matter because aerobic microorganisms produce heat in composting mass [7]. The temperature undergoes considerable changes due to a calorific effect, resulting from oxidative cleavage of covalent bonds in the substances during composting [9]. All composting processes are known to go through tree stages: mesophilic, thermophilic, and cooling.

The initial temperature of the composting mass was 25°C and after 48 hours rapidly increased to 56°C. The third day of composting, the temperature dropped to 39°C and the day after increased again to a peak of 44°C. Afterward, the composting mass started to cool until the compost and ambient temperatures levelled (Figure 1).

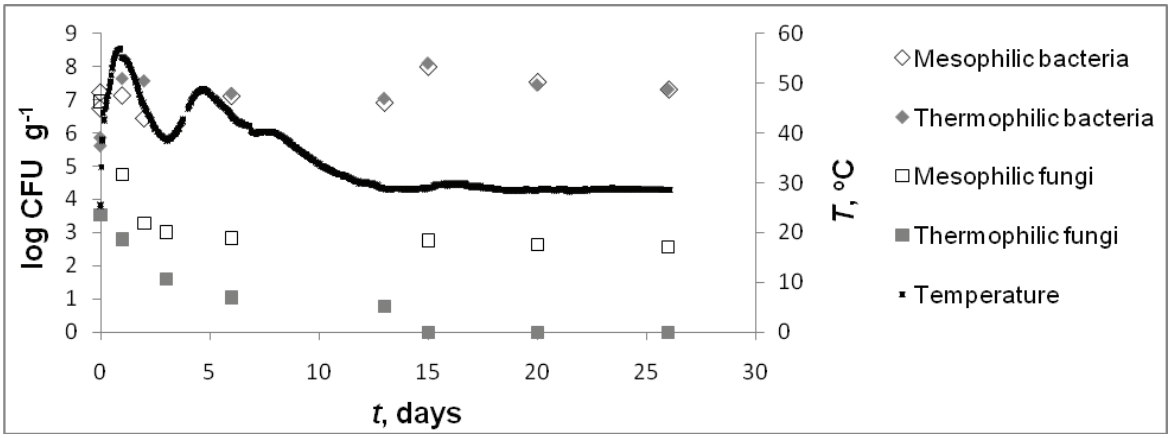


Figure 1. Temperature variations in composting mass and growth of microorganisms during 26 days of composting

The mesophilic stage usually starts at the beginning of a process during which the microorganisms undergo adaptation and proliferate [9]. The temperature levels in the composting mass tended to increase and reached 50-60°C due to the energy released from the biochemical reactions of the mesophilic microorganisms. Increased temperature enabled the growth of thermophilic microorganisms and their activity. In this phase, metabolic heat started to decrease as a result of biodegradation of macromolecules that uses a large amount of energy, and temperature started to drop [1]. It enabled the regrowth of mesophilic microorganisms. The secondary temperature peak that occurred were possibly a result of delayed microbial growth (recovered mesophilic microbial population) in the outer portions of composting mixture, either due to the water leached from the top, or lower heat removal rate due to the predominance of low constant aeration rate, or both [10]. At the end of the experiment, the organic components of waste undergo their final degradation and the temperature curve was typical of laboratory composting process and indicated that the system was operating satisfactorily.

The growth of both the mesophilic (20-45°C) and thermophilic (45-70°C) bacteria and fungi, at various stages of the composting process, was determined (Figure 1). The microbial species involved in the degradation of the substrate and their number has been changing with the change of the temperature in reactor. During the first day of the experiment, the number of mesophilic bacteria increased from 5.49×10^{6} to 1.35×10^{7} and at day fifteen up to 9.83×10^{7}. After that, their number slowly started to decrease. The exponential growth (4.17×10^{5} to 4.23×10^{7}) of thermophilic bacteria started after the first day because the temperature was about 50°C and until the end of composting their number increased no further. Bacteria are mostly responsible for starting the composting process because they consume the available soluble nutrients, which produces metabolic heat [11]. From the start of experiment, the number of mesophilic (5.48×10^{4}) and thermophilic (3.43×10^{3}) fungi decreased and until the end of process only mesophilic fungi were detected (6.31×10^{2}).

2.2.2. Emission of Ammonia and Carbon Dioxide

Ammonia and carbon dioxide are the main gases released during composting of tobacco waste and the obtained results of experiments are presented in Figures 2, 3 and 4.

2.2.2.1. Ammonia Evolution and Influence of pH Value on its Emission

Ammonia emissions have been proposed in some works as an indicator of the biological activity in composting materials with high nitrogen content [5]. Tobacco waste has high nitrogen content and low C/N ratio. It is known that temperature and pH are two main factors, which have influence on ammonia emission from the composting mass. High temperature and pH value affects ammonia volatilization, thus non-volatile ammonium ions are converted to the volatile ammonia form [5]. The pH values of composting mass ordinarily vary from weakly acidic to neutral. Due to the formation of ammonia it becomes alkaline, what is closely related to the activity of microorganisms participating in the process of compost formation [9].

Figure 2 (a) and (b) shows the evolution of ammonia in the exhaust gas and presence in condensate depending on temperature in reactor. It can be seen that concentration of ammonia in the exhaust gas and in condensate is lower during the initial phase with high temperature. In later phase of process, the ammonia emission was higher due to the transformation of biodegradable organic N to ammonium [5].

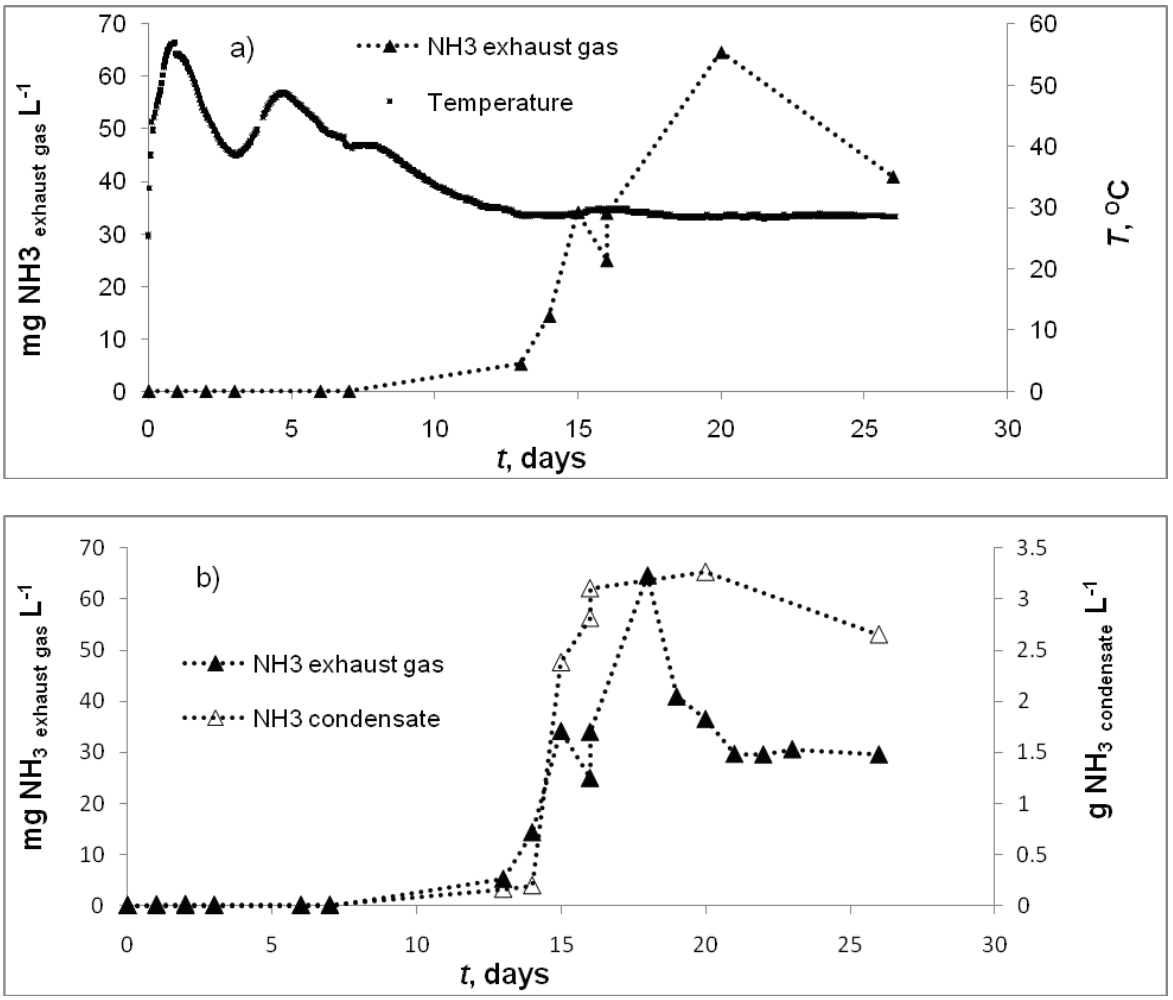


Figure 2. Presence of ammonia in condensate versus temperature (a) and correlation of evolution of ammonia in exhaust gases and in condensate (b) during 26 days of composting

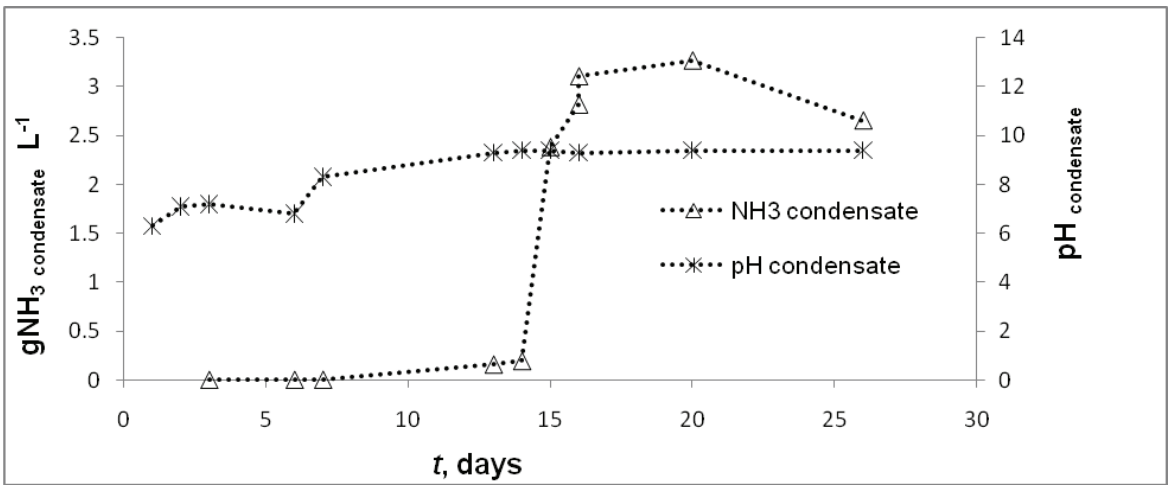


Figure 3. Evolution of ammonia in condensate and pH value of condensate during composting

From Figures 2 (b) and 3 it can be seen that on day 13 the concentration of ammonia in exhaust gas and in condensate increased with increasing of pH value of condensate. The increase of pH value during the composting process is due to the production of ammonium ions as a result of the ammonification process [12]. At day twenty, the emission of ammonia was still high. Apparently, the emission of NH_3

was influenced by pH condition of composting mass and its moisture content, microbial activity and continued aeration [13].

During the composting process, the pH value of condensate increased from an initial pH of 6.3 to 7.2 in the first 3 days and after 10 days to pH=9. Changes in pH value of condensate over reaction time corresponded well with variations in concentration of ammonia in condensate evolved from the biodegradation of the organic nitrogenous compounds [14]. These results correspond well with the general theory that variations in pH value are in relation with ammonia-ammonium equilibrium in the compost mixture. Furthermore, the pH value (pH = 9) of compost and condensate increased no more, but maintained in the same alkaline range during the subsequent period (Figure 3).

2.2.2.2. Evolution of Carbon Dioxide

The dynamics of CO_2 release in the compost reactor is highly influenced by the temperature regime. Equation (1) and (2) describe the production of CO_2, and equation (3) the absorption of CO_2 in the hydroxide solution [15].

$$C_5H_{19}O_3N + 12.5O_2 \rightarrow 10CO_2 + NH_3 + 8H_2O \quad (1)$$

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O \quad (2)$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad (3)$$

Figure 4 shows that emission of carbon dioxide is proportional with temperature and high microbial activity during the first 6 days. CO_2 evolved in the exhaust gases peaked at the same time. Thus, the emission rate of CO_2 during first two days was around 30.0 g CO_2 kg_{VT0}^{-1} and reached maximum value at day 6 with amount of 55.0 g CO_2 kg_{VT0}^{-1}.

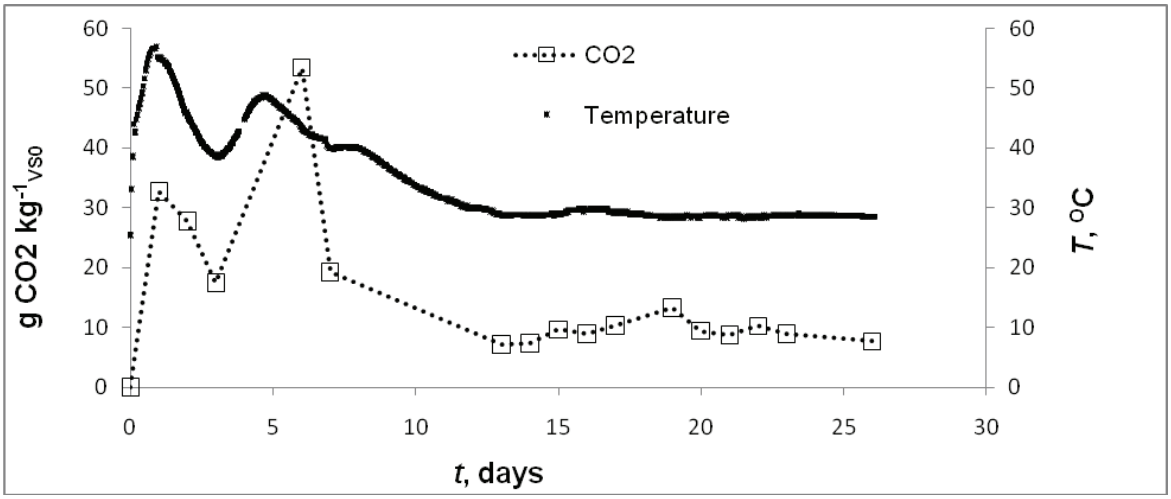


Figure 4 The evolution of carbon dioxide versus temperature during the composting of tobacco waste

Because of the intense biodegradation of organic fraction of waste between the second and the sixth day the temperature and evolution of CO_2 increased. The variation of CO_2 concentration during that period is in correlation with bacterial activity and with reaction temperature (Figures 1 and 4). After 10 days, the concentration of carbon dioxide became lower and until the end of process remained between 8.0 and10.0 g CO_2 kg_{VS0}^{-1}.

2.2.3. C/N Ratio and Conversion of Substrate during Composting of Tobacco Waste

The C/N ratio has frequently been used to describe the course of organic waste degradation and it is widely accepted that a high substrate C/N ratio implies a low mineralization rate due to N deficiency [16]. The initial carbon and nitrogen ratio is the most important index of compost quality. Based on the nutritional requirements of the microbes that are active in composting, C/N ratio of the organic matter should be in the order of 20-25 parts carbon to 1 part nitrogen; a declination from this ratio leads to slow composting process [1].

The initial C/N ratio of tobacco waste was 21 and it was gradually decreasing with increasing of conversion of volatile solids, expressed as degradation of organic matter in waste solid (Figure 5). The most intense degradation is evident in the first 13 days, i.e. in the first half of the composting process.

The nitrogen as ammonium ions remained in composting mass until the day 15 when the volatilization of ammonium ions start (Figure 3). At the end of composting the conversion of substrate was 45%, C/N ratio was 10 and the compost as a product possessed a satisfactory agronomic value.

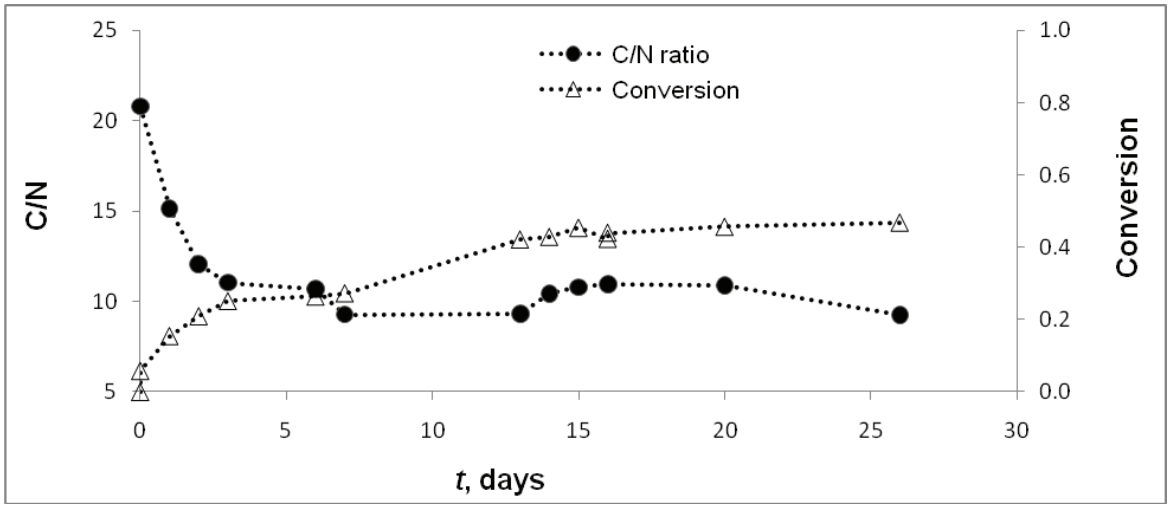


Figure 5 C/N ratio versus conversion of tobacco waste during 26 days of composting

3. CONCLUSIONS

During 26 days of composting of tobacco waste in a closed reactor the following has been recorded. Initial pH value of compost substrate was 6.5 and initial C/N ratio 21 and at the end of composting process was 9 and 10 respectively.

From the second to fifth day temperature oscillated between 56°C and 50°C, due to delayed microbial growth in lower portions of tobacco waste. At different stages of composting noticed were a change in the number and type of microorganisms.

The C/N ratio, pH value and temperature influenced on ammonia emissions. At the beginning of process the concentration of volatile ammonia was low and then was increased with increasing of pH value (pH = 9) of composting mass. The total concentration of ammonia in condensate was 2.972 g kg_{VS0}^{-1} after 26 days.

The most of carbon dioxide evolved during the first 6 days of composting process due to the highest activity of microorganisms. The cumulative evolved CO_2 during 26 days of composting was 302.0 g CO_2 kg_{VS0}^{-1}.

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REFERENCES

[1] N. Saithep, S. Dheeranupatana, P. Sumrit, S. Jeerat, S. Boonchalearmkit, J. Wongsanoon and C. Jatisatienr, Composting of tobacco plant waste by manual turning and forced aeration system, Journal of Science and Technology 02 (2009) 248-260.

[2] N. Saithep, S. Dheeranupatana, P. Sumrit, S. Jeerat, S. Boonchalearmkit, J. Wongsanoon and C. Jatisatienr, Composting of tobacco plant waste by manual turning and forced aeration system, Journal of Science and Technology 02 (2009) 248-260.

[3] T.-J. Hu, G.-M. Zeng, D.-L. Huang, H.-Y. Yu, X.-Y. Jiang, F. Dai, G.-H. Huang, Use of potassium dihydrogen phosphate and sawdust as adsorbents of ammonical nitrogen in aerobic composting process, Journal of Hazardous Materials 141 (2007) 736-744.

[4] E. Pagans, X. Font, A. Sanchez, Biofiltration for ammonia removal from composting exhaust gases, Chemical Engineering Journal 113 (2005) 105-110.

[5] E. Pagans, R. Barrena, X. Font, A. Sanchez, Ammonia emissions from the composting of different organic wastes. Dependency on process temperature, Chemosphere 62, (2006) 1534-1542.
[6] Institute, Austrian Standardization, Austrian Standard S 2023, Analytical methods and quality control for waste compost, Vienna 1986.
[7] T. Osada, K. Kuroda, M. Yonaga, Determination of nitrous oxide, methane, and ammonia emissions from a swine waste composting process, J Mater Cycles Waste Manag. 2 (2000) 51-56.
[8] S. Duraković, S, Opća mikrobiologija, Zagreb, Zagreb 1996
[9] A.D. Neklyudov, G.N. Fedotov, A.N. Ivankin, Aerobic Processing of Organic Waste into Compost, Biochemistry and Microbiology 42 (2006) 341-353.
[10] Y. Liang, J.J. Leonard, J.J.R. Feddes, W.B. Mcgill, Influence of carbon and buffer amendment on ammonia volatilization in composting, Bioresource Technology 97 (2003) 748-761.
[11] F. Briški, Z. Gomzi, A. Hublin and M. Vuković, Aerobno kompostiranje otpadaka voća i povrća: modeliranje procesa, Kemija u industriji 52 (2003) 95-102.
[12] B. Beck-Friis, S. Smars, H. Jonsson; H. Kirchmann, Gaseous Emissions of Carbon Dioxide, Ammonia and Nitrous Oxide from Organic Household Waste in a Compost Reactor under Different Temperature Regimes, J. agric. Engng Res. 78 (2001) 423-430.
[13] Y.-K. Jeong, S.-J. Hwang, Optimum doses of Mg and P salts for precipitating ammonia into struvite crystals in aerobic composting, Bioresource Technology 96 (2005) 1-6.
[14] S.-H. Kwon, D.-H. Lee, Evaluation of Korean food waste composting with fed-batch operations II: using properties of exhaust gas condensate, Process Biochemistry 39(2004) 1047-1055.
[15] T. Haug, Roger, The Practical Handbook of Compost Engineering, Chapter 9, Lewis Publishers, United States of America 1993, pp. 326-327.
[16] M.P. Bernal, C. Paredes, M.A. Sanchez-Monedero, J. Cegarra, Maturity and stability parameters of composts prepared with a wide range of organic wastes, Bioresource Technology 63 (1998) 91-99.

ANALYSIS OF MONITORING AIR QUALITY AND POLLUTANT EMISSION GENERATED BY ROAD TRAFFIC IN THE CITY OF ZAGREB

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Abstract

The greatest impact on air pollution in the city of Zagreb has road vehicles which are mostly responsible for air contamination. Shown in percentages the number are: NO_X – 35%, CO – 44%, SO_X – 7%, Pb – 38%, NMVOC - 16%, suspended particles -30%, according to data of Central Bureau of Statistics for the year 2007. Until the year 2010 in Zagreb there were 12 measuring sights installed, of which six as a part of city network. The measurements show that the quality of air is third category it comes to PM_{10} on one measuring sight, second category when it comes to NO_2 and ozone on three measuring sights, PM_{10} on four measuring sights. In relation to the other harmful components the quality of air is first category, which means that the measured values are under recommended values, the air is clean or slightly contaminated, so we can conclude that the air quality has considerably improved in comparison to the '60-s, the '70-s, '80-s and even the '90-s. Especially big problems are intersections because they were not built for the large amount of traffic as there is today and traffic lights control is not yet traffic-oriented. Some of the suggestions for the decreasing emission of harmful components in exhaust gases emissions in Zagreb are: reconstruction of road network (emphasis on intersections), introduction of traffic oriented control, exploitation of ITS for conduction and better organization of transport stimulation of "clean" cars import, fuel quality improvement etc.

Keywords: *air pollution, intersection, monitoring of air pollution*

1. INTRODUCTION

The total number of registered road motor vehicles in Croatia in the year 2008 was 2.021.936, out of which 20.5% were registered in the city of Zagreb [1]. Due to unfavorable engine operating conditions, relatively low driving speeds (below 80km/h), poor quality of fuel, and high numerical presence of motor vehicles, road motor vehicles represent the primary air polluters in the city of Zagreb. Air quality in Croatia has been monitored since the 1960s when also the West-European countries started to deal with the same issues. Since that time the air quality has been continuously improved in the populated areas where in the past the concentrations of sulfur (IV) oxide and fumes were even three times as high as today. In the Republic of Croatia, based on the Air Quality Act, air quality measurements are performed by the State Network for Continuous Air Quality Monitoring using the local networks. The structure of the measuring network for monitoring of air pollution in a certain urban area is a dynamic process which is changed, harmonized and improved depending on the new scientific knowledge [2]. In the city of Zagreb six urban and three state measuring stations have been installed, as well as four measuring stations for special purposes. In the last decade, there has been a substantial increase in the number of vehicles in the city of Zagreb, by more than 60%. Generally, the traffic in the region of the city of Zagreb participates with high share in the total emission of carbon (IV) oxide (CO_2), carbon (II) oxide (CO), nitrogen oxides (NOx), sulfur (IV) oxides (SO_2), volatile organic substances (NMVOC) and particulates. There is an especially high level of nitrogen oxides and NMVOC compounds which interact and cause the creation of ground-level ozone, which is especially expressed during the summer season [3].

High influence on the reduction of air pollution is by EKO-test which started to be applied for petrol vehicles on 18 April 2001, and for Diesel vehicles in 2002, as well as the fact that since 2005 the use of leaded fuel has been banned [4,5]. The reduction of polluting substance emissions from road vehicles includes the control of the quantity of emissions from vehicles and traffic control measures, which requires unity of the action policy at local and national levels. The traffic system of the city of Zagreb can be optimized even without constructing new traffic routes, by introducing intelligent traffic control, with the possibility of organizational change at intersections, and by establishing a secondary system for the control and management, which was shown also by the computer simulation. In this way it is possible to achieve energy and ecological efficiency, that is, reduction of HC, CO, VOC, and NOx by 50% [6].

The paper will present an overview and analysis of the condition of studying exhaust gases generated by road vehicles in the city of Zagreb, as well as the proposals of measures for their reduction.

2. ELABORATION

2.1. Regulations and Testing of Exhaust Gases in the City of Zagreb

Croatia is in the pre-accession procedure for full EU membership, which means that the development of legal regulations in Croatia will be based on the transfer of EU acquis communautaire in all areas, including the area of environmental protection, which means also the area of air quality. Therefore, over the last years, an entire series of acts have been brought that need to be implemented and which is, according to past experiences of the transition states, a complex organizational, technical and financial process. The basic documents that define the air quality policy in the Republic of Croatia include:

- Environmental protection strategy with National Plan of acting on the environment,
- Environment protection act,
- Air protection act.

These documents regulate the bringing of a series of bylaws which, among other things, determine: the method of assessing air quality, the method of monitoring air quality, the limit values of airborne pollutants, requirements for technical appliances and fuel, control of implementation, requirements for the quality of data and measurements. The international agreements were accepted and confirmed by the Republic of Croatia and integrated into the legal system, which regulates the area of environmental protection and air quality monitoring, also stipulate systemic monitoring and exchange of data on air quality condition, especially regarding the assessment of cross-border distance transfer of pollution as well as the assessment of the impact on other parts of the environment. By coming into force of the Regulations on modifications and amendments of the Regulations on technical inspections of vehicles in the Republic of Croatia on 18 April 2001 as part of regular technical inspection the exhaust gases on petrol engines started to be tested, and on 28 April 2002 the tests started to be applied to Diesel engine vehicles. The EKO-test is performed during the regular technical inspection and it is a condition that has to be fulfilled for a vehicle to be considered roadworthy at a technical inspection station. One of the reasons why road vehicles are primary air polluters in the city is also partial failure at the EKO-test of 4.25% since Zagreb citizens perform 37% of their trips by passenger cars [7]. The reason for worry is also the growing trend in the number of passenger cars, and the reduction in the volume of public urban transport, and relative old age of vehicles. Thus, the number of passenger vehicles per 1,000 citizens increased from 233 in 1981 to 517.9 vehicles per 1,000 citizens in 2008 [1]. Because of air quality monitoring the cities with more than 40,000 citizens, including the city of Zagreb, have the obligation of constantly monitoring the concentrations of pollutants significant for the air pollution sources of the region, and to compare the measured concentrations with the values that serve for air quality assessment. In Zagreb this is dealt with by the Institute for Medical Research that performs measurements at 13 measuring stations in the wider region of the city, out of which six are urban, and three state stations, and four measuring stations for special purposes. In order to harmonize the measuring network for air pollution monitoring in Zagreb, one measuring station each has been located in the city centre, and in its northern, eastern, southern and two in the western part, which is a total of six measuring stations. Regarding the level of air pollution, the regions, including the area of the City of Zagreb, can be classified into three categories: (i) Category I - pure or slightly polluted air; (ii) Category II – moderately polluted air; and (iii) Category III- excessively polluted air.

Analyzing air pollution in Zagreb from 2001 to 2009, one can come to the conclusion that the biggest problem of pollution is from nitrogen oxides, airborne particulates and ground-level ozone, which means that air in relation to these pollution parameters was of Category II, i.e. moderately polluted. The tolerant values have been exceeded, for the third year in a row, for PM parameter, so that the air in the western part of the city was of Category III i.e. excessively polluted. In the area of the city of Zagreb the data on emissions into the air from industrial plants, energy plants, energy heating plants and thermal power plants have been collected, and the data have been entered into the Air Emission Cadastre (KEO) which is an element of the Cadastre of Environmental Emissions. The emissions of the main pollutants (CO, NMOC, NOx, SOx and PM) generated by road transport have been evaluated, i.e. calculated by using the EMEP/CORINAIR methodology which is implemented for the EU countries. For the calculation needs COPERT III method has been used (Road Transport Emission Factors Calculator). The assessment of the main pollutant emissions from the traffic sector of the city of Zagreb is presented in Table 1 [8].

Table 1. Orientation assessment of emissions from the traffic sector of the city of Zagreb

Parameters of pollution	Quantity of emission (t)
CO	7890
NO_X	2474
NMVOC	2217
PM	276,2
CO_2	641193
SO_2	426

This refers to the orientation assessment performed on the basis of the number of registered vehicles. The assumption was used that an average vehicle in the urban area travels about 5000 km annually. With the data on the vehicle emission factors, the final assessment of pollution from mobile emission sources was found. The table shows that in the city the emissions are mostly from carbon (IV) oxides.

Table 2. Summary presentation of pollutant emissions (t per year) for the city of Zagreb

Emission from sources/ Pollutant	TE-TO EL-TO	Non energy sources	Process technology	Heating, steam, hot water	Households and institutions	Transport	Total
CO	482.97	2.54	13.74	25.11	-	7890.00	8414.36
CO_2	1192343.60	1441.21	89215.45	221564.01	-	641193.00	2145757.27
SO_2	4086.66	9.32	22.81	309.78	3612.00	426.00	8466.57
NO_X	1119.00	0.48	95.89	613.93	1051.00	2474.00	5354.30
Overall particles	44.15	13.73	44.06	45.91	1375.00	276.20	1799.00

In the emissions the traffic accounts for about 30%, heating plants, preparation of warm water and other, for about 11%, energy sources with a bit more than 0.5% etc. An increasing use of passenger vehicles has become the dominant problem regarding air quality in the city area. Regardless of this referring to newer generation of vehicles with reduced emissions and vehicles that use higher quality fuels, the increase is continuing and causing an increase in the total emissions especially in the peak traffic and on congested traffic routes. Table 2 presents a summary of the emissions for the city of Zagreb for the period from 2001 to 2009 [9].

2.2. Road Traffic as Source of Air Pollution in the City of Zagreb

In the city of Zagreb the highest impact on air pollution is from road vehicles due to unfavorable conditions of engine operation, relatively low driving speed, insufficient fuel quality and large number of vehicles, because of the high percentage of defective vehicles (in 2008 there were 21.4% defective vehicles in a total of 1775354 inspected vehicles according to data of the Croatian Centre for Vehicles).

Table 3. Emissions of pollutants from road traffic in Croatia from 2000 to 2007 in % in relation to overall emission [1]

Road transport	CO%	SO_2%	NO_X%	NMVOC%	Particles TSP%	Particles PM2.5%	Particles PM10%
2000	45.3	8.9	43.6	23.9	-	-	-
2003	41.9	9.1	39.4	25	18.6	-	7
2004	40	12.1	40	20.7	19.4	-	7.3
2005	45.6	12.1	36.9	17.4	5.8	30	7.6
2006	42.5	13.2	36.4	16.1	5.8	33	7.7
2007	44	7.4	34.5	15.8	22.9	32.7	30

Table 4. Emissions of heavy metals from road traffic from 2000 to 2007 in % in relation to overall emission [1]

Road transport	Pb	Cu	Zn
2000	92.9	-	-
2003	78.8	78.4	82.3
2004	70.6	82	84.2
2005	53.43	81.8	81.73
2006	38.36	81.98	81.36
2007	38.56	82.12	82.37

The number of registered vehicles in 2008 was 414,353 in Zagreb. In Croatia the total number of road vehicles from 1999 to 2008 increased by 53%, whereas the number of passenger cars increased by 4-5% [7]. Although the share of passenger cars in the total number of vehicles is decreasing, it is still at the high 76%, which is why it represents the main problem from the aspect of air pollution by exhaust gases. Table 3 presents the emissions of pollutants generated by road traffic in Croatia in a seven-year period in percentages compared to the total emission, and Table 4 shows emissions of heavy metals in the same period [1]. What can be seen is that the respective period marked a significant decline in lead and its compounds from 92.9% in 2000 to 38.56% in 2007. However, in the same period there was a significant increase in the emission of particulates because of the increase in the number of Diesel vehicles. Since in the overall number of registered vehicles in the Republic of Croatia the city of Zagreb accounts for about 20% i.e. one fifth, it may be concluded that road vehicles are the largest source of air pollution especially by carbon (II) oxide, nitrogen oxides, particulates and metals in the overall sedimentary substance. In the situation of such high increase in the number of motor vehicles such as the one in Zagreb, there comes inevitably to significant difficulties in the traffic system flow, particularly in the historical centre whose streets, primarily constructed for pedestrians, fail to withstand this pressure, and a lot is said by the data from the European Green Paper about the urban traffic that due to traffic congestions and diseases caused by exhaust gases from traffic, almost 100 billion euro i.e. 1% GDP are lost annually [6]. The regulation and organization of traffic flows in road traffic network of the city of Zagreb, which, except for the smaller rail system, accepts all transport means, is extremely unfavorable. Because of the restrictive regulation, numerous unnecessary bans and obligations, i.e. unfavorably directed street network, the intersection capacities have been reduced by more than 20%. This reflects negatively both on the expenditures and on environmental pollution. The total quantity of pollutant emissions from road traffic are significantly affected by the traffic density, i.e. vehicle flow at intersections. With the increase in the number of vehicles the traffic network of the city of Zagreb is characterised by the increase in the queuing time at traffic lights, which increases also both fuel consumption and emissions. Table 5 shows the values of pollutants obtained on the basis of air pollution measurement in Zagreb in 1990s. Although the values of pollutants have significantly decreased, the relations have not changed significantly. With the increase in the traffic density the amount of emissions increases linearly.

Table 5. Values of airborne pollutants in relation to traffic density [7]

Concentration (mg m^{-3})				
Roads with density traffic			Roads wit dullness	
Pollutant	Medium value	Maximum value	Medium value	Maximum value
CO	28	70	1	5
Pb	0.008	0.037	0.0005	0.0015
NO_2	0.1	0.23	0.025	0.032
SO_2	0.16	0.7	0.018	0.032
dim	0.644	1.235	0.245	0.251

In Zagreb in autumn 2002 from 24 to 29 October a seven-day pilot measurement of air pollution levels at seven city intersections was carried out [10]. The measurement included intersections in the strict city centre as well as open intersections at the entries into the city centre. The traffic count provided data on the number of vehicles, vehicle structures and traffic congestions at intersections and the surrounding traffic routes. The application of the Trafficware-Synchro 4 software, Traffic Signal Coordination Software, was used to make the computer image of the current condition of traffic routes and intersections and traffic flows, where the software processed the actual traffic situations in the current moment without trying to influence it by means of software parameters. In this way the image of the fuel consumption and the image of exhaust gas emissions (NOx, CO and VOC) are obtained. Table 6. shows the values obtained in this way as the basic situation.

Using the example of this intersection we can see that the grade separation of the intersection achieves the effects of greater throughput capacity of the intersection, better connection of the intersections in the network, which results in lower congestion at the intersection, smaller waiting queues for left turns, and consequently also lower emission of harmful substances. By considering the network of surrounding traffic routes and intersections we can see that some intersections, which until the leveling had no congestions, now start to receive greater flow of vehicles that may result in congestions i.e. shifting of the congestion to the adjacent intersections. The Traffic-SimTraffic, Traffic Signal Simulation Software, have been used to make computer-controlled simulation of the traffic situation in the duration of 10 minutes, and new values of the mentioned parameters are presented in Table 6 as improved situation. The data were processed according to the following criteria:

- all the current traffic flows have been kept according to values and directions;
- the directions, number and size of traffic lanes at intersections have been kept;
- the same traffic light cycle has been kept;
- all other infrastructure factors have been kept;
- detector coordinated automatic signal-safety devices control has been introduced into the traffic light operation, automatic traffic flow management has been regulated by means of intersection passing speed.

Table 6. Energy and ecological efficiency at the Slavonska avenija - Radnička cesta - Heinzlova ulica intersection [10]

Intersection Slavonska avenija - Radnička cesta - Heinzlova ulica		
Indicators:	Basic situation	Improved situation
Total period of travelling (hours)	153	91
Total travelled transit (km)	2611	2611
Average speed (km h^{-1})	17	29
Consumption of fuel (liter)	889	483
Efficiency of fuel consumption (km lit^{-1})	29	54
Emission CO (g)	16530	8990
Emission NO_X (g)	3190	1730
Emission VOC (g)	3810	2070
Stopping of vehicle (total all/one average)	6095/1.01	3853/0.64
Indicators for simulation of 10 min		
Total travelled time (hour)	40	38.8
Total travelled transit (km)	765.3	771.1
Average speed (km h^{-1})	20	21
Consumption of fuel (liter)	305.8	250.6
Efficiency of fuel consumption (km lit^{-1})	2.5	3.1
Emission CO (g)	9960	6133
Emission NO_X (g)	725	503
Emission VOC (g)	203	154
Stopping of vehicle	1569	1327

2.3. Results Obtained by Computer Simulation

Under the title of basic situation and improved situation, the data about the emission of harmful substances, about the fuel consumption, fuel consumption efficiency, lost time necessary to pass an intersection, speed and volume of traffic flows, etc. have changed. In the computer processing the software uses data and calculation methods which have been applied and verified by the US organization "Federal Highway Administration Research" and the data processing procedure under the title "CORSIM". Table 6 shows the essential indicators for energy efficiency and environmental protection, through their reduction or increase. Computer simulation indicates significant possible reductions in environmental pollution (lower emissions) from road traffic by using telematic systems to control traffic as well as improved throughput capacity of traffic flows, even without their reconstruction. The analysed Slavonska avenija - Radnička cesta - Heinzlova ulica intersection was grade separated in 2006, and the seven-day measurement was repeated after the reconstruction from 24 to 29 October. Figs. 1. and 2. show the levels of concentrations of NO2 and PM10 before and after the reconstruction.

