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The influence of mineral admixtures on sulfate resistance of limestone cement pastes aged in cold $MgSO_4$ solution

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Abstract

The influence of slag (S), fly ash (FA) and silica fume (SF) on the sulfate resistance of limestone cements was evaluated. Hardened pastes were exposed to $MgSO_4$ solution at 5 °C. Visible changes of the samples during the exposure were followed. Absorption of sulfate was measured and changes in mineralogical composition were evaluated by thermogravimetric analysis and X-ray diffraction (XRD). It was found that among admixtures used, only the addition of silica fume to limestone cement significantly improved its sulfate resistance. Cement with lower contents of C_3A and C_3S also showed favorable performance compared to cement having higher contents of these minerals. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Thermal analysis; Limestone cements; Sulfate attack; Blended cement

1. Introduction

The usage of limestone cements and the usage of limestone powder in concrete have tremendously increased over the last few years. Taking into account that EN 197-1 was harmonized in 2000 by CEN, one should expect an even further rise of limestone usage for these purposes. Limestone is used not only for low-performance concrete and applications but also for advanced applications and high-performance concrete [1–4]. The application of limestone powder in concrete also increases the probability of sulfate attack, associated with thaumasite formation, at low temperature under humid conditions.

When an appropriate source of carbonate ions such as limestone powder is present in cement paste mortar or concrete and when they are in humid and cold environment, thaumasite could form as a result of sulfate attack [5–15] through one of the following reactions (Reactions (1)and (2)):

$$C_3S_2H_3 + C\overline{C} + 2C\overline{S}H_2 + \overline{C} + 23H \rightarrow 2(C\overline{C} \cdot CS \cdot C\overline{S}H_{15}) \qquad (1)$$

$$C_3A \cdot 3C\overline{S} \cdot H_{32} + C_3S_2H_3 + 2C\overline{C} \rightarrow 2(C\overline{C} \cdot CS \cdot C\overline{S}H_{15}) + C\overline{S}H_2 + AH_3 \qquad (2)$$

Whereas conventional sulfate attack targets primarily the aluminate phase, the thaumasite form of sulfate attack involves a process where nonbinder material forms from C-S-H, which is the main binder in cement-based materials. The whole mechanism of thaumasite formation is still not fully understood. Notably the knowledge of the possible influence of different mineral admixtures on the sulfate resistance of limestone cement seems to be rather incomplete and is certainly not very extensive. Some authors suggested that the presence of mineral admixtures like blast furnace slag (S), fly ash (FA) and silica fume (SF) in limestone cement could improve the resistance to the thaumasite form of sulfate attack [6]. Crammond and Halliwell [16] studied the influence of fly ash and blastfurnace slag on sulfate resistance of limestone-filled mortars at low temperatures. They found that slag improved the resistance to the thaumasite form of sulfate attack but fly ash did not. Zelić et al. [17], for example, studied the influence of silica fume addition on the sulfate resistance of limestone cement at room temperature. Bensted and Munn [18] critically discussed the results published by Zelić et al. [17] and found that obtained data are very valuable but

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Table 1
Cement mixtures with different mineral admixtures and cement types

Sample	Cement	Limestone (%)	Mineral admixture
1	100% OPC	0	0
2	80% OPC	20	0
3	85% OPC	0	15% S
4	65% OPC	20	15% S
5	85% OPC	0	15% FA
6	65% OPC	20	15% FA
7	90% OPC	0	10% SF
8	70% OPC	20	10% SF
9	100% SRPC	0	0
10	80% SRPC	20	0

S = slag; FA = fly ash; SF = silica fume; OPC = ordinary Portland cement; SRPC = sulfate-resistant Portland cement.

stressed that since the thaumasite formation seemed to be the most critical problem in the performance of limestone cement under sulfate attack, the data would only be complete if experiments were also performed at low temperatures.

Taking into account all these facts, it would be extremely important to perform further experiments to enlarge the knowledge about the influence of mineral admixtures on the performance of limestone cement under sulfate attack at low temperature. If admixtures have any positive effect on the sulfate resistance of limestone cement, it will be very convenient to design mixtures with specified properties just by mixing limestone cement with an appropriate admixture.

