

Waste Phosphogypsum – Toward Sustainable Reuse in Calcium Sulfoaluminate Cement Based Building Materials

N. Franković Mihelj^{a,*}, N. Ukrainczyk^b, S. Leaković^c, and Juraj Šipušić^b

^aEnvironmental Protection and Energy Efficiency Fund, Ksaver 208, Zagreb, Croatia

^bFaculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, Zagreb, Croatia

^cPetrokemija d.d., Aleja Vukovar 4, 44320 Kutina, Croatia

Original scientific paper

Received: August 28, 2012

Accepted: December 6, 2012

¹part of this work was presented at, and published in the proceedings of *3rd International Symposium on Environmental Management*, Eds. Koprivanac, N., Kušić, H., Lončarić Božić, A., Zagreb, Faculty of Chemical Engineering and Technology, University of Zagreb, 26–28. October 2011.

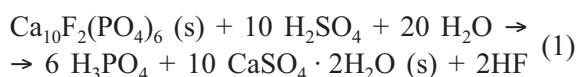
The Croatian fertilizer plant Petrokemija d.d. – Kutina produces phosphoric acid by the wet process natural phosphate rock sulfuric acid digestion. Unfortunately, large quantities of phosphogypsum are produced by this process as an unwanted byproduct. In this work, calcium sulfoaluminate cement production has been investigated as a possible way of phosphogypsum reuse. Due to the use of large quantities of industrial byproducts of various origins for calcium sulfoaluminate cement production, radionuclide activity has been determined and found to be lower than permissible levels. Mechanical properties of standard 3:1 mortar specimens have been determined from 5 kg pilot scale batches, and 28-day compressive strengths are somewhat less than 20 MPa. Mineralogical composition of calcium sulfoaluminate cement prepared has been determined by qualitative X-ray diffraction powder analysis showing the presence of Klein compound but also sulfoferrite that could contribute to the further increase in long-term strength.

Key words:

Phosphogypsum, calcium sulfoaluminate cement, waste management, reuse of phosphogypsum

Introduction

The Croatian fertilizer plant Petrokemija d.d. – Kutina is an industrial complex consisting of production units for ammonia, nitric acid, urea, sulfuric acid, phosphoric acid, mineral fertilizers, carbon black and bentonite clay. Phosphogypsum (PG) is a byproduct from the production of phosphoric acid by the wet process whereby natural phosphate rock is mixed with sulfuric acid. The resulting solid phase of calcium sulfate is separated from the solution of phosphoric acid by filtration. Commercial wet process is classified according to the hydrated form in which calcium sulfate crystallizes (as anhydrite, CaSO_4 ; hemihydrate, $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ or dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)¹. The underlying chemical transformation of raw materials in the dihydrate process operated at Petrokemija plant is shown by Eq. 1.



The usual plant operation generates 4.9 tons of phosphogypsum per ton of phosphoric acid (calculated as 100 % P_2O_5). Phosphoric acid as a valuable product is recovered from phosphogypsum slurry by initial filtering and three stages of subsequent filter cake washing to ensure a satisfactory recovery of soluble P_2O_5 . The desired degree of phosphorous-bearing liquid separation from the filter cake is vacuum-assisted and the remaining phosphogypsum filter cake is repulped with water and then pumped as approximately 25 % by weight solids-containing suspension to the phosphogypsum tailing facility. The increasing quantity of phosphogypsum, in excess of 4 million tons at tailing facility of Petrokemija phosphoric acid plant, has triggered a serious investigation of possible phosphogypsum reuse^{2–4}.

PG properties depend upon the nature of the phosphate rocks used, the plant operation efficiency, the disposal method, and the age, location and depth of landfill⁴. Petrokemija imports phosphate rock from Morocco (Khouribga). A compari-

*Corresponding author e-mail: nirvana.fm@fzoeu.hr

Table 1 – Typical chemical analysis of various phosphate rocks (mass fraction, %), taken from European Fertilizer Manufacturers Association booklet¹

