

Short communication

Immobilization of calcium sulfate contained in demolition waste

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Abstract

This paper presents the results of a laboratory study undertaken to examine the treatment of demolition waste containing calcium sulfate by means of calcium sulfoaluminate clinker (CSA). The quantity of CSA necessary to entirely consume calcium sulfate was determined. Using infrared spectrometry analysis and X-ray diffraction, it was shown that calcium sulfate was entirely consumed when the ratio between CSA and calcium sulfate was 4.

Standard sand was polluted by 4% calcium sulfate. Two solutions were investigated:

- either global treatment of sand by CSA,
- or immobilization of calcium sulfate by CSA, followed by the introduction of this milled mixture in standard sand.

Regardless of the type of treatment, swelling was almost stabilized after 28 days of immersion in water.

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1. Introduction

In Europe, the gypsum content of recycled aggregates varies from 0.03% in concrete rubble to more than 6% in some sieving sands. Gypsum occurs in finely dispersed form and originates mainly from plaster work [1]. The presence of gypsum has a negative effect on the material quality for reasons of solubility and low hardness and density. For example, the solubility of plaster (calcium sulfate hemi-hydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) is 2.3 g/L at 20 °C. Therefore, when plaster polluted aggregates are disposed in unlined landfills, a series of biological and chemical reactions can occur that have the potential for adverse environmental impacts. When these aggregates get wet, some of the sulfate from gypsum dissolves in water. If this “leachate” reaches groundwater, contamination with sulfate may result. Fortunately, sulfate is not a risk on the same magnitude as chemicals such as lead or arsenic, but high sulfate concentrations do impact negative qualities to the water [2,3]. High levels in water can impart a taste

and when combines with magnesium or sodium can produce a laxative effect. Sodium sulfate (Glauber’s salt) and magnesium sulfate (Epsom’s salt) are both naturally occurring and well known laxatives. Sulfate also contributes to the high total dissolved solids (TDS) concentrations observed in groundwater at many C&D debris landfills. Another issue results from the conversion of dissolved sulfate to hydrogen sulfide (H_2S). H_2S is a foul-smelling gas (often compared to rotten eggs) and odor complaints are a common problem.

These properties prevent the use of gypsum containing products as unbound elevation or foundation material. Additionally, gypsum affects the hardening reactions during concrete production. In cement bound applications, an excess of sulfates causes loss of strength, expansion and disintegration of concrete. Sulfate attack is related to the expansive character of ettringite formation by reaction of the sulfate present in concrete with the hydrated calcium aluminate of the hardened and rigid cement matrix. Sulfates, in the form of gypsum, are added to the clinker during the grinding process. The purpose of gypsum is to slow the hydration of aluminates and thus prevent a “flash set” of concrete. The initial or primary ettringite formation occurs shortly after the water has been added to the

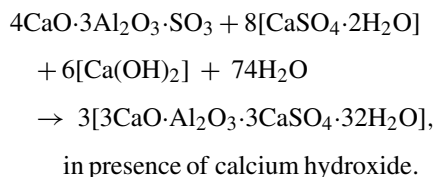
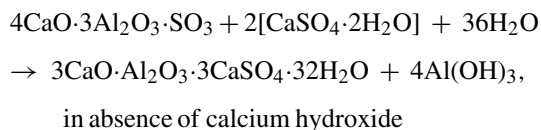
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cement but before the concrete reaches its initial set. Ettringite formation does not necessarily produce a damaging effect [4–9]. When it occurs homogeneously and immediately (within hours or days) in a mixture or in a deformable concrete – early ettringite formation (EEF) – the related expansion does not cause any significant localized disruptive action. This happens when ground gypsum present in cement reacts with anhydrous calcium aluminate (C_3A) within some hours (set regulation). The amount of gypsum which is needed as set regulator for cement is limited: at most 3.5–4% as SO_3 depending on cements, which is equivalent to about 7–8% by mass of cement. An excess of gypsum with respect to this amount 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.

