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Use of jarosite/alunite precipitate as a substitute for gypsum in Portland cement

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Abstract

The possibility of replacing the natural gypsum, used in cement production, by a jarosite/alunite chemical precipitate was investigated. This precipitate is a by-product of a new hydrometallurgical process, which was developed in order to treat economically low-grade nickel oxide ores. For this purpose, nine mixtures were produced by substituting gypsum, from 0% to 100%, by the jarosite/alunite precipitate. All samples were tested by determining the setting time, compressive strength, grindability and content of water soluble chromium. Furthermore, XRD analysis was used to determine the hydration products after 2, 7, 28 and 90 days. The jarosite/alunite precipitate was produced from a real laterite heap leach liquor by precipitation at atmospheric pressure, during a series of six runs. More specifically, iron and aluminum were precipitated at 95 °C. That was accomplished by gradually raising the initial pH of the leach liquor to an equilibrium pH value of 3.5, at such a rate as to keep supersaturation of iron and aluminum below a critical value.

Keywords: Cement; Gypsum; Jarosite/alunite; By-product; Hydration

1. Introduction

The general trend of today for the industrial wastes or by-products, which are produced in industrial countries, is to develop alternative ways for their exploitation in order to eliminate the cost of disposal and avoid soil and water contamination. Many of these undesirable industrial materials contain significant amounts of inorganic ingredients that can be used in the production of Portland cement clinker.

The Laboratory of Metallurgy of the National Technical University of Athens has developed a new integrated hydrometallurgical method, suitable to treat, efficiently and economically, low-grade nickel oxide ores. It involves heap leaching of the ore by dilute sulphuric acid at ambient temperature, purification of the leach liquors and recovery of nickel and cobalt [1–3].

In the framework of the above method, a new process of leach liquors purification was invented relating to the removal of iron, aluminum and chromium, as existing methods were not satisfactory. This process relates to the precipitation of the above metals as crystalline, easily filterable chemical precipitates of the jarosite/alunite type, at atmospheric pressure [4,5]. The precipitation occurs according to the following hydrolysis reaction [6–9]:

$$2[Fe_2(SO_4)_3]_{(aq)} + [Al_2(SO_4)_3]_{(aq)} + M_2SO_4 + 12H_2O \rightarrow 2M[Fe_2Al(SO_4)_2(OH)_6]_{(s)} + 6H_2SO_4$$

The idea of substituting natural gypsum by the jarosite/alunite precipitate in order to produce Portland cement was based on the high sulphate content of the mineralogical phases and the need to find an industrial use for this by-product. Besides, it is assessed that the

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cost of using the jarosite/alunite precipitate would be lower than that of quarrying, grinding, and transporting of natural gypsum [10].

Replacement of natural gypsum by non-calcium sulphate salts was investigated by Bombled [11], who found out that the non-calcium cations affected the rheological properties of cements pastes. More specifically, the sulphates of zinc, iron, potassium and sodium decreased both the plasticity and the setting time of the cement pastes. It has also been found [12,13] that the presence of Cr^{3+} retards the setting time.

Another important factor that should probably be taken into account is the SO_3 content. It is known that there is an optimum SO_3 content [12,14], yielding the highest strength. This optimum value normally increases with age and may very well extend beyond the SO_3 limits set by the standard specifications. The optimum amount at early ages is closely related to the amount of SO_3 necessary for proper retardation so it will be influenced by the same factors, that is, the amount and reactivity of C_3A, the quantity of soluble alkalies, the cement fineness and the reactivity of the SO_3 bearing compositions. Proper SO_3 optimization is usually worthwhile as a deviation of 1% SO_3 from the optimum value (or range) can result in a decrease in strength by 5 MPa or more, at 28 days, according to the EN 196-1 test procedure. In addition, the effect of Cr^{3+} (which is present in jarosite/alunite precipitate) improves the crystal growth of ettringite but reduces the strength of hardened ettringite [12,13].

In the present work a series of runs was conducted to produce the jarosite/alunite precipitate from a real laterite heap leach liquor by precipitation, at atmospheric pressure, to be used as a substitute of gypsum in cement production. Nine different mixtures were produced by substituting gypsum from 0% to 100% with the above precipitate. All mixtures were tested for setting time, compressive strength, grindability and water-soluble chromium, in order to determine optimum percentage of substitution.

