



Short communication

Valorization of phosphogypsum as hydraulic binder

T. Kuryatnyk, C. Angulski da Luz, J. Ambroise, J. Pera*

Laboratoire Génie Civil et Ingénierie Environnementale (LGCE), Institut National des Sciences Appliquées de Lyon,
Domaine Scientifique de la Doua, Bâtiment J. Tuset, 12, Avenue des Arts, 69 621 Villeurbanne Cedex, France

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ABSTRACT

Phosphogypsum (calcium sulfate) is a naturally occurring part of the process of creating phosphoric acid (H_3PO_4), an essential component of many modern fertilizers. For every tonne of phosphoric acid made, from the reaction of phosphate rock with acid, commonly sulfuric acid, about 3 t of phosphogypsum are created. There are three options for managing phosphogypsum: (i) disposal or dumping, (ii) stacking, (iii) use-in, for example, agriculture, construction, or landfill. This paper presents the valorization of two Tunisian phosphogypsums (referred as G and S) in calcium sulfoaluminat cement in the following proportions: 70% phosphogypsum–30% calcium sulfoaluminat clinker. The use of sample G leads to the production of a hydraulic binder which means that it is not destroyed when immersed in water. The binder including sample S performs very well when cured in air but is not resistant in water. Formation of massive ettringite in a rigid body leads to cracking and strength loss.

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1. Introduction

Phosphogypsum is a by-product from the production of phosphoric acid by the wet process. In this process, the raw phosphate is treated by sulfuric acid and, besides the main product which is phosphoric acid (H_3PO_4), gypsum and a small quantity of hydrofluoric acid are obtained. For every tonne of phosphoric acid made, about three tonnes of phosphogypsum are yielded. It is estimated that more than 22 million tonnes of anhydrous P_2O_5 are produced annually worldwide, generating in excess of 110 million tonnes of gypsum by-product [1]. Residual phosphogypsum is highly acidic (pH 1). Commercial uses, in agriculture and in manufacturing gypsum board and Portland cement, consume less than a few percent of this by-product. The vast majority is disposed of on land in gypsum stacks or is discharged into water bodies. Worldwide, four methods are being used by the phosphate industry to dispose of surplus phosphogypsum, namely: (i) discharging to water bodies; (ii) backfilling in mine pits; (iii) dry stacking; and (iv) wet stacking.

Phosphogypsum consists primarily of calcium sulfate dihydrate with small amounts of silica, usually as quartz, and unreacted phosphate rock. Radium and uranium, as well as minor amounts of toxic metals, namely, arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver and phytotoxic fluoride and aluminum are also present in phosphogypsum and its pore water. The concentra-

tions of heavy metals and radionuclides depend on the composition of the phosphate rock feed. Aside from piling up in significant quantities wherever phosphate is processed, phosphogypsum also effuses radon gas which is radioactive. This means that phosphogypsum is inherently radioactive at some level. Exposure to high enough quantities, such as working for many years in a dust filled environment or through drinking water, could introduce enough radiation into the body to have the same effects as uranium refining tailings [2–5].

There are several areas of utilization for phosphogypsum. The two main fields are conversion of phosphogypsum to plaster and plaster products and replacement of natural gypsum in cement production. Unfortunately, high energy consumption is needed to dry phosphogypsum and the utilization of phosphogypsum is therefore limited [1,6].

By far, the biggest issue facing Tunisia's phosphate industry today is pollution. The Gulf of Gabes between Sfax, Gabes, and the Kerkennah Islands is one of the most polluted places in all of the Mediterranean Sea. This is a result of several factors including not treating the liquid effluent streams of the refineries, and the massive accumulation of phosphogypsum piles which are unprotected from the elements. It is estimated that 10 million tonnes of phosphogypsum are annually produced. In Tunisia, phosphogypsum is currently contained by dumping it in large warehouses. When it rains or when the wind blows, phosphogypsum gets spread around the general vicinity of these warehouses. Long hot and dry summers in Tunisia mean that there are many phosphogypsum particulates floating around in the atmosphere. To deal with the phosphogypsum, Tunisia has decided to bury it somewhere in the interior of the country where it will have minimal environmental impact [7].

