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THE EFFECTS OF VARYING GYPSUM CONTENT ON THAUMASITE FORMATION IN A CEMENT:LIME:SAND MORTAR AT 5°C

M. E. Gaze
Building Research Establishment, Garston, Herts, UK

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ABSTRACT

An air entrained cement:lime:sand mortar containing high purity powdered calcite was crushed and portions stored in water together with varying quantities of gypsum. All mixes are stored at 5°C. The reaction products were monitored at intervals over a period of several months by means of X-ray diffraction analysis. Ettringite, later followed by thaumasite was produced by mixes of high gypsum content but only ettringite was obtained for the lower gypsum contents. © *1997 Elsevier Science Ltd*

Introduction

Sulphate attack in mortars and concretes is usually ascribed to the formation and expansive properties of the mineral ettringite, $3CaO.Al_2O_3.3CaSO_4.31H_2O$, a consequence of attack on the calcium aluminate hydrates of the hydrated cement. However, sulphate attack may also involve the formation of thaumasite, $CaSiO_3.CaCO_3.CaSO_4.15H_2O$, which has been discussed, amongst others in (1), (2), (3) and (4). The requirements for rapid thaumasite formation have been described as a supply of sulphate and carbonate ions in the presence of active alumina plus constant conditions of high relative humidity and a temperature of around 4°C. The formation of thaumasite is particularly pernicious because it involves attack on the calcium silicate hydrates and may ultimately reduce a mortar or concrete to a sludge.

The present work describes a study of the effects of adding different weights of gypsum ($CaSO_4.2H_2O$) to previously prepared and set mortar tablets, which were crushed before use to facilitate reaction. Each tablet/gypsum mixture was stored in water at 5 °C and the reaction products monitored at intervals using X-ray diffraction analysis (using a Siemens automated X-ray Diffractometer and CuKα radiation).

Experimental

Mortar Used. An air entrained cement:lime:sand mortar (proportions by volume 1:1:5.5) containing an ordinary portland cement with a tricalcium aluminate (C_3A) content of 8.1%, a commercially available powdered lime, ($Ca(OH)_2$) and a quartz-rich G sand. High purity powdered calcite (25% by weight of the portland cement) was added as part of the aggregate. The air content was 11.1% and the water/cement ratio = 1.1. Chemical analysis of the portland cement is given in Table 1.

TABLE 1

Chemical Analysis of Cement %

SiO_2	20.40	
TiO_2	0.26	
Al_2O_3	4.79	
Fe_2O_3	2.70	
CaO	65.80	
MgO	0.89	Bogue calculations
K_2O	0.68	C_4AF = 8.2
Na_2O	0.16	C_3A = 8.1
P_2O_5	0.03	C_3S = 62.3
Mn_3O_4	0.06	C_2S = 11.5
BaO	0.04	
SrO	0.05	
SO_3	2.63	
LOI	1.22	
Free lime	1.70	

The mortar was prepared as for the BRE mortar durability test (5), ie was laid between pairs of water saturated, surface dry bricks so as to produce 10 mm thick mortar beds which would be subjected to as little suction during laying as possible. The beds were separated from the bricks after 1 day's moist curing and then returned to moist storage. Twenty eight days after casting, the beds were cut to provide 28 x 34 mm tablets. It was calculated that each tablet contained approximately 1.8 g cement. Each tablet was subsequently ground to pass a 600 µm sieve.

Gypsum Ccontents. The amounts of reagent-grade gypsum added to the crushed set tablets were 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 2.0 and 3.0 g. The total sulphate to which the tablets were exposed was a little higher because of the sulphate content (mainly gypsum) of the portland cement itself. Chemical analysis of the cement gave an SO_3 content of 2.63% which would add the equivalent of 0.1 g gypsum per tablet to the above quantities. In the text, the mixes are referred to by their added rather than total gypsum content.

Test Method. Each tablet was crushed and kept in a plastic beaker with 200 ml of water and the requisite amount of gypsum. The beakers were covered with glass petri dishes to reduce evaporation without preventing atmospheric carbonation and stored at 5°C for 21 days. After this, the contents were removed and placed in sealed plastic jars and returned to storage at 5°C for the remainder of the test period. This routine was adopted to allow a degree of carbonation to occur since Bensted and Varma (6) reported that CO_2 absorption from the air appears to promote thaumasite formation but it was envisaged that the tablets might have to be stored for a long time, risking total carbonation.