Thus, the sulfate content is a major criterion in the valorization of the construction and demolition waste as secondary aggregate. Immobilization of sulfate can be achieved by chemical binding in the form of ettringite and other calcium sulfoaluminates. Mixture compositions based on Portland, high alumina and blast furnace slag cements have been defined [10].

This paper examines the feasibility of treating demolition waste containing gypsum by calcium sulfoaluminate clinker (CSA), in order to immobilize calcium sulfate. Sulfo-belite clinkers, also called sulfoaluminate-belite clinkers, contain the phases belite ($2CaO \cdot SiO_2$) and yeelimite, or tetracalcium trialuminate sulfate ($CaO \cdot 3Al_2O_3 \cdot SO_3$) as their main constituents. When CSA clinker hydrates in the presence of gypsum ($CaSO_4 \cdot 2H_2O$), ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$)

is formed according to the following reactions [10]:



The properties of these cements have been described in the literature [10–22].

In the present study, the first investigation was carried out on plain pastes. It consisted in optimizing the quantity of CSA necessary to entirely consume calcium sulfate. In a second step, standard sand was polluted by 4% calcium sulfate. Two solutions were investigated: either global treatment of sand by CSA, or immobilization of calcium sulfate by CSA, followed by the introduction of this milled mixture in standard sand. The performances of these polluted mortars were assessed.

2. Materials

The CSA used in this study, presented the following composition:

- yeelimite ($4CaO \cdot 3Al_2O_3 \cdot SO_3$): 66.4%,
- belite ($2CaO \cdot SiO_2$): 15.6%,
- mayenite ($12CaO \cdot 7Al_2O_3$): 7.1%,
- perovskite ($3CaO \cdot Fe_2O_3 \cdot TiO_2$): 9.9%.

The source of calcium sulfate was plaster: $CaSO_4 \cdot 0.5H_2O$. Standard siliceous sand (EN 196-1) was used as aggregate. Nor-

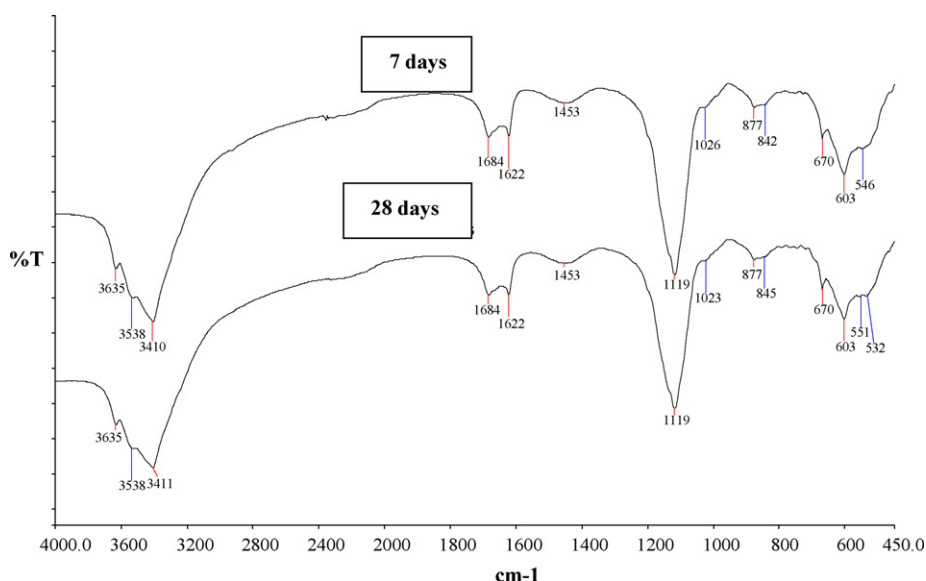


Fig. 1. IR spectra of the mixture composed of 40% plaster and 60% CSA.

Table 1
Composition of plain pastes (wt.%)

Plaster	CSA
40	60
30	70
20	80

mal Portland cement (NPC), class CEM I 52.5, according to the European Standard EN 197-1, was utilized to prepare mortars.