* Corresponding author at: LGCE-INSA LYON, Domaine Scientifique de la Doua, Bâtiment J. Tuset, 12, Avenue des arts, 69621 Villeurbanne Cedex, France.
Tel.: +33 4 72 43 82 96; fax: +33 4 78 94 98 07.

E-mail address: Jean.Pera@insa-lyon.fr (J. Pera).

Table 1
Chemical composition of phosphogypsums and natural gypsum (wt%)

Oxides	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	MgO	P ₂ O ₅	SO ₃	LOI
G (%)	1.9	0.2	31.9	0.7	0.1	1.4	44.7	24.2
S (%)	1.8	0.1	31.8	0.9	0.3	1.2	44.7	24.8
N (%)	0.4	0.1	33.4	ND	0.1	ND	44.2	21.4

Some ways of valorization have also been investigated. Concerning Tunisia, the natural gypsum of good quality exists in many regions. This gypsum is employed among others to manufacture plaster for which consumption at the national level is less than 0.1 million tonnes per year. The purification of phosphogypsum for use in the plaster industry is not competitive for Tunisia. Not purified phosphogypsum was used in the fabrication of bricks and

Table 2
Physical and chemical properties of phosphogypsums and natural gypsum

Property	G	S	N
Average diameter of the particle size distribution (μm)	20	20	20
BET surface area (m ² /g)	27.4	19.1	0.8
Blaine specific surface area (m ² /kg)	320	270	337
pH	1.95	1.80	8.5
Soluble phosphates (mg/L)	933	594	<0.1
Soluble sulfates (mg/L)	1960	2020	1594

blocks by static press process [8], or in embankment construction [9]. The characterization of the Sfax phosphogypsum has pointed out a low radioactivity level, compared to other phosphogypsum in the world, but a very bad behaviour towards immersion. Phosph-

