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## Calcium Sulfoaluminate Eco-Cement from Industrial Waste

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In this paper, the potential benefits offered by calcium sulfoaluminate cement (CSA) production from industrial wastes or by-products already present in Republic of Croatia have 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 CSA. Mass fraction of Ye'elimite, the principal hydraulic mineral in the prepared CSA was determined by quantitative X-ray powder diffraction. Calculated phase composition based on 18 sub-systems of five-component assemblages, each containing five clinker phases, showed promising results. The hydration behavior of CSA clinkers was investigated by calorimetric and Vickers hardness tests. In conclusion, CSA production offers an alternative and feasible method of industrial waste minimization.

*Key words:*

*Calcium sulfoaluminate cement, waste minimization, phosphogypsum, electric arc furnace slag, coal bottom ash*

### Introduction

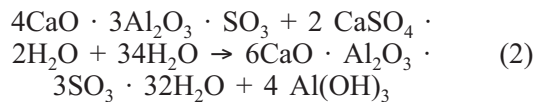
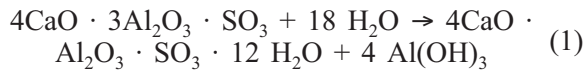
CO<sub>2</sub> emissions due to human activity and extensive use of natural resources pose a serious threat to future sustainable development as well as trigger climatic change. The cement industry accounts for up to 5–7 % of CO<sub>2</sub> emissions<sup>1</sup> due to the large global production of 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<sup>2,3</sup> 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 CO<sub>2</sub>”<sup>1</sup> and “low energy” cement due to the much lower CO<sub>2</sub> emissions and energy consumption during its production, and has

therefore been extensively investigated in recent years.<sup>4–8</sup> At same mixing water to cement ratios and achieved degrees of hydration the obtained porosity of cement pastes made from CSA 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 CSA, especially in that of the AFt type<sup>4</sup> hydration products (mainly ettringite). About one million tons of CSA type cements are produced annually in China,<sup>7</sup> 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, reduces both the temperature and the time of the firing process.<sup>8</sup> On a large-scale manufacture, the firing process can be performed in conventional rotary kilns used for PC manufacture.<sup>9</sup> Throughout this paper, cement mineralogy nomenclature is used (C=CaO, A=Al<sub>2</sub>O<sub>3</sub>, S=SiO<sub>2</sub>, s=SO<sub>3</sub>, F=Fe<sub>2</sub>O<sub>3</sub>, M=MgO). Ye'elimite (4CaO · 3Al<sub>2</sub>O<sub>3</sub> · SO<sub>3</sub> i.e. C<sub>4</sub>A<sub>3</sub>S in shortened ce-

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ment 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:<sup>5,6</sup>



Depending on the proportion of the individual mineral phases in the clinker and the content of calcium sulphate, CSA may perform as non-expansive high early strength cements, or as expansive cements. Development of the rigid skeletal structure followed by formation of ettringite results in expansive cement. Contrary, ettringite formation preceding the development of the rigid skeletal structure gives non-expansive CSA cement.

In the presence of the iron minerals in the raw mixture, a considerable amount of iron may form a solid solution of the ferrite phase type  $\text{Ca}_2(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_5$  where  $x$  may range from 0–0.7.<sup>10</sup> The ferrite phase exhibits a higher reactivity than in ordinary PC, contributing to both the early strength development and long term strength of the CSA. This higher reactivity is most likely due to its formation at lower firing temperature.<sup>10</sup> The  $\text{C}_2\text{F}$  starts forming at about 1100 °C and at higher temperatures it incorporates alumina, which finally attains the composition  $\text{C}_6\text{AF}_2$ . To obtain Ye'elimite ( $\text{C}_4\text{A}_3\text{S}$ ) and to avoid its decomposition as well as decomposition of  $\text{CaSO}_4$  at higher temperatures, the firing temperature in the manufacture of CSA must not exceed 1300 °C (especially if reusing the waste as raw materials). Belite ( $\text{C}_2\text{S}$ ) is usually present in its  $\beta$  modification, but sometimes also in  $\alpha$  form. Belite, as well as ternesite ( $\text{C}_5\text{S}_2\text{S}$ , also called sulfo-spurrite) have only a very small contribution to early strength development, but are mainly responsible for the late strength of the CSAC. Ternesite can be formed as an intermediate phase, from about 900 °C<sup>8</sup> and decomposes above 1200–1280 °C to  $\text{C}_2\text{S}$  and  $\text{CaSO}_4$ .

In this work, the potential benefits offered by CSA cement production from industrial waste materials already present in Republic of Croatia have been addressed for the first time. The main raw material components are: waste phosphogypsum from mineral fertilizer production, electric arc furnace slag (EAFS) from 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 CSA cement. Theoretical calculations were done in order to investigate the appropriate raw composition for obtaining the CSAC clinker. The mineralogical composition of the samples was investigated by XRD powder diffraction. The hydration behavior of CSA clinkers was investigated by calorimetric and Vickers hardness tests.