3. Investigation on plain pastes

Plain pastes containing different amounts of plaster and CSA were hydrated at water to solids ratio of 0.35. The composition of pastes is given in Table 1.

These pastes were stored in Plexiglas moulds ($\phi = 20$ mm, $h = 40$ mm) for 7 and 28 days, respectively, and then analyzed by means of infrared spectrometry and X-ray diffraction. The IR spectra are presented in Figs. 1–3.

Figs. 1 and 2 point out the presence of bands at 603 and 670 cm^{-1} , characterizing the presence of residual plaster in the mixtures containing 40 and 30% plaster, respectively. The amount of CSA was not sufficient to consume all the plaster present in these mixtures. Fig. 3 shows that plaster was entirely consumed in the mixture containing 20% plaster and 80% CSA. This result was confirmed by X-ray diffraction. This technique also pointed out that the main product of hydration was ettringite. To entirely consume the plaster present in the mixture, the following condition has to be met: $\text{CSA/plaster} \geq 4$.

4. Investigation on mortars

Two approaches have been undertaken:

- in the first one, standard sand was first polluted by plaster and then treated by CSA,

Table 2
Compositions of treated sand (g)

Component	CSA/plaster	
	1.5	2.33
Standard sand	1296	1296
Plaster	54	54
CSA	81	126
Water	220	220

- in the second one, plaster was first mixed with CSA and hydrated for 7 days, then milled and introduced in standard sand.

Standard mortars were cast using NPC and these sands. Their dimensional variations were compared to those of control mortar cast with pure sand, when immersed in water. The amount of plaster present in the sand was 4%, by mass.

4.1. Results of the first approach

In this approach, only two CSA/plaster ratios have been investigated: 1.5 (60% CSA + 40% plaster) and 2.33 (70% CSA + 30% plaster). The compositions of treated sands are presented in Table 2.

After 7 days of hydration in sealed bags, these sands were crushed to get particles smaller than 3 mm. The crushing was difficult due to the hardness of the treated sand, and therefore, this phenomenon has to be taken into account in an industrial process.

Standard mortars were cast using NPC and either pure, or polluted, or treated sand, in the following proportions:

- sand: 1350 g,
- NPC: 450 g,
- water: 225 g (pure or polluted sand) or 285 g (treated sand).

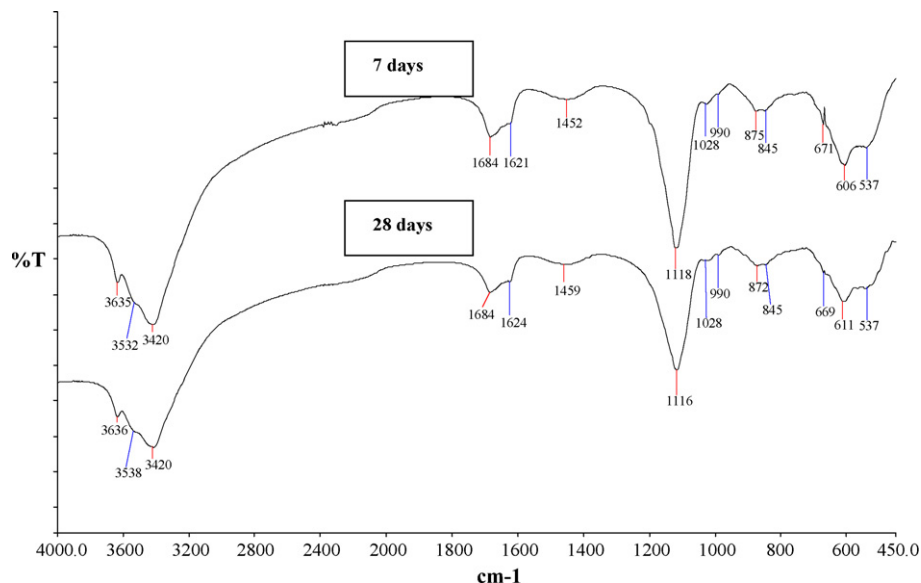


Fig. 2. IR spectra of the mixture composed of 30% plaster and 70% CSA.