Mass fraction, w(component)/ %	CEI-Russia	South Africa-Phalaborwa	Morocco-Khouribga	USA Florida	Senegal	Togo
Grade, *BPL%	84	80	73	75	80	80
P ₂ O ₅	38.9	36.8	33.4	34.3	36.7	36.7
CaO	50.5	52.1	50.6	49.8	50	51.2
SiO ₂	1.1	2.6	1.9	3.7	5.0	4.0
F	3.3	2.2	4.0	3.9	3.7	3.8
CO ₂	0.2	3.5	4.5	3.1	1.8	1.5
Al ₂ O ₃	0.4	0.2	0.4	1.1	1.1	1.0
Fe ₂ O ₃	0.3	0.3	0.2	1.1	0.9	1.0
MgO	0.1	1.1	0.3	0.3	0.1	0.1
Na ₂ O	0.4	0.1	0.7	0.5	0.3	0.2
K ₂ O	0.5	0.1	0.1	0.1	0.1	0.1
SO ₃	0.1	0.2	1.6	0.1	–	0.3
Cl	–	–	0.1	–	–	0.1
SrO	2.9	0.3	0.1	–	–	–

*BPL – Basic Phosphate of Lime (Bone Phosphate of Lime)

son among the most common phosphate rocks chemical composition^{1,5,6} is given in Table 1.

Phosphate rock from Morocco, mainly used by “Petrokemija” d.d., enables smooth production process, i.e. good overall efficiencies may be obtained, gypsum cake is reasonably filterable etc. However, increased concentration of heavy metals should be expected in phosphoric acid and acidic PG slurry water (transporting water). As far as trace elements are concerned⁶, Morocco phosphate rock is characterized by increased chromium and nickel content

(Table 2.). Zinc is usually not an issue, but due to elevated content in the phosphate rock, its concentration is increased in both phosphoric acid and recycling water.

Raw phosphogypsum contains 15–30 % moisture and over 50 types of impurities, such as organic matter, soluble and insoluble phosphates and free phosphoric and sulfuric acid, fluorine compounds and fluor-silicates, admixtures combined sodium and potassium, rare earth and radioactive elements⁴⁻⁷.

Table 2 – Trace elements in various phosphate rocks¹

Content / ppm	CEI-Russia	South Africa-Phalaborwa	Marocco-Khouribga	USA Florida	Senegal	Togo
Rare earth elements	6800	4200	900	600	-	-
U ₃ O ₈	11	134	185	101	124	-
As	10	13	13	11	53	12
Cd	1.2	1.3	15	9	18	53
Cr	19	1	200	60	6	-
Cu	37	102	40	13	-	-
Hg	33	0.1	0.1	0.02	0.2	0.6
Ni	2	2	35	28	-	-
Pb	-	11	10	17	5	-
Zn	20	6	200–400	70	-	-

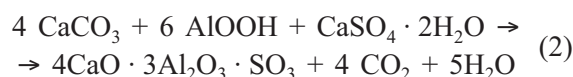
A number of industrial processes, such as fertilizer production and processing activities, can cause naturally occurring radioactive materials (NORM) to become concentrated at levels above natural background in byproduct waste streams. NORM that accumulates in industrial waste streams is referred to as “technologically enhanced NORM”, or TENORM (Technologically Enhanced Naturally Occurring Radioactive Material). Phosphate ores are naturally radioactive and their radioactivity originates mainly from ^{226}Ra , ^{238}U and ^{232}Th .

Wet processing of phosphate rock causes the selective separation and concentration of naturally occurring radium (^{226}Ra), uranium (^{238}U) and thorium (^{232}Th): about 80 % of ^{226}Ra is concentrated in PG while nearly 86 % of ^{238}U and 70 % of ^{232}Th end up in the phosphoric acid. 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 not just due to legal prohibitions, but also due to 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.

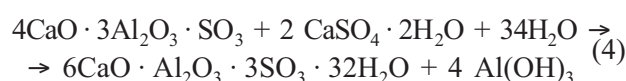
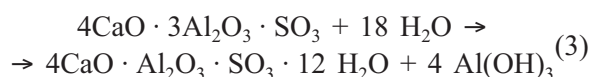
Determining the types of impurities present can be very important when defining waste management processes and environmental policies such as public health risk assessment. It has been found that no exposure of the particular *public member* in Kutina municipality is at any time greater than 1 mSv per year due to existence of PG tailing facility^{2,7}.

This fact justifies all present or future efforts leading to technological enrichment of TENORM PG product to be used in various new products and to the benefit of Kutina municipality inhabitants. Phosphogypsum could serve as a raw material for calcium sulfoaluminate cement production^{3,8}. This work investigates the feasibility of PG reuse in building materials based on calcium sulfoaluminate cement. The results obtained from reuse of raw byproduct materials already present in Republic of Croatia are reported for the first time.