## Elaboration

### CSA vs. PC: Assessment of energy saving and CO<sub>2</sub> emission

CSA can lay claim to being a very attractive “high-performance” cement mainly due to following reasons:<sup>4–8</sup>

- low energy and low CO<sub>2</sub> emission associated with its production;
- ability to form cements, mortars and concretes with high early and late strengths;
- shrinkage compensating abilities;
- potential for good durability, especially in saline marine environments, and the protection it provides to embedded steel (as well as resistance to alkali-silica reaction).<sup>1</sup> However, more research is required to establish the durability of concretes made from CSA cements.

Next, the energy requirement and environmental impact of CSA and PC production is quantitatively compared. The energy balances and CO<sub>2</sub> emissions depend on the efficiency of the kiln and fuel. Indications of these balances are shown in Table 1, regarding the firing process, grinding process and CO<sub>2</sub> emission. For the purpose of such comparison, we consider a standard grade PC product (CEM II/B-M(S-V) 42,5N) which is blended with 15 mas. % of supplementary addition (granulated blast furnace slag and fly ash). Due to low CaCO<sub>3</sub> content, in relation to OPC, the CO<sub>2</sub> emissions are markedly reduced in CSA clinkers. Furthermore, economic benefits of CSA over PC in specific fuel (per kilogram of cement produced) and CO<sub>2</sub> 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 firing the kiln was divided into two segments (Table 1):

- influence of the firing temperature, and
- influence of the amount of raw material.

Literature values were used for firing temperature and amount of raw material<sup>1</sup> for both types of

Table 1 – Ecological and economical benefits of CSA over PC

Process	Parameter	CSA	PC (Cem II)	Savings in regard to the PC
Sintering	Temperature	1200 °C Lower heat loss	1450 °C (3.1 GJ/t cem)	~5 % (0.15 GJ/t cement)
	Amount	0.3 t CaCO <sub>3</sub> / t cement	0.85 t CaCO <sub>3</sub> / t cement	0.55 t CaCO <sub>3</sub> / t cement
		1.25 t raw / t cement	1.6 t raw / t cement	0.6 GJ/t* 0.35 t raw / t cement
	Total saving			> 1.1 GJ/t cement
Grinding	raw materials for sintering	0,3 t CaCO <sub>3</sub> / t cement bauxite 10 %	0,85 t CaCO <sub>3</sub> / t cement (16 kWh / t cem.)	~28 %**
	cement clinker	sintered = low energy re- quirement, ~40 % less than for PC	partly melted = huge energy requirement (36 kWh/ t cem.)	~40 %
		Total saving		
	CO <sub>2</sub> emission	Raw material (CaCO <sub>3</sub> )	0.3 t CaCO <sub>3</sub> / t cement	0.85 t CaCO <sub>3</sub> / t cement
0.132 t CO <sub>2</sub> / t cem. (2.48 GJ/t cem.)			0.374 t CO <sub>2</sub> / t cement (3.1 GJ/t cem.)	
FUEL		90 kg CO <sub>2</sub> /GJ	90 kg CO <sub>2</sub> /GJ	20 %
		223 kg CO <sub>2</sub> / t cem.	279 kg CO <sub>2</sub> / t cement	
Total saving			42.5 %	
Waste management	bottom ash ~12 %		ash + EAFS = 10 % (35 HRK/t waste) 3.5 HRK/t cement	11.2 HRK / t cement***
	EAFS ~30 %			
	phosphogypsum ~15 % (35 HRK/t waste)			
	14.7 HRK/t cement			

\*considering 60 % of energy for CaCO<sub>3</sub> decomposition (1.78 GJ/t CaCO<sub>3</sub>) for conversion to per ton of cement

\*\*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.

\*\*\*currency exchange, 1 Euro ~7.58 HRK

cements. Energy consumption for the formation of CSA 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 CSA, and because the fraction of the CaO is formed from CaSO<sub>4</sub> instead of CaCO<sub>3</sub>. A potential problem in industrial manufacture may be the partial thermal decomposition of CaSO<sub>4</sub> during firing the raw material, which may call for an appropriate technology to control the SO<sub>3</sub> emission. However, the emission of CO<sub>2</sub> and NO<sub>x</sub> is significantly reduced<sup>12</sup>. The energy requirement for the

grinding process of CSA clinker is much lower than that of ordinary PC clinker (Table 1). The values in Table 1 show the assessment of energy savings in the grinding process of raw materials (before sintering), as well as cement clinker (after sintering). According to the known stoichiometric amount of the raw material that needs to be ground, the savings in energy are estimated at about 28 %, while the overall savings are estimated at about 33 %.

