Faculty of Chemical Engineering and Technology
University of Zagreb

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

SEM 2011

Conference Proceedings

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

Sponsored by:

CEMEX

3rd International Symposium on

Environmental Management

Towards Sustainable Technologies

October 26 – 28, 2011, Zagreb, Croatia

CONFERENCE PROCEEDINGS of SEM2011

Publisher:
Faculty of Chemical Engineering and Technology, University of Zagreb,
Marulićev trg 19, 10000 Zagreb, Croatia

Phone: +385 1 4597 281, Fax: +385 1 4597 260, E-mail: office@fkit.hr

Editors:
Natalija Koprivanac, Hrvoje Kušić and Ana Lončarić Božić

Logo:
Edi Murgić

A CIP catalogue record for this book is available from the National and University Library in Zagreb under 780938

ISBN 978-953-6470-56-3

3rd International Symposium on Environmental Management

Towards Sustainable Technologies

October 26 – 28, 2011, Zagreb, Croatia

Organized by:

Faculty of Chemical Engineering and Technology, University of Zagreb
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)

Under the auspice of:

Croatian Parliament; Ministry of Environmental Protection, Physical Planning and Construction; Ministry of Science, Education and Sport; Ministry of the Sea, Transport and Infrastructure; Ministry of Environment and Spatial Planning of Kosovo; Office for Sustainable Development of Monte Negro; University of Zagreb; University of Split; Croatian Academy of Engineering; Croatian Environment Agency; Environmental Protection and Energy Efficiency Fund; Croatian Chamber of Economy; American Chamber of Commerce in Croatia (Green Building Council); Croatian Business Council for Sustainable Development; Energy Institute Hrvoje Požar; The Institute of Economics, Zagreb; The Croatian Association of Engineers; Croatian Society of Chemical Engineers; Croatian Chamber of Architects; District of Cazin (BIH)

Scientific and Organizing Committee

President: Natalija Koprivanac
Roko Andričević, Anđelka Bedrica, Felicita Briški, Besim Dobruna, Neven Duić, Mark Gero, Zlata Hrnjak-Murgić, Tonka Kovačić, Savka Kučar-Dragičević, Dragan Kukavica, Stanislav Kurajica, Hrvoje Kušić, Stjepan Leaković, Danuta Leszczynska, Ana Lončarić Božić, Nenad Mikulić, Ljubomir Miščević, Zoran Nakić, Lidija Pavić-Rogošić, Gordana Pehnec-Pavlović, Davor Romić, Suad Rošić, Nenad Smodlaka, Siniša Širac, Martina Šumenjak, Vesna Tomašić, Branko Tripalo, Đurđa Vasić-Rački

International Scientific Advisory Board

Prof. Dr. I. Balcioglu (TUR), Prof. Dr. F. Bašić (HR), Prof. Dr. M. C. Cann (USA), Prof. Dr. D. D. Dionysiou (USA), Prof. Dr. S. Esplugas (ESP), Dr. F. Evers (NED), Prof. Dr. M. Giaoutsi (GRE), Prof. Dr. P. Glavič (SLO), Dr. C. Hey (GER), Prof. Dr. M. Hraste (HR), Dr. Lj. Jeftić (HR), Prof. Dr. M. Kaštelan-Macan (HR), Prof. Dr. V. Kaučič (SLO), Prof. Dr. B. Kunst (HR), Prof. Dr. J. Leszczynski (USA), Prof. Dr. A. Magerholm Fet (NOR), Prof. Dr. A. Majcen Le Marechal (SLO), Prof. Dr. M. Metikoš-Huković (HR), Prof. Dr. P. Novak (SLO), Prof. Dr. G. Li Puma (UK), Prof. Dr. M. Schreurs (GER), Prof. Dr. M. Scoullos (GRE), Dr. S. Švaljek (HR), Dr. V. Vađić (HR), Prof. Dr. G. Varallyay (HUN), Prof. Dr. D. T. Waite (AUS), Prof. Dr. T. Winnicki (PL)

IRON-ALUMINUM SOLID SOLUTION IN KLEIN'S COMPOUND

Juraj Šipušić*, Neven Ukrainczyk, Marina Đopar

Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia

* e-mail: jsipusic@fkit.hr

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.

$$3CaCO_3 + 3Al_2O_3 + CaSO_4\times 2H_2O \rightarrow 4CaO\times 3Al_2O_3\times SO_3 + 3CO_2 + 2H_2O \qquad (1)$$

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 $\lambda(\mathrm{CuK}_\alpha) = 0.15418$ 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.

