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

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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 Portland cement clinker. For that reason, two samples of raw meals were prepared, one with ordinary raw materials, as a reference sample ($(PC)_{Ref}$) and another with 1% jarosite–alunite precipitate ($(PC)_{J/A}$). Both raw meals were sintered at 1450 °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 Portland cement clinker. 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.

Keywords: Portland 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, aluminium and chromium of the jarosite–alunite types. The jarosite–alunite group of isostructural minerals is described by the general formula $M(Fe_xAl_yCr_z)(SO_4)_2(OH)_6$, in which M may be Na^+, K^+, NH_4^+ or H_3O^+ and $x+y+z=3$. For $x=3$, the formula represents jarosite, whereas for $y=3$ it represents alunite. The above precipitate is produced at some stage of a new hydrometallurgical process, 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 [1–3].

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

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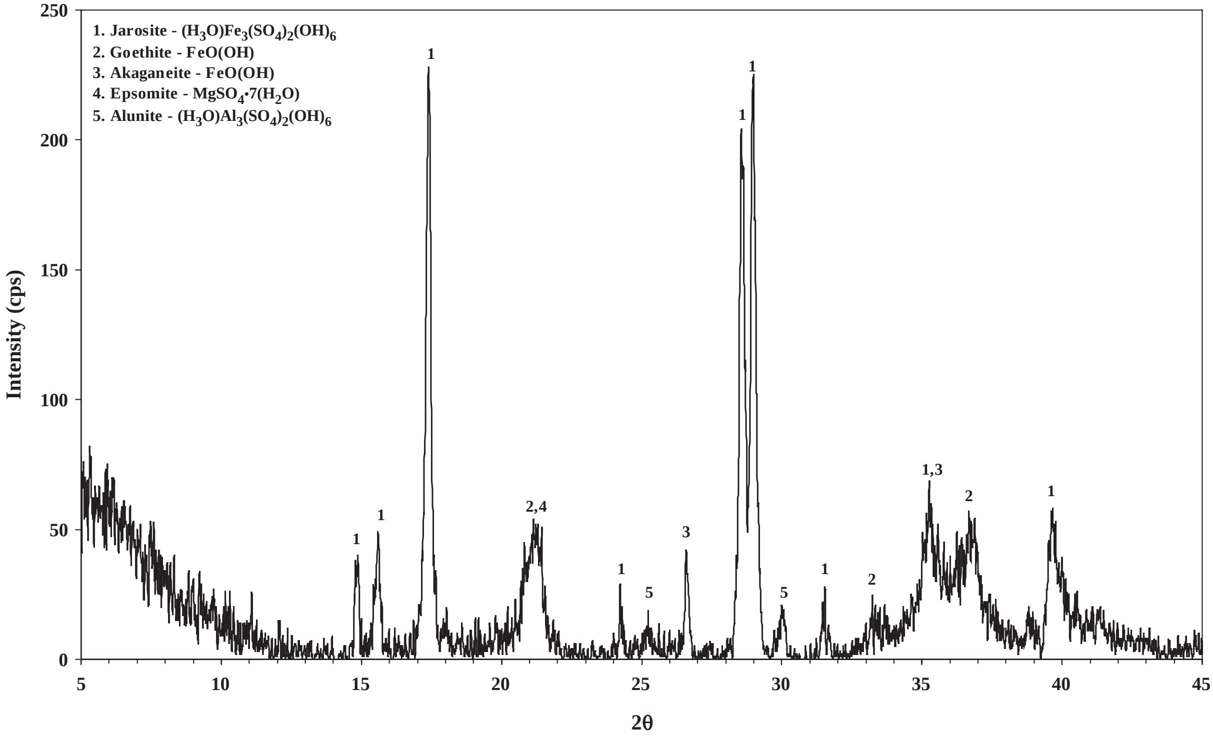


Fig. 1. Mineralogical phases of jarosite–alunite precipitate.