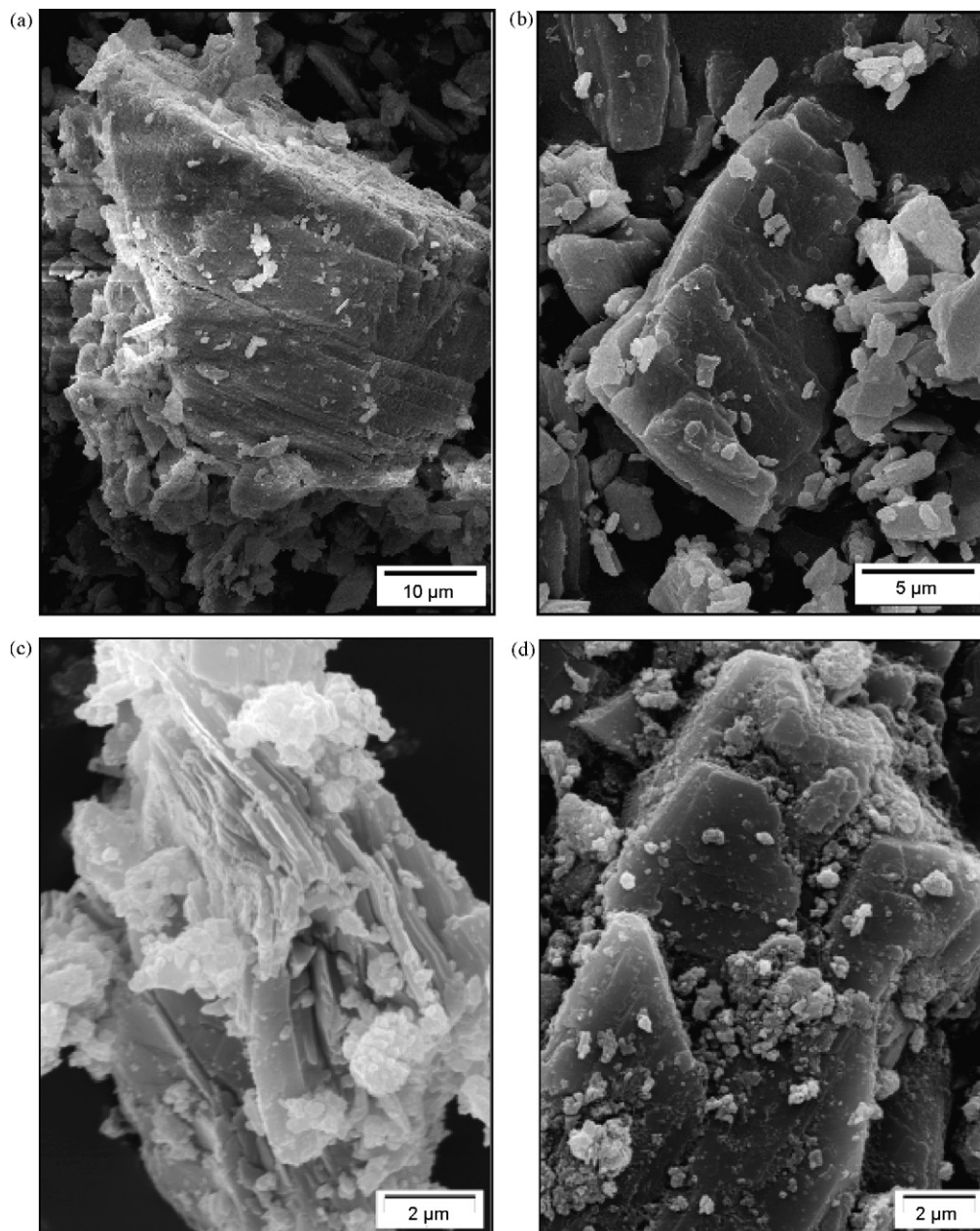
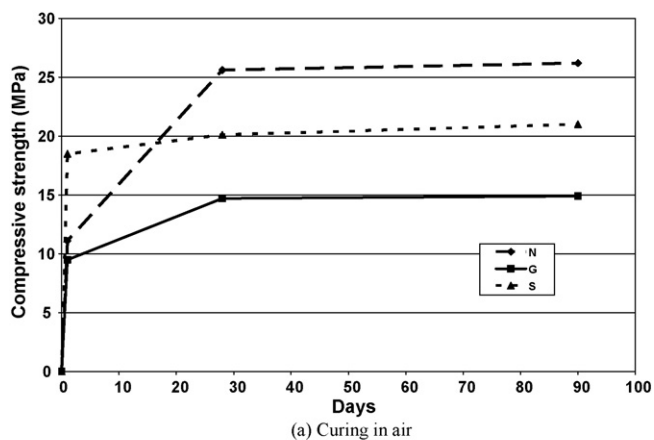
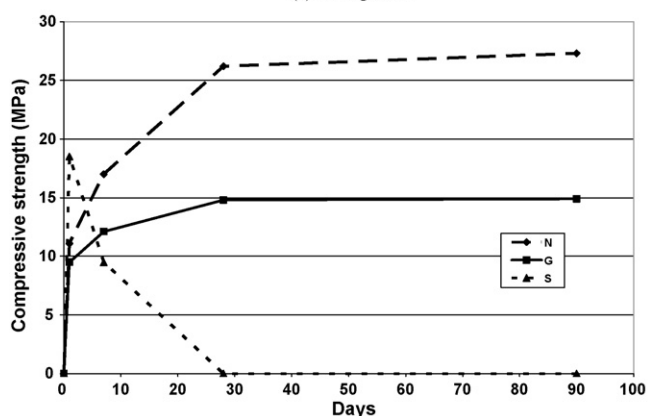


Fig. 1. Morphology of natural gypsum (a and b), phosphogypsum G (c), and phosphogypsum S (d)



(a) Curing in air



(b) Curing in water

Fig. 2. Compressive strength versus time.

ogypsum was treated by limestone sand and cement, for road use [10,11].

In the present study, Gabes and Skhira phosphogypsums were utilized in the design of calcium sulfoaluminate cement (CSA), in the following proportions: phosphogypsum/calcium sulfoaluminate clinker = 70/30. The main properties of calcium sulfoaluminate cement are presented in the literature [12–20]. The engineering properties of this new type of binder are described in the present study. They are compared to those developed by a binder containing natural gypsum instead of phosphogypsum.