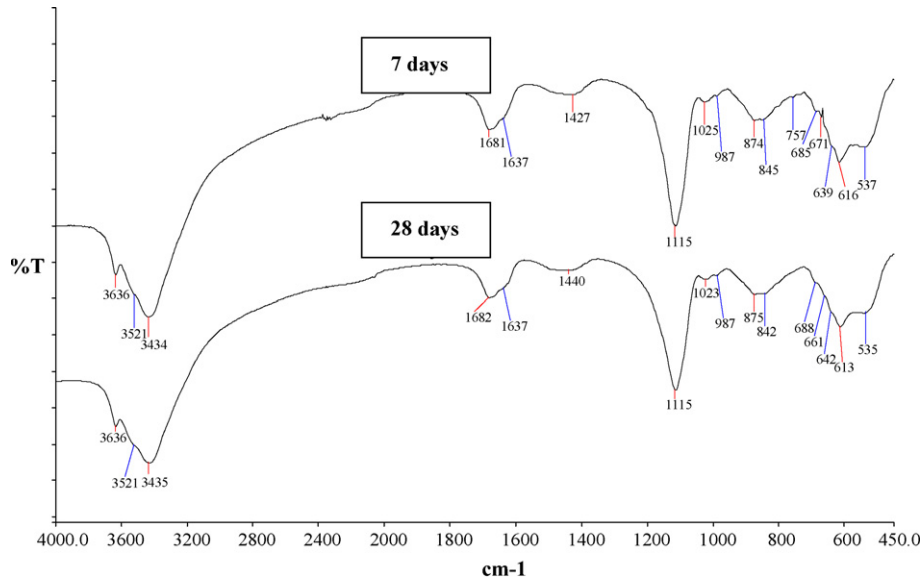


Fig. 3. IR spectra of the mixture composed of 20% plaster and 80% CSA.

The quantity of water was adjusted to get the same workability. The samples were demoulded after 24 h and immersed in water at 20 °C. The dimensional variations of the different mortars are shown in Fig. 4.

Fig. 4 points out that the mortar containing polluted sand (4% plaster) developed continuous swelling, reaching 915 μm/m at 90 days of age. For pure or treated sand, swelling was stabilized after 7 days of immersion in water. The swelling obtained at 90 days for the different mortars is presented in Table 3.

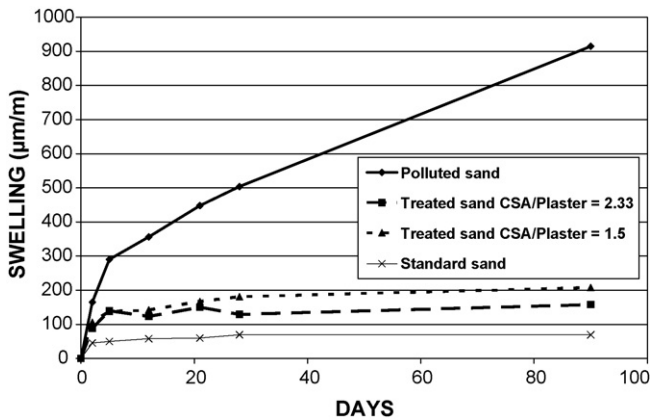


Fig. 4. Swelling of mortars cast with treated sand vs. time.

Table 3 Swelling of mortars after 90 days of immersion in water

Type of sand	Swelling at 90 days (μm/m)
Pure	69
Polluted (4% plaster)	915
Treated CSA/plaster = 2.33	158
Treated CSA/plaster = 1.5	208

Table 3 proves the efficiency of the treatment. Adding CSA to plaster reduces swelling of the mortars by about 80%.

The 90-day compressive strength of the different mortars is shown in Table 4. The higher quantity of mixing water in mortars containing treated sands explains the lower strength obtained by these mortars.