2. Methods

Ten different mixtures were prepared according to Table 1. Among these mixtures, five contained 20% of limestone powder while others were reference samples. Blastfurnace slag, fly ash and silica fume were used as mineral admixtures. Two different types of cement were used in these mixtures. The chemical analyses and characteristics of these two cements and of mineral admixtures used are shown in the Table 2.

Mixtures were mixed with water in W/C ratio of 0.5. Then, pastes were molded into plastic cylindrically shaped molds and tightly closed by rubber stoppers. After 28 days of aging at room temperature ($T = 20 \pm 1$ °C) and in humid atmosphere (RH = 50–70%), test prisms were separately immersed into 2% $MgSO_4$ solution. Test prisms were approximately 9 mm in diameter and 80 mm in height. Immersed samples were put into the refrigerator where the temperature was maintained at 5 °C. Every month, the sulfate solution was replaced by a freshly prepared one. Samples were visually inspected once a week in order to note any changes. At different time periods (3 and 5 months), the hydration was stopped by acetone drying. Crushed samples were soaked with acetone for 1 h, vacuum filtered and rinsed by diethyl ether. Samples were dried at 40 °C for 3 h and then crushed to powder. Samples were stored in tightly closed glass containers prior to analysis. Finally, exposed and unexposed samples were analyzed by thermal analysis (TA) and X-ray powder diffraction (XRD). Wet chemical procedure was used for the evaluation of sulfate absorption during the exposure. Samples were dissolved and sulfate was precipitated as $BaSO_4$, which was subsequently determined gravimetrically. The procedure was performed according to the standard for chemical analysis of cement EN 196-2.

Thermogravimetric analyses were performed on a SDT 2960 simultaneous thermal analyzer (TA Instruments, USA). After 15-min equilibration at 40 °C, the temperature was raised at 10 °C/min up to 600 °C. The analyses

Table 2
Chemical analyses and characteristics of starting materials

	OPC	SRPC	S	FA	SF	Limestone
CaO (%)	63.2	61.6	45.1	6.7	0.0	54.8
SiO_2 (%)	20.5	23.3	38.7	47.7	Min. 95	0.4
Fe_2O_3 (%)	2.9	4.9	1.7	8.4	0.3	0.1
Al_2O_3 (%)	4.8	3.8	9.2	24.7	0.1	0.1
SO_3 (%)	3.1	2.3	2.8	1.9	< 0.1	0.1
K_2O (%)	0.86	0.7	0.3	2.4	< 0.1	0.02
Na_2O (%)	0.27	0.2	0.3	2.1	< 0.1	0.04
MgO (%)	2.3	2.2	5.3	2.6	0.8	0.5
C (%)	n.d.	n.d.	n.d.	n.d.	1.5[a]	n.d.
$CaCO_3$ (%)	n.d.	n.d.	n.d.	n.d.	n.d.	97.9[a]
Mineral composition[b]						
C_3S	56.2	34.5	n.d.	n.d.	n.d.	n.d.
C_2S	16.4	40.8	n.d.	n.d.	n.d.	n.d.
C_3A	7.8	1.8	n.d.	n.d.	n.d.	n.d.
C_4AF	8.8	14.9	n.d.	n.d.	n.d.	n.d.
Specific surface area						
BET (m^2/g)	n.d.	n.d.	n.d.	n.d.	22	n.d.
Blaine (m^2/kg)	480	368	337	240	n.d.	500

n.d. = not determined.

[a] Determined by thermal analysis.

[b] Calculated according to Bogue equations.

Table 3
Visual observations on exposed samples

Sample	3 Months	5 Months
1	1	1
2	2	3
3	0	1
4	2	3
5	1	1
6	2	3
7	0	0
8	0	1
9	0	0
10	0	1

0 = no visible changes, 1 = appearance of first visible cracks, 2 = numerous cracks on the sample, 3 = totally disintegrated sample.

were performed in 100-ml/min N_2 flow. Powder diffraction was performed on a Philips PW 1710 diffractometer from 8° to 40° 2θ in step scan mode with 0.04° steps and counts of 2 s per step.

3. Results and discussion

3.1. Visual observations

Table 3 shows the results of visual observations of immersed samples after 3 and 5 months of exposure. Changes are expressed with numbers from 0 to 3, which represent the degree of damage caused by sulfate attack.