At intervals, a small portion of the solids was removed and subjected to analysis by X-ray diffraction (XRD). Indicator papers were used to provide an approximate guide to the solution pH.

Results and Discussion

The XRD results are given in Tables 2 and 3. Ettringite was present at all the ages examined and occurred before the formation of thaumasite. This latter was first detectable for mixes containing 0.6 g or more of gypsum between days 31 and 42, in trace or small amounts. The thaumasite contents of these mixes increased with time, becoming significant at later ages.

Figure 1 shows the XRD traces for the 2.0 g mix showing the development of thaumasite over a period of time.

In contrast, thaumasite was not found at any age for gypsum contents of 0.05-0.2 g. The 0.4 g mix appeared to be a borderline case, producing only ettringite up to the late age of 70 days after which traces of thaumsite were detectable. In this case, though, there was not much increase in thaumasite content thereafter. Figure 2 shows the final XRD traces for the 0.2-0.6 g mixes (age 240 days) covering this apparent transition.

Overall, the 0.05-2.0 g group produced only small amounts of ettringite rising to just about moderate for the 0.4 g mix. The higher sulphate containing mixes produced significant amounts of both ettringite and thaumasite, the latter probably becoming predominant for the 2.0 and 3.0 g mixes. Gypsum was detectable throughout for the 2.0 and 3.0 g mixes but a decline in strength of the gypsum pattern over time indicated that even these relatively large quantities were being consumed.

Portlandite, $Ca(OH)_2$, was always present and the pH of the solutions remained high throughout at around 12.5; conditions favouring the stability of the calcium silicate hydrates. However the formation of thaumasite implies that some decomposition of the C-S-H must

TABLE 2

XRD Analysis (0.05-0.4 g Added Gypsum)

Age in days	Added Gypsum in Grams			
	0.05 g	0.10 g	0.20 g	0.40 g
9	E (v small)	E (small)	E (small)	E (small)
21	E (small)	E (small)	E (small)	E (small)
42	E (small)	E (small-mod)	E (small)	E (small-mod)
52	E (small)	E (small-mod)	E (small-mod)	E (small-mod)
70	E (small)	E (small)	E (small-mod)	E (moderate) T (trace)
100	E (small)	E (small)	E (small-mod)	E (moderate) T (trace)
140	E (small)	E (small)	E (small-mod)	E (moderate) T (trace)
240	-	-	E (small-mod)	E (moderate) T (trace)

E = Ettringite; T = Thaumasite

TABLE 3

Age in days	Added Gypsum in Grams			
	0.60 g	0.80 g	2.00 g	3.00 g
9	E (small) G (small)	E (small) G (moderate)	E (small) G (v strong)	E (small) G (v strong)
21	E (moderate)	E (moderate) G (small)	E (moderate) G (v strong)	E (small-mod) G (v strong)
42	E (mod-strong) T (small)	E (mod-strong) T (small-mod)	E (strong) G (strong) T (small-mod)	E (moderate) G (v strong) T (small-mod)
52	E (mod-strong) T (small)	E (strong) T (small-mod)	-	-
59	-	-	E (strong) G (moderate) T (moderate)	E (strong) G (strong) T (moderate)
70	E (strong) T (moderate)	E (strong) T (strong)	E (small-mod) G (moderate) T (strong)	E (mod-strong) G (strong) T (strong)
100	E (small) T (strong)	E (strong) T (strong)	E (small-mod) G (small) T (strong)	E (mod-strong) G (mod-strong T (strong)
140	E (strong) T (strong)	E (strong) T (strong)	E (mod-strong) G (v small) T (v strong)	E (mod-strong) G (moderate) T (v strong)
240	E (strong) T (strong)	-	-	-

E = Ettringite; T = Thaumasite; G = Gypsum

have occurred even under these conditions. It is generally considered that calcium sulphate does not attack the C-S-H but the present work would suggest that this is not necessarily true when calcite is present.