Table 3
Properties of calcium sulfoaluminate clinker

Chemical analysis	
Oxides	%
SiO ₂	4.7
Al ₂ O ₃	37.4
CaO	39.2
TiO ₂	1.6
MgO	1.7
P ₂ O ₅	0.2
SO ₃	8.8
LOI	0.9
Physical properties	
Average diameter of the particle size distribution (mm)	16
BET surface area (m ² /g)	1.05
Blaine-specific surface area (m ² /kg)	450

Table 4
Mineralogy of calcium sulfoaluminate clinker (wt%)

Phase	Chemistry	%
Yeelimite	Ca ₄ Al ₆ O ₁₂ SO ₄	73.5
Larnite	β-Ca ₂ SiO ₄	16.1
Perovskite	Ca ₃ Fe ₂ TiO ₉	6.9
Mayenite	Ca ₁₂ Al ₁₄ O ₃₃	0.6
Periclase	MgO	1.7
Anhydrite	CaSO ₄	1.0
Quartz	SiO ₂	0.2

2. Experimental

2.1. Materials

Natural gypsum (N) and two different types of Tunisian phosphogypsum (G and S) were investigated. The amount of pure gypsum was determined by the mass loss observed in the TGA curve in the temperature range 140–180 °C. For pure gypsum, this mass loss is 20.9% and corresponds to the loss of two molecules of water. Here, we obtained 19.1% for G, 19.4% for S, and 19.5% for N, which correspond to respective pure gypsum contents of 91.4% for G, 92.8% for S, and 93.2% for N. The chemical composition of N, G and S is shown in Table 1. Na₂O and P₂O₅ are present in phosphogypsums, while they are not detectable in natural gypsum. Other properties are presented in Table 2. The pH of phosphogypsums was particularly low (1.8–1.95), while that of natural gypsum was 8.5. Phosphogypsums contained more soluble phosphates and sulfates than natural gyp-

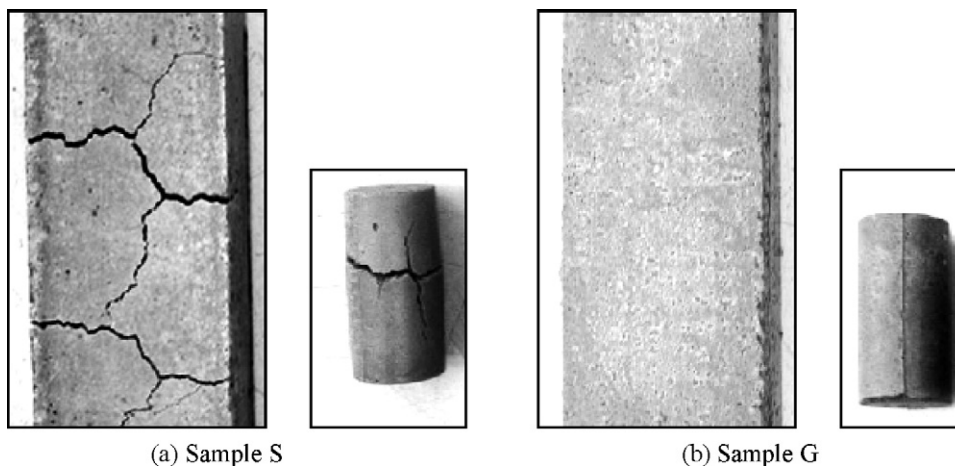


Fig. 3. Cracking of sample S after more than 7 days of immersion in water.

