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EKO-CEMENT IZ PROIZVODNOG OTPADA

ECO-CEMENT FROM INDUSTRIAL WASTE

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ABSTRACT

The manufacture of portland cement (PC) consumes huge amount of raw materials and fossil fuels contributing significantly to the overall anthropogenic CO_2 emission. Calcium sulfoaluminate cement (CSAC) is a promising alternative binder to PC due to lower limestone requirement and significantly lower sintering temperature for CSAC production than for PC. Furthermore, the product is much easier to grind than PC. 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. Qualitative mineral composition of CSAC had been determined by X-ray diffraction analysis (XRD), and mass fraction of Klein's compound (the principal hydraulic mineral) had been determined by quantitative XRD. Rate of heat generation during hydration of CSAC prepared had been determined by microcalorimetry. Volume stability, compressive and flexural strength of standard size specimens had been determined. In conclusion, CSAC production offers an alternative and feasible way of industrial waste minimization.

KEYWORDS: *calcium sulfoaluminate special cement, waste minimization, phosphogypsum, electric arc furnace slag, coal bottom ash.*

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1. INTRODUCTION

Calcium sulphoaluminate cement 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 [10]. At same mixing water to cement ratios and achieved degrees of hydration the obtained porosity of cement pastes made from calcium sulphoaluminate cement 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 calcium sulphoaluminate cement, especially in that of the AFt type [10] hydration products. About million tons of calcium sulphoaluminate cement type cements are produced annually in China [14], where special cement standards were issued. To manufacture calcium sulphoaluminate cement 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 [9]. Throughout the paper cement mineralogy shortend notation was used (C=CaO, A=Al_2O_3, S=SiO_2, s=SO_3, F=Fe_2O_3, M=MgO, T=TiO_2). Kleinite ($4CaO \cdot 3Al_2O_3 \cdot SO_3$ i.e. C_4A_3s in shortened cement mineralogy notation) 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, calcium sulphoaluminate cement 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 [10]. 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 calcium sulphoaluminate cement is between 30 – 40% [3]. Belite has only very small contribution to early strength development, but is mainly responsible for the ultimate strength of the calcium sulphoaluminate cement. 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 $CaSO_4$.

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. 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. Therefore, Phosphogypsum could serve as a raw material for calcium sulfoaluminate cement production [1]. In this work, calcium sulfoaluminate cement production from various industrial by-products had been investigated. The main hydraulically active mineral of calcium sulfoaluminate cement is Kleinite, $4CaO \cdot 3Al_2O_3 \cdot SO_3$, formed by the following high-temperature chemical reaction:

$$4\,CaCO_3 + 6\,AlOOH + CaSO_4 \cdot 2H_2O \rightarrow 4CaO \cdot 3Al_2O_3 \cdot SO_3 + 4\,CO_2 + 5H_2O \qquad (1)$$

In other words, it could be stated that Kleinite is prepared from the mixture of limestone, bauxite and phosphogypsum in right proportions. For the first time, mineral Kleinite had been prepared in early 1960 [7], but its hydration had been thoroughly investigated only recently [1, 3, 9, 10, 14]. Kleinite reacts with water and dissolved gypsum added during milling of calcium sulfoaluminate clinker, giving up calcium monosulfate aluminate hydrate and ettringite as main hydration products [2]:

$$4CaO\cdot 3Al_2O_3\cdot SO_3 + 2\ CaSO_4\cdot 2H_2O \rightarrow 6CaO\cdot Al_2O_3\cdot 3SO_3\cdot 32H_2O + 4\ Al(OH)_3 \quad (2)$$

Glasser and Zhang [6] calculated the optimal gypsum addition to the calcium sulfoaluminate clinker between 20-25%, based on the main hydration reaction (Eq. 3). Production of calcium slufoaluminate cement is highly attractive because of the lower firing temperatures, lower CO_2 emissions and use of industrial wastes and by-products as raw materials [1].

2. EXPERIMENTAL

2.1 Raw materials

Phosphogypsum, coal bottom ash and electric arc furnace slag are three industrial waste materials used for calcium sulfoaluminate cement production, while final bulk chemical composition was adjusted by bauxite and limestone addition relying on the results of mineral phase equilibrium investigation by Sahu and Majling [11].

2.2 Mixing and firing

All the raw materials used had been separately milled in planetary mill Pulverisette 5, using steel balls and bowl and sieved through the wire sieve of 125 micrometer mesh. Each component of the final batch had been carefully weighted and dry mixed in ordinary ball mill. The raw meal had been transferred to the large ceramic crucible and fired in gas furnace at temperature of 1170 °C for 3 hours. The fired clinkers were relatively soft and friable, and were easy to grind.

2.3 X-ray fluorescent analysis

Chemical composition of calcium sulfoaluminate cement samples had been determined by X-ray fluorescence analysis using Oxford LAB-X3500 instrument.

2.4 X-ray powder diffraction

X-ray powder diffraction (XRD) for a qualitative phase analysis was conducted on calcium sulfoaluminate clinkers prepared. The samples were milled by hand in corundum pestle and crucible and then mounted in sample holder. The powder diffraction patterns were gathered over the range of 5-50° 2θ at a step of 0.02° for 1 s collection time. All the measurement were performed using Shimadzu XRD-6000.

2.4.1 Quanitative X-ray powder diffraction

We employed the quantitative X-ray diffraction (QXRD) by using the adiabatic principle with auto flushing [4, 5, 8] as a proven suitable method for quantifying the minerals in cement. Rutile was used as a standard in this study. In this work, C_4A_3s in prepared sample is quantified based on the Chung method: i.e. determined by additional mixing of synthesised pure C_4A_3s 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 in the required stoichiometric mole proportion, dried at 105 °C and fired at 1150 °C, for 4 h in an air atmosphere electric furnace. Each sample prepared for QXRD was mixed with 10 mass % of rutile. Appropriate corrections for peak overlap were meticulously applied by inference to the (measured) intensities of the pattern due to the pure phases.

2.5 Hydration calorimetry

Semiisothermal hydration microcalorimetry was performed for selected clinkers at 20 °C. The water to cement ratio was maintained at 0.50 for all the measurements. Rate of heat evolution during first 24 hours of hydration was measured. Other details of semiisothermal microcalorimeter construction and operation had been described previously [12, 13].

2.6 Mechanical property measurement

Compressive strengths were measured on halves obtained after flexural strength determination on standard 40×40×160 mm prisms. The water to cement ratio was maintained at 0.44 for all the measurements. After 1 day of curing, the molds were removed. The specimens were cured in a 20±1 °C water bath until flexural and compressive strength determination. The flexural and compressive strengths were measured after 2 and 28 days of curing.

Table 1. 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	-	-	-
Bottom ash	54	23	7	5	-	-	-	-	-
Bauxite	3.5	57	22.5	1	0.5	-	2.5	< 1	-
Phosphogypsum	-	-	-	40	-	-	-	-	58

Table 2. Raw meal composition for calcium sulfoaluminate cement firing.