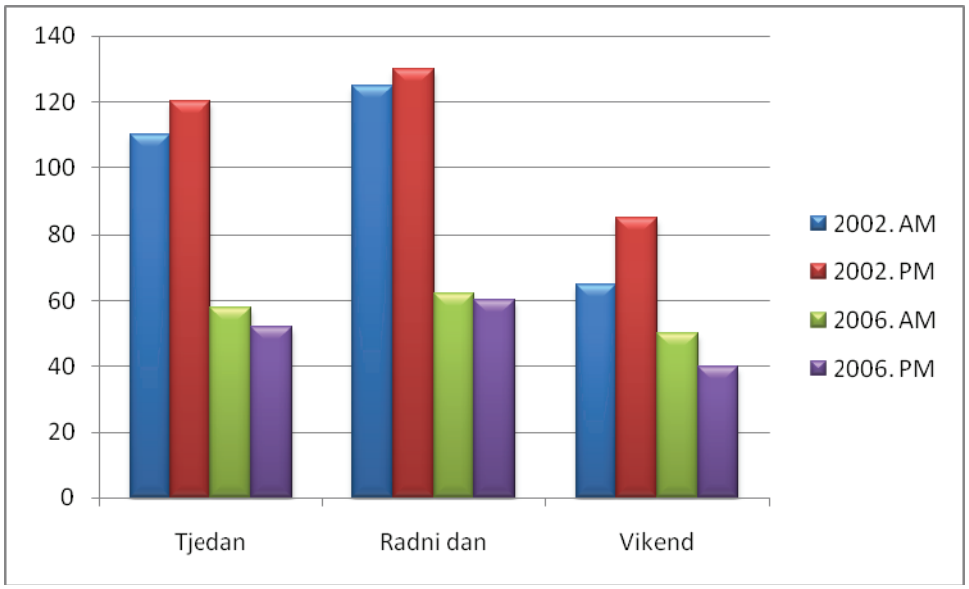


Figure 1. Levels of concentration of NO_2 at Slavonska avenija - Radnička cesta - Heinzlova ulica intersection during the measuring periods in 2002 and 2006 [11]

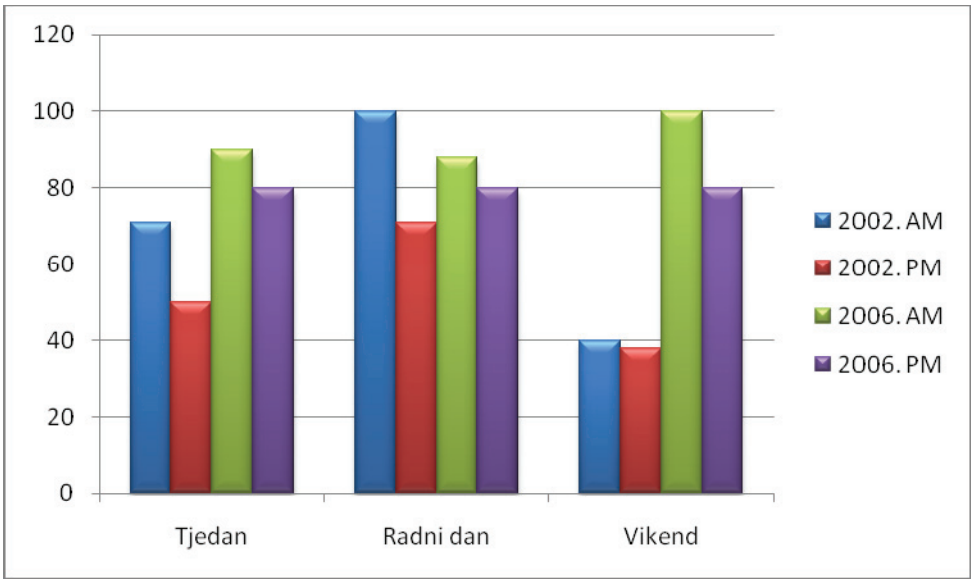


Figure 2. Levels of concentration of PM10 at Slavonska avenija - Radnička cesta - Heinzlova ulica intersection during the measuring periods in 2002 and 2006 [11]

During the seven-day measurement in 2002, higher values of NO_2 concentrations were recorded in comparison to concentrations from 2006. Lower NO_2 concentrations after the construction of the

overpass in spite of the assumed traffic density indicate the justification of constructing the overpass. Its construction has prevented the formation of long queues of vehicles at traffic lights. Also, the year 2002 marked higher values of concentrations during the morning hours as consequence of accumulation of pollution during the formation of long queues. This effect was marked during 2006 because of the construction of the overpass and higher traffic throughput capacity. For the reduction of exhaust gases emissions at intersections it is of primary importance to increase the throughput capacity, thus avoiding the delay of vehicles and increasing the speed of passing through the intersection.

The given examples show that this can be achieved in two ways: by reconstruction and adaptive traffic light management. A partial solution (only reconstruction or only a new telematic system) would not give the desired results.

3. CONCLUSIONS

The starting position of the sustainable traffic of the city of Zagreb is the proven fact that the needs for traffic connection within the city as well as with its region cannot be satisfied by the passenger car, but rather primarily by high-quality public urban transport. High-quality solutions in Zagreb and the region can be achieved by systemic investment into synchronized development of the current systems of public transport: urban-suburban rail, tram, and bus, as well as gradual development of light urban rail of an under- and above ground rail system.

The most threatened parts of the city are the industrial zones and traffic nodes. Whereas air pollution in the industrial zone has no major relations to road traffic, at traffic nodes road traffic is the main cause of pollution.

By analyzing the air pollution in the city of Zagreb from 2001 to 2009, it may be concluded that in the city the biggest problem was the pollution by nitrogen oxides, airborne particulates and ozone (ground-level ozone), which means that the air in relation to these parameters of pollution was of category II, that is, moderately polluted. The tolerant values were exceeded for PM10 parameter, so that the air in the western part of the city was of category III, that is, excessively polluted.

The traffic system of the city of Zagreb can be optimized without constructing new traffic routes, but rather by introducing intelligent transport management, with possible organizational changes at intersections, and by establishing the accompanying supervision and control system which has been shown also by the computer simulation. Reduction of HC, CO, NO_x and VOC even up to 50% can be seen at the analyzed intersection.

In order to monitor and analyze the influence of road traffic on air pollution in the future as well, it is necessary to undertake the following measures:

- It is recommended to introduce new measuring parameters at the stations of local measuring network, which are used to monitor closely the imission concentrations of air pollution. At the current measuring stations of the local network (where this is not the case) it is recommended to upgrade the measuring system by introducing measurements of PM 2.5 particulates and BTX (benzene) parameters in compliance with the Regulations on the limit values of pollutants in the air. In this way the influence of the pollution parameters on air quality and health of people will be additionally monitored.
- Introduce target, periodical monitoring of pollutants from traffic at measuring stations of special purposes. Because of the excessive air pollution by PM10 particulates in the western part of the city, and moderate pollution by ozone, nitrogen oxides and particulates at the majority of the measuring stations of local network, it is recommended to introduce prefabricated measuring stations of small dimensions which would allow correct determination of imission of pollutants generated by traffic. The data obtained in this way form the basis for the evaluation and improvement of measures against traffic pollution. Taking into consideration the distribution of the current measuring stations, both government and local ones, and the assessment of the busiest routes and intersections with the frequent occurrence of traffic jams, it is recommended to introduce a subsystem of measuring stations, including the measurements in the city centre. The plan is to move three such measuring stations at certain time intervals (1-3 years) to extremely busy traffic routes. The planned measuring parameters are the particulates, benzene (BTX), nitrogen oxides, sulfur (IV) oxides, hydrogen sulfide and ozone.
- Enable data transfer with all local automatic measuring stations to the central unit with adequate information system for transfer and processing of results in order to combine the measuring data and for constant supervision of air quality condition in Zagreb.

REFERENCES

[1] N. Štrumberger, Onečiščivanje zraka u ovisnosti o protoku vozila, Ceste i mostovi 38 (1992) 305-308.
[2] I. Bernard, Usporedba zagrebačkog prometnog sustava s prometnim sustavima evropskih gradova. Zelena akcija, Zagreb, 2008.
[3] J. Blašković Zavada, J. Zavada, N. Štrumberger, Trendovi naknadne obrade ispušnih plinova dieselovih motora, Suvremeni promet 25 (2005) 351-355.
[4] ECOINA: Program zaštite i poboljšanja kakvoće zraka u Gradu Zagrebu, Zagreb, 2008
[5] www.dzs.hr
[6] N. Štrumberger, T. Kljak: Utjecaj tehnologije inteligentnih transportnih sustava na zaštitu okoliša u prometu, Suvremeni promet, 22 (2002) 72-76.
[7] M. Jednaček, Parametri kvalitete goriva i njihovi učinci na ponašanje goriva u primjeni, Goriva i maziva, 48 (2009) 121-130.
[8] S. Bešlić, Z. Zenzerović, Statističke metode analize utjecaja prometa na okoliš. Suvremeni promet 22 (2002) 395-401.
[9] J. Golubić, V. Kolar, Ekološki aspekti optimizacije prometa na raskrižjima u Gradu Zagrebu. Znanstveni skup: Prometna problematika grada Zagreba. Zagreb, 2006.
[10] I. Bešlić, K. Šega, Onečišćenje zraka dušikovim dioksidom i lebdećim česticama na nadvožnjaku Slavonske avenije i Radničke ceste u Zagrebu. Znanstveni stručni skup Tehnologije zaštite zraka, Tuheljske toplice, 2008.
[11] www.zagreb.hr

PHOTOCATALYTIC TREATMENT OF AIR: HOW TO DEAL WITH THE PROBLEM OF TIO_2 DEACTIVATION

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Abstract

In this study photocatalytic oxidation of toluene, used as model VOCs in the gas phase on different types of Ti-based catalytic materials was investigated. The objective of this work was to find out additional information regarding activity and stability of catalyst during photocatalytic treatment of the polluted air. Two designs of the photoreactor were used: classical type of an annular reactor and annular reactor with recirculation. All measurements were performed at room temperature, atmospheric pressure and at constant initial toluene concentration, relative humidity and total flow rate of the reaction mixture. Some experiments were carried out with catalysts thermally treated on different temperatures (350-450 °C). It was found out that thermal treatment of deactivated photocatalyst at higher temperature is efficient method of TiO_2 reactivation. According to results presented in this paper problem of catalyst deactivation can be partially solved by using annular reactor with recirculation of one part of reaction mixture entering the reactor.

Keywords: *annular photocatalytic reactor, deactivation, reactivation, TiO_2, toluene oxidation*

1. INTRODUCTION

Heterogeneous photocatalysis has been intensely studied over the past decade, mostly in connection with the treatment of wastewater and air purification and its potential application in medicine and energy conversion [1-11]. Fujishima and Honda [12] were the first to describe the photocatalytic process, which related to electrolysis of water in a photoelectrochemical electrode with the use of TiO_2 as a photocatalyst. However, the examples of commercial application of photocatalysis and their application in real systems are still insignificant compared to the interest this topic arouses among the scientists. Up to date research scientists have been focused mostly on photocatalysis of water and much less of gas phase and air protection [12]. However, over past few years the interest has rapidly changed what is best shown by the fact that there are currently over 120 patents based on photocatalytic air purification [4].

One of the greatest challenges in the design and operation of any catalytic process is the prevention of catalyst degradation. Although catalyst deactivation is inevitable for most processes, the rate of decay can be minimized through understanding and control of the deactivation process, i.e. through control of catalyst properties, process variables (temperature, concentration, flow rate, etc.), feedstock impurities and methods of reactants and catalyst contact [13].

In our previous work [14], we focused on the photocatalytic oxidation (PCO) of toluene in the gas phase over UV-illuminated thin layer of titanium dioxide. An attempt was made to investigate dependence of the reaction rate on various operating variables (such as water content, inlet toluene concentration and gas flow rate). Like other researchers who have dealt with similar reaction system [15-19] we noticed the existence of the catalyst deactivation. The purpose of the present work was to find out additional information regarding: (i) causes of TiO_2 deactivation, (ii) methods of catalyst reactivation or avoiding of catalyst deactivation and (iii) design considerations to prevent or minimize effect of catalyst deactivation. Several catalysts based on titanium were prepared and their photocatalytic activity was compared in particular with that of commercially purchased Degussa P-25 TiO_2.

2. ELABORATION

2.1. Experimental

2.1.1. Photocatalyst Preparation

Four samples of Ti-based materials were used to prepare photocatalytic layer. The characteristics of the catalytic samples and the code used for indicating them throughout the text are summarized in Table 1. The photocatalyst labeled TP1 was prepared using the commercial TiO_2 powder supplied by *Degussa*, now *Evonik* (Aeroxide P-25). According to manufacturer data approximately 70 % of P-25 has the anatase crystal structure and the remainder the rutile structure. TP2 was commercial Millenium PC 500 provided by *Crystal* and its crystal structure was primarily based on anatase (> 99 %).

TA1 sample was home-made TiO_2 (100 % of anatase) prepared by the sol–gel method: an appropriate amount of tetrabutyl titanate was slowly dissolved into ethanol, then a mixture of dilute aqueous solution of nitric acid and ethanol was added to the above solution under stirring conditions. The reaction mixture had the following molar composition: Ti^{4+}: H_2O: $H^+(HNO_3)$: C_2H_5OH = 1: 4: 0.015: 12. The solution was strongly stirred until the gels were formed and then placed at room temperature for 10-15 h, followed by being washed with deionized water, then filtered and dried at 80 °C. Thus obtained samples were calcined in air at 300 °C for 2h.

The parent SBA15 support was prepared by the method of Zhao et al. [20] by means of neutral triblock copolymer surfactants. Titanium was grafted by post-synthesis [21]. The photocatalyst was labeled TS1.

The Ti-based catalytic layer was coated on the inner wall of the outer tube of the annular reactor using homogeneous suspensions (1g Ti-based material/100 ml isopropanol) of certain powder materials. Modified spin coating process was used for preparation of very thin layers of the photocatalyst.

Table 1. The properties of the photocatalyst employed in this work

Photocatalyst sample	Composition	Manufacturer
TP1	TiO_2 P-25 (70 % anatase + 30 % rutile)	*Degussa (*now *Evonik)*
TP2	TiO_2 PC 500 (> 99 % anatase)	*Crystal*
TA1	TiO_2 (ca. 100 % anatase)	home made
TS1	Ti-SBA-15	home made

2.1.2. Annular Photocatalytic Reactor System Set-Up

The photocatalytic oxidation of toluene was performed in an annular photoreactor equipped with an 8 W fluorescent black light blue lamp (*Sylvania*, UVA light at 315-400 nm). High purity synthetic air (20.5% O_2 in N_2, *Messer*) was used as oxidant. The photoreactor feed stream resulted from mixing a dry air in a saturation flask containing distilled water at 20 ˚C and a dry air stream with toluene (*Aldrich)* at the specified flow rates of the gas carrier through the saturators. Flow rates were regulated using the mass flow controllers (*Cole Palmer*). The secondary air flow was introduced into the mainstream in order to dilute the reaction mixture and to obtain the desired concentration of the reactant at the reactor inlet. The reaction gas mixture flowed between the reactor's inner and outer tube. The inner tube was made of quartz glass because of its transparency for UV light. Two configurations of photoreactor were used: classical type of an annular photocatalytic reactor (designed to be run in a single-pass) and annular reactor with recirculation. All measurements were carried out at the initial concentration of toluene of $2.68 \cdot 10^{-3}$ g dm^{-3}, relative humidity (RH) of 50 %, and at total flow rate of reaction mixture of $40 \cdot 10^{-3}$ dm^3 min^{-1}. The membrane peristaltic pump was applied to circulate a particular amount of the fluid containing a reactant to the reactor entrance. Experiments were performed in the range of the recirculation flow rate, v_R from 0.5 to 2.5 dm^3 min^{-1}. The rates of the photocatalytic oxidation of toluene were based on the difference in toluene concentration before and after UV illumination at the steady-state conditions.

2.1.3. TiO_2 Reactivation

Reactivation of TiO_2 (P25) photocatalyst was achieved by thermal treatment in the air atmosphere. Thermal treatment was carried out in a furnace *Nabertherm* L5/11/B180 at different temperatures (350, 400 and 450 °C). The temperature was increased slowly up to desired temperature and then keeping the catalyst at this temperature for 2 hours.

2.4. Analytical methods

Toluene concentrations were measured on-line by gas chromatograph (*Shimadzu* GC-2014) equipped with a flame ionization detector. The measurement system included highly purified nitrogen as carrier gas and *Carbowax 20M* column (length 3m, i.d. 2 mm). Analysis was performed using a program package *Shimadzu GCSolution*®. The operating conditions of the GC were as follows: column temperature of 120 °C, detector temperature of 250 °C. Additionally, a high performance liquid chromatograph (*Shimadzu Prominence*) equipped with UV/Vis detector (λ= 210 nm) was used to analyze the intermediate products over deactivated TiO_2 catalyst. Small amount of deactivated catalyst (0.02 g) was suspended in methanol for several hours to extract adsorbed organic compounds and the resulting solution was examined with HPLC using *Waters Spherisorb ODS2* column (length 15 m, i.d. 0.46 mm). Instrument calibration was performed using standard solutions of benzaldehyde and benzoic acid (5 mM) or their equimolar solution (0.1 mM).

2.2. Results and Discussion

Deactivation of the photocatalyst is among the most severe practical problems, and its importance is reflected by the large number of papers claiming to solve it [4,15,16,19,22]. Different approaches are reported in the literature, but usually they are related to various post treatment of undesired by-products formed under reaction conditions, of which the following are important to mention: thermal treatment at elevated temperatures (> 400 °C) [23], photocatalytic treatment using simultaneous UV illumination and exposure to humidified air [15,24], ozone purging in the presence of water vapor [25], washing with alkaline solutions [26], etc. Another approach to eliminating or moderating deactivation is through modifications of catalyst composition and/or process or process conditions.

In this work different catalysts are used with purpose to investigate their photocatalytic activity and stability during photocatalytic oxidation of toluene, used as model volatile organic compound (VOC). The laboratory photoreactor used in the first set of experiments was an annular reactor designed to run in a single-pass mode. Dependence of toluene conversion on time of UV illumination for all catalyst is presented in Fig. 1.

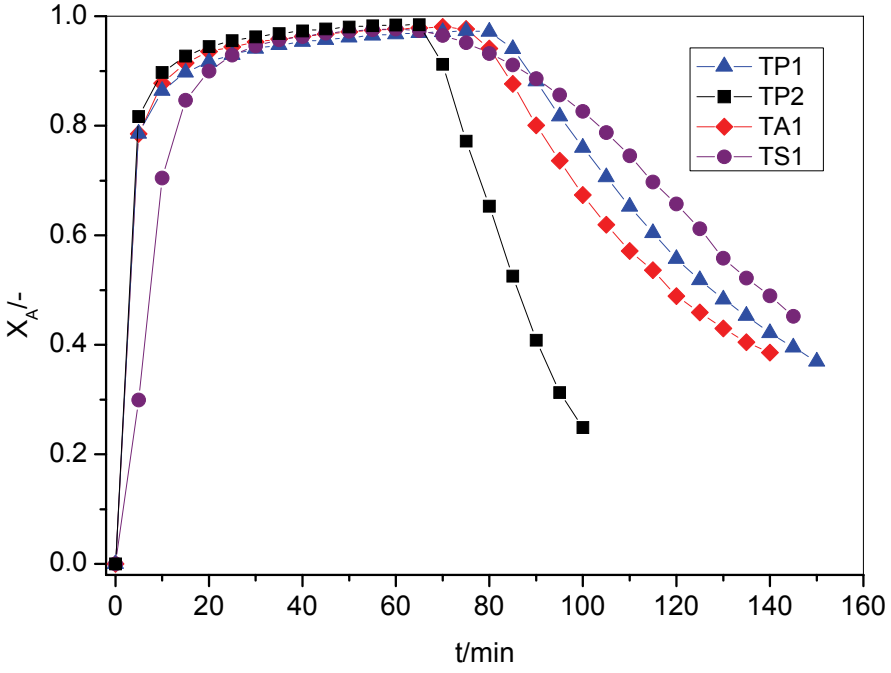


Figure 1. Conversion *vs.* exposure time to UV lamp for different PCO catalysts (annular reactor without recirculation)

The results indicate that the shape of curves is very similar regardless of photocatalyst applied. Surprisingly, the Ti-SBA-15 showed even better results than the TiO_2 P-25, especially at longer exposure time of photocatalyst to UV illumination. Generally, three characteristic periods can be observed on the curves. The first period can be considered as a period of initiation. During this period toluene conversion rapidly increases and reaches a maximum value, which indicated that the process is nonstationary. The

most likely explanation of such behavior is a time-dependent increase in photocatalyst activity, which can be attributed to the formation of hydroxyl radicals. As can be seen this period is very short and lasts for about 10 min, depending on the reaction conditions. This is followed by a period of constant toluene conversion or constant activity of photocatalyst (maximum conversion was cca. 0.98), after which conversion starts to decrease with illumination time, indicating deactivation of the photocatalyst. It may be noted that the home-made photocatalyst, designed as TA1 shows greater stability (slower decrease of activity) compared to commercial TP2, regardless of the almost identical chemical composition (both were in almost anatase form). Obviously, the stability of the photocatalyst is affected by the method of its preparation. Reason for more stable TS1 photocatalyst is not clear, however its higher stability probably can be correlated with the possibility of competitive adsorption of water and toluene molecules and subsequent desorption of photooxidation products from the surface of the catalyst.

In our previous work [14] deactivation of the photocatalyst was observed. FTIR experiments performed over deactivated catalyst have confirmed the presence of benzaldehyde and benzoic acid adsorbed on the surface of the TiO_2, which led to the blocking of the active sites. In this study additional experiment are conducted to confirm these results. Results of HPLC analysis, as shown in Fig. 2, once more confirmed adsorption of benzoic acid on deactivated TiO_2 catalyst.

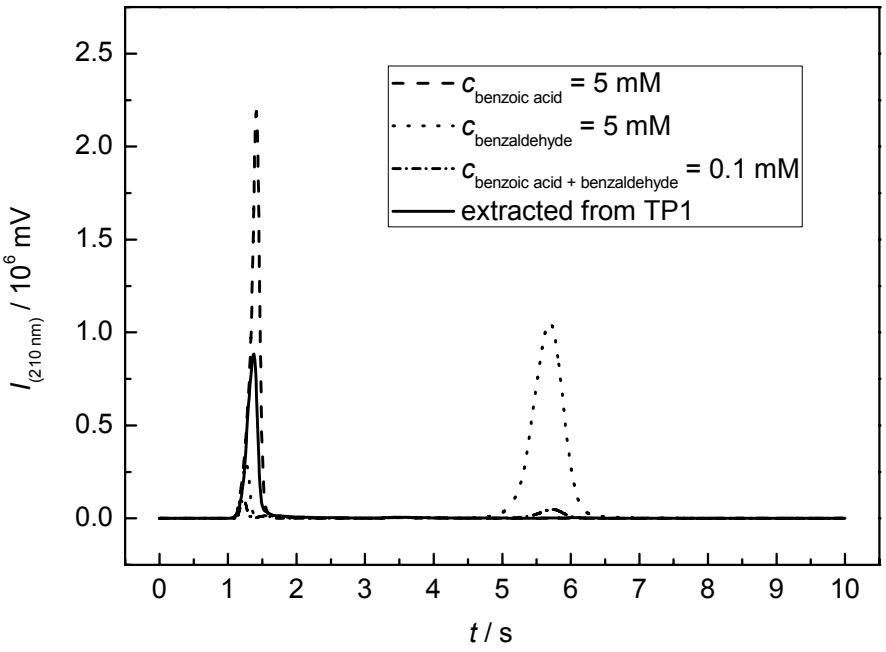


Figure 2. Identification of the adsorbed surface species responsible for the deactivation of the photocatalyst.

Next task was to find an appropriate way of catalyst's reactivation. First of all, it is necessary to draw attention to a common mistake regarding use of the terms „reactivation“ and „regeneration“ in a number of papers that may be encountered in the literature. As a rule, a catalyst is reactivated when the reactivated catalyst is less expensive than the fresh one, whereas the very reactivation process depends heavily on deactivation mechanism. On the other hand, catalyst regeneration is cost-efficient procedure only if catalysts are based on precious metals. Regeneration of metal catalysts usually includes their chemical decomposition, separation of metals from solution or concentration of metal salts.

The influence of thermal treatment on toluene conversion at different time of illumination is shown on Fig. 3. As can be seen, thermal treatment was found to be very efficient method, especially at temperature of 450 °C. It was also observed colour change of the catalyst during the reactivation, i.e. the catalyst has changed colour from light-yellow to white. It may be noted that heat pre-treatment leads to a slower decline of catalyst activity regardless of treatment temperature. Complete reactivation of the catalyst treated at 450 °C was in accordance with the thermal stability of the oxidation intermediates that block the active sites on the surface of catalyst. The temperature required for complete oxidation of benzaldehyde and benzoic acid is 360 and 420 °C, respectively [22]. Thus, reactivation of the catalyst required a temperature of 420 °C or slightly higher, as was the case in this work.

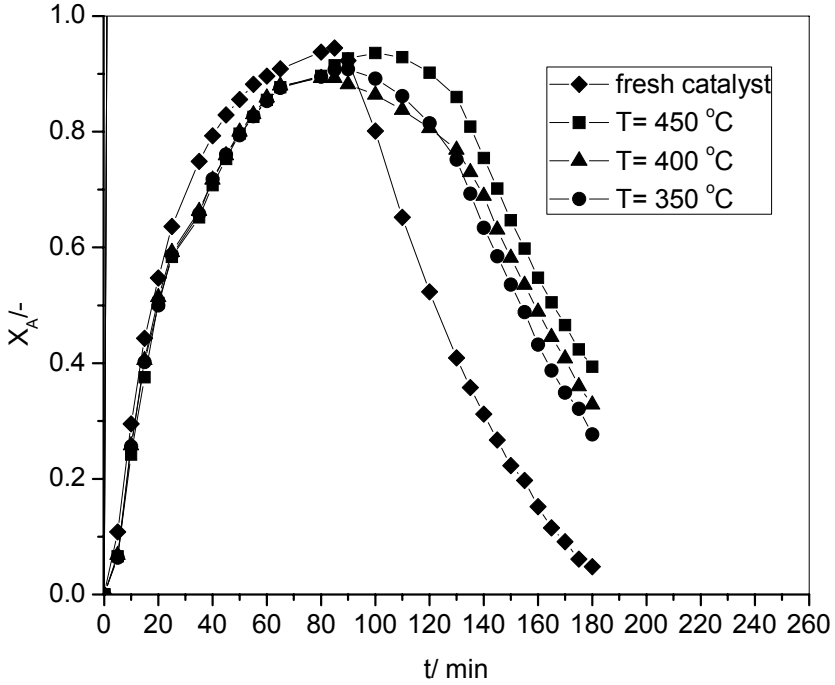


Figure 3. Influence of the thermal treatment on the photocatalyst activity and stability (TP1 catalyst).

Another approach to fight deactivation is by changing the flow mode inside the reactor. One way to achieve this is to use the annular reactor with mixing of reaction mixture accomplished by recirculation.

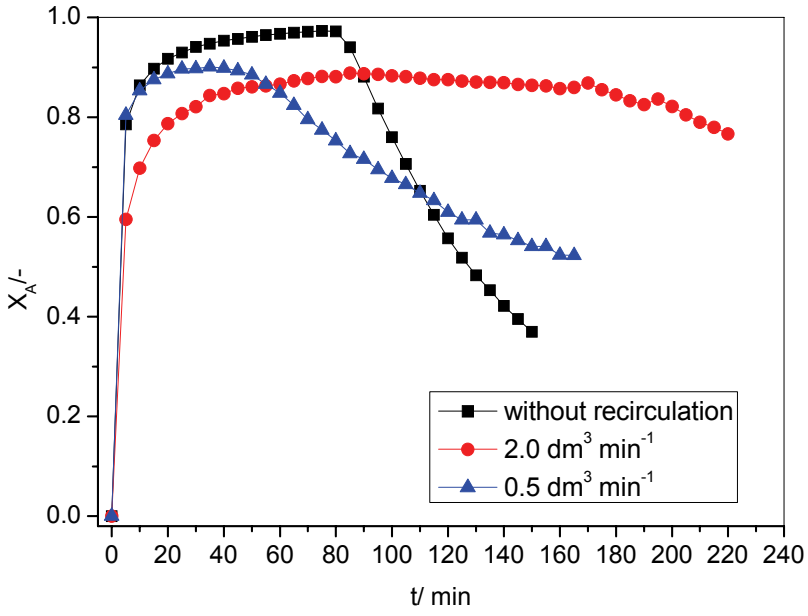


Figure 4. Conversion vs. exposure time to UV lamp for different recirculation flows (TP1 photocatalyst)

Comparison of results obtained using commercial TP1 photocatalyst located in classic type of annular reactor (without recirculation) and in an annular reactor at different recirculation flow rates is given in Fig. 4. Similar results were observed with the use of other photocatalysts (Fig. 5). Decreased conversion ascribed to catalyst deactivation was intense in reactor without recirculation because of much lower linear velocity of the reaction feed over catalyst surface. On the other hand, in reactor with recirculation the linear velocities were considerably higher so that accumulation of reaction intermediates was difficult. Obviously, photocatalytic properties were also affected by the recirculation flow rate.

The increase of the recirculation flow rate lead to decrease of the photoactivity in the series: TP1> TA1>TP2>TS1. Apparently, the stability of catalysts, i.e. resistance to deactivation was improved using the annular reactor under recirculation mode.

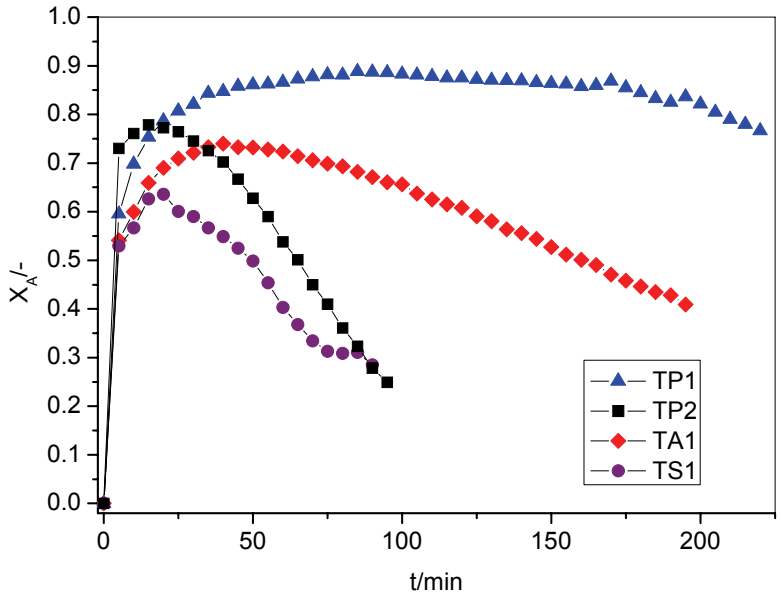


Figure 5. Conversion vs. exposure time to UV lamp for different catalysts (recirculation flow rate of 2 dm^3 min^{-1})

3. CONCLUSIONS

The photocatalytic oxidation of toluene over different type of Ti-based catalytic materials was carried out in the photocatalytic annular reactor operated in two different flow modes: classic type of annular reactor and annular reactor with recirculation. The analysis of the conversion *vs* illumination time curves showed that all catalysts have very high activity depending on the reaction conditions and catalysts used. Three characteristic periods were observed on time-conversion curves: i) the period of the initiation, ii) the period of constant activity and iii) the period of decreasing activity (catalyst deactivation). Decreasing activity of the catalyst was explained by the adsorption of benzoic acid as reaction intermediates on the active sites, which was confirmed by FT-IR and HPLC analysis of used (deactivated) catalyst. Thermal treatment of deactivated photocatalyst on the higher temperature was found to be an efficient method of catalyst reactivation. The catalytic activities of the Ti-based materials located in the classic type of annular reactor (without recirculation) were quite similar. The increase of the recirculation flow rate lead to slower decrease of the catalyst activity. Finally, the stability of photocatalysts, i.e. their resistance to deactivation can be improved using the annular reactor under recirculation mode.

Acknowledgements
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REFERENCES

[1] A. Mills, S. L. Hunt, An overview of semiconductor photocatalysis, J. Photochem. Photobiol. A: Chem. 108 (1997) 1-35.
[2] A. Mills, S.-K. Lee, A web-based overview of semiconductor photochemstry-based current commercial applications, J. Photochem. Photobiol. A: Chem.152 (2002) 233-247.
[3] Y. Paz, Composite titanium dioxide photocatalysts and the "adsorb & shuttle" approach: A review, Solid State Phenomena 162 (2010) 135-162.
[4] Y. Paz, Application of TiO_2 photocatalysis for air treatment: Patents'overview, Appl. Catal. B: Environ. (2010)
[5] G. B. Raupp, A. Alexiadis, M. M. Hossain, R. Changrani, First-principles modeling, scaling laws and design of structured photocatalytic oxidation reactors for air purification, Catal.Today 69 (2001) 41-49.
[6] J. Zhao, X. Yang, Photocatalytic oxidation for indoor air purification: a literature review, Building and Environ. 38 (2003) 645-654.

[7] M. R. Hoffman, S. T. Martin, W. Choi, D. W. Bahnemann, Enviromental applications of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69-96.
[8] H. Huang, W. Li, Destruction of toluene by ozone-enhanced photocatalysis: Performance and mechanism, Appl. Catal. B: Environ. 102 (2011) 449-453.
[9] I. Salvadó-Estivill, A. Brucato, G. Li Puma, Two-dimensional modeling of a flat-plate photocatalytic reactor for oxidation of indoor air pollutants, Ind. Eng. Chem. Res. 46 (2007) 7489-7496.
[10] I. Salvadó-Estivill, D.M. Hargreaves, G. Li Puma, Evaluation of the intrinsic photocatalytic oxidation kinetics of indoor air pollutants, Environ. Sci. Tech. 41 (2007) 2028-2035.
[11] N. Quici, M. L. Vera, H. Choi, G. Li Puma, D. D. Dionysiou, M. I. Litter, H. Destaillats, Effect of key parameters on the photocatalytic oxidation of toluene at low concentration in air under 254 + 185 nm UV irradiation, Appl. Catal. B: Environ. 95 (2010) 312-319.
[12] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 37 (1972)
[13] C.H. Bartholomew, R.J Farrauto, Fundamentals of Industrial Catalytic Processes, John Wiley & Sons, New Jersey, 2006.
[14] V. Tomašić, F. Jović, Z. Gomzi, Photocatalytic oxidation of toluene in the gas phase: Modelling an annular photocatalytic reactor, Catal. Today 137 (2008) 350-356.
[15] O. d'Hennezel, P. Pichat, D. F. Ollis, Benzene and toluene gas-phase photocatalysis degradation over H2O and HCL pretreated TiO_2: by products and mechanisms, J. Photochem. Photobiol. A: Chem.118 (1998) 197-204.
[16] R. Méndez-Román, N. Cardona-Martínez, Relationship between the formation of surface species and catalyst deactivation during the gas-phase photocatalytic oxidation of toluene, Catal. Today 40 (1998) 353-365.
[17] R-D. Sun, A. Nakajima, T. Watanabe, K. Hashimoto, Decomposition of gas-phase octamethyltrisiloxane on TiO_2 thin film photocatalysts-catalytic activity, deactivation, and regeneration, J. Photochem. Photobiol. A: Chem. 154 (2003) 203.-209.
[18] C. Xie, Z. Xu, Q. Yang, N. Li, D. Zhao, D. Wang, Y. Du, Comparative studies of heterogeneous photocatalytic oxidation of heptane and toluene on pure titania, titania–silica mixed oxides and sulfated titania, J. Mol. Catal. A: Chem. 217 (2004) 193-201.
[19] J. Jeong, K. Sekiguchi, W. Lee, K. Sakamoto, Photodegradation of gaseous volatile organic compounds (VOCs) using TiO_2 photoirradiated by an ozone-producing UV lamp: decomposition characteristics, identification of by-products and water-soluble organic intermediates, J. Photochem. Photobiol. A: Chem. 169 (2005) 279-287.
[20] D. Zhao, J. Freng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores, Science 279 (1998) 548-552.
[21] F. Chiker, J.P. Nogier, F. Launay and J.L. Bonardet, New Ti-SBA mesoporous solids functionnalized under gas phase conditions: characterisation and application to selective oxidation of alkenes, Appl. Catal. A 243 (2003), 309-321.
[22] L. Cao, Z. Gao, S.L. Suib, T.N. Obee, S.O. Hay, J.D. Freihaut, Photocatalytic oxidation of toluene on nanoscale TiO_2 catalysts: Studies of deactivation and regeneration, J. Catal. 196 (2000) 253-261.
[23] M.M. Ameen, G.B. Raup, Reversible catalyst deactivation in the photocatalytic oxidation of diluted *o*-xylene in air, J. Catal. 184(1999) 112-122.
[24] H. Einaga, T. Ibusuki, S. Futamura, Improvement of catalyst durability by deposition of Rh on TiO_2 in photooxidation of aromatic compounds, Environ. Sci. Tech. 38 (2004) 285-289.
[25] W. Wang, L.W. Chiang, Y. Ku, Decomposition of benzene in air streams by UV/TiO_2 process, J. Hazard Mater. 101 (2003) 133-146.
[26] R.D. Sun, A. Nakajima, T. Watanabe, K. Hashimoto, Decomposition of gas phase octamethyltrisiloxane on TiO_2 thin film photocatalysts-catalytic activity, deactivation, and regeneration, J. Photochem. Photobiol. A: Chem. 154 (2003) 203-209.

CO_2-FLUE GAS SEPARATION FOR A COAL FIRED POWER PLANT

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Abstract

CO_2 is one of the main pollutants for global warming and climate-change effect. In order to carry on power generation by fossil fuel, CCS technologies are required to reduce the environmental impact by CO_2 emissions. Currently, chemical absorption is the preferred option for CO_2 capture by post combustion.The detailed description of the CO_2 removal process using mono-ethylamine (MEA) as a solvent for coal-fired power plant is present in this paper. The model was implemented in Aspen Plus and possible chemical reactions are introduced using an electrolyte wizard. The rate based Electrolyte NRTL activity coefficient model was used in the Aspen Plus with 25[$^{w}/_{w}$] % MEA solution and 0.25[mol CO_2/mol MEA] as lean CO_2 loading. The removal efficiency was specified as a design specification option in Aspen Plus with the variation of Distillate rate in the stripper. With the help of sensitivity analysis, optimal parameters were selected for packed bed absorber and stripper column. The complete removal process with re-circulating solvent back to the absorber was implemented with the sequential modular method in Aspen Plus. The most significant cost related to CO_2 capture is the energy requirement for re-generating solvent, i.e. re-boiler duty. Parameters' effects on re-boiler duty were studied, resulting increased re-boiler duty with the packing height and absorber packing diameter, absorber pressure and solvent temperature. On the other hand, with the flue gas temperature, re-boiler duty is decreased. Re-circulating solvent with make-up stream was added to the system to get lowest possible energy demand. The re-boiler duty requirement on 85% of CO_2 removal was calculated as 4120 kJ/kg CO_2 after several iterations. The temperature profiles are used to check the model behaviour.
Keywords: *Carbon capture, Aspen Plus, Simulation, Re-boiler duty, Temperature profile*

1. INTRODUCTION

Due to the large number of fossil fuel based power plants, bulk amount of CO_2 is releasing to the atmosphere. In order to maintain the atmospheric green house gases, mitigation technologies have to be developed. Post combustion capture technologies are the best and widely used method for CO_2 recovery process. CO_2 capture by absorption and stripping process is currently considered as the most feasible option for CO_2 removal from fossil fuel fired power plants. The main drawback of this technology is energy consumption and the capital cost. Post combustion CO_2 capture technology with amine solvent is a reactive system. Hence, mass transfer of CO_2 from the bulk vapour to the liquid solvent and chemical reactions between amine and flue gas are the main two phenomena to be considered.