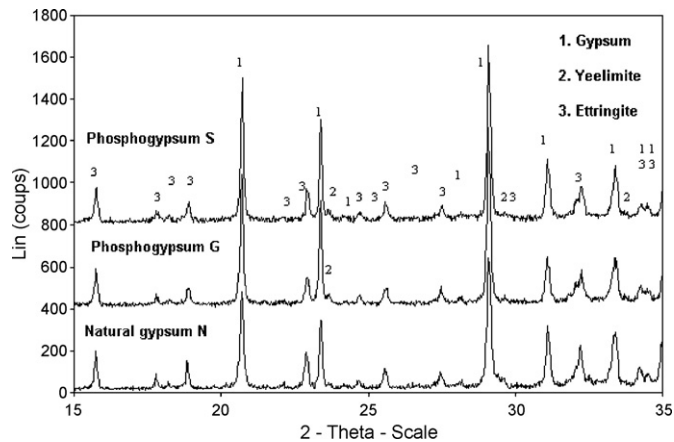


Fig. 4. XRD patterns of pastes immersed in water for 7 days.

sum. Phosphogypsums presented the same average diameter of the particle size distribution than natural gypsum but their BET surface area was 20–30 times higher. This is explained by the morphology of these materials assessed by scanning electron microscopy (SEM) and presented in Fig. 1. The morphology of sample N is an example of a sheeted structure with parallel layers containing crystalline inclusions (Fig. 1a and b). The structure of sample G is very porous (Fig. 1c) and it is composed of sheets and very small crystals. Tabular crystals of gypsum are found in sample S (Fig. 1d) but they are small.

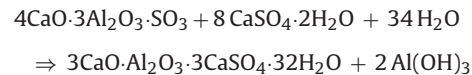
The characteristics of calcium sulfoaluminate clinker (CK) are shown in Table 3. CK is a commercial Chinese product supplied by the Belitex company. It is industrially produced in a rotary kiln. Its mineralogy was assessed by X-ray diffraction (Table 4). The amount of yeelimite, also called “Klein’s compound”, was very high: 73.5%.

Table 5
EDAX analysis of ettringites

Elements (%)	N	G	S
Al	16	17	21
S	26	28	28
Ca	58	55	51

This phase and mayenite are responsible of the development of early age strength.

In the present study, calcium sulfoaluminate clinker was added to improve the water resistance of phosphogypsum, according to the following reaction:



Mixtures of yeelimite and gypsum yield ettringite ($3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$) and gibbsite [$\text{Al}(\text{OH})_3$] as products of hydration. These hydrates are insoluble in water.

2.2. Preparation of pastes and mortars

Each cement (70% G, N or S + 30% CK) was hydrated at $W/C = 0.30$, and cast in Plexiglas mini-cylinders ($\varnothing = 20\text{ mm}$, $h = 40\text{ mm}$). The samples were demolded at 24 days of age. Then, they were cured in water at 20°C . These pastes were used for X-ray diffraction, DTA-TGA, and SEM analyses.

Standard mortars were prepared with these binders. Their composition was as follows:

- binder: 450 g;
- standard sand: 1350 g;
- water: 225 g.