2. Experimental

Six (6) runs were conducted to produce the jarosite/alunite precipitate, according to the method which was 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 [4]. 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 (4 l), 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 avoid the production of an amorphous precipitate. The parameters of the runs were: temperature 95 °C, equilibrium $pH = 3.5$, addition of jarosite precipitate as seed material (20 g/l), reaction $time = 12$ h.

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.

During the first two runs, the neutralizing agent used was magnesium carbonate (industrial grade) in the form of a slurry with water (100 g/l). However, it exhibited slow reactivity and, consequently, high reaction times and consumption were induced. For this reason, magnesium carbonate was replaced by a slurry of magnesium oxide (100 g/l) in the next runs.

Nine (9) different mixtures were produced, with 95% clinker content, by replacing gypsum, from 0% to 100%, with jarosite/alunite precipitate and the grindability index of each mixture was determined (as the ratio of specific surface to mill revolution). Furthermore, all samples were analyzed for water soluble Cr^{6+} by treating the solid cement with water ($w/c = 10$), at ambient temperature, for 15 min. Liquors samples were subsequently reacted with diphenylcarbizide in acid solution to produce a pink color. The absorbance of the solution was then measured at a wavelength of 540 nm by a spectrophotometer [15]. The setting times of cement samples were determined using the European Standard EN 196-3 [16]. Compressive strengths at 2, 7 and 28 days were also measured according to EN 196-1 [17].

Finally, the cement paste samples, which had been prepared by mixing 300 g of ground mixtures with 75 ml of water, were examined by XRD analysis. These pastes were left to cure for 2, 7, 28 and 90 days.

3. Results and discussion

The chemical analysis of the feed solution used for the production of the jarosite/alunite precipitate is shown in Table 1. All jarosite/alunite precipitates settled down quickly and were easily filtered. They were determined as jarosites/alunites by XRD analysis, as can be seen in Fig. 1. Their chemical analyses are shown in Table 2.

Table 1
Chemical analysis of the feed solution

Element	Concentration (g/l)
Fe	21.8
Ni	5.3
Co	0.3
Al	9.3
Cr	0.8
Mn	0.9
Mg	7.6

The corresponding results of the iron, aluminum and chromium simultaneous precipitation are shown in Table 3. Iron and aluminum precipitation reached 99% and 96%, respectively. The consumption of neutralizing agents for the six runs ranged from 40 to 50 g/l leach solution, for the MgO, and 60–75 g/l leach solution, for the $MgCO_3$. The precipitate production was approximately 65 g/l leach solution.

The chemical analyses of the jarosite/alunite precipitate, produced by mixing of the produced precipitates, clinker and gypsum are given in Table 4. The mineralogical composition of the clinker, as well as the composition of the nine mixtures produced, are shown in Tables 5 and 6, respectively.

Grindability index of each sample was determined and is presented in Table 7. The grindability index reaches its maximum values when 75% and 100% of gypsum is substituted by the jarosite/alunite. The precipitate, which is an easily grindable material, results in an increase of the grindability index of the mixtures produced.

The samples were analyzed for water soluble Cr^{6+} and the corresponding values are, also, given in Table 7. The water-soluble chromium (Cr^{6+}) appeared to decrease as the quantity of gypsum, replaced by the jarosite/alunite precipitate, increased. As can be shown in Table 7, the reference mixture, that had been produced by 95% clinker and 5% gypsum (sample 1), presented a Cr^{6+} value of 75 ppm, as the result of Cr^{3+} oxidation, contained in the raw meal, under the oxidizing conditions in the rotary kiln. On the contrary, the Cr^{6+} value of sample 9, produced by total replacement of gypsum with jarosite/alunite, was determined at 14 ppm. This