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 [5–8]. 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 Portland cement. 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 a typical Portland cement clinker. For that reason, two samples of raw meals were prepared, one with ordinary raw materials, as a reference sample ($(PC)_{Ref}$), and another with 1% jarosite–alunite precipitate ($(PC)_{J/A}$). The produced clinkers were analyzed chemically and mineralogically by XRD and optical microscopy. The clinkers were then mixed with gypsum and 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.

Table 1
Chemical analysis of raw materials for the production of Portland cement clinkers

Oxides	Content of raw materials (%)			
	Limestone	Schist	Bauxite	Jarosite–alunite precipitate
SiO_2	0.09	55.56	4.81	1.20
Al_2O_3	0.04	9.66	46.96	16.55
Fe_2O_3	–	7.12	33.34	39.66
CaO	55.44	5.75	0.33	–
MgO	0.17	9.55	0.36	–
K_2O	0.02	1.04	0.25	–
Na_2O	0.02	1.32	0.05	–
LOI	43.79	8.89	10.26	20.00
SO_3	–	–	–	17.34
TiO_2	–	0.52	2.38	–
Cr_2O_3	–	0.21	0.41	1.36
NiO	–	–	–	0.95
CoO	–	–	–	0.05

2. Experimental

The mineralogical phases of the precipitate used, which were determined by XRD analysis, are shown in Fig. 1. This precipitate was mixed with other raw materials, such as limestone, schist and bauxite, in appropriate proportions in order to produce the raw meal to be tested for the production of Portland cement clinker ($(PC)_{J/A}$). A reference raw meal

Table 2
Composition of the raw meals for the production of Portland cement clinkers

Raw meals	Raw meals composition (%)			
	% Limestone	% Schist	% Bauxite	% Jarosite–alunite precipitate
$(PC)_{Ref}$	73.50	24.91	1.59	–
$(PC)_{J/A}$	73.03	24.97	1.00	1.00

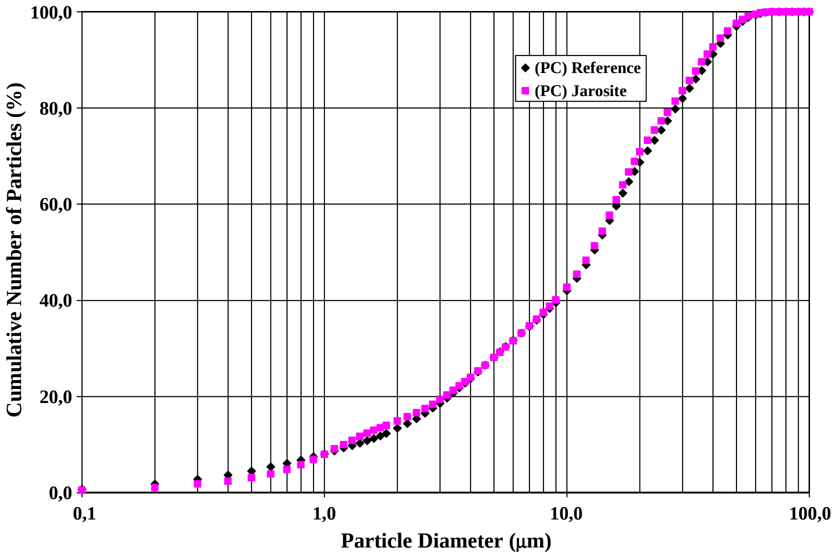


Fig. 2. Particle size distributions of cement samples by a laser scattering analyzer.

($(PC)_{Ref}$), without jarosite–alunite precipitate, was also synthesized for reasons of comparison. The chemical analyses of the raw materials used are given in Table 1. Based on those, and by using a computational software program, the proportion of raw materials was derived and is presented in Table 2.

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 a furnace at 500 °C, the temperature was increased to 1000 °C, at which the samples remained for 20 min, and, finally, the temperature was further increased to 1450 °C. The samples were sintered for 50 min. 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. The clinkers produced were analyzed by chemical analysis, X-Ray Diffraction and optical microscopy.