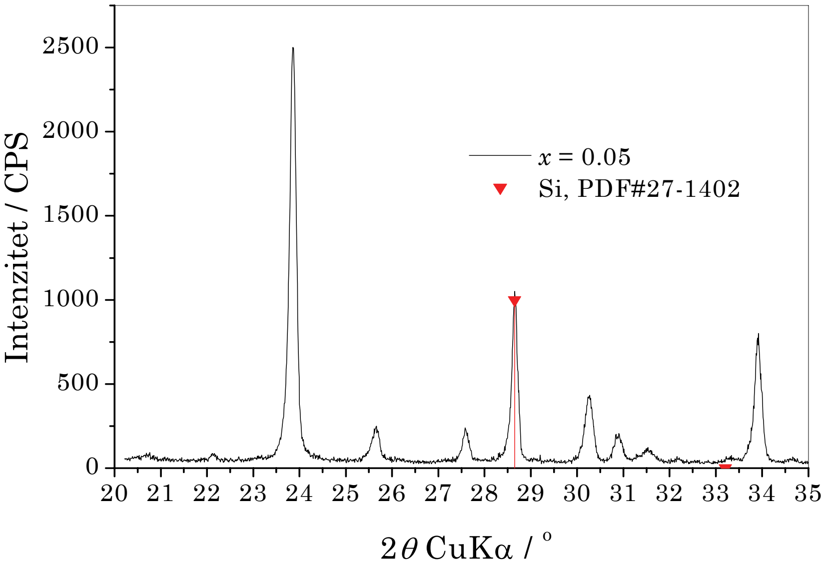

Figure 1. X-ray diffraction of calcined mixture of precursor materials corresponding to the following potential composition of Klein compound, $C_4A_{3(1-x)}F_{3x}s$, where x=0.05. The position of silicon standard (10% by mass) is marked red.

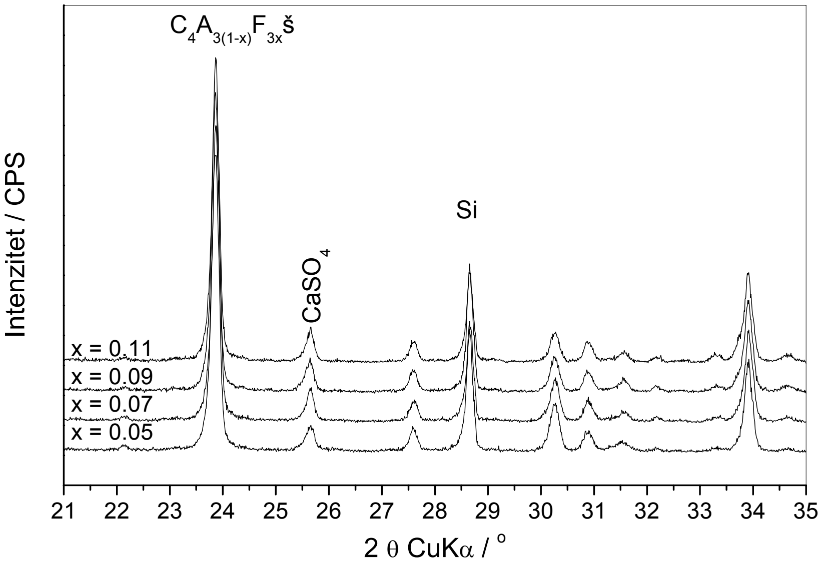

Figure 2. X-ray diffraction of calcined mixtures of precursor materials corresponding to the following potential composition of Klein compound, $C_4A_{3(1-x)}F_{3x}s$, where x=0.05, 0.07, 0.09 and 0.11. Traces of anhydrite mineral, $CaSO_4$, is present in the calcined samples