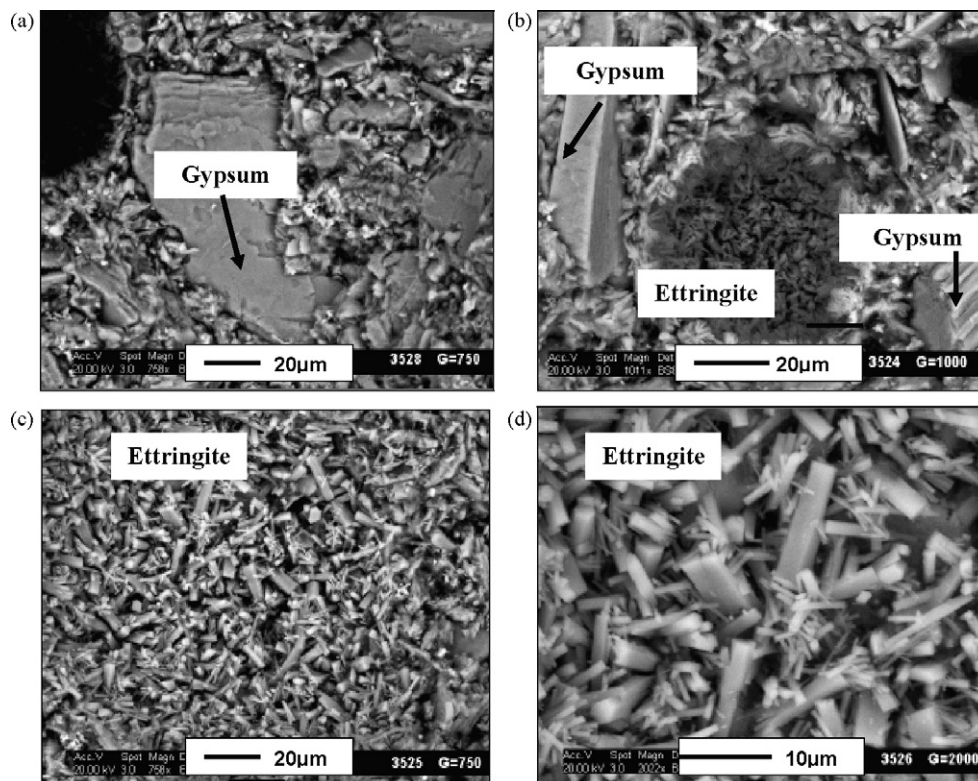


Fig. 5. ESEM analysis of sample N after 7 days of immersion in water.

Prismatic samples (40 mm × 40 mm × 160 mm) of mortar were cast. All mortars were demolded after 24 h. One series of samples was kept at 20 °C in sealed plastic bags until the age of ($d - 1$) days, with $d = 7, 28,$ and 90 . The second series of specimens was stored in water at 20 °C until the age of ($d - 1$) days. Then, all the samples were stored at 20 °C and 50% RH for 24 h and subjected to mechanical testing.

3. Results and discussion

3.1. Compressive strength

As shown in Fig. 2, curing conditions have not any influence on the strength of mortars containing either natural gypsum (N) or phosphogypsum G. The level of strength is lower with phosphogypsum but remains acceptable. As the strength does not decrease versus time for specimens immersed in water, it can be concluded that hydraulic binders are obtained with samples N and G.

The behaviour of mortars containing phosphogypsum S is quite different: in air, the strength is very good, but becomes nil for specimens immersed in water for more than 7 days. Cracking appears for such samples as seen in Fig. 3.

3.2. Microstructure

The hydration evolution of pastes immersed in water was followed by X-ray diffraction analysis at different ages: 1, 7, 28, and 90

days. After one day of hydration, ettringite was the single hydrate observed by X-ray diffraction in each paste. Residual gypsum and yeelimite were observed. As cracking occurred in sample S after more than 7 days of immersion in water, it seemed interesting to compare the different XRD patterns at this age (Fig. 4). There is not any significant difference between the different samples: ettringite precipitates and residual gypsum and yeelimite are still present. The quantities of ettringite are very close. This result means that the cracking of sample S is not due to higher precipitation of ettringite but can be attributed to different crystallizations. This was verified by SEM (scanning electron microscopy) and environmental scanning electron microscopy (ESEM). For ESEM analysis, samples are not gold covered and the applied pressure is limited to 5.9 Torr.

ESEM analysis of sample N is presented in Fig. 5. Several crystals of unreacted gypsum are present in the matrix: large plates (Fig. 5a), and tabular crystals (Fig. 5b). Different morphologies of ettringite are found: either short and thick rods or thin needles. Ettringite precipitates as well in the matrix (Fig. 5a) as in pores (Fig. 5b–d).

ESEM and SEM analyses of sample G are shown in Fig. 6. Gypsum is present as large plates (Fig. 6a and c). Massive ettringite appears within the matrix (Fig. 6a and c) while thin and short rods precipitate in pores (Fig. 6b and d).

