

# Examination of the jarosite–alunite precipitate addition in the raw meal for the production of sulfoaluminate cement clinker

M. Katsioti<sup>a</sup>, P.E. Tsakiridis<sup>b,\*</sup>, S. Leonardou-Agatzini<sup>b</sup>, P. Oustadakis<sup>b</sup>

<sup>a</sup> School of Chemical Engineering, Laboratory of Analytical and Inorganic Chemistry, National Technical University of Athens, Greece

<sup>b</sup> School of Mining and Metallurgical Engineering, Laboratory of Metallurgy, National Technical University of Athens, Greece

Received 14 January 2005; received in revised form 14 September 2005; accepted 14 September 2005  
Available online 11 October 2005

## Abstract

The aim of the present research work was to investigate the possibility of adding a jarosite–alunite chemical precipitate, a waste product of a new hydrometallurgical process developed to treat economically low-grade nickel oxides ores, in the raw meal for the production of sulfoaluminate cement clinker. For that reason, two samples of raw meals were prepared, one contained 20% gypsum, as a reference sample ((SAC)<sub>Ref</sub>) and another with 11.31% jarosite–alunite precipitate ((SAC)<sub>J/A</sub>). Both raw meals were sintered at 1300 °C. The results of chemical and mineralogical analyses as well as the microscopic examination showed that the use of the jarosite–alunite precipitate did not affect the mineralogical characteristics of the so produced sulfoaluminate cement clinker and there was confirmed the formation of the sulfoaluminate phase (C<sub>4</sub>A<sub>3</sub>S̄), the most typical phase of this cement type. Furthermore, both clinkers were tested by determining the grindability, setting time, compressive strength and expansibility. The hydration products were examined by XRD analysis at 2, 7, 28 and 90 days. The results of the physico-mechanical tests showed that the addition of jarosite–alunite precipitate did not negatively affect the quality of the produced cement.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Sulfoaluminate cement; Characterization; Hydration; Compressive strength

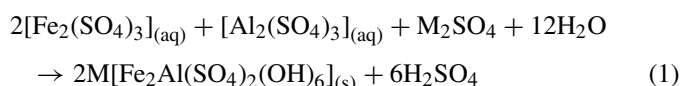
## 1. Introduction

The general trend of today for the industrial wastes or by-products, which are produced in industrial countries, is to examine alternative ways for their exploitation in order to eliminate cost of disposal and avoid soil and water contamination. Many of these undesirable industrial materials contain significant amounts of inorganic ingredients, such as oxides of silicon, aluminum, calcium and iron, which, at suitable combinations, can be used in the production of either Portland cement clinker or other special cement types.

Such a material is a crystalline chemical precipitate, consisting of basic sulfate salts of iron, aluminum and chromium of the jarosite–alunite types. The jarosite–alunite group of isostructural minerals is described by the general formula M(Fe<sub>x</sub>Al<sub>y</sub>Cr<sub>z</sub>)(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, in which “M” may be Na<sup>+</sup>, K<sup>+</sup>,

NH<sub>4</sub><sup>+</sup> or H<sub>3</sub>O<sup>+</sup> and  $x + y + z = 3$ . For  $x = 3$ , the formula represents jarosite, whereas for  $y = 3$  it represents alunite.

The precipitate is produced at some stage of a new hydrometallurgical process [1–3], which was developed at the laboratory of Metallurgy of the National Technical University of Athens in order to extract, economically and efficiently, nickel and cobalt from low-grade nickel oxide ores. According to the above process, the ores are subjected to heap leaching with dilute sulfuric acid and the resulting leach liquors, containing nickel, cobalt, iron, aluminum and chromium, are then treated, at atmospheric pressure and at temperatures not exceeding 100 °C, to remove iron, aluminum and chromium before nickel and cobalt recovery [3]. The jarosite–alunite precipitation is a hydrolysis reaction and can be represented by the equation:



The application of the Toxicity Characteristic Leaching Procedure (TCLP) test [4] has shown the jarosite–alunite precipitate

\* Corresponding author. Tel.: +30 210 7722234; fax: +30 210 7722218.  
E-mail address: ptsakiri@central.ntua.gr (P.E. Tsakiridis).

to be environmentally stable and safe to be rejected in a tailings pond. It should also be noted that this precipitate, coming from the treatment of nickel oxide ores, does not contain hazardous elements, such as Cd, As or Hg, by contrast with the jarosite precipitate produced during the hydrometallurgical extraction of zinc from sulfide ores. However, it is important to find use for this jarosite–alunite precipitate in order to reduce the cost of the hydrometallurgical process by avoiding the construction of a large landfill.

It is well known that various industrial wastes, such as metallurgical slags, fly ash, glass, ceramics from the electronic industry, spent catalysts from refineries, sludge from waste water treatment and others, have been successfully used in clinker production [5–7]. These materials are added to the feedstock in such a proportion that the desirable mineralogical composition is achieved. However, the so far published literature has given little attention to the use of hydrometallurgical wastes, such as jarosite–alunite precipitate, in the production of sulfoaluminate cement.