In the chemical absorption, flue gas enters the absorber at the bottom whilst the solvent enters at the top. The reactions start between MEA and CO_2 while flowing through the column (packing bed). An un-reacted gas leaves the column at the top, while the CO_2 rich solvent discharges at the bottom. The rich solvent goes through the heat exchanger to increase the temperature before sending it to the stripper section. The heated rich MEA stream then goes to the stripper at the top. In the stripper, steam is used for the regeneration process. Finally, separated acid gases leave the stripper at the top. The lean MEA then leaves the system at the bottom of the stripper and goes through the heat exchanger. The MEA and water are added to the lean MEA stream to balance the component before recycled back to the absorber unit.

The main problem with installing capture plant to the fossil fuel fired power industry is operating cost. Installation of capture plant causes to increase the electricity unit cost. The main point that requires considering operating cost is the energy requirement to run the carbon capture process. Therefore, it is necessary to perform research on this topic to reduce the operating cost and to improve the existing technologies to capture the high amount of CO_2. This paper primarily focuses on developing the model for gas treating plant of CO_2 from the coal-fired power plant flue gas and simulates the adaptable model to reduce the re-boiler duty.

2. ELABORATION

2.1. Model Implementation

A simulation of a 500MW coal fired power plant flue gas is considered. The flue gas composition and inlet conditions are extracted from the literatures [1]. The comprehensive flow sheet is developed in Aspen Plus for CO_2 removal with 85% efficiency. The suitable operating conditions are selected and sensitivity analysis is performed to check the validity of the parameters. A simplified flow sheet of the implemented model which employs CO_2 capture by absorption/stripping with an aqueous amine solution is shown in Figure 1.

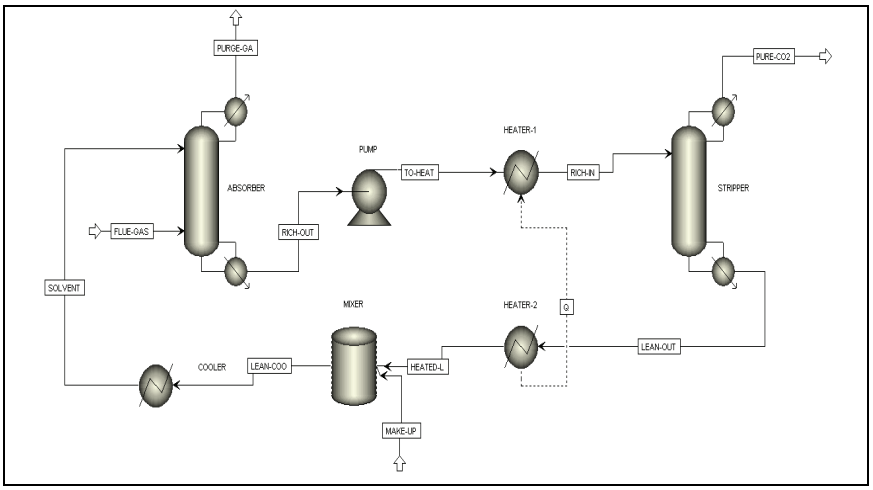


Figure 1: Process flow diagram

2.1.1. Operating conditions

The process flow diagram is developed to capture 85% of CO_2 from coal fired power plant flue gas. Absorber and stripper are the main two unit operation blocks in the capture process. Inlet flue gas and solvent stream are supplied at 313K and absorber is operating at 1bar absolute pressure. The rich solvent stream is heated up to 388K using a heat exchanger unit before sending it to stripper section for maximum performance. The stripper is operating at 1.9 bar absolute pressure and reflux ratio (fraction of the condensed is coming back to the stripper section) and distillate rate (flow rate of the PURE-CO_2 line) are used to implement the stripper unit. The inlet flue gas stream data are selected from Alie [1] and tabulated in Table 1.

Table 1: Flue gas stream conditions [1]

Parameter	Coal fired power plant flue gas	Composition	
		Major components	Value (mol %)
Flow Rate (kg/s)	673.4	H_2O	8.18
		N_2	72.86
Pressure (bar)	1.1	CO_2	13.58
		O_2	3.54
Temperature (K)	313	H_2S	0.05

The main component in the pure gas stream of the stripper is CO_2 and the rest of that is MEA and water. High temperature (393K) steam (produce in the re-boiler) is used to remove the CO_2 from the solvent. Steam is produced in the re-boiler and main energy requirement in the process is related to re-boiler duty. Therefore, the CO_2 capture model is implemented to reduce the re-boiler duty so that energy requirement can be minimized.

The operating conditions of absorber and stripper section are tabulated in Table 2. Due to several reasons Aspen Plus Rad-Frac model is selected for absorber and stripper:

- It is the active unit operation model for vapour- liquid absorption and stripping section.
- The simulation time is faster for Rad-Frac column in comparison with other available options.
- Fewer convergence problems compared to other available options in Aspen Plus.

Table 2: Absorber and stripper parameters selection

	Absorber	Stripper
Block type	Rad-Frac column	Rad-Frac column
Operating system	Rate based No Condenser and Re-boiler	Rate based Partial vapour condenser and
Number of stages	15	15
Feed stages	Flue gas in: 15 (from the top) MEA: 1	Rich IN: 2 (from the top)
Product stages	Purge gas: 1 Rich-MEA: 15	Pure CO_2: 1 Lean-MEA: 15
Packing type	PALL type metal	FLEXIPAC metal
Packing size	D:16m & H:22m	D:15M & H: 20m
Pressure	1bar	1.9 bar

Packed columns are used for the model development and the type of the packing is selected to get better operating conditions. The packing height, section diameter, packing factor and material are important factors and tabulated below (Table 2). The number of stages is selected to obtain high accuracy and feed, and product stages are decided on better physical phenomena with required output.

2.1.2. Property method selection

A property method is defined as a collection of property calculation routes. Each unit operation model requires property method to perform the calculation [2]. Mainly, four different property methods are available for CO_2+ MEA system:

- ELECNRTL - handle very low and high concentrations of aqueous and mixed solvent systems.
- ENTRL-HF- similar to the ELECNRTL property method except that it is uses the HF equation of state for vapor phase calculation model.
- ENTRL-HG - similar to the ELECNRTL property method except it uses the Helgeson model for standard property calculations.
- AMINES - this property method uses Kent-Eisenberg correlation for K-values and enthalpy calculation.

Out of them, the ELECNRTL model is selected for the simulation of the CO_2 capture process and electrolyte wizard is used to develop the simulation kinetics and reactions. The ELECNRTL is the most versatile electrolyte property method as it can handle very low and high concentrations of aqueous and mixed solvent systems. The solubility of gases can be modeled with Henry's law and required coefficients are available in databanks. For the calculation of vapor phase properties, the Redlich-Kwong equation of state is used.

2.1.3. Thermodynamic behaviour

The acid gases in the flue gas are weak acid electrolytes, and amines are weak organic base electrolytes. Combination of those two forms partially ionizes or partially dissociates aqueous solution in reacting system. The reacting system can be expressed as dissociation of components as below [3], equations (1)-(7).

Water: $2H_2O \leftrightarrow OH^- + H_3O^+$ (1)

Hydrogen sulfide: $H_2O + H_2S \leftrightarrow HS^- + H_3O^+$ (2)

Hydrogen bisulfide: $H_2O + HS^- \leftrightarrow S^{2-} + H_3O^+$ (3)

Carbon dioxide: $CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$ (4)

Bicarbonate: $HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$ (5)

Protonated alkanolamine: $MEAH^+ + H_2O \leftrightarrow MEA + H_3O^+$ (6)

Hydrolysis reaction: $MEACOO^- + H_2O \leftrightarrow MEA + HCO_3^-$ (7)

Equilibrium constants are required for each of the above equations to continue their vapour/liquid mole fraction calculations. It can be calculated by equation (8).

$$\ln K_j = A_j + \frac{B_j}{T} + C_j \ln T + D_j T \quad (8)$$

Equilibrium constant values are imported from the literature sources [4] and tabulated in Table 3.

Table 3. Constant values of equilibrium constant equations [4]

Parameter	Reaction 1	Reaction 2	Reaction 3	Reaction 4	Reaction 5	Reaction 6	Reaction 7
A_j	132.89	214.58	-9.74	231.46	216.05	-3.038	0.52
B_j	-13445.9	-12995.4	-8585.47	-12092.1	-12431.7	-7008.3	-2545.53
C_j	-22.47	-33.55	0	-36.78	-35.48	0	0
D_j	0	0	0	0	0	-0.00313	0

It is important to understand the kinetics of the reactions. The kinetic equations (9) and (10) and reverse reactions (11) and (12) are replacing rate model equations (4) and (7).

$CO_2 + OH^- \rightarrow HCO_3^-$ (9)

$MEA + CO_2 + H_2O \rightarrow MEACOO^- + H_3O^+$ (10)

$HCO_3^- \rightarrow CO_2 + OH^-$ (11)

$MEACOO^- + H_3O^+ \rightarrow MEA + CO_2 + H_2O$ (12)

The kinetic expression is defined in Aspen Plus and given below with constant values, equation (13).

$$r_j = k_j \left(\frac{T}{T_0}\right)^{n_j} \exp\left[-\frac{E_j}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (13)$$

Table 4 presents the constant values taken for the simulation in Aspen Plus for kinetic calculation. The given values are extracted from the Aspen Plus available databanks and checked with literatures to confirm the accuracy.

Table 4: Rate constant values

Parameter	Reaction 9	Reaction 10	Reaction 11	Reaction 12
k_j	4.32e+13	9.77e+10	2.38e+17	2.7963e+20
n_j	0	0	0	0
E_j (J/mol)	55433	41236	123222	72089
T_O (K)	298	298	298	298

2.1.4. Parameter selection

In the amine-H_2S-CO_2-H_2O system, where the amine is MEA and eight ionic species (OH^-, H_3O^+) and four molecular species (H_2O, H_2S, CO_2, MEA) are present in the liquid phase. Therefore, pure component parameters, binary parameters as well as electrolyte parameters have to be introduced in order to implement the process model. If any of the parameters are missing, it can be estimated with molecular structure, or using regression with experimental data. The Aspen Plus physical property system contains built in parameters for the electrolyte NRTL model. The databank contains energy parameters and other electrolyte parameters for molecular-electrolyte and electrolyte-electrolyte systems.

2.2. Results and Discussion

Sensitivity analysis is performed to understand the parameters' effect on re-boiler duty. Therefore, initially open loop model was developed for the simulation, and absorber packing height, diameter of the packing bed, absorber pressure, solvent and flue gas temperatures are varied to check the effect on re-boiler duty. Figure 2 (a-e) represents the re-boiler duty variation with listed parameters. In order to study the effect of one parameter on energy consumption in the re-boiler, other parameters of the absorber column are kept constant.

The re-boiler duty is decreasing with the increase of absorber packing height, packing diameter, absorber pressure and solvent temperature (Figure 2-a, b, c, d). The attained rich loading increased with the increase in the absorber packing height and packing diameter. Therefore, the re-boiler duty to process unit mass of CO_2 is reduced and the total energy requirement decreased. Similarly, re-boiler duty decreased with the increase of absorber pressure due to higher CO_2 removal efficiency with high absorber operating pressure. An analysis is carried out to examine the effect of solvent and flue gas temperature of the system (Figure 2-d and e). Re-boiler duty decreased with the increase of solvent temperature. Reverse is applicable to flue gas temperature effect. The re-boiler duty for those cases did not differ significantly. Hence, solvent and flue gas temperature does not have a significant effect on re-boiler duty.

The efficiency of the CO_2 removal (85%) is achieved with distillate rate variation in the stripper. However, before lean MEA stream recycled back to the absorber, rest of the 15% has to be removed from the system to get material balances. The CO_2 removal amount in the purge gas stream is calculated. That value is closer to 15% and some amount of CO_2 is circulating through the process. Therefore, an exact amount of 15% CO_2 can be corrected by adjusting open loop MEA inlet flow rate to the absorber. Amount of MEA and H_2O losses during the process are added to the make up stream to balance the system and lean MEA stream is recycled back to the absorber.

Finally, the closed-loop CO_2 removal process is considered for the re-boiler duty calculation and further analyzing. Re-boiler duty is calculated as 4120 kJ/kg CO_2 for the 85% CO_2 removal process for coal fired power plant. Compared with the literatures [5], re-boiler duty is approximately equal with literature values (4000 kJ/kg CO_2). Temperature profiles as well as CO_2 loading profile (Figure 3) are studied to understand the behaviour of the absorber process.

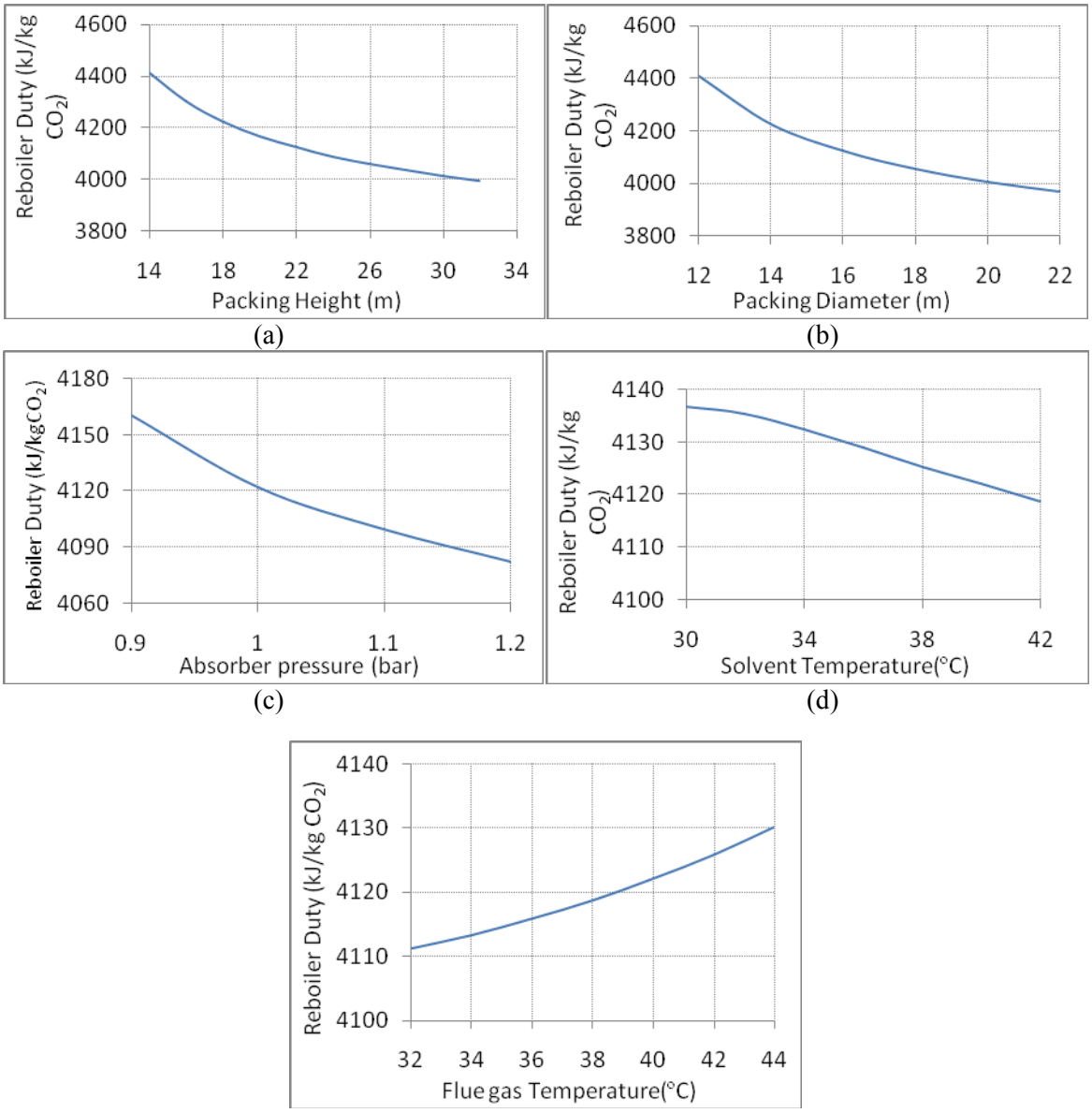


Figure 2. Re-boiler duty variation with parameters (a-e)

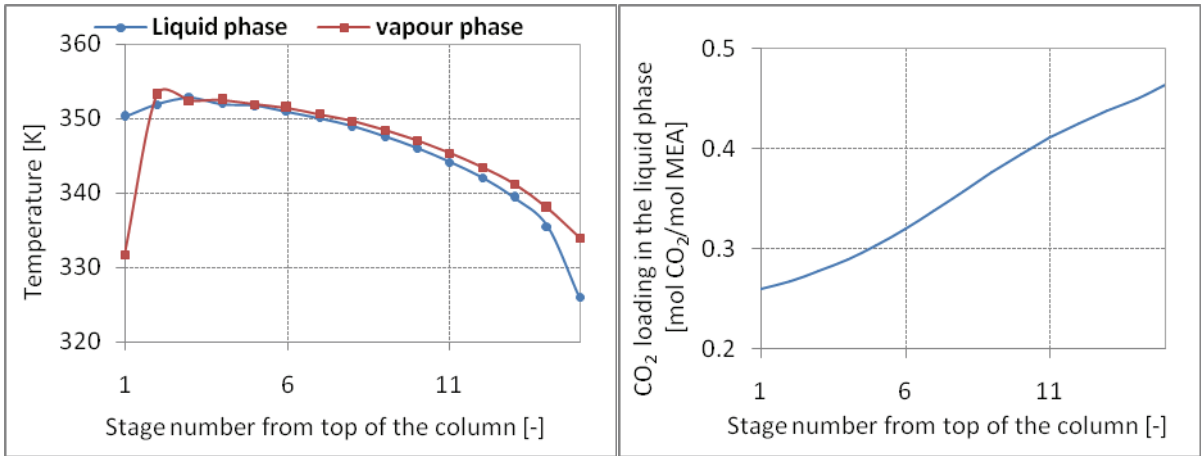


Figure 3: Temperature profiles and CO_2 loading profile in absorber

3. CONCLUSIONS

The implemented model is properly working and converging for coal fired flue gas system. Efficiency of the system is designed as 85% according to the industrial conditions. The stripper distillate rate was varied to achieve the specified efficiency. The MEA and water requirement for make up stream were calculated as 0.174 kg/s and 32.78 kg/s. In this case study coal power plant flue gas has been considered for CO_2 removal process. Model was implemented to achieve 85% CO_2 removal efficiency. Aspen Plus electrolyte NRTL property method was used to simulate the process.

The re-boiler duty depends on several factors. The sensitivity analysis was performed to check the parameters' effect on re-boiler duty. Re-boiler duty was decreasing with absorber packing height and packing diameter, absorber operating pressure and solvent temperature. Re-boiler duty was increased with the flue gas temperature. However, packing height and diameter as well as absorber pressure have significant effect on re-boiler duty. The re-boiler duty was calculated as 4120 kJ/kg CO_2 for the 85% CO_2 removal closed loop process for coal fired power plant. This can be reduced with further optimization steps. Temperature profiles as well as CO_2 loading were analyzed in absorber and stripper to study the model behaviour. The absorber tends to exhibit a temperature bulge at the top of the column for both liquid and vapour phase. Temperature bulge is due to highly exothermic reactions at the top of the column.

List of Symbols

CCS	carbon capture and sequestration
MEA	monoethanolamine
K_j	equilibrium constant for thermodynamic model
A, B, C, D	constants
T	temperature [K]
E_j	activation energy [J / mol]
R	gas constant [J / mol K]
k_j	rate coefficient
j	index

REFERENCES

[1] C.F. Alie, CO_2 Capture with MEA: Intergrating the Absorption Process and Steam Cycle of an Existing Coal-Fired Power Plant. Master Thesis, University of Waterloo, Canada, 2004.

[2] Aspen Technology, Inc Aspen Plus 2006 Documentation, Aspen Physical Property Methods, USA, 2006.

[3] A.D. Michael, A model of vapour-liquid equilibria for acid gas-alkanolamine-water systems. PhD Thesis, University of Texas, USA, 1989.

[4] S. Freguia, Modelling of CO_2 removal from Flue Gas with Mono-ethanolamine. Master Thesis, University of Texas, Austin, 2002.

[5] A. Kothandaraman, Carbon dioxide capture by Chemical Absorption: A Solvent Comparison Study. PhD Thesis, Massachusetts Institute of Technology, USA, 2010.

THE SYNTHESIS AND ITS CHARACTERISTICS OF MOLYBDENUM DOPED TiO_2 PHOTOCATALYST FOR DYE SENSITIZED SOLAR CELLS

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Abstract

Molybdenum ion-doped titanium dioxide (TiO_2) samples were prepared by wet ball milling. The samples were made of TiO_2 powder. The samples were characterized by XRD, XPS, UV-vis diffuse reflectance spectroscopy and FE-SEM. The photocatalytic activity of those catalysts was investigated by photocatalytic degradation of methanol and methyl orange under UV and visible light irradiation for the liquid phase. The catalyst doped with Molybdenum performs high properties for photodegradation purposes. It was found that the amount of doped Molybdenum ion plays significant role in affecting its photocatalytic activity and Molybdenum dopant with optimum content enhances photocatalytic activity under visible light.

Keywords: *Titanium dioxide, photocatalyst, ball milling method, molybdenum ion doping, visible light*

1. INTRODUCTION

TiO_2 is a semiconductor which turns to a high-energy state by receiving light energy, and releases electrons from its illuminated surface. We now that the necessary wavelength of irradiating spectrum is approx. 380 nm, which determines that the light needed to activate TiO_2 is ultraviolet light. We reduced binding energy for making visible light sensitive TiO_2. Doped TiO_2 can harvest visible light photons. Therefore we can improve efficiency of DSSC (Dye Sensitized Solar Cells). Transition metal doped anatase titanium dioxide (TiO_2) samples were prepared by wet mechanical alloying. Many researchers doped TiO_2 by transition metals [1], doping decreases band gap energy of TiO_2 for solving this problem. Metal particles on the surface of TiO_2 (Fig. 1.) leads to a reduced band gap and charge separation. TiO_2 not only shift the band gap to the visible, but improve the photocatalytic efficiency [2].

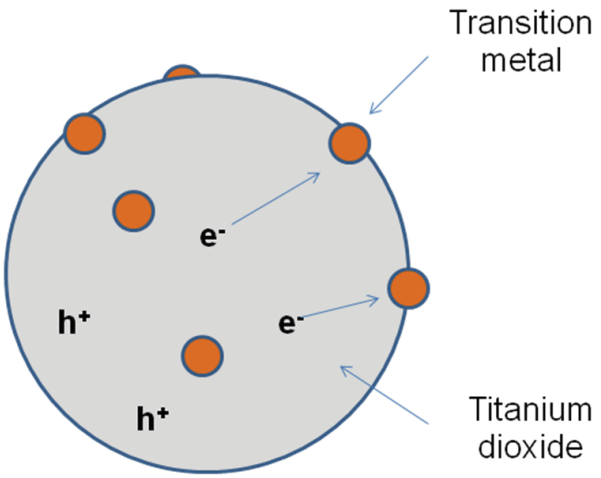


Figure 1. Inhibition of recombination mechanism

There are various methods for doping TiO_2 photocatalyst. Such as: hydrothermal hydrolysis, solvothermal method, impregnation and calcinations and mechanical alloying [3]. But most methods are difficult to use or expensive. Most of required and remained after fabrication chemicals are hazardous for environment. Wet ball milling synthesis method of Molybdenum-ion-doped TiO_2 [4] is very comfortable especially for industrial use. It is relatively non hazardous and environment amicable. Processed chemicals are recyclable. The photocatalytic activity depends on doping method, dopant metal, ion nature and its concentration. We developed various concentrations of dopant for different methods. This makes TiO_2 visible light reactive. Because of high photocatalytic activity enhanced TiO_2 can be used in dye synthesized solar cells.

In this paper, we reported the fabrication of TiO_2 powder doped with MoO3 with HCl. Titanium dioxide doped by MoO_3 with HCl performed high photocatalytic activity. The samples were characterized by X-Ray diffractometry (XRD), X-ray Photoelectron spectroscopy (XPS), UV-Vis diffuse reflectance spectroscopy. The photodegradation of Methylene orange (MO) (dye) was chosen as a probe reaction to measure the photocatalytic activity of different samples. Sample exhibited high photocatalytic activity under visible light. Therefore we decided to utilize it in Dye sensitisized solar cells. There is another advantage of doping by metal. When photocatalytic particles are allowed to carry transition metal, electrons are drawn to the transition metal. This inhibits the recombination of electrons and positive holes, thereby ensuring the stable formation for charge carriers more effectively than undoped TiO_2.

2. ELABORATION

2.1. Experimental Procedure

The Molybdenum ion doped TiO_2 was fabricated by wet ball milling method. The wet ball milling of TiO_2 was carried out in the ball mill produced by company Mirae Mechatronics Co. Required amount of DI water and HCl were mixed with MoO3. By hydrochloric acid PH was adjusted to 3.0 and was added Titanium dioxide (powder). The solution was ball milled with alumina balls in plastic bottle for 24 hours. The solution was rinsed with water several times in order to remove Cl^-. Afterwards, the resulted TiO_2 powder was dried in oven under air atmosphere and ground using agate mortar.

To make paste for DSSC TiO_2 [5] powder was mixed with acetic acid and Polyethylene glycol (PEG). All chemicals were analytical grade and were used without purification.

2.2. XRD Results

Anatase TiO_2 exhibits higher photocatalytic activity then rutile and brookite and amorphous. It can be seen that all TiO_2 samples are well-developed anatase structure. There are no peaks of Molybdenum oxide in sample. Because of Molybdenum amount is too small it cannot be determined by XRD. The XRD patterns of Mo-doped TiO_2 powder are showed in Fig. 2.

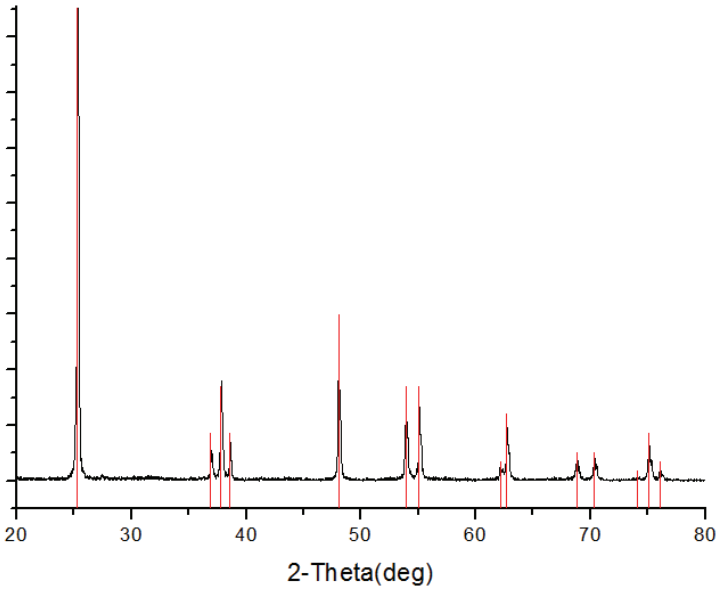


Figure 2. XRD pattern of Fe doped TiO_2 photocatalyst

2.3. UV Visible Diffuse Reflectance Spectra

The diffuse reflectance spectra for the molybdenum ion doped Titanium dioxide are shown in Fig. 3. We can observe higher intrinsic absorption and shift from UV spectra to higher wavelength. A higher absorption was performed for doped TiO_2. The color of undoped TiO_2 is white, but molybdenum ion doped is light blue. The higher absorption and such color were attributed to the existing of molybdenum on the surface of TiO_2 particles.

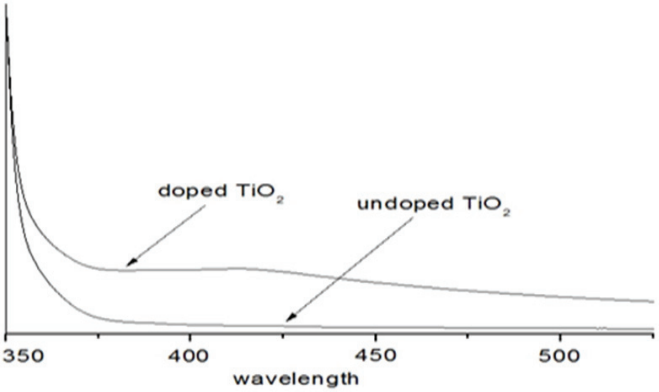


Figure 3. UV-vis reflectance spectra for Molybdenum doped TiO_2

2.4. X-ray Photoelectron Spectroscopy

The XPS spectra of Ti 2p and O 1s electrons of Mo doped TiO_2 powder are shown in Figs. 4(a), 4(b) and 4(c).

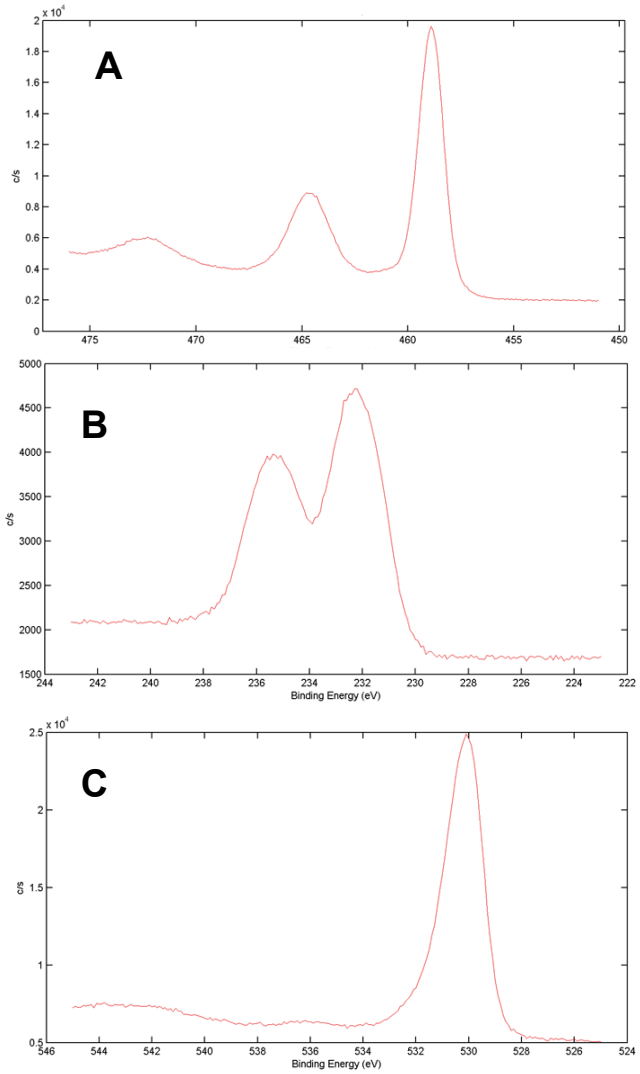


Figure 4. XPS spectra of Ti 2p (a), Mo 3d (b) and O 1s (c) electrons of Mo doped TiO_2 powder

The binding energy of Ti 2p at 458.42 eV shifting from 452 eV of metallic Ti, it means the signal of Ti in TiO_2 lattice, and that of O 1s at 531 eV is assigned to metallic oxide [6,7].

Table 1. XPS data

XPS binding energies (eV) of the elements present at the surface of TiO2 specimen			
Element	Ti(2p)	O(1s)	Mo(3d)
Binding energy	458.42 eV	534.00 eV	233.28 eV
amount at%	20.61	63.74	3.99

Table 1 summarizes the information about elemental composition and binding energies by XPS. The amounts of Molybdenum calculated from these XPS data are higher than the nominal one. The only reasonable tentative explanation is that in this sample an external surface molybdenum rich area has been formed [8].

2.5. EDX Analysis

EDX analysis of Mo doped TiO_2 powder was used to measure elements amount. XPS can observe only 5 nm deep into surface, but EDX can penetrate about 2A. As shown in Fig. 5. Molybdenum exists on the surface of TiO_2. Small contamination of residual Chlorine can be found also (Table 2). This is due to the not perfect rinsing of powder by water after doping. There are small contaminations such as Aluminum and Carbon due to alumina balls and plastic bottles used in experiment.

Table 2. EDX data

Element	Weight%	Atomic%
O K	46.57	70.26
Cl K	0.97	0.66
Ti K	39.35	19.83
Mo L	2.79	0.70

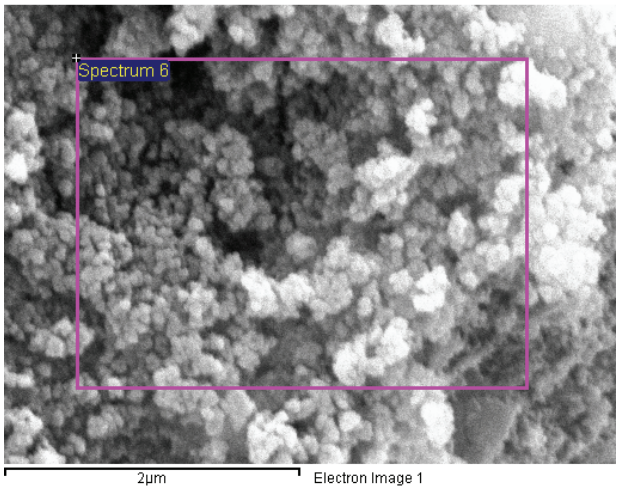


Figure 5. EDX survey image

2.6. Application to Dye Synthesized Solar Cell

Efficiency of DSSC solar cell fabricated using doped TiO_2 is higher than fabricated using undoped one (Table 3). Undoped sample demonstrated efficiency around 5.04%, but doped one showed 5.28% efficiency. 10% more efficient! Fill factor improved from 55.34% to 57.89%. This is due to the higher light absorption and lower recombination rate.

Table 3. Comparison between DSSC using doped and undoped TiO_2

	Undoped TiO_2 DSSC	Doped TiO_2 DSSC
Jsc (A m^{-2})	1.217×10^2	1.215×10^2
F.F(%)	55.34	57.89
Efficiency (%)	5.04	5.28

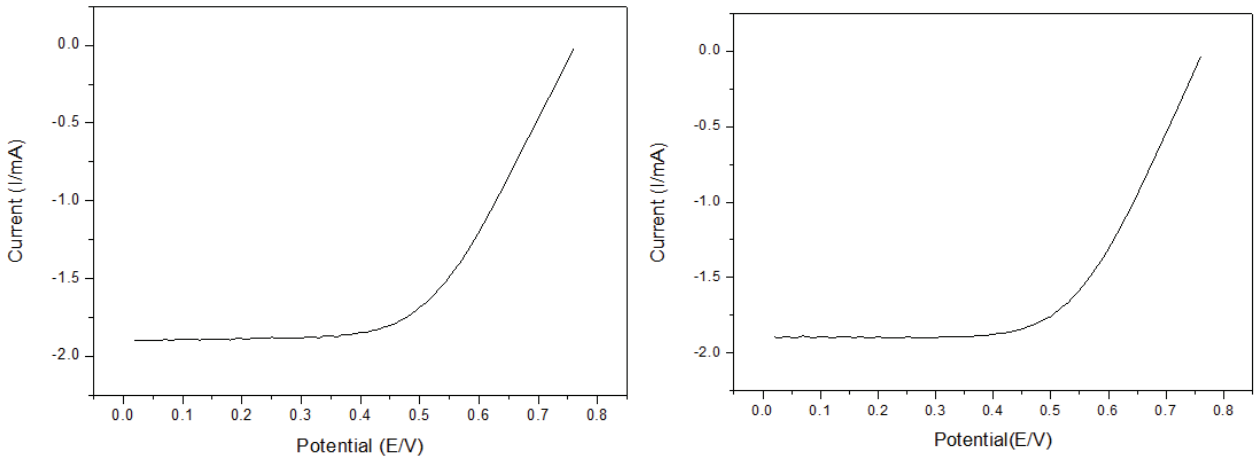


Figure 6. Comparison between DSSC using undoped and doped TiO_2

3. CONCLUSIONS

The paper investigated usage of Molybdenum doped TiO_2 for fabricating DSSC. Higher efficiency doped DSSCs were obtained. According to the experimental data reported in this review, it is possible to say that DSSCs fabricated using doped TiO_2 are more efficient than fabricated by undoped TiO_2. Wet ball milling method is simple and applicable for DSSC efficiency improvement. Process and used chemicals are relatively non hazardous, safe and recyclable. It is really important issue for environment.

REFERENCES

[1] J. Zhu, W. Zheng, B. He, J. Zhang, M. Anpo, Characterization of Fe-TiO_2 photocatalysts synthesized by hydrothermal method and their photocatalytic reactivity for photodegradation of XRG dye diluted in water, J. Mol. Catal. A: Chem. 216 (2004) 35-43.

[2] Michael Nolan, Electronic coupling in iron oxide-modified TiO2 leads to a reduced band gap and charge separation for visible light active photocatalysis, Phys. Chem. Chem. Phys., 2011, 13, 18194-18199.

[3] Z. Li, W. Shen, W. He, X. Zu, Effect of Fe-doped TiO_2 nanoparticle derived from modified hydrothermal process on the photocatalytic degradation performance on methylene blue, J. Hazard. Mater. 155 (2008) 590-594.

[4] F.-J. Zhang, W.-C. OH, Visible light photocatalytic properties of novel molybdenum treated carbon nanotube/titania composites, Bull. Mater. Sci., 34(3) (2011) 543-549.

[5] Seigo Ito, Peter Chen, Pascal Comte, Mohammad Khaja Nazeeruddin, Paul Liska, Pe´ter Pe´chy and Michael Gra¨tzel Fabrication of Screen-Printing Pastes From TiO2 Powders for Dye-Sensitised Solar Cells, Prog. Photovolt: Res. Appl. DOI: 10.1002/pip.768

[6] M Maeda, T Yamada, Photocatalytic activity of metal-doped titanium oxide films prepared by sol-gel process, J. Phys. 61 (2007) 755-759.

[7] J. Pouilleau, D. Devilliers, H. Goult, Surface study of a titanium-based ceramic electrode material by X-ray photoelectron spectroscopy, J. Mater. Sci. 32 (1997) 5645-5651.