Component	**sample 1**	**sample 2**	**sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**
Phosphogypsum	12%	18%	30%	20%	25%	25%	12.5%
Electric arc furnace slag	12%	0%	19%	32%	20%	27%	33.75%
Bottom ash	12%	18%	18%	0%	22%	10%	12.5%
Limestone	42%	46%	25%	25%	25%	25%	31.25%
Bauxite	22%	18%	8%	23%	8%	13%	12.5

Table 3. Results of chemical analysis and semiquantitative X-ray fluorescence analysis of calcium sulfoaluminate cement clinkers sample 1 and sample 2.

Property, %	**sample 1**	**sample 2**
Moisture	0,11	0,10
L. O. I.	0,35	0,27
Insoluble residue	10,69	6,23
CaO, free	0,07	0,15
SiO_2	21,14	17,45
Fe_2O_3	10,52	6,76
Al_2O_3	16,41	16,65
CaO	37,65	44,91

MgO	2,19	0,54
SO_3	6,93	10,76
Cl	0,0038	0,0175

3. RESULTS AND DISCUSSION

Phosphogypsum is very pure and contains small amounts of impurities, mainly SiO_2 and fluoride. Because of more than 95% gypsum content, PG is a potentially valuable industrial by-product. In the raw meal for calcium sulfoaluminate cement production, phosphogypsum is main source of sulfate needed for Kleinite formation. For the preparation of calcium sulfoaluminate cement, beside phosphogypsum another two industrial by-products had been used: coal bottom ash and electric arc furnace slag. Despite very similar chemical composition to the fly ash, coal bottom ash is not so widely used as cement clinker additive, mostly due to the presence of unburned char, coarser particle size, less specific surface area and potentially smaller reactivity in cement. Electric arc furnace slag is by-product of steel production and refinement in electric furnaces, available in large quantities. Chemical composition of used raw materials (in mass %) is presented in **Table 1**. The calcium slufoaluminate cement sample clinkers were formulated attempting to obtain different contents of cement mineral phases (**Table 2**). Seven series of calcium sulfoaluminate clinkers were synthesized. The final chemical composition of raw meal for calcium sulfoaluminate cement production had been adjusted by bauxite and limestone addition (**Table 2**). Chemical composition of the calcium sulfoaluminate clinkers prepared had been determined by X-ray fluorescent analysis, shown in **Table 3**.

After homogenization and firing, the calcium sulfoaluminate clinker obtained had been analyzed by X-ray powder diffraction (**Figs 1 and 2**), revealing the presence of Kleinite, $4CaO·3Al_2O_3·SO_3$, sulfospurrite, $5CaO·2SiO_2·SO_3$, anhidrite, $CaSO_4$, belite, $2CaO·SiO_2$, feritte phase, $4CaO·Al_2O_3·Fe_2O_3$ and titanium bearing perovskite like phase $3CaO·Fe_2O_3·TiO_2$. Although the true composition of feritte phase is uncertain due to the possibility of iron-aluminium substitution in solid solution, the relative quantity of ferrite phase is larger for sample 1 that contains more iron oxide than sample 2 (**Table 3**).

Kleinite is main mineral in calcium sulfoaluminate clinkers prepared. Its hydration with water and dissolved gypsum is very rapid giving up rapid strength gain. However, the presence of other minerals is also important, because their reactivity with water is lower. It is interesting to observe large quantity of belite and sulfospurite in both samples due to the relatively high SiO_2 content (**Table 3**). Belite and sulfospurite in the cement clinker hydrate slowly and contribute to strength in latter stages of hydration.

Mass fraction of Klein's compound in the prepared calcium sulphoaluminate cement as determined by quantitative X-ray powder diffraction (**Table 4**) was shown to be in the range 27 to 32 mass %, **Table 4**. As the optimal C_4A_3s content in non-expansive calcium sulphoaluminate cement is between 30 – 40% [3, 10] one can conclude that calcium sulphoaluminate cement production offers an alternative and feasible way of the investigated industrial waste minimization.

Rate of heat generation on water addition (due to wetting, dissolution and hydration reactions in general) of samples prepared is shown in **Figure 3**. The rate of heat generation is typical of cement hydration, i.e. initial rapid heat generation is due to the initial wetting and dissolution of minerals, presumably mostly Kleinite and anhydrite followed by nucleation and growth of hydrate phases, mostly ettringite. The dormant period is clearly observed in case of sample 2, but is overlapped by other processes in case of sample 1 hydration. The maximum rate of heat generation occurs between 200-400 minutes and 400-700 minutes for samples 1 and 2 respectively, followed by gradual decrease up to 24 h hydration. It is worth noting that monotonically decaying period of hydration after 400 minutes and 700 minutes for samples 1 and 2 respectively could be fitted as single exponentially decay curve. However it is more important to observe qualitatively similar hydration behavior of samples 1 and 2. Rapid heat evolution starts immediately as water is added to the cement clinker. The heat effect is greater for sample 2 than for sample 1 and is well separated from the following process that could be observed as a shoulder on the main hydration peak between 200 and 300 minutes. Analogous process for sample 1, clearly visible between 50-100 minutes of hydration is overlapped with both initial heat evolution and main hydration peak. The main hydration peak is composed of two exothermic processes that are partially separated in case of sample 2 hydration, but are highly overlapped for sample 1 hydration. After maximal rate of heat liberation, the hydration processes monotonically slow down.

Pilot scale 5 kg batches yielded enough calcium sulfoaluminate cement clinker for comprehensive testing. Calcium sulfoaluminate cement batches had been prepared with the addition of 5 and 10% gypsum to further test development of strength according to the HRN EN-197-1:2005. It was interesting to observe chocolate brown color of cement mortars. The color of the calcium sulfoaluminate cement mainly depends on the quantity and oxidation state of iron compounds, and changes from yellowish- brown up to dark brown had been observed, depending on the initial composition and firing conditions.