Table 4 90-Day compressive strength of mortars (first approach)

Type of sand	Compressive strength (MPa)
Pure	76
Polluted (4% plaster)	83
Treated CSA/plaster = 2.33	49.4
Treated CSA/plaster = 1.5	37.8

Table 5 Composition of mortars prepared with treated plaster (g)

Component	CSA/plaster		
	1.5	2.33	4
Standard sand	1222	1185	1117
Treated plaster	128	164	233
NPC CEM I 52.5	450	450	450
Water	225	225	225

Table 6 Swelling observed at 90 days with the two types of treatment

Type of treatment	CSA/plaster		
	1.5	2.33	4
Treated sand	208	158	n.a.
Treated plaster	210	195	170

4.2. Results of the second approach

Plaster was hydrated in the presence of CSA at W/S = 0.35 in the following proportions: CSA/plaster = 1.5, 2.33 and 4. After 7 days of hydration in plastic bags, pastes were milled to get particles smaller than 200 μm. These fine particles were introduced in sand to prepare standard mortars with NPC. The composition of mortars is shown in Table 4. The quantity of plaster present in each mortar was 4%.

The swelling of mortars immersed in water is presented in Fig. 5. The swelling observed with such mortars was in the same range than that observed for mortars cast with treated sand, as shown in Tables 5 and 6.

As shown in Table 7, the second approach allows better compressive strength. This approach keeps the W/C constant and therefore, there is a drastic increase in the compressive strength:

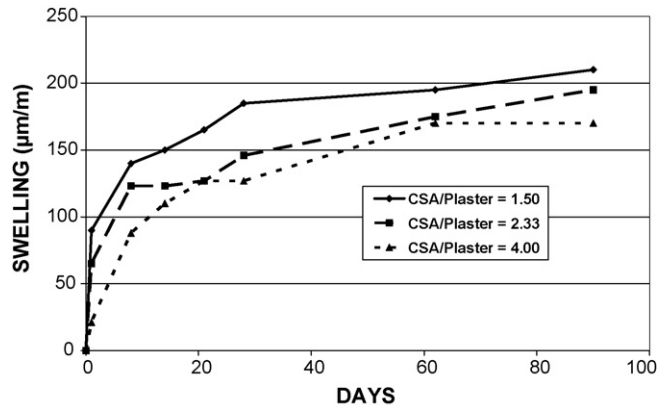


Fig. 5. Swelling of mortars cast with treated plaster vs. time.

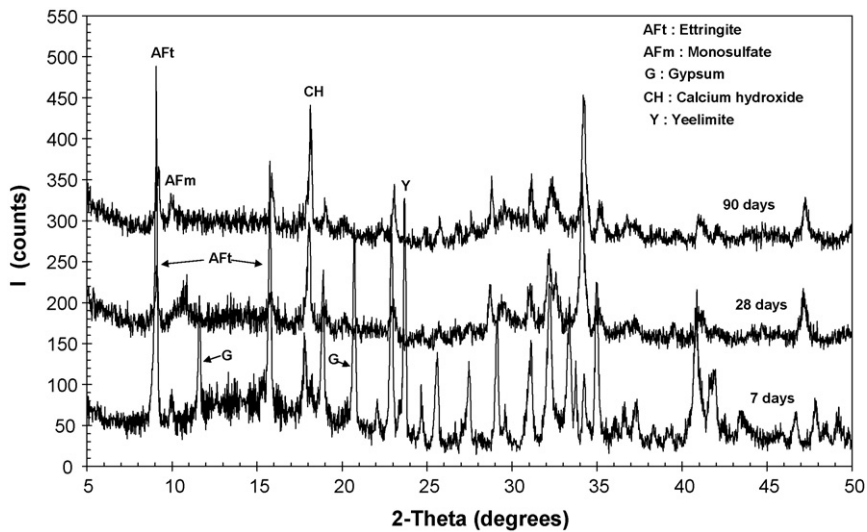


Fig. 6. Products of hydration in mortars cast with treated plaster: CSA/plaster = 1.5.