No monosulphate was found even in low gypsum mixes but Kuzel and Pollman (7) have reported that, where the composition is such that the conversion of ettringite to monosulphate might be expected, this is suppressed in the presence of carbonate ions. Instead, ettringite is preserved with the crystallisation of hemicarbonate, $3CaO.Al_2O_3.\frac{1}{2}CaCO_3.\frac{1}{2}Ca(OH)_2.11.5H_2O$, monocarbonate, $3CaO.Al_2O_3.CaCO_3.11H_2O$ or both. Two very small peaks, which could have indicated the presence of trace amounts of monocarbonate were found in all the mixes up to and including 0.4 g. These persisted at all ages for the 0.05 and 0.1 g mixes, up to 21 days for the 0.2 but only 9 days for the 0.4 g mix. These peaks are illustrated in Figure 3 which shows the relevant portion of the XRD trace for the 0.05 g mix at age 140 days together with the two strongest lines of the monocarbonate standard.

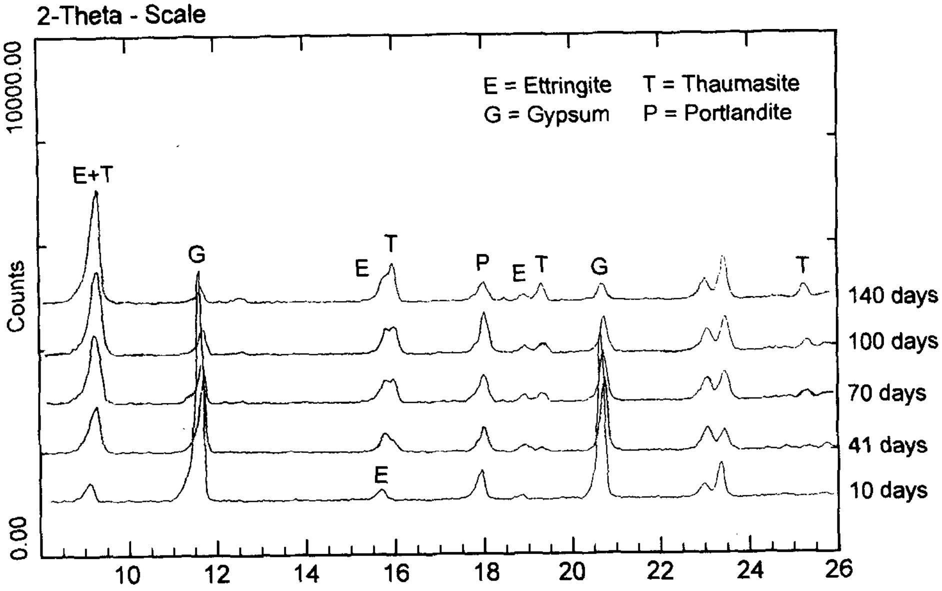

FIG. 1.
Development of thaumasite in 2.0 g mix.

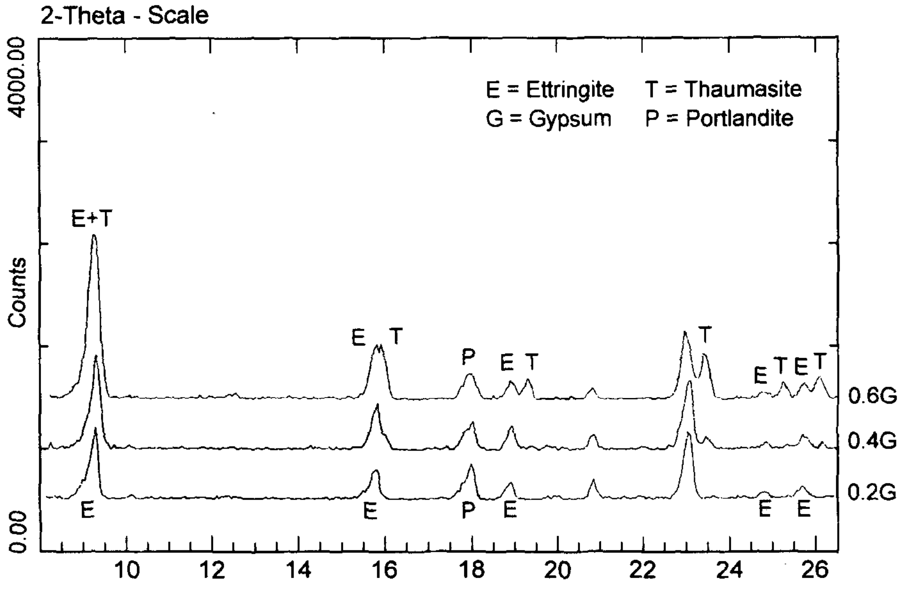

FIG. 2.
0.2 g, 0.4 g, 0.6 g gypsum mixes age 240 days.