Table 1 also presents the ecological and economic benefits of CSA over PC regarding the CO<sub>2</sub> emission. The basic fee for CO<sub>2</sub> emissions in Croatia was taken to be 14 – 18 HRK per ton of CO<sub>2</sub> (1 EUR ~7.58 HRK). The reaction of CaCO<sub>3</sub> decomposition (CaCO<sub>3</sub> → CaO + CO<sub>2</sub>) forms 44

mas. % of CO<sub>2</sub>. The emission of CO<sub>2</sub> per ton of cement is calculated according to the amount of the CaCO<sub>3</sub> raw material needed for the production of cement. For PC, this emission amounts 0.374 t CO<sub>2</sub> / t cem. (0.85 t CaCO<sub>3</sub> / t cem. · 0.44), while for CSA, the savings amount to 0.242 t CO<sub>2</sub> / t cement (Table 1). Beside the CO<sub>2</sub> emission from CaCO<sub>3</sub>, there is also a significant emission resulting from fuel combustion. According to the Cement Data Book by W. H. Duda<sup>11</sup>, the value of the energy requirement for 1 t of cement and the amount of CO<sub>2</sub> emissions, the estimated emission from fuel combustion was calculated (e.g. for CSA 2.48 GJ / t cem. · 90 kg CO<sub>2</sub> / GJ = 223 kg / t cem). The assessment of waste management savings is given in the last row of Table 1.

The uses of PG are still limited and the 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 d.d. – Kutina, Croatia is determined as non-hazardous waste and Petrokemija d.d. has been granted a permit for the retention of phosphogypsum. Therefore, it is possible to prepare calcium sulfoaluminate cement from phosphogypsum and other industrial by-products.

## Experimental

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

- electric arc furnace slag (EAFS), *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 2. 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.

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<sup>-1</sup> 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. 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.

We employed quantitative X-ray diffraction (QXRD) by using the adiabatic principle with auto flushing<sup>13–15</sup> 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<sub>2</sub>)<sup>16</sup> or corundum (Al<sub>2</sub>O<sub>3</sub>)<sup>15</sup>. The rutile used in this study had a narrow particle size distribution around approximately 0.4 μm, which would reduce the microabsorption effect. XRD analysis of chosen standard rutile showed no traces of anatase. In this work, C<sub>4</sub>A<sub>3</sub>S in the 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<sub>2</sub>) in a 50:50 weight ratio. For the synthesis of C<sub>4</sub>A<sub>3</sub>S, precipitated calcite (CaCO<sub>3</sub>, analytical grade purity, Kemika), anhydrite (CaSO<sub>4</sub>, analytical grade purity, Kemika) and gibbsite (Al(OH)<sub>3</sub>, Sigma-Aldrich) were 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. The cement samples were milled in a ring agate mortar and sieved below 40 μm to maximize the number of particles analyzed, improve powder homogeneity and packing characteristics, and 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 applied meticulously by inference to the (measured) intensities of the pattern due to the pure phases. Measurement uncertainty of the QXRD analysis is discussed further in section Results and discussion.

## Calorimetric measurement

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 thickness 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  $1\mu\text{V}$ ) 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 (Fig. 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  $T = 20\text{ }^{\circ}\text{C}$  ( $\pm 0.03\text{ }^{\circ}\text{C}$ ).

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

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

where:

$C_p$  – effective heat capacity of the calorimeter,  $\text{J }^{\circ}\text{C}^{-1}$

$\beta$  – cooling constant of the calorimeter,  $\text{h}^{-1}$

$m$  – 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 ( $\beta$ ) was estimated by nonlinear regression of the exponential solution of Newton's law of cooling to the transient experimental results.

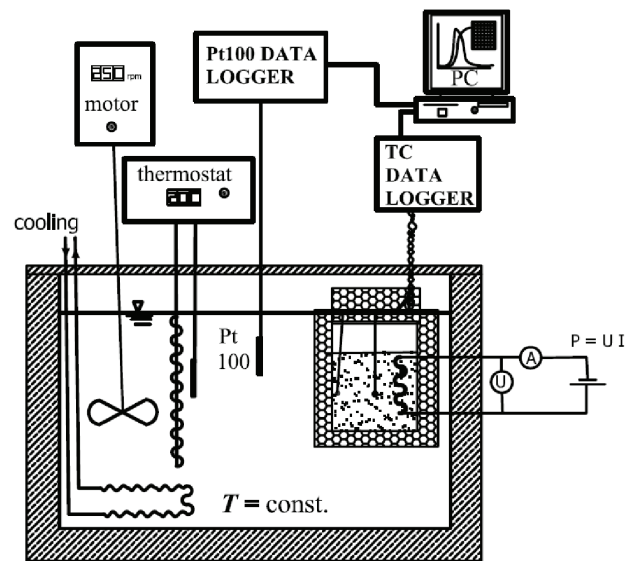


Fig. 1 – Scheme of the calorimetric measurement set-up

### Vickers hardness

The Vickers hardness test (Zwick) was performed on hydrated cement pastes at 7th day after mixing. A diamond indenter was applied (200 g of load) into the polished surfaces of the cement pastes. After removal of indenter an imprint was measured by optical microscopy (magnification of 100 times) and by means of image analysis (ImageJ software).

