MATRIB 2013
International conference on materials, tribology, recycling
Vela Luka, 27- 29 June 2013

KINETIC STUDY OF CALCIUM SULFOALUMINATE CEMENT HYDRATION

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Original scientific paper / Izvorni znanstveni rad

Abstract

Calcium sulfoaluminate cement (CSAC) is an alternative binder to Portland cement (PC). Advantages in producing CSAC over PC are in lower CO_2 emission and lower energy consumption.

In this paper, a variety of industrial wastes, namely phosphogypsum, coal bottom ash and electric arc furnace slag were used as raw materials to provide additional environmental advantages in production of calcium sulfoaluminate cement. Hydraulic minerals in the prepared CSA were determined by X-ray powder diffraction. Rate of heat generation during hydration had been determined by calorimetric measurements. It was observed that the main heat generation peak can exhibit two exothermic processes. A numerical model for the hydration kinetics is proposed, based on solving a system of two differential kinetic equations, for two interdependent reactions, employing Runge-Kutta IV method.

In conclusion, CSAC production offers an alternative and feasible method of industrial waste minimization.

Keywords: calcium sulfoaluminate cement, waste minimization, calorimetry, hydration kinetics, numerical modeling.

Sažetak

Kalcij sulfoaluminatni cement (CSAC) je hidratno vezivo koje se može upotrijebiti umjesto Portland cementa (PC). Prednosti proizvodnje CSAC u odnosu na PC su manja emisija CO_2 te ušteda energije.

U ovome radu, za proizvodnju CSAC korišteni su otpadni fosfogips, ložišni pepeo i troska, što dodatno pridonosi ekološkoj atraktivnosti ovog cementa. Sinteriranim uzorcima određen je mineraloški sastav metodom rendgenske difrakcije (XRD). Brzina oslobađanja topline tijekom hidratacije pripravljenog CSAC određena je mikrokalorimetrijski. Uočeno je da se glavni maksimum oslobađanja reakcijske topline sastoji od dva procesa. Predložen je numerički model za opis kinetike hidratacije koji se osniva na rješavanju sustava od dvije spregnute nelinearne diferencijalne jednadžbe metodom Runge-Kutta IV.

Na osnovu 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 aluminatni cement, zbrinjavanje otpada, kalorimetrija, kinetika hidratacije, numeričko modeliranje.

INTRODUCTION

The cement industry accounts for up to 5-7 % of CO_2 emissions [1] due to the large global production of cement (2 billion tons per year) and due to the high temperatures involved in its production, along with the large quantity of calcareous materials needed per ton of cement produced. However, the cement industry has the potential to reuse vast quantities of various industrial wastes and by-products [2, 3] by their incorporation, as raw material for clinker production or by adding them during the final grinding of clinker. Calcium sulfoaluminate (CSA) cement had been recognized as a ''low CO2'' [1] and "low energy" cement due to the much lower CO_2 emissions and energy consumption during its production, and has therefore been extensively investigated in recent years [4-10]. About one million tons of CSA type cements are produced annually in China [9], where special cement standards have been issued. To manufacture CSA 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 (PG), reduces both the temperature and the time of the firing process [10]. On a large-scale manufacture, the firing process can be performed in conventional rotary kilns used for PC manufacture. Throughout this paper, cement mineralogy nomenclature is used (C=CaO, A=Al2O3, S=SiO2, s=SO3, F=Fe2O3, M=MgO). Ye'elimite (4CaO˙3Al2O3˙SO3 i.e. C4A3s in shortened cement mineralogy notation) is the principal mineral phase responsible for the early strength development during cement hydration. Ye'elimite reacts with water and dissolved gypsum added during milling of calcium sulfoaluminate clinker, giving up calcium monosulfate aluminate hydrate (Eq. 1) and ettringite (Eq. 2) together with amorphous aluminium hydroxide as main hydration products [7, 8]:

$$4CaO\cdot 3Al_2O_3\cdot SO_3 + 18\ H_2O \rightarrow 4CaO\cdot Al_2O_3\cdot SO_3\cdot 12\ H_2O + 4\ Al(OH)_3 \qquad (1)$$

$$4CaO\cdot 3Al_2O_3\cdot SO_3 + 2\ CaSO_4\cdot 2H_2O + 34H_2O \rightarrow 6CaO\cdot Al_2O_3\cdot 3SO_3\cdot 32H_2O + 4\ Al(OH)_3 \qquad (2)$$

Potential benefits offered by CSA cement production from industrial waste materials already present in Republic of Croatia have been studied recently [4, 5]. Because of radioactivity and its harmful consequences, commercial use of PG in the world is very limited. However, our previous studies showed promising results toward sustainable reuse in calcium sulfoaluminate cement based building materials [5]. In this paper, the hydration kinetics of the prepared CSAC was investigated by further calorimetric measurements. The mineralogical composition of the samples was investigated by XRD powder diffraction.

EXPERIMENTAL

Materials

To formulate the clinkers, three industrial by-products were used as raw materials:

- electric arc furnace slag (ES), *Sisak Ironworks d.d.* (Sisak, Croatia);
- coal bottom ash (BA), *Plomin Power Plant II* (Plomin, Croatia);
- phosphogypsum (PG), *Petrokemija d.d.* – Kutina (Kutina, Croatia).

Their chemical oxide composition is shown in Table 1. To correct the bulk chemical and mineralogical composition, two additional raw materials were employed:

- Bauxite (Bx), *CALUCEM* cement plant (Pula, Croatia);
- limestone, p.a. Kemika Zagreb.