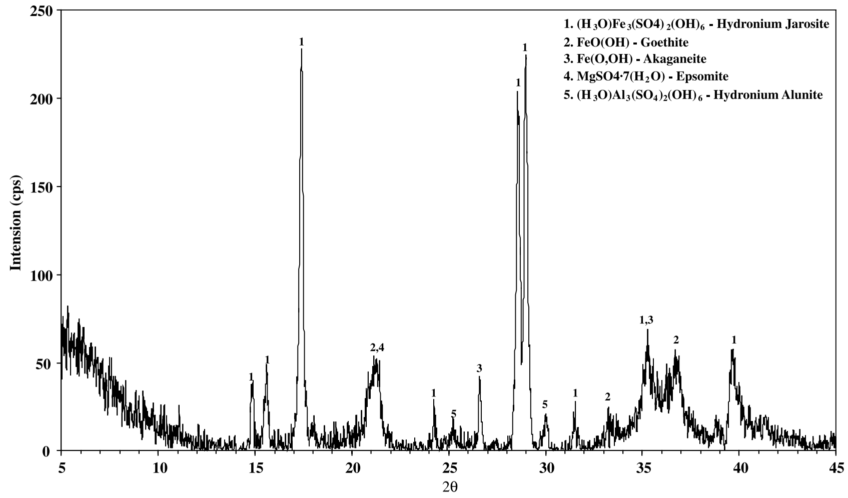

Fig. 1. Mineralogical phases of jarosite/alunite precipitate.

Table 2
Chemical analyses of the precipitates produced

Element	Content (%)					
	Run no.					
	1	2	3	4	5	6
Fe	27.76	29.12	24.80	26.40	27.91	25.82
Ni	0.45	0.41	0.84	0.76	0.62	0.46
Co	0.03	0.03	0.04	0.04	0.03	0.04
Mg	0.31	0.29	0.28	0.25	0.32	0.29
Mn	0.03	0.03	0.02	0.03	0.02	0.02
Al	8.76	9.03	10.21	11.01	10.31	9.89
Cr	0.91	0.92	0.97	0.94	0.90	0.92
SO_4^{-2}	20.80	19.42	22.68	20.50	21.40	20.35

Table 3
Metals precipitated and nickel–cobalt losses

Run no.	% Fe precipitated	% Al precipitated	% Cr precipitated	% Ni loss	% Co loss
1	98.95	95.10	90.62	5.28	9.30
2	99.25	95.77	91.80	5.09	8.80
3	97.42	94.70	88.30	8.32	9.80
4	97.15	93.86	89.52	7.85	9.34
5	99.20	96.42	92.60	6.44	7.81
6	98.85	95.60	90.97	5.54	8.50

Table 4
Chemical analysis of clinker, gypsum and jarosite/alunite precipitate

Oxides	Content of raw materials (%)		
	Clinker	Gypsum	Jarosite–alunite precipitate
SiO_2	22.23	–	1.20
Al_2O_3	5.27	–	18.55
Fe_2O_3	3.65	–	39.66
CaO	65.06	34.30	–
MgO	1.31	–	0.46
MnO	–	–	0.04
K_2O	0.78	–	–
Na_2O	0.65	–	–
CaO_f	0.53	–	–
LOI	0.26	20.85	20.00
SO_3	0.66	44.98	17.34
TiO_2	–	–	–
Cr_2O_3	0.96	–	1.36
CoO	–	–	0.05

Table 5
Mineralogical composition of clinker

Mineralogical phases	% Composition
C_3S	51
C_2S	25
C_3A	7.8
C_4AF	11
LSF	91

decrease of Cr^{6+} value could probably be attributed to the presence of Mn^{2+}, in the jarosite/alunite precipitate, which reduces Cr^{6+} to Cr^{3+}, while it is oxidized to Mn^{4+}.

The setting times of the cement mixtures, determined by the European Standard EN 196, are given in Table 8. As can be shown, the increase of the jarosite/alunite substitution in the cement mixtures results in lower setting times. This can be attributed to the decrease of the water soluble SO_3, present in jarosite/alunite precipitate compared to the natural gypsum. Furthermore, as was mentioned before, the presence of Fe^{3+} and Cr^{3+} ions in the jarosite/alunite precipitate instead of Ca^{2+} in the natural gypsum, can lead to a higher decrease in plasticity and shortening of setting time. This decrease reached its highest levels at 75% and 100% of gypsum replacement, where the "flash set" phenomenon was observed because of lack of sufficient Ca^{2+} and SO_4^{2-} ions. Consequently, it was impossible to control initial hydration of the aluminate phase (C_3A).