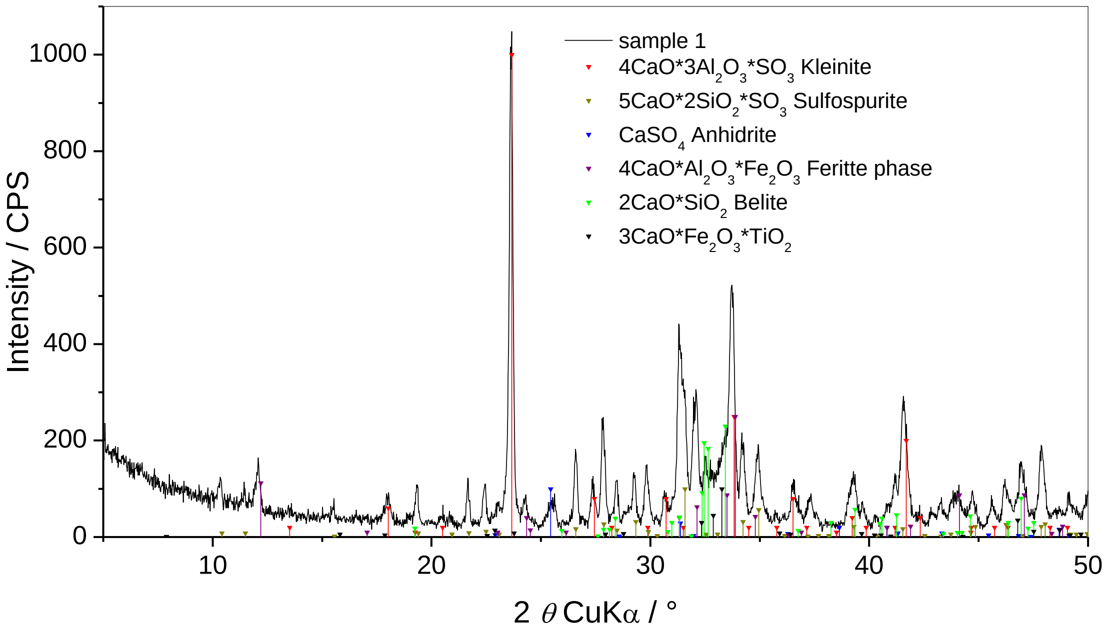

Figure 1. Result of X-ray powder diffraction analysis of sample 1 prepared.

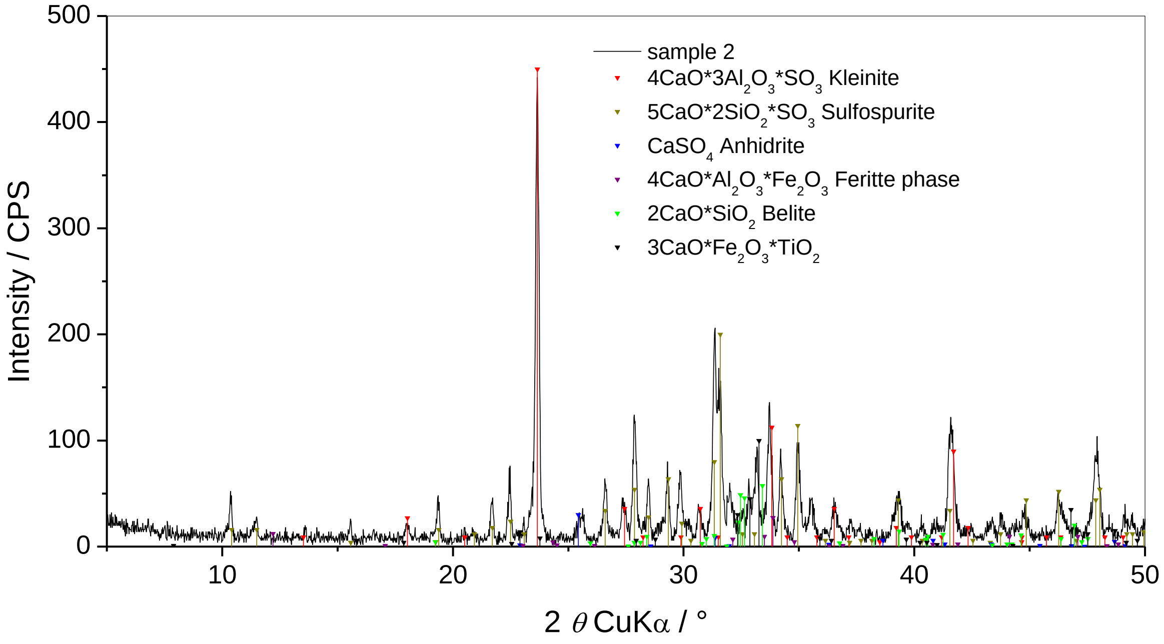

Figure 2. Result of X-ray powder diffraction analysis of sample 2 prepared.

Table 4. Results of the quanitative X-ray powder diffraction analysis.

Sample	3	4	5	6	7
w(Kleinite), %	28.1	27.1	31.3	32.0	29.2

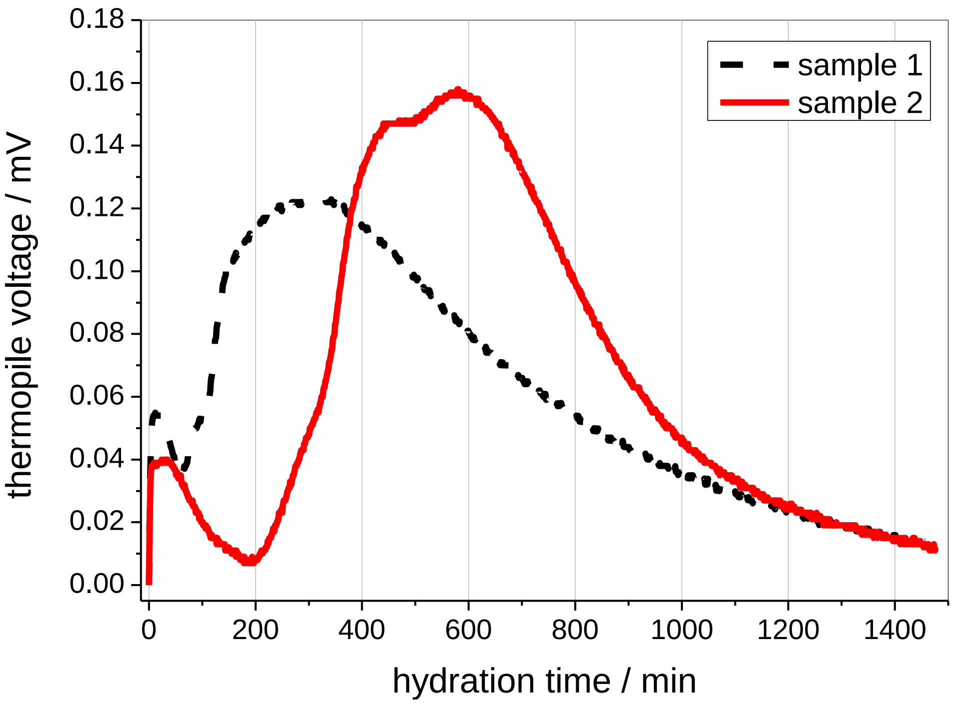

Figure 3. Rate of heat generation, proportional to the thermopile voltage, due to the hydration of samples 1 and sample 2 in microcalorimeter at 20 °C and water to cement ratio, *w*/*c*=0.5.

Table 5. Properties of calcium sulfoaluminate cements prepared from pilot scale batches with the 5%, and 10% gypsum addition.