The main hydraulically active mineral of calcium sulfoaluminate cement is Kleinite or Klein compound, $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$, formed by heating the mixture of limestone, bauxite and phosphogypsum at high-temperature as shown below:



For the first time, mineral Kleinite⁹ was prepared in early 1960, but its hydration behavior has been investigated only recently^{10,11}. Kleinite reacts with water and dissolved gypsum added during milling of calcium sulfoaluminate clinker, giving up calcium monosulfate aluminate hydrate (Eq. 3) and ettringite (Eq. 4) together with amorphous aluminium hydroxide as main hydration products^{10,12}:



Glasser and Zhang¹¹ and Chen and Juenger¹³ calculated the optimal gypsum addition to the calcium sulfoaluminate clinker between 20–25 %, based on the main hydration reaction (Eqs. 3 and 4). Production of calcium sulfoaluminate cement is highly attractive because of the lower firing temperatures, lower CO₂ emissions and use of industrial wastes and byproducts as raw materials^{3,8}.

Experimental

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 with the addition of bauxite and limestone. The batch formulations were developed previously¹⁴, relying on the results of mineral phase equilibrium investigation by Sahu and Majling¹⁵.

Mixing and firing

All the raw materials used were separately milled in planetary mill Pulverisette 5, using steel balls and bowl, and sieved through a wire sieve of 125 micrometer mesh. Each component of the final batch was carefully weighed and dry mixed in ordinary ball mill.

The raw meal was transferred to a large ceramic crucible and fired in a gas furnace at temperature of 1170 °C for 3 hours. The fired clinkers were relatively soft and friable, and easy to grind.

TGA analysis of raw meal mixture

Mass loss of raw materials mixture was observed by NETZSCH STA409 simultaneous DTA/TGA instrument in synthetic air flow over the

sample of 30 cm³ min⁻¹ and nitrogen protective flow over TGA balance at a rate of 150 cm³ min⁻¹.

X-ray fluorescent analysis

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

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 a corundum pestle and crucible and then mounted in a sample holder. The powder diffraction patterns were gathered over the range of 5–50° 2θ at a step of 0.02° for a collection time of 1 sec. All the measurements were performed using Shimadzu XRD-6000.

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 the first 24 hours of hydration was measured. Other details of semiisothermal microcalorimeter construction and operation have been described previously¹⁶.

Flexural and compressive strength 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.

Gamma spectrometry measurements

Gamma spectrometry measurements were conducted at the Institute for Medical Research and Occupational Health, Unit for Radiation Protection, in Zagreb. ²²⁶Ra activity was determined by alpha spectrometric measurements using silicon charged particle detector with active area of 450 mm² and counting duration of at least 60 000 s. Gamma spectrometric analysis was conducted using HPGe and/or Ge(Li) detectors with electronic units and gamma spectrometric software on a personal computer.

Results and discussion

Quality of phosphogypsum produced in Petrokemija d.d. has been regularly monitored by both the Petrokemija works laboratory and the laboratory of the Institute for Public Health and Occupational Health in Zagreb. Typical analysis of PG made in February 2008. (PG1), and in July 2010. (PG2 and PG3), are shown in Table 3.

Table 3 – Chemical composition of phosphogypsum at the Petrokemija tailing facility. The rest of the composition is organic matter, free acids and other minor elements.

Mass fraction, w(component)/%	PG1	PG2	PG3
Total P ₂ O ₅	0.30	0.59	0.48
CaO	25.40	31.59	33.64
SO ₃	46.03	47.67	53.46
MgO	0.0005	0.006	0.002
F	0.22	2.15	1.18
Fe	0.009	0.045	0.006
Al	0.039	0.095	0.075
Na	0.008	0.010	0.010
Cd	2.00	0.52*	0.37*
SiO ₂	0.94	7.53	1.09
H ₂ O	14.64	7.34	4.72

*Cadmium concentration in ppm

It is seen that phosphogypsum is very pure and contains small amounts of impurities, mainly SiO₂ 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 the main source of sulfate needed for Kleinite formation. For the preparation of calcium sulfoaluminate cement, beside phosphogypsum, two other industrial by-products were 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 a byproduct of steel production and refinement in electric furnaces available in large quantities. Chemical composition¹⁷ of bottom ash and EAFS is shown in Table 4.