The clinkers were crushed and ground in a Bond ball mill to a specific surface area of about 3950 cm^2/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 dispersion unit for 60 s.

The water soluble SO_3 content in the clinkers was measured and the ground clinkers were mixed with industrial $CaSO_4 \cdot 2H_2O$, so that the produced laboratory cements contained about 3% total soluble SO_3.

Compressive strength measurements were conducted at the ages of 2, 7, 28 and 90 days on mortar prisms (dimensions 40 × 40 × 160 mm), prepared and tested in accordance with European Standard EN 196-1 [9]. The normal consistency and setting times of cement pastes were determined using a

Table 3
Results of grindability tests

Number of sample	$(PC)_{Ref}$	$(PC)_{J/A}$
Mill revolutions	4200	4150
Specific surface (Blaine-cm^2/gr)	3940	3950
Grindability index	0.94	0.95
Specific gravity (g/cm^2)	3.15	3.17
% SO_3	2.75	2.58

Table 4
Chemical analysis of the Portland cement clinkers

Oxides	Content of the produced cement clinkers (%)	
	$(PC)_{Ref}$	$(PC)_{J/A}$
SiO_2	21.36	22.58
Al_2O_3	4.86	4.08
Fe_2O_3	3.51	4.13
CaO	63.17	62.57
MgO	3.97	3.95
K_2O	0.22	0.19
Na_2O	0.17	0.15
SO_3	0.038	0.052
TiO_2	0.2	0.22
CaO_f	1.51	0.85
NiO	–	0.02
CoO	–	0.01
Cr_2O_3	0.1	0.12
LOI	0.32	0.42

Table 5
Mineralogical composition of the produced Portland cement clinkers

Mineralogical phases	Cement clinkers composition (%)	
	$(PC)_{Ref}$	$(PC)_{J/A}$
C_3S	48.91	49.6
C_2S	24.43	27.3
C_3A	6.95	3.8
C_4AF	10.67	12.5