It can be seen that samples that are based on ordinary Portland cement and contained limestone exhibited lower sulfate resistance in comparison with reference samples. Considering the effect of mineral admixtures on the sulfate resistance, only silica fume significantly influenced the behavior of limestone cements. The sample containing silica fume and limestone (Sample 8) showed quite good resistance even after 5 months of exposure. On the other hand, the use of sulfate-resistant low-alite cement in combination with limestone also showed good resistance (Sample 10).

3.2. Sulfate absorption

Fig. 1 shows the contents of sulfate (expressed as SO_3) in exposed and unexposed samples. Two main points can be seen in this figure:

1. Samples with limestone absorbed more sulfate than reference samples particularly in the period between 3 and 5 months. After 5 months, they also contained more SO_3 than reference samples.
2. The addition of silica fume significantly reduced the absorption of sulfate for both samples, without and with limestone (Samples 7 and 8). After 5 months, Sample 8 (limestone + silica fume) contained less SO_3 than cement with no additions (Sample 1).

It can be concluded that among mineral admixtures used in this study, only silica fume significantly influenced the absorption of sulfate into the samples and thus the resistance to sulfate attack in tested conditions.

3.3. Thermal analysis

In order to estimate the changes of mineralogical composition in samples, thermal analysis was performed. Fig. 2

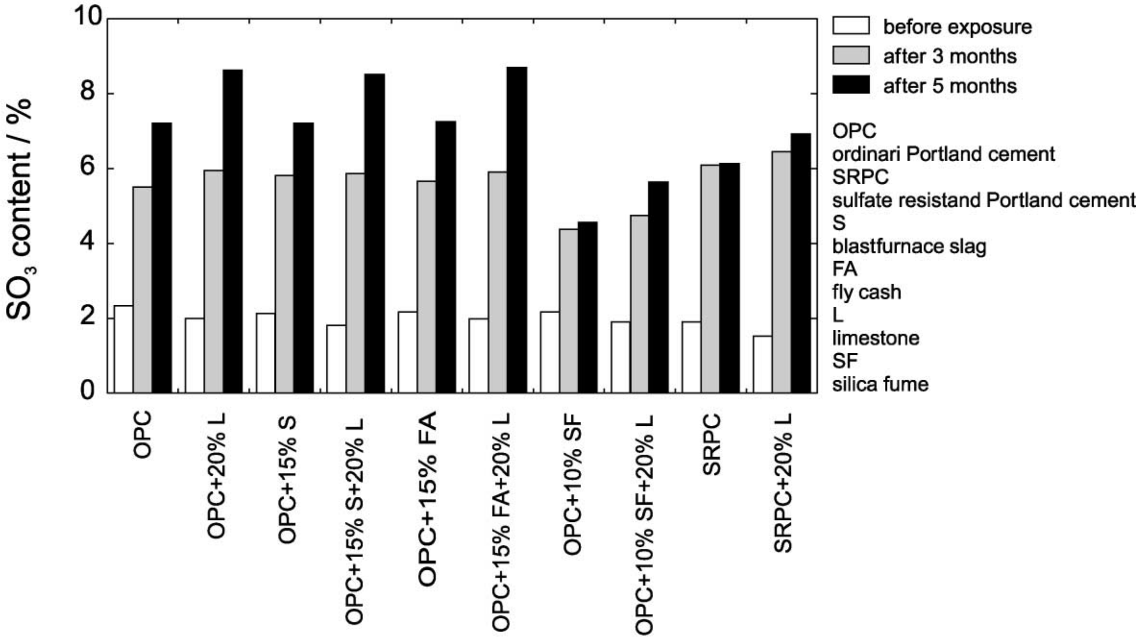

Fig. 1. The influence of cement paste composition on sulfate absorption rate.