### Results and discussion

The CSA sample clinkers were formulated attempting to obtain different contents of cement mineral phases (Table 3). Five series of CSA clinkers were synthesized. The chemical oxide composition is calculated from the known chemical oxide composition of each raw material (Table 2) and their proportions (Table 3) 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 aimed to achieve different cement clinker formulations and then emphasize the differences between derived cements. The main drawback was the difficulty to estimate the correct amount of each phase after clinking 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  $1200\text{ }^{\circ}\text{C}$  for 1 h. Partial melting of the material occurred at  $1250\text{ }^{\circ}\text{C}$ .

Table 2 – Chemical composition of used raw materials (in mass %)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	MnO	TiO <sub>2</sub>	Na <sub>2</sub> O + K <sub>2</sub> O	SO <sub>3</sub>
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	–	–	–	31.6	–	–	–	–	47.7

Table 3 – Experimental plan: Mass fraction of raw materials and calculated chemical composition used for the preparation of CSA clinkers

CSA 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	12.50
bauxite	8.00	23.00	8.00	13.00	10.00
coal bottom ash	18.00	0.00	22.00	10.00	13.40
EAFS	19.00	32.00	20.00	27.00	32.85
Chemical composition (mass %)					
CaO	31.59	38.75	32.27	36.09	44.67
Al <sub>2</sub> O <sub>3</sub>	11.58	17.31	12.69	12.96	11.99
SiO <sub>2</sub>	15.42	5.45	18.19	11.16	14.23
CaSO <sub>4</sub>	30.23	19.89	25.02	24.97	12.55
Fe <sub>2</sub> O <sub>3</sub>	11.17	18.60	11.83	14.82	16.57

### XRD analysis of employed industrial waste

The composition of EAFS is based on component compositions of type CaO–SiO<sub>2</sub>, CaO–FeO, CaO–SiO<sub>2</sub>–MnO, CaO–Al<sub>2</sub>O<sub>3</sub>, CaO–FeO–SiO<sub>2</sub> and CaO–SiO<sub>2</sub>–FeO–MgO (Table 6).<sup>17</sup> X-ray diffraction analysis, shown in Figure 2, indicated the following principally represented minerals in investigated EAFS: F (Fe), srebrodolskite (C<sub>2</sub>F), brownmillerite (C<sub>4</sub>AF), wustite (FeO), magnetite (Fe<sub>3</sub>O<sub>4</sub>), mayenite (C<sub>12</sub>A<sub>7</sub>), and belite (C<sub>2</sub>S). Figure 3 shows the X-ray diffraction analysis of the coal bottom ash (Plomin) used for preparation of the CSA. It can be seen that a significant portion of the ash sample is amorphous (glassy), while the crystalline phases identified are  $\alpha$ -quartz and mullite, which is in accordance with the chemical composition (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> make 75–80 % of the ash) shown in Table 2.

### Phase formation

Figures 4 and 5 present X-ray diffraction analysis of the obtained CSA sample clinkers from the raw mixture with the chemical composition shown in Table 3. The main mineral phases identified are:

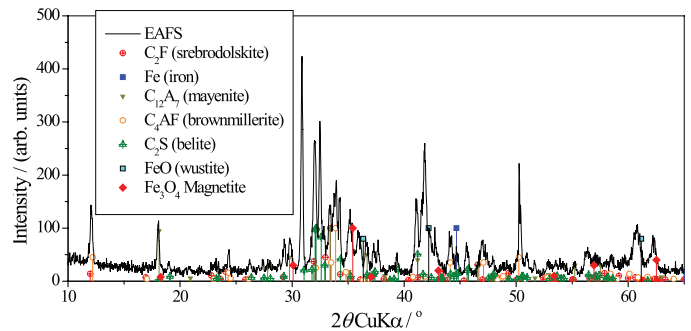


Fig. 2 – X-ray diffraction analysis of electric arc furnace slag (EAFS, Sisak)

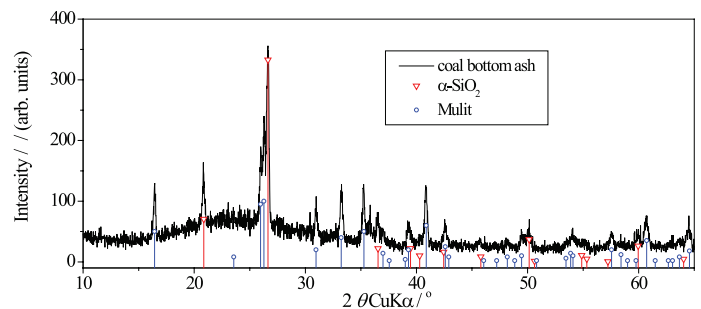


Fig. 3 – X-ray diffraction analysis of coal bottom ash (Plomin)