Property	**unit**	**5% gypsum added**		**10% gypsum added**	
		Sample 1	**Sample 2**	**Sample 2**	**Sample 2**
Le Chatellier expansion		0	0	0	0
Flexural strength, 2 days	N/mm^2	2.3	2.6	2.1	2.3
Flexural strength, 28 days	N/mm^2	3.3	3.5	2.8	3.4
Compressive strength, 2 days	N/mm^2	9.5	11.4	11.1	13.3
Compressive strength, 28 days	N/mm^2	12.9	17.1	14.9	18.3

Properties of calcium sulfoaluminate cements prepared from pilot scale batches with the 5%, and 10% gypsum addition are shown in **Table 5**. From the results of **Table 3** and **Table 5**, it could be concluded that higher density and higher insoluble residue content is due to the greater Fe_2O_3 quantity in sample 1. Lower strengths observed for sample 1 are also due to the higher SiO_2 quantity in sample 1, giving up more belite and sulfospurite that both hydrate slowly. It could be argued that increasing specific surface of cements and addition of more gypsum would result in greater flexural and compressive strengths of standard mortar samples.

4. CONCLUSIONS

Calcium sulphoaluminate cement materials are a potentially very attractive high-performance eco-cement. The potential benefits offered by calcium sulphoaluminate cement 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 calcium sulphoaluminate cement.

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. 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. Therefore, Phosphogypsum could serve as a raw material for calcium sulfoaluminate cement production.

Seven series of calcium sulfoaluminate clinkers were synthesized attempting to obtain different contents of cement mineral phases. Mass fraction of Klein’s compound in the prepared calcium sulphoaluminate cement as determined by quantitative X-ray powder diffraction was in the range 27 to 32 mass %. Measured mechanical properties of calcium sulfoaluminate cements prepared from pilot scale batches with the 5%, and 10% gypsum addition show promising results. In conclusion, calcium sulphoaluminate cement production offers an alternative and feasible way of industrial waste minimization.

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EKO-CEMENT IZ PROIZVODNOG OTPADA

ECO-CEMENT FROM INDUSTRIAL WASTE

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SAŽETAK

Proizvodnja portland cementa (PC) troši velike količine sirovina i fosilnih goriva, te značajno doprinosi sveukupnoj emisiji CO_2. Kalcij sulfoaluminatni cement (CSAC) je relativno nova vrsta hidratnog veziva koju je moguće uporabiti umjesto portland cementa. Proizvodnja kalcij sulfoaluminatnog cementa zahtijeva manju količinu vapnenca i značajno niže temperature za završetak reakcije, a konačni proizvod lakše se melje od portland cementa. Svaka od nabrojanih prednosti proizvodnje CSAC značajno smanjuje utrošak energije i emisiju CO_2.

U ovom radu istražene su moguće prednosti proizvodnje CSAC uporabom proizvodnog otpada već prisutnog u Republici Hrvatskoj u velikim količinama. Kao sirovine za proizvodnju CSAC korišteni su: fosfogips, ložišni pepeo iz termoelektrane i šljaka električnih peći za rafinaciju čelika. Kvalitativni mineraloški sastav CSAC određen je metodom rendgenske difrakcije (XRD), a maseni udio Kleinovog spoja (glavnog hidratno aktivnog minerala CSAC) određen je metodom kvantitativne rendgenske difrakcije. Brzina oslobađanja topline tijekom hidratacije pripravljenog CSAC određena je mikrokalorimetrijski, a volumna postojanost, tlačna i savojna čvrstoća određeni su na pripravljenim uzorcima standardnih dimenzija. Na osnovi rezultata istraživanja slijedi da je proizvodnja CSAC iz proizvodnih otpadnih materijala moguća, a ujedno se na taj način zbrinjava velika količina otpada na održivi način.

KLJUČNE RIJEČI: *kalcij sulfoaluminatni cement, zbrinjavanje otpada, fosfogips, šljaka, ložišni pepeo*

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1. UVOD

Kalcij sulfoaluminatni cement se intenzivno istražuje unazad nekoliko godina stoga što je za njegovu proizvodnju potrebna znatno manja količina energije (engl. „low energy cement”) nego za proizvodnju Portland cementa (PC) [10]. Uz isti vodocementni omjer ili isti stupanj napredovanja hidratacije poroznost paste sulfoaluminatnog cementa je značajno manja od paste uobičajenog cementa opće namjene, PC. Manja je poroznost posljedica stehiometrije kemijskih reakcija hidratacije, tj. veće količine kemijski vezane vode u produktima hidratacije sulfoaluminatnog cementa, posebice AFt faza, u odnosu na PC [10]. U Kini se godišnje proizvede oko milijun tona kalcij sulfoaluminatnog cementa [14] prema odgovarajućem nacionalnom standardu. Proizvodnja kalcijevog sulfoaluminatnog cementa temelji se na žarenju odgovarajuće smjese sirovina pri temperaturi od 1200-1300 °C. Uporaba fosfogipsa koji je industrijski nusproizvod pri proizvodnji fosfatne kiseline u smjesi sirovina dovodi do smanjenja potrebne temperature i vremena u procesu proizvodnje [3]. U industrijskim razmjerima proces proizvodnje kalcijevog sulfoaluminatnog cementa odvija se u rotacijskim pećima uobičajenim u proizvodnji Portland cementa [9]. U ovom radu koristi se skraćena notacija uobičajena u kemiji cementa (C=CaO, A=Al_2O_3, S=SiO_2, s=SO_3, F=Fe_2O_3, M=MgO, T=TiO_2). Kleinov spoj ($4CaO \cdot 3Al_2O_3 \cdot SO_3$ tj. C_4A_3s u skraćenoj notaciji) je glavna mineralna faza koja doprinosi brzom razvoju čvrstoće tijekom hidratacije. Ovisno o udjelu pojedinih mineralnih faza u klinkeru i posebno udjelu kalcijeva sulfata, moguće je pripraviti volumno postojan kalcij sulfoaluminatni cement visoke rane čvrstoće ili ekspanzivni cement. Ova je razlika posljedica nastanka etringita prije (volumno postojan) ili nakon (ekspanzija) razvitka krutog skeleta čestica cementa. Kako bi se spriječila ekspanzija, etringit mora nastati u odsutnosti slobodnog CaO [10]. Ipak, određena količina CaO u kalcij sulfoaluminatnom cementu je poželjna jer doprinosi visokim ranim čvrstoćama i brzom razvoju čvrstoće. Optimalni udio C_4A_3s u volumno postojanom (ne-ekspanzivnom) kalcij sulfoaluminatnom cementu je između 30 – 40 % [3]. Belit, dikalcijev silikat C_2S, malo doprinosi razvoju rane čvrstoće materijala, no kasnija, polagana hidratacija doprinosi konačnoj čvrstoći sulfoaluminatnog cementa. Ternesit ili sulfospurit, C_5S_2s, nastaje pri oko 900 °C i raspada se iznad 1200-1280 °C u belit, C_2S, i anhidrit, $CaSO_4$ [3].