[8] M.I. Litter, J.A. Navio, 1999, Photocatalytic properties of iron-doped titania semiconductors. J. Photochem. Photobiol. A: Chem. 98 (1999) 171-181

COST-BENEFIT ANALYSIS IN EXPLOITATION OF STONE

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Abstract

Cost-benefit analysis (CBA) is an economic decision-making approach, used in the assessment of whether a proposed project is worth doing. CBA involves comparing the total expected costs of each option against the total expected benefits, to see whether the benefits outweigh the costs, and by how much. In this study, besides analysis of other impacts, CBA was used in Environmental Impact Assessment (EIA) process of stone exploitation as an objective method enabling easier decision making about acceptance of the project. Evaluating of the project has been performed by determining the appreciable discounted net values (difference between total benefits and total costs) and immeasurable benefits and costs as a measure for the project acceptance. By financial analysis of appreciable parameters of the social benefits in particular EIA study, the positive results were determined, *i.e.* benefits for wider community will be larger than costs. By analysis of financially immeasurable parameters of social benefits, negative results were obtained, *i.e.* it was estimated that costs for wider community will be negligibly larger than benefits. Still, due to significantly larger financial measurable benefits for the society in comparison to costs, and negligibly larger financial immeasurable costs, it can be concluded that particular project of stone exploitation is acceptable from the CBA point of view.
Keywords: *cost-benefit analysis, environmental impact assessment, stone exploitation, decision making*

1. INTRODUCTION

Cost-benefit analysis (CBA) is a method that finds, quantifies and adds all the positive factors *i.e.* benefits of the planned action for the social well-being. Moreover, CBA technique identifies, quantifies and subtracts all the negative factors *i.e.* costs. The difference between benefits and costs indicates whether the planned action is advisable for the society. CBA has been successfully applied in developed countries to environmental issues and policies, including the use and conservation of natural resources [1]. The findings could inform economically efficient choices and contribute to social welfare. The valuation of environmental assets could link human and natural systems to ensure ecologically sustainable development [2]. In this work, CBA was used in Environmental Impact Assessment (EIA) of stone exploitation in Republic of Croatia as an additional support in decision making process of acceptance of the proposed project. The obligation of performing of EIA process for particular project is prescribed by Environmental Protection Act [3], paragraph 3, *i.e.* subparagraph 35. of Annex I of Regulation EIA [3], which are the competence of Ministry of Environmental Protection, Physical Planning and Construction of Republic of Croatia.

2. ELABORATION

2.1. Theory

Within the EIA process, two basic methods of CBA have been developed [4]. The first one relies on determination of appreciable discounted net benefits and costs which can be expressed in money terms. The other one is based on immeasurable benefits and costs *i.e.* impacts which can not be expressed in currency. Instead, it can be presented through different scales of values comparison.

2.1.1. Appreciable Discounted Net Benefits and Costs of the Project for the Society

From the point of view of the society, valuable (financially) appreciable benefits of the project the impacts which increase the economic potential of the society can be defined, while under the costs (losses) all generally accepted negative impacts according the goals of the social development have been considered. In the process of assessment of valuable (financially) appreciable benefits the cases in which

the society in general gets the welfare in any way from the proposed project (expressed in cash flow) will be taken into the account as follows:

- value added tax (VAT, 23 %) on every one-time basis investments in mining works, equipment, technical documentation and administrative procedure,
- value added tax (23 %) which will be paid on the value of the equipment in the case of it's replacement during the exploitation period,
- value added tax (23 %) which will be paid on the value of sold products (total income). In this case total income will be realized just for the part of the product which is sold to the end customers. The residual product which will be used by Hrvatske šume will be accounted by accounting (internal) prices, excluded VAT,
- value added tax (23 %) on all material costs (material, energy, services etc.) during exploitation period which are imposed to taxation (so called pre-tax). Mentioned amounts of VAT which will be paid by the suppliers of materials and services also present a benefit for the society,
- value added tax (23 %) which is accounted as a difference between VAT charged from the annual total income of the project holder and VAT accounted for material and services in annual production costs (so called pre-tax),
- taxes on employees salary (estimated on the level of 21 % of gross salary),
- corporate income tax (20 %)
- VAT (23 %) on the cost accounted in the form of internalized fees prescribed by current legislative (mentioned fees present a cost for the wider community since it's include a fee for environment loading which will be generated by the project),
- the fee for concession of mineral resources exploitation (includes the fee for excavated amount of mineral resources and the fee for the engaged surface).

Mentioned benefits differ because some are one-time basis, while the others are achieved annually through the whole period of exploitation. In the group of one-time basis the following benefits can be included:

- VAT on one-time basis investments necessary for the project realization,
- VAT on the equipment value in the case of it's replacement during the exploitation period.

The following could be considered as direct annual benefits for the society:

- VAT presented as a difference between VAT charged from the annual total income and VAT accounted for material and services (so called pre-tax),
- tax on achieved gross salaries,
- tax on achieved annual income,
- VAT on the cost accounted in the form of internalized fees prescribed by current legislative,
- the fee for excavated amount of mineral raw materials and the fee for the engaged surface.

For the assessment of appreciable discounted net values the internal environmental costs expressed as environmental fees paid for the use and/or protection of different component of the environment have been taken into the account. Since it has been paid in government budget they can be addressed as the benefit for the social community but since their purpose is the fee for the cost and loading of the environment by the project, engaged surface and overall spatial loading by the project, these costs can be considered as the cost of the social community.

2.1.2. Immeasurable Benefits and Costs of the Project for the Society

For the assessment of immeasurable benefits and costs for the society different scales of values whereas particular immeasurable impacts ranks according to intensity have been used. The ordinal scale has been used mostly. It enables statistical evaluation of the results by statistical method and was used for the analysis of immeasurable benefits and costs of the exploitation field studied in this work.

2.2. Results and Discussion

2.2.1. The costs of Project Realization (Investment)

The costs of project realization are shown in Table 1.

Table 1. The costs of project realization

The costs of project realization	Number of units	Unit value (kn)	Total (kn)
I. Existing machinery and equipment			
Deepwell drill	1	1.844.247.00	1.844.247.00
Loader	1	1.342.611.00	1.342.611.00
Bulldozer	1	1.475.397.00	1.475.397.00
Vehicle for workers and fuel transportation	1	184,425.00	184,425.00
Mobile crusher	1	2.286.866.00	2.286.866.00
Motor vehicle	1	110.655.00	110.655.00
I. TOTAL			7.244.200.00
II. Planned objects and investments			
Containers, oil separator, chemical toilet, oil eco containers etc.		50.000.00	50.000.00
Project documentation		350.000.00	350.000.00
II. TOTAL			400.000.00
III.			
Fence	685 m	12	8.220.00
Drainage channels system with precipitation tanks	1	38.500.00	38.500.00
Patio for oil and grease separator	1	82.000.00	82.000.00
III. TOTAL			128.720.00
II. + III.			528.720.00
OVERAL			7.772.920.00

2.2.2. The Costs of Project Running (The Structure of Annual Production, Overall Annual Turnover, Overall Production Costs and Their Structure, Realized Profit)

2.2.2.1. Structure of Annual Production, Overall Annual Turnover

The amount of exploited rock mass will be 40.000 m^3 coalesced rock (c.r.), i.e. 56.000 m^3 mealy rock (m.r.) per year, in fraction of 60 mm. From that amount, 60 % (33.600 m.r.) will be used for the sell on the market and profit generation. Overall turnover in one year of exploitation can be calculated by using following expression: $OT = Q_r \times C_r$, whereas:

OT overall turnover accomplished by sell, (kn)
Qr total amount of rock mass assigned to sell,
= 33.600 m^3 m.r.
C_r average market value of 1 m^3 of rock mass, (kn/m^3)
80.00 kn/m^3 m.r.

OT = 33.600 m^3 m.r./yr × 80.00 kn/m^3 m.r. = **2.688.000.00 kn/yr**

2.2.2.2. Overall Production Costs and its Structure

Overall production costs consider annual production costs during project realization including gross salary, energy, necessary drilling materials, loading, transportation, maintenance etc and have been presented in Table 2.

Table 2. Annual production costs

1.	Gross salary*	516.000.00 kn
2.	Oil fuel (70.171 × 9.21)	646.274.91 kn
3.	Engine oil (452 × 30)	13.560.00 kn
4.	Hydraulic oil (218.5 × 50)	10.925.00 kn
5.	Hydraulic hoses (2 × 350)	700.00 kn
6.	Motor vehicle tire (2 × 2.400)	4.800.00 kn
7.	Loader tire (1 × 25.000)	25.000.00 kn
8.	Drill crown (1 × 1.600)	1.600.00 kn
9.	Drill pipe (1 × 3.000)	3.600.00 kn
10.	Riogel (1.080 × 11)	11.880.00 kn
11.	Explosive AN-FO (14.640 × 5.2)	76.128.00 kn
12.	Nonel igniter (150 × 34)	5.100.00 kn
13.	Nonel connector (150 × 15)	2.250.00 kn
14.	Electrical igniter (6 × 8)	48.00 kn
15.	The fee for excavated amount of mineral raw material (40.000 m^3 × 1.4 × 21.92 kn/m^3 × 7.5 %)	92.064.00 kn
16.	The fee for the engaged surface (4.68 × 2.000.00 kn/ha)	9.360.00 kn
17.	Amortization of 8 % of equipment value (7.244.200.00 × 0.08)	579.536.00
18.	Amortization of 5 % on facilities and previous investment (80.000.00 × 0.05)	4.000.00 kn
19.	Spare parts 6 % of amortization for equipment (579.536.00 × 0.06)	34.772.16 kn
20.	Investment and current maintenance 10 % of amortization for equipment (579.536.00 × 0.10)	57.953.60 kn
21.	Amortization of 8 % on environmental protection investment	10.168.00 kn
22.	Rehabilitation (46.800 m^2 × 7 kn/m^2 = 327.600.00 kn/10 god)	32.760.00 kn
23.	The costs of other environmental protection measures and monitoring program measures	5.000.00 kn
24.	The fees (for exploitation, regulation, water protection, gas emissions)	47.135.82 kn
OVERAL		**2.190.615.49 kn**

Average gross salary exceeds 8.000.00 kn and manager 11.000.00 kn. Annual salary amount is (8.000.00 kn × 12 months × 4) + (11.000.00 kn × 12 months × 1) = 516.000.00 kn

2.2.2.3. Realized Profit

Realized profit has been calculated on the basis of determined overall turnover and overall costs. Realized profit during a year of quarry running exceeds 2.688.000.00 kn/yr and includes 60 % of overall project realization costs. Profit can be calculated on the basis of following expression: Ppr = OT – C, whereas:

OT overall turnover in one year, (kn)
= 2.688.000.00 kn

C 60 % from overall realization costs,
= 1.314.369.29 kn

Ppr = 2.688.000.00 – 1.314.369.29 = **1.373.630.71 kn**

2.2.3. Internal Benefits and Costs of the Project

Internal costs of the project are defined by the economic instruments of Republic of Croatia and consider payment of the fees prescribed by legislative. In the case of this exploitation field obligation of the following fees is prescribed:

- building unit fee
- water use fee
- water regime fee
- water protection fee
- gas emissions fee
- excavated amount mineral raw materials fee
- engaged surface fee

2.2.3.1. Building Unit Fee

The Law about Energy Protection and Efficiency Fund [5] determine obligation for payment of particular fee, implementing regulations for it's application has not been brought yet.

2.2.3.2. Water Use Fee

According to the Regulations concerning the calculation and payment of fees for water use [6, 7] the fee for the obligor in particular case exceeds 270.10 kn/yr.

2.2.3.3. Water Regime Fee

According to the article 21., paragraph 1 of the Act on Water Management Financing [8] and Directive on Water Regime Fee [6], the amount of the fee for the outdoor business areas of trade and services aimed to conducting economic and other activities including quarries has been determined regarding surface and exceeds 0.20 kn/m^2/yr.

So, water regime fee has been calculated according expression $F_{WR} = A \times 0.20$ kn/m^2/yr, whereas:

A area of the exploitation field (m^2),
= 46.800 m^2

F_{WR} = 46.800 m^2 × 0.20 kn/m^2/yr = 9.360.00 kn/yr.

2.2.3.4. Water protection fee

The amount of the fee has been determined by Directive on Water Regime Fee [6]. The amount of water protection fee according to the Ordinance on accounting and payment of the water protection fee [9] has been calculated according to the expression $F = A_F \times W \times k_1 \times k_2$, whereas:

F water protection fee,
A_F amount of fee – 0.90 kn/m^3,
W the amount of rainfall per year (0.861 m – water gauge per 1 m^2)
0.861 m × 46.800 m^2 = 40.294,80 m^3
k_1 the value which depends on the extent of impact on water quality decrease – 1.0 (for the obligators who do not need water permit and has been connected on water supply system)
k_2 counts just in case when obligator discharges it's wastewater in the public drainage system with wastewater treatment facility
F = 0.90 kn/m^3 × 40.294.80 m^3 × 1 = 36.265.32 kn

2.2.3.5. Gas Emissions Fee

The fee for harmful gas emissions generated by motor vehicles has been determined by Directive on unit fees, corrective coefficients and detailed criteria for determination of special environmental fee on motor vehicles [10]. Gas emissions fee generated by all motor vehicles operating on the particular exploitation field exceeds 1.240.40 kn/yr.

2.2.3.6. Excavated Amount Mineral Raw Materials Fee

The fee for excavated amount of mineral raw materials fee is paid every three months on the basis of exploited amount of mineral raw materials (40.000 m^3/yr. of c.r. × 1.4 = 56.000 m^3/yr. of m.r.) and multiplies by 7.5 % from production cost of mineral raw material (21.92 kn/m^3). Overall annual amount of the fee for the exploitation of mineral raw materials exceeds 92.064.00 kn.

F_{DU} = 40.000 m^3/yr. × 1.4 × 21.92 kn/m^3 × 7.5 % = 92.064.00 kn/yr.

2.2.3.7. Engaged surface fee

According to the Directive on the fee for concession for exploitation of mineral raw materials [11] the engaged surface fee exceeds 2.000.00 kn/ha of engaged surface of approved exploitation field.

F_{ES} = 4.68 ha × 2.000.00 kn/ha = 9.360.00 kn.

2.2.3.8. Brought Forward and Restricted Claim Fee on the Forest and Forestry Land under the Property of Republic of Croatia

Since the land of particular exploitation field is property of Republic of Croatia, it is necessary to assure forest and/or forestry land easement right before exploitation of mineral raw materials. So, concessionaire is obliged to pay easement right fee which consists of forest fee, forestry land fee and forest functions of general benefit decrease fee. This fee will not be accounted as benefit for the society, but the amount of stated fees will be estimated in order to express appreciable discounted net costs for the community caused by the project.

Forest/forestry land fee

The amount of forest/forestry land fee has been determined by Hrvatske šume ltd. and exceeds 1.561.35 kn/ha, so for the particular exploitation field of 4.68 ha range amounts 7.307.14 kn

Forest functions of general benefit decrease fee

Forest functions of general benefit include:

- protection of soil, roads and other infrastructure from erosion and flooding,
- impact on water regime and hydroenergetic system,
- impact on soil fertility and agriculture production,
- impact on climate,
- protection and improvement of human environment,
- generation of oxygen and atmosphere purification,
- recreational, touristic and health function,
- impact on fauna and hunting,
- protection of forest and forest with special allocation [12].

Total value of forest functions of general benefit exceeds 451.290 points and each point is valued 1 kn so for particular exploitation field forest functions of general benefit decrease fee amounts 451.290.00 kn. The annual amount of the fee is calculated by dividing of total fee amount (458.597.14 kn) on equal amounts concerning the number of years of easement (with estimated duration of exploitation of 10 yr) which exceeds 45.859.71 kn/yr.

2.2.4. Immeasurable Benefits and Costs of the Project for the Society

For the particular exploitation field, 12 financially immeasurable impacts which pose a benefits and costs for the society were chosen. The recognized impacts were categorized in four groups as follows:

- impacts on biodiversity,
- impacts on human environment,
- impacts on natural resources,
- impacts on social community.

The estimated intensity of the each impact (defined by the expert team) was determined by addition of corresponding value (according Table 3). Since determined values of ordinal scale consider only the range, it is necessary to present it for quantitative analysis, *i.e.* perform certain transformations [13]. It was performed according to:

$$(i - 0.5)/M, \quad i = 1, \ldots M,$$

whereas: M - upper scale value (for the particular exploitation field M = 12),
i - any value from the scale (1 – 12).

The values obtained by this transformation can be processed arithmetically, *i.e.* summarized and present the final cost and benefit difference which consider the result of cost benefit analysis.

Table 3. Evaluation of immeasurable environmental impacts

Activity impact	Impact intensity	Value according to Directives	Scoring
Positive	Very weak		0 – 2
	Moderate		3 – 5
	Significant		6 – 8
	Very strong		10 and more
Negative	Very weak	Up to recommendable	0 – 2
	Moderate	Between recommendable and limited	3 – 5
	Significant	Above limitation	6 – 8
	Very strong		9 – and more

3. CONCLUSIONS

CBA is one of the methods that have been applied in Republic of Croatia for defining environmental accessibility of mineral raw materials exploitation. CBA defines appreciable discounted net benefits (contribution to the national budget) as well as immeasurable ones. Mineral resources are the state property (all the Croatian citizens) and should be treated rationally since it presents a national wealth. By the analysis of appreciable discounted net values, the positive results were determined (1.375), *i.e.* the benefit for wider social community will be larger than the costs. By the analysis of immeasurable costs, negative results were obtained (-0.168), *i.e.* costs for the wider social community will be slightly larger than benefits. Mentioned impacts will not cause significant changes of current situation since proposed project consider expansion of the existing exploitation field. Having in mind all mentioned above (significantly larger appreciable discounted net values for the society in comparison to costs and slightly larger immeasurable costs in comparison to costs), it can be concluded that the project is acceptable from the cost benefit analysis point of view.

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REFERENCES

[1] C. Price, Valuation of unpriced products; contingent valuation, cost-benefit analysis and participatory democracy, Land Use Policy 17 (2000) 187-196.
[2] B.R. Howarth, S. Faber, Accounting for the value of ecosystem services, Ecol. Econ. 41 (2002) 421-429.
[3] http://www.mzopu.hr/default.aspx?id=7257
[4] G. Munda, Cost-benefit analysis in integrated environmental assessment: some methodological issues, Ecol. Econ. 19 (1996) 157-168.
[5] The Law about Energy Protection and Efficiency Fund, Official Gazette 107/03
[6] Directive on Water Protection Fee, Directive on Water Use Fee, Directive on Water Regime Fee, Official Gazette 82/10
[7] Ordinance on Accounting and Charging of Water Use Fee, Official Gazette 84/10
[8] Act on Water Management Financing, Official Gazette 107/95, 19/96, 88/98, 150/05
[9] Ordinance on Accounting and Charging of Water Protection Fee, Official Gazette 83/10
[10] Directive on unit fees, corrective coefficients and detailed criteria for determination of special environmental fee on motor vehicles, Official Gazette 02/04
[11] According to the Directive on the fee for concession for exploitation of mineral raw materials Official Gazette 158/09
[12] Ordinance on Forest Management, Official Gazette 111/06, 141/08
[13] T. Hastie, R. Tibshirani, J. Friedman, The Elements of Statistical Learning: Data Mining, Inference and Prediction, second ed., Springer, New York, 2009.

SUBCRITICAL WATER - A PERSPECTIVE REACTION MEDIA FOR BIOMASS PROCESSING TO CHEMICALS

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Abstract

Biomass and water are recognized as a key renewable feedstock in sustainable production of chemicals, fuels and energy. Subcritical water (SubCW), or commonly referred as hot compressed water (HCW), is the water above the boiling and below critical point (CP; 374°C, 22.1 MPa). It has gained a great attention during the last few decades as a green, cheap and nontoxic reagent for conversion of biomass to valuable chemicals due to unique thermo-physical and transport properties, which greatly differ from water at normal state. Interests of our investigations are hydrothermal reactions of biomass with subcritical water and design of processes for production of valuable chemicals. The experiments were done with microcrystalline cellulose as a model biomass in batch reactor at the temperature range 220°-300°C. The main products in liquid, gaseous and solid phase were determined and quantified by the various analytical techniques. The conversions to each group of products were found to strongly depend on the temperature and residence time. The results are used to discuss the influence of reaction conditions and physical-chemical properties of subcritical water on the occurring chemical reactions. Some general conclusions are made about hydrothermal degradation pathways of real biomass at such conditions.

Keywords: *biomass, subcritical water (SubCW), hydrothermal conversion, bio-oils*

1. INTRODUCTION

Due to a still excessive reliance on nonrenewable resources and environmentally unacceptable production processes, the chemical industry is under increasing pressure and continuous improvement in performance, enabling more sustainable and safer production. The main technological challenge lies in the "green chemical engineering" which comprises the selection of renewable raw materials, integration of material constrains, cost and safety and increasing of energy and material efficiency in production and services 0. Biomass and water are recognized as a key feedstock for a sustainable chemical industry, which provide entirely novel opportunities for production, nowadays predominantly based on fossil resources 0.

Biomass, commonly referred to lignocellulose, has a complex structure. It is constituted by three main structural components: cellulose, hemicelluloses and lignin arranged themselves in cross-linked three-dimensional resinous structure. The most abundant components are carbohydrates, in general composed of C_6- and C_5- sugars that form cellulose and hemicelluloses, representing almost 75 % of biomass weight 0. The second most abundant chemical component is lignin (20-25 % of biomass weight). Lignin is a complex, cross-linked polymer built of substituted phenols that form large molecular structures. It acts as reinforcing agent, giving mechanical strength to biomass by gluing the fibers between the cell walls to each other. These main constitutional substances represent the valuable raw material in transformation processes for production of chemicals and fuels. In this context, hydrothermical processes with water in subcritical or supercritical state have gained increased attention in the last decades. As a cheap, environmentally friendly reaction medium with unique properties 0 water at elevated temperatures and pressures is widely investigated in numerous processes to obtain valuable products, as is reported in review by G. Brunner 0.

Subcritical water (SubCW) is pressurized water at temperatures above its boiling point under ambient pressure and below critical point (T_c=374°C, p_c=22.1 MPa, ρ=320 kg m^{-3}). Within a region close to critical conditions (near-critical or subcritical region), water properties are becoming more sensitive to pressure and temperature changes. Above the critical point, water is called supercritical water (SCW) and its properties vary between liquid-like and gas-like with changing the temperatures and pressures without

any phase transition. The most relevant properties of water at different temperatures and pressures are summarized in Table 1.

Table 1. Properties of water at various temperatures and pressures

	Water	Subcritical water		Supercritical water	
Temperature (°C)	25	250	350	400	400
Pressure (Mpa)	1	50	25	250	500
Density (g cm^{-3})	1	0.80	0.60	0.17	0.58
Dielectric constant, ε	78.5	27.10	14.07	5.9	10.5
Ion product, K_W	10^{-14}	$10^{-11.2}$	10^{-12}	$10^{-19.4}$	$10^{-11.9}$
Heat capacity, C_P (J g^{-1} K^{-1})	4.22	4.86	10.10	13.0	6.8
Dynamic viscosity η (mPa s)	0.89	0.11	0.064	0.03	0.07
Compressibility	no	slightly increased, but still liquid		yes	

The most relevant properties of SubCW are miscibility, solvent's dielectric constant, ionic product, electrolytic solvent power, transport properties (viscosity, diffusion coefficients and ion mobility), hydrogen bonding, etc. These properties are strongly influenced by the temperature and water density so they could be manipulated as parameters to enhance reaction selectivity to desired products. The dielectric constant decreases by temperature, making SubCW more similar to hydrocarbon solvents. For this reason solubility of hydrophobic organic compounds and light gases in subcritical water is increased. The ionic product of subcritical water ($K_w=[H^+][OH^-]$) increases with temperature and is greater by 1 to 2 orders of magnitude than at the ambient temperatures, so SubCW has an important role in acid- and base-catalyzed reactions (e.g. biomass hydrolysis). Furthermore, good transport properties (high diffusion coefficient and thermal conductivity and low viscosity) make SubCW more similar to gases than liquids, enabling the increasing of reaction rates in processes in SubCW. These properties of SubCW greatly impact biomass decomposition, mainly through reactions of solvolysis, depolymerisation of biomass's main compounds (cellulose, hemicelluloses and lignin) and further decomposition of monomers by cleavage, dehydration, decarboxylation, deammination and rearrangements of reactive fragments 0. In such complex processes, different products are synthesized depending on biomass type (composition), process conditions and catalysts applied.

Biomass conversion rate and a yield of each group of products is strongly influenced by many factors like are reaction temperatures, water properties, reactor system, catalysts implied, heating rate, biomass properties, etc.0. Our investigations are focused on transformations of microcrystalline cellulose, as a model biomass, in SubCW. In this work experiments in temperature range 220°-300°C have been conducted. The influence of reaction conditions and physical-chemical properties of subcritical water on the chemical reactions and products distribution were investigated.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Materials

Microcrystalline cellulose was obtained from Merck. Deionized water having the resistivity of 18 MΩ cm^{-1} was obtained by water purification apparatus (ELGA, Veolia). Sugar standards (glucose, cellobiose, fructose, galactose, ribose, etc.) and high-purity reagents for HPLC analysis were purchased from Sigma-Aldrich.

2.1.2. Experimental Methods

Experiments of the microcrystalline cellulose conversions were carried out in stirred batch reactor made from HT/HP 1.4980 steel tube (volume capacity=60 ml) at temperature range 220°-300°C and equivalent pressure. The suspensions of 3 g cellulose in 30 ml deionized water were prepared and were charged in the reactor. The reactor was heated by electrical wire-heater to the desired temperature of

220°-300°C. The reaction temperature and pressures were measured by K-type thermocouple and pressure sensor connected to reactor interior. After a defined reaction time, the reactor was quickly immersed in ice bath to immediately stop the reaction. The gaseous products (in cases, when the gases were produced) were collected in preweighed sample-bags. The liquid and solid contents in the reactor were separately collected as water-soluble, acetone-soluble and acetone-insoluble fractions. The reactor content was filtered using a paper-filter. The water in the filtrate was evaporated under vacuum at 60°C, and the water-soluble (WS) fraction was recovered. The water-insoluble fraction was washed three-times with acetone, as same as reactor walls, and acetone soluble (AS) and acetone insoluble or solid residue (SR) fractions were obtained (Fig. 1.). Acetone was evaporated under vacuum at 40°C and acetone soluble fraction (AS), as same as solid residue (SR) were weighed.

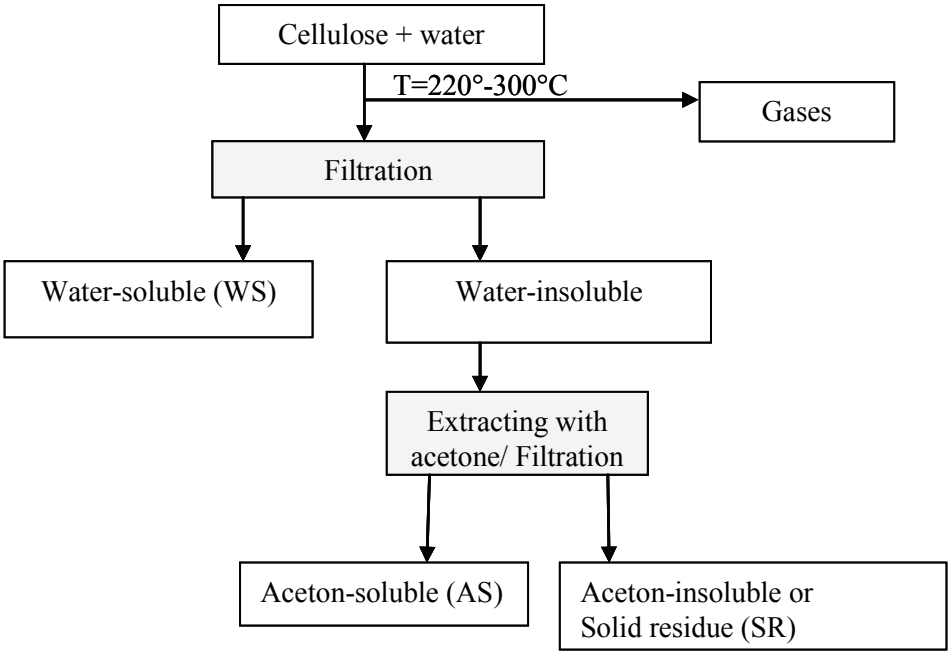


Figure 1. Fractionation of reaction products.

2.1.3. Analysis

The liquid water soluble phase was analyzed for sugars decomposition products. The sugars were analyzed and quantified by HPLC instrument with ELDS detector (Agilent). The gaseous phase was analyzed and quantified for H_2, CO, CO_2 and CH_4 by GC (Shimadzu 2010). The solid residue spectra were recorded using an IR-spectrophotometer within the range of 4000-400 cm^{-1} by KBr pelletization method. The experiments at each condition were done in duplicate and average value was used.

2.2. Results and Discussion

2.2.1. Effect of Reaction Temperature on Cellulose Conversion

The effect of temperature on cellulose conversion rate is demonstrated in Fig. 2., which shows conversion percent (on the basis of initial amount of cellulose) for residence time 0-60 min for three temperatures: 220°, 250° and 300°C. It is clear that decomposition of cellulose increases with increasing reaction temperature and residence time first, and then decreases with further increasing of temperature to 250° and 300°C. At temperature 300°C almost 92 % of initial cellulose decomposes in only 5 min, but after that, conversion drastically decreases. This is a result of competitions of two reactions, hydrolysis and repolymerization, occurring parallel in reaction systems with subcritical water. In general, the cellulose is subjected first to hydrolysis and depolymerization into oligosaccharides (DP=2-6) and monosaccharides (glucose) by water diffusion to the cellulose surface and then to rearrangement/decomposing of glucose to various decomposition (pyrolitic) products: fructose, 5-hydroxymetylfurfural (5-HMF), furfural, pyruvaldehyde, dihydroxyacetone, glyceraldehydes, glycolaldehyde, erythrose. Hydrolysis is enhanced by increased ionic product with temperature to ~ 10^{-11} at 300°C. At higher temperatures and/or longer reaction time, isomerization, fragmentation and repolymerization of these small compounds into liquid oils, gases and char occurs 0.

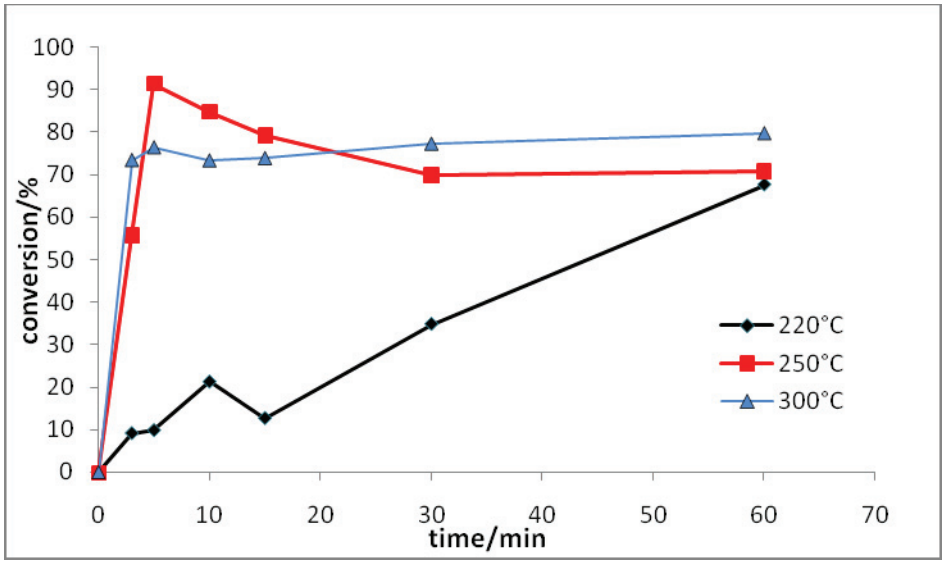


Figure 2. Effect of residence time on conversion of microcrystalline cellulose at temperatures 220°C, 250° and 300°C.

2.2.1. Effect of Reaction Temperature on Various Product Distribution

The mentioned competing effect on reactions of hydrolysis and repolymerization was also observed from results of water-soluble (WS) and acetone soluble (AS) quantification, in accordance with residence time and temperature. Furthermore, visual observation of color changes of WS and AS samples collected during the reactions were consistent with results from analysis, as is presented on Fig. 3.

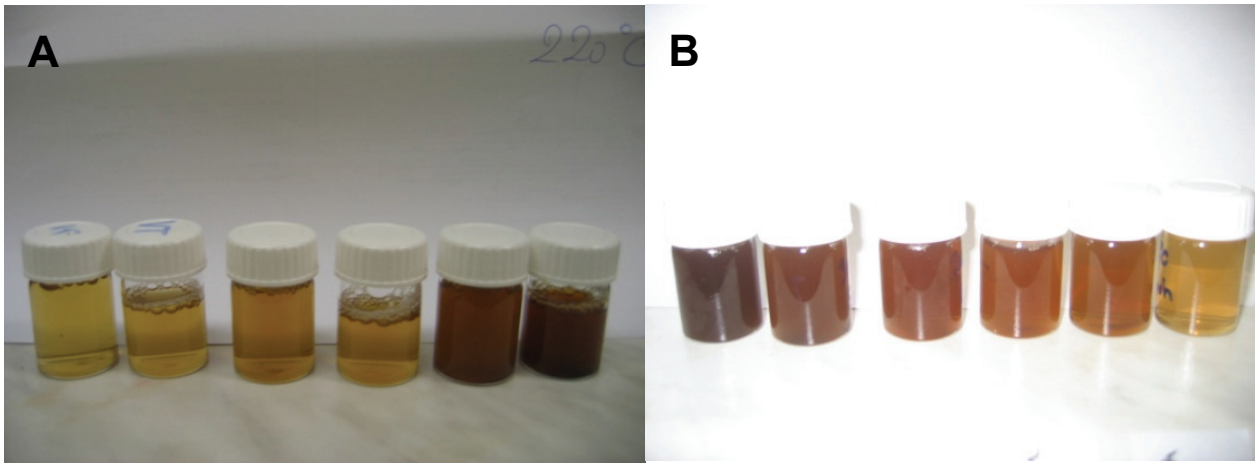


Figure 3. Changes in color during the reaction of cellulose suspension in SubCW: a WS phase collected at a) 220°C and b) 300°C at time 0-60 min.

It was found that at 220°C conversion of cellulose to WS was increased by increasing the reaction time and has achieved value of 33.6 wt% on the basis of initial cellulose. Acetone soluble phase (AS) yield is minor at 220°C.This finding shows that the hydrolysis at temperature of only 220°C is very slow reaction, and decomposition of hydrolysis products to oils or gases is negligible. At temperatures of 250° and even 300°C, conversion of cellulose to WS products has reached the maximum only after 5 min (to about 40 wt %) and 3 min (to about 12.3 wt %). After that, their concentration has started to decrease with residence time, as could be observed from Fig. 3.

The dominance of condensation/depolymerization at higher temperatures is confirmed also from results of cellulose conversion yield to acetone soluble (AS), solid residue (SR) and gaseous phase. Increasing of the yield of AS phase is more evident at 300°C, indicating that viscous hydrophobic bio-oils (often called bio-crude) was formed. Bio-oil mainly consists of hydrophobic phenols and its derivates, ketones, carboxylic acids, long-chain alkanes etc.0 The maximum conversion to AS phase was reached after 60 minutes at 250°C, and only after 3 minutes at 300 C. The gases phase formation was obvious at higher temperatures and longer residence time, what was observed by final pressure in reactor

after cooling it down to room temperature. On the contrary, char formation was the highest at 250°C and 60 min reaction time (up to 65 wt%) with decreasing tendency at 300°C, indicating that significant gasification starts with T>300°C. The similar results were found in literature elsewhere 0. The solid residues were characterized also by a FTIR spectrophotometer to confirm structural changes during the reactions in SubCW. The disappearance of characteristic absorption peaks of black solid residues (e.g. cellulose at 1423 and 3398 cm^{-1}) occurs drastically with increasing the reaction time and temperature, confirming the observations about cellulose transformations mentioned before. Although gases phase has been observed at 250°C at longer residence time (in negligible quantities), analyses of gas composition on GC were done only for samples at 300°C. The main gases were CO_2 and CO, only small amounts of H_2 and CH_4 have been detected.

Thus, results from this study of cellulose conversion, as a model biomass, conducted in subcritical water, could be used to predict major reactions also for conversion of other biomass feedstock. Properties of water at temperatures 220°C-300°C change obviously, determining the reaction pathways and product distribution. Besides the temperature (and water properties) also residence time implicates indirectly on differences in product type (and reaction mechanism). In batch reactors, residence time of mixture is long, enabling the secondary reactions of the hydrolysis products and increased yield of oil and char, and low yield of sugars. The comparative study of reactions of cellulose and HCW in batch- and flow-type of reactor systems shows, that in flow-type reactor system cellulose hydrolyze results in minimal pyrolyzed products, whereas in batch-type higher yields of pyrolyzed products are detected 0. From this reason, it is very important to investigate fundamental reaction of biomass degradation in appropriate reactor system and conditions, to avoid secondary reactions of primary products. At high temperatures, sugar decomposition could be very fast e.g only few seconds is needed for decomposition of glucose at temperatures higher than 300°C 0. Due to this reason, reactions at higher pressures and temperatures (supercritical water) are, in general, investigated in semi-continuous or continuous reactors.

3. CONCLUSIONS

An experimental work was done with aim to highlight the main reactions pathways of microcrystalline cellulose in subcritical water, as a model biomass at temperature ranging from 220°C to 300°C. The results show that various products occur. The liquid products were separated regarding their solubility in water and acetone. A water soluble phase (WS) represents mostly cellulose decomposition products, like are sugar monomers and monomer degradation products (organic acids, 5-HMF, aldehydes etc.). Acetone soluble phase, referred also as bio-oil, mainly consists of hydrophobic phenols and its derivates, ketones, carboxylic acids, long-chain alkanes etc. Significant gaseous phase was observed only at 300°C, indicating that non-catalytic gasification of biomass occurs only at temperatures above 300°C.

The conversion of cellulose strongly depends on temperature and subcritical water properties. By the increasing of temperature, the conversion is increased, but only at temperatures around 220°C. Any further increase in temperature and reaction time leads to re-polymerization of primary products (pyrolysis) to bio-oils (here separated as AS) and solid product “char”. So, conversion of cellulose is mostly completed in 3 minutes at 300°C, but prolonging the reaction will result in un-desirable secondary reactions. From this reasons, a proper reactor design must be applied to ensure a high reaction selectivity and minimization of undesired products.

REFERENCES

[1] J.F. Jenck, F. Agterberg, M.J. Droescher, Products and processes for a sustainable chemical industry: a review of achievements and prospects, Green Chem. 6 (2004) 544-556.

[2] P.R. Gruber, M. Kamm, Biorefineries - Industrial Processes and Products, Wiley-VCH, New York, 2006.

[3] A. Kruse, E. Dinjus, Hot compressed water as reaction medium and reactant-Properties and synthesis reactions, J. of Supercritical Fluids 39 (2007) 362-380.

[4] G. Brunner, Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes, J. of Supercritical Fluids, 47 (2009) 373-381.

[5] S.S. Toor, L. Rosendahl, A.Rudolf, Hydrothermal liquefaction of biomass: A review of subcritical water technologies, Energy, 36 (2011) 2328-2342.