The raw materials were ground and sieved below 125 μm. They were then wet homogenized in a planetary mill (FRITSCH, Pulverisette 5, α-alumina pot and grinding balls), according to desired proportions (weighted on analytical balance, homogenized for 5 min at 250 rpm with addition of demineralized 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^{-1} and natural cooling rate of the furnace). CSA clinker samples were milled in a ring agate mortar (very easily, i.e. with low energy requirement) and sieved below 125 μm.

Experimental plan

Three series of compositions of samples were investigated as shown in Tables 2-4. Table 2 shows the experimental plan of Series I clinker compositions (in mass %). In a Series II (Table 3) was designed to investigate clinkers with a lower content of phosphogypsum. In Series III (Table 4) the latter addition of phosphogypsum (added later after clinker milling but before cement paste mixing) on the hydration behavior is investigated. To a blended mixture different amounts of phosphogypsum are added: 10 %, 15 % and 20 %. Measurements are done with clinker samples II1 and II4 (from Series II, Table 3). The mixture labels are given in Table 4.

Table 1. Chemical composition of used raw materials in mass % (Bx-boxite, BA-bottom ash, PG-phosphogypsum, ES- slag).

material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	TiO_2	$Na_2O + K_2O$	SO_3
ES	11	2	30	33	13	6	-	-	-
BA	54	23	7	5	-	-	-	-	-
Bx	3.5	57	22.5	1	0.5	-	2.5	< 1	-
PG	-	-	-	31.6	-	-	-	-	47.7

Tablica 2. Clinker composition (mass %), Series I (Bx-boxite, BA-bottom ash, PG- phosphogypsum, ES-slag); calcium carbonate = 25 % in all samples

Series I	Notation	I1	I2	I3	I4
Bx	**a**	23	18	13	8
BA		0	0	10	10
PG		30	30	30	30
ES		22	27	22	27
Bx	**b**	23	18	13	8
BA		0	0	10	10
PG		25	25	25	25
ES		27	32	27	32
Bx	**c**	23	18	13	8
BA		0	0	10	10
PG		20	20	20	20
ES		32	37	32	37

Table 3. Clinker composition (mass %), Series II: lower PG (Bx-boxite, BA-bottom ash, PG-phosphogypsum, ES- slag, Cc - calcium carbonate)

Notation	II1	II2	II3	II4	II5	II6
Cc	31.25	29.40	27.77	31.25	29.40	27.77
Bx	16.25	15.30	14.40	10.00	9.40	8.80
BA	12.50	11.75	11.10	12.50	11.75	11.11
PG	12.50	17.65	22.20	12.50	17.65	22.22
ES	27.50	26.00	24.40	33.75	31.76	30.00

Table 4. Clinker-phosphogypsum mixtures (in mass %) for Series III

Notation	PG	Clinker II1	Clinker II4
III1a	10	90	-
III1b	15	85	-
III1c	20	80	-
III4a	10	-	90
III4b	15	-	85
III4c	20	-	80

XRD analysis

The mineralogical composition of the ground samples was investigated by XRD powder diffraction. Shimadzu XRD 6000 (Japan) diffractometer with a CuKα radiation (30 kV, 30 mA) was used.

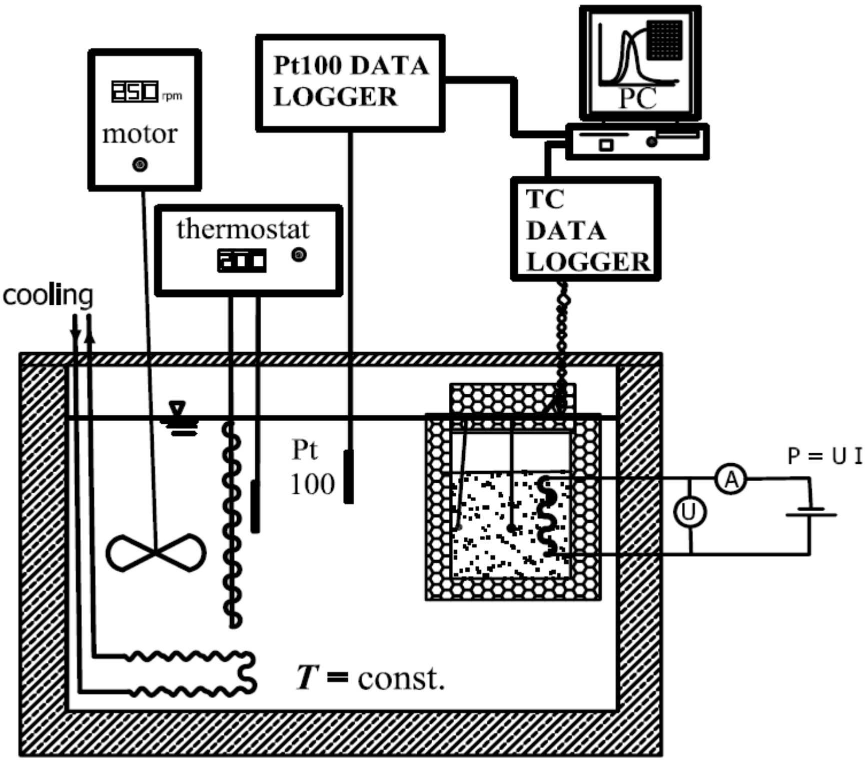

Figure 1. Scheme of the calorimetric measurement set-up.