The final chemical composition of raw meal for calcium sulfoaluminate cement production was

Table 4 – Chemical composition of bottom ash (coal fired power plant at Plomin, Croatia) and electric arc furnace slag (Sisak, Croatia)

Mass fraction, w(component)/%	Bottom ash	EAFS
CaO	5.43	38.42
Fe ₂ O ₃	10.33	24.20
SiO ₂	49.64	11.01
Al ₂ O ₃	25.16	8.67
MgO	–	10.22
MnO	–	5.47
Na ₂ O	–	0.07
K ₂ O	–	0.04
SO ₃	0.19	–

adjusted by bauxite and limestone addition (Table 5.). The range of interesting compositions was determined previously¹⁴. Chemical composition of the calcium sulfoaluminate clinkers prepared was determined by X-ray fluorescent analysis, shown in Table 6.

Table 5 – Raw meal composition for calcium sulfoaluminate cement production

Mass fraction, w(component)/ %	sample C1	sample C4
Phosphogypsum	12	18
Electric arc furnace slag	12	0
Bottom ash	12	18
Limestone	42	46
Bauxite	22	18
Sum:	100	100

During firing of raw meal charge one could observe significant mass loss (about 20 %) due to the decomposition of phosphogypsum (water loss), bauxite mineral diaspore and calcite from limestone, shown in Fig. 1. However, due to the lower limestone proportion in the raw meal (~0.65 tons of CaCO₃ per ton of sulfoaluminate clinker, based on the composition C4) than for Portland cement production (~1.10 tons of CaCO₃ per ton of Portland cement clinker, based on average 62 % of CaO in clinker), the mass loss is also lower. It also follows that CO₂ emission per 1 kg of sulfoaluminate clinker produced is also lower than for Portland cement clinker production. This fact, along with the lower temperatures needed for production and easy

Table 6 – Results of chemical analysis and semiquantitative X-ray fluorescence analysis of calcium sulfoaluminate cement clinkers prepared

Mass fraction, w(component)/%	sample C1	sample C4
Moisture	0.11	0.10
Loss on ignition	0.35	0.27
Insoluble residue	10.69	6.23
free CaO	0.07	0.15
SiO ₂	21.14	17.45
Fe ₂ O ₃	10.52	6.76
Al ₂ O 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
F	–	–

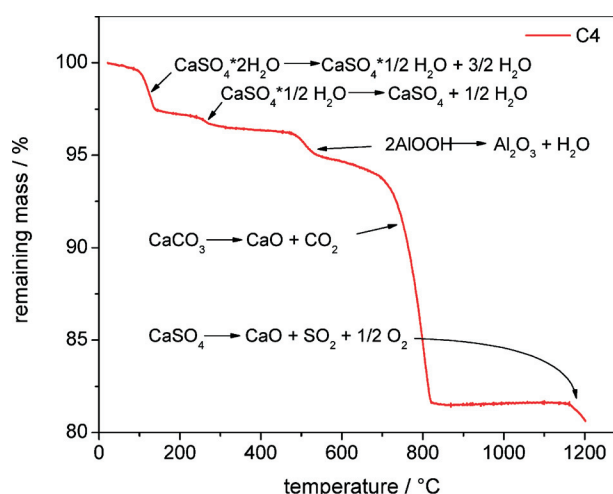


Fig. 1 – Result of TGA analysis of raw materials mixture for CSAC production, sample C4

grinding make calcium sulfoaluminate cement highly attractive. Exhaust gases have not been analyzed and thus the fate of fluoride is not certain. However, it could be argued that there is a possibility of fluoride incorporation in clinker minerals, similar as for Portland cement¹⁸. After homogenization and firing, the calcium sulfoaluminate clinker obtained was analyzed by X-ray powder diffraction (Figs. 2 and 3), revealing the presence of Kleinite, $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$, sulfospurrite, $5\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{SO}_3$, anhydrite, CaSO_4 , belite, $2\text{CaO} \cdot \text{SiO}_2$, ferritte phase, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ and titanium bearing perovskite like phase $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$. Although the true composition of ferritte phase is uncertain due to the