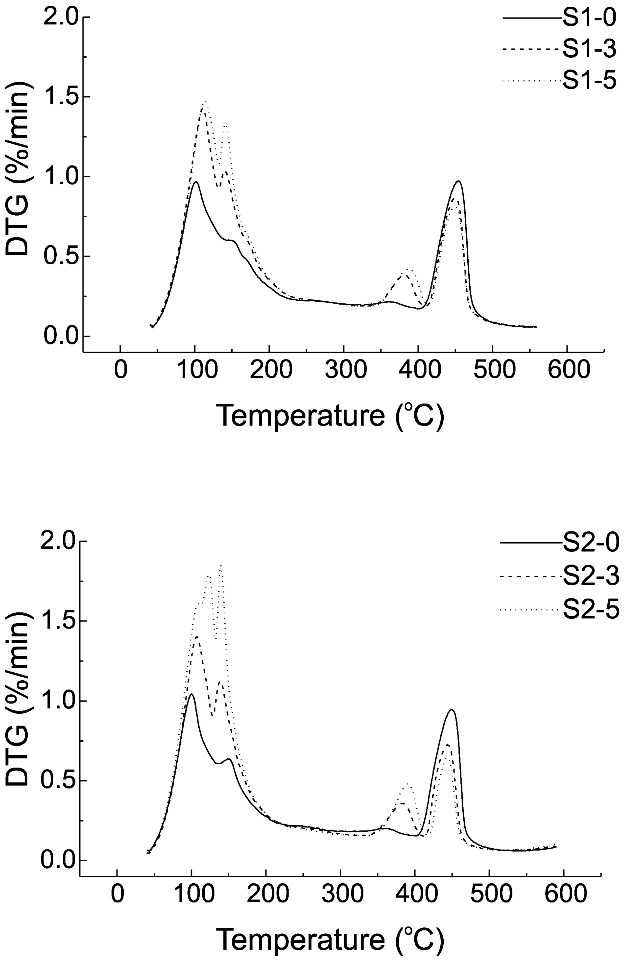

Fig. 2. DTG curves of Samples 1 and 2 after different periods of exposure to cold $MgSO_4$ solution (before exposure, after 3 months and after 5 months of exposure). The influence of limestone addition on the sulfate resistance.

shows differential thermogravimetric curves (DTG curves) of Samples 1 and 2 after different times of exposure to $MgSO_4$ solution.

Under sulfate attack in both samples, a part of $Ca(OH)_2$ (onset temperature at approximately 400 °C) was replaced by $Mg(OH)_2$ (onset temperature at approximately 350 °C) through Reaction (3):

$$Ca(OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2 \quad (3)$$

This process seems to be more pronounced in Sample 2, which is in agreement with the results of sulfate absorption. After 5 months of exposure, Sample 2 contained 4.7% of $Mg(OH)_2$, whereas Sample 1 contained only 3.5%. On the contrary, Sample 1 contained 11.2% of $Ca(OH)_2$ but Sample 2 only contained 6.9%. At temperatures up to 250 °C, where most interesting sulfate phases (ettringite, thaumasite and gypsum) loose crystal water, there were no differences between samples up to 3 months. After 5 months under sulfate attack, the peaks of Sample 2 were much more pronounced than that of Sample 1. This is again in agreement with stronger absorption of sulfate into samples containing limestone between 3 and 5 months of exposure. We can see a very strong decomposition peak at about 145 °C in Sample 2, which could be assigned to decomposition of ettringite and thaumasite. It is known from the literature that ettringite and thaumasite could not be detected separately by thermal analysis [19] and it should be borne in mind that thaumasite, as a product of deterioration process, is poorly crystallized and that it could also form solid solution with ettringite [20]. The peak at about 125 °C in the DTG curve of Sample 2 is most likely to be connected with the decomposition of gypsum. Gypsum probably appears in two reactions in limestone cements. The first reaction is related to $Ca(OH)_2$ (Eq. (3)) and the second one is connected with the formation of thaumasite (Eq. (2)). The peak (shoulder) at about 100 °C represents the decomposition of C-S-H gel. Gypsum and C-S-H gel decomposition were not well resolved up to 3 months of exposure, so only one single peak appeared in the DTG curves. In Sample 1, significantly less gypsum, ettringite and thaumasite were detected after 5 months. These results were also in agreement with results obtained by XRD analysis (Fig. 3).