Calorimetry

The heat of hydration evolution was measured by means of a self-adopted laboratory isoperibolic calorimeter. The employed calorimeter consists of an insulating container (composed mainly of styrofoam cups with stoppers), temperature sensor, and thermostated bath, as shown in Figure 1. The temperature change in the calorimeter is measured by K-type thermocouples (wire thicknes of 0.2 mm). Temperature is stored every 15 seconds by a data logger PICO Logger TC-08 (Pico Technology Ltd., UK: 20 bits, 8 channels, voltage resolution 1μV) connected to PC with *PicoLog for Windows* software. The thermocouples were calibrated using high accuracy Pt 100 probe. Thermocouple cold junction is held at room temperature and sensed by a precision thermistor in good thermal contact with the input connectors (on thermal block) of the measuring instrument. In order to assure good cold junction compensation, a change of its temperature is kept as low as possible.

The cement and appropriate amount of water was left to reach thermal equilibrium (overnight) before manual mixing in the calorimeter. The calorimeter (Figure 1) consists of a glass sample holder (29 mm in diameter and 50 mm in height) and surrounding insulation. Sample holder is quantitatively filled with a cement paste sample (prepared with 10 g of cement for all mixtures) and put into the insulating body which is immersed in temperature controlled water bath T = 20 °C (±0.03 °C).

The evolved heat of hydration per gram of cement (J g^{-1}) was calculated by employing the lumped-parameter heat transfer model:

$$Q(t) = \frac{C_p}{m}\left(\Delta T(t) + \beta \int_0^t \Delta T(t)\right) \tag{3}$$

where: C_p – effective heat capacity of the calorimeter, J $^{o}C^{-1}$
β – cooling constant of the calorimeter, h^{-1}
m – cement mass, g

The following calorimeter parameters were estimated: the heat loss constant, the cooling constant, and the effective heat capacity. The calibrations were done by applying a known voltage to a known electrical resistance (thin constantan wire) embedded in a block of hardened cement paste. The heat loss from the calorimeter to the surrounding was obtained from a steady state condition measurement (the voltage was applied until the steady state was achieved). In steady state the heat loss equals the heating power dissipating on the embedded resistance wire. The cooling constant of the calorimeter was obtained from the transient temperature response after switching off the Joules heat in the calorimeter. The cooling constant (β) was estimated by nonlinear regression of the solution of Newton's law of cooling to the transient experimental results.

RESULTS AND DISCUSSION

Figures 2 - 4 present X-ray diffraction analysis of the obtained CSA sample clinkers. The main mineral phases identified are: Ye'elimite (C_4A_3s), anhydrite ($CaSO_4$), ternesite (C_5S_2s, also called sulfospurite), ferrite phase (C_4AF with varying amount of Al and Fe), and magnetite (Fe_3O_4).

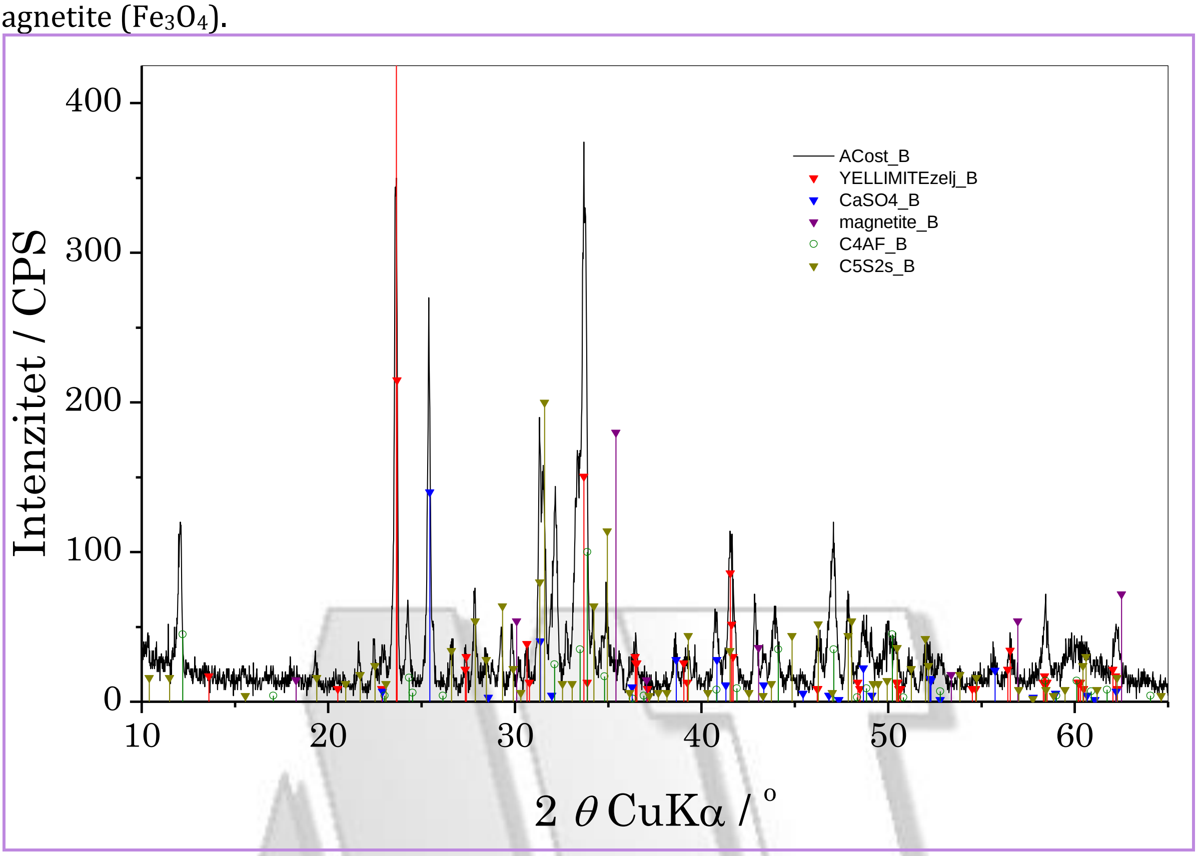

Figure 2. Diffractograms of clinker sample I1c (Table 2)