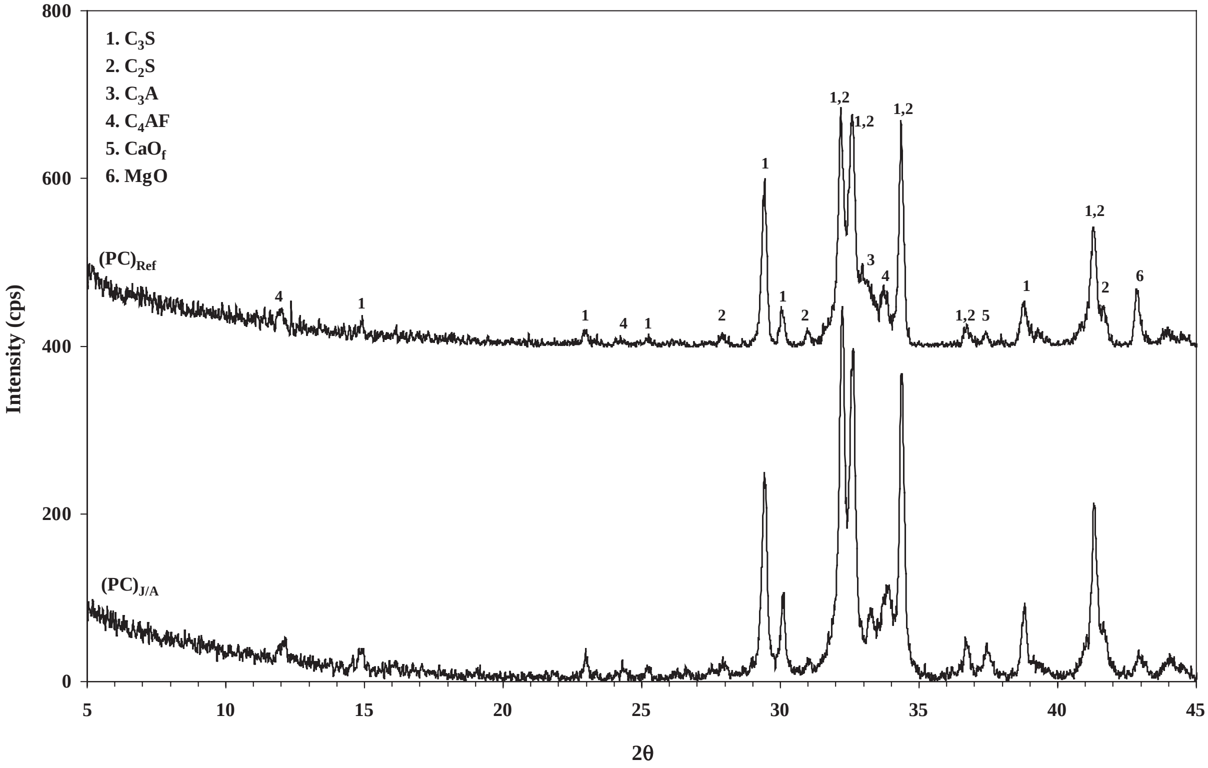


Fig. 3. X-ray diffraction of Portland cement clinkers with and without jarosite–alunite precipitate.

Vicat apparatus according to the European Standard EN 196-3 [10]. Expansions of the cement pastes were determined by Le Chatelier method.

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

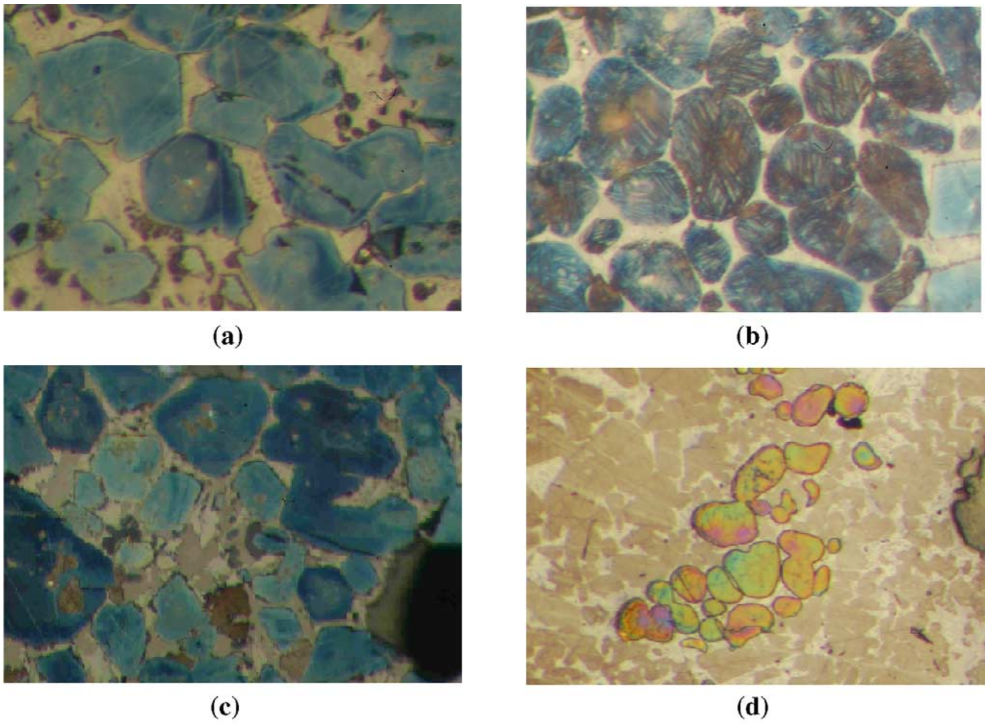
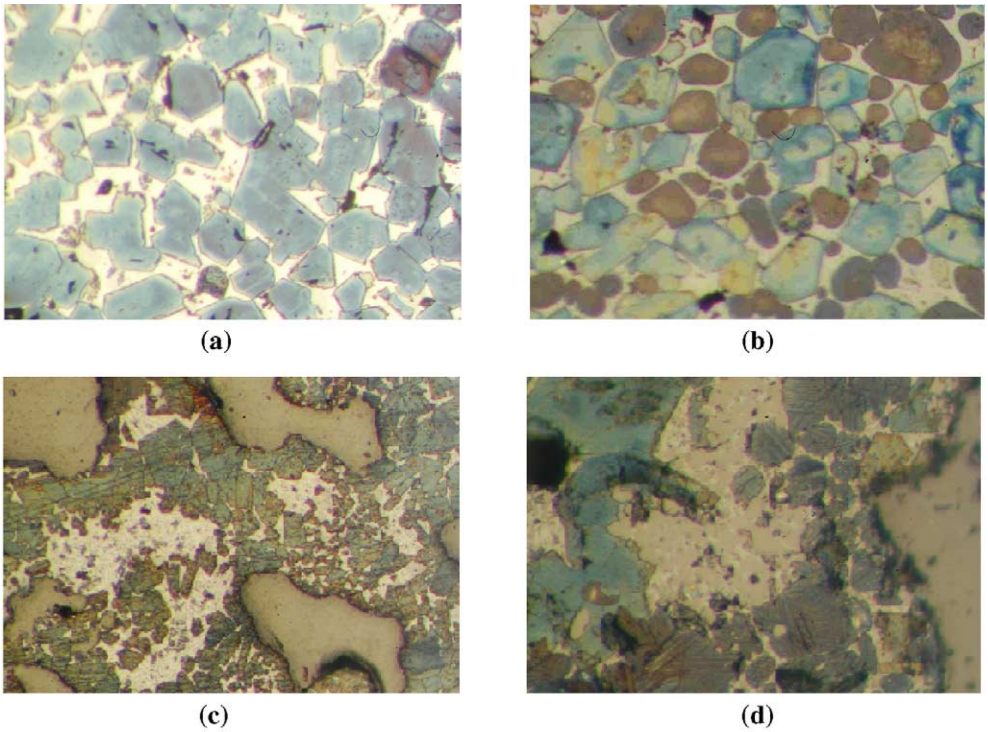