[6] Y. Yu, H. Wu, Characteristics and Precipitation of Glucose Oligomers in the Fresh Liquid Products Obtained from the Hydrolysis of Cellulose in Hot-Compressed Water, Energy Fuels, 24 (2010) 1963-1971.
[7] A. Kruse, A. Gawlik, Biomass conversion in water at 330-410 C and 30-50 MPa-Identification of key compounds for indicating different chemical reaction pathways, Ind. Eng. Chem. Res, 42 (2003) 267-279.
[8] S. Kumar, R.Gupta, Hydrolysis of Microcrystalline Cellulose in Subcritical and Supercritical Water in a Continuous Flow Reactor, Ind. Eng. Chem. Res., 47 (2008) 9321-9329.
[9] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, N. Takeda, T. Adschiri, K. Arai, Cellulose hydrolysis in subcritical and supercritical water, J. of Supercritical Fluids, 13 (1998) 261-268.
[10] M. Sasaki, T. Adschiri, K.Arai, Kinetics of cellulose conversion at 25 MPa in sub- and Supercritical water, AIChE Jour. 50 (2004) 192-202.
[11] K.Echara, S. Saka, A comparative study on chemical conversion of cellulose between the batch-type and flow-type systems in supercritical water Cellulose, 9 (2002) 301-311.
[12] B.M.Kabyemela, T.Adschiri, R.M.Malaluan, K.Arai, Rapid and selective conversion of glucose to erythrose in supercritical water, Ind.Eng.Chem.Res. 38 (1999) 2888- 2895.

ALTERNATIVE PROCESSES FOR REMOVING ORGANIC SULFUR COMPOUNDS FROM PETROLEUM FRACTIONS

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Abstract

In this work the processes for removing sulfur from fuels, and problems related thereto, including conventional and improved processes of hydrodesulfurization, and alternative technologies and processes for obtaining fuel with extremely low sulfur content, which are in the process of research and development, are discussed. It is anticipated that alternative processes, that are already developed or that are being researched, will be applied as an addition to the currently most used process of hydrodesulfurization, which is based on selective heterogeneous catalysts. New achievements in the development of hydrodesulfurization process regarding new catalysts and reactors, as well as research and development possibilities of adsorption and extraction processes and of biodesulfurization process are reviewed.

Keywords: *sulfur, petroleum fractions, alternative process, desulfurization*

1. INTRODUCTION

One of the major tasks of the petroleum industry is the production of gasoline and diesel fuels with ultra low sulfur content. Current legislation limits the maximum content of sulfur in gasoline and diesel fuels to 10 mg kg^{-1}. Reducing sulfur content in fuels is important in order to reduce their impact on the environment and protect the public health. Effect of the sulfur from the fuels on the environment is mainly associated with its conversion into sulfur oxides that form during combustion in the engine. Beside the facts that it pollutes the environment and affects air quality, sulfur is also harmful to modern vehicles more sensitive to the quality and purity of the fuel. A higher concentration of sulfur in fuels significantly decreases the efficiency and lifetime of emission gas treatment systems in cars [1-4].

2. ELABORATION

2.1. Advanced Hydrodesulfurization Processes

Hydrodesulfurization (HDS), a mild form of hydrocracking, is a refining process used for removing organic sulfur compounds from petroleum fractions. Compounds like thiols, sulfides, and thiophenes can be readily removed from petroleum fractions by using conventional HDS catalysts, sulfidized $CoMo/Al_2O_3$ i $NiMo/Al_2O_3$, and reactors, but the efficiency towards the removal of refractory sulfur compounds, such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), is greatly reduced. Applying new techniques and technologies new types of CoMo and NiMo catalysts, with increased hydrogenation activity and selectivity, were developed. Also, new reactor designs were developed including the reactors with multiple levels or the reactors with different catalyst structures.[5-10] Furthermore, HDS catalysts with excellent desulfurization efficiency were developed by combining new types of catalytically active species, such as noble metals, and new carrier materials, such as the ones based on improved amorphous silica-alumina (ASA). However, the use of noble metals in HDS processing is limited by their susceptibility to sulfur poisoning. In order to increase the catalysts resistance to sulfur poisoning, new types of bi-functional HDS catalysts were developed. The processing in HDS plants that use catalysts based on noble metals is conducted in two or more steps which include multilevel catalyst systems in order to achieve deep desulfurization and hydrogenation. Other ways to improve the HDS process include changing the direction of reaction streams, i.e. conduct the hydrodesulfurization counter currently (Figure 1) and using ebullated catalyst bed reactor. [5-13].

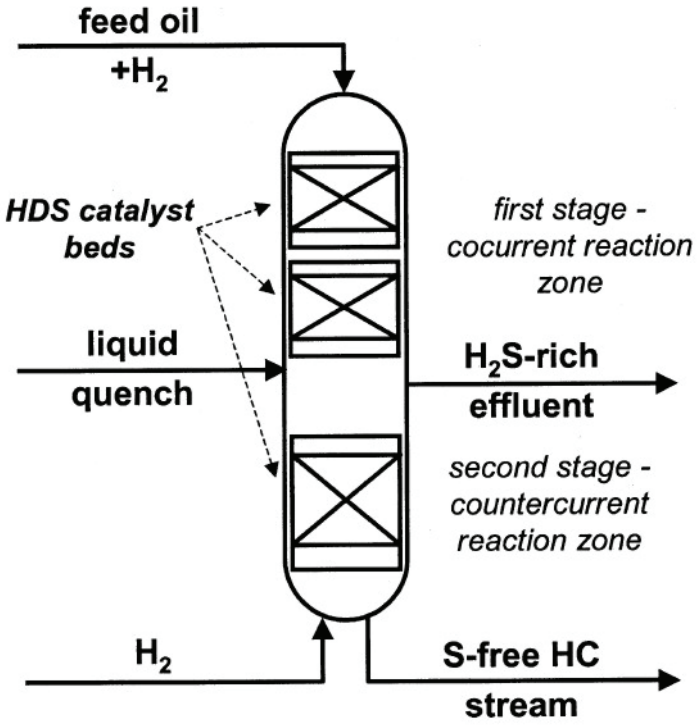


Figure 1. Schematic of the counter current HDS process.[7]

2.2. Adsorptive Desulfurization

Adsorption can be used for desulfurization of petroleum fractions based on the ability of solid adsorbent material to selectively adsorb organic sulfur compounds. There are two types of adsorptive desulfurization: adsorptive desulfurization during which physical and/or chemical adsorption of organic sulfur compounds takes place on the surface of the adsorbent, and reactive adsorption desulfurization during which organic sulfur compounds react with chemical species on the surface of the adsorbent and the sulfur is chemically bound, usually in the form of sulfide, while the newly formed hydrocarbon compound is released in to the feed. The efficiency of adsorptive desulfurization is for the most part influenced by the adsorbent properties: capacity, selectivity, stability and ability to regenerate.[7-9,14] Materials that are being used as adsorbents for desulfurization include different forms of activated carbon, zeolite, metallic oxides and porous metals.[15]

Mužic et al.[15,16-20] have conducted several studies of adsorptive desulfurization of diesel fuel using commercially available activated carbons as adsorbents. The fixed bed adsorption experiments by Mužic et al.[19,20] where activated carbon SOLCARB C3 (Chemviron Carbon, Belgium) was used to treat a diesel fuel resulted with output sulfur concentrations of less than 0,7 $mgkg^{-1}$. The calculations by Mužic et al.[26] have shown that fixed bed adsortive desulfurization of a previously hydro-treated diesel fuel could be carried out on industrial scale. For the feed capacity of around 10^5 kgh^{-1} a two fixed bed column system with each bed depth of 17,32 m and activated carbon SOLCARB C3 load of 93,5 t must be used to achieve ultralow sulfur concentration and enable continuous 24 hour a day operation.

Mužic et al.[21] have studied the removal of DBT from model gasoline by batch adsorptive desulfurization and the best results were achieved with Y-zeolite which removed the most of DBT in shortest time. It was determined that for the Y-zeolite there is less heterogeneity in the system, higher probability that chemisorption is the prevailing mechanism and the mono-molecular layer is being formed.

2.2.1. Reactive Adsorption Desulfurization – S-Zorb Process

Reactive adsorption desulfurization is a process where metal based adsorbent bonds the sulfur on the surface and forms disulfide. In the USA the S-Zorb process was developed for removing sulfur from gasoline and diesel fuels by reactive adsorption (Figure 2).[6,7,9,14]

S-Zorb process is based on fluidized bed technology and is conducted at relatively severe conditions, temperatures between 340 and 400 °C and pressures between 2 and 20 bars, in order to achieve better kinetics. The sulfur atom in organic sulfur compound is first adsorbed on the surface after which it reacts with the adsorbent and the newly formed hydrocarbon is released in to the main feed flow. It is presumed

that the adsorbent is based on a reduced metal which reacts with sulfur and forms metallic sulfides. The used adsorbent is continuously removed from the reactor and transported in to the regeneration chamber. The sulfur is removed from the surface of the adsorbent by burning and the formed SO_2 is sent to the sulfur plant. The adsorbent is then reduced with hydrogen and is recycled back to the reactor. The process schematic is shown on Fig. 3. [5,7,9,14].

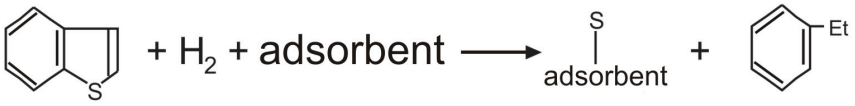


Figure 2. S Zorb reactive adsorption schematic [6]

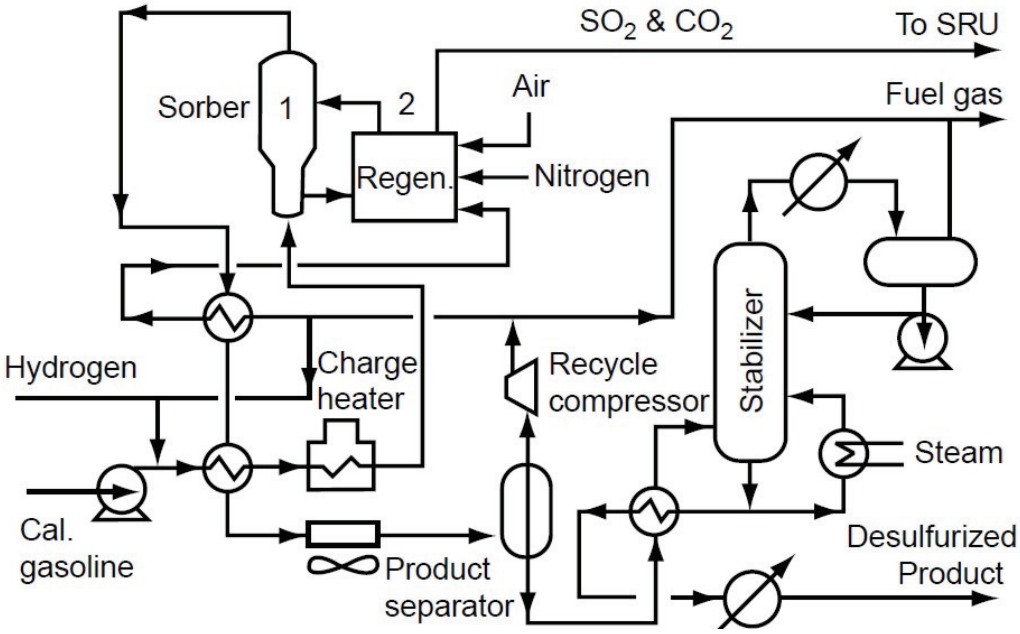


Figure 3. S-Zorb process schematic.[9]

2.3. Extractive Desulfurization

The extraction can be used for desulfurization because of higher solubility of organic sulfur compounds in appropriate solvent than other hydrocarbons present in a petroleum fraction. The organic sulfur compounds are being removed from the feed into the solvent after which the mixture of solvent and feed is separated. The organic sulfur compounds are removed from the solvent by distillation and the solvent is recycled. The extractive desulfurization process schematic is shown on Figure 4.[7,9,14]

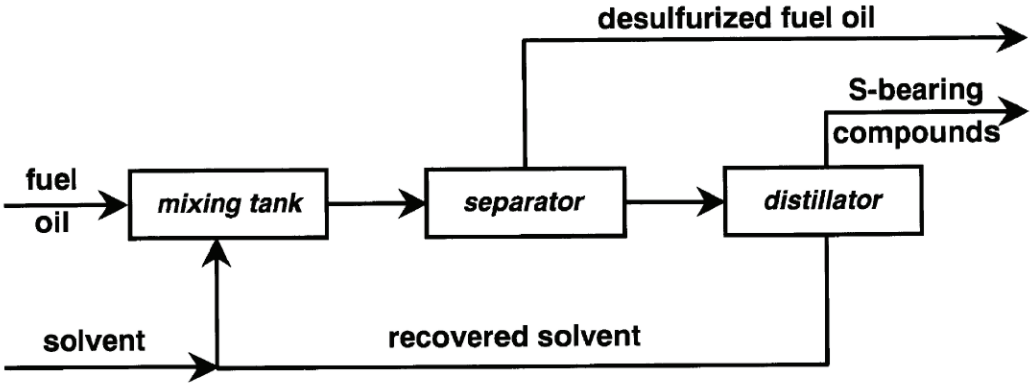


Figure 4. Extractive desulfurization process schematic.[7]

The advantages of the extractive desulfurization include the possibility of conducting it at relatively low temperatures and pressures; it requires standard industrial equipment for operation and can easily be integrated in the refineries. In order for the process to be efficient several conditions must be met: organic sulfur compounds must be fully soluble in the solvent, the solvent must have a different boiling point in relation to the removed organic sulfur compounds and the solvent must be nontoxic and relatively cheap so the process can be economically viable. Satisfactory levels of desulfurization of between 50 and 90% were achieved with sulfolane, acetone, ethanol, polyethylene glycol and some nitrogen containing solvents.[9,14]

Adžamić et al.[22,23] have carried out studies on possibilities of removing organic sulfur compounds from FCC gasoline by batch extraction with sulfolane. The removal efficiencies of up to 89% of total sulfur content were achieved. It was determined that sulfolane is highly selective of mercaptanes and lighter tiophenes. Also, it was determined that its selectivity is lower for heavier thiophenes so that the sulfur content which remains in the rafinate is mostly made up of lighter thiophene compounds.

An industrial size process called Sulf-X was developed for extractive desulfurization of FCC gasoline with sulfolane and it was commercially used in Sisak Refinery (INA – Industrija nafte d.d., Croatia). The extraction was carried out in columns, i.e. extractors with perforated plates.

Eβer et al.[24] give a good recent overview on the desulfurization with different types of ionic liquids, particularly on the most promising water-stable and less costly 1-n-butyl-3methylimidazolium octylsulphate. Given the poor extraction of alkylthiols and sulfides, the formation of liquid-clathrates and π–π interaction is assumed to be the main driving force for extraction. Furthermore, nitrogen compounds are found to be more efficiently extracted than sulfur compounds. The main problems are the extraction efficiency of limited number of organic sulfur compounds for particular ionic liquid, cross-solubility of hydrocarbons and the regeneration of expensive ionic liquid compounds.

2.3.1. Extractive distillation desulfurization

GTC Technology Inc. has developed an extractive distillation desulfurization process GT-DeSulf™ for removing organic sulfur compounds from FCC gasoline without octane number loss and increase in hydrogen consumption. The GT-DeSulf™ process utilizes a proprietary aromatics selective solvent, which is effective in extracting thiophenic sulfur species and aromatics, and to a limited extent, mercaptans and sulfides as well. Since olefins are not extracted, it is indeed a 'selective' desulfurization system. The application is, however, limited to a light and a middle FCC cut, with specified boiling point range of up to 180 °C. A desulfurized/dearomatised olefin rich gasoline stream and an aromatic stream containing the sulfur compounds are formed after treatment in a GT-Desulf™ reactor. The first stream is directly used as a gasoline blend stock. The aromatics fraction with the sulfur compounds is sent to a HDS reactor. The GT-Desulf™ process is economically favorable due to an integrated approach to the refinery processing (segregated sulfur removal and aromatics recovery) and lower hydrogen consumption since less FCC naphtha is treated in the HDS reactor.[5,7,14]

2.4. Oxidative Desulfurization

Oxidative desulfurization is a process during which organic sulfur compounds are oxidized and are subsequently removed from the feed by a separation method. Separation methods used for separating oxidized sulfur containing compounds from fuel streams include extraction, adsorption, distillation and thermal decomposition. During oxidative desulfurization the refractory sulfur compounds, such as DBT, are oxidized to form sulfones. Sulfones have higher polarity compared to the source sulfur compounds and that is why are more easily removed from petroleum fractions.

In practice the oxidative desulfurization process has encountered some technological and economical problems such as product loss during extraction stage. Also, oxidative desulfurization process is a source of new, so called, sulfonic waste which requires special treatment.[7,9,14,24,25]

The research of oxidative desulfurization is being conducted using different oxidizers including nitrogen oxides and acids such as NO/NO_2 and HNO_3, t-butyl-hypochlorite, highly toxic RuO_4, persulfate based oxidizers, and H_2O_2-H_2SO_4 systems. The introduction of stringent fuel sulfur content regulations the most used oxidizers became hydrogen peroxides such as H_2O_2, tert-butyl hydroperoxide (TBHP) with catalyst support, in-situ formed per-acids, organic acids, phosphate acid and heteropolyphosphate acids, Fe-tetra amido macrocyclic ligand (Fe-TAML), Fenton and Fenton-like compounds, as well as solid catalysts such as the ones based on titanium-silica, W-V-TiO_2, solid bases such as MgLa metal oxides or hydrotalcites, Fe oxides and oxidizing catalysts based on monoliths. These compounds can effectively oxidize organic sulfur compounds into sulfones with less residue formation.[7,14,25-29]

The advantages of oxidative desulfurization, in comparison to conventional HDS, include the requirement of rather moderate reaction conditions, no need for expensive hydrogen and higher reactivity of aromatic sulfur compounds in oxidation reactions since the electrofilic reaction with sulfur atom is enhanced by higher electron density of aromatic rings. Alkyl groups attached to the aromatic ring increase the electron density on the sulfur atom even more. The reactivity is also dependent on the type of catalyst.

SulphCo Inc. has developed an oxidative desulfurization process which utilizes ultrasound power during H_2O_2 sulfur oxidation in the presence of tungsten phosphoric acid. Ultrasound decreases the reaction time by one order of magnitude. The SulphCo process operates at 70–80 °C under atmospheric pressure. The residence time for the ultra-sound reactor is reported to be only 1 min. Desulfurization efficiencies for crude oil and diesel of up to 80 and 98% sulfur removal were achieved.[7,14,30]

Lyondell Chemical Co. and UOP LLC in cooperation with EniChem S.p.A have developed a t-butylhydroperoxide (TBHP) based commercial oxidative desulfurization processes that depending on the version utilizes extraction or adsorption for sulfone separation. The biggest advantage of this kind of single liquid system is simple reactor engineering, enabling the application of a fixed bed column (Figure 5). Major drawback is the high price of TBHP, and the waste treatment of t-butyl alcohol as an accompanied product, as well as sulfone waste treatment. t-butyl alcohols could find use as potential octane boosting compounds for gasoline.[14,28,31]

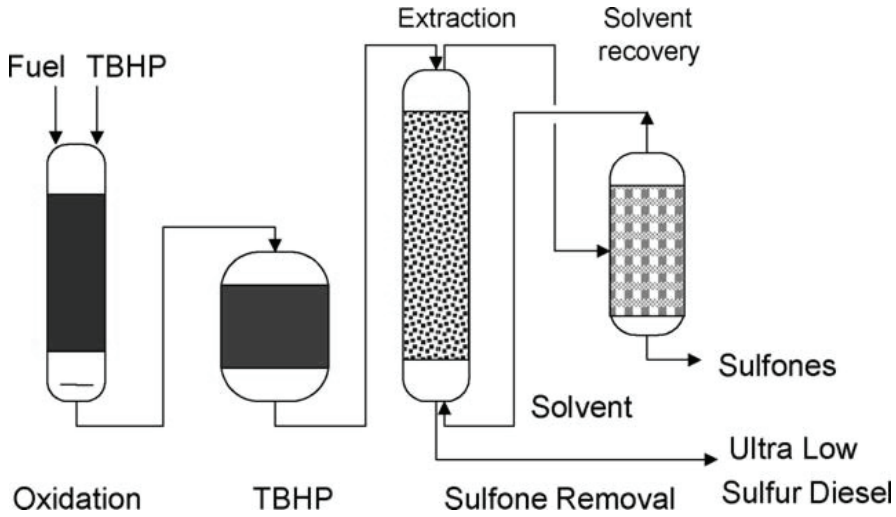


Figure 5. Schematic of the Lyondell Chemical oxidative desulfurization process.[14]

2.5. Photochemical Extractive Desulfurization

Photochemical extractive desulfurization process combines photochemical reactions with extraction of the organic sulfur compounds with an aqueous-soluble solvent. The organic sulfur compounds are irradiated by UV or visible light in a specially designed photoreactor and are oxidized. The polar compounds formed are rejected by the non-polar hydrocarbon phase and are concentrated in the solvent. Photochemical reaction is assisted by a photosensitizer species such as 9,10-dicyanoanthracene (DCA). Acetonitrile, which provides relatively high solubility of initial and oxidized sulfur compounds, was found to be the most suitable solvent. After photooxidation, the solvent and the hydrocarbon phases are separated, as in extractive desulfurization. In addition, the recovery of aromatics from the solvent and recovery of the photosensitizer from the solvent and desulfurized hydrocarbon stream must be done to increase product yield and economic efficiency. Aromatics are usually recovered by liquid–liquid extraction using light paraffinic solvents and are subsequently blended into the desulfurized fuel stream. DCA is removed by adsorption, using a silica gel as an adsorbent. It can be returned to the process after desorption with aqueous solution of acetonitrile. All of these processes are rather common refinery processes can be easily integrated into the refinery and do not require special equipment or conditions. This photooxidation process showed a high selectivity to remove organic sulfur compounds from light oils, catalytic-cracked gasoline and vacuum gas oils. For fuels with higher aromatics content, efficiency is slightly lower but it was claimed that above 99% of the sulfur was removed from a vacuum gas oil.[7]

2.6. Biodesulfurization

Biodesulfurization is a process that removes organic sulfur compounds from fossil fuels using enzyme-catalyzed reactions. Certain microbial biocatalysts have been identified that can biotransform sulfur compounds found in fuels, including ones that selectively remove sulfur from DBT heterocyclic compounds (Figure 6).

Energy Biosystems Inc. has developed a biodesulfurization process which involves the removal of organic sulfur compounds from distillate or naphtha streams using bacteria. The distillate stream is first mixed with an aqueous media containing the bacteria, caustic soda and nutrients for the bacteria. Enzymes in the bacteria first oxidize the sulfur atoms and then cleave some of the sulfur–carbon bonds. The sulfur leaves the process in the form of hydroxyphenyl benzene sulfonate, which can be used commercially as a feedstock to produce surfactants. Designs based on pilot plant studies combine biodesulfurization with conventional hydrotreating to produce low sulfur diesel fuel.[9]

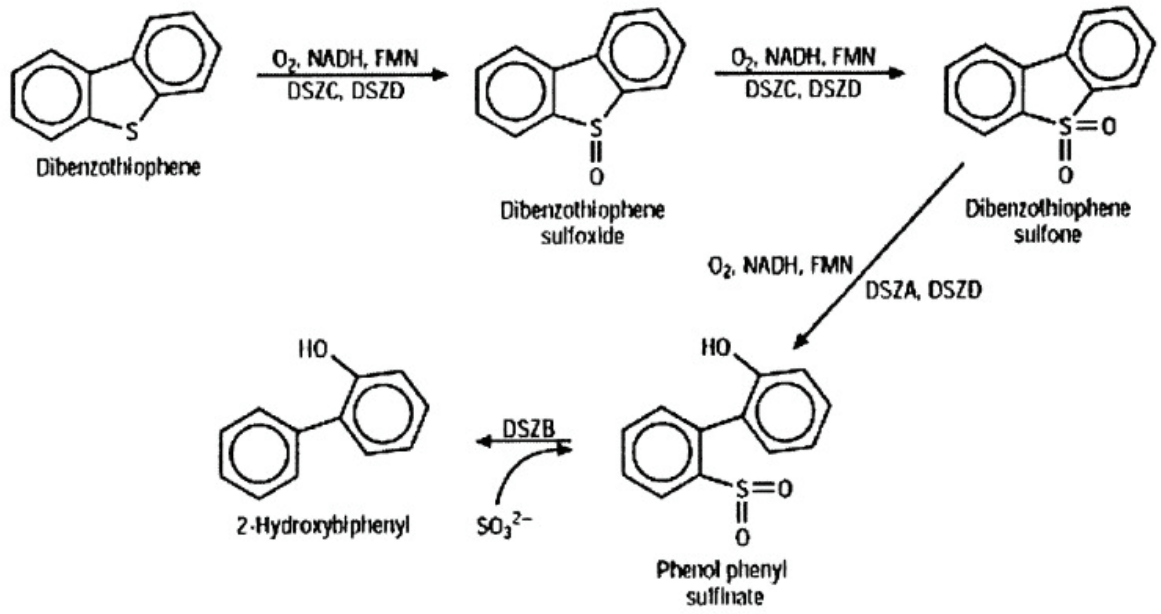


Figure 6. The pathway of biological desulfurization of DBT various bacterial species.[9]

Biodesulfurization, which operates under ambient temperature and pressure, is expected to be a complement and a promising alternative to HDS. However, biodesulfurization of fuels is still not a commercial technology because some problems have to be solved. Stability and life-time of biocatalyst are two crucial factors. In order to solve these problems, cell immobilization, which has been widely studied and applied in recent years, is considered to be a potential method. Recent discoveries related to biodesulfurization mechanisms may lead to commercial applications of biodesulfurization through engineering recombinant strains for over-expression of biodesulfurization genes, removal of end product repression, and/or by combining relevant industrial and environmental traits with improvements in bioprocess design. With bioprocess improvements that enhance biocatalyst stability, achieve faster kinetics, improve mass transfer limitations, temperature and solvent tolerance, as well as broaden substrate specificity to attack a greater range of heterocyclic compounds, biocatalysis may be a cost-effective approach to achieve the production of low sulfur gasoline.[9,32]

3. CONCLUSIONS

The alternative desulfurization processes including advanced HDS processes, separation processes adsorption and extraction, oxidation and biodeuslufirazion processes are being developed because conventional HDS process experiences difficulties in producing fuels in accordance with latest regulations, i.e. environmentally friendly fuels. From the technological stand point it was prudent to first try to improve the current HDS catalysts and reactors, but it soon became clear that if significant advancement should be made new types of HDS catalysts and reactor designs had to be developed. At the

same time the research and development of adsorptive, extractive and oxidative desulfurization and biodesulfurization processes intensified. Up to this point there were several successful commercial processes installed in the refineries including reactive adsorption S-Zorb process and extractive desulfurization Sulf-X process. However, for the most part these alternative desulfurization processes are still being researched and developed in laboratories and pilot plants, but some very encouraging results indicate real economic viability and that widespread commercial application is not far away. It should be noted that more research is needed and all processes should be able to find their place on the market.

REFERENCES

[1] F. Pardal, G. Tersac, Comparative reactivity of glycols in PET glycolysis, Polym. Degrad. Stab. 91 (2006) 2567-2578.

[1] Z.Y. Zhang, T.B. Shi, C.Z. Jia, W.J. Ji, Y. Chen, M.Y. He, Adsorptive removal of aromatic organosulfur compounds over the modified Na-Y zeolites. Appl. Catal. B: Environ, 82 (2008) 1–10.

[2] X. Ma, L. Sun, C. Song, A new approach to deep desulfurization of gasoline, diesel fuel and jet fuel by selective adsorption for ultra-clean fuels and for fuel cell applications. Catal. Today 77 (2002) 107–116.

[3] Y.A. Alhamed, H.S. Bamufleh, Sulfur removal from model diesel fuel using granular activated carbon from dates' stones activated by ZnCl2, Fuel 88 (2009) 87–94.

[4] J.H. Kim, X. Ma, A. Zhou, C. Song, Ultra-deep desulfurization and denitrogenation of diesel fuel by selective adsorption over three different adsorbents: a study on adsorptive selectivity and mechanism, Catal. Today 111 (2006) 74–83.

[5] S. Brunet, D. Mey, G. Perot, C. Bouchy, F. Diehl, On the hydrodesulfurisation of FCC gasoline: a review, Appl. Catal. A-Gen. 278 (2005) 143-172.

[6] C. Song, An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, Catal. Today 86 (2003) 211–263.

[7] I.V. Babich, J.A. Moulijn, Science and technology of novel processes for deep desulfurization of oil refinery streams: a review, Fuel 82 (2003) 607–631.

[8] P. Baeza, G. Aguila, F. Gracia, P. Araya, Desulfurization by adsorption with copper supported on zirconia, Catal. Commun. 9 (2008) 751–755.

[9] C. Song, X. Ma, New design approaches to ultra-clean diesel fuels by deep desulfurization and deep dearomatization, Appl. Catal. B-Environ. 41 (2003) 207–238.

[10] M. Breysse, G. Djega-Mariadassou, S. Pessayre, C. Geantet, M. Vrinat, G. Perot, M. Lemaire, Deep desulfurization: reactions, catalysts and technological challenges, Catal. Today 84 (2003) 129–138.

[11] V. Rabarihoela-Rakotovao, S. Brunet, G. Perot, F. Diehl, Effect of H_2S partial pressure on the HDS of dibenzothiophene and 4,6-dimethyldibenzothiophene over sulfided $NiMoP/Al_2O_3$ and $CoMoP/Al_2O_3$ catalysts, App. Catal. A-Gen. 306 (2006) 34–44.

[12] S. Haji, Y. Zhang, D. Kang, M. Aindow, C. Erkey, Hydrodesulfurization of model diesel using Pt/Al_2O_3 catalysts prepared by supercritical deposition, Catal. Today 99 (2005) 365–373.

[13] R.M. Navarro, P. Castano, M.C. Alvarez-Galvan, B. Pawelec, Hydrodesulfurization of dibenzothiophene and a SRGO on sulfide $Ni(Co)Mo/Al_2O_3$ catalysts. Effect of Ru and Pd promotion, Catal. Today 143 (2009) 108–114.

[14] E. Ito, J.A. van Veen, On novel processes for removing sulphur from refinery streams, Catal. Today 116 (2006) 446–460.

[15] M. Mužic, K. Sertić-Bionda, Z. Gomzi, S. Podolski, S. Telen, Study of diesel fuel desulfurization by adsorption, Chem. Eng. Res. Des. 88 (2010) 487–495.

[16] M. Mužic, K. Sertić-Bionda, Z. Gomzi, Kinetic and Statistical Studies of Adsorptive Desulfurization of Diesel Fuel on Commercial Activated Carbons, Chem. Eng. and Technol. 31 (2008) 355-364.

[17] M. Mužic, K. Sertić-Bionda, T. Adžamić, Z. Gomzi, Š. Podolski, Optimization of diesel fuel desulfurization by adsorption on activated carbon, Chem. Eng. Transact. 17 (2009) 1549-1554.

[18] M. Mužic, K. Sertić-Bionda, Z. Gomzi, A Design of Experiments Investigation of Adsorptive Desulfurization of Diesel Fuel, Chem. Biochem. Eng. Q. 24 (2010) 253-264.

[19] M. Mužic, Z. Gomzi, K. Sertić-Bionda, Modeling of the Adsorptive Desulfurization of Diesel Fuel in a Fixed-Bed Column, Chem. Eng. Technol. 33 (2010) 1137-1145.
[20] M. Mužic, K. Sertić-Bionda, T. Adžamić, Desulfurization of Diesel Fuel in a Fixed Bed Adsorption Column: Experimental Study and Simulation, Pet. Sci. Technol., In Press.
[21] M. Mužic, K. Sertić-Bionda, T. Adžamić, Adsorptive Removal of Dibenzothiophene from Model Gasoline Solution, Proceedings of the 37th International Conference of Slovak Society of Chemical Engineering, Slovakia, 2010.
[22] T. Adžamić, K. Sertić-Bionda, Z. Zoretić, Desulfurization of FCC gasoline by extraction with sulfolane and furfural, Nafta 60 (2009) 7-8.
[23] T. Adžamić, K. Sertić-Bionda, N. Marčec-Rahelić, Modeling of FCC Gasoline Desulfurization Process by Liquid Extraction with Sulfolane, Pet. Sci. Technol. 28 (2010) 1936-1946.
[24] J. Eβer, P. Wasserscheid, A. Jess, Deep desulfurization of oil refinery streams by extraction with ionic liquids, Green Chem. 6 (2004) 316-322.
[25] M.C. Capel-Sancheza, P. Perez-Presasa, J.M. Campos-Martin, J.L.G. Fierroa, Highly efficient deep desulfurization of fuels by chemical oxidation, Catal. Today 157 (2010) 390-396.
[26] S. Dhir, R. Uppaluri, M.K. Purkait, Oxidative desulfurization: Kinetic modelling, J. Hazard. Mater. 161 (2009) 1360–1368.
[27] P.S. Tam, J.R. Kitrell, J.W. Eldridge, Desulfurization of Fuel-Oil by Oxidation and Extraction. 1. Enhancement Of Extraction Oil Yield, Ind. Eng. Chem. Res. 29 (1990) 321-324.
[28] D. Wang, E.W. Qian, H. Amano, K. Okata, A. Ishihara, T. Kabe, Oxidative desulfurization of fuel oil Part I. Oxidation of dibenzothiophenes using tert-butyl hydroperoxide, Appl. Catal. A-Gen. 253 (2003) 91–99.
[29] Y. Hangun, L. Alexandrova, S. Khetan, C. Horwitz, A. Cugini, D.D. Link, B. Howard, T.J. Collins, ACS Petr. Chem. Div. Prepr. 47 (2002) 42.
[30] Y. Dai, Y. Qi, D. Zhao, H. Zhang, An oxidative desulfurization method using ultrasound/Fenton's reagent for obtaining low and/or ultra-low sulfur diesel fuel, Fuel Process. Technol. 89 (2008) 927–932.
[31] F.J. Liotta, Y. Han, Production of Ultra-Low Sulfur Fuels by Selective Hydroperoxide Oxidation, Lyondell Chemical Company, NPRA Anual Meeting, Newtown Square, PA, 2003.
[32] Y. Hou, Y. Kong, J. Yang, J. Zhang, D. Shi, W. Xin, Biodesulfurization of dibenzothiophene by immobilized cells of Pseudomonas stutzeri UP-1, Fuel 84 (2005) 1975–1979.

IRON-ALUMINUM SOLID SOLUTION IN KLEIN'S COMPOUND

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Abstract

Over again, much attention has been given to the development of special cement clinkers, leading to energy saving and better environmental management. One of such cements is the calcium sulfoaluminate cements (CSAC), an economical and environmental friendly alternative to Portland cement. The key mineral of CSAC is the Klein's compound ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$ i.e. C_4A_3s in shortened cement mineralogy notation), because of its hydration reaction ability to produce ettringite. C_4A_3s based cements are used commercially in increasing quantities, but several aspects of its solid state production as well as hydraulic reactivity appear to be difficult to control. It is known that iron-aluminum substitution influence its reactivity. In order to investigate iron-aluminum solid solution in C_4A_3s, the following bulk compositions were made, $C_4A_{3(1-x)}F_{3x}s$, where x equals: 0.05, 0.07, 0.09, 0.11, 0.13, 0.15, 0.17 and 0.19. Qualitative X-ray diffraction analysis (XRD) of samples prepared revealed only partial iron-aluminum substitution at 1100 °C, the rest of the iron giving up minerals: magnetite (Fe_3O_4), ferrite phase ($C_2(A,F)$) and srebrodolskite (C_2F).

Keywords: *special cement, Klein compound, solid solution, X-ray powder diffraction*

1. INTRODUCTION

Climate change is a global environmental issue of the 21st century and also one of the biggest challenges for the mankind. The effects of climate change, especially emission of greenhouse gases are more and more visible every day and those changes also have adverse influence on global economy, environment and society. Having in mind the growth of population, it is a prerequisite for the industry to find new improved ways of energy, material resources and waste management in a sustainable way. The cement industry is not to be excluded because cement production needs vast quantity of raw materials and fuel followed by large CO_2 emissions. Nowadays, cement factories are proactive regarding industrial ecology because waste materials and by-products of various origins are used in the manufacture of ordinary Portland cement (OPC) or other special cements either as a supplementary fuel or raw meal component. A possible route for production of new calcium sulfoferoaluminate (CSAF) special cement from waste materials is depicted in this work. By developing an alternative way of waste reuse, the risk of possible water and/or soil pollution as well as a cost of its remediation is significantly lowered. Further benefit of this practice is lower consumption of natural resources. It is estimated that cement industry contributes up to 7% of total anthropogenic emissions of CO_2, while current worldwide cement production is of the order of 2 billion tons per year. Since concrete as a building (construction) material has no alternative, the cement industry is actively involved in, and contributes to the solution of the greenhouse gases emission and climate change. Recent investigations of calcium sulfoferoaluminate special cements seem promising in that direction because it has a great potential of waste gypsum reuse, along with bottom ashes, electric arc furnace slags (EAFS) etc. Calcination temperature is lower for CSAF cement than during the production of ordinary Portland cement and the final product is also easier to grind. Main mineral of CSAF cement is Kleinite, C_4A_3s. CSAF cements are used commercially in increasing quantities, but several aspects of its solid state production as well as hydraulic reactivity appear to be difficult to control. It is known that iron-aluminum substitution influence this reactivity.

In cement chemistry it is a usual practice to use shortened notation of complex chemical composition of numerous minerals (see Table 1). Accordingly, the composition of Kleinite, $3CaO{\times}3Al_2O_3{\times}CaSO_4$ is written as C_4A_3s.

Table 1. Shortened symbol notation used in cement chemistry

Oxide	CaO	Al_2O_3	SiO_2	SO_3	Fe_2O_3	H_2O	MgO	TiO_2
Symbol	C	A	S	s	F	H	M	T

1.1. Calcium Sulfoaluminate

In the four component phase diagram $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}SO_3$, there are two ternary compounds: calcium sulfoaluminate and calcium sulfosilicate [1]. Calcium sulfoaluminate ($Ca_4(Al_6O_{12})(SO_4)$, or C_4A_3s), gives up mineral Kleinite and is also known as Klein compound. It is prepared by calcination of the appropriate oxide mixture at temperatures 1250-1300 °C [2-5] according to the equation 1.

$$3CaCO_3 + 3Al_2O_3 + CaSO_4{\times}2H_2O \rightarrow 4CaO{\times}3Al_2O_3{\times}SO_3 + 3CO_2 + 2H_2O \quad (1)$$

This compound is stable up to the temperature of 1350-1400 °C.

Crystal structure of Klein compound consists of the three dimensional lattice of AlO_4 tetrahedra in corners with Ca^{2+} and SO_4^{2-} ions in cavities formed by AlO_4 tetrahedra. This compound belongs to the tetragonal system [4]. At temperatures in excess of about 1350 °C Kleinite becomes unstable and begins to decompose [6]. Al^{3+} within the structure of C_4A_3s could be partially substituted by Fe^{3+} ions [7]. Reactivity with water decreases as the iron substitution increases.

2. ELABORATION

2.1. Experimental

2.1.1. Materials

The following materials: $CaCO_3$, *pro analysi*, Kemika, Zagreb; $Al(OH)_3$, Alcoa, Ohio; $Fe(NO_3){\times}9H_2O$, E. Merck, Darmstadt; and $CaSO_4{\times}2H_2O$, *pro analysi*, E. Merck, Darmstadt, had been used for preparation of the raw mixes with the selected oxide composition. Pure Si powder (Shimadzu Corporation, Japan) had been added to the synthesized materials prior to X-ray powder diffraction analysis.