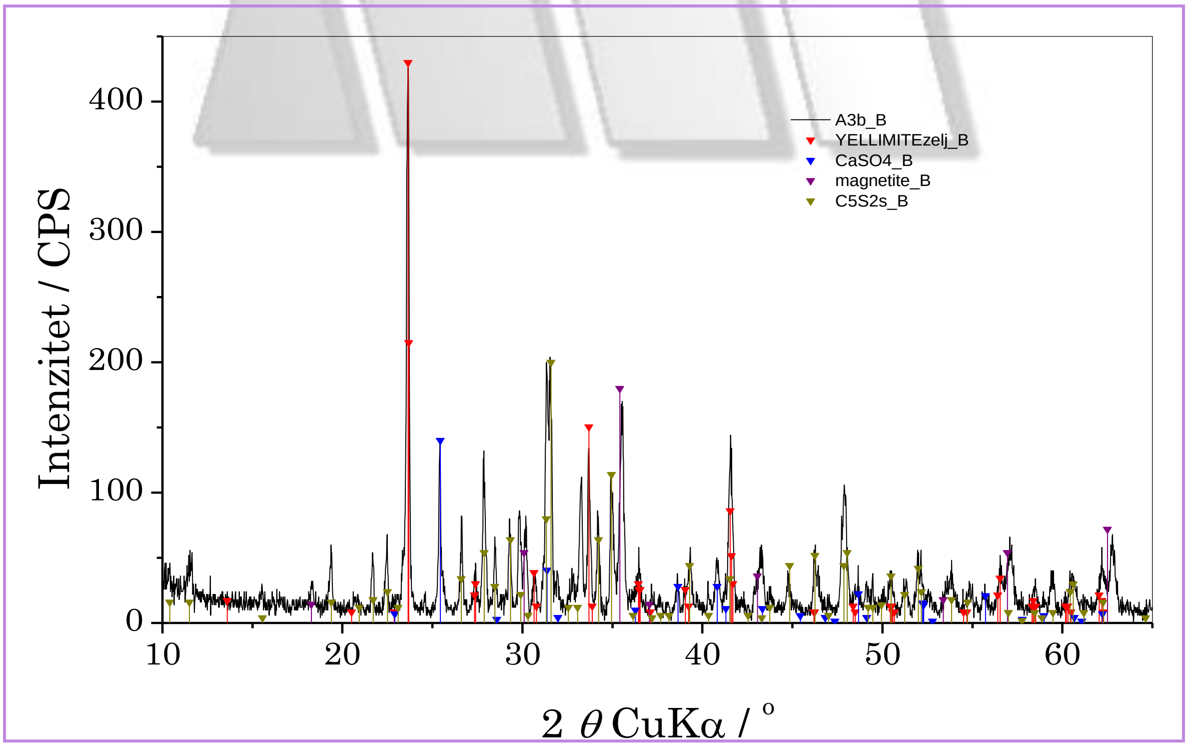

Figure 3. Diffractograms of clinker sample I3b (Table 2)

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 identified 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 partially melted and were hard to separate from the porcelain pots, further mineralogical analysis at temperatures higher than 1200 °C were not performed. Figure 2 and 3 show diffractograms of a clinker samples from the Series I, Table 2, namely I1c and I3b, respectively. From the results presented in the Figures 2 and 3, it can be concluded that the presence of the ferrite phase excludes the formation of ternesite, and vice versa.

Diffractograms of samples II1, II5, II6 from the Series II (Table 3), designed to investigate clinkers with a lower content of phosphogypsum, are depicted in Figure 4. Comparing Figures 2 and 4 one can observe smaller diffraction intensity of $CaSO_4$ in reference to Ye'elimite phase.