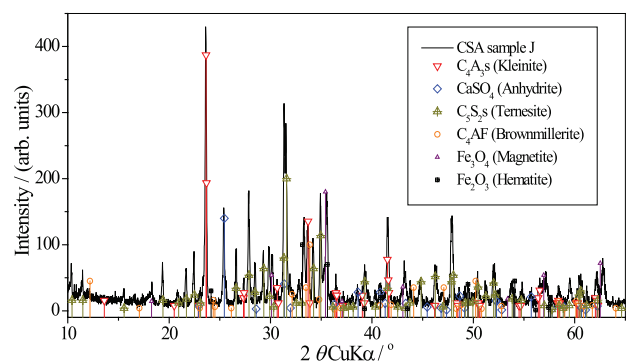


Fig. 4 – X-ray diffraction analysis of CSA cement sample J

Ye'elimite (C<sub>4</sub>A<sub>3</sub>S), anhydrite (CaSO<sub>4</sub>), ternesite (C<sub>5</sub>S<sub>2</sub>S, also called sulfospurite), ferrite phase (C<sub>4</sub>AF with varying amount of Al and Fe), and magnetite (Fe<sub>3</sub>O<sub>4</sub>). It is worth noting that hematite

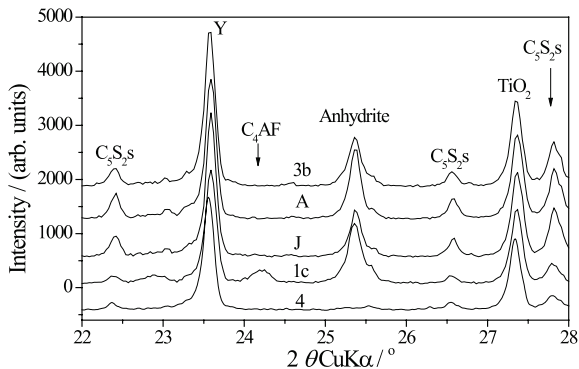


Fig. 5 – Quantitative X-ray diffraction analysis of prepared CSA cement samples, (Y –  $C_4A_3S$ )

( $Fe_2O_3$ ) 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 sulfo spurrite) 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. From the results presented in the Figures 4 and 5, it can be concluded that the presence of the ferrite phase excludes the formation of ternesite, and vice versa.

Mass fraction of Ye'elimite in the prepared CSA as determined by quantitative X-ray powder diffraction (Fig. 5) was shown to be in the range of 27 to 32 mass %, Table 4. The employment of conventional (non-Rietveld) XRD methods to quantify minerals in clinker could be unreliable. The uncertainty of the result is mainly associated to the preferred orientation effects (the powder method assumes that the ground crystallites are randomly oriented, which is not the case when the structures are platy or needle-shaped). Preferred orientation problem can be solved by spray-drying, when the poly-mineral irregular particles become spherical. However, mostly this is not practical. Practically the effect can be almost eliminated by grinding to particle sizes less than 1  $\mu m$ , and back-loading the specimen holders. Nowadays, the effect is most commonly corrected in the Rietveld refinement procedure. However, a problem in Rietveld quantification of CSA is the missing of satisfying structural model of Ye'elimite. Schmidt and Pollmann<sup>18</sup> employed an empirical method by identification of a isostructural phase with similar stoichiometry and lattice parameters and validated the accuracy of the Rietveld method for CSA systems on different synthetic clinkers, obtained from pure synthetic phases.

They concluded that only the preferred orientation of  $CaSO_4$  has to be taken into account. Investigating the back-loading and front-loading sample preparation procedure resulted in a standard error of the mean for Ye'elimite to be 0.93 and 0.26, respectively. Shape of clinker particles as well as cubic structure of Ye'elimite could result in favourable (near random) orientation of Ye'elimite crystallites. Rietveld quantification of CSA gave 36.1 % for Ye'elimite in prepared samples, which is in reasonable agreement to values obtained in this paper. Also, the calculated phase composition in work by Schmidt and Pollmann<sup>18</sup> yielded reasonable estimates to Rietveld quantification.

In order to investigate the appropriate raw composition for obtaining CSA eco-cement from the aforementioned industrial raw materials a computer code to calculate a theoretical phase composition is developed. The mineralogical composition of clinker can be calculated quantitatively according to the Bogue method, or its modification.<sup>10</sup> The Bogue method is a solution of a set of linear simultaneous equations, each giving the total fraction of one of the main oxides, namely  $CaO$ ,  $SiO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$  and  $SO_3$  for Portland cement, which can be determined/measured for the initial mixture. The set of five equations can then be solved for the unknown fractions of the five-component system. Only the simplified approach is employed here that disregards the existence of solid solutions in the formed phases.