2.1.2. Preparation and homogenization of precursor materials

Eighth raw mixes of precursor materials with increasing iron oxide content, according to the following bulk oxide composition: $C_4A_{3(1-x)}F_{3x}s$, where x equals: 0.05, 0.07, 0.09, 0.11, 0.13, 0.15, 0.17 and 0.19 had been synthesized (Table 2). In all of the samples prepared the mass of the $CaCO_3$ and $CaSO_4{\times}2H_2O$ remains constant, while the mass of the $Fe(NO_3)_3{\times}9H_2O$ increases as the mass of the $Al(OH)_3$ decreases.

Table 2. Masses of precursor materials used for raw mixes of selected bulk oxide composition corresponding to $C_4A_{3(1-x)}F_{3x}s$, where $0.05 < x < 0.19$

sample	x	$m(CaCO_3)$, g	$m(Al(OH)_3)$, g	$M(Fe(NO_3)_3{\times}9H_2O)$, g	$m(CaSO_4{\times}2H_2O)$, g
1	0.05	10.0086	14.8205	4.0399	5.7390
2	0.07	10.0086	14.5085	5.6559	5.7390
3	0.09	10.0086	14.1965	7.2718	5.7390
4	0.11	10.0086	13.8845	8.8878	5.7390
5	0.13	10.0086	13.5725	10.5037	5.7390
6	0.15	10.0086	13.2605	12.1197	5.7390
7	0.17	10.0086	12.9484	13.7357	5.7390
8	0.19	10.0086	12.6364	15.3516	5.7390

Precursor materials had been weighted on analytical balance, and wet homogenized in planetary mill (Pulverisette 5, Fritsch GmBh, Germany) for 5 min at 250 rpm.

2.1.3. Drying of precursor mixes

After wet homogenization in planetary mill, dense suspension of precursor materials had been dried in drying chamber at 130 °C.

2.1.4. Calcination of precursor mixes

Precursor mixes prepared had been calcined in laboratory furnace at 1100 °C for 4 hours (in porcelain crucibles with lids). Heating rate was 10°C min^{-1}, and after soaking, the furnace left to cool naturally.

2.1.5. Grinding of Calcined Samples

Calcined mixes had been comminuted by hand in mortar with pestle. All of the samples had been easy to grind.

2.1.6. X-Ray Powder Diffraction of Calcined Mixes

Mineralogical phase composition of calcined samples had been determined by X-ray powder diffraction analysis on H-6000 manufactured by Shimadzu, Japan. Characteristic copper X-ray radiation had wavelength of $\lambda(CuK_\alpha) = 0.15418$ nm.

2.2. Results

The iron-aluminum solid solution of Kleinite mineral had been studied. Previous study of iron-aluminum solid solution of characteristic minerals of calcium aluminate cement had shown that large differences in calculated potential phase composition arise by not taking into account the formation of iron-aluminum solid solution [8]. Mixture of precursor materials with bulk oxide composition corresponding to $C_4A_{3(1-x)}F_{3x}s$, where x takes the following values: x = 0.05, 0.07, 0.09, 0.11, 0.13, 0.15, 0.17, 0.19 had been prepared, homogenized, dried and calcined at 1100 °C for 4 hours. The samples prepared had ochre color that is more intense for greater iron addition. Elementary silicon had been added to the calcined samples (10% by mass), and results of X-ray powder diffraction are shown in Figs. 1-3.

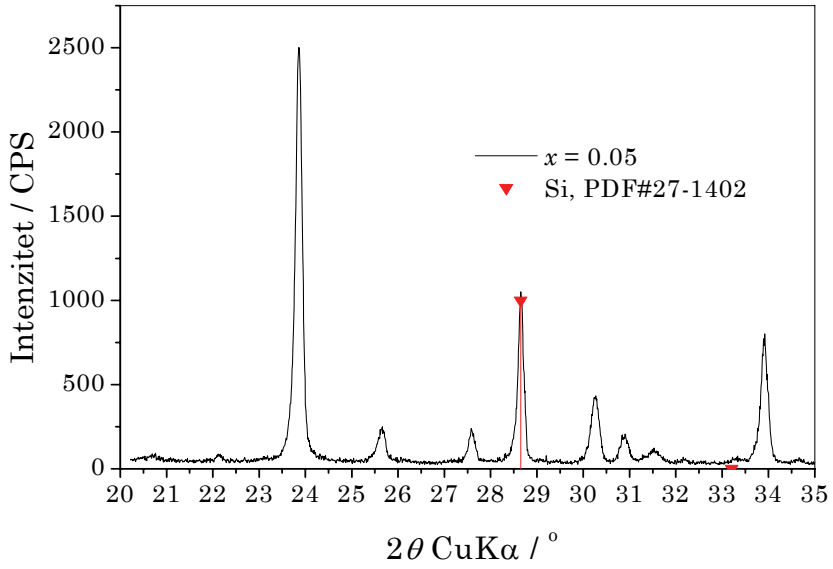


Figure 1. X-ray diffraction of calcined mixture of precursor materials corresponding to the following potential composition of Klein compound, $C_4A_{3(1-x)}F_{3x}s$, where x=0.05. The position of silicon standard (10% by mass) is marked red.

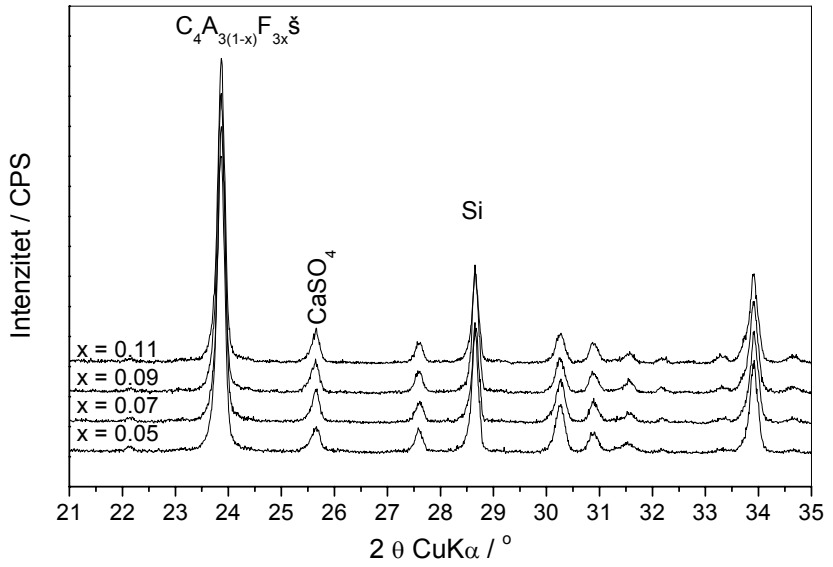


Figure 2. X-ray diffraction of calcined mixtures of precursor materials corresponding to the following potential composition of Klein compound, $C_4A_{3(1-x)}F_{3x}s$, where x=0.05, 0.07, 0.09 and 0.11. Traces of anhydrite mineral, $CaSO_4$, is present in the calcined samples

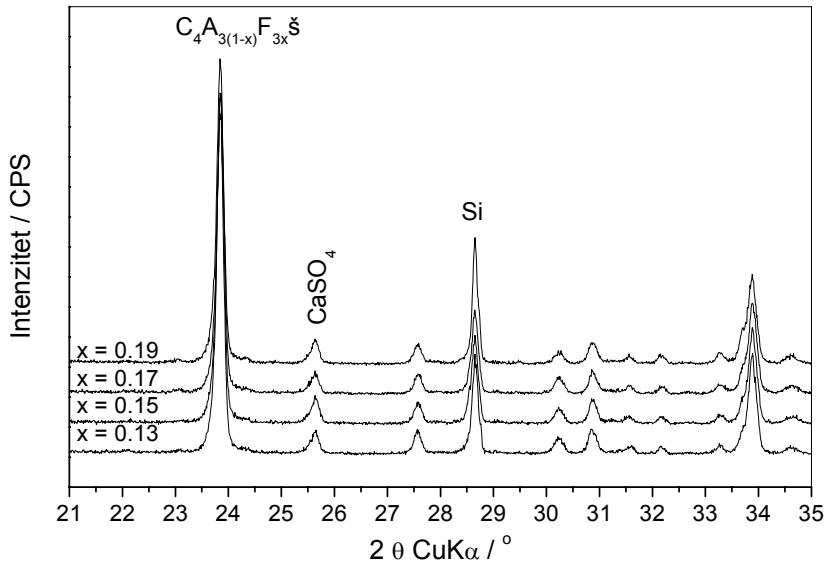


Figure 3. X-ray diffraction of calcined mixtures of precursor materials corresponding to the following potential composition of Klein compound, $C_4A_{3(1-x)}F_{3x}s$, where x=0.13, 0.15, 0.17 and 0.19. Traces of anhydrite mineral, $CaSO_4$, is present in the calcined samples.

The systematic offset of the diffractogram had been corrected relative to diffraction peak of silicon (most intense reflection (111), at 28.443° 2θ CuK_α, PDF#27-1402). In the Table 3, the corrected position of the diffraction peak of Kleinite is given

Table 3. Diffraction peak position of Klein compound for the 8 calcined samples prepared.

$x(Fe_2O_3)$	Kleinite, raw data	Si, raw data	Offset vs. Si	Kleinite, corrected
*0	-	-	-	*23.662
$^{\$}$0.05	-	-	-	$^{\$}$23.640
0.05	23.858	28.653	-0.210	23.648
0.07	23.869	28.661	-0.218	23.651
0.09	23.86	28.658	-0.215	23.645
0.11	23.864	28.658	-0.215	23.649
0.13	23.842	28.656	-0.213	23.629
0.15	23.849	28.649	-0.206	23.643
0.17	23.851	28.652	-0.209	23.642
0.19	23.844	28.653	-0.210	23.634

*- literature data, PDF#33-0256
$^{\$}$- literature data, PDF#51-0162

Beside the presence of Kleinite in the calcinded samples prepared, traces of anhydrite ($CaSO_4$) and magnetite (Fe_3O_4) are also detected. Beside the determined positions of diffraction peak of Kleinite in the samples prepared, in the Table 3, the literature data on the position of the diffraction peak of Kleinite containing iron (x=0.05) and without iron are also given. Results are depicted in Fig. 4, where the dotted horizontal line corresponds to the position of Kleinite (containing iron, x=0.05) diffraction peak (2θ =23.640° CuKα, PDF#51-0162).

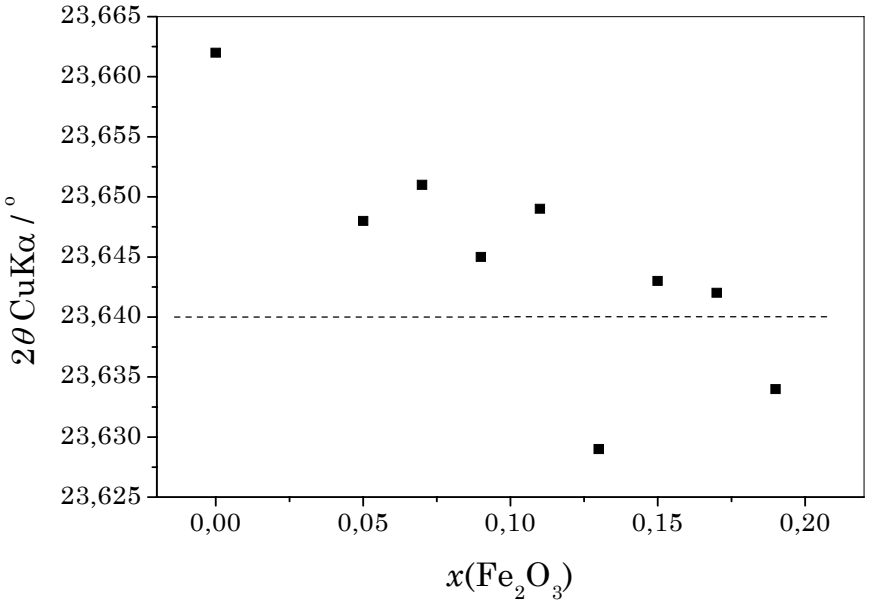


Figure 4. Dependence of Kleinite diffraction peak position on the bulk chemical oxide composition corresponding to: $C_4A_{3(1-x)}F_{3x}s$, where x equals: 0.05, 0.07, 0.09, 0.11, 0.13, 0.15, 0.17 and 0.19. The dotted horizontal line corresponds to the position of Kleinite (containing iron, x=0.05) diffraction peak (2θ =23.640° CuKα, PDF#51-0162)

2.3. Discussion

Ordinary Portland cement mainly consists of minerals alite (C_3S) and belite (C_2S) which contribute to the strength and durability of the prepared binders and concrete. Calcium aluminate cement is another type of cement and is also continuously produced during last 100 years (on a much smaller scale). Calcium aluminate cement consists mainly of calciumaluminate mineral (CA) that is responsible for its rapid hardening characteristics. Mineralogical composition of inorganic binders is not exhausted by those two main types of cements, because there exist a number of other mineral assemblages with interesting hydraulic properties and various potential applications. By addition of gypsum or anhydrite as a component of cement raw mix (consisting mainly of CaO, SiO_2, Al_2O_3 and Fe_2O_3), a new mineral appears, Kleinite or Klein compound, of the following chemical composition: C_4A_3s. Cement materials containing Kleinite belong to the class of sulfoaluminate cements [1]. Sufoaluminate cements could be further divided with respect to the other main minerals as: calcium sulfoaluminate-bellite, calcium sulfoaluminate-ferrite, or calcium sulfoferroaluminate-bellitni cements, etc.

Mineral composition of calcium sulfoferroaluminate cement is quite complex because of large number of mineral phases [9] that could be present within this (at least) fivecomponent system formed by the following oxides: CaO, Al_2O_3, SO_3, SiO_2 and Fe_2O_3. Some of the compounds form iron-aluminum solid solutions. This research addresses the question of main compound (Kleinite) iron-aluminum solid solutions. Starting from the pure precursor materials ($CaCO_3$, $Al(OH)_3$,×$CaSO_4$×1/2H_2O and $Fe(NO_3)_3$×9H_2O), a number of potential solid solutions compositions had been prepared ($C_4A_{3(1-x)}F_{3x}s$, where x = 0.05, 0.07, 0.09, 0.11, 0.13, 0.15, 0.17, 0.19). Qualitative X-ray diffraction analysis of the samples calcined at 1100 °C for 4h showed traces of magnetite (Fe_3O_4), ferrite phase ($C_2(A,F)$), srebrodolskite (C_2F) and anhydrite ($CaSO_4$) beside Kleinite, main mineral product. Elementary silicon added as a standard to the samples prepared, enabled precise determination of diffraction peak position. It had been established that Kleinite diffraction peak position does depend on the quantity of iron-oxide in raw mixture. The exact position of Kleinite diffraction peak for x=0 and x=0.05 is known (Table 3), and it was argued that iron-aluminum solid solution has its 5% maximum/limit [1]. It is thus possible to determine actual composition of Kleinite (regarding the iron-aluminum solid solution) from the X-ray diffraction data. Unfortunately, two preparations of Kleinite (x=0.13 i x=0.19, Fig. 4) apparently show greater iron-aluminum substitution. This point needs further clarification because Andac and Glasser [10], based on the results of microcrystal chemical composition determination, had shown that significant deviations from idealized stoichiometry of Kleinite are likely to appear. The following compositions of monocrystals had been determined by electron microprobe: $Ca_{3.82}Al_{6.11}S_{1.02}O_{16}$, $Ca_{3.78}Al_{5.80}Fe_{0.30}S_{1.02}O_{16}$,

etc. Frequently cited iron-aluminum solid solution of Kleinite is about 2-3%, and 5% iron-aluminum substitution is referred to as an upper limit.

3. CONCLUSIONS

Kleinite is a main mineral of calcium sulfoaluminate cements and its reactivity is influenced by iron-aluminum solid solution composition. Kleinite solid solution forms spontaneously during production from the iron impurities present in the raw meal. The usual iron-aluminum solid solution substitution reported is about 2-3%, while its maximum is about 5%. The rest of iron-oxides present in calcium sulfoaluminate cement raw meal forms a new iron bearing phases, i.e. magnetite (Fe_3O_4), ferrite phase ($C_2(A,F)$) and srebrodolskite (C_2F).

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REFERENCES

[1] I. Odler, Special inorganic cements, E&FN Spon, London, 2000.
[2] L. Santoro, R. Garofano, G.K. Valenti, Calcium sulphoaluminate made from phosphogypsum and its hydration properties, in *Proceedings 8th ICCC*, *Rio de Janeiro*, (1986) Vol. 4, pp. 389-394.
[3] J. Havlica, S. Sahu, Thermodynamics and kinetics in the system $Ca_4(Al_6O_{12})(SO_4)$-$CaSO_4 \cdot 2H_2O$-H_2O up to 75 °C, in *Proceedings 9th ICCC*, *New Delhi*, (1992) Vol. 4, pp. 157-163.
[4] P. Zhang, *et al*. The crystal structure of C_4A_3S, in *Proceedings 9th ICCC*, *New Delhi*, (1992) Vol. 3, pp. 201-208.
[5] J.H. Sharp, C.D. Lawrence, R. Yang, Calcium sulfoaluminate cements - low-energy cements, special cements or what. *Advances in Cement Research* 11 (1999) 3-13.
[6] F. Puertas, M.T.B. Varela, S.G. Molina, Kinetics of thermal decomposition of C_4A_3S□ in air. *Cement and concrete research* 25 (1995) 572-580.
[7] M. Muntean *et al*. Synthesis of calcium sulfoferroaluminates and their properties. *Materiale de Constructii (Bucharest)* 281 (1998) 60-64 [ref. CA 129/57741]
[8] I. Mijakovac, Preparation and investigation of mineral phases of calcium aluminate cements (in Croatian)/Graduate work, *Faculty of Chemical Engineering and Technology,* (2002) Zagreb.
[9] J. Beretka *et al*. Hydraulic behaviour of calcium sulfoaluminate-based cements derived from industrial process waste. *Cement and Concrete Research* 23 (1993) 1205-1214.
[10] M. Andac, F.P. Glasser, Microstructure and microchemistry of calcium sulfoaluminate cement. *Materials Research Society Symposium Proceedings* 370 (1995) 135-142.

SUSTAINABLE ENVIRONMENT MANAGEMENT IN CERAMIC TILES PRODUCTION

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Abstract

Ceramic industry in the world has a significant impact to the environment due to emissions to the air, soil and water that adversely affects wildlife, people and human health. The negative impacts of ceramic industry can be reduced by investing in better and cleaner technology. In this work is described the methodology for diminishing of harmful influences to the environment and its application. The production process of ceramic tiles in mono-firing technology is described. The possibilities for diminishing of harmful influence of particular phases of this process are analyzed. This paper describes the application of new methods to assess the impact and reduce the environmental impact of ceramic industry: methodology of clean production and method for increasing of energy efficiency (ECO-Energy Conservation Opportunity). The clean production methodology enables the evaluation of particular phases of life cycle of ceramic tiles by choosing of weight coefficients of particular criteria. The environmental influences are reduced by increasing the energy efficiency of production also. The presented results were analyzed by applying cleaner production methods and other methods for increasing energy efficiency and diminishing of harmful influences to the environment. These methods were applied in ceramic tiles factory KIO Keramika d.o.o. in Orahovica. This factory works by technology of mono-firing according to the standards HRN EN I 14 411 group B III part L. The certified management systems by standards ISO-9001 and ISO 14001 are used.

Keywords: ceramic tiles, sustainable development, life cycle assessment, ECO indicator, increase energy efficiency, cleaner production

1. INTRODUCTION

During the strong industrial development in the sixties and seventies of the last century the impact of production processes on pollution environment increased. In the eighties, the great progress in technology of production of ceramic tiles was development of a tunnel kiln for mono-firing. In one burning the body and glazer burnt in a single layer, thus reducing gas consumption per unit area from 5.0 to 2.5 m^3. By reducing gas consumption, emissions of harmful substances into the atmosphere are reduced. In recent years, manufacturers and consumers tend to produce and apply the products produced by processes that are acceptable from the standpoint of preserving the environment. Such products are called environmentally friendly products [1].

This tendency is present in the production of ceramic tiles too. It is therefore important to analyze the possibility of reducing the impact of ceramic tile production on the environment and take action to reduce the impact of the process through the introduction of new environmentally friendly technologies. Cleaner production and energy efficiency methodologies are included in the strategy applied in the industry of ceramic tiles KIO d.o.o. Tiles declared standard EN 14 411 I III group B annex L are produced in this company by mono-firing technology. The company has introduced and certified management system according to ISO-9001 and ISO 14001.

2. ELABORATION

2.1. Sustainable Development and Ceramic industry

The environmental legislation initially focused on protecting water and air, and then to control waste. In the seventies the theory of waste management was based on dilute and disperse principle, while the

newer theories are based on the prevention of waste. Efforts invested so far are apparently not sufficient, because the global environmental situation continues to deteriorate: energy consumption is growing, greenhouse gases, stacks, use of drinking water are all limited in agricultural soils are still unresolved, the area preserved and further reduce the crop, the list of endangered species longer, etc.

In recent years the importance of ceramic tiles as a building material is growing. Increasingly used for wall cladding and flooring. The development of techniques and technology of new materials today resulted in manufacturing tiles with outstanding characteristic of the aesthetic look as natural materials, marble, wood and stone.

2.1.1. Ceramic Tiles Production Process

The production of ceramic tiles consists of several sub-processes:

(i) Preparation of the raw tiles including: preparation of mass by wet grinding; preparation of granules by atomizing mass; pressing of granules in molds under the heavy pressure; drying of pressed tiles in vertical dry kilns; and

(ii) Preparation of glaze by wet grinding; icing by depositing of glaze on the raw warm tile; burning of raw tile.

(iii) Sorting; visual control and selection of tiles in classes according to the standard EN 14411.

After selection, the tiles are packed in the card box, arranged on the palette, and wrapped by foil.

In Fig.1 the schematic diagram of ceramic tiles production process by mono-firing technology is presented.

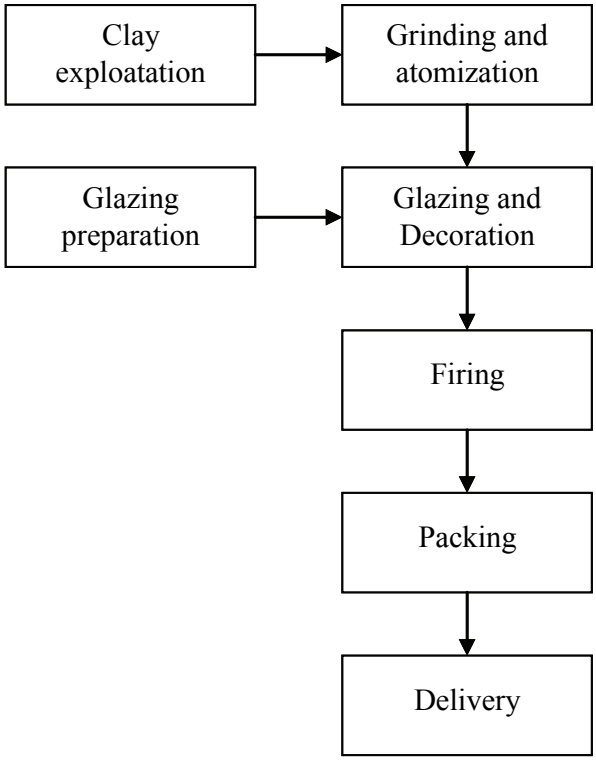


Figure1. Schematic diagram of ceramic tiles production process; mono-firing technology.

2.1.1.1. Environmental Influence

The influence on the environment is observed over the life cycle of ceramic tiles. Production process influences the environment through emissions, waste and usage of resources and materials. The most significant influences of ceramic industry on the environment are: gaseous emissions, water consumption and wastewater generation, consumptions of energy, waste and transport.

The of ceramic industry influence the environment is affecting the earth, water and the air [2]. The influence on earth is expressed through the consumption raw material, mainly clays, which are used for production of mass, the tile body, and other materials, mineral raw material and metal oxides used for production of frits and glazes.

Table 1.Influences of ceramic industry on environment

LIFE CYCLE PHASE	RAW MATERIALS	ENERGY	POLLUTION
Exploatation of raw materials	-clay -nonplastic materials	-electrical -oil -gasoline	gaseous emission
Reparation	-water -electrolyte	electrical	water
Spray drier	milling mass	gas	-steam -heat
Pressing	clay powder	electrical	-water -clay
Drying	raw tiles	-gas -electrical	dust
Glazing	-water -glue -poliglycol	electrical	chemicals
Firing	glazed tiles	-gas -electrical	-toxic gases -heat
Packing	-carton -wood -plastic	electrical	waste package
Utilization	-water -detergents	-	detergents

The influence on water is expressed through the consumption of relatively large amounts of water, which is used in the production process, and through the wastewater. The dirty polluted water is fed out to rivers and evaporates in the air via the water steam and gases, which emerges by burning of gas during processes of burning of tiles. There exists the strong influence on the environment, which has been expressed through the large consumption of gas and electricity. Influence of ceramic industry on the environment is presented in the Table 1.

2.1.1.2. Emission of Gasses

The process of burning in ceramic industry is significantly improved in last 20 years. Considerable improvements concerning the influence on the environment are achieved. Change from double-burning to mono-burning reduced the use of tunnel ovens and the high filling of carriage and reduced emissions of gases caused by tiles burning. Development of new technologies enables the modern ceramic industry lower costs in comparison to that before 20 year.

During burning of ceramic tiles by natural gas as a fuel, emerge NO_2 and CO_2, whose concentrations should be within allowed limits. In burning process of raw tiles, the largest are the emissions of water steam to the atmosphere that takes out 0,613 L/m^2 of tiles, causing warming up the atmosphere.

2.1.1.3. Water Consumption and Water Pollution

The water consumption depends on production technology and types of product, but in any case is relatively large [3]. It is reduced by usage of recycled wastewaters that is applied in KIO Keramika d.o.o. Water that is necessary for wet preparation of mixture for the tile mass evaporates completely during atomizing and burning. Water necessary for the preparation of glaze for the filling of mills finishes in the glaze that is inflicted during the glazing process. This water evaporates in the burnings process also. Water used for the mills washing finishes partially as wastewater. The part of that water is fed back to process with the exhaust glaze to the glaze preparation process and is used instead of the frit for some products. Water used in glazing process for device washing is partially discharged into river, and partially fed back to the process. The total water drawback is 6.5 L/m^2 consisting of water for washing of atomizing device and water in exhaust glaze waste.

2.1.1.4. Waste

The most significant influence of ceramic tile industry on the environment is waste that emerges during production of ceramic tiles, and emissions in the water and the gas in the atmosphere [4]. Waste that emerges during the process is represented by exhaust oil and paper, wooden pallets, plastic materials, metal waste, accumulators, fluorescent tubes and packing. The toxic waste, from the material which cannot be reused in the production process, is collected separately by legislative requirements in a way regulated by the standard ISO 14001 that is applied in the Management system of KIO Keramika d.o.o.

2.1.1.5. Transport

The production of ceramic tiles causes the increase of traffic on roads, so that daily production of 12.000 m^2 means around 6 trucks daily.

2.1.1.6.. Laying of ceramic tiles

Ceramic tiles are used for floor and walls covering and as final material. Ceramic tiles are laid down on the base using the connecting layer. The gap between tiles should be filled by special material. Materials for the connecting layer, adhesives, used for lying down and filling the gap are not harmful and their influence on the environment is completely limited [4].

2.1.1.7. Utilization of Ceramic Tiles

Because of good characteristics the tiles are strong, have the ruggedized structure, ruggedized are to abrasion and do not release metals because of the high chemical inertia, so do not have influence on the environment. The release of metals, or the ablution, is checked for tiles that are in touch with the food. The emission of tiles to environment is not greater than emissions of other materials in the atmosphere. The tiles radioactivity is low [5]. The tiles are dump proof. If they are exposed to fire, do not release toxic substances nor steam, therefore have no harmful influence on the health [6]. Thanks to good features ceramic tiles are exceptionally safe and hygienic. In phases of usage there is no emissions, for the cleaning uses the water with the supplement detergent, however in this case this wastewater does not consider. In the end of life cycle, after more years of usage, inevitably are tiles removing, transport and the disposal on the dump site construction waste.

2.1.2. Methods for Reducing the Influence on the Environment

It is possible to reduce the influences of ceramic tiles on the environment in all phases of manufacturing process, as presented in the Table 1.

2.1.2.1. Cleaner Production Methodology

The methodology of cleaner production is applied in many companies giving considerable savings. By definition of United Nations for the industrial development organization (UNIDO) the cleaner production is a continued application of comprehensive preventive strategy of environmental protection. It is applied on production process of products and services, in order to increase the efficiency and reduce the risk for men and environment. The raw materials and energy are used more efficiently. The usage of dangerous and toxicants is reduced, emissions and waste are reduced also.

The cleaner production is applied on diminishing of influences of products during whole life cycle of products and services from development, design and usages up to final disposals of tiles as ceramic reject in the end. The flows of materials and energy are analyzed in the production process in production stages. Inputs are quantified, and values are expressed financially. Data about quantities are checked so that corrections are carried out. Priorities and goals are determined as well as the plan of application [7].The gathered data on input materials are analyzed and calculated casualties on the reject.

Table 2.Activities scheduled in cleaner production methodology

Phase	Activity
I	Project preparation Preliminary estimation Action planning and Project organization
II	Analyzing
III	Feasibility
IV	Implementation
V	Utilization

The data from material balance, especially value of reject, are considered and protective actions are attempted because of the reject diminishing. The generating of ideas for improvement is done using brainstorming. The model is taken from business decision-making for idea selection in this project, which is often used in the environmental protection. In Table 3 is presented the example of environmental impact assessment, that is in view of decision models in the management environment best processed [8].

Form of decision-making in the environmental protection is represented by general expression given equation (1) (maximizations of total efficiency):

$$U_D(a^*) = \max U_i = \max \sum_{j=1}^{n} (W_j)(u_{ij}) \quad (1)$$

where:
W_j- weight coefficient of criterion,
U_i- total efficiency of alternative and
$U_D(a^*)$ -value of chosen mode.

The determination of weight coefficients W_j is predented in Table 3.

Table 3. Weight coefficients as a function of criteria

	Weight coefficients establishing						
Criterion	C_1	C_2	C_3	C_4	C_5	Raw sum	W_j
C_1	x	1	1	1	1	4	0.4
C_2	0	x	1	0	1	2	0.2
C_3	0	0	x	0	1	1	0.1
C_4	0	1	1	x	1	3	0.3
C_5	0	0	0	0	x	0	0
			Total			10	1.00

2.1.2.2 Power Efficiency Increasing Methodology

The method for increasing of energy efficiency (ECO-Energy Conservation Opportunity) is applied in order to reduce the energy consumption in stages of ceramic tiles production, the influence on the environment and total costs of energy. This method includes six possibilities for energy savings of largest gas users: atomizing device and kiln. Saving is achieved using the kiln waste heat in the atomizing device. It includes saving of electricity by modernization of lighting system in the production plant and the application of frequency converters in drives. This method of energy efficiency is realized in few phases: energy management establishment, increasing atomizer efficiency, exploitation of smoke gases, warmth lighting efficiency improvement, frequency converters controlled drives. The second phase is project phase in which particular points and modes are determined based on energy consumption data, in which the actions are done to increase the energy efficiency.

2.2. Results and Discussion

The diminishing of amount of resulting ceramic reject and write-down of water consumption arise by applying of chosen methods in ceramic tiles manufacturing.

2.2.1. Waste Diminishing

Good results on reject diminishing are fulfilled by the application of described clean production project in period of five years. Fig.2 represents the reject diminishing in relation to the reject in year 1997. The 6% of reject is used in the production process. This percentage is returned back in the production process. The reject amount, which has finished in the environment, is calculated by usage of data about the percentage of reject.

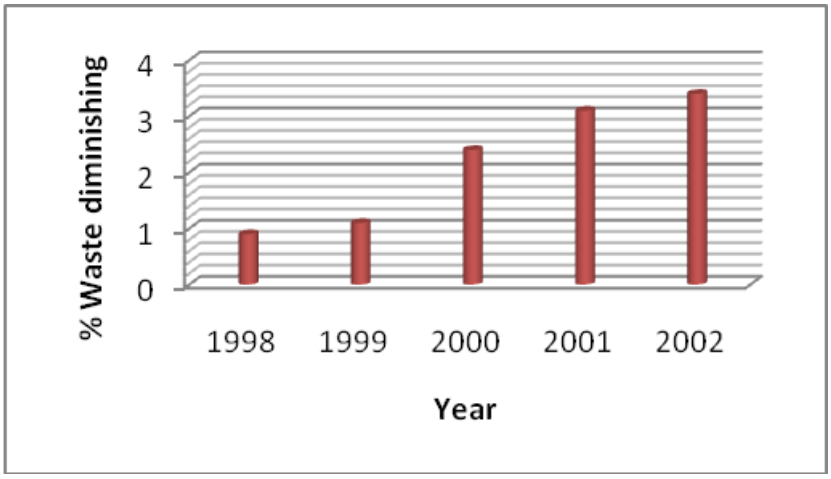


Figure.2. The waste diminishing based on waste in 1997.

2.2.2. Water Consumption Diminishing

Favorable results are achieved by application of described clean production project and suggested ideas for the diminishing of consumption in five years period. The water consumption data are presented on Fig.3. The savings in water consumptions is calculated yearly so is saved totally 99.910,8 m^3 in period from 1997 to 2003.

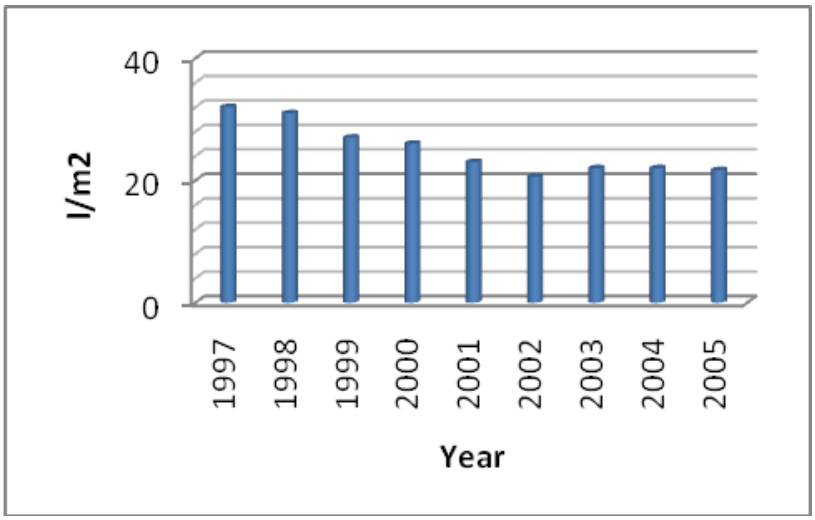


Figure 3. The water consumption diminishing

2.2.3. Gas and Electrical Energy Diminishing

The savings in consumptions of electricity and gas and reduced influence on the environment are achieved by application of model in real process. This method is also significant because reduces the gas consumption for around 5 % yearly, separately on the atomizer reduces for 20 %. The waste gases, which emerge by burning of natural gas, CO_2 and NO_2 from tiles firing kilns, are used for mud pre-heating in the atomizer. Based on reject diminishing data reduced gas consumption is calculated. Increasing the energy efficiency includes the recuperation as the main method of gas savings. Profitability of such project is achieved through the reduced gas and electricity consumption. On Fig.4 are presented the savings in natural gas consumption due to the decrease of reject.

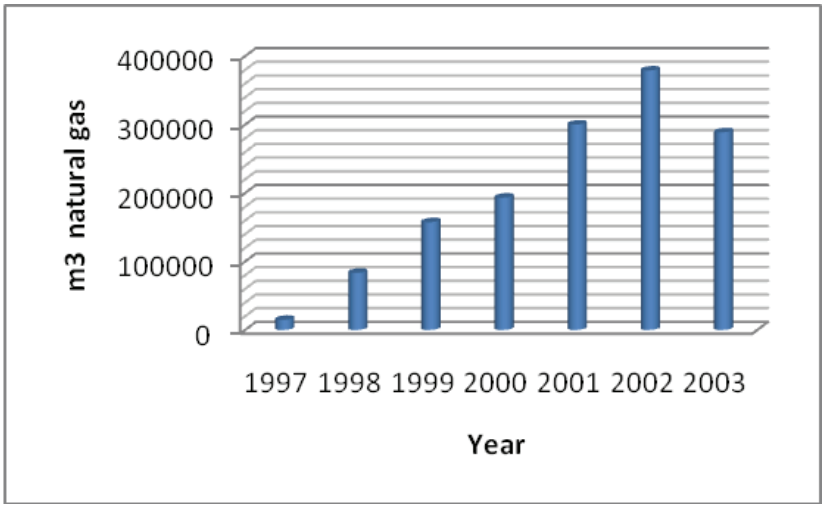


Figure 4. The gas consumption and diminishing after waste reduction

2.2.4. Power Efficiency Improvement

The methodology for establishing energy savings demands very precise measurements, repeating the measurement, and verification of obtained results. The basic energy consumption is measured before installation of frequency converters, using the short-term measurement of final consumers. These measures would need adequately characterizing 24-hour, seven-day weekly consumption of electricity.

The identical measurement is performed after installing of frequency converters. The constant measurement are performed in cases when cannot assume different loads of engines in advance. Improvement of lighting system and the application of light-fittings with the higher efficiency coefficient achieves reducing the consumption of electricity necessary for the lighting.

2.2.5. Diminishing Influence on Environment

The diminishing of influences of ceramic tiles on the environment by the application of Green model comprises in the write-down of influences of particular production phase of ceramic tiles. For easy reference obtained results after application of model in plants KIO Keramika d.o.o. are presented in Table 4.

Table 4.Green Model diminishing of influence on environment

Phase	Enivironmental influence	Reduction results
Raw preparation	Water consumption	From 32 to 22 L/m^2
Spray drier	Gas consumption	499.929 Nm^3 in 2005 569.120 Nm^3 in 2006
Spray drier	Electric power	407.128 kWh in 2005 412.736 kWh in 2006
Glazing	-Water consumption -Pigment consumption	Toxic mat. Group 2 0,62% in 2005
Firing	Gas emission	Gas reduction 40% CO_2, NO_2 – 40%

3. CONCLUSIONS

The methodologies for diminishing of harmful influences on environment are described in this paper. The results achieved by its application are presented. The technological manufacturing process of ceramic tiles is described and possibilities of decreasing the harmful influence of particular phases this process are analyzed.

The diminishing of influences of ceramic tiles on the environment by application of Green model is resumed on write-down of influence during particular phases of life cycle. The cleaner production methodologies and increase of energy efficiency are usable in ceramic industry so can be recommended for write-down of harmful influences of ceramic tiles industry on environment. The results achieved by application of described Green methodology in last few years in the real production are presented, which shows large possibilities of achieving reduced harmful influence on the environment.