In searching for the possible mechanisms of sulfate resistance improvement of limestone cement by the addition of silica fume, a DTG analysis of Sample 8 after 5 months of exposure was performed. In Fig. 4, DTG curves of Samples 2 and 8 after 5 months of exposure were compared. Sample 8 originally contained silica fume and limestone, while Sample 2 contained only limestone. The difference can be clearly seen in the region where sulfate phases in the samples (ettringite, thaumasite and gypsum) loose crystal water. Sample 8 had significantly less gypsum. Also, the peak associated with ettringite and thaumasite (140–150 °C) was significantly lower if compared with Sample 2. It can be concluded that silica fume at least suppressed the evolution of sulfate phases in limestone cements under sulfate attack and in that way also improved the sulfate resistance of limestone cement.

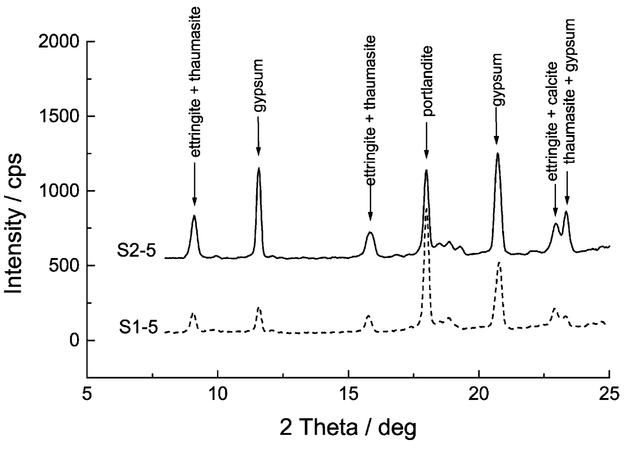

Fig. 3. XRD patterns for Samples 1 and 2 after 5 months of exposure to cold $MgSO_4$ solution.

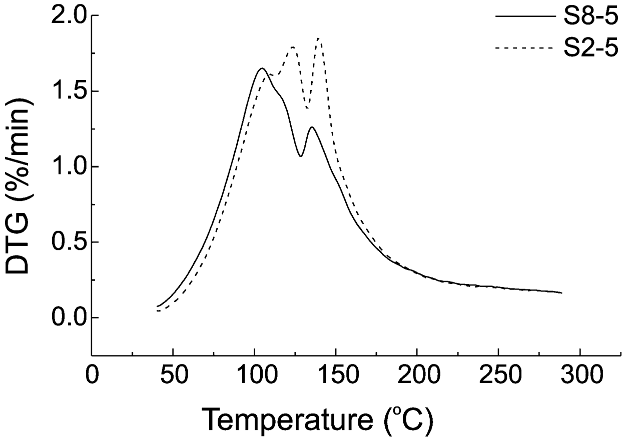

Fig. 4. DTG curves of Samples 2 and 8 after 5 months of exposure to cold $MgSO_4$ solution. The influence of silica fume on the resistance of limestone cement.

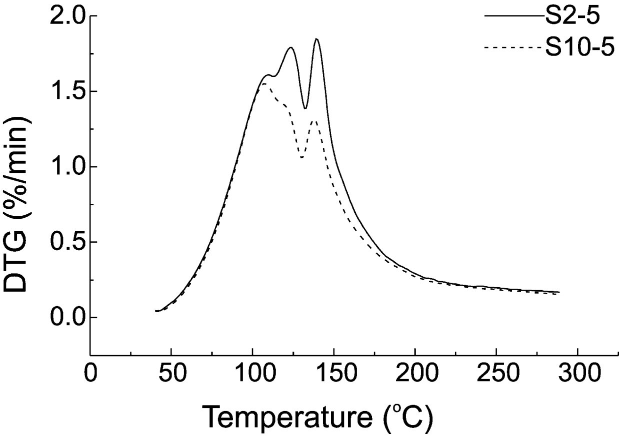

Fig. 5. DTG curves of Samples 2 and 10 after 5 months of soaking in cold $MgSO_4$ solution. The influence of clinker type on the resistance of limestone cement.