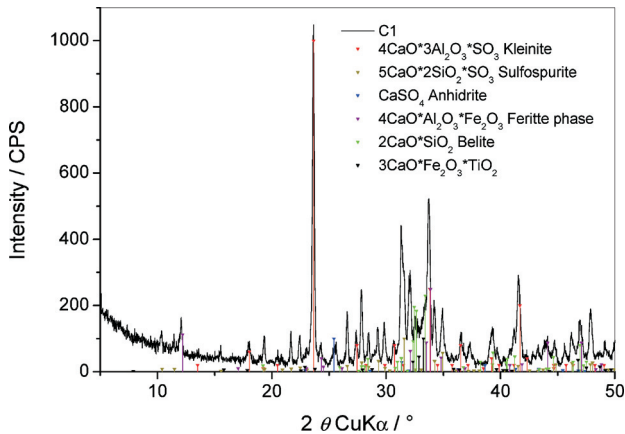


Fig. 2 – Result of X-ray powder diffraction analysis of sample C1

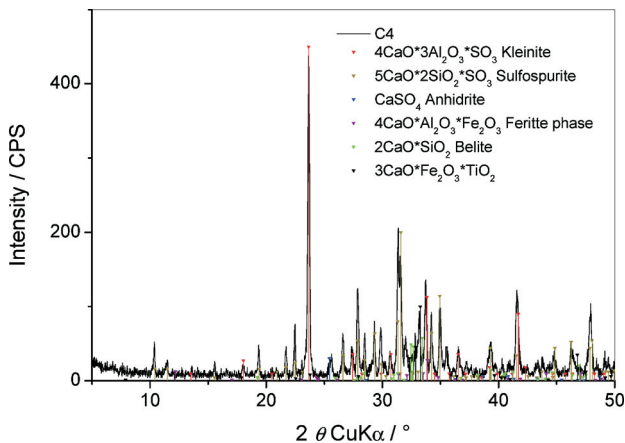


Fig. 3 – Result of X-ray powder diffraction analysis of sample C4

possibility of iron-aluminium substitution in solid solution, the relative quantity of ferrite phase is larger for sample C1 that contains more iron oxide than sample C4 (Table 6). Furthermore, the chemical composition of Kleinite is also uncertain because it forms iron-aluminium solid solution¹⁹.

Kleinite is the main mineral in the prepared calcium sulfoaluminate clinkers. 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, and they form polymineral grains. The prevailing opinion²⁰ on cement hydration states that the degree of hydration of different minerals in cement is approximately the same because of the presence of polymineral grains. The core of the polymineral particle is shielded by the hydration products and outer minerals, so even after long hydration period one could find a certain amount of rapid hardening minerals. It is interesting to observe the large quantity of belite and sulfo spurrite in both samples due to the relatively high

SiO₂ content (Table 6). Belite and sulfo spurrite in the cement clinker hydrate slowly and contribute to strength in latter stages of hydration.

Rate of heat generation on water addition (due to wetting, dissolution and hydration reactions in general) of the samples prepared is shown in Fig. 4. 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 the case of sample C4, but is overlapped by other processes in case of sample C1 hydration. The maximum rate of heat generation occurs between 200–400 minutes and 400–700 minutes for samples C1 and C4 respectively, followed by gradual decrease up to 24 h hydration. It is worth noting that the monotonically decaying period of hydration after 400 minutes and 700 minutes for samples C1 and C4 respectively, could be fitted as a single exponentially decay curve. However, it is more important to observe qualitatively similar hydration behavior of samples C1 and C4. Rapid heat evolution starts immediately as water is added to the cement clinker. The total heat effect (i.e. the integral of the obtained heating rate signal) evolved during the first 24h is 8 % greater for sample C4 than for sample C1. The main hydration peak of sample C4 exhibits two exothermic processes represented as a shoulder on the main hydration peak between 200 and 300 minutes. Analogous process for sample C1, clearly visible between 50–100 minutes of hydration is overlapped with both initial heat evolution and main hydration peak. After maximal rate of heat liberation, the hydration processes monotonically slow down.