(a) (b) (c) (d)

Fig. 4. Microstructure of Portland cement clinker without jarosite–alunite precipitate. (a) Well formed alite crystals (× 500). (b) Cluster C_2S (× 500). (c) Large crystals of C_3A (× 500). (d) Small clusters of CaO_f (× 200).



(a) (b) (c) (d)

Fig. 5. Microstructure of Portland cement clinker with jarosite–alunite precipitate. (a) Well formed alite crystals (× 500). (b) Crystals C_2S scattering among alite (× 500). (c) High percentage of C_4AF (× 500). (d) MgO cluster detection (× 500).

temperature 20 ± 2 °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 3. Both cement samples gave similar results.

The chemical analysis and the potential mineral composition of the Portland clinkers produced are given in Tables 4 and 5, respectively. As the tables show, the addition of the jarosite–alunite precipitate by 1% did not seem to affect its chemical and mineralogical composition.

The XRD analyses of the produced Portland clinkers are given in Fig. 3. As can be seen, the addition of the 1% jarosite–alunite precipitate did not affect the mineralogical composition of the produced clinkers. In both clinker types, the main mineralogical phases, C_3S, C_2S, C_3A and C_4AF, were well formed. The $(PC)_{Ref}$ clinker contained more C_3A and less C_4AF than the $(PC)_{J/A}$ clinker. These differences were attributed to the partial replacement of bauxite with jarosite–alunite, which is higher in iron and lower in aluminum than the former. CaO_f was relatively higher in the reference synthesis, probably due to its higher content of CaO. Finally, the alite phase (C_3S) in both cases has the monoclinic form.