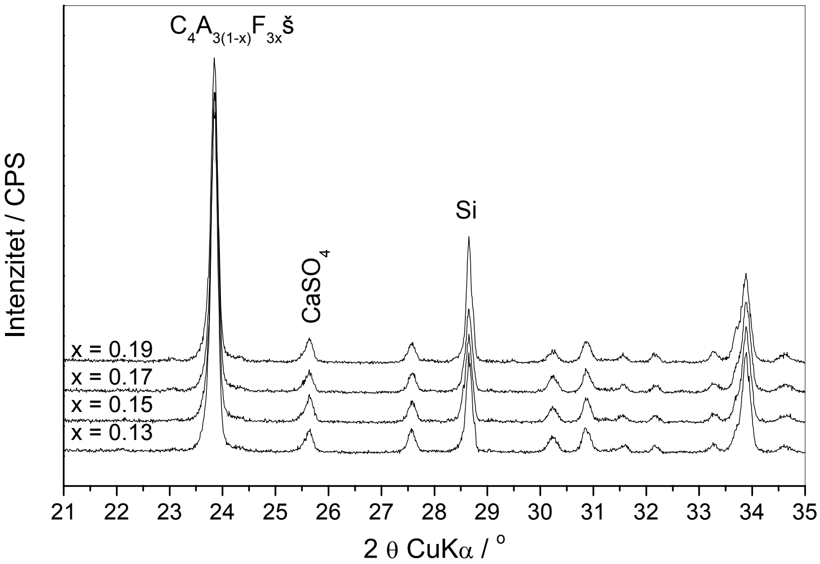

Figure 3. X-ray diffraction of calcined mixtures of precursor materials corresponding to the following potential composition of Klein compound, $C_4A_{3(1-x)}F_{3x}s$, where x=0.13, 0.15, 0.17 and 0.19. Traces of anhydrite mineral, $CaSO_4$, is present in the calcined samples.

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).

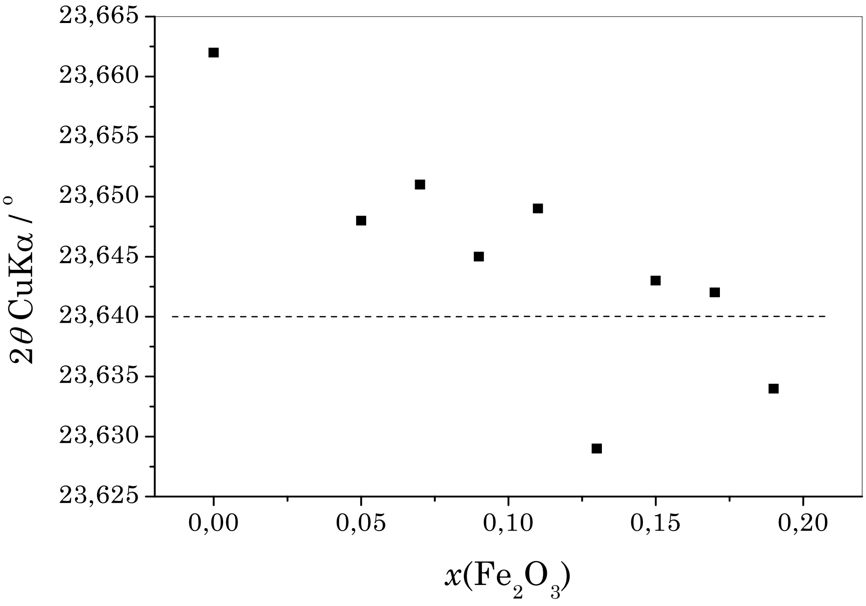

Figure 4. Dependence of Kleinite diffraction peak position on the bulk chemical oxide composition corresponding to: $C_4A_{3(1-x)}F_{3x}s$, where x equals: 0.05, 0.07, 0.09, 0.11, 0.13, 0.15, 0.17 and 0.19. The dotted horizontal line corresponds to the position of Kleinite (containing iron, x=0.05) diffraction 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 ($CaCO_3$, $Al(OH)_3$,$\times CaSO_4\times 1/2H_2O$ and $Fe(NO_3)_3\times 9H_2O$), 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).

Acknowledgment
The authors acknowledge support from the Croatian Ministry of Science, Education and Sports under project's no. 125-1252970-2983 "Development of hydration process model".

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.