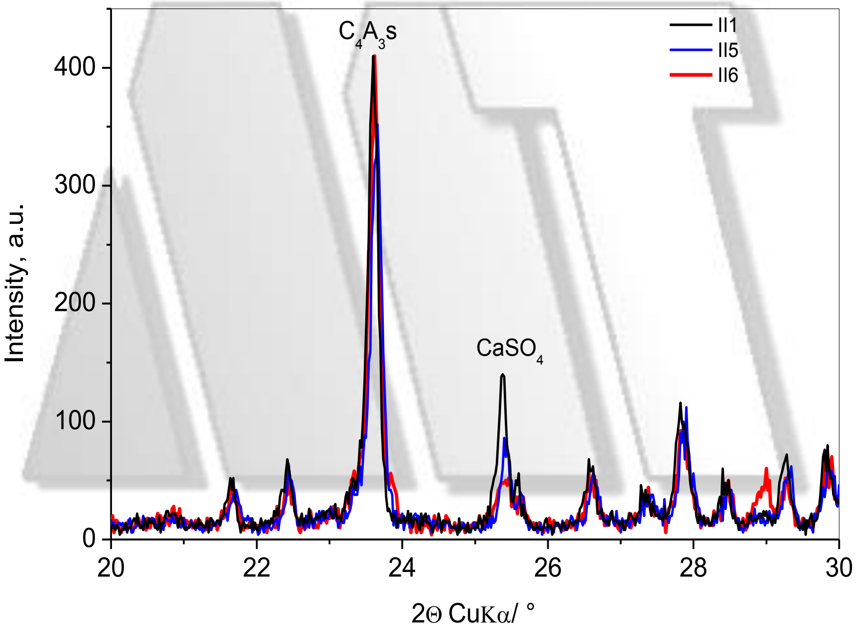

Figure 4. Diffractograms of samples II1, II5, II6 from the Series II (Table 3)

Figure 5 shows diffractograms of hydrated sample II4b (i.e. in which 15 % of phosphogypsum is added during mixing of the clinker with water, Table 4). The sample was hydrated for 14 days at 20 °C. The main hydration product indentified are ettringite, $CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O$, and aluminate gel ($AH_3$). There is also a small quantity of calcium monosulfate aluminate hydrate, $4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12\ H_2O$. The diffraction intensities of Ye'elimite (C_4A_3s) phase have almost completely disappeared, thus showing a high reactivity of this mineral.

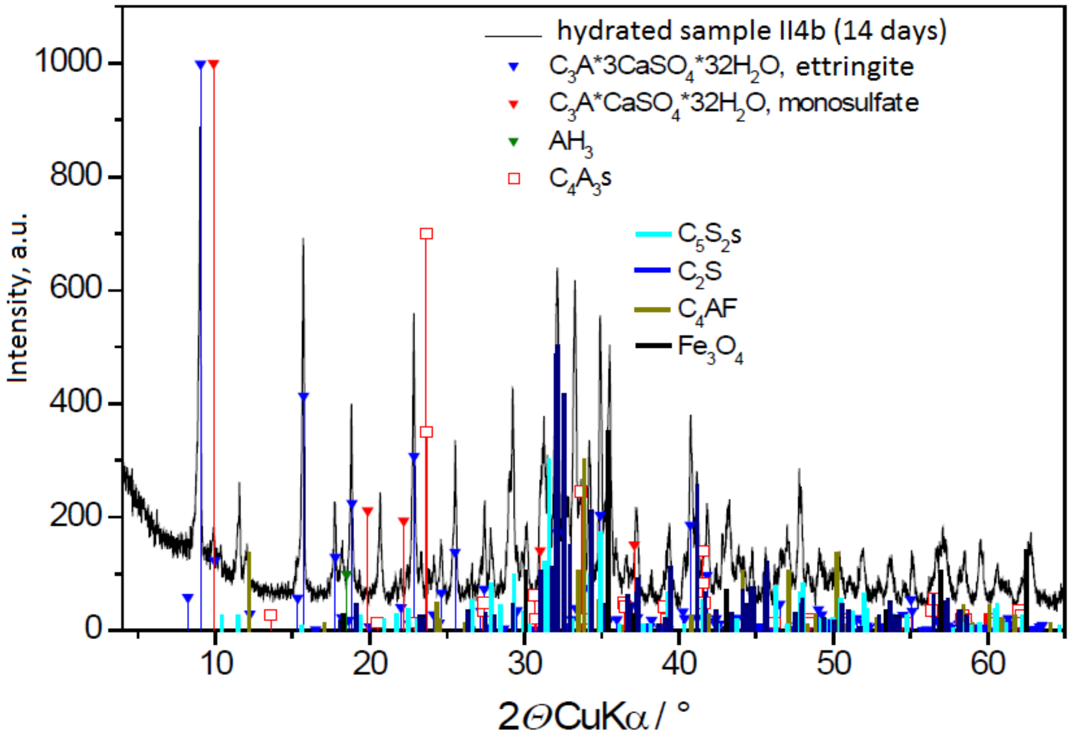

Figure 5. Diffractograms of hydrated sample II4b (Table 4)

Figure 6 shows temperature response of calorimeter during hydration of some of the samples from Series I (Table 2). The calculated cumulative heat evolved during hydration is given in Figure 7. Figure 8 shows cumulative heat evolved during hydration of samples from the Series III (Table 4). The results show that the hydration of the prepared cements is very rapid. Also it shows the complexity of the overall hydration, that is composed of many reaction processes, indicated by occurrence of multiple peaks in temperature difference response or rate of heat generation.

Furthermore, the hydration process of sulphoaluminate cement is marked by an obvious acceleration period, but the dormant period is not obvious due to overlaps of other processes (e.g. formation of gypsum from $CaSO_4$) or does not exist. During the acceleration period which lasts typically few hours, the hydration progresses rapidly. This period determines the early-age-strength development and final set of low sulphoaluminate cement. This period corresponds to the main exothermic peak in the hydration (derivative) curve.

Comparison of heating rates of samples from the Series I and III (Table 2 and 4) is given in Figure 9. The rate of heat generation on water addition are in general due to wetting, dissolution and hydration reactions of cement minerals. The observed 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 Ye'elimite and anhydrite followed by nucleation and growth of hydrate phases, mostly ettringite. The dormant period is observed in case of sample I3b, but is overlapped by other processes in case of hydration of samples III4b and III4c. The initial rate of heat evolution (first maximum) is higher for higher amounts of phosphogypsum (added later after clinker milling but before cement paste mixing).