ESEM and SEM analyses of sample S are shown in Fig. 7. The matrix seems denser than that of sample G. Gypsum is present as large plates (Fig. 7a, c and d). Ettringite is not found in pores and precipitates in the matrix. Massive ettringite is essentially found (Fig. 7a, b and d). The EDAX analysis carried out on the different

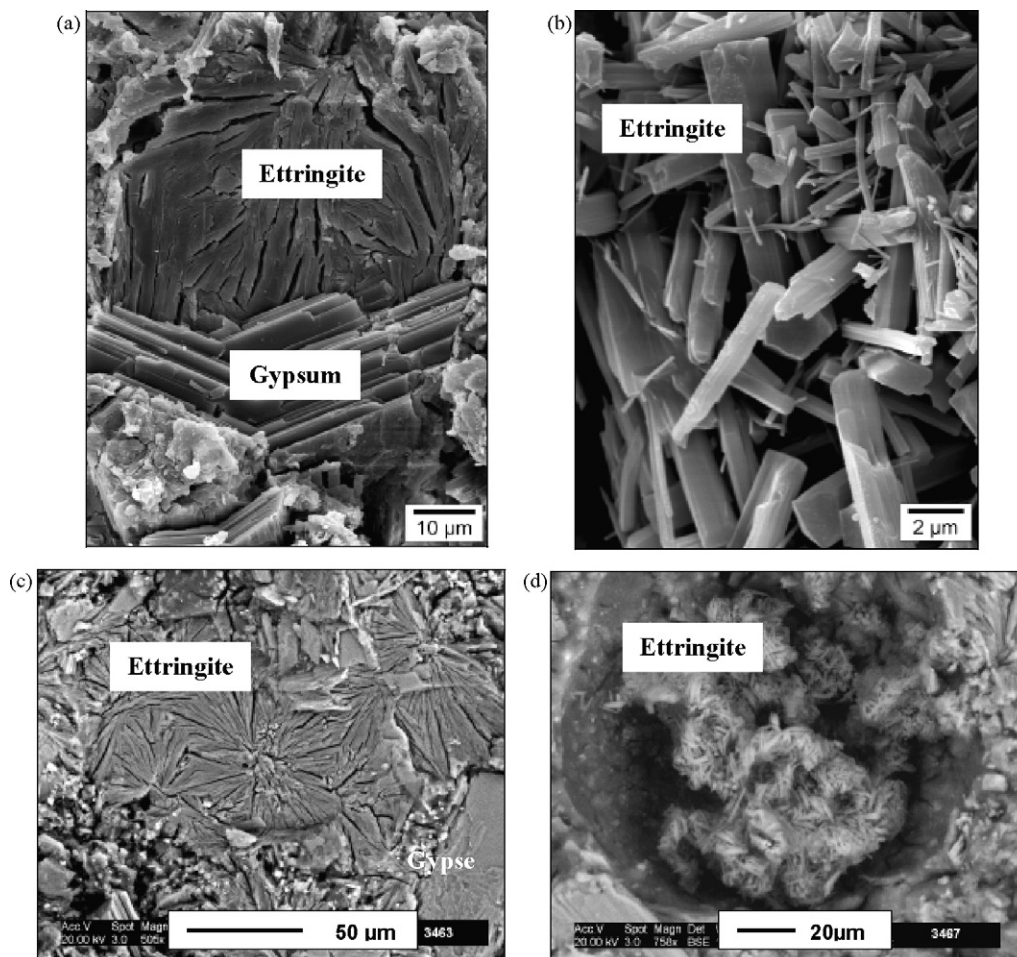


Fig. 6. SEM (a and b) and ESEM (c and d) analyses of sample G after 7 days of immersion in water.