The microstructure of the Portland cement clinkers was examined by optical microscopy in polished sections. The addition of the jarosite–alunite precipitate by 1% 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, especially in the $(PC)_{J/A}$ synthesis. Both clinkers contained more or less euhedral alite, and they exhibited coalescence of alite crystals. In the case of $(PC)_{J/A}$, the alite crystals appeared well-formed, with size 35 μm. On the other hand, the size of C_3S, in the case of $(PC)_{Ref}$, was about 40 μm. In the optical microscope, belite was observed as bluish or brownish rounded crystals, rich in lamellas. No differences in the microstructure of belite between $(PC)_{Ref}$ and $(PC)_{J/A}$ clinkers were detected. In the reference clinker, the belite crystals existed mainly in nests and appeared as clusters. In the $(PC)_{J/A}$ clinker, belite crystals were few and evenly distributed in relation to alite, indicating that the clinkering reaction had proceeded extensively in the direction of alite and that the raw mix was much more homogenous. Finally, in the $(PC)_{J/A}$ clinker, the liquid phase occurred as uniformly

Table 6
Results of setting time and expansibility

Sample	$(PC)_{Ref}$	$(PC)_{J/A}$
Initial time (min)	145	160
Final time (min)	225	200
Water of normal consistency (%)	23.2	24.8
Expansion (mm) (Le Chatelier)	1.5	1.0

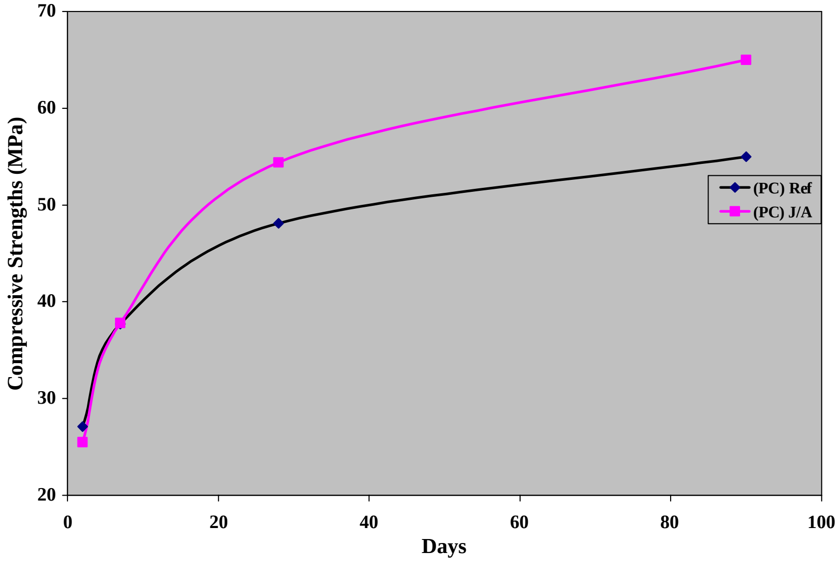


Fig. 6. Compressive strengths of the cements produced.

distributed fine crystals, whereas, in the case of $(PC)_{Ref}$, large crystals of C_3A were observed.

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 6. 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 [10].

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 $(PC)_{J/A}$ clinker, showed higher com-