The main maximum of rate of heat generation occurs around 2.3 h and 3.7 h for samples III4a and III4bc, respectively, followed by gradual decrease up to 20 h hydration. It is interesting to observe qualitatively similar hydration behavior of samples III4a III4b and III4c. The main hydration peak of sample I3b exhibits two exothermic processes represented by peaks at around 3.4 h and 6.4 h of hydration. Comparing the total heat evolved after about 20h of hydration (in Figure 6) it can be observed that the sample I3b has the maximal evolved heat, and that the higher is the additions of phosphogypsum (added during paste mixing) the lower is the measured cumulative heat evolved up to 20 h of hydration.

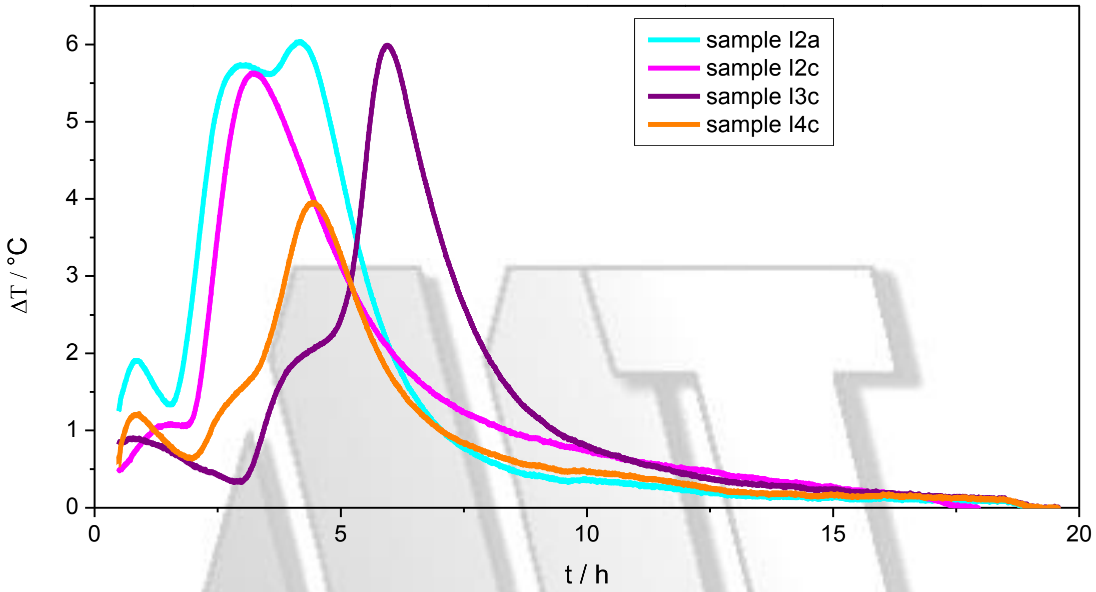

Figure 6. Temperature response of calorimeter for hydration of samples from the Series I (Table 2)

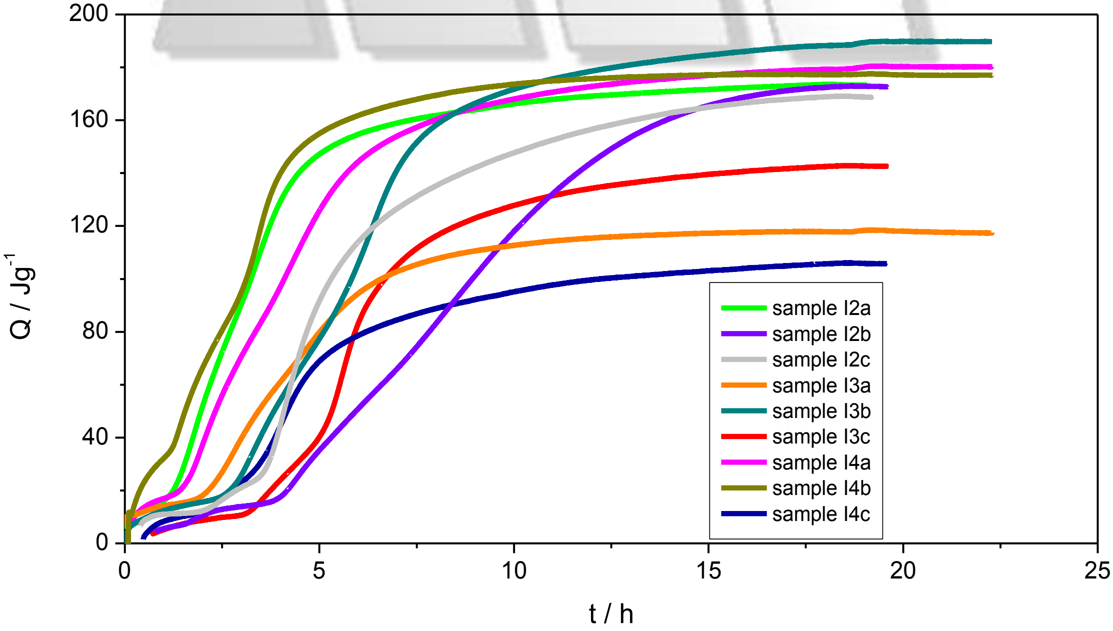

Figure 7. Cumulative heat evolved during hydration of samples from the Series I (Table 2)