On the other hand, the manufacture of Portland cement consumes not only a vast amount of energy but generates also undesirable CO<sub>2</sub> emissions. Much attention in recent years has been given to the development of a new generation of cements with the aim of saving energy [8]. To this end, blended cements have been successfully developed by the concrete industry. Nevertheless, blended cements have to be incorporated in more products and have to provide improved engineering properties like improved resistance to chemical attack, freeze-thaw and alkali-aggregate reactions in order to play a greater role in the construction industry. One such cement containing the main phases C<sub>2</sub>S, C<sub>4</sub>A<sub>3</sub> $\bar{S}$ , C<sub>4</sub>AF and CaSO<sub>4</sub> has been developed and reported by many researchers [9–11]. This special cement contains calcium sulfoaluminate instead of high-temperature and hence high-energy tricalcium silicate and tricalcium aluminate. Raw mixes for C<sub>4</sub>A<sub>3</sub> $\bar{S}$  clinkers differ from those of Portland cement in that they contain significant amounts of sulfates; therefore, the reactions and products are different from those found in Portland cement production [12–14].

The aim of the present research work was to investigate the possibility of using the jarosite–alunite precipitate as a raw material for the production of sulfoaluminate cement clinker. For that reason, two samples of raw meals were prepared, one contained 20% gypsum, as a reference sample ((SAC)<sub>Ref</sub>) and another with 11.31% jarosite–alunite precipitate ((SAC)<sub>J/A</sub>). The produced clinkers were analyzed chemically and mineralogically by X-ray diffraction and optical microscopy. The final cement samples were tested for grindability, setting times, compressive strengths and expansibility. The hydration products were determined by XRD analysis at the ages of 2, 7, 28 and 90 days.

## 2. Experimental

### 2.1. Materials

Six runs were conducted to produce the jarosite–alunite precipitate, according to the method developed by the Laboratory

of Metallurgy of the National Technical University of Athens, in order to remove the aluminum and chromium from laterite leach solutions, in a crystalline and filterable form [3]. The runs were conducted in 5 l, five-necked, round bottomed split reactors, that were fitted with glass stirrers, vapor condensers, thermometers and a pH electrode. Real laterite leach solution (4l), pre-neutralized to pH 1.1 at ambient temperature, was placed in each flask and was heated to 95 ± 0.5 °C by an electric thermomantle. The temperature of the liquid was controlled by a FISONs controller and the pH was measured using a METTLER 465-50-T-S7 combined pH electrode, specially designed for semi-solid and boiling water solutions. Ferrous iron was oxidized using hydrogen peroxide. The pH of the solution was slowly raised to a pre-determined equilibrium value, by adding a neutralizing agent. During the precipitation process, the rate of pH increase was kept low in order to control supersaturation of aluminum and chromium and to avoid the production of an amorphous precipitate. The parameters of the runs were: temperature 95 °C, equilibrium pH 3.5, addition of jarosite–alunite precipitate as seed material (20 g/l), reaction time = 12 h.

The sintering process applied was common for the production of both types of cement clinkers. The raw meals were shaped in small spheres, with a diameter of 2 cm, and dried at 110 °C. Then, they were placed inside an oven at 500 °C, the temperature was increased to 1000 °C, at which the samples remained for 30 min and, finally, the temperature was further increased to 1300 °C. The samples were sintered for 30 min [8,14]. At the end of the sintering process, the samples were removed from the furnace and left to cool inside a desiccator in order to avoid the effects of air and moisture.

### 2.2. Methods

The chemical analysis of the feed solution used for the production of the jarosite–alunite precipitate was determined by atomic absorption spectrophotometry (Perkin-Elmer Model 4100) and it is shown in Table 1. At the end of the runs, the content of each reactor was filtered under vacuum. The resulting precipitates were washed with water by re-pulping, dried overnight at 110 °C and weighed. Their chemical analyses are shown in Table 2. The XRD analysis (Fig. 1) showed that the mixed precipitated consisted mainly of jarosite and less alunite due to its lower concentration in the laterite leach liquor. The chemical analyses of the raw materials used are given in

Table 1  
Chemical analysis of the feed solution

Element	Concentration (g/l)
Fe <sup>3+</sup>	21.8
Ni <sup>2+</sup>	5.3
Co <sup>2+</sup>	0.3
Al <sup>3+</sup>	9.3
Cr <sup>3+</sup>	0.8
Mn <sup>2+</sup>	0.9
Mg <sup>2+</sup>	7.6