Fosfogips nastaje kao industrijski nusproizvod proizvodnje fosfatne kisline, a zbog tehnološkog procesa proizvodnje sadrži povećani sadržaj prirodnih radioaktivnih nuklida (TENORM, engl. technologically enhanced naturally occuring radiactive material). Zbog radioaktivnosti i njezina štetna djelovanja, komercijalna uporaba fosfogipsa u svijetu je vrlo ograničena. Američka agencija za zaštitu okoliša (EPA) zabranila je uporabu fosfogipsa u SAD, a dozvoljeno je samo odlaganje fosfogipsa unatoč tome što bi se mogao komercijalno primijeniti u ograničenim količinama.

Fosfogips iz proizvodnje „Petrokemije d.d.“ iz Kutine, Hrvatska, je s obzirom na kemijski sastav i sadržaj radionuklida klasificiran kao neopasni otpad i dozvoljeno je njegovo odlaganje. Stoga je fosfogips moguće uporabiti kao sirovinu za proizvodnju kalcij sulfoaluminatnog cementa [1]. U ovom radu je istražena priprava kalcij sulfoaluminatnog cementa iz više otpadnih materijala. Najvažnija hidratno aktivna mineralna faza u kalcijevom sulfoaluminatnom cementu je Kleinov spoj, $4CaO \cdot 3Al_2O_3 \cdot SO_3$, koji nastaje tijekom visokotemperaturnih kemijskih reakcija:

$$4\,CaCO_3 + 6\,AlOOH + CaSO_4 \cdot 2H_2O \rightarrow 4CaO \cdot 3Al_2O_3 \cdot SO_3 + 4\,CO_2 + 5H_2O \qquad (1)$$

Drugim riječima, Kelinov spoj se pripravlja iz odgovarajuće smjese vapnenca, boksita i fosfogipsa. Ovaj je mineral prvi puta pripravljen 60-tih godina prošlog stoljeća [7], no njegova je hidratacija detaljno istražena tek unatrag nekoliko godina [1, 3, 9, 10, 14]. Kleinov spoj reagira sa vodom i otopljenim gipsom dodanim tijekom mljevenja kalcij sulfoaluminatnog klinkera, pri čemu nastaju kalcijev monosulfat aluminat hidrat i etringit kao glavni produkti reakcije hidratacije, uz nešto aluminatnog gela [2]:

$$4CaO\cdot 3Al_2O_3\cdot SO_3 + 2\ CaSO_4\cdot 2H_2O \rightarrow 6CaO\cdot Al_2O_3\cdot 3SO_3\cdot 32H_2O + 4\ Al(OH)_3 \quad (2)$$

Glasser i Zhang [6] su na temelju ove kemijske reakcije (2) izračunali optimalnu količinu gipsa dodanog kalcij sulfoaluminatnom klinkeru, što iznosi 20-25 % od mase klinkera. Proizvodnja kalcij sulfoaluminatnog cementa je interesantna stoga što je potrebna niža temperatura rotacijskih peći, manje su emisije CO_2, te se u proizvodnji rabi veliki udio industrijskih otpadnih materijala kao sirovina [5].

2. EKSPERIMENTALNI DIO

2.1 Sirovine za proizvodnju kalcij sulfoaluminatnog cementa

Industrijski otpadni materijali: fosfogips nastao tijekom proizvodnje fosfatne kiseline, ložišni pepeo termoelektrane na ugljen i troska električnih peći za taljenje čelika su uporabljeni za proizvodnju kalcij sulfoaluminatnog cementa. Konačni je kemijski sastav smjese sirovina podešen dodatkom boksita i kalcita, ponajviše s obzirom na rezultate istraživanja fazne i kemijske ravnoteže u sustavu CaO-Al_2O_3-SO_3-SiO_2-Fe_2O_3 autora Sahu i Majling [11].

2.2 Miješanje i pečenje

Sve su sirovine odvojeno samljevene u planetarnom mlinu Pulverisette 5, sa čeličnim posudama i kuglicama, te prosijane kroz žičano sito veličine svjetlog otvora od 125 mikrometara. Svaka je komponenta konačne smjese sirovina pažljivo odvagana, a smjesa sirovina je homogenizirana u kugličnom mlinu, na suho. Homogena smjesa je prenesena u keramičke lončiće za žarenje te paljena u plinskoj peći na temperaturi od 1170 °C tijekom 3 sasta. Pripravljeni klinker je nakon hlađenja relativno porozan i krhak te se lako melje.

2.3 Kemijska analiza metodom rendgenske fluorescentne analize

Kemijski sastav kalcij sulfoaluminatnog cementa određen je metodom rendgenske fluorescentne analize na uređaju Oxford LAB-X3500.

2.4 Rendgenska difrakcijska analiza

Za potrebe rendgenske difrakcijske analize (određivanja kvalitativnog i kvantitativnog faznog sastava) uzorci klinkera su ručno usitnjeni u kornudnom tarioniku te stavljeni u nosač uzorka, a difraktogram je snimljen u području kuta od 5-50° 2θ uz korak od 0.02° i vrijeme integracije od 1 sekunde, na uređaju proizvođača Shimadzu, Japan, XRD-6000.

2.4.1 Kvantitativna rendgenska difrakcijska analiza

Kvantitativni sastav kalcij sulfoaluminatnog klinkera određen je obradom rezultata rendgenske difrakcijske analize Chungovom metodom [4, 5, 8], koja se uobičajeno primjenjuje za cementne materijale. Rutil, TiO_2, je dodan kao standard, a maseni udio C_4A_3s u klinkeru određen je uz pomoć dodatnih rezultata rendgenske difrakcijske analize smjese sintetiziranog C_4A_3s u smjesi sa rutilom (50:50, po masi). Mineral C_4A_3s pripravljen je iz taložnog kalcita ($CaCO_3$, čistoće *pro analysi*, Kemika), anhidrita ($CaSO_4$, čistoće *pro analysi*, Kemika) i gibsita ($Al(OH)_3$, Sigma-Aldrich) mokro homogeniziranih u planetarnom mlinu prema stehiometriji kemijske reakcije. Gusta suspenzija osušena pri 105 °C paljena je u laboratorijskoj peći u atmosferi zraka na 1150 °C tijekom 4 sata. Svaki je uzorak za kvantitativnu rendgensku difrakcijsku analizu pomiješan sa 10% rutila (po masi), a intenzitet je difrakcijskih maksimuma korigiran s obzirom na prisutne faze.

2.5 Kalorimetrijsko praćenje hidratacije cementa

Hidratacija cementa pri 20 °C praćena je semiizotermnom mikrokalorimetrijom. Vodocementni omjere bio je 0,50 u svim mjerenjima, a brzina razvoja topline hidratacije mjerena je tijekom prva 24h. Drugi detalji o kontrukciji i radu semiizotermnog mikrokalorimetra opisani su prethodno [12, 13].