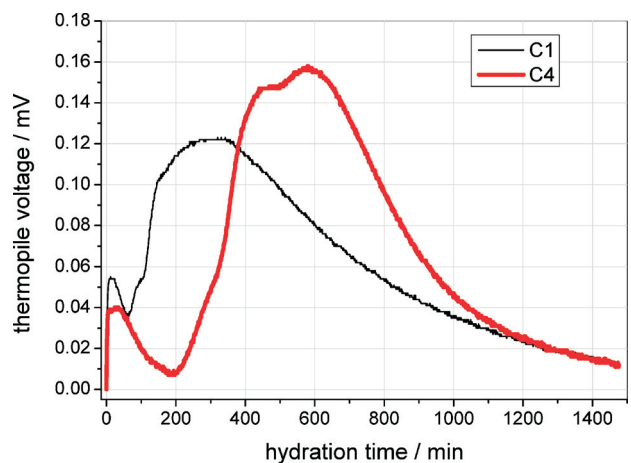


Fig. 4 – Rate of heat generation, proportional to the thermopile voltage, due to the hydration of samples C1 and C4 in microcalorimeter at 20 °C and water to cement ratio, $w/c=0.5$

Pilot scale 5 kg batches yielded enough calcium sulfoaluminate cement clinker for comprehensive testing. Calcium sulfoaluminate cement batches were prepared with the addition of 5 and 10 % gypsum to further test development of strength according to the HRN EN-197-1:2005. Filling of a standard three-prism mould is shown in Fig. 5. It is interesting to observe the 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 to dark brown, depending on the initial composition and firing conditions²¹.



Fig. 5 – Filling of standard three-prism mould.

Properties of calcium sulfoaluminate cements prepared from pilot scale batches with the 5 % and 10 % gypsum addition are shown in Table 7. From the results of Table 6 and Table 7, it could be con-

cluded that higher density and higher insoluble residue content is due to the greater Fe_2O_3 quantity in sample C1. Lower strengths observed for sample C1 are also due to the higher SiO_2 quantity in sample C1, giving up more belite and sulfoferrite 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.

The most important source of PG radioactivity is reported to be ^{226}Ra and therefore, from the radiation protection point of view and the protection of the public from TENORM exposures originating from waste piles, storage and *processing* of the PG the primary radionuclide of concern is ^{226}Ra . Measurements of nuclide radioactivity (Table 8) of the calcium sulfoaluminate clinkers C1 and C4 prepared have shown that calculated α -activity of the samples are lower than permissible levels by one order of magnitude while calculated β -activities are two orders of magnitude lower than permissible levels. Final result, *i.e.* the calculated relative number according to the legislative act NN 60/2008 poses no restrictions to the use of the composition similar to the sample C1 with 10 % of gypsum added as building material, while materials similar as sample C4 could be used only up to 80 %.

Conclusions

This work shows that it is possible to prepare calcium sulfoaluminate cement from phosphogypsum and other industrial byproducts already present in Republic of Croatia. Since bauxite is the most expensive component of the raw meal, its quantity is deliberately kept low. Increasing the

Table 7 – Properties of calcium sulfoaluminate cements prepared from pilot scale batches with the 5 %, and 10 % gypsum addition

Property	Measuring unit	5 % gypsum added		10 % gypsum added	
		C1	C4	C1	C4
Density	g cm^{-3}	3.092	2.942	2.996	2.937
Specific surface area (Blaine)	$\text{cm}^2 \text{g}^{-1}$	2630	2766	2428	2708
Standard consistency	%	26.0	25.6	26.0	26.4
Le Chatelier expansion	mm	0	0	0	0
Initial setting time	min	55	49	86	47
Final setting time	min	76	79	117	77
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

Table 8 – Results of radioactive isotope measurements for samples of C1 and C4 of calcium sulfoaluminate cement clinker with the 10 % gypsum addition

Radionuclide	Specific activity / Bq kg ⁻¹	
	sample C1 + 10 % gypsum	sample C4 + 10 % gypsum
²³⁸ U	(6,731±0,344)E+1	(7,608±0,390)E+1
²³² Th	(6,453±0,105)E+1	(6,717±0,133)E+1
²³⁵ U	(7,937±0,393)E+0	(8,713±0,428)E+0
²²⁶ Ra	(1,684±0,011)E+2	(2,475±0,025)E+2
²²⁸ Ra	(6,453±0,105)E+1	(6,717±0,133)E+1
²¹⁰ Pb	(3,605±0,553)E+1	(5,202±0,633)E+1
⁴⁰ K	(9,211±0,200)E+1	(3,195±0,086)E+1
Calculated specific activity / Bq kg ⁻¹		
α -emitters	1,076A10 ⁶ < 1A10 ⁷	1,200A10 ⁶ < 1A10 ⁷
β -emitters	8,625A10 ⁵ < 1A10 ⁸	1,01A10 ⁶ < 1A10 ⁸
Relative number*		
	0,915 < 1	1,208 > 1