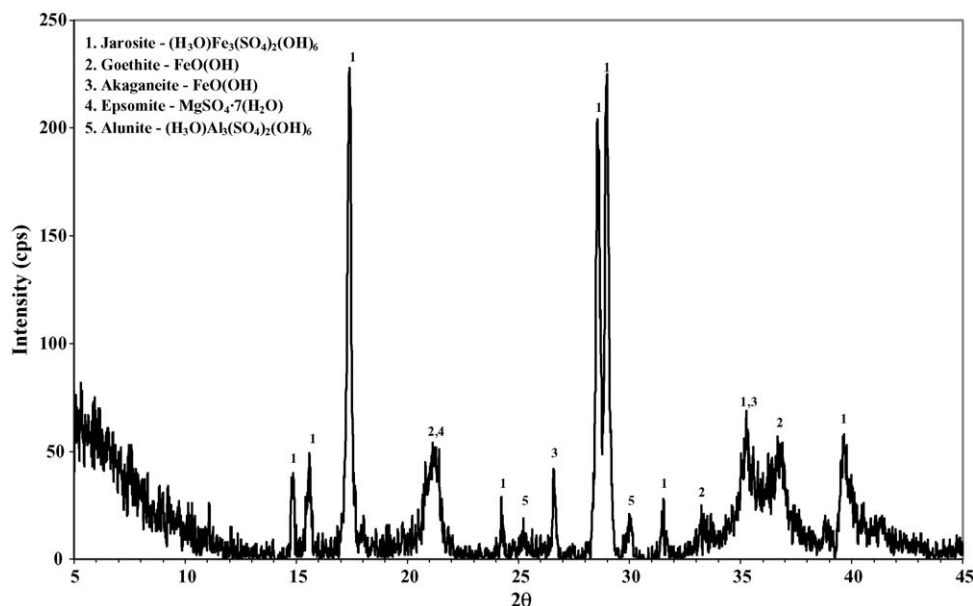


Fig. 1. Mineralogical phases of jarosite–alunite precipitate.

**Table 3.** Based on those, and by using a computational software program, the syntheses of the four raw meals were derived and are presented in **Table 4**.

The clinkers microstructure was examined by optical microscopy. The microscopic observation of the polished impregnated samples was achieved using a Jenapol optical microscope in reflected light. Their mineralogical phases were determined by XRD analysis, using a Siemens D5000 diffractometer with nickel-filtered Cu  $K\alpha_1$  radiation ( $=1.5405 \text{ \AA}$ , 40 kV and 30 mA).

The clinkers were continuously crushed and ground in a Bond ball mill to a specific surface area of about  $3950 \text{ cm}^2/\text{g}$ . Particle size distributions were measured by a laser scattering particle size distribution analyzer (Cilas: Model 1064). An amount of 0.1 g of sample powder was put in 100 ml of ethanol and underwent dispersion treatment by an ultrasonic unit for 60 s.

Compressive strength measurements were conducted at the ages of 2, 7, 28 and 90 days on mortar prisms (dimensions  $40 \text{ mm} \times 40 \text{ mm} \times 160 \text{ mm}$ ), prepared and tested in accordance with European Standard EN 196-1 [15]. The normal consist-

**Table 2**  
Chemical analysis of the precipitates produced

Element	Content (%) at run no.					
	1	2	3	4	5	6
Fe <sup>3+</sup>	27.76	29.12	24.80	26.40	27.91	25.82
Ni <sup>2+</sup>	0.45	0.41	0.84	0.76	0.62	0.46
Co <sup>2+</sup>	0.03	0.03	0.04	0.04	0.03	0.04
Mg <sup>2+</sup>	0.31	0.29	0.28	0.25	0.32	0.29
Mn <sup>2+</sup>	0.03	0.03	0.02	0.03	0.02	0.02
Al <sup>3+</sup>	8.76	9.03	10.21	11.01	10.31	9.89
Cr <sup>3+</sup>	0.91	0.92	0.97	0.94	0.90	0.92
SO <sub>4</sub> <sup>2-</sup>	20.80	19.42	22.68	20.50	21.40	20.35

**Table 3**  
Chemical analysis of raw materials for the production of sulfoaluminate cement clinker

Oxides	Content of raw materials (%)				
	Limestone	Schist	Bauxite	Gypsum	Jarosite–alunite precipitate
SiO <sub>2</sub>	0.09	55.56	4.81	–	1.20
Al <sub>2</sub> O <sub>3</sub>	0.04	9.66	46.96	–	16.55
Fe <sub>2</sub> O <sub>3</sub>	–	7.12	33.34	–	39.66
CaO	55.44	5.75	0.33	34.3	–
MgO	0.17	9.55	0.36	–	–
K <sub>2</sub> O	0.02	1.04	0.25	–	–
Na <sub>2</sub> O	0.02	1.32	0.05	–	–
LOI	43.79	8.89	10.26	20.85	20.00
SO <sub>3</sub>	–	–	–	44.98	17.34
TiO <sub>2</sub>	–	0.52	2.38	–	–
Cr <sub>2</sub> O <sub>3</sub>	–	0.21	0.41	–	1.36
NiO	–	–	–	–	0.95
CoO	–	–	–	–	0.05

ency and setting times of cement pastes were determined using a Vicat apparatus according to the European Standard EN 196-3 [16]. Expansions of the cement pastes were determined by Le Chatelier method [16].