REFERENCES

[1] http://www.cbi.eu/marketinfo/cbi/?action=showDetails&id=167
[2] V. Hocenski, Z. Hocenski, S. Vasilic, Application of Results of Ceramic Tiles Life Cycle Assessment due to Energy Saving and Environment Protection, Proceedings of the IEEE International Conference on Industrial Technology, ICIT 2006, / Hori, Takamasa (ur.), Mumbai (India), IEEE, 15-17 Dec. 2006. 2972-2977.
[3] G. Busani, C. Palmonari, G.Timellini, Piastrelle ceramiche & ambiente. Emissioni gassose, acque, fanghi, rumore, Ed. EDI.CER, Sassuolo, 1995.
[4] V. Gallo, I. Bernardini, G. Timellini, A. Tenaglia, F. Cremonini, R. Bullini, S. Degli Esposti, Indagine sulla tossicologia degli adesivi per la posa delle piastrelle ceramiche, Atti Conv. Naz., I rischi dell'uso di sostanze chimiche in edilizia, Bologna, 29-30/5/90, Ed. Monduzzi, Bologna (1990) 165-206.
[5] L. Bruzzi, S. Cazzoli, R. Mele, A. Tenaglia, Radioactivita naturale nei prodotti ceramici per edilizia: le piastrelle ceramiche, Ceramica Acta, 3 (1991) 27-33.
[6] C. Palmonari, F. Vaughan, Behaviour of building materials in a fire, Centro Ceramico, Basilea, 1979.
[7] V. Hocenski, Ceramic tiles wastes diminishing in factory KIO d.d. Orahovica by clean production methodology, 7th International Conference on Waste Management, Zagreb (Croatia), 13-15 Nov, 2002. 58-64.
[8] L. Canter, Environmental Impact Assessment, Mc.Graw-Hill, 1995.

HYDRATION STUDY OF ORDINARY PORTLAND CEMENT IN THE PRESENCE OF LEAD(II) OXIDE

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Abstract

The aim of this work is to investigate the effect of the addition of lead(II) oxide on hydration heat and specific conductivity of a CEM I Portland cement. The measurements were made at 20 ^{o}C, defined water/solid ratio, W/S = 0.5 and different contents of lead(II) oxide (0 – 1 wt. %). The heats production during hydration were determined by differential microcalorimetry up to 48 hours of hydration and the specific conductivity by a digital conductometer. Thermal gravimetric analysis (TGA) was employed in the characterization of the cement structure. The hydration heat results show that the addition of lead(II) oxide affect the cement hydration kinetics. Kinetic curves show that higher content of lead(II) oxide slow down the hydration processes and the heat values are lower. Addition of lead(II) oxide significantly delays the time appearance of the maximum conductivity. Setting time is prescribed by standard for a particular type of cement and can be determined based on the appearance of specific conductivity maximum, which occurs at the setting time. Acceptable share of lead(II) oxide is the one at which time the appearance of the conductivity maximum permitted standard limits. It was found that the acceptable amount of lead (II) oxide in cement system is w = 0,25 wt. %.

Keywords: *stabilization/solidification (S/S), hydration heat, specific conductivity, differential microcalorimetry, thermogravimetric analysis (TGA)*

1. INTRODUCTION

Solidification/stabilization (S/S) is a technique for immobilizing hazardous wastes in binding materials, mostly cement-based, to delay the release of toxic components to the environment. Waste material is often S/S treated and is then landfilled or recycled into new building materials [1-3]. Among metal wastes, those containing Pb represents a serious issue. Pb derivatives are employed in mining and metallurgic industries, manufacture of coating pigments, imprint and typographer and plastic incineration. In humans, Pb exposure can lead to a wide range of biological effects depending on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system [4].

Ordinary Portland cement (OPC) is often used as the binding agent on its own, or in combination with cement replacement materials, which may be hydraulic (cement kiln dust) or pozzolanic (pulverized fuel ash, slag etc.) in nature [5].

A great number of studies investigated the effect of lead on the hydration of cement phases. Lead retards the setting of cement due to the formation of compounds which cover the silicate phases. Glasser [6] reported that calcium silicate hydrates (C – S – H) and calcium sulfoaluminate hydrates are largely responsible for the retention of Pb. Using X-ray diffraction Hamilton et al [7] do not identify any lead compounds in cement/lead oxide system after a 28-day curing time and they concluded that lead compounds in cement matrices are amorphous. Tashiro et al reported that common hydration products are formed during the hydration of C_3A in the presence of PbO. But it decreases the compressive strength of C_3A [8].

In the present study, a PbO was solidified and stabilized by different proportion of OPC. This work has examined the effect of PbO on hydration processes using differential microcalorimetry, conductometry and TG analysis. The main task of this study is to determine an acceptable amount of PbO in the cement system for its successful stabilization and solidification.

2. ELABORATION

2.1. Materials and Methods

2.1.1. Materials and Sample Preparation

All the measurements were carried on using OPC and different content of lead(II) oxide. OPC (according to EN-197 CEM I) was obtained from CEMEX Croatia cement plant (Kaštel Sućurac, Croatia). Its chemical composition and physical properties are shown in Table 1 and 2. Lead(II) oxide, PbO, p.a., was obtained from P.P.H. Polskie Odezynniki Chem-Gliwice, Poland.

Samples for microcalorimetrical measurements were prepared by mixing cement and 0 - 1 wt. % of PbO. The total mass of the solid sample was constant and it was 4 g. Water to solid ratio of 0.5 was used for all mixes and measurements were carried out at a temperature of 20 ^{o}C.

Samples for conductometrical measurements were prepared in the same way as the samples for microcalorimetrical measurements, except the total mass of the solid sample was 100 g.

Cement pastes for TG analysis were hydrated 28 days in a thermostat at a temperature of 20 ^{o}C. After this curing time they were ground and sieved through a standard 4900 mesh/cm^2 sieve.

Table 1. Chemical composition of OPC

Compositions (%)	**OPC**
SiO_2	22.85
Al_2O_3	4.81
Fe_2O_3	2.79
CaO	65.23
MgO	1.61
K_2O	1.89
Na_2O	0.18
Loss of ignition	0.04

Table 2. Physical and mechanical properties of OPC

Physical property	**Value**
Specific surface according to Blaine (cm^2 g^{-1})	3300
Standard consistency (%)	26
Setting time – start (min)	85
Setting time – end (min)	150
Average flexural strength (MPa)	
after 3 days	6.26
after 28 days	8.44
Average compressive strength (MPa)	
after 3 days	33.5
after 28 days	50.7

2.1.2. Differential Microcalorimetry

The microcalorimetrical measurements used to examine the interferences with a waste stabilization process were conducted by means of a differential microcalorimeter of the conduction-isoperibolic type [9]. An ALMEMO 2290-8 data logger was used to register heat effects of the hydration processes in the microcalorimeter, monitoring the change of voltage d$U = f(t)$. The recorded values were processed by a computer program on a computer, obtaining the values of the hydration heat, the relative reaction degree, and the heat-release rate for the given hydration conditions.

2.1.3. Conductivity

The conductometrical measurements used to provide the conductivity in the cement pastes were conducted by means of an ISKRA MA 5964 microprocessor conductometer connected to a computer via a RS 232 C digital output. The conductometrical cell electrode was made of stainless steel with a constant C = 0.285 cm^{-1}.

2.1.4. TG analysis

Thermal analysis were performed on a Pyris 1 TGA at 20 ^{o}/min from 50 to 850 ^{o}C in 10 ml/min N_2.

2.2. Results and Discussion

To determine the effect of PbO on OPC hydration, the method of continuous observing of early hydration, microcalorimetry, was applied, which monitors heat released during hydration. Heat released heats the operating cell of a differential microcalorimeter [10], causing a difference of temperatures between the operating and the referent cell, measured as tension difference, dU, by thermocouples. Figure 1 shows the thermovoltage curves for samples of OPC with different additions of PbO. On microcalorimetrical curve for OPC is observed very pronounced second maximum. Increasing the share of PbO maximums assume lower values and the occurrence of the maximum registered in the later hydration times.

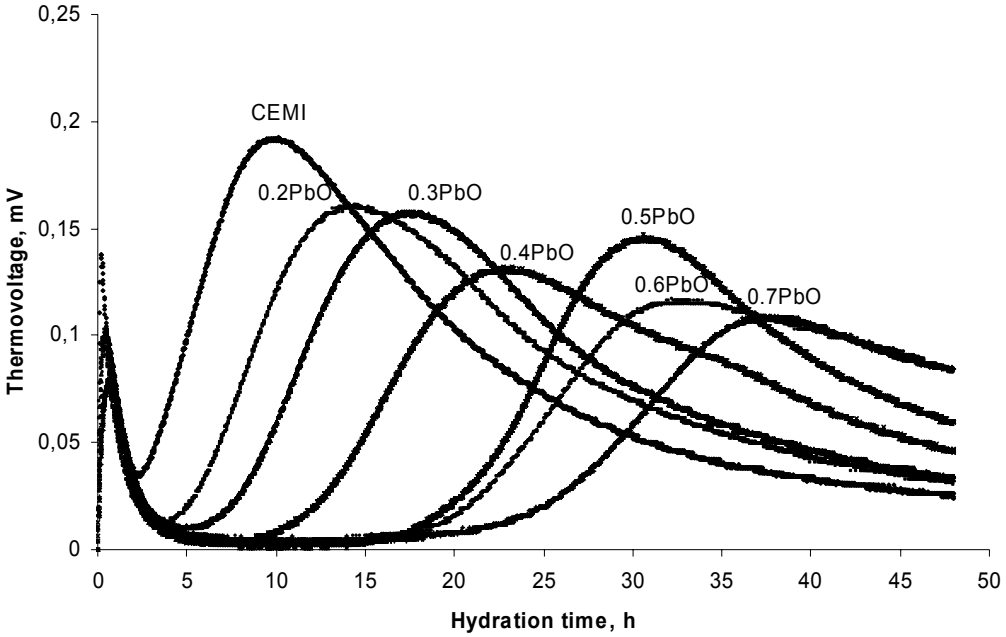


Figure 1. Thermovoltage curves (dU = f(t)) for the samples with addition of PbO

Specific conductivity of cement pastes was continuously observed in order to use these curves to determine the conductivity maximums, which indicate the binding time of the cement pastes. Time to appearance of the maximum can be used as a parameter for estimating the share of PbO, which does not delay the binding of cement paste more than the standard allowed time for the beginning and end of the binding. The introduction of PbO into the reaction system leads to slower hydration, but hydration curves have a typical shape with somewhat less intensity of the specific conductivity (Figure 2).

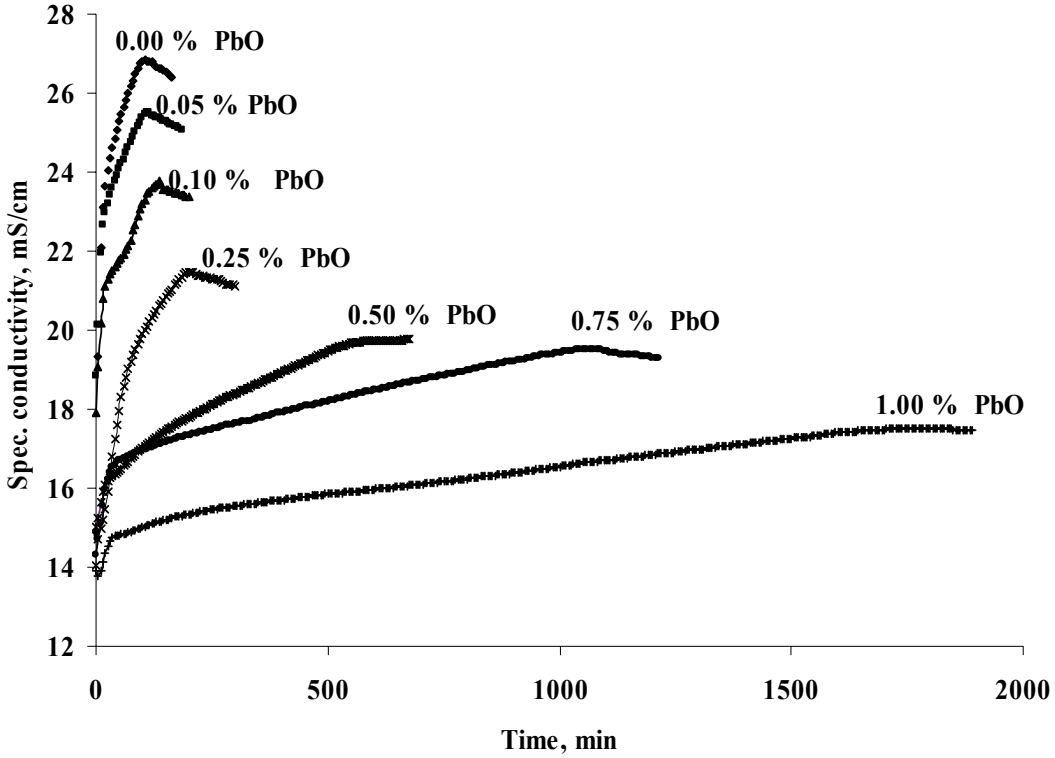


Figure 2. Specific conductivity of cement paste containing PbO

According to the technical specification [11] and standard [12] for OPC, the beginning of binding time should occur after 60 minutes. For the practical application, the end of binding time should happen in time below 200 minutes. It was found that PbO addition to the cement-water system is acceptable up to 0.25 wt. % (Table 3). An increased share of PbO over 0.25 wt. % significantly delay the beginning of binding time and for the system is not acceptable.

Table 3. Time to maximum appearance for various addition of PbO

Addition of PbO, wt %	Time to maximum appearance, min
0.00	105
0.05	115
0.10	135
0.25	205
0.50	560
0.75	1060
1.00	1780

Figure 3 shows the thermal curves obtained on heating a hydrated cement samples cured for 28 days. Several losses appear on these curves. The first between 100 – 200 ^{o}C corresponds to the decomposition of the nearly amorphous hydrates, mainly CSH as well as sulphoaluminate hydrates. The decomposition continues gradually, as evidenced by the slow loss in mass between 200 and 450 ^{o}C. A great loss then occurs corresponding to the decomposition of Portlandite ($Ca(OH)_2$). The loss of weight around 700 ^{o}C was assumed to represent decomposition of $CaCO_3$. The addition of PbO shifts the peaks to the left and sees a higher mass loss.

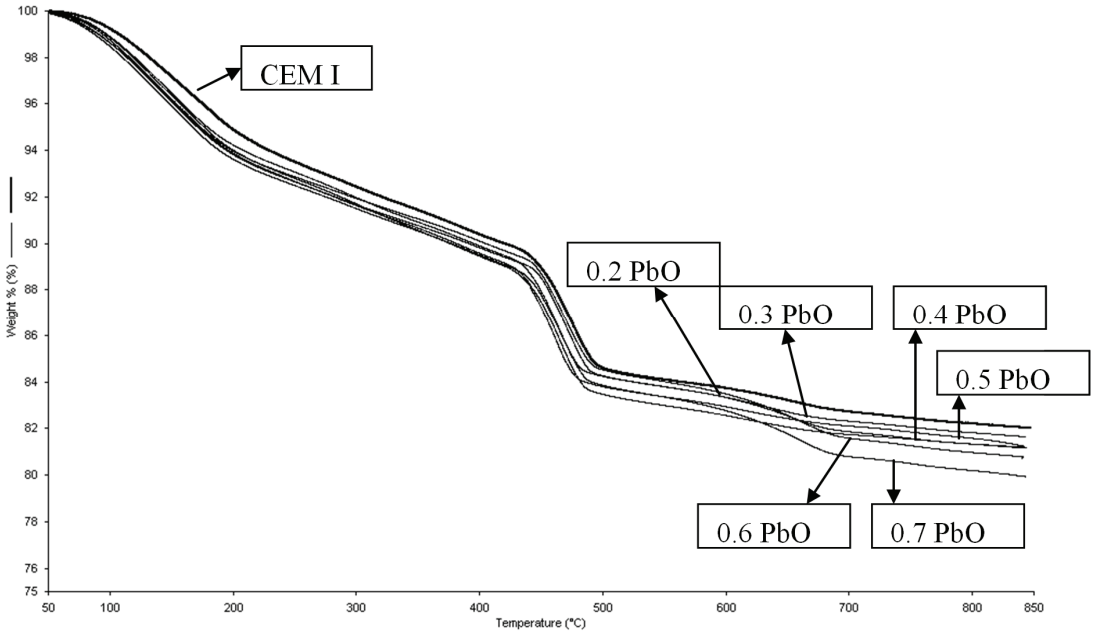


Figure 3 Thermal analysis of a hydrated cement sample with addition of PbO, cured for 28 days

3. CONCLUSIONS

The hydration heat results show that the addition of lead(II) oxide affect the cement hydration kinetics. Kinetic curves show that higher content of lead(II) oxide slow down the hydration processes and the heat values are lower.

Addition of lead(II) oxide significantly delays the time appearance of the maximum conductivity.

It was found that the acceptable amount of lead (II) oxide in cement system is w = 0,25 wt. %.

REFERENCES

[1] R.D. Spence, C. Shi, Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes. Boca-Raton: CRC Press, 2005.

[2] E. Martens, D. Jacques, T. Van Gerven, L. Wang, D. Mallants, Geochemical modeling of leaching of Ca, Mg, Al, and Pb from cementitious waste forms, Cement Con. Res. 40 (2010) 1298-1305.

[3] Q.Y. Chen, M. Tyrer, C.D. Hills, X.M. Yang, P. Carey, Immobilisation of heavy metal in cement-based solidification/stabilization: A review, Waste Manag. 29 (2009) 390-403.

[4] M.A.C. Gollmann, M.M. da Silva, A.B. Masuero, J.H. dos Santos, Stabilization and solidification of Pb in cement matrices, J. Hazard. Mater. 179 (2010) 507-514.

[5] Z. Giergiczny, A. Krol, Immobilization of heavy metals (Pb, Cu, Cr, Zn, Cd, Mn) in the mineral additions containing concrete composites, J. Hazard. Mater. 160 (2008) 247-255.

[6] F.P. Glasser In: R.D. Spencer (Editor), Chemistry and Microstructure of Solidified Waste Forms, Lewis Publishers, Boca Raton, FL (1993) 1–40.

[7] I.W. Hamilton, N.M. Sammes, Encapsulation of steel foundry dusts in cement mortar, Cem. Concr. Res. 29 (1999) 55– 61.

[8] C. Tashiro, J. Oba, The effects of Cr_2O_3, $Cu(OH)_2$, ZnO and PbO on the compressive strength and the hydrates of the hardened C_3A paste, Cem. Concr. Res. 9 (1979) 253– 258.

[9] R. Krstulović, P. Krolo, T. Ferić, Microcalorimetry in cement hydration process, Periodica Polytehnica 33 (1989) 315-321.

[10] R. Krstulović, P. Dabić, A conceptual model of the cement hydration process. Cem. and Concr. Res. 30 (2000) 693-698.

[11] Technical specification for CEM I 42,5 R Sv. Juraj

[12] EN 196-3, Test Methods for Cement, CEN/TC 51.

WASTE PHOSPHOGYPSUM CHARACTERIZATION – TOWARD SUSTAINABLE REUSE

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Abstract

The Croatian fertilizer plant Petrokemija d.d. - Kutina produces phosphoric acid by the wet process natural phosphate rock sulfuric acid digestion. Phosphoric acid librated from apatite mineral is further used in fertilizer formulation. Unfortunately, large quantities of the phosphogypsum (PG) are produced by this process as an unwanted by product. The usual plant operation generates 4.9 ton of phosphogypsum per 1 ton of phosphoric acid (calculated as 100% P_2O_5). Since 1983, when the phosphogypsum pond has been formed and wet stacking has been applied, 8.4 million tons of PG had been disposed. PG tailing facility is located about 5 km from the plant at the very edge of the Natural Protected area Lonjsko Polje. Most favorable improvements, from the point of environmental protection and sustainability, should bring about any possible reuse of phosphogypsum. In order to evaluate reuse potential of phosphogypsum we investigated its chemical and mineralogical composition and physical properties of the as collected wet slurry and dried phosphogypsum. Radioactive nuclide content of the PG is of special concern and limits its possible applications. In this work an overview of PG pond present state and near future projection along with recent legislative changes in Croatia is given. It is concluded that comprehensive characterization is necessary for safe waste management and several material recovery routes proposed.

Keywords: *phosphogypsum, chemical characterization, waste management, reuse of phosphogypsum*

1. INTRODUCTION

The Croatian fertilizer plant Petrokemija d.d. - Kutina is an existing industrial complex consisting of production units for ammonia, nitric acid, urea, sulphuric acid, phosphoric acid, mineral fertilizers, carbon black and bentonite clay, located in the municipality of Kutina in the County of Sisak-Moslavina. It was founded in 1968, and manufactures mineral fertilizers, clay-based products, carbon black and many various products.

Phosphogypsum (PG) is a by-product from the production of phosphoric acid by the wet process whereby natural phosphate rock is mixed with sulfuric acid. The resulting solid phase of calcium sulfate is separated from the solution of phosphoric acid by filtration. Commercial wet process is classified according to the hydrated form in which crystallizes calcium sulfate (as anhydrite, $CaSO_4$, hemihydrate, $CaSO_4 \cdot ½\ H_2O$ or dihydrate, $CaSO_4 \cdot 2H_2O$).

Underlying chemical transformation of raw materials in the dihydrate process operated at Petrokemija plant is shown by Eq. 1.

$$Ca_{10}F_2(PO_4)_6\ (s) + 10\ H_2SO_4 + 20\ H_2O \rightarrow 6\ H_3PO_4 + 10\ CaSO_4 \cdot 2H_2O\ (s) + 2HF \quad (1)$$

The usual plant operation generates 4.9 ton of phosphogypsum per 1 ton of phosphoric acid (calculated as 100% P_2O_5). Phosphoric acid as a valuable product is recovered from phosphogypsum slurry by initial filtering and three stages of subsequent filter cake washing to ensure a satisfactory recovery of soluble P_2O_5. The desired degree of phosphorous bearing liquid separation from the filter cake is vacuum assisted and the remaining phosphogypsum filter cake is re-pulped with water and then pumped as approximately 25% by weigth solids containing suspension to the phosphogypsum tailing facility. Simplified flow diagram of the Petrokemija phosphoric acid plant [1] is shown in Fig. 1. The tailing facility (Fig. 2.) is situated 5 km southwest from Kutina on the margins of Nature Park „Lonjsko Polje“, and its north dam is also the right bank of Kutinice river. The tailing facility consists of 4 ponds, which are defined by 6 m high brimmed earth dams with a crown width of 3m and a slope ratio of 1:3. Since 1983, when the phosphogypsum pond has been formed and wet stacking has been applied, 8.4 million tons of PG had been disposed.

The tailing facility occupies an area of approximately 166 ha, and the main pollutants are: transport acidic water and phosphogypsum retaining on the tailing facility, and calcium fluorides and flour-silicic acids, retaining on the waste water treatment plant. Petrokemija d.d. participated in feasibility study for the remediation of the phosphogypsum tailing facility project funded by European Union Phare 2006, and some results are presented in this paper, especially phosphogypsum radioactivity [2].

This paper reviews the different environmental impacts associated with PG storage and classifies the methods described in the literature for recycling and minimizing the negative effect of this waste with special overview to Petrokemija PG.

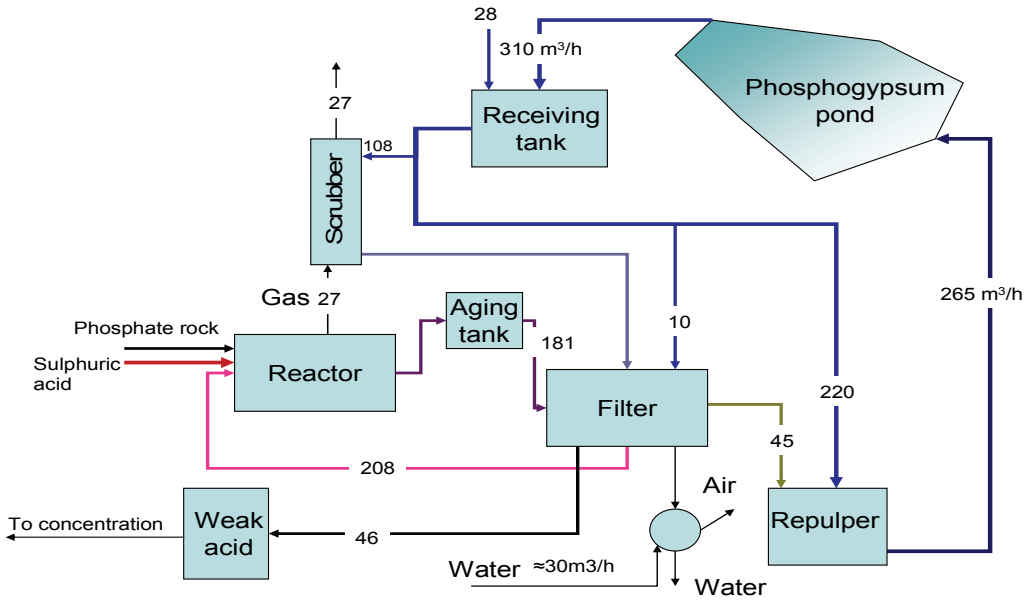


Figure 1. Simplified flow diagram of the phosphoric acid plant [1]



Figure 2. Phosphogypsum disposal pond.

2. ELABORATION

2.1. Characterization of phosphogypsum

PG properties are dependent upon the nature of the phosphate rocks used, the plant operation efficiency, the disposal method, and the age, location and depth of landfill [3]. Petrokemija imports phosphate rock from Morocco (Khouribga). A comparison among the most common phosphate rocks chemical composition is given in Table 1.

Table 1. Typical chemical analysis of various phosphate rocks (% by mass)

Deposits	CEI-Russia	South Africa-Phalaborwa	Marocco-Khouribga	USA Florida	Senegal	Togo
Grade %BPL(nominal)	84	80	73	75	80	80
P_2O_5	38.9	36.8	33.4	34.3	36.7	36.7
CaO	50.5	52.1	50.6	49.8	50	51.2
SiO_2	1.1	2.6	1.9	3.7	5.0	4.0
F	3.3	2.2	4.0	3.9	3.7	3.8
CO_2	0.2	3.5	4.5	3.1	1.8	1.5
Al_2O_3	0.4	0.2	0.4	1.1	1.1	1.0
Fe_2O_3	0.3	0.3	0.2	1.1	0.9	1.0
MgO	0.1	1.1	0.3	0.3	0.1	0.1
Na_2O	0.4	0.1	0.7	0.5	0.3	0.2
K_2O	0.5	0.1	0.1	0.1	0.1	0.1
Organics	-	0.1	0.3	0.5	-	-
Organic C	0.1	-	-	0.2	0.4	0.1
SO_3	0.1	0.2	1.6	0.1	-	0.3
Cl	-	-	0.1	-	-	0.1
SrO	2.9	0.3	0.1	-	-	-

Phosphate rock from Morocco enables smooth production process, i.e. good overall efficiencies may be obtained, gypsum cake is reasonably filterable etc. However, increased concentration of heavy metals should be expected in phosphoric acid and acidic PG slurry water (transporting water). As far as trace elements are concerned, Morocco phosphate rock is characterized by increased chromium and nickel content (Table 2.). Zinc is usually not an issue, but due to elevated content in the phosphate rock, its concentration is increased in both phosphoric acid and recycling water.

Table 2. Trace elements in various phosphate rocks (ppm)

Content	CEI-Russia	South Africa-Phalaborwa	Marocco-Khouribga	USA Florida	Senegal	Togo
Rare earth elements	6800	4200	900	600	-	-
U3O8	11	134	185	101	124	-
As	10	13	13	11	53	12
Cd	1.2	1.3	15	9	18	53
Cr	19	1	200	60	6	-
Cu	37	102	40	13	-	-
Hg	33	0.1	0.1	0.02	0.2	0.6
Ni	2	2	35	28	-	-
Pb	-	11	10	17	5	-
Zn	20	6	200-400	70	-	-

Raw phosphogypsum contains 15-30% moisture and over 50 types of impurities, such as organic matter, soluble and insoluble phosphates and free phosphoric and sulfuric acid, fluorine compounds and fluor-silicates, admixtures combined sodium and potassium, rare earth and radioactive elements [4-7]. Phosphogypsum has physical and chemical properties similar to those of natural gypsum. Phosphogypsum readily dissolves in rainwater in a similar way as natural gypsum and its dissolution does not depend on pH. However, properties of an entire phosphogypsum pile differ from those of gypsum of the same size. A phosphogypsum pile contains numerous very fine phosphogypsum particles. The specific surface of phosphogypsum particles is exceptionally large and as a result the

phosphogypsum pile dissolves more rapidly than a gypsum mass of the same size. Thus particle size distribution influences the performance of phosphogypsum dumps. If a closed uncovered phosphogypsum pile is continuously exposed to rainwater infiltrations it will develop karst features such as solution channels and cavities. Prolonged leaching of phosphogypsum in stacks leads to flushing of trapped acids, metals and metalloids. Therefore, aged and leached PG material display near neutral pH and lower trace element content. The mobility of trace elements depends on their physico-chemical bonding, i.e. if they are adsorbed onto the surface of PG crystals or are within its crystal structure. It seams that cadmium and strontium may substitute for calcium in the calcium sulphate crystal lattice, uranium may be adsorbed onto the surface of calcium sulphate crystals and selenium may be adsorbed onto iron oxyhydroxides. The finer particles fractions of phosphogypsum (<20 μm) tend to have higher fluorine, heavy metals, metalloids and radionuclide concentrations than the coarser fractions [8]. Quality of phosphogypsum produced in Petrokemija d.d. has been regularly monitored by both the Petrokemija works laboratory and the laboratory of the Institute for Public Health and Occupational Health in Zagreb. Typical analysis of PG made in February 2008. (sample 1), and in July 2010. (sample 2 and 3), are shown in Table 3.

Table 3. Chemical composition of phosphogypsum at the Petrokemija tailing facility [9]

Parameter	sample 1 Value (% by mass)	sample 2 Value (% by mass)	sample 3 Value (% by mass)
Total P_2O_5	0.3	0.59	0.48
Soluble P_2O_5	0.034	0.02	0.02
Unreacted P_2O_5	0.100	0.31	0.23
CaO	25.4	31.59	33.64
SO_3	46.03	47.67	53.46
MgO	0.0005	0.006	0.002
F	0.22	2.15	1.18
Fe	0.009	0.045	0.006
Al	0.039	0.095	0.075
Na	0.008	0.01	0.01
Cd	0.0002	0.52 mg kg^{-1}	0.37 mg kg^{-1}
SiO_2	0.94	7.53	1.09
H_2O	14.64	7.34	1.72
Calcination loss	20.76	19.90	21.22

Takeda and Parreira [10] made a physical characterization of phosphogypsum (specific gravity 2.308 g/cm^3) produced by Fosfertil (Brazil). Particle size distribution curve showed that phosphogypsum is a silty material without plasticity, and its other physical properties are also similar to those found by other researchers [11,12].

2.2. Phosphogypsum radioactivity

A number of industrial processes, such as fertilizer production and processing activities, can cause naturally occurring radioactive materials (NORM) to become concentrated at levels above natural background (BG) in by product waste streams. NORM that accumulates in industrial waste streams is referred to as "technologically enhanced NORM", or TENORM [2]. Phosphate ores are naturally highly radioactive and their radioactivity originates mainly from ^{238}U and ^{232}Th.

Wet processing causes the selective separation and concentration of naturally occurring radium (^{226}Ra), uranium (^{238}U) and thorium (^{232}Th): about 80% of ^{226}Ra is concentrated in PG while nearly 86% of ^{238}U and 70% of ^{232}Th end up in the phosphoric acid. Determining the types of impurities present can be very important when defining waste management processes and environmental policies such as public health risk assessment. In the Republic of Croatia, by definition listed in Radiation Protection legal Act, TENORM, is not subject to regulatory control under the Radioactive Waste policy Act. At this time, the TENORM is not classified as a LLW (Low Level Waste) either. Therefore PG as a TENORM product is

hardly to be treated as hazardous waste due to its radioactivity levels and regulatory definition. This is why the exposure dose and dose rate originating from ^{226}Ra and ^{222}Rn in PG have to be assessed in order to evaluate the *public health risk* due to external exposure and/or internal exposure to PG. Standard individual public member exposure as outlined by the EU Directive, IAEA, UNSCEAR2000 give the adequate and clear input parameters and premises needed to work out a qualitative public health risk and impact assessment due to TENORM exposures originating from fertilizer production, production of PG and any other associated waste streams. It is a usual practice to express radioactivity of TENORM as a single number that combines the radioactivity contributions from different isotopes [13]. The analyzed PG from the tailing facility in Kutina is definitely TENORM material. External hazard index, H_{ex}, internal hazard index, H_{in} and radium equivalent index, Ra_{eq}, calculated from the data measured are not less than 1 (unity) indicating that the existing PG is not to be used in construction material products *alone*. PG has to be mixed to a certain volume extent with third party materials (clay or else) containing much less TENORM assuring the H_{ex} and H_{in} of the final PG product to become less than 1. This mixing process is to be fairly and constantly monitored by licensed technical services.

At all times, it is important to have in mind that radiation protection of people (public members as defined in EU basic safety standard legislation) from TENORM exposures is to be defined using the *occupancy factors* and equivalent exposure dose rate calculations. In that way it is shown and justified that despite the fact that $H_{ex} > 1$, $H_{in} > 1$ and $Ra_{eq} > 1$ for the PG at tailing facility near Kutina no exposure of the particular public member in Kutina municipality is at any time greater than 1 mSv per year due to existence of PG tailing facility.

This fact justifies all present (or future) effort leading to technological enrichment of TENORM PG product to be used in various new products and on the benefit of Kutina municipality inhabitants.

According to above statements the PG tailing facility in Kutina is radiological defined as normal tailing facility site where no specific safety or security procedures regarding radiation protection of environment or public are to be performed. Radioactivity from TENORM PG is not polluting the ground waters or agricultural soil in the vicinity of the tailing facility. PG is dispersed by air in the form of suspended air particles and this is the only pathway through which the surface PG from tailing facility can be dispersed over the environment causing diverse hazards to public health. The radiological characterization of specific PG tailing facility site at Kutina municipality showed that this specific industrial site in Croatia is radiological very stable[2] and that no harm to the environment or public is to be expected if the facility is managed as till now in the future too. The Institute for Medical Research and Occupational Health determines radionuclides in Petrokemija phosphogypsum [9,14] , and the results are shown in Table 4.

Table 4. Concetration of radionuclides in phosphogypsum

Radio nuclide	Phosphogypsum on tailing facility	Phosphogypsum from filter
	Activity (Bqkg^{-1})	
^{238}U	86.9 ± 30.3	56.2 ± 22.9
^{232}Th	6.2 ± 1.1	5.0 ± 1.1
^{235}U	5.7 ± 1.1	3.0 ± 0.3
^{226}Ra	533.2 ± 15.1	309.4 ± 11.4
^{228}Ra	6.2 ± 1.1	3.0 ± 0.3
^{40}K	33.8 ± 4.6	15.2 ± 3.6
^{137}Cs	0.7 ± 0.2	0.1 ± 0.04

Many studies were carried out concerning the concentration of radioelements in the phosphogypsum [15-27]. Reguigui et. al. [28] investigated the Tunisian phosphogypsum as a function of storage time, and they noticed a decreasing tendency of the concentration for ^{238}U and ^{232}Th going from the most recent sample to the oldest. Concentration of ^{226}Ra remains constant within the piles during the storage. Measurements of the ^{232}Th series confirmed that thorium fractionates to the phosphoric acid during the production process. Other fields of modern reuse of PG are to be considered only together with proper monitoring and radiological characterization regarding the specific planned and purpose (like agricultural use enriching the soil quality for certain variety of plants or else).

2.3. Environmental impact

Impact of PG on the landscape is obvious. There is monitoring system of phosphogypsum facility surrounding that includes air quality monitoring, monitoring of surface and ground water quality as well as analyses of phosphogypsum and technological water in accordance with environmental protection regulation. Fortunately, as a part of environmental policy in Petrokemija, there are some very promising rehabilitation activities in progress which are the ongoing efforts to start with the final stage of covering and planting on the parts of the tailing facility where the retention of gypsum is finalized. Since the first phase when phosphogypsum dike was finished, the stabilization and vegetative cover of the site was planned. The key prerequisite for efficient disposal stabilization is the right choice of plant species that form strong roots, deeply and thickly grow through surface layer of substrate by forming thick overground vegetative cover that protects the disposal from extreme weather conditions. The experiment was started in the springtime of 2009 and the best results gave calcium fluoride (industrial waste in phosphoric acid wastewater treatment plant) as substrate and seeded species false indigo bush (Amorpha fruticosa) and grass mixtures with high content of red fescue (Festuca rubra) [29].

2.4. Reuse of produced phosphogypsum at Kutina

Nowadays there is a great interest in using PG as an alternative raw material for many applications because it contains more than 95% $CaSO_4 \cdot 2H_2O$. PG has great economic potential and possible reuse would have positive environmental impact. The main industries for potential reuse of PG are based in road construction, agricultural fertilizer use, dumpsite remediation and landfill covering, ceramic production, cement industry and manufacturers of construction material and many ways of valorization of PG have also been investigated [30-43]. PG as a raw material has a potential in Croatia, because all the surveyed activities show a positive and satisfactory trend. The fastest implementation could appear in the production of cement. Cement manufacturers possess high level of knowledge regarding PG, which could lead to fast reuse in replacing natural gypsum within the production process. One attractive application of PG is currently under study in Croatia with possible reuse of large quantities of PG for special (sulfoaluminate) cement production [44-52].

3. CONCLUSIONS

Because of radioactivity and its harmful consequences, commercial use of PG in the world is very limited. The USA Environmental Protection Agency (EPA) has prohibited any use in the United States. Only stacking of PG was allowed, despite the fact that there are many potential commercial applications. The uses of PG are still limited and reason for this is not just in the legal prohibitions, but also the fact that PG as a raw material is relatively new, so companies need a certain period of adjustment to start using it. Besides the USA, other countries have not made enough in the field of using PG, which precludes systematic exploitation.

The new waste framework directive (2008/98/EC) anyhow excluded PG from the list of wastes and has introduced concepts of „by-product“ and „end of waste status“. Bref documents address clearly the priorities to identify economical potential (reuse, recover) of PG. So, the overall objective is to understand market opportunities for the phosphogypsum product on national and international level.

Based on chemical and radionuclide analysis phosphogypsum from Petrokemija is determined as non-hazardous waste and Petrokemija d.d. has been granted a permit for the retention of phosphogypsum. Regarding the aforementioned PG properties, further research is still needed to evaluate overall suitability of PG reuse for each specific application.

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REFERENCES

[1] Description of phosphoric acid plant with process flow sheet, Material received from Petrokemija d.d., April 2009.

[2] B. Nikov, E. Spitaler, Development of hazardous waste management system, including the identification and management of “hot spot sites” in Croatia, PHARE 2006, I 00B, Process Engineering and Treatment Methodology Screening-Fertilizer Plant Kutina, 2009.