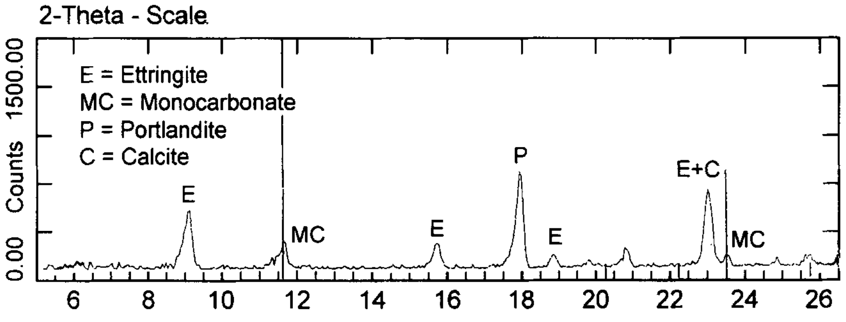

FIG. 3.
0.05 g mix age 140 days.

The results suggest that a minimum amount of sulphate is required for the production of thaumasite which, in the present case, was found to lie somewhere between 0.2-0.4 g added gypsum, or, if the cement's SO_3 content is included, 0.3-0.5 g. This gives a reasonable correlation with the amount of gypsum required to totally convert the cement's C_3A/alumina content to ettringite. Each tablet contained approximately 1.8 g cement which would contain 0.15 g C_3A and a total alumina content of 0.086 g, the former requiring 0.29 g and the latter 0.44 g gypsum for complete conversion to ettringite.

If thaumasite is formed via the conversion of ettringite then this could suggest that only relatively pure ettringite in a stable situation is suitable for conversion. It could also suggest that the conversion actually requires the presence of excess sulphate ions. For instance, the overall compositional changes involved are the import of silica and calcium carbonate and the expulsion of alumina. If the reaction mechanism was such that the latter could combine with lime and calcium sulphate to form additional ettringite then the alumina would effectively be 'rehoused' in the same situation in which it started, the overall change being represented as: -

$$\text{Ettringite} + \left(SiO_2 + CaCO_3\right) \xrightarrow[Ca\left(OH_2\right)]{CaSO_4} \text{Thaumasite} + \text{additional Ettringite}$$

The work suggests that there are some cases where the quantity of sulphate is such that only ettringite can form but this does not imply that any particular concentration or sulphate class, as defined in BRE Digest 363 (8), would confer immunity to the thaumasite form of sulphate attack. In the field, continuous absorption of sulphate is possible so that significant quantities may be taken up over a period of time, even from a low sulphate environment (9). This was not generally the case in the present work, since the solutions were not replenished as the gypsum was absorbed. The 2.0 and 3.0 g mixes could be considered as exceptions to this since solid gypsum was present throughout and therefore replenishment of the solution could take place. Interestingly, the starting sulphate concentration of the solution would have been that of a saturated gypsum solution and therefore designated as a moderately aggressive Class 2 situation (8). Nevertheless continuous absorption resulted in a large sulphate uptake and abundant ettringite and thaumasite formation.

Although the tests were carried out on a crushed building mortar a similar sequence of events was indicated for a deteriorated concrete foundation examined by Crammond and Halliwell (9). This contained a limestone aggregate and had been exposed to groundwater containing primarily calcium sulphate. These authors found that early stages of attack on this concrete were characterized by the formation of ettringite, later stages by the presence of thaumasite.

Conclusions

1. The work described indicates that a minimum amount of sulphate is required for thaumasite formation. This appears to be associated with the alumina content of the cement.
2. In the samples examined during the course of this investigation, the formation of thaumasite was preceded by ettringite formation.
3. Thaumasite formation, which implies some C-S-H breakdown, occurred in solutions of high pH where free lime was also present. This suggests that calcium sulphate can cause attack on the calcium silicate hydrates under some circumstances.

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