**Table 4**  
Composition of the raw meals for the production of sulfoaluminate cement clinkers

Raw meals	Raw meals composition (%)				
	Limestone	Schist	Bauxite	Gypsum	Jarosite–alunite precipitate
(SAC) <sub>Ref</sub>	47.85	15.28	16.52	20.35	–
(SAC) <sub>J/A</sub>	52.35	–	30.89	5.45	11.31

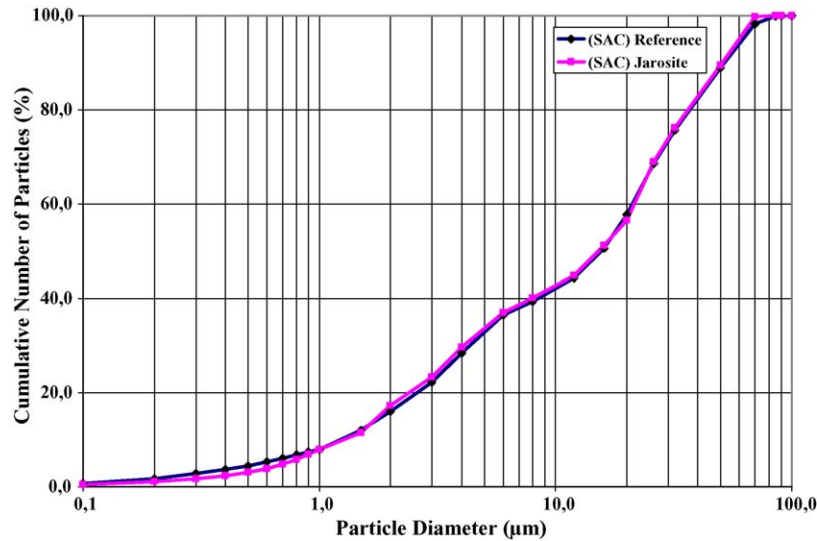


Fig. 2. Particle size distributions of sulfoaluminate cement samples by a laser scattering analyzer.

For the study of the hydration products, the cement pastes were prepared by mixing 300 g of ground mixtures with 75 ml of water. They were then cured in a tap water at a temperature  $20 \pm 2^\circ\text{C}$ . At the ages of 2, 7, 28 and 90 days, the hydration was stopped by means of acetone and ether extraction and the hydration products were determined by XRD analysis.

### 3. Results and discussion

The results of particle size distributions by a laser scattering analyzer are given in Fig. 2. The grindability index of each sample was determined and is presented in Table 5. Both cement samples gave similar results.

The chemical analysis and the Bogues potential mineralogical composition of the sulfoaluminate cement produced are given in Tables 6 and 7, respectively. As the tables show, the addition of the jarosite–alunite precipitate by 11.31% did not seem to affect significantly its chemical and mineralogical composition.

The XRD analyses of the produced sulfoaluminate cement clinkers are given in Fig. 3. As can be seen, the addition of the 11.31% jarosite–alunite precipitate did not affect significantly the mineralogical composition of the produced clinker. The presence of  $\text{C}_4\text{A}_3\bar{\text{S}}$  and the entire absence of sulfate spurrite confirmed the formation of the typical sulfoaluminate-based cement at the final sintering temperature of  $1300^\circ\text{C}$ . Further-

Table 6  
Chemical analysis of the sulfoaluminate cement clinkers

Oxides	Content of the produced cement clinkers (%)	
	(SAC) <sub>Ref</sub>	(SAC) <sub>J/A</sub>
SiO <sub>2</sub>	15.20	14.30
Al <sub>2</sub> O <sub>3</sub>	13.10	14.20
Fe <sub>2</sub> O <sub>3</sub>	4.08	9.40
CaO	51.40	49.80
MgO	0.52	0.51
K <sub>2</sub> O	0.20	0.24
Na <sub>2</sub> O	0.10	0.17
SO <sub>3</sub>	14.20	9.70
TiO <sub>2</sub>	1.05	1.24
CaO <sub>f</sub>	0.14	0.20
LOI	0.11	0.13

more, the  $\text{C}_4\text{A}_3\bar{\text{S}}$  phase, which was formed, did not decompose at that temperature, a fact that was confirmed by the absence of  $\text{C}_3\text{A}$  phase. In the case of adding jarosite–alunite precipitate, the higher proportion of  $\text{C}_4\text{AF}$  phase was attributed to the high content of iron oxide in the precipitate. No  $\text{CaO}_f$  was determined. The proportion of  $\text{C}_2\text{S}$  (belitic phase) in the (SAC)<sub>J/A</sub> clinker was relatively lower compared to (SAC)<sub>Ref</sub>, due to the lower concentration of silicon oxide in the initial synthesis.

