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Use of gypsum/brucite mixed precipitate instead of gypsum in Portland cement

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Abstract: The possibility of replacing the natural gypsum used in cement production by a chemical precipitate consisting of gypsum ($CaSO_4{\cdot}2H_2O$) and brucite ($Mg(OH)_2$), 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. More specifically, it is obtained by hydrolytic precipitation of magnesium at temperatures not exceeding 80 °C, from sulfate solutions which result from heap leaching of nickel oxide ores with dilute sulfuric acid at ambient temperature, using calcium hydroxide as a neutralizing agent. The mixture generally consists of 20–30% non-fibrous magnesium hydroxide, 60–75% gypsum and any excess of calcium hydroxide, depending on the precipitation conditions. In the present work, a mixture was produced by hydrolytic precipitation at 25 °C, using 1.1 times the stoichiometric quantity of $Ca(OH)_2$ required to precipitate all of the magnesium. The possibility of using the above precipitate as a substitute for gypsum in cement was examined by testing four different cement mixtures, one reference sample, containing 4.5% gypsum and 0.5% anhydrite ($(PC)_{Ref}$) and another three with 4.1%, 5.2% and 6.3% of gypsum/brucite mixed precipitate ($(PC)_{B/G}$), in the place of gypsum. All samples were tested by determining the grindability, setting time, expansion and compressive strength. The results of the physico-mechanical tests showed that the replacement of natural gypsum by the above precipitate did not affect negatively the quality of the produced cements.

Keywords: cement; gypsum; brucite; by-product; hydration

1 INTRODUCTION

There is a general trend today towards developing alternative means of exploiting industrial wastes or by-products 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 for treating, efficiently and economically, low-grade nickel oxide (laterite) ores. It involves heap leaching of the ore by dilute sulfuric acid at ambient temperature, purification of the leach liquor and recovery of nickel and cobalt.[1–4] A typical composition of the pregnant solution produced from heap leaching of Greek low-grade nickeliferous laterites with sulfuric acid is: $Ni^{2+} = 5.0\,g\,dm^{-3}$, $Co^{2+} = 0.6\,g\,dm^{-3}$, $Fe^{3+} = 22.0\,g\,dm^{-3}$, $Al^{3+} = 6.0\,g\,dm^{-3}$, $Cr^{3+} = 1.0\,g\,dm^{-3}$, and $Mg^{2+} = 8\,g\,dm^{-3}$. Iron, aluminium and chromium are removed from the leach liquor by hydrolytic precipitation after which nickel and cobalt are recovered from the purified liquor by solvent extraction. The resulting final solution contains only magnesium, which must also be removed in order to:

(i) allow recycling of the purified barren solution to the heap leaching stage;
(ii) obtain a magnesium-containing precipitate with commercial value and, thus, improve the cost-effectiveness of the whole process.

The majority of the cement plants in Greece mainly use natural gypsum to prevent rapid setting of cement. The partial or total replacement of gypsum by materials which contain calcium sulfate has been instigated by the increasing availability of low-cost by-products containing calcium sulfate. The idea of substituting natural gypsum by a gypsum/brucite mixed precipitate in order to produce Portland cement was based on its high sulfate content and the need to find an industrial use for this by-product. Besides, it is assessed that the cost of using the gypsum/brucite mixed precipitate would be lower than that of quarrying, grinding, and transporting natural gypsum.

The rapid hardening (or flash set) of cement pastes due to the reaction of tricalcium aluminate (C_3A)

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with water is usually prevented by adding a substance which acts a retarder. The cement industry has been using natural gypsum ($CaSO_4{\cdot}2H_2O$) as a first choice material. The addition of a sulfate-bearing material, also affects apart from the setting time, the strength development of the hydrated cement paste and avoids shrinkage. However, if the addition of the above mentioned material exceeds a certain limit, it can lead to substantial expansion of concrete.[5–7] This is the main reason why cement standards define an upper limit to the gypsum content. The required amount of gypsum in a specific cement type increases with the amount of C_3A in the clinker and the fineness of the cement. Modification of the sulfate-bearing admixture to the reactivity of the tricalcium aluminate (C_3A) is, therefore, of significant importance in retarding setting and improving the strength development.