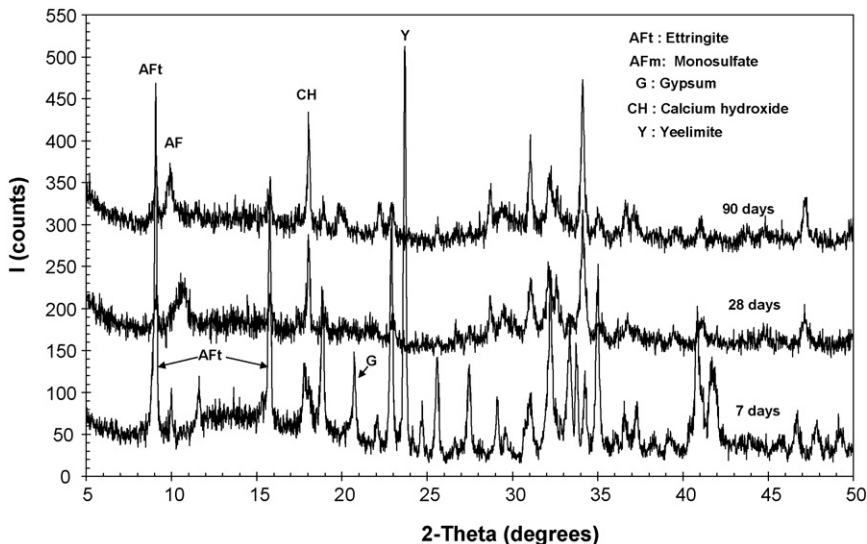


Fig. 7. Products of hydration in mortars cast with treated plaster: CSA/plaster = 2.33.

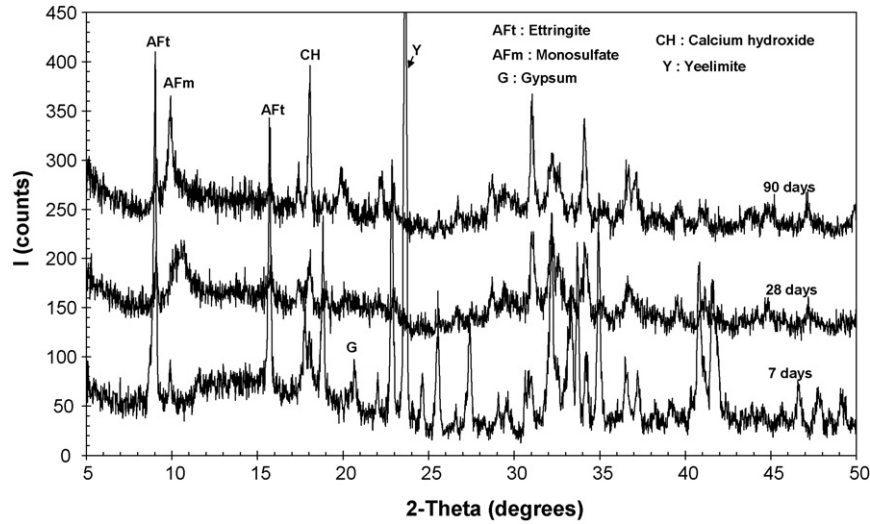


Fig. 8. Products of hydration in mortars cast with treated plaster: CSA/plaster = 4.

Table 7
90-Day compressive strength obtained with the two types of treatment

Type of treatment	CSA/plaster		
	1.5	2.33	4
Treated sand	49.4	37.8	n.a.
Treated plaster	73.8	69.5	67

- +49% for CSA/plaster = 1.5,
- +84% for CSA/plaster = 2.33.

The products of hydration appearing in these mixtures until 90 days are shown in Figs. 6–8. Gypsum is present at 7 days but disappears at 28 days to produce ettringite and some monosulfate. In all mixtures, yeelimite is entirely consumed at 28 days. The amount of monosulfate increases as the CSA/plaster ratio increases. The SEM investigation confirms these results, as shown in Figs. 9 and 10, which perfectly point out the presence of monosulfate in the matrix at 90 days of age.