Table 7  
Bogues mineralogical composition of the produced sulfoaluminate cement clinkers

Mineralogical phases	Cement clinkers composition (%)	
	(SAC) <sub>Ref</sub>	(SAC) <sub>J/A</sub>
C <sub>2</sub> S	46.25	44.90
C <sub>4</sub> AF	12.46	16.37
$\text{C}_4\text{A}_3\bar{\text{S}}$	21.35	28.35
CaSO <sub>4</sub>	19.80	10.18

Table 5  
Results of grindability tests

	Sample	
	(SAC) <sub>Ref</sub>	(SAC) <sub>Jar</sub>
Mill revolutions	2650	2550
Specific surface (Blaine-cm <sup>2</sup> /g)	3710	3720
Grindability index	1.40	1.46
Specific gravity (g/cm <sup>3</sup> )	3.07	3.10



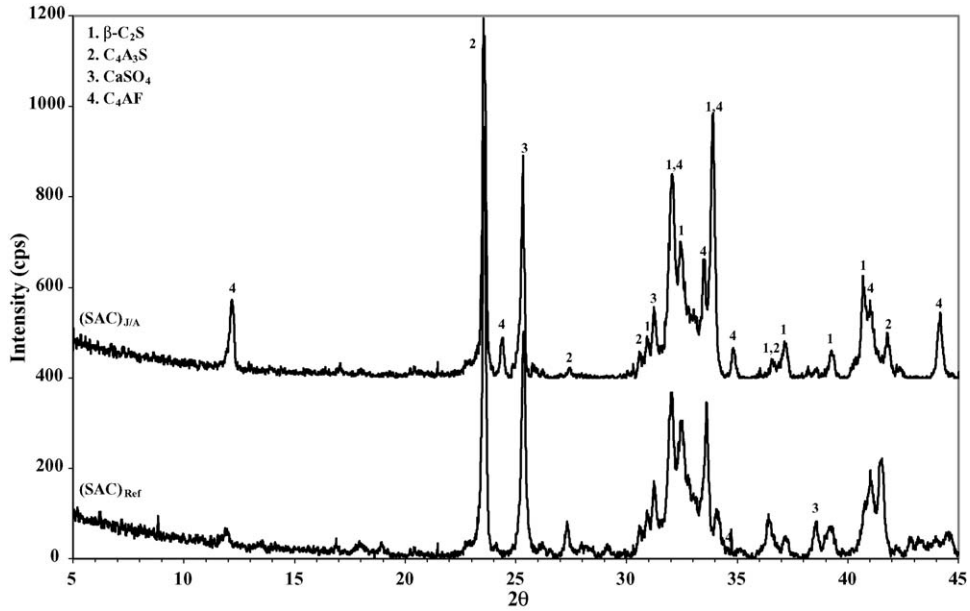


Fig. 3. X-ray diffraction of sulfoaluminate cement clinkers with and without jarosite–alunite precipitate.

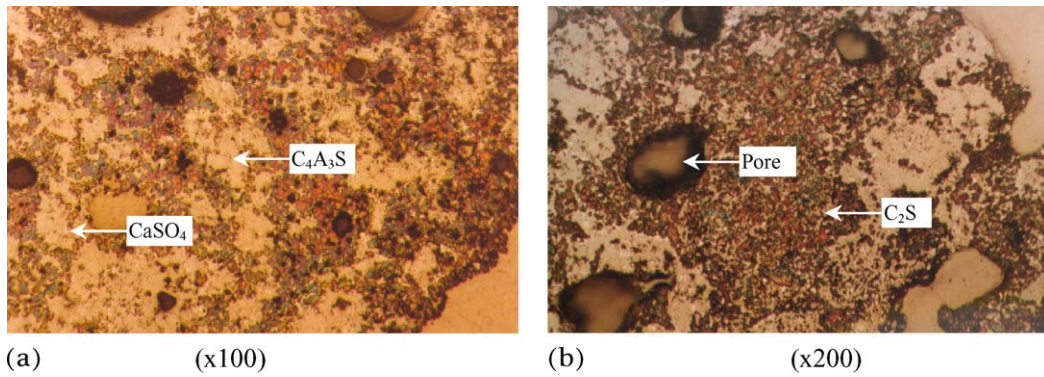


Fig. 4. (a and b) Microstructure of sulfoaluminate cement clinker without jarosite–alunite precipitate.