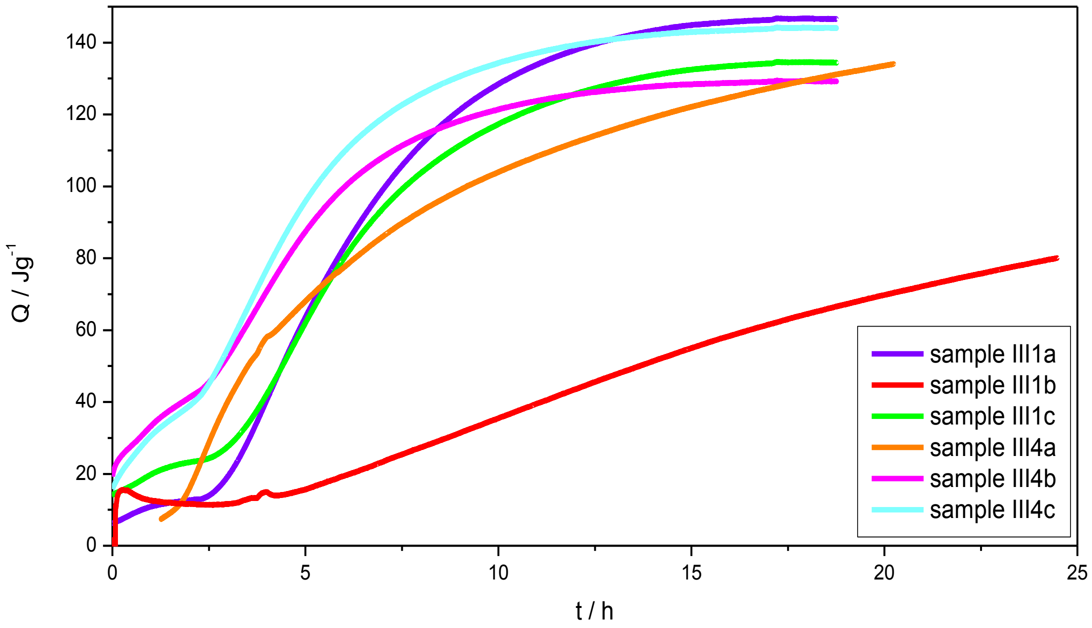

Figure 8. Cumulative heat evolved during hydration of samples from the Series III (Table 4)

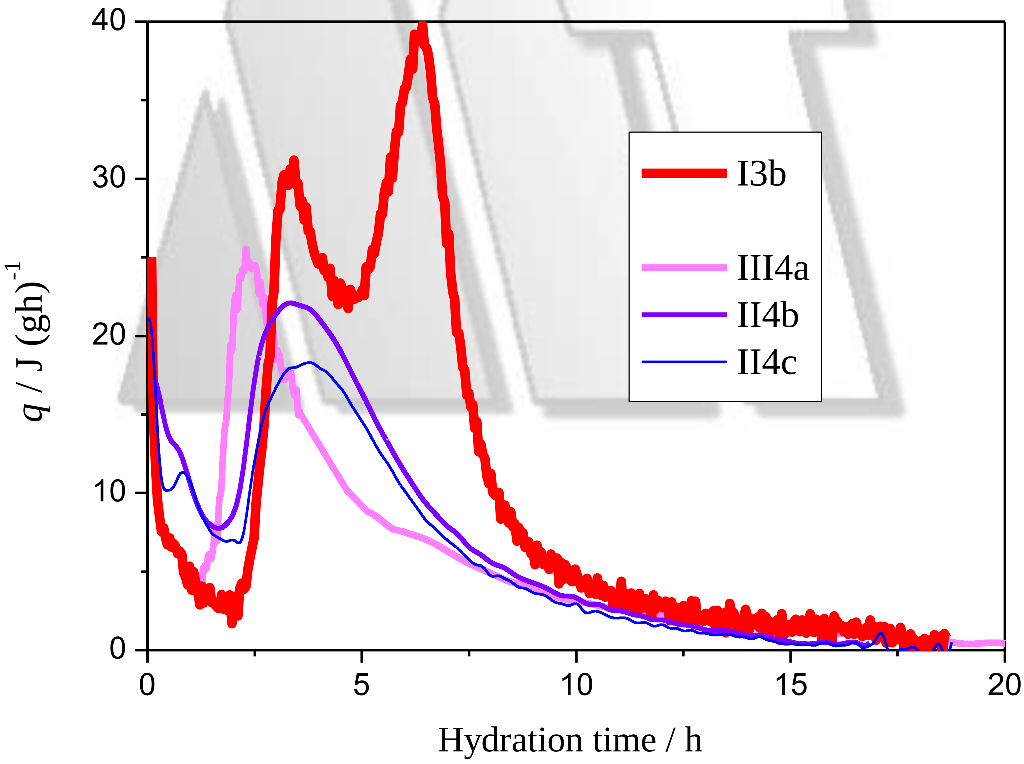

Figure 9. Comparison of heating rates of samples from the Series I and III (Table 2 and 4)