Theories on the cement hydration process suggest that, upon contact with water, the $CaSO_4$-bearing materials dissolve to give sulfate anions, which react with the C_3A grains forming ettringite, as shown by eqn (1):[8,9]

$$3CaO\ Al_2O_3 + 3CaSO_4{\cdot}2H_2O + 26H_2O \longrightarrow 3CaO\ Al_2O_3 3CaSO_4{\cdot}32H_2O \quad (1)$$

The ettringite crystals formed create a thin coating around the anhydrate cement grains, preventing the quick reaction of C_3A with water:

$$2[3CaO\ Al_2O_3] + 21H_2O \longrightarrow 4CaO\ Al_2O_3{\cdot}13H_2O + 2CaO\ Al_2O_3{\cdot}8H_2O \longrightarrow 2[3CaO\ Al_2O_3{\cdot}6H_2O] + 9H_2O \quad (2)$$

Replacement of natural gypsum by non-calcium sulfate salts was investigated by Bombled, who found out that the non-calcium cations affected the rheological properties of cement pastes.[10] 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, yielding the highest strength.[11,12] This optimum value normally increases with age and may 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, and so it will be affected by the amount and reactivity of C_3A, the quantity of soluble alkalis, 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.[5]

In the present experimental work a mass of mixed gypsum/brucite precipitate was first produced by precipitation from a real laterite heap leach liquor. Cement mixtures were then prepared and tested for grindability, setting time, expansion and compressive strength.

2 EXPERIMENTAL

The solution used for the production of gypsum/brucite precipitate was a sample of real leach liquor, which had been produced by heap leaching of a Greek nickel oxide (laterite) chloritic ore with diluted sulfuric acid. Iron, aluminium and chromium were removed by hydrolytic precipitation, after which nickel and cobalt were recovered by solvent extraction. The final solution had a composition of 12.2 g dm^{-3} Mg and a pH of 5.5.

The precipitation of gypsum/brucite was carried out in 5 dm^3, five-necked, round-bottomed split reactors at 25 °C, using 1.1 times the stoichiometric quantity of $Ca(OH)_2$ required to precipitate all of the magnesium. Calcium hydroxide was added in solid form. The reaction time was approximately 2 h. Equilibrium pH was around 10. The precipitate was dried at 80 °C and kept in a desiccator. Further details of the precipitation process, as developed by the Laboratory of Metallurgy of the National Technical University of Athens, have been published elsewhere.[13,14] The precipitate obtained as described above was analysed chemically and mineralogically by X-ray diffraction (XRD), using a Siemens D5000 diffractometer with nickel-filtered $CuK\alpha_1$ radiation (=1.5405 Å), 40 kV and 30 mA. To get an idea of its morphology, a sample of the precipitate was also examined by scanning electron microscopy (SEM) with a Jeol 6100 Scanning Electron Microscope using 10 kV accelerating voltage. The particle size distribution of the produced precipitate was measured by a Cilas-Model 1064 laser diffraction particle size distribution analyser. This was carried out using 0.1 g of powder in 100 cm^3 of ethanol, dispersed using an ultrasonic dispersion unit for 60 s.

Four cement mixtures were produced, one reference sample containing 4.5% gypsum and 0.5% anhydrite ($(PC)_{Ref}$) and another three with 4.1%, 5.2% and 6.3% of gypsum/brucite precipitate ($(PC)_{B/G}$), instead of gypsum. The grindability index of each mixture was determined, as the ratio of the specific surface to the number of mill revolution. The setting times of the samples were determined using the European Standard EN 196-3, and the expansion of the cement pastes by the Le Chatelier method.[15] Compressive strengths at 2, 7, and 28 days were also measured according to EN 196-1.[16]

3 RESULTS AND DISCUSSION

The chemical analyses of the gypsum/brucite mixed precipitate, clinker and gypsum used are given in Table 1. The particle size distribution of the gypsum/brucite precipitate is given in Fig 1. It was found that 50% of the mixed precipitate was below 6 µm, whereas 100% of the material was below 20 µm. The mean diameter of the precipitate was computed at 6.9 µm.

The main mineralogical phases of the mixed precipitate (Fig 2) were gypsum ($CaSO_4{\cdot}2H_2O$) and brucite ($Mg(OH)_2$). The main peaks, which

Table 1. Chemical analysis of clinker, gypsum and gypsum/brucite mixed precipitate

	Content (%)		
Oxides	Clinker	Gypsum	Gypsum/brucite precipitate
SiO_2	22.23	—	—
Al_2O_3	5.27	—	—
Fe_2O_3	3.65	—	—
CaO	65.06	34.3	25.91
MgO	1.31	—	18.92
K_2O	0.78	—	—
Na_2O	0.65	—	—
SO_3	0.66	44.98	31.34
Cr_2O_3	0.96	—	—
CaO_f	0.53	—	—
LOI	0.26	20.85	23.83

CaO_f, free CaO in the clinker; LOI, loss of ignition.