The microstructure of the sulfoaluminate cement clinkers was examined by optical microscopy in polished sections. The addition of the jarosite–alunite precipitate by 11.31% did not seem to affect its microstructure and the formation of its characteristic mineralogical phases (Figs. 4 and 5).  $CaO_f$  was dispersed

among other phases, in low percentages, in both cases. In the optical microscope, belite was observed as bluish or brownish rounded crystals, rich in lamellas. No differences in the microstructure of belite between (SAC)<sub>Ref</sub> and (SAC)<sub>JA</sub> clinkers were detected. Belite, which was the main mineralogical

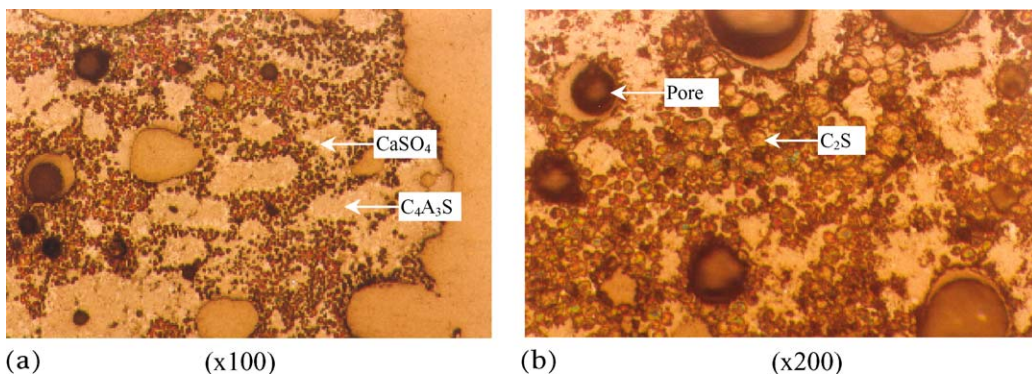


Fig. 5. (a and b) Microstructure of sulfoaluminate cement clinker with jarosite–alunite precipitate.

Table 8  
Results of setting time and expansibility

	Sample	
	(SAC) <sub>Ref</sub>	(SAC) <sub>J/Ar</sub>
Initial time (min)	60	55
Final time (min)	105	95
Water of normal consistency (%)	25.6	26.7
Expansion (mm) (Le Chatelier)	1.3	1.1

phase, was observed in a very fine crystal form and dispersed in the ferrite and sulfoaluminate phases. The second significant phase in these clinkers was the phase of  $C_4A_3\bar{S}$ , which could be easily distinguished from the others. No  $C_3A$  was observed, indicating that  $C_4A_3\bar{S}$  had not been decomposed at the final sintering temperature of 1300 °C. The phase of  $CaSO_4$  was entrapped in the sulfoaluminate phase. In the case of (SAC)<sub>J/Ar</sub> the addition of jarosite–alunite precipitate by 11.31%, resulted in higher proportion of  $C_4AF$  phase, a fact that was attributed to the higher content of iron oxide in the jarosite–alunite precipitate.

The water requirement and setting time, determined by Vicat probe and Vicat needle apparatus, as well as the results of expansion are reported in Table 8. The obtained values showed that the use of jarosite–alunite precipitate in the raw meal only slightly affected the water content for standard consistency and the setting times. The expansion measured, according to the Le Chatelier process, was well below the maximum accepted value of 10 mm [16].

The mortars of the samples under investigation were tested for compressive strengths after 2, 7, 28 and 90 days of curing. The obtained results are shown in Fig. 6. The mortar, which contained the (SAC)<sub>J/Ar</sub> clinker, showed similar compressive strengths with the (SAC)<sub>Ref</sub>. This fact confirms the probabili-

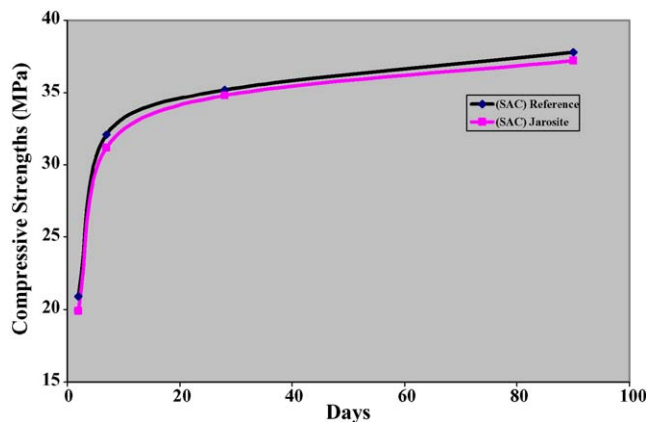


Fig. 6. Compressive strengths of the sulfoaluminate cements produced.

ty of jarosite–alunite utilization in the raw meal for the cement production.