2.6 Mjerenje mehaničkih svojstava standardnih uzoraka

Miješanjem standardnog pijeska, vode i pripravljenog kalcij sulfoaluminatnog cementa, uz vodocementni omjer od 0,44 pripravljen je cementi mort za punjenje standardnih kalupa. Nakon 24h njege u vlažnom zraku, standardne prizme dimenzija 40×40×160 mm izvađene su iz kalupa, te dalje njegovane u vodi pri 20±1 °C, sve do trenutka određivanja savojne i tlačne čvrstoće. Savojna i tlačna čvrstoća određene su nakon 2 i 28 dana njege, a čvrstoća na tlak određena je na polovicama standardnih prizmi dobivenih nakon određivanja savojne čvrstoće.

Tablica1. Kemijski sastav uporabljenih sirovina (maseni udio, %).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	TiO_2	$Na_2O + K_2O$	SO_3
Troska električne peći	11	2	30	33	13	6	-	-	-
Ložišni pepeo	54	23	7	5	-	-	-	-	-
Boksit	3.5	57	22.5	1	0.5	-	2.5	< 1	-
Fosfogips	-	-	-	40	-	-	-	-	58

Tablica 2. Sastav smjesa sirovina za pripravu kalcijevog sulfoaluminatnog cementa

Komponenta	**uzorak 1**	**uzorak 2**	**uzorak 3**	**uzorak 4**	**uzorak 5**	**uzorak 6**	**uzorak 7**
Fosfogips	12%	18%	30%	20%	25%	25%	12.5%
Troska električne peći	12%	0%	19%	32%	20%	27%	33.75%
Ložišni pepeo	12%	18%	18%	0%	22%	10%	12.5%
Vapnenac	42%	46%	25%	25%	25%	25%	31.25%
Boksit	22%	18%	8%	23%	8%	13%	12.5

Tablica 3. Rezultati kemijske analize i semikvantitativne rendgenske fluorescentne analize klinkera kalcij sulfoaluminatnog cementa, uzorak 1 i uzorak 2.

Svojstvo, %	**uzorak 1**	**uzorak 2**
Vlaga	0,11	0,10
Gubitak žarenjem	0,35	0,27
Netopljivi ostatak	10,69	6,23
CaO, slobodni	0,07	0,15

SiO_2	21,14	17,45
Fe_2O_3	10,52	6,76
Al_2O_3	16,41	16,65
CaO	37,65	44,91
MgO	2,19	0,54
SO_3	6,93	10,76
Cl	0,0038	0,0175

3. REZULTATI I RASPRAVA

Fosfogip sadrži male količine primjesa, ponajviše SiO_2 i fluorida. Budući da sadrži više od 95% gipsa, fosfogips je ekonomski vrlo interesantan industrijski nusproizvod. U smjesi sirovina za proizvodnju kalcij sulfoaluminatnog cementa, fosfogips je glavni izvor sulfata potrebnih za nastanak Kleinova spoja. Za pripravu kalcij sulfoaluminatnog cementa, osim fosfogipsa rabe se i dva druga industrijska nusproizvoda: ložišni pepeo od gorenja ugljena i troska električnih peći za proizvodnju čelika. Unatoč tome što ložišni pepeo ima vrlo sličan kemijski sastav letećem pepelu, puno se manje koristi kao dodatk cementu zato jer sadrži i neizgorenu čađu, čestice su veće nego kod letećeg pepela, a specifična površina i reaktivnost u cementu su manje. Troska električnih peći je nusproizvod proizvodnje čelika te je dostupna u velikim količinama. Kemijski sastav uporabljenih sirovina (maseni udio, %) prikazan je u **Tablici 1**. Sastavi smjesa sirovina za pripravu kalcij sulfoaluminatnog klinkera formulirani su kako bi se dobio različit udio mineralnih faza (**Tablica 2**). Pripravljeno je sedam serija kalcij sulfoaluminatnog klinkera. Konačni kemijski sastav smjese sirovina podešen je dodatkom boksita i vapnenca (**Tablica 2**). Kemijski sastav pripravljenih kalcij sulfoaluminatnih klinkera određen je metodom rendgenske fluorescentne analize, te je pokazan u **Tablici 3**.

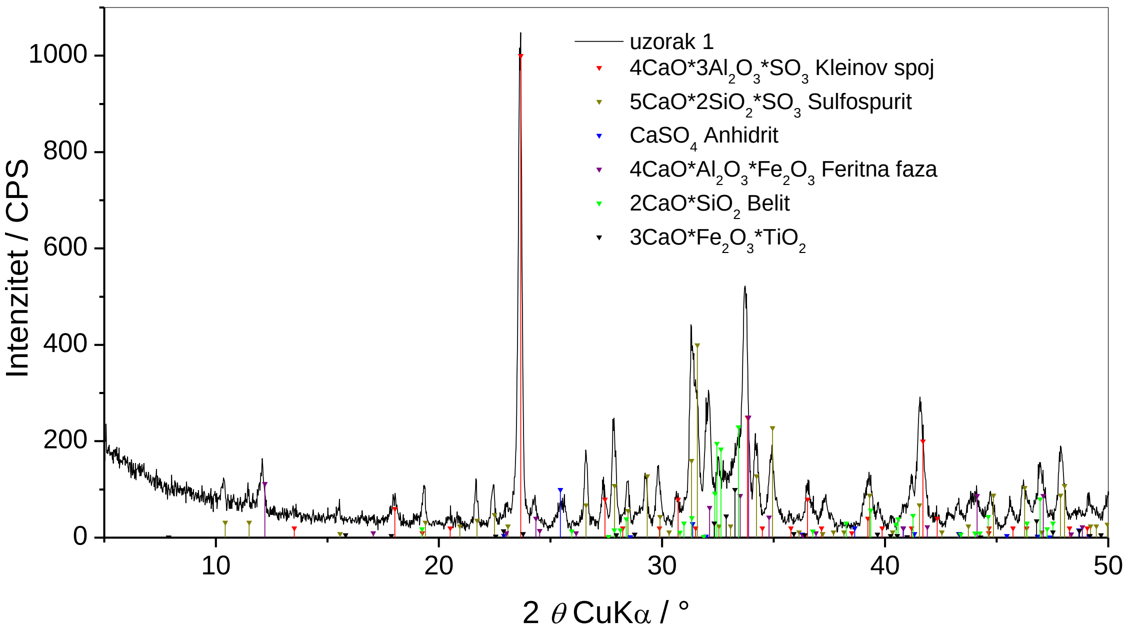
Nakon homogenizacije i paljenja mineraloški sastav kalcij sulfoaluminatnog klinkera određen je metodom rendgenske difrakcijske analize (**Slike 1 i 2**), ukazujući na prisutnost: Kleinova spoja, $4CaO{\cdot}3Al_2O_3{\cdot}SO_3$, sulfospurita, $5CaO{\cdot}2SiO_2{\cdot}SO_3$, anhidrita, $CaSO_4$, belita, $2CaO{\cdot}SiO_2$, feritne faze, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ i perovskitu sličnih faza koje sadrže titan $3CaO{\cdot}Fe_2O_3{\cdot}TiO_2$. Iako je pravi sastav feritne faze nepoznat zbog mogućnosti zamjene aluminija željezom, udio zamjene u čvrstoj otopini veći je za uzorak 1 nego za uzorak 2 jer uzorak 1 sadrži više oksida željeza nego uzorak 2 (**Tablica 3**).