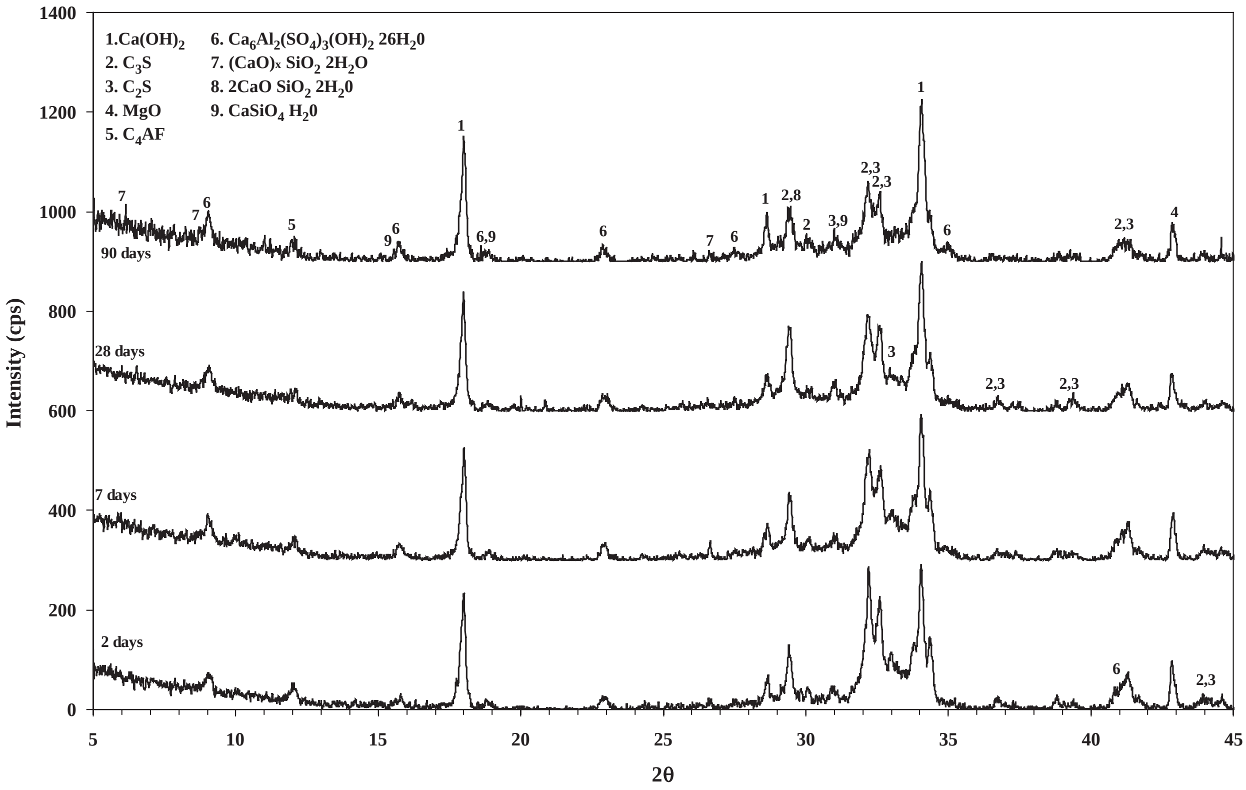


Fig. 7. X-ray diffraction of $(PC)_{Ref}$ pastes at 2, 7, 28 and 90 days.