[3] A. Arman, R. K. Seals, A preliminary assessment of utilization alternatives for phosphogypsum, Proceedings of the Third International Symposium on Phosphogypsum, Orlando, FL, 1990, FIPR Pu. No. 01-060-083; 562-575.
[4] M.B. Rajković, Classification of Phosphogypsum as a waste material from the aspect of environmental protection, Belgrade, 2003.
[5] M.B. Rajković, V. Hadžić, I. Molnar, Waste phosphogypsum from chemical industry: status, applications and perspective, Naučni Institut za ratarstvo i povrtarstvo, Novi Sad, Serbia, 1995.
[6] M.B. Rajković, M.M. Mitrović, Phosphogypsum surface characterization using scanning electron microscopy, 5th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 27–29, 2000, Belgrade, Serbia.
[7] M.B. Rajković, Applications of phosphogypsum, 2nd Yugoslav conference „Theory and technology of sintering“, TEOTES 95, SANU and Technical Faculy in Čačak, 4-9th Sep. 1995, Čačak, Serbia, R-P-26, pp 42.
[8] M.B. Rajković, D. Tošković, A New Procedure of Phosphogypsum Purification in Order to Diminish the Content of Radionuclides, Hung. J. Ind. Chem. 30(3) (2002) 219-227.
[9] Institute for Medical Research and Occupational Health, Unit for Radiation Protection, Gamma Spectrometric Analyses of phosphogypsum from Petrokemija d.d. Institute for Medical Research and Occupational Health, Detection of Dispersion Pathways of Ionizing Radiation in the Course of Phosphoric Acid Production, Report for 2007, Zagreb, Croatia, 2008.
[10] M.C. Takeda, A.B.Parreira, The use of cement-stabilized phosphogypsum mixes in road construction, International Conference on Geotechnical and Geological Engineering, 19-24th Nov. 2000, Melbourne, Australia, pp. 966-971.
[11] W. F. Chang, M. I. Mantell, Engineering properties and construction applications of phosphogypsum, University of Miami press, Coral Gables, Florida, (1990) pp. 203.
[12] R. Taha, R. K. Seals, M. Tittlebaum, D. Saylak, Environmental Characteristics of By-product Gypsum, Transportation Research Record, 1486 (1995) 21-26.
[13] H.M. Diab, S.A. Nouh, A. Hamdy, S.A. El-Fiki, Evaluation of natural radioactivity in a cultivated area around a fertilizer factory, Journal of Nuclear and Radiation Physics, 3(1) (2008) 53-62.
[14] I. Prlić, E. Spitaler, Development of hazardous waste management system, including the identification and management of “hot spot sites” in Croatia, 00D Radiological characterization of Phosphogypsum Tailing Facility-Fertilizer Plant Kutina, 2009.
[15] P.M. Rutherford, M.J. Dudas, J.M. Arocena, J. Environ. Qual., 24 (1995) 307.
[16] J.L. Aguado, J.P. Bolivar, Czech. J. Phys., 49, Suppl. SI (1999) 269.
[17] M. N. Alam, M. I. Chowdhury, M. Kamal, S. Ghose, H. Banu, D. Chakraborty, Appl. Radiation Isotopes, 48 (1997) 1165.
[18] M. Azouazi, Y. Ouahidi, S. Fakhi, Andres, J. Ch. Abbe, M. Benmansour, J. Environ. Radioact., 54 (2001) 231.
[19] B. Mazzilli, V. Palmiro, C. Saueia, M. B. Nisti, Radiochemical characterization of Brazilian phosphogypsum, J. Environ. Radioact., 49 (2000) 113-122.
[20] W. C. Burnett, A. W. Elzerman, J. Environ. Radioact., 54 (2001) 27.
[21] P. M. Rutherford, M. J. Dudas, J. M. Arocena, Sci. Total Environ., 180 (1996) 201.
[22] P. M. Rutherford, M. J. Dudas, R. A. Samek, Sci. Total Environ., 149 (1994) 1.
[23] C. D. Hull, W. C. Burnett, J. Environ. Radioact., 32 (1996) 213.
[24] P. Haridasan, C. G. Maniyan, P. M. B. Pillai, A. H. Khan, J. Environ. Radioact., 62 (2002) 287.
[25] W. M.Kanno, H. L. Rossetto, M. F. de Souza, M. F. Maduar, M. P. de Campos, B. P. Mazzilli, High strenth phosphogypsum and its use as a building material, The Natural Radiation Environment-8th International Symposium
[26] M. Lysandrou and I. Pashalidi: Uranium chemistry in stack solutions and leachates of phosphogypsum disposed at a coastal area in Cyprus, Journal of environmental radioactivity, 99 (2008) 359-366.
[27] A. Luca, R. Margineanu, M. Sahagia, A. C. Watjen, Activity measurements of technically enhanced naturally occurring radionuclides (TENORM) in phosphogypsum, Applied Radiation and Isotopes 67 (2009) 961-963.
[28] N. Reguigui, H. Sfar Felfoul, M. Ben Ouezdou, P. Clastres, Journal of Radioanalytical and Nuclear Chemistry, Vol. 264, No. 3 (2005) 719 – 722.

[29] Preliminary results of plant species and substrate investigation for soil stabilization and greening of phosphogypsum dump (in Croatian), Conference proceeding "Tehnologije zbrinjavanja otpada i zaštite tla", Zadar, Croatia, 2009.
[30] T. Kuryatnyk, I. Angulski da Luz, C. Ambroise, J. Pera, Valorization of phosphogypsum as hydraulic binder, Journal of Hazardous Materials 160 (2008) 681-687.
[31] S. Gaidučis, R. Mačiulaitis, A. Kaminskas, Eco-balance features and significance of hemihydrate phosphogypsum reprocessing into gypsum binding materials, Journal of civil engineering and management 15(2) (2009) 205-213.
[32] A. Kaminskas, S. Gaidučis, R. Mačiulaitis, Influence of granulated milled slag glass additive on hemihydrate phosphogypsum hardening, Materials science 13(3) (2007) 224-228.
[33] J. Cesniene,: Influence of phosphatic impurities on the anhydrite binding material of phosphogypsum, Ceramics–Silikaty 51 (3) (2007) 153-159.
[34] M.B. Rajković, D.V. Tošković, Investigation of the possibilities of phospho-gypsum application for building partitioning walls-elements of a prefabricated house, APTEFF, 33 (2002) 1-174.
[35] A. I. Akin, S. Yesim, Utilization of weathered phosphogypsum as set retarder in Portland cement, Cement and Concrete Research 34 (4) (2004) 677-680.
[36] C. Papastefanou, S. Stoulos, A. Ioannidou, M. Manolopoulou, The application of phosphogypsum in agriculture and the radiological impact, Journal of Environmental Radioactivity 89 (2) (2006) 188-198.
[37] L. Reijnders, Cleaner phosphogypsum, coal combustion ashes and waste incineration ashes for application in building materials, A review. Building and Environment 42 (2) (2007) 1036-1042.
[38] S. Weiguo, Z. Mingkai, Z. Qinglin, Study on lime-fly ash- phosphogypsum binder. Construction and Building Materials 21 (7) (2007) 1480-1485.
[39] C. Koopman, Purification of gypsum from the phosphoric acid production by recrystalization with simultaneous extraction. PhD thesis, TU, Delft, 2001.
[40] S. Manjit, Treating waste phosphogypsum for cement and plaster manufacture, Cement and Concrete Research 32 (7) (2002) 1033-1038.
[41] R. Beretka, M. Cioffi, G.L. Marrovcoli, G.K. Valenti: Energy-saving cements obtained from chemical gypsum and other industrial wastes, Waste Management 16 (1996) 231-235.
[42] P. Arjunan, M. Silsbee, D. Roy, Sulfoaluminate-belite cement from low-calcium fly ash and sulfur-rich and other industrial by products, Cement and Concrete Research 29 (1999) 1305-1311.
[43] C. Ferreira, A. Riberio, L. Ottosen, Possible application for municipal solid waste fly ash, Journal of Hazardous Materials B 96 (2003) 211-222.
[44] L. Santoro, R. Garofano, G.K. Valenti, Calcium sulfoaluminate made from phosphogypsum and its hydration properties, in Proceedings 8 th ICCC, Rio de Janeiro, Vol. 4, (1986) pp. 389 – 394.
[45] J. Havlica, S. Sahu, Thermodynamics and kinetics in the system $Ca_4(Al_6O_{12})(SO_4)$-$CaSO_4 \cdot 2H_2O$-H_2O up to 750°C, in Proc. 9th ICCC, New Delhi, Vol. 4, (1992) pp. 157–163.
[46] P. Zhang et al., The crystal structure of $C_4A_3\,\overline{S}$, in Proceedings 9 th ICCC, New Delhi, Vol. 3, (1992) pp. 201 – 208.
[47] J. H. Sharp, C. D. Lawrence, R. Yang, Calcium sulfoaluminate cements – low-energy cements, special cements or what. Advances in Cement Research 11 (1999) 3 – 13.
[48] F. Puertas, M. T. B. Varela, S.G. Molina, Kinetics of thermal decomposition of $C_4A_3\,\overline{S}$ in air. Cement and Concrete Research 25 (1995) 572 – 580.
[49] M. Mentean et al., Synthesis of calcium sulfoferroaluminates and their properties. Materiale de Constructii (Bucharest) 281, (1998) 60 – 64.
[50] K. Ogawa, D.M. Roy, $C_4A_3\,\overline{S}$ hydration, ettringite formation and its expansion mechanism. Cement and Concrete Research 11 (1981) 741 – 750; 12 (1982) 101 -109.
[51] Dutch Notes on BAT for the Phosphoric Acid Industry (http://www.infomil.nl/_legsys/bref/NL-phosa.pdf)
[52] European Commission, Integrated Pollution Prevention and Control, Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers (http://www.eippcb.jrc.es)

IMPLEMENTING SUSTAINABILITY INTO CROATIAN PUBLIC BUILDING STANDARD

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Abstract

The public standard facilities and the society itself need to be an example of ecological technologies and practices, to be the economy generator, to represent energy self-sufficiency and to be an implement association of sustainable principles. A mutual collaboration of all participants of building process accomplishes the advantages of sustainable building. They also raise the investments of energy effective and renewable technologies of private and corporative sector. The sustainability is a positive contribution to society. Only sustainable projects will be feasible on the long turn, on the condition of existing building regulations. Sustainability has become a principle of our age. The definition of sustainable building draws attention for need of design guidelines that will be an integral part of defining the sustainable topics within legal act. The first step is implementing the principles of sustainable design into legal acts within general conditions of all public competitions for public standard facilities - facilities whose building is financed within local self-government and government budget. So this kind of the measurement is applicable right away. The next step is to implement the sustainable design into law regulations. In that way all the regulations become the obligation for all facilities of this kind. The implementation will have full value only if it has a clear political support, and if it is constantly analyzed and improved. Implementing Sustainability into Croatian Architecture would help additional funding of Public Building by EU funds, which would cause a positive impact on society in general.

Keywords: *sustainability, competitions, Croatian public building standard, legislation*

1. INTRODUCTION

Physical planning is of great significance to the quality studying and research of environment. Vital urban areas with opportunities for living near offices and basic services reduce the amount of time wasted, money spent, and pollution created as a result of lengthy commutes to and from work, which means that people will have more time to spend with family (the average European spends 1.2 hours driving to and from work per day), save more money (almost €1500 per year at the current price of petrol), and breath cleaner air (almost 3000 kilograms of CO2 will be kept out of the atmosphere). According to the Centre for Renewable Energy Sources (CRES), European buildings account for 50% of carbon dioxide emissions, 35% of material consumption, 45% of energy demand, and 10-35% of waste that goes to a landfill [1]. A *peripheral moment* (the term peripheral moment is used in a book The Peripheral Moment by I. Rupnik and represents a decade 1999 – 2010 of architectural experimentation in Croatia) [2] in a Croatian architecture has resulted with a various competitions. Partly it's because of construction boom in last decade, partly because of Public Procurement Act (Official Gazette no. 117/2001 & 197/2003). However, only a few of them dealt with some topics of sustainability. The Croatian architecture just recently started to catch up a step concerning sustainability in designing new buildings or renovation projects. This approach will bring about a new trend in Croatian architecture. All maintained is only with theoretical projects and seminars and less with realizations. The article deals with the way of popularization of sustainability in Croatian architecture and the architect's emerging role in Croatian sustainable society (Fig. 1).

2. ELABORATION

2.1. Research Method

In Croatia, in the last decade, there was an unprecedented building boom trend, as a resulted from public competitions and therefore many realizations of PBS buildings. The authors participated in more public competitions, worked on technical studies and realized a few PBS projects. Only a few preparations of the competitions have a study with some elements of sustainability guidelines.

The conducted competitions were followed and analyzed from the competitions announcement until the results. None of them were realized. Then the existing regulations were inspected. At the end there is a conclusion and proposition for further acting.

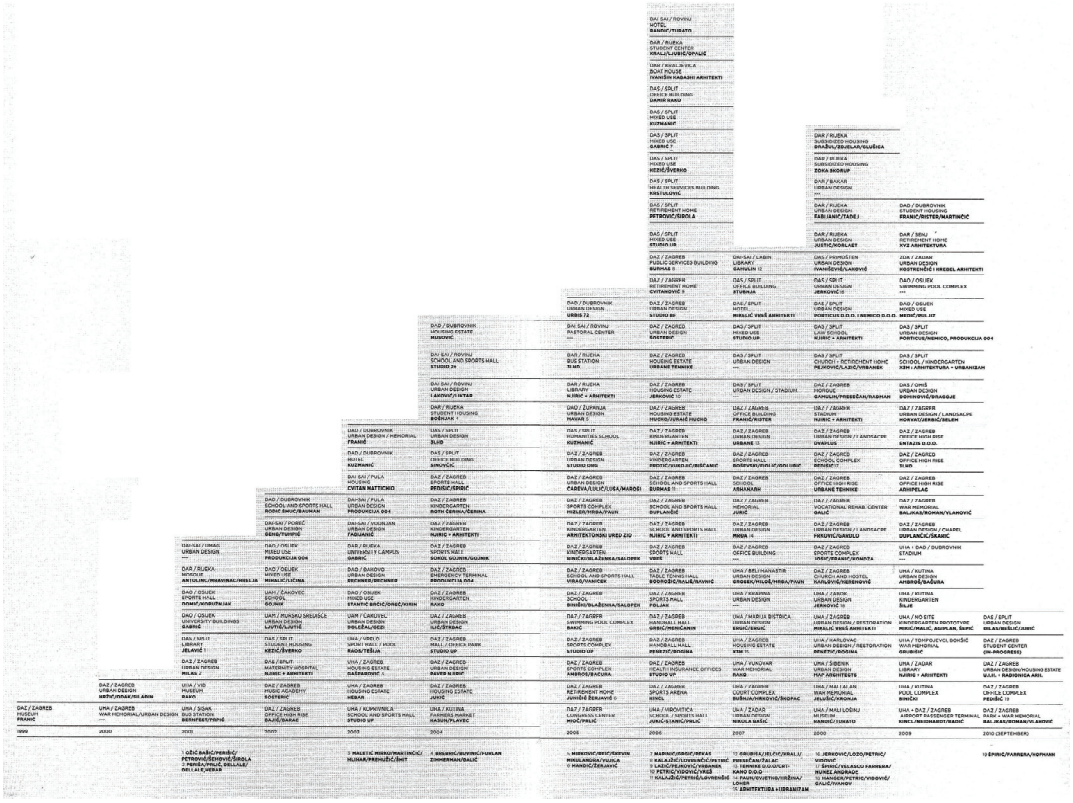


Figure 1. “Peripheral moment”

2.2. Sustainability and Public Building Standard

The term of sustainability is constantly supplemented. Most commonly quoted definition of sustainable construction is one of Brundtland’s reports that describe sustainable development as “development that enables them to meet the needs of present generations without compromising the needs of future generations” [3]. Sustainability is a complex area that requires a multidisciplinary approach and the participation of various professions and disciplines. It manifests itself at an economic, cultural and social level and on the preservation and improvement of the environment. Sustainability in the construction process is implemented through several different aspects of physical planning, use of energy sources, use of sustainable materials and to create a pleasant environment. “This definition clearly speaks about the long-term, overriding issue of sustainability: we should be living off of income and not stored capital. In other words, our society should be striving to live off of renewable resources and not one-time resources” [4]. “Philosophically, many embraced sustainable development as a moral obligation. However today's basically definition of sustainable development concept includes mutually interwoven economic, social and environmental dimension” [5]. Sustainable building is one of the meaningful segments of sustainable development and includes: appropriation of building materials that don’t harm the environment, energy efficient building and waste reduction management and building demolition. Sustainable development is a political and a global concept and major operational challenge is to find best way to translate it to the local level. For architecture and urban planning, it takes the form of the fundamental objective too, and creates the possibility of ideation and application of innovative models of "architectural structure" and "urban development" with increased sensitivity of environmental, political, cultural and financial components. Such an approach will ultimately lead to greater sensitivity and integration between regional, rural and urban strategic component development and construction [6]. Instruments that have proven to be good, and have demonstrated it through the contests that were held, are only the Public Building Standard (PBS) or the sustainable building design of public facilities. PBS implies nurseries, kindergartens, schools, community centers, student and elderly residences, children’s homes, places of care, hospitals, sport facilities like gymnasiums and swimming pools, administrative buildings, fire and police stations, prisons, community centers, religious centers, cultural facilities,

museums, libraries, performing arts centers – facilities whose building are financed within local self-government and state budget or with public-private initiatives. It is important that such facilities are social responsible and non-profit. They should be self sufficient and not the society's burden. "Civic facilities become flexible for new areas of urban life. They behave as focal points for cultural life, service nodes, gathering venues and driving forces of activity, extending their influence far beyond the walls that host them" [7]. The public sector facilities and the society itself need to be an example of ecological technologies and practices, and should be the economy generator, to represent energy self-sufficiency and to implement association of sustainable principles. The sustainability is a positive contribution to society. It serves the general good.

2.3. Positive Steps in Sustainability Regulations in Europe

An assessment of sustainable building according to standardized criteria introduces several international certificates. Such certificates provide added value to the investment. Leading national Sustainable Building certificators are: LEED, American; BREEAM, British; Green Star, Australian; CASBEE, Asian; DGNB, German; ÖGNI – Austrian (Fig. 2.).



Figure 2. Rating systems around the world

There are no universal criteria and definitions or methods, but everyone have similar rating system. Each of them creates standards for themselves. Depending on the legislation certification can be binding but in most countries is voluntary. For example, as the DGNB is established in its region, it began looking for bringing influence on the European region scale. "The foundation of the DGNB system is thoroughly international. It integrates all of the important requirements imposed by EU legislation and standards" says Dr. Christine Lemaitre, CEO of the DGNB [8] (Fig. 3.). DGNB is based on current European standards and building regulations and contains the European data sets required to carry out life cycle assessments. Eventually, Croatia could take over it and began networking in order to learn from one another's successes. Ecological, economical and socio-cultural issues are focal points in the planning, construction and operation of buildings. The criteria in the DGNB's core system define sustainable building in six evaluation areas:

- *Ecological quality* such as: global warming potential, ozone depletion potential, risks to the local environment, sustainable use of resources
- *Economic quality* such as: building related life-cycle costs and suitability for third-party use
- *Sociocultural and functional quality* such as: thermal comfort in the winter and in the summer, interior air hygiene, acoustic and visual comfort, quality of outdoor spaces, handicapped accessibility, space efficiency, suitability for conversion, assurance of design and urban development quality in a competition, social integration

- *Technical quality* such as: fire prevention, sound insulation, quality of building envelope, ease of use and equipment quality, durability, ease of dismantling and recycling
- *Process quality* such as: quality of project preparation, optimization and complexity of planning method, construction site / construction process, management
- *Site quality* such as: conditions in the micro-environment, access to transportation, proximity to use-specific facilities, connections to public services, legal situation for planning, extension options

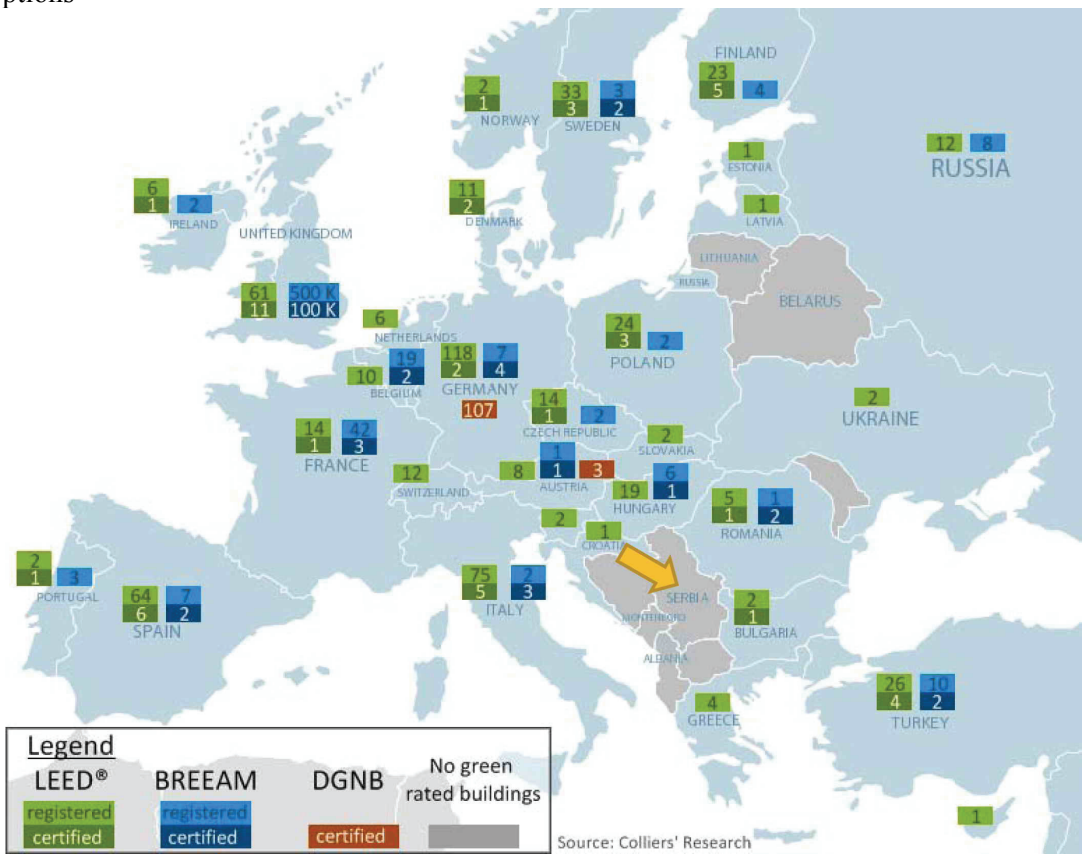


Figure 3. Green building in Europe

Each field contains special criteria that can be designed and weighted differently depending on the occupancy profile; each field is also viewed over the building's entire life cycle. If the building fulfills the criteria, it receives the DGNB Certificate in gold, silver or bronze, depending on the degree of fulfillment.

2.4. State of Croatian Regulations concerning Topics of Sustainability

Until now various events, such as forums, seminars, congresses, were trying to popularize sustainability in Croatia. In 2007 year Faculty of Architecture and Faculty of Engineering in Zagreb and Holcim launched a Forum on Sustainable Building. Later, Zagreb Energy Week from year 2010 and Symposium *Proto!Ekologike Arhipelag* Istra from year 2011 emerged. The Congress of Croatian Architects has been recognized as the central gathering place for all the relevant professions. The 3rd Congress' of Croatian Architects primary goal was to discuss the basic assumptions shaping our daily activities with the aim of adopting guidelines for the very concrete and necessary changes that will ensure the quality and sustainable development of our environment. Its intention was to put it as backbone of a national "Architectural Policy 2013" and to encourage the widest possible range of participants to actively contribute to the condition in space, to observe with a critical eye, and to suggest long-term strategies for reconstruction based on concrete interventions [9]. Beside these events, several institutions deal with sustainable building. The main institution is Ministry of Environmental Protection, Physical Planning and Construction, which launched Green Building Council in Croatia and Croatian Association of Energy Certifiers (HUEC) and Environmental Protection and Energy Efficiency Fund of Croatia. Energy Institute Hrvoje Požar is founded on a long lasting tradition of scientific research in the energy sector directing towards the fulfillment of requirements of the Republic Croatia and deals with national

energy programs. And finally we must mention Croatian Chamber of Architects that should be along with Ministry in the leading role in implementing sustainability into PBS. In addition to the building legislation there are also other parts of legislation and other regulations that are relevant for sustainable construction, although not directly targeted to the building sector, such as: environmental protection and environmental assessment, restrictions of certain emissions and waste management. One of the first entries of sustainability is implemented in National Environmental Strategy from 2002. "Croatia wishes to focus efforts to sustainable development and to align environmental objectives with the long-term national, social and economic interests" [10]. Then follows the Projections Of Greenhouse Gas Emissions with Croatian GHG Projections for the period 1990-2020 [11]. In the Environmental Protection Act, Strategy For Sustainable Development from 2009 among other things says: "The Strategy for Sustainable Development of the Republic of Croatia presumes a process of deliberation and negotiation for the purpose of reaching a consensus in order to determine priority economic, social and environmental challenges and the measures with which to respond to those challenges. The Ministry of Environmental Protection, Physical Planning and Construction is responsible for coordination and drafting of the Strategy, with all the necessary institutional support" [12]. But within the strategy, the construction is not mentioned as an important factor in the environment preservation. From year 2018 all new houses in the European Union will need to be energy self-sufficient. Croatian legislation is slowly coming into line with EU regulations.

2.5. Discussion

During last ten years in Croatia number of public facilities strongly grew. That happened in *peripheral moment* – a decade of architectural experimentation in Croatia – a ten-year cycle of competitions. As Eve Blau said there is a freedom of the periphery in the distance from power and all that it entails: "the absence of strong institution and systems of patronage, the lack of material resources and political authority. It is distance from power, rather than unremitting chance that creates opportunities for architecture" [2]. Unlike architecture, sustainability needs a power to be conducted, and sustainable architecture needs PBS and regulations as an opportunity to start his path. Architectural associations must take responsibility for the next generations. Implementation of sustainable design in Croatia architecture will contribute to end the decade of experimentation, but could also be a new challenge in form. Here are few case studies that represent sustainable topics: public urban and architectural competition for The Borongaj Campus of the University of Zagreb, public architectural and urban competition for Craft Centre Blato in Zagreb and public architectural competition for Typical Timber Structure Nursery Case.

2.5.1. Case study 1: The Borongaj Scientific and Academic Campus of the University of Zagreb, 2011

The founding premise for the Borongaj campus is to focus on the environment and sustainability. In partnership with industry, government and academic leaders, Borongaj as a green campus will provide the intellectual capital, experiential infrastructure, financial capacity and presentation opportunities to showcase novel and necessary approaches to efficient energy and natural resources utilization, the development of alternative energies, creative food production and distribution processes and many other elements related to serving Croatia, Europe and the world. The University of Zagreb has a firm commitment in promoting sustainable development. As a member it will be obliged to sign and practice in the International Sustainable Campus Network (ISCN). The key goals of ISCN members are:

- Sustainable construction, renovation and campus operation
- Sustainable campus master planning, development and community integration
- Linking facilities, research and education for sustainable development [13]

The Borongaj Campus should be an ecological oasis and a point of reference for the production and use of green energy in the city. It will be a place of developing and implementing contemporary approaches to design and maintenance of the environment as well as using economical and energy-efficient building technologies. Borongaj should be a polygon for testing sustainability principle for both the University and the City of Zagreb. The competitors have to design the campus based on the sustainable construction and environment through use and production of all types of renewable and alternative energy which can be rationally produced and used on the spot. They should take into account that the most rational and environmentally friendly technologies should be used as well as those that will return resources invested into the energetic field as fast as possible, based on the Croatian state incentives and the EU directives. The competition should please the obligations through three concerns: urbanism, architecture and installation. (i) *Concerning urbanism:* optimal urban volume disposition rationally indented architectural volume composition, greenery around the buildings. (ii) *Concerning architecture*: efficient building insulation based on principle of "1-litre house" whenever possible, all glass surfaces should be equipped

with active sun protection system. (iii) *Concerning installation*: alternative energy sources that have a possibility of transferring to renewable energy sources [14]. It is rear example of competition for public projects of this scope and significance in Croatia in last ten years. It is also unique example of implementing a sustainable approach in general conditions of competition preparations for planning and designing with obligation. But, the guidelines of the Expert group for the sustainable construction where much more defining installation conditions, and much less dealing with urban planning and architectural design. Such a large dominantly urban and architectural competition should focuses more on the complex issues of urban planning.

2.5.2. Case study 2: Craft Centre Blato in Zagreb, 2010

Croatian Chamber of Trades and crafts with Municipality of Zagreb in year 2010 organized the competition for Craft Centre with a high school in Blato district. Competition consists of several different programs: secondary craft school, shopping centre, business centre facilities, hotel, bank and other accompanying contents. Competition guidelines have some entries concerning energy efficiency and energy savings but as a whole, sustainability wasn't main criteria. In assessing the competition work, essential criteria were: physical and functional program requirements represented with 20% share, formal and spatial qualities represented with 20%, subjective Court jury member represented with 20%, targets development of the tender includes represented with 10%, efficiency represented with 10%, energy efficiency and energy savings represented with 10%, stage construction and relations between different parts of the task represented with 10% [15].

2.5.3. Case study 3: Typical Timber Structure Nursery, 2009

Project *Timber is first!* [16] carried by Croatian Chamber of Economy, Ministry of Regional Development, Forestry and Water Management and Association for forest management 'Croatian woods' with Association of Croatian architects, started a joint architectural competition for typical kindergarten of wooden construction. This competition means to enhance use of timber materials and architectural methodology in development of timber-construction kindergartens. Natural materials, with ecological substance are put first, especially woods of Croatian origin. Demands are made in regard to mobile wooden construction from monolith timber, laminated panels and other wooden products. Competition presumed optimal kindergarten orientation, spatial concept and design that should meet demands of energetic efficiency and use of sustainable energy sources that are dependent on future real location of particular building. In process of future developing, sustainable installation should be observed like alternative energy sources that have a possibility of transferring to renewable energy sources.

These elements also were taken into consideration as a part of final judgment:

- Functional, esthetic, design and spatial qualities
- Adaptability to changing locations conditions and spatial demands
- Rational wooden construction system
- Economy in construction and maintenance
- Energetic efficiency and use of sustainable energy sources

This could be the best and the only real example of implementation of sustainable conditions into competitions conditions for architectural design. Regretfully, further project development led to half-way solution [17].

2.6. Outcome - Regulated Sustainability Topics for PBS

These three examples show that all of them are PBS and that their competition programs have implemented some of sustainable building design guidelines. Also it is characteristic that nothing happened after the competitions. During April 2005., the *Croatian Chamber of Architects* and the *Croatian Architects Association* drew up the proposal of the *Ordinance on tender of architectuel and urban field*, which has been accepted and published in year 2006 [18]. The Ordinance points out that the competition is confirmed as a comparative method of getting high quality concept designs of public and private buildings, planning and expansion of towns and settlements. The competition may ask the functional, formal, environmental, technical and economic tasks. It aims to improve the overall quality of design, construction and design [19]. The first step to implement the principles of sustainable design into Croatian architecture is regulation of legal acts. It should be agreement between the state and the municipal and public sector. Sustainable design should be the basic task of competition. Beside that, the Competion Procedure (the fifth section of The Ordinance) could set up additional requirements for sustainable design such as:

- mandatory requirement for PBS in *Competition Vacancy Notices* (art. 34.)
- studies on sustainability in *Other substrate and competition documentation* (art. 35.)
- presentation of applied project measurements on sustainability in *Competition work* (art. 36.)
- sustainability request in *Evaluation criteria* (art. 37.)
- lectures on the topic of sustainability in *Colloquium* (art. 42.) [20]

Its target is to create user friendly and widely accepted framework for implementing sustainable topics in performance of buildings. This requirements should be manadatory for all PBS and optional for all other facilities. The jurisdiction of these requirements should belong to *Croatian Chamber of Architects* and the *Association of Croatian Architects*. In this way such step could be applied immediately. Economic prosperity in general aside, the benefit of sustainable design is inevitable. "It is Confirmed that minimal increases in upfront costs of about 2% to support green design would, on average, result in life cycle savings of 20% of total construction costs -- more than ten times the initial investment" [21]. Today it is estimated that investment in green building in Croatia is up to 5% more expensive than a standard investment in the building [22]. All large investments in Croatia need to undergo the procedure of competition too. That justifies the implementation of sustainable design into *Ordinance on tender of architecture and urban field* [20]. Once a new occupancy profile has been adopted, the pilot phase begins. This would make architects protagonists of social progress. It would be follow principles of sustainable development. The next step of implementing the sustainable design into law regulations is a part of *Ministry of Environmental Protection, Physical Planning and Construction* jurisdiction. This refers to implementing the sustainable design requirements into *Physical Planning and Building Act* [23] as a legal base, and other supporting Ordinances. Particularly that refers to *Essential principles for technical quality of building* (article 14. of *Physical Planning and Building Act*) for which the sustainable design should be one of the most important demands. In that way all the regulations will become the obligation of PBS and optional for other facilities. The scheme is developed essentially for building projects and all of them must meet the basic requirement level of assessment criteria in order to be granted a site and building permit. "Projects should be characterized by a high degree of social responsibility, not only in relation to materials and production but also regarding positive, social spaces encouraging intimacy and community. The objective of sustainability has holistic approach to create value ranging from social values to location-determined, infrastructural, demographic and climatic values. It is possible to save most of the energy consumption simply by designing and situating correctly in relation to the surrounding urban landscape and climate. Achieving sustainability is about making the right design decisions" [24]. The implementation will have full value only if it had a clear political support and if it is constantly analyzed and improved. Implementing Sustainability into Croatian Architecture would help additional co-funding of PBS by EU funds, which would cause a positive impact on our everyday living and working environments and on society in general. "The innovation of the public implicates that the future is not based on negating the past, but on understanding the transition. And in Croatia it runs on a very fast train" [25].

3. CONCLUSIONS

Building is one of the meaningful segments of sustainable development and includes: appropriation of building materials that don't harm the environment, energy efficient building and waste reduction management and building demolition. This way the definition of sustainable building draws attention for need of design guidelines that will be an integral part of defining the sustainable building within legal act. The first step to implement the principles of sustainable design into Croatian architecture is regulation of legal acts. Sustainable design should be incorporated into *Ordinance on tender of architectural and urban field.* These requirements should be mandatory for all PBS and optional for all other facilities. In this way such step could be applied immediately. In Croatia all PBS projects should undergo the procedure of competition. The next step is to implement the sustainable design into *Essential principles for technical quality of building* of *Physical Planning and Building Act* for which it should be one of the most important requirements. Implementing Sustainability into Croatian Architecture would help additional funding of PBS by EU funds, which would cause a positive impact on society in general. The public sector facilities and the society itself need to be an example of ecological technologies and practices, be the economy generator, represent energy self-sufficiency and implement sustainability principles. Burden of implementation should not be put on the private sector, private investment is expected to see benefits of sustainable development eventually. Sustainable building should educate the

public and set up the standard and new economic concept of responsibility. That also raises the investments of energy effective and renewable technologies from private and corporative sector. The sustainability is a positive contribution to society. This article attempts not to bring a finished implementation of sustainability regulation but to set up a thesis about the logic of introducing topics of sustainability in the building environment through the construction of PBS, not only as an example for other construction sectors, but also to private capital, and finally, the resident. The public sector is in the service of sustainable building practices. Sustainable approach is the opportunity to use design to change our environment.

REFERENCES

[1] Green building council of Croatia, Why build green (info@gbccroatia.org)
[2] I. Rupnik, A Peripheral Moment: Experiments in Architectural Agency, Actar, New York, 2010.
[3] ED, Our Common Future, Oxford University Press, Oxford, UK, 1987.
[4] J. Judelson (2009.), Sustainable Retail Development - New Success Strategies, International Council of Shopping Centers, Springer, New York. 2009.
[5] Ž.Kordelj – De Villa, P.Stubbs, M.Sumpor, Participatory Governance for Sustainable Development, Ekonomski institut, Zagreb, 2009, 1-35.
[6] LR Simposium PROTO!EKOLOGIKE ARHIPELAG ISTRA 2011., Speculative Materialism In Architecture
[7] A. Fernández Per, Civilities. Reviving the Heart of the City, Civilities I, A+T Architecture Publishers, 2007.
[8] Certification System, The DGNB Certificate. Your system for sustainable quality. German Sustainable Building Council, Copyright 2011
[9] 3rd Congress of Croatian Architects, ARCHITECTURAL POLICY 2013, Split, 2010.
[10] National Environmental Strategy, Republic of Croatia Ministry of Environmental Protection, Physical Planning and Construction, Zagreb, 2002. (Official Gazette No. 46/02, 2002)
[11] Projections Of Greenhouse Gas Emissions, Republic of Croatia Ministry of Environmental Protection, Physical Planning and Construction, Prepared by EKONERG, Zagreb, 2004.
[12] Strategy for Sustainable Development of the Republic Of Croatia, Zagreb, 2009. (Official Gazette 110/07)
[13] B. Baletić, M. Kovačević, L. Moneta, The Borongaj Campus of the University of Zagreb, A Systems View, University of Zagreb, Zagreb, 2010
[14] The Borongaj Campus Public Competition Programme for Elaboration of a Preliminary Urban and Architectural Design, University of Zagreb, Zagreb, October, 2010.
[15] Craft Centre Blato Public Competition Programme for Elaboration of a Preliminary Urban and Architectural Design, City of Zagreb, Zagreb, 2009.
[16] Timber is first!, Croatian Chamber of Economy, Ministry of Regional Development, Forestry and Water Management and Association, 2007-2009.
[17] Typical Timber Structure Nursery Public Competition Programme for Elaboration of a Preliminary Architectural Design, Croatian Chamber of Economy with Association of Croatian Architects, Zagreb, 2008.
[18] Competitions of a Urban and Architectural Design, Croatian Chamber of Architects, Zagreb, 2007.
[19] Flooding of architectural competitions during the summer drought, NN/Zadar newspaper/PressCut
[20] Ordinance on tender of architecture and urban field, Croatian Chamber of Architects, Zagreb, 2006. (Official Gazette no. 1127/06, 2006)
[21] G. H. Kats, Green Building Costs and Financial Benefits, Massachusetts Technology Collaborative, Massachusetts, USA, 2003.
[22] Vedrana Likan, Does it make sense to build green, 4. Croatian Forum on Sustainable Building, 2010.
[23] Physical Planning and Building Act, Croatian Parlament, 2011. (Official Gazette 76/07, 38/09, 55/11, 90/11)
[24] Henning Larsen Architects, Sustainability (www.henninglarsen.com/architecture/sustainability.aspx)
[25] L. F. Martinez de Maration, The innovation of public, Man and Space 03/04 2008, 62-65.

CEMEX

Alternative fuels in cement plants – sustainable development based on industrial ecology

Cement plants have a significant role to play in helping to overcome Croatian waste management problems

Alternative fuels, as various kinds of processed waste material left after all other options for recycling or reusing are exhausted, can be used in cement kilns as a substitute for fossil fuels. Besides the decrease of necessity for the use of non-renewable energy sources fossil fuels are, their use also decreases total carbon emissions, thus influencing greenhouse effects.

This is exactly what Croatian cement plants are now obligated to do – drop their CO2 emissions in accordance to the Kyoto protocol by the beginning of 2013. Croatian CEMEX, a part of the worldwide CEMEX group, utilized examples of extensive European practice that used alternative fuels for over forty years. CEMEX's plants in Europe substitute up to 70 percent of fuels with alternative ones in their production, from different types of biomass to industrial and communal waste.

There are multiple benefits that come out of the use of waste as alternative fuel in cement industry; not only does it help industry deal with climate change, it also help communities deal with waste management issues in a modern and safe way and preserve natural resources.



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