Kleinov spoj je glavni hidratno aktivni mineral u pripravljenom kalcij sulfoaluminatnom klineru. Njegova hidratacija sa vodom i otopljenim gipsom je vrlo brza te dolazi do brzog porasta čvrstoće. Ipak, važna je i prisutnost drugih minerala zato jer je njihova reaktivnost s vodom manja. Interesantno je primijetiti velike količine belita i sulfospurita u oba uzorka zbog relativno velikog udjela SiO_2 (**Tablica 3**). Belit i sulfospurit hidrataiziraju vrlo polako te čvrstoći cementa pridonose tek u kasnijem razdoblju hidratacije.

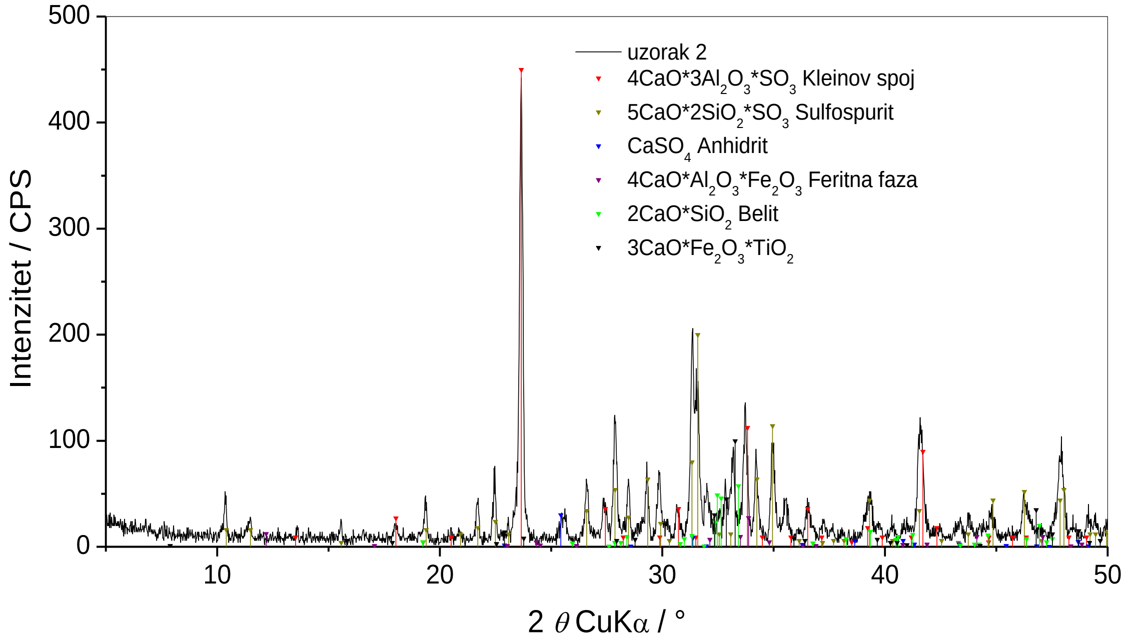
Maseni udio Kleinova spoja u pripravljenom kalcij sulfoaluminatnom cementu određen je kvantitativnom difrakcijom rendgenskih zraka (**Tablica 4**), te je pokazano da iznosi od 27 do 32 % mase uzorka. Budući da je optimalni udio C_4A_3s u volumno postojanom kalcij sulfoaluminatnom cementu između 30 – 40 % [3, 10] zaključuje se da je proizvodnja kalcij sulfoaluminatnog cementa alternativni i ostvarljiv put smanjenja količine navedenih industrijskih otpadnih materijala.

Brzina generacija topline po dodatku vode (zbog kvašenja površine, otapanja minerala i drugih fizikalno-kemijskih reakcija) pripravljenih uzoraka prikazana je na **Slici 3**. Brzina generacije topline je uobičajena za hidrataciju cementa, tj. brzo početno oslobađanje topline kao posljedica kvašenja površine i otapanja minerala, vjerojatno ponajviše Kleinova spoja i anhidrita praćeno je nukleacijom i rastom hidratanih faza, većinom etringita. Razdoblje indukcije se jasno vidi u slučaju hidratacije uzorka 2, no preklopljeno je sa drugim egzotermnim procesima u slučaju hidratacije uzorka 1. Najveća brzina hidratacije vidljiva prema najvećoj brzini generacije topline nastupa tijekom razdoblja od 200-400 minuta od trenutka dodatka vode za uzorak 1, te tijekom 400-700 minuta od trenutka dodatka vode za uzorak 2, nakon čega slijedi monotoni pad brzine generacije topline do završetka mjerenja nakon 24 sata. Napominje se da je razdoblje monotono padajuće brzine hidratacije nakon 400 odnosno 700 minuta moguće opisati jednom krivuljom eksponencijalnog pada, no to nije dalje istraživano. Važnije je istaknuti kvalitativno slično ponašanje tijekom hidratacije za uzorke 1 i 2. Brzi razvoj topline započinje odmah po dodatku vode cementnom klinkeru. Toplinski je efekt veći za uzorak 2 nego za uzorak 1, te je dobro razdvojen od sljedećih procesa koji se očituju kao rame na glavnom piku hidratacije nakon 200 do 300 minuta. Sličan je proces u slučaju uzorka 1 vidljiv nakon svega 50-100 minuta hidratacije, te je preklopljen i sa pikom početne generacije topline i glavnim pikom hidratacije klinkera. Glavni pik hidratacije klinkera sastoji se od dva egzotermna procesa koji su djelomično razdvojeni u slučaju hidratacije uzorka 2, no jako su preklopljeni u slučaju hidratacije uzorka 1. Uskoro nakon što je postignuta najveća brzina generacije topline, hidratacija monotono usporava, sve do završetka mjerenja nakon 24 sata hidratacije.