The compressive strengths at 2, 7 and 28 days, as well as the % SO_3 content, were also determined and the results are given in Table 9. At the age of 2 days, there is a slight decrease in the strength value, while at the age of 7 days the changes are not significant, in comparison with the reference mixture (sample 1: 95% clinker and 5% gypsum). However, in the case of 25% and 50% replacement, at the age of 28 days, a decrease, ranging from 4 to 6 MPa, was acknowledged. Moreover, at the replacement levels of 75% and 100%, the rate of the hydration reaction appeared to be decreasing, resulting in lower compressive strengths (39.26 and 31.4 MPa, respectively). The retarding of the compressive strength could be attributed to the shortening of setting time because of the decrease in water soluble SO_3 and the increase of Cr^{3+} in the mixtures with jarosite/alunite.

Finally, the cement paste samples, which had been prepared by mixing 300 g of ground mixtures with 75 ml of water, were examined by XRD analysis. The pastes were left to cure for 2, 7, 28 and 90 days. The XRD of the mixture with no jarosite/alunite, as well as the mixture with 20% replacement, are given in Figs. 2 and 3, respectively. The XRD analyses of the above samples suggested that the clinkers with no jarosite/alunite

Table 6
Composition of samples

Number of sample	1	2	3	4	5	6	7	8	9
% Clinker	95.00	95.00	95.00	95.00	95.00	95.00	95.00	95.00	95.00
% Gypsum	5.00	4.75	4.50	4.25	4.00	3.75	2.50	1.25	0
% J/A	0	0.25	0.50	0.75	1.00	1.25	2.50	3.75	5.00
% Substitution of gypsum from J/A	0	5	10	15	20	25	50	75	100

Table 7
Results of grindability test

Number of sample	1	2	3	4	5	6	7	8	9
Mill revolutions	4200	4275	4400	4400	4300	4150	3900	3700	3750
Specific surface (Blaine-cm^2/gr)	3945	3950	3950	3970	3960	3970	3970	3965	3985
Grindability index	0.94	0.92	0.90	0.90	0.92	0.96	1.02	1.07	1.06
Specific gravity (g/cm^2)	3.15	3.15	3.15	3.15	3.14	3.15	3.15	3.15	3.16
Water soluble Cr^{6+} (ppm)	75	77	67	68	65	41	43	30	14

Table 8
Determination of setting time

Number of sample	1	2	3	4	5	6	7	8	9
Initial time (min)	145	145	155	150	150	90	60	20	15
Final time (min)	225	220	215	205	215	165	105	32	25
Water of normal consistency (%)	23.2	23.2	23.4	23.7	23.6	24.6	25.6	36*	35*

* Flash set.

Table 9
Results of compressive strength

Number of sample	1	2	3	4	5	6	7	8	9
% SO_3	2.75	2.69	2.63	2.56	2.50	2.44	2.13	1.81	1.99
Strength (MPa) 2 days	27.1	24.3	25.1	25.1	24.0	23.3	19.4	0.6	0.7
Strength (MPa) 7 days	37.7	37.7	36.6	37.7	36.5	34.7	34.1	2.3	3.0
Strength (MPa) 28 days	48.1	44.2	44.4	44.5	44.4	44.2	41.67	39.26	31.4