* calculated according to the Croatian legislative act: čl. 35 NN 60/2008

quantity of bauxite and phosphogypsum would increase the quantity of Klein compound and mechanical strength, but due to the radioactive nuclide content of phosphogypsum, its quantity should be kept low. Compressive strength of the standard 3:1 mortar prisms of the CSAC prepared is somewhat less than 20 MPa. Those material formulations are unsuitable for load-bearing parts of construction but could find applications in soil stabilization or preparation of base layers of roads, where mechanical strength is not of prime importance. Long-term investigations are still needed to fully characterize other important aspects of these materials in exploitation, e.g. freeze/thaw resistance, volume stability, reinforcement corrosion, chloride ingress etc. The samples C1 and C4 containing 36 % by mass of waste materials, seem to be well balanced between required mechanical properties, specific radioactivity and bauxite content of the raw meal. Measurements of nuclide radioactivity (Table 8) of the prepared calcium sulfoaluminate clinkers show no restrictions to the use of the composition similar to the sample C1 (with 10 % of gypsum added) as building material, while materials similar to sample C4 could be used only up to 80 %. Regarding the aforementioned PG properties, further research is still needed to evaluate overall suitability of PG use for each specific application.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support from the Croatian Ministry of Science, Education and Sports under project no. 125-1252970-2983 "Development of hydration process model", and thank Petrokemija d.d. fertilizer plant for providing site specific data, as well as Holcim Hrvatska d.o.o. Koromačno for technical assistance.

References

- Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry, Booklet No. 4 of 8: Production of phosphoric acid, Copyright 2000 – European Fertilizer Manufacturers' Association, pp. 9.
- Prlić, I., Spitaler E., PHARE 2006 Development of hazardous waste management system, including the identification and management of "hot spot sites" in Croatia, Volume I 00A The qualitative public health risk and impact assessment, (2009).
- Odler, I., Special Inorganic Cements, E&FN Spon, London (2000).
- Renteria-Villalobos, M., Vioque, I., Mantero, J., Manjón, G., J. Hazard. Mater. **181** (2010) 193–203.
- Tayibi, H., Choura, M., Lopez, F.A., Alguacil, F.J., Lopez-Delgado, A, J. Environ. Manage. **90** (2009) 2377–2386.
- Beddow, H., Black, S., Read, D., J. Environ. Radioactiv. **86** (2006) 289–312.
- UNSCEAR. Report of the United Nations Scientific Committee on the Effects of Atomic Radiation, United Nations 2000, New York.
- Arjunan, P., Silsbee, M. and Roy, D., Cem. Concr. Res. **29** (1999) 1305–1311.
- Klein, A., US Patent No. 3,155,526, 3 Nov 1963; 4 pp.
- Bernardo, G., Telesca, A., Valenti, G. L., Cem. Concr. Res. **36** (2006) 1042–1047.
- Glasser, F. P., Zhang, L., Cem. Concr. Res. **21** (2001) 1881–1886.
- Winnefeld, F., Lothenbach, B., Cem. Concr. Res. **40** (2010) 1239–1247.
- Chen, I.A., Juenger, M.C.G., J. Mater. Sci. **46** (2011) 2568–2577.
- Ukrainczyk, N., Franković Mihelj, F., Šipušić, J., Calcium sulphoaluminate eco-cement from industrial waste, 3rd International Symposium on Environmental Management, Faculty of Chemical Engineering and Technology, University of Zagreb, 2011, pp. 158–165.
- Sahu, S., Majling, J., Cem. Concr. Res. **23** (1993) 1331–1339.
- Ukrainczyk N., Chem. Eng. Sci. **65** (2010) 5605–5614.
- Sofilić, T., Merle, V., Rastovčan-Mioč, A., Ćosić, M., Sofilić, U., Archives of Metallurgy and Materials **55** 3 (2010) 657–668.
- Kacimi, L., Simon-Masseron, A., Salem, S., Ghomari, A., Derriche, Z., Cem. Concr. Res. **39** (2009) 559–565.
- Andac, O., Glasser, F. P., Adv. Cem. Res. **6** (1994) 57–60.
- Scrivener, K. L., Capmas, A., Calcium aluminate cement, in: Lea's chemistry of cement and concrete, 4th Ed., P.C. Hewlett (Ed.), Elsevier, 2006.
- Ichikawa, M., Komukai, Y., Cem. Concr. Res. **23** (1993) 933–938.