Poluindustrijskom pripravom šarži od po 5 kg klinkera kalcij sulfoaluminatnog cementa raspolagalo se sa dovoljno materijala za sveobuhvatna laboratorijska ispitivanja karakteristična za praćenje procesa proizvodnje Portland cementa. Kalcij sulfoaluminatni cement pripravljen je iz klinkera dodatkom 5 odnosno 10% mase gipsa kako bi se ispitala čvrstoća prema normi HRN EN-197-1:2005. Interesantno je primijetiti neuobičajenu čokoladnu boju cementnog morta. Boja kalcij sulfoaluminatnog cementa najviše ovisi o količini i stupnju oksidacije spojeva željeza, te se mijenja od žuto-smeđe do tamno smeđe, ovisno o početnom sastavu i uvjetima paljenja.



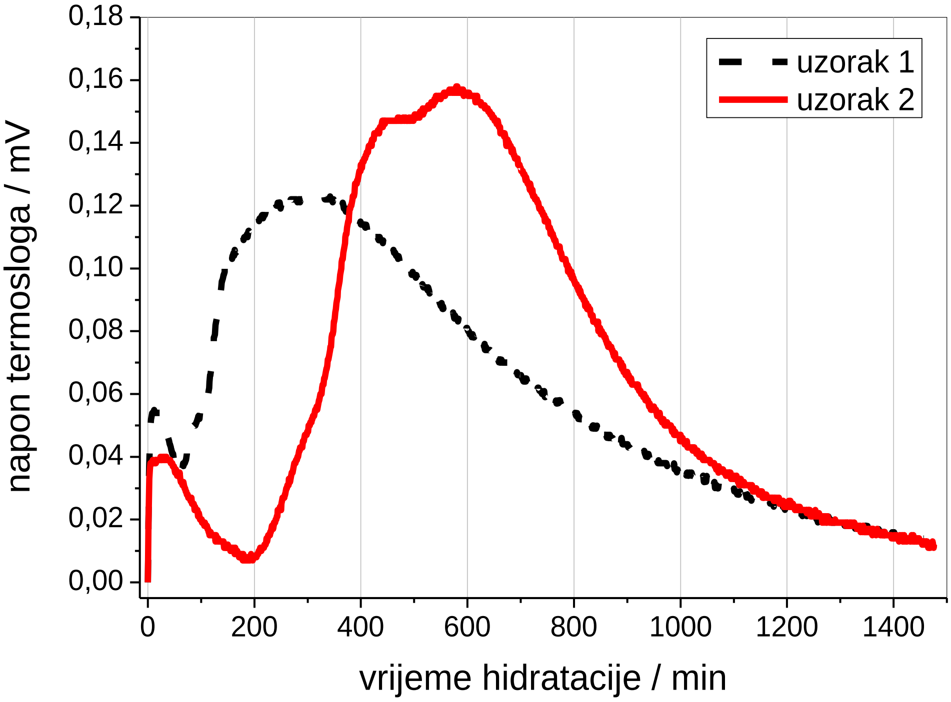
Slika 1. Rezultat rendgenske difrakcije klinkera uzorka 1.



Slika 2. Rezultat rendgenske difrakcije klinkera uzorka 2.

Tablica 4. Rezultat kvanititativne rendgenske difrakcijske analize.

Uzorak	3	4	5	6	7
w(Kleinova spoja), %	28.1	27.1	31.3	32.0	29.2



Slika 3. Prikaz brzine generacije topline proporcionalne naponu termosloga u mikrokalorimetru tijekom hidratacije uzoraka 1 i 2 pri 20 °C i vodocementni omjer, *v*/*c*=0.5.

Tablica 5. Svojstva kalcij sulfoaluminatnog cementa pripravljenog u poluindustrijskom mjerilu, uz dodatak 5% i 10% mase gipsa.

Svojstvo	**Mjerna jedinica**	**5% dodatka gipsa**		**10% dodatka gipsa**	
		uz. 1	**uz. 2**	**uz. 1**	**uz. 2**
Eksp. po Le Chatelieru	mm	0	0	0	0
Savojna čvrstoća, 2 dana	N/mm^2	2.3	2.6	2.1	2.3
Savojna čvrstoća, 28 dana	N/mm^2	3.3	3.5	2.8	3.4
Tlačna čvrstoća, 2 dana	N/mm^2	9.5	11.4	11.1	13.3
Tlačna čvrstoća, 28 dana	N/mm^2	12.9	17.1	14.9	18.3

Svojstva kalcij sulfoaluminatnog cementa pripravljenog u poluindustrijskom mjerilu, uz dodatak 5% i 10% mase gipsa prikazana su u **Tablici 5**. Iz rezultata prikazanih u **Tablici 3** i **Tablici 5**, može se zaključiti da je veća gustoća i veći udio netopljivog ostatka posljedica većeg udjela Fe_2O_3 u uzorku 1. Manja čvrstoća uzorka 1 također je posljedica većeg udjela SiO_2 u uzorku 1, te posljedično tome i veće količine belita koji polagano hidratizira. Na temelju drugih spoznaja može se pretpostaviti da će veća specifična površina cementa i dodatak veće količine gipsa doprinijeti većim savojnim i tlačnim čvrstoćama uzoraka standardnog cementnog morta.

4. ZAKLJUČCI

Kalcij sulfoaluminatni cement može se nazvati eko-cementom dobrih primjenskih svojstava. Proizvodnjom kalcij sulfoaluminatnog cementa iz otpadnih materijala koji se u velikim količinama već nalaze u Republici Hrvatskoj ostvaruje se niz ušteda. Uporabom industrijskih otpadnih materijala: fosfogipsa, ložišnog pepela i troske električnih peći kao sirovina za proizvodnju kalcij sulfoaluminatnog cementa ekološki pozitivno utječe na okoliš.

Uporaba fosfogipsa još je uvijek ograničena, a razlozi nisu samo zakonska ograničenja nego i činjenica da je fosfogips relativno novi otpadni materijal te je industriji potrebno određeno vrijeme prilagodbe prije nego što ga počinju koristiti. Na temelju kemijskog sastava te sadržaja radionuklida fosfogips iz proizvodnje Petrokemije, d.d. u Kutini smatra se neopasnim otpadom, te je Petrokemiji d.d. omogućeno daljnje odlaganje fosfogipsa. Stoga je fofogips moguće uporabiti kao sirovinu za proizvodnju kalcij sulfoaluminatnog cementa.

Sedam priprava kalcij sulfoaluminatnig klinkera sadrže različite udjele hidratno aktivnih mineralnih faza. Maseni udio Kleinova spoja u pripravljenim klinkerima određen je kvantitativnom difrakcijom rendgenskih zraka, a kreće se od 27 do 32 %. Mehanička svojstva određena ispitivanjem poluindustrijskih šarži uz dodatak 5% i 10% gipsa pokazuju ohrabrujuće rezultate. Na temelju sve navedenog zaključuje se da je proizvodnja kalcij sulfoaluminatnog cementa moguć i ostvariv način smanjenja količine industrijskog otpada.

5. ZAHVALA

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