Sahu and Majling<sup>19</sup> proposed a tentative internally consistent model for phase compatibility relationship in the C-S-A-F-s oxide system. The model is based on phase diagrams and phase equilibrium studies for the phase compatibility data in the indi-

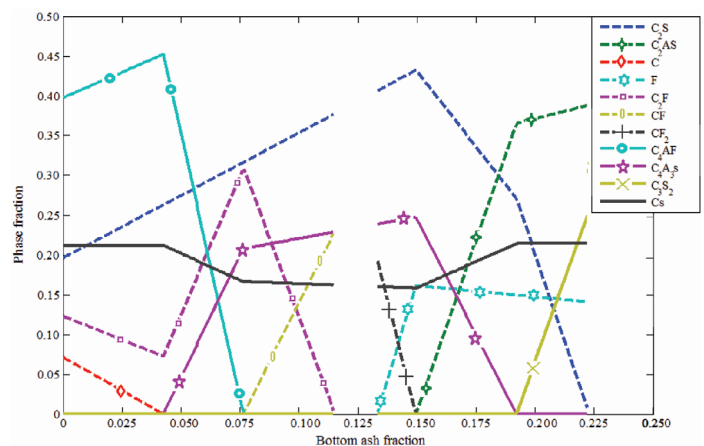


Fig. 6 – Change in phase fraction prediction as a function of variation in a mass fraction of bottom ash (and EAFs fraction, please see text while fixing mass fraction of calcite (31.25 %), bauxite (10.00 %) and phosphogypsum (12.50 %) as in sample 4 (Table 3)

vidual binary, ternary, and quaternary subsystems of the C-S-A-F-s system. In this paper, the eighteen phase assemblages, each containing five phases, as established by Sahu and Majling,<sup>19</sup> are considered for theoretical quantification. Their phase compatibility relationships enable computation (quantification) of the of clinkers' phase composition and easy investigation (i.e. by. reducing the number of experiments) of the potential raw mix compositions for the synthesis of CSA.

The calculation of the potential phase composition of CSA clinkers is implemented as a computer program for the setting in the Matlab to calculate the phase composition of clinkers. The code first calculates the chemical composition of the mixture based on the mass fractions of the used raw materials and their chemical compositions. Then, as a main contribution of the Matlab program, all the 18 sub-systems of equations are solved, each comprising of a set of 5 equations with 5 unknowns. The phase assemblage of all 18 sub-systems<sup>19</sup> is listed later as a table in Figure 7. For the sub-system No. 1, the phase assemblage is C<sub>2</sub>S, C, C<sub>3</sub>A, C<sub>4</sub>AF and C<sub>4</sub>A<sub>3</sub>S, and the equations are:

$$m_i = m_{C_2S} w_{i_{C_2S}} + m_C w_{i_C} + m_{C_3A} w_{i_{C_3A}} + m_{C_4AF} w_{i_{C_4AF}} + m_{C_4A_3S} w_{i_{C_4A_3S}} \quad (4)$$

where  $i$  represents each of the five mass balances corresponding to the five oxides: C, A, S, s, and F. Equations for other 17 sub-systems (Table in Figure 7) were obtained in an analogous way (therefore not shown here as they can be reproduced). The output of the algorithm first calculates the unknown fractions of the five-component system for all 18 sub-systems, and then extracts the true phase composition of the clinker indicated as the only true so-

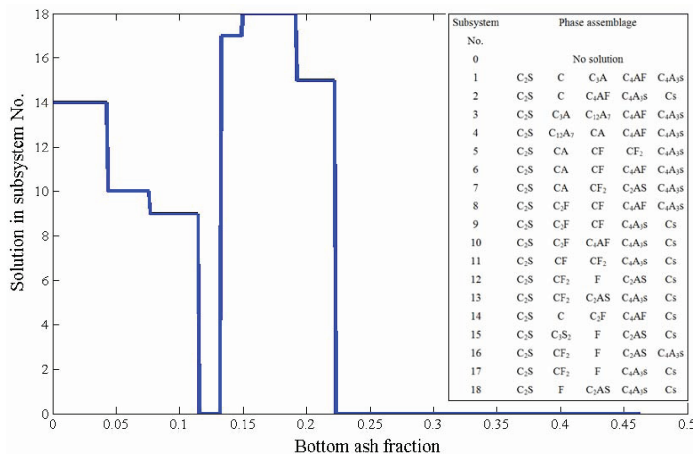


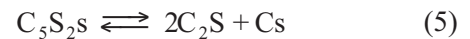
Fig. 7 – Change of the subsystem number with a true compositional solution for simulation parameters as in Fig 5

Table 4 – Comparison of calculated and measured values for mass fraction (in mass %) of Ye'elimite in clinkers

Sample	3b	J	1c	A	4
QXRD	32.0	28.1	27.1	31.3	29.2
Model	–*	–*	32.8	–*	24.0

\*No solution found

lution of all 18 subsystems. The true solution is found by the condition that a summation of all 5 mass fractions should yield 100 % within a prescribed tolerance (e.g. of  $\pm 0.1$  %) and that each of the individual mass fraction should lie within 0 to 1 interval. The model does not consider the existence of ternesite (C<sub>5</sub>S<sub>2</sub>S), but instead the phases C<sub>2</sub>S and Cs as compatible pairs. Ternesite is formed as an intermediate phase, and is expected to decompose above 1200–1280 °C according to:



It could be concluded that the formed ternesite was not decomposed in our mixtures due to the relative low firing temperatures and/or because of the relatively short time of firing. It can be argued that the calculations could be used still considering the reversible reaction eq. (5). Therefore, depending on the degree of the reaction of decomposition (Eq. 5) the reacted mixture could comprise up to 6 phases (instead of the 5 phases-model, which corresponds to full decomposition of ternesite) or only 4 phases in the scenario when the decomposition degree is 0 %. Although the Bogue calculation did not consider the formation of a solid solution, the quantity of Ye'elimite in the CSA cement clinkers was reasonably close to their predicted composition (Table 4 and Fig 6). This shows promising results for employing the composition calculation to effectively predict CSA cement clinker phase composition from its industrial by-product raw materials oxide composition. The calculated mass fraction of sample 4 is: 0.408, 0.010, 0.183, 0.240, and 0.160, for C<sub>2</sub>S, F, CF<sub>2</sub>, C<sub>4</sub>A<sub>3</sub>S, and Cs, respectively. The calculated mass fraction of sample 1c is: 0.1483, 0.0996, 0.0906, 0.3280, and 0.3335, for C<sub>2</sub>S, F, CF<sub>2</sub>, C<sub>4</sub>A<sub>3</sub>S, and Cs, respectively. Table 4 shows that for some compositions there was no solution found with the Matlab program. Furthermore, by comparing the theoretical and experimental results, it can be observed that the experimental amount of Ye'elimite in sample 4 is higher than in sample 1c, but the Bogue calculations show an opposite tendency (i.e. predicts a higher value for sample 1c). This could be attributed both to the accuracy of the QXRD measurement and to the limitations of the employed simplified Bogue calculations that does not con-



sider the solid solution effect. For more accurate predictions, a modified Bogue calculation should be employed that accounts for the solid solution reality of produced phases. However, more research is needed in order to obtain all the input parameters for such an advanced model, and is currently underway.

Further, the potential use of the Matlab program is demonstrated in the example in Fig 6. The phase fraction is calculated for a fixed mass fraction of calcite, bauxite and phosphogypsum to 31.25 %, 10.00 % and 12.50 %, respectively (corresponding to the sample 4 in Table 3.). The remaining amount to 100 % is composed of bottom ash and EAFS. Therefore, an increase in the amount of bottom ash would result in the decrease of the EAFS in order to keep the balance. Fig 6 shows the change in the predicted phase fraction as a function of the change in the amount of bottom ash and EAFS. This was calculated by internally iterating the Bogue calculations for incremental changes in bottom ash and EAFS. The change of the corresponding subsystem number with a true compositional solution is shown in Fig 7. These two figures clearly depict regions where no solution could be found by the Bogue calculations for these compositional cases. Regions with no theoretical output are detected for bottom ash fraction of around 12.5 % and after 22.5 % for a simulation scenario presented in Fig 6. The right side limit is due to the fact that the used calculations are confined to the portion of the system in which  $C_2S$  is present.<sup>19</sup> For other mixture compositions (e.g. as in Table 4) behaviors are quantitatively different. In this paper, only simulation derived from sample 4 is presented to show the potential use of the Matlab program for investigating the effect of raw mixture (i.e. bottom ash and EAFS mass addition) to the mineralogical composition of clinker.

### Hydration study

The hydration behavior of CSA clinkers were investigated by calorimetric and Vickers hardness tests. Both the influence of the different clinker mixtures and the addition of phosphogypsum on the hydration behavior are investigated. Measurements are done with clinker samples 3b and 4 (Table 5). The 3b clinker was directly mixed with water, while to a mixture with the sample clinker 4 different amounts of phosphogypsum are added: 10 %, 15 % and 20 %. The mixtures are labelled 3b, 4\_10, 4\_15 and 4\_20, respectively.

Figure 8 presents the results of the rate of the heat of hydration, obtained by differentiating the cumulative heat of hydration curve. Rate of heat generation on water addition are in general due to wetting, dissolution and hydration reactions of ce-

Table 5 – Experimental results on Vickers hardness (samples hydrated for 7 days) and evolved heat of hydration (after 20 h)

Sample	w(PG)* / %	A / $\mu\text{m}^2$	$H_{v,7d}$ / MPa	$Q_{20h}$ / $\text{Jg}^{-1}$
3b	0	16030	109.0	189
4_10	0.10	56676	34.6	97
4_15	0.15	42361	46.3	129
4_20	0.20	22340	87.6	144

\* mass fraction of phosphogypsum (PG) added during paste mixing

ment 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'elite and anhydrite followed by nucleation and growth of hydrate phases, mostly ettringite. The dormant period is observed in case of sample 3b, but is overlapped by other processes in case of hydration of samples 4\_15 and 4\_20. The initial rate of heat evolution (first maximum) is higher for higher amounts of phosphogypsum (added later during cement paste mixing). The main maximum of rate of heat generation occurs around 2.3 h and 3.7 h for samples 4a and 4bc, respectively, followed by gradual decrease up to 20 h hydration. It is interesting to observe qualitatively similar hydration behavior of samples 4\_10, 4\_15 and 4\_20. The main hydration peak of sample 3 b exhibits two exothermic processes represented by peaks at around 3.4 h and 6.4 h of hydration.