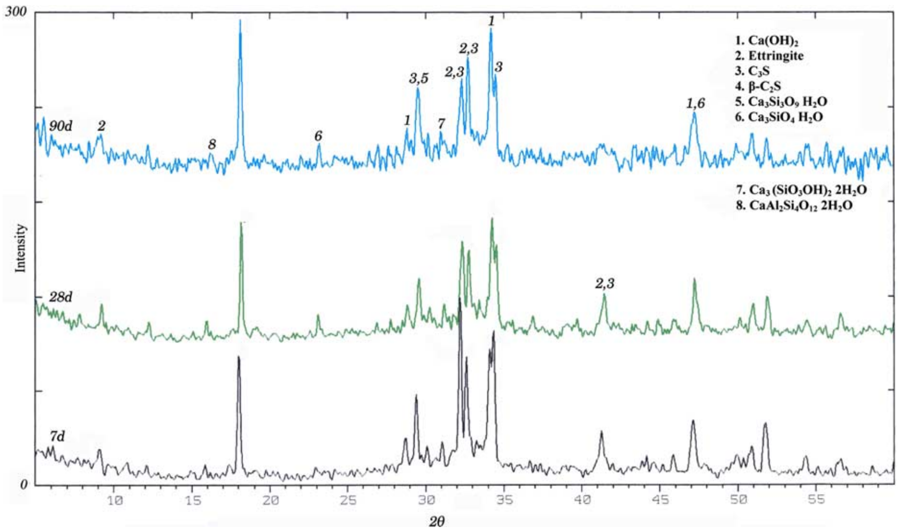

Fig. 2. X-ray diffraction of reference mixture (sample 1—no gypsum substitution) at 7, 28 and 90 days.

addition contained more portlandite [$Ca(OH)_2$] and less ettringite than the samples which contained jarosite/alunite as a substitute for gypsum. This indicates that the hydration rate in the first case is higher. The presence of jarosite/alunite favors the formation of ettringite, probably because of the presence of cations such as Cr^{3+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Al^{3+} in the precipitate [12,13].

The fact that the grindability index, setting time and compressive strengths were similar to those obtained with the mixture with no jarosite/alunite addition (sample 1), lead to the conclusion that the optimum mixture was the one, in which 20% (sample 5) of the gypsum had been replaced by the jarosite/alunite precipitate.

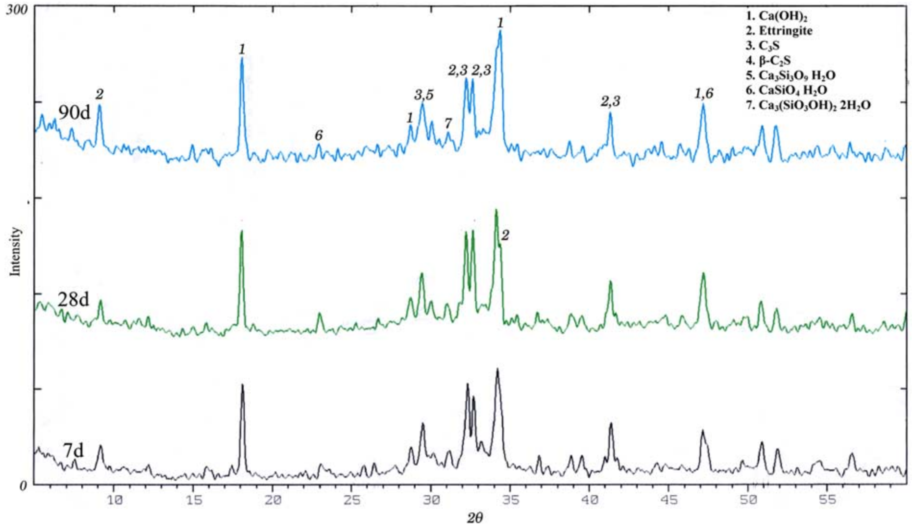

Fig. 3. X-ray diffraction of sample 5 (20% gypsum substitution) at 7, 28 and 90 days.

4. Conclusions

In this paper, the possibility of using jarosite/alunite as a substitute for natural gypsum in cement production was investigated. More specifically, a jarosite/alunite precipitate was produced from a real laterite leach solution, according to a novel method developed by the Laboratory of Metallurgy of the National Technical University of Athens. According to this method, iron and aluminum were precipitated by 99% and 95%, respectively at 95 °C. That was accomplished by gradually raising the initial pH of the leach liquor to an equilibrium pH value of 3.5 at such a rate as to keep supersaturation of iron and aluminum as low as possible, within a practical period of time (up to 12 h). The evaluation of the data of chemical analyses, X-ray diffraction analyses, grindability tests, measurements of setting time and compressive strengths, showed that the substitution of jarosite/alunite for gypsum up to 20% does not affect the properties of the cement mixtures produced. Higher substitution leads to shortening of the setting time and to a decrease of water-soluble chromium Cr^{6+} and compressive strengths values.

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