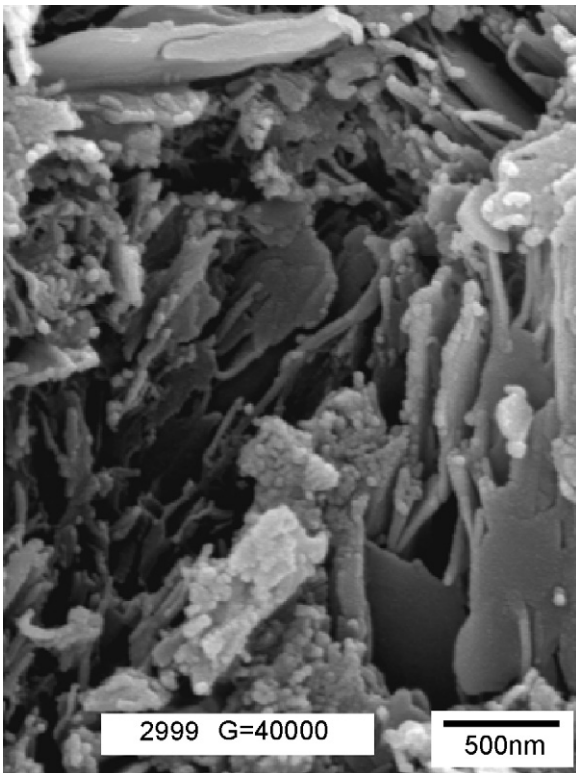


Fig. 9. Presence of monosulfate in mortars cast with treated plaster (90 days): CSA/plaster = 4.

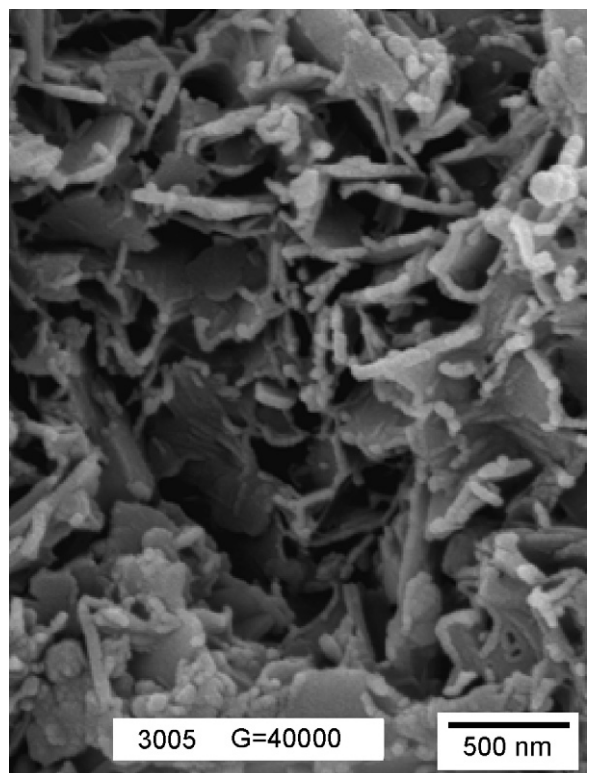


Fig. 10. Presence of monosulfate in mortars cast with treated plaster (90 days): CSA/plaster = 2.33.

5. Conclusions

The use of calcium sulfoaluminate clinker (CSA) is efficient to stabilize the swelling of mortars containing sand polluted by plaster. The consumption of plaster is completed when the ratio between CSA and plaster reaches 4. The reduction of swelling is effective for CSA/plaster values higher than 1.5: the swelling drops by 80%. Two ways of treatment are possible: either treating directly the polluted sand or separating plaster from the sand and treating this plaster by CSA before re-introducing it in mortar. This second treatment keeps the W/C constant and allows better strength. The microstructural investigation shows that gypsum is entirely consumed at 28 days to produce ettringite and monosulfate. The quantity of monosulfate increases as the CSA/plaster ratio increases.

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