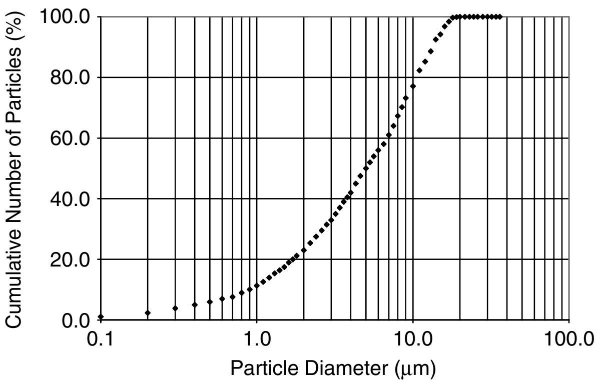


Figure 1. Particle size distributions of the gypsum/brucite mixed precipitate by a laser scattering analyser.

correspond to $CaSO_4{\cdot}2H_2O$, were sharper and with higher intensity, compared with those of $Mg(OH)_2$, whose peaks displayed lower intensity and higher peak width. The above differences were attributed to the differences in grain size and degrees of crystallinity of the two main products. Specifically, the main peaks of $Mg(OH)_2$ characterize a fine crystallized material with no well-developed crystals, whereas the main peaks of $CaSO_4{\cdot}2H_2O$ reveal a well-crystallized compound. The detection of small quantities of $CaCO_3$ and $(Ca,Mg_3)(CO_3)_4$ could be attributed to the partial carbonation of brucite and calcium hydroxide that had not been consumed during precipitation.

The above conclusions were also confirmed by electron microscopic observations. As shown in Fig 3,

Table 2. Mineralogical composition of clinker

Mineralogical phase	Composition (%)
C_3S	51.2
C_2S	25.2
C_3A	7.8
C_4AF	11.1
LSF	91.2
AR	1.4
SR	2.49
Na_2O_{eq}	1.4
Liquid phase	26.8

Table 3. Cement mixtures

	Mixture No			
Component	$((PC)_{Ref})$	$((PC)_{B/G})_1$	$((PC)_{B/G})_2$	$((PC)_{B/G})_3$
Clinker (%)	95.0	95.5	94.2	93.0
Gypsum (%)	4.5	—	—	—
Anhydrite (%)	0.5	0.4	0.6	0.7
Gypsum/ brucite (%)	—	4.1	5.2	6.3

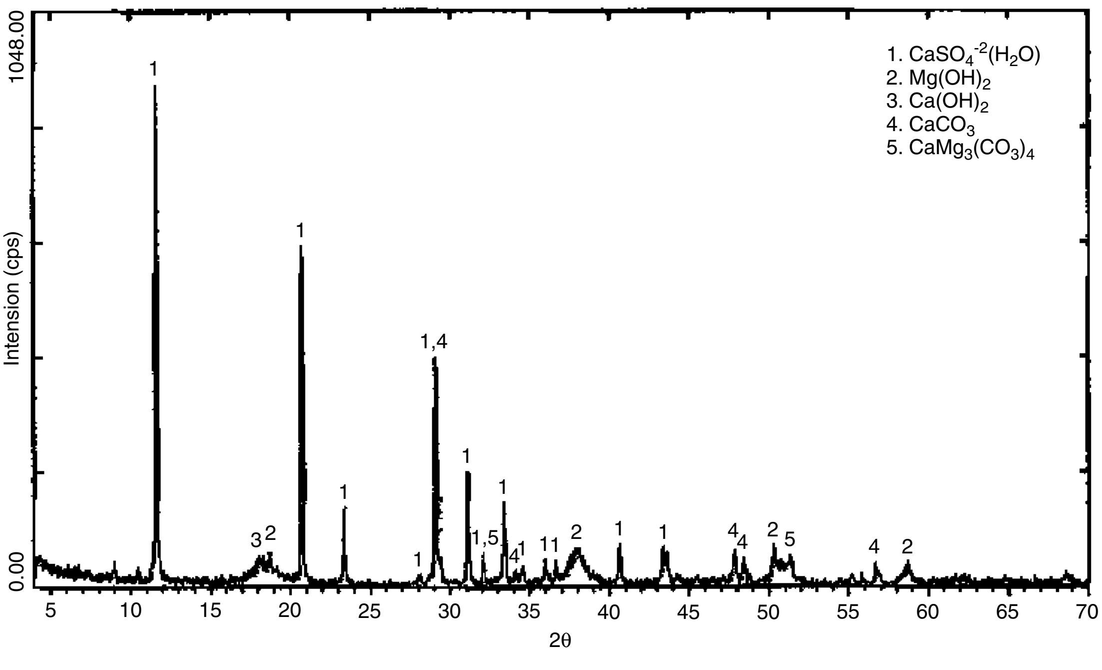
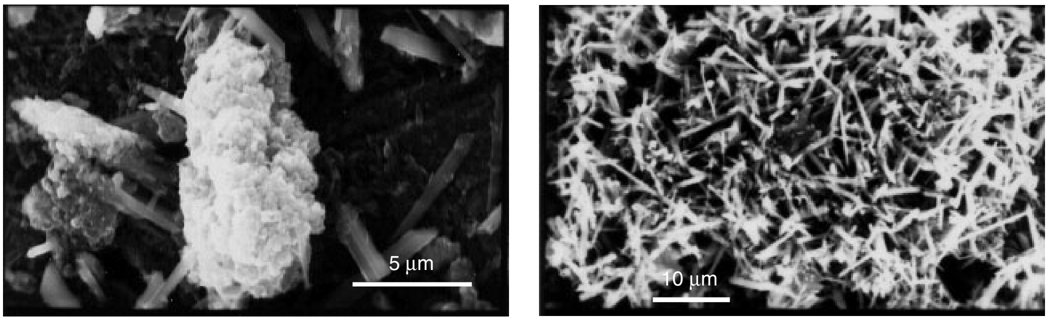