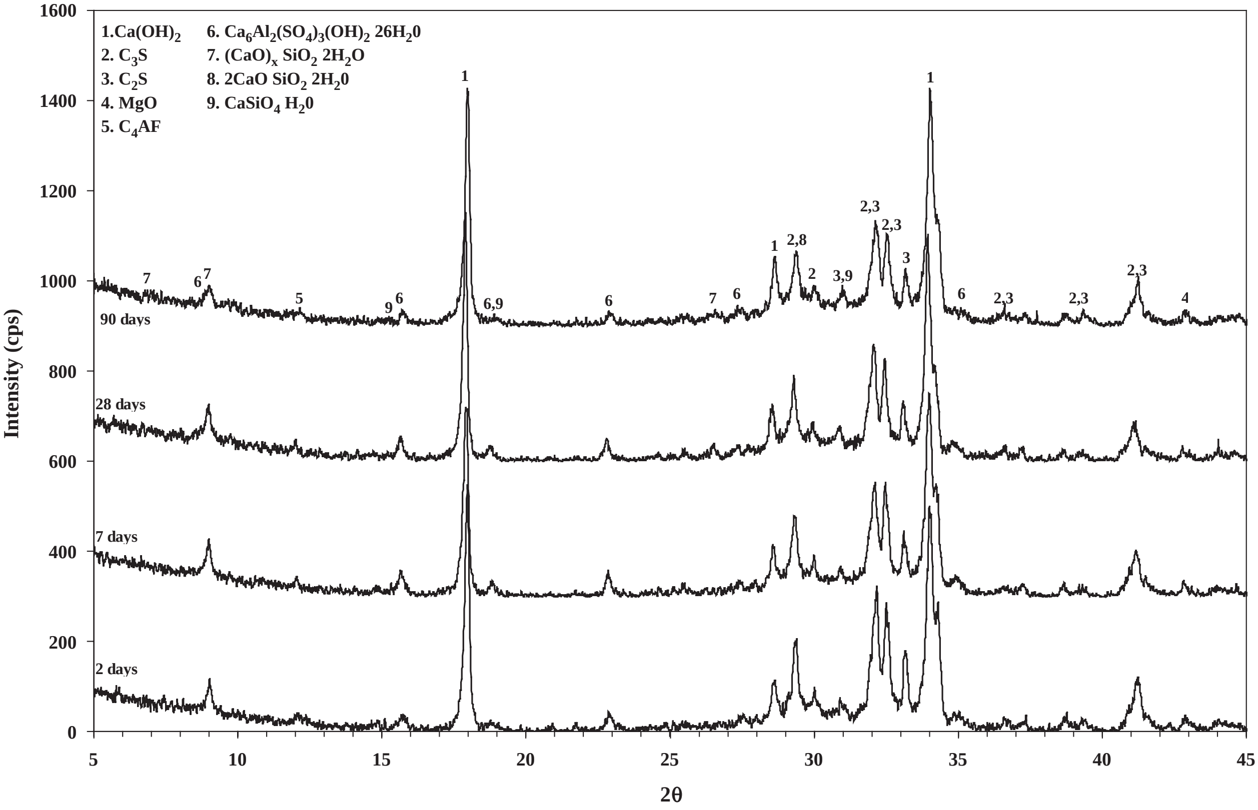


Fig. 8. X-ray diffraction of $(PC)_{J/A}$ pastes at 2, 7, 28 and 90 days.

pressive strengths than the $(PC)_{Ref}$, especially at the ages of 28 and 90 days, a fact that was attributed to the higher content of C_2S and C_3S in the $(PC)_{J/A}$ clinker.

The XRD patterns of the $(PC)_{Ref}$ and $(PC)_{J/A}$ samples, hydrated at 2, 7, 28 and 90 days, are presented in Figs. 7 and 8, respectively. In both cases the diffraction peaks of ettringite, CSH, and $Ca(OH)_2$ crystallized phases appeared in all samples obtained during hydration. The peaks of C_3S and C_2S phases diminish, especially at the age of 90 days. The higher peaks of $Ca(OH)_2$, in the case of $(PC)_{J/A}$, indicate a higher hydration rate than the $(PC)_{Ref}$ sample at the ages of 2 and 7 days. Following the hydration progress through the peaks of $Ca(OH)_2$ at the ages of 28 and 90 days, it was possible to observe a higher intensity of these peaks in the case of $(PC)_{J/A}$.

4. Conclusions

The addition of jarosite–alunite precipitate by 1% in the raw meal did not affect either the sintering or the hydration process during Portland cement production. More specifically, the sample with jarosite–alunite presented the following characteristics:

- ➢ The alite phase occurred as small well-formed crystals.
- ➢ The belite crystals were few and evenly distributed in relation to alite, indicating that the clinkering reaction had proceeded extensively in the direction of alite and that the raw mix was homogenous.
- ➢ The liquid phase occurred as fine crystals, uniformly distributed.
- ➢ The values for setting times and water content for standard consistency and expansion were similar to those obtained from the reference ordinary Portland cement sample and within the standard limits.
- ➢ 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 sulphuric acid, can be utilized as a raw material in cement production.

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