The XRD patterns of the (SAC)<sub>Ref</sub> and (SAC)<sub>J/Ar</sub> samples, hydrated at 2, 7, 28 and 90 days, are presented in Figs. 7 and 8, respectively. In both cases, after 2 days of hydration the sulfoaluminate phase has been extensively hydrated. The  $CaSO_4$  phase also seems to be slightly reduced as having been consumed in hydration. The hydration of the above compounds results in the formation of ettringite. After 2 days, in both cases, the peak of  $C_2S$  indicates that the hydration of this phase has not yet started. After 7 days of hydration  $C_4A_3\bar{S}$  has been completely hydrated, while the hydration of  $C_2S$  seems to have commenced, in both samples. The peak of the ferrite phase, at 28 days, was significantly reduced, indicating an almost complete hydration of this phase. At 28 days the hydration of the belite phase still proceeds with relative slow rate. The small amount of  $Ca(OH)_2$  formed by this process seems to form (in combination with  $CaSO_4$  and  $C_4A_3H_6$ ) ettringite, as its peak still increases. The higher peaks

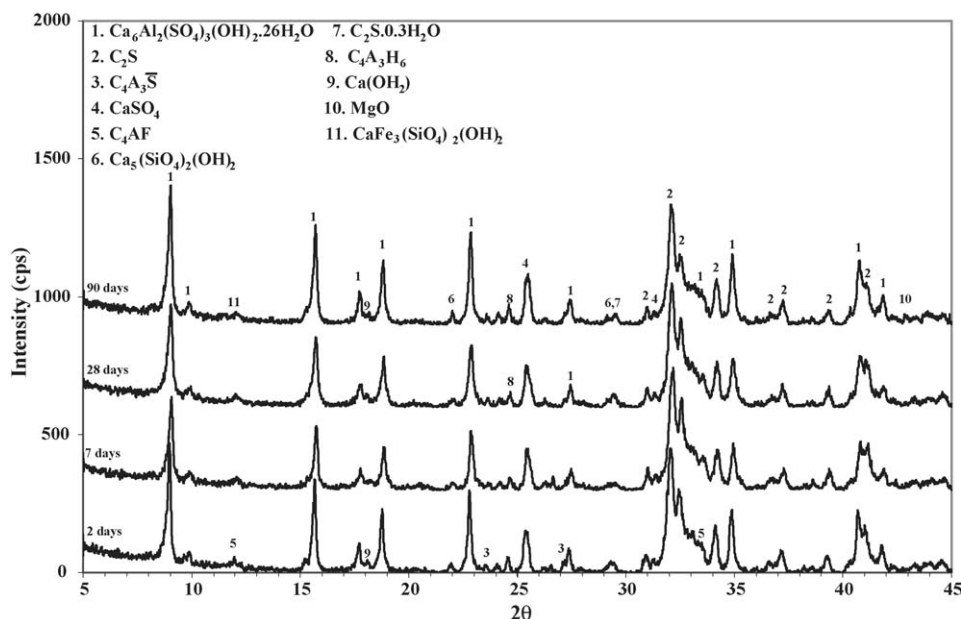


Fig. 7. X-ray diffraction of (SAC)<sub>Ref</sub> pastes at 2, 7, 28 and 90 days.

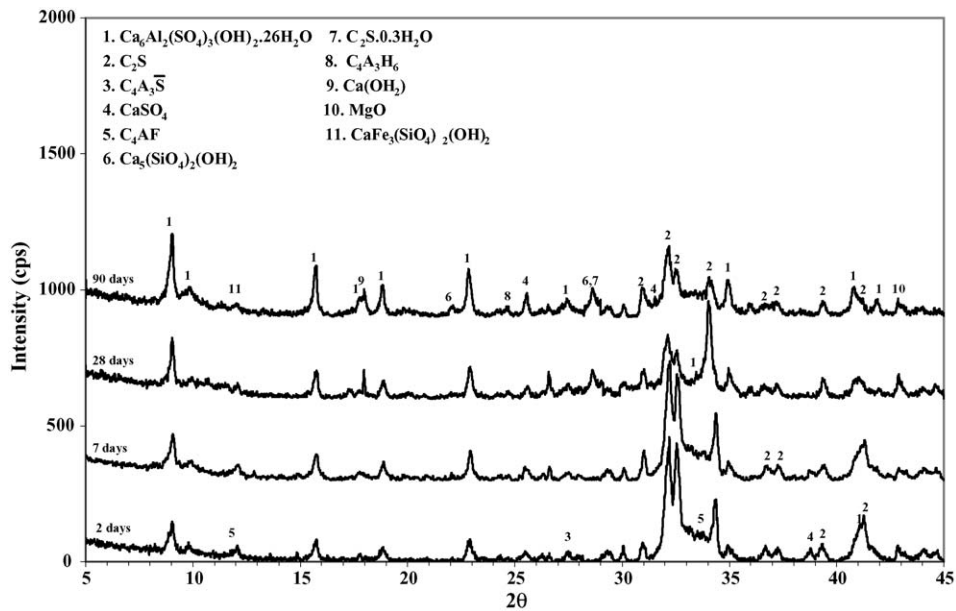


Fig. 8. X-ray diffraction of (SAC)<sub>J/A</sub> pastes at 2, 7, 28 and 90 days.

of  $\text{Ca}(\text{OH})_2$ , in the case of (SAC)<sub>J/A</sub>, indicates a higher hydration rate than the (SAC)<sub>Ref</sub> sample, especially at the ages of 28 and 90 days. Finally, at 90 days of hydration the increase of the ettringite peak was attributed as above.