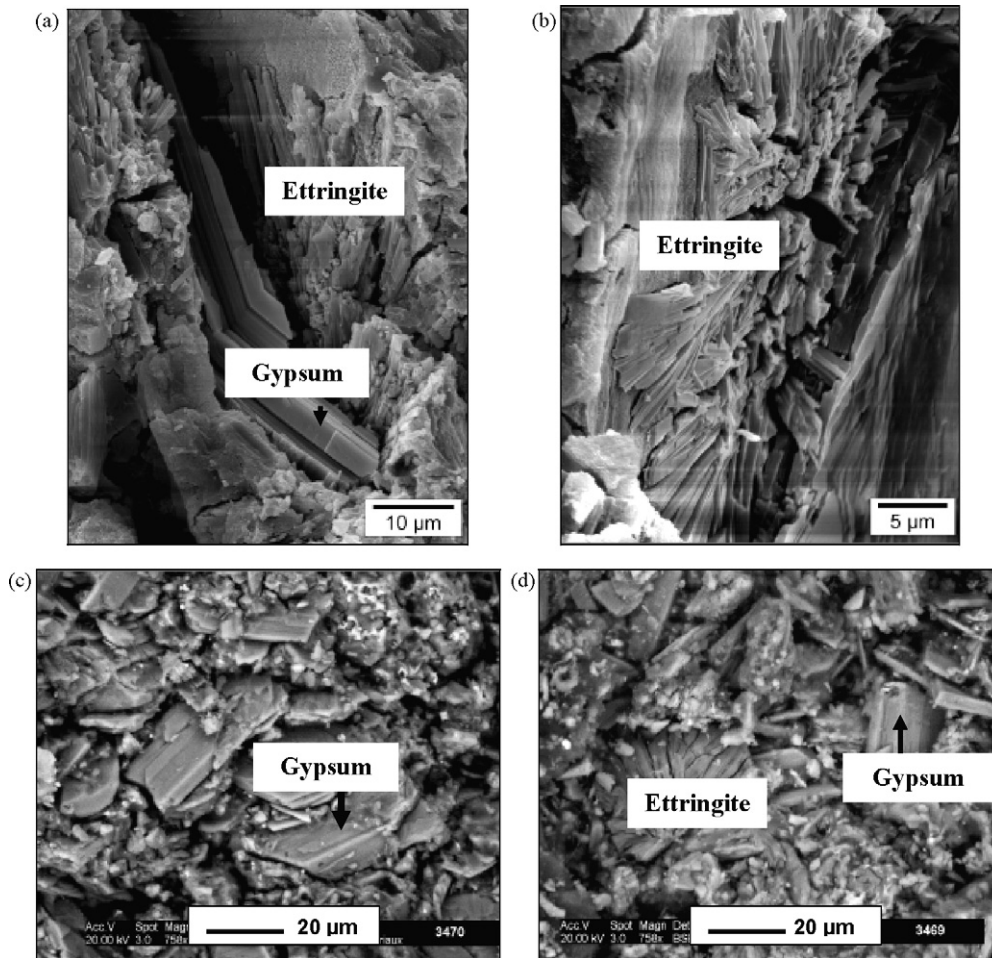


Fig. 7. SEM (a and b) and ESEM (c and d) analyses of sample S after 7 days of immersion in water.

types of ettringite found in samples N, G, and S is presented in Table 5. It clearly appears that ettringite S has a composition different from that of ettringites N and G: more aluminium and less calcium.

Therefore, the cracking of sample S can be explained as follows: precipitation of massive ettringite less rich in calcium within a dense and strong matrix. S mortar presented a compressive strength of 18.5 MPa at one day which is nearly the double of that presented by mortars G and N. As reported in the literature [21], the formation of ettringite in a rigid body produces cracking, spalling, and strength loss. When it occurs homogeneously and immediately (within hours or days) in a mixture or in a deformable concrete – early ettringite formation (EEF) – the related expansion does not cause any significant localized disruptive action. An excess of gypsum could favor ettringite formation after setting and could cause undesirable cracking effects due to the expansion which accompanies the formation of ettringite when it is formed in hardened and rigid concrete. In this case, ettringite forms heterogeneously and later (months or years) – delayed ettringite formation (DEF) – in a rigid body and produces cracking, spalling, and strength loss. Therefore, only DEF – and not EEF – is associated with a damaging sulfate attack.

4. Conclusions

This study shows that phosphogypsum can constitute an interesting resource for the development of low-cost housing materials.

From the results obtained, it is possible to draw the following conclusions:

- (1) It is possible to get a water resistant binder by mixing 70% phosphogypsum to 30% calcium sulfoaluminate clinker if ettringite precipitates in the pores of the matrix as short and thin needles.
- (2) The precipitation of massive ettringite within the matrix leads to cracking when mortars are immersed in water.
- (3) The use of such binder may be recommended to design low-cost building materials in developing countries possessing large amounts of phosphogypsum: concrete blocks, renders or screeds.

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