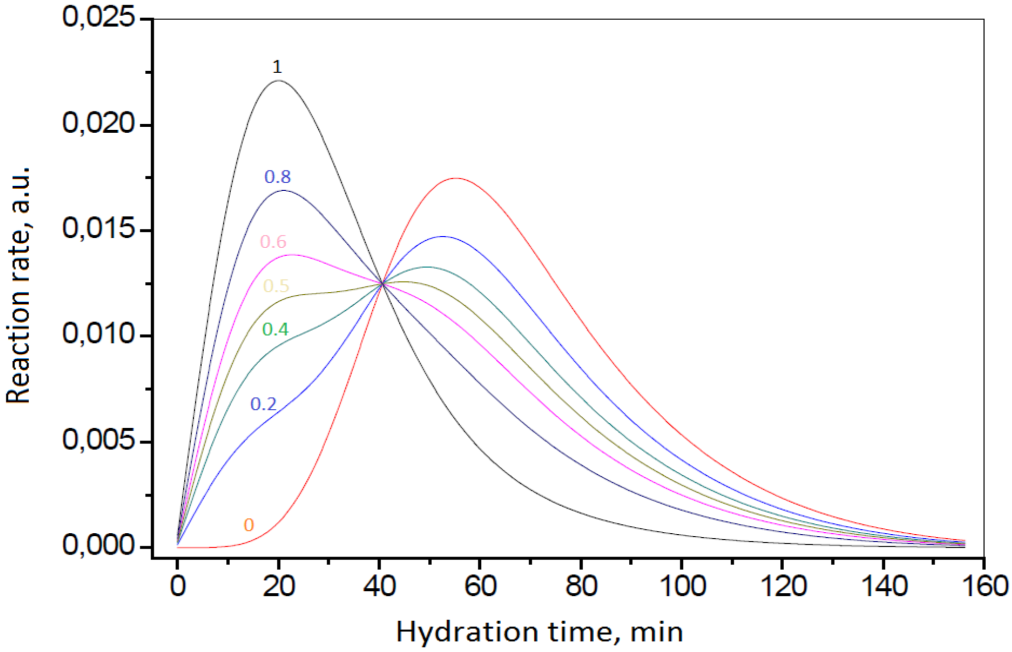

Figure 10. Numerical simulation of overall reaction rate during hydration of eq. (1) and (2) by varying the mixing fraction (i.e. their relative contributions)

The main explanation for the two exothermic processes in main hydratin peak (e.g. I3b hydration curve in Figure 9) is that under the condition of insufficient gypsum, the ettringite crystal transforms to calcium monosulphoaluminate hydrate (AFm). When there is gypsum in solution available for reaction, the main hydration reaction follows eq (1). When the gypsum is consumed, the hydration proceeds to form monosulphoaluminate hydrate as a main hydration product as well as to transform the initially precipitated ettringite. Similar results on two-stage mechanism of the overall hydration process are reported also in work of Zhou at al. [11].

Next, a numerical model for the hydration kinetics is proposed to describe the two exothermic processes (corresponding to reaction eq. 1 and 2) of the main heat generation peak. The model is based on solving a system of two differential kinetic equations, for two interdependent reactions:

$$\frac{d\alpha}{dt} = f(\alpha,\xi) \qquad (3)$$

$$\frac{d\xi}{dt} = g(\alpha,\xi) \qquad (4)$$

where the eq. (3) calculates the rate of the reaction (1), and the eq. (3) calculates the rate of the reaction (2), taking into account their mutual interdependence. The system of equations was solved by Runge-Kutta IV method. Figure 10 shows preliminary numerical simulation results. The overall reaction rate was plotted as a function of the mixing fraction (i.e. their relative contributions) of individual reactions. It can be concluded that there is a good qualitative agreement with experimental results, when focusing only on the description of the main hydration peak. This shows a promise on improving the existing kinetic modelling of CSAC hydration [11] by introducing the analogue model for describing the hydration of the other reaction. The extended modelling approach is, thus, composed of a coupled system of two differential kinetic equations, that could describe the convolution of the two peaks into the main hydration peak.

CONCLUSION

To provide additional environmental advantages in production of calcium sulfoaluminate cement a variety of industrial wastes, namely phosphogypsum, coal bottom ash and electric arc furnace slag can be used as raw materials.

The main mineral phases identified in synthesized clinkers were: Ye'elimite (C_4A_3s), anhydrite ($CaSO_4$), ternesite (C_5S_2s,), and ferrite phase. It was observed that the presence of the ferrite phase excludes the formation of ternesite, and vice versa.

The calorimetric study shows that the initial hydration starts immediately after the sulphoaluminate cement is mixed with water, mostly due to Ye'elimite and anhydrite dissolution. The initial rate of heat evolution is higher for higher amounts of phosphogypsum added during cement paste mixing. The hydration reaction is followed by very quick nucleation and growth of hydration products, mostly ettringite. The higher is the quantity of phosphogypsum, added after clinker milling but before cement paste mixing, the lower is the measured cumulative heat evolved up to 20 h of hydration.

The main heat generation peak can exhibit two exothermic processes. A numerical model for the hydration reaction kinetics is proposed, based on solving a system of two differential kinetic equations, for two interdependent reactions. Namely, the two reactions could be an initial formation of ettringite when there is enough $CaSO_4$, and subsequent reaction to produce monosulfate.

ACKNOWLEDGEMENT

The authors acknowledge the support from the Croatian Ministry of Science, Education and Sports under project's no. 125-1252970-2983 "Development of hydration process model", and thank the Power Plant Plomin (Plomin, Croatia), Petrokemija d.d. – Kutina (Kutina, Croatia), and Sisak Ironworks d.d. (Sisak, Croatia), for providing their industrial by-products, the CALUCEM cement plant (Pula, Croatia) for providing bauxite raw material, as well as Mateja Šnajdar, Ana Čale, Tamara Hruška, and Lucija Samac for assistance with part of the experimental work.

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