#### 4. Conclusions

The addition of jarosite–alunite precipitate by 11.31% in the raw meal did not affect either the sintering or the hydration process during sulfoaluminate cement production. More specifically, the sample with jarosite–alunite presented the following characteristics:

- $\text{C}_2\text{S}$  was the main phase and was observed in very fine crystal form and dispersed in the ferrite and sulfoaluminate phases.
- $\text{C}_4\text{A}_3\bar{\text{S}}$  was not decomposed at the final sintering temperature of  $1300^\circ\text{C}$ , a fact that was confirmed by the absence of  $\text{C}_3\text{A}$ . The phase of  $\text{CaSO}_4$  was entrapped in the sulfoaluminate phase.
- The higher proportion of  $\text{C}_4\text{AF}$  phase was attributed to the higher content of iron oxide in the jarosite–alunite precipitate.
- The values for setting times, water content for standard consistency and expansion were similar to those obtained with the reference sulfoaluminate cement sample.
- The compressive strengths were at least as high as those of the reference sample during hydration.

It is thus concluded that the jarosite–alunite residue, produced during hydrometallurgical treatment of nickel oxide ores with sulfuric acid, can be utilized as a raw material in cement production, at no cost to the producer, contributing, in this way, to reduction of the process cost.

#### Acknowledgements

The authors are grateful to the General Secretariat for Research and Technology of Greece for financial support in the framework of the Program “Industrial Exploitation of the Solid Wastes Produced from Hydrometallurgical Treatment of Greek Laterites – PENED 99”. They also express their warmest thanks to Mr. J. Marinou, Director in Quality Assurance and R&D Manager of Hercules Cement Company of Greece, for his constant advice.

#### References

- [1] S. Agatzini-Leonardou, D. Dimaki, Recovery of nickel and cobalt from low-grade nickel oxide ores by heap leaching with dilute sulfuric acid at room temperature, Greek Patent 910,100,234 (1991).
- [2] S. Agatzini-Leonardou, D. Dimaki, Method for extraction of nickel and/or cobalt from nickel and/or cobalt oxide ores by heap leaching with a dilute sulfuric acid solution, prepared from sea water, at ambient temperature, Greek Patent 1,003,569 (2000).
- [3] S. Agatzini-Leonardou, P. Oustadakis, J. Zafiratos, Removal of aluminum and chromium from nickel–cobalt sulfate solutions, Greek Patent 1,003,419 (1999).
- [4] U.S. E.P.A., Method 1311, Toxicity characteristic leaching procedure, Test methods for evaluating solid wastes physical/chemical methods, United States Environmental Protection Agency, 1994.
- [5] F.M. Lea, The Chemistry of Cement, third ed., Edward Arnold Publishers, 1970.
- [6] M. Singh, S.N. Upadhyay, P.M. Prasad, Preparation of iron rich cements using red mud, Cement Concrete Res. 27 (1997) 1037–1046.
- [7] R. Taha, A. Al-Rawas, K. Al-Jabri, A. Al-Harthy, H. Hassan, S. Al-Oraimi, An overview of waste materials recycling in the Sultanate of Oman, Resour. Conserv. Rec. 41 (2004) 293–306.
- [8] P.K. Mehta, Investigation on energy saving cement, World Cement Technol. 11 (1991) 166–177.
- [9] M. Ali, S. Gopal, S.K. Handoo, Studies on the formation kinetics of calcium sulfo-aluminate, Cement Concrete Res. 24 (1994) 715–720.

- [10] J.H. Sharp, C.D. Lawrence, R. Yang, Calcium sulfoaluminate cements—low-energy cements, special cements or what? *Adv. Cement Res.* 11 (1999) 3–13.
- [11] J. Beretka, B. de Vito, L. Santoro, N. Sherman, G.L. Valenti, Hydraulic behavior of calcium sulfoaluminate-based cements derived from industrial process wastes, *Cement Concrete Res.* 23 (1993) 1205–1214.
- [12] J. Majling, S. Sahu, M. Vlana, D.M. Roy, Relationship between raw mixture and mineralogical composition of sulphoaluminate belite clinkers in the system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SO}_3$ , *Cement Concrete Res.* 23 (1993) 1351–1356.
- [13] P. Arjunan, M.R. Silsbee, D.M. Roy, Sulfoaluminate-belite cement from low-calcium fly ash and sulfur-rich and other industrial by-products, *Cement Concrete Res.* 29 (1999) 1305–1311.
- [14] V. Kasselouri, P. Tsakiridis, C. Malami, B. Georgali, C. Alexandridou, A study on the hydration products of a non-expansive sulfoaluminate cement, *Cement Concrete Res.* 25 (1995) 1726–1736.
- [15] EN 196-1, Methods of testing cement—determination of compressive strength (1994).
- [16] EN 196-3, Methods of testing cement—determination of setting time and soundness (1994).