Figure 2. Mineralogical phases of the gypsum/brucite mixed precipitate.



(a) Brucite agglomerate among gypsum crystals

(b) Needle-like crystals of $CaSO_4.2H_2O$

Figure 3. Scanning electron microscopy micrographs of the gypsum/brucite mixed precipitate.

Table 4. Results of grindability tests

	Mixture No			
Parameter	((PC)$_{Ref}$)	((PC)$_{B/G}$)1	((PC)$_{B/G}$)2	((PC)$_{B/G}$)3
Mill revolutions	4200	3500	3400	3300
Spec surface Blaine $cm^2\ g^{-1}$	3955	3940	3950	3970
Grindability index	0.94	1.13	1.16	1.20
Specific gravity ($g\ cm^{-2}$)	3.14	3.15	3.14	3.13
SO_3 of mixture (%)	2.9	2.5	3.0	3.5

Table 5. Results of setting time–expansion of the cement mixture produced

	Mixture No			
Parameter	((PC)$_{Ref}$)	((PC)$_{B/G}$)1	((PC)$_{B/G}$)2	((PC)$_{B/G}$)3
Initial time (min)	145	105	120	135
Final time (min)	225	135	160	200
Water of normal consistency (%)	23.2	27.6	26.5	25.6
Expansion (mm) (Le Chatelier)	2	1.5	1	1.5

Table 6. Results of compressive strength

	Mixture No			
Parameter	((PC)$_{Ref}$)	((PC)$_{B/G}$)1	((PC)$_{B/G}$)2	((PC)$_{B/G}$)3
Mortar flow (%)	98	101	95	91
Strength (MPa), 2 days	26.4	23.4	27.3	29.3
Strength (MPa), 7 days	38.4	36.0	38.0	39.6
Strength (MPa), 28 days	46.3	44.6	46.8	47.3

the magnesium hydroxide precipitates were in the form of aggregates of fine crystallites. The aggregates had an irregular shape and a homogeneous size of about 8 µm (longest dimension). On the other hand, gypsum consisted of needle-like crystals of 5–15 µm in length and 1–3 µm in diameter.

The mineralogical composition of the clinker used as well as the composition of the four mixtures produced are shown in Tables 2 and 3, respectively. The clinker was co-ground with gypsum or gypsum/brucite mixed precipitate in a ball mill of 1.5 kg capacity. The grindability index of each mixture was determined and is presented in Table 4. As the precipitate was a fine material, its increase in the mixture composition caused an increase of the mixture grindability index. The grindability index reaches its maximum values when 6.3% of gypsum/brucite precipitate is used as a substitute for gypsum.

The setting times of the cement mixtures are given in Table 5. As the table shows, the replacement of gypsum with the gypsum/brucite precipitate accelerates the cement setting, but within acceptable limits. It is proposed that this is because the SO_3 contained in the precipitate is less soluble than that of natural gypsum. Also, an increase in the precipitate content in the cement mixture increases cement setting times.

The mortars of the mixtures under investigation were tested for compressive strength after 2, 7, and 28 days of curing. The results obtained are shown in Table 6. The mortars that contained the mixed gypsum/brucite precipitate showed similar compressive strength values with the reference material and satisfy the specified limits set by EN 196-1. This finding confirms the potential for the precipitate to be used as a substitute for gypsum in cement production.

4 CONCLUSIONS

Under the experimental conditions of the present research work, a precipitate was obtained composed of well-crystallized gypsum ($CaSO_4{\cdot}2H_2O$) and aggregates of fine crystallites of brucite ($Mg(OH)_2$). The mixture exhibited excellent filtering properties.

The addition of the above precipitate, instead of natural gypsum, by 4.1%, 5.2% and 6.3% in clinker did not adversely affect the properties of the cement mixtures produced.

More specifically, all the cement mixtures tested presented similar characteristics, such as grindability, compressive strength and expansion, with the reference sample.

Regarding the setting times of the mixtures, the replacement of natural gypsum with the gypsum/brucite precipitate accelerated the cement setting, within acceptable limits, a fact which was attributed to the lower solubility of SO_3 contained in the precipitate than that in natural gypsum.

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