There are two possible reasons that could be proposed for the observed action of silica fume on limestone cement. Firstly, it is well known that silica fume decreases the content of $Ca(OH)_2$ in hardened cement paste and in this way also decreases the rate of $Ca(OH)_2$ conversion to $CaSO_4{\cdot}2H_2O$. This fact causes the absorption of sulfate ions into hardened cement paste to diminish and also lessens the damage associated with the crystallization of gypsum within the paste. Secondly, silica fume generally decreases the porosity of hardened cement paste [21] and thus also suppresses the mobility of sulfate ions into the paste. In this way, the absorption of sulfate can be further reduced and therefore the sulfate resistance improved. Considering the proposed reasons, one may predict that blast furnace slag and, especially, fly ash can also improve sulfate resistance of limestone cements to some extent, as both admixtures react with lime. As mentioned previously, it was reported [16] that slag addition improved sulfate resistance of limestone-filled cement mortar, but the degree of slag replacement in that research was very high compared to our mixtures. The fact that the addition of fly ash had no positive effect was also stated in that study. Probably the hardened samples should have been cured for a longer time before the exposure to show this effect, since the reaction of fly ash and slag with lime was slow compared with that of silica fume. This can be also seen from TGA measurements of portlandite content for samples after 28 days of hydration and before they were exposed to $MgSO_4$ solution (Table 4). It can be seen that samples containing silica fume had significantly less $Ca(OH)_2$ than other samples (compared with samples contained slag and fly ash).

Table 4
Content of $Ca(OH)_2$ in cement pastes after 28 days of hydration and before exposure to $MgSO_4$ solution

Sample	$Ca(OH)_2$ (%)
1	19.7
2	17.9
3	18.4
4	16.0
5	16.4
6	14.7
7	15.0
8	12.7
9	14.1
10	11.1

$Ca(OH)_2$ was determined by TGA.

Approximately the same amount of $Ca(OH)_2$ content was present in Samples 7–10. This fact can be explained by the low C_3S content of the SRPC and can also be related to the low sulfate absorption during the exposure. On the other hand, low absorption of sulfate may be the consequence of low C_3A content in these cements. The influence of different types of clinker on sulfate resistance of limestone cements can be seen from DTG analysis of Samples 2 and 10 shown in Fig. 5.

It can be seen that the combination of limestone with sulfate-resistant Portland cement (Sample 10) showed a smaller content of gypsum. Also, the peak assigned to ettringite and thaumasite was lower than in the case of Sample 2. It seems logical that less ettringite was formed since Sample 10 contained less C_3A, and less gypsum was probably formed because of the low $Ca(OH)_2$ content. On the other hand, the conversion of ettringite to thaumasite (Eq. (2)) was also lower since the ettringite content was low, and the formation of gypsum through this reaction was also decreased. Because gypsum, ettringite and thaumasite were formed to a lower extent, the structure of the pastes was less damaged and consequently the penetration of sulfate ions hindered.

4. Conclusions

Limestone cements were susceptible to sulfate attack at low temperatures and this was connected with thaumasite formation. This fact is becoming more and more important also with the increased usage of limestone cements in Europe. European standard EN 197-1 allows for the possibility of combining different mineral admixtures with limestone as major components of CEM II/-M type of cement, where the maximum permitted replacement of cement clinker is limited to 35%. Different combinations of major components offer also the possibility of optimising cement properties among which durability is one of the most important. So, it is important to know how admixtures such as slag, fly ash and silica fume influence the resistance of limestone cements to thaumasite sulfate attack in order to have the possibility of designing the optimal composition of such types of cements.

Due to the lack of relevant data in the literature, we attempted in this study to elucidate the problem, but further research work should be done in the future, since the properties of mineral admixtures also vary considerably and so few results could hardly be generalised. In addition, we also tested the influence of mineral composition of cement clinker (C_3A, C_3S) on the thaumasite sulfate attack resistance of limestone cements.

It was found that the addition of silica fume to limestone cement significantly improved its sulfate resistance. It was shown that the absorption of sulfate and the formation of sulfate minerals in the cement paste was decreased by the addition of silica fume. The use of low-content C_3A and C_3S limestone cement also showed better sulfate resistance than ordinary limestone cement. Fly ash and slag did not significantly change the sulfate resistance of the limestone cements investigated in this study.

It was concluded that thermal analysis is a valuable tool for the investigation of sulfate attack in cements and should be used in this field of applications. In combination with other methods (XRD), the formation of minerals during sulfate attack can be followed. TGA can be also easily used for quantitative measurements without the calibration of the procedure. Unfortunately, however, the minerals ettringite and thaumasite cannot be detected separately by thermal analysis.

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