Total heat evolved after about 20h of hydration is given in Table 5. It can be observed that the sample 3b 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. Furthermore, the highest heat of hydration for sample

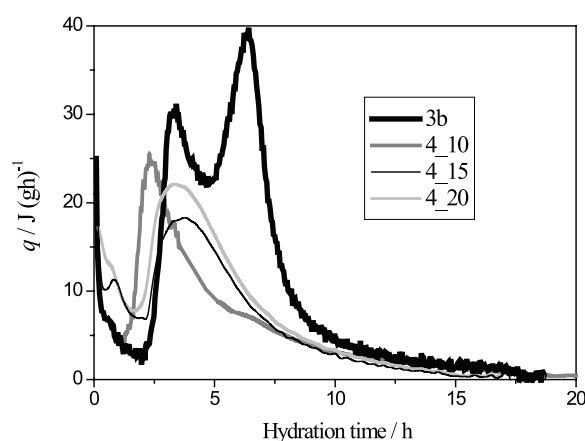


Fig. 8 – Rate of heat of hydration measured by isoperibolic calorimeter

3b is in agreement with the QXRD data that show the highest amount of Ye'elimite in that sample.

Results of Vickers hardness test of samples hydrated for 7 days are also shown in Table 5. The results indicate that the hardness (and thus compressive strength) increases with the fraction of added phosphogypsum. It must be stressed that due to the porosity within the hardened cementitious material, the Vickers indentation did not give an expected square-based pyramid imprint (as commonly observed for metals), and the characteristic diagonals could not be distinguished. Therefore, the obtained Vickers hardness results are only semi-quantitative. Heat evolution could provide an approximation on a relative amount of achieved hydration degree. The trend of results on the measured cumulative heat evolved up to 20 h of hydration are in agreement with trend of results on Vickers hardness. The higher the hardness is, the higher is the evolved heat. Furthermore, it is interesting to compare the amount of Ye'elimite in the clinker samples (Table 5) with the initial composition (i.e. mass fractions) of raw materials (Table 3). Basically, in a fired clinker, the 3b sample has a higher amount of phosphogypsum than the sample 4, that is mainly compensated by lower limestone content. The highest Ye'elimite content could explain the best mechanical properties and the highest hydration heat obtained for the 3b sample.

As the obtained  $C_4A_3S$  content in CSA are close to the ones obtained in other studies,<sup>4,18</sup> and the calorimetric measurements showed significant reactivity, while the Vickers test indicated a development of mechanical properties, it can be concluded that CSA production offers an alternative and feasible way of the investigated industrial waste minimization.

## Conclusion

An elaboration is made to quantitatively compare the energy requirement and environmental impact of CSA and PC production. The manufacture of portland cement (PC) consumes huge amounts of energy and has a significant  $CO_2$  emission. Calcium sulfoaluminate cement (CSA) is a promising alternative binder to PC due to: a) lower limestone requirement in CSA; b) about 200 K lower sintering temperature for CSA than for PC; and c) much easier grinding of the fired CSA. Each of these arguments considerably reduces energy consumption and  $CO_2$  emissions from cement manufacture. Therefore, CSA materials are a potentially very attractive high-performance eco-cement.

The potential benefits offered by CSA production from industrial wastes or by-products already

present in the Republic of Croatia have 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 CSA. Five series of CSA clinkers were synthesized in the attempt to obtain different contents of cement mineral phases. Mass fraction of Ye'elimite in the prepared CSA as determined by quantitative X-ray powder diffraction (QXRD) ranged from 27 to 32 mass %.

Theoretical phase composition of the clinkers from different raw mixtures compositions were calculated using Bogue calculations. The computational procedure of phase compatibility and quantification in the C-S-A-F-s systems relevant to CSA clinkers show promising performance. For more accurate predictions, a modified Bogue calculation that accounts for the solid solution reality of produced phases could be employed.

The hydration behavior of CSA clinkers investigated by calorimetric and Vickers hardness tests were in good agreement with QXRD. In conclusion, CSA production offers an alternative and feasible method for minimization of industrial waste.

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## A list of symbols with measurement units

A	– $Al_2O_3$
A	– surface area, $\mu m^2$
BA	– coal bottom ash
C	– CaO
$C_p$	– effective heat capacity of the calorimeter, $J\ ^\circ C^{-1}$
CSA	– calcium sulfoaluminate cement
EAFS	– electric arc furnace slag
F	– $Fe_2O_3$

$H$	– Vickers hardness, MPa
$M$	– MgO
$m$	– cement mass, g
$PC$	– portland cement
$PG$	– phosphogypsum
$S$	– SiO <sub>2</sub>
$s$	– SO <sub>3</sub>
$T$	– temperature, °C
QXRD	– quantitative X-ray powder diffraction
$Q$	– heat of hydration, J g <sup>-1</sup>
$q$	– Rate of heat of hydration, J g <sup>-1</sup> h <sup>-1</sup>
$w$	– mass fraction
$\beta$	– cooling constant of the calorimeter, h <sup>-1</sup>

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