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Cement & Concrete Composites 25 (2003) 857–860

Cement & Concrete Composites

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Formation of thaumasite in synthetic cement mineral slurries

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Abstract

In order to investigate the effect of alite polymorphism on the susceptibility of cements to thaumasite formation, slurries were prepared from magnesium sulphate solution and mixtures of calcium carbonate with synthetic cement preparations plus additions of 0%, 1% or 2% w/w alumina. Two synthetic cement preparations were used; a co-prepared mixture of monoclinic alite ($\sim C_{54}S_{16}AM$) with β-C_2S (designated A) and a ~99% pure, primarily triclinic C_3S (designated B). The slurries were prepared after the manner of Gaze [Cement Concrete Res. 27(2) (1997) 259] and maintained in a state of continual agitation at 5 °C for 100 days. After this period, the slurries were dried and characterised using X-ray diffraction. In slurries made with A, both ettringite and thaumasite (or a solid solution thereof) were detected, the apparent ratio of the former to the latter increasing with alumina addition. No gypsum was detected. In slurries made with B, the only sulphate phase detected was gypsum.

This interesting observation leads to a number of avenues for discussion;

- that alumina must be present in sufficient quantities *within the clinker or gel structure*, rather than as an addition, to initiate TF;
- that TF is only initiated by C_2S, not C_3S;
- that TF cannot be initiated by triclinic C_3S.

Keywords: Alite; Alumina; Monoclinic; Triclinic; Slurry

1. Introduction

The thaumasite form of sulfate attack has been the subject of much investigation by the cement research community over the last few years and an expert group has recently reported [1]. The laboratory conditions required to optimise formation of thaumasite from normal cementitious materials, aggregates, additives and sulfate sources have now been clearly established [2,3]. The role of some of the additives, in particular alumina, is still not fully clear. The intention in this study was to study thaumasite formation in slurries formed using 'synthetic' calcium silicate minerals, in the absence of C_3A, C_4AF or other major impurities present in Portland cements. It was intended also to determine the effect of various additions of active alumina.

2. Materials and methods

Two samples of synthetic cement materials were used in the study. The first (designated type A) was a mixture of monoclinic alite ($\sim C_{54}S_{16}AM$) and belite prepared according to Lambert [4]. The composition of the mixture used in this investigation was shown by means of quantitative XRD and confirmed by NMR analysis to be approximately 50:50 alite:belite. The average molar C:S ratio was 2.55 (standard deviation [SD] 0.43) according to EDXA performed by BRE (Table 1). The second sample (designated type B) was a nominally pure triclinic C_3S supplied by BRE. Subsequent detailed XRD analysis of the 31.5–33° 2θ region after Taylor [5] indicated that some monoclinic alite was probably also present in the sample. The average molar C:S ratio was 3.44 (SD 0.44), similarly determined by EDXA, indicating some enrichment with respect to calcium although no free lime was detected in the samples.

The method used to form thaumasite was based on that of Gaze [6]. Pastes samples containing approximately

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doi:10.1016/S0958-9465(03)00112-4

Table 1
EDXA spot analyses of synthetic cement materials (% w/w; [standard deviation])

	CaO	SiO_2	Al_2O_3	MgO
Type A[a]	60.3 [3.7]	25.7 [3.1]	1.67 [0.63]	0.40 [0.30]
Type B[b]	69.1 [5.1]	21.8 [2.7]	0.30 [0.28]	0.03 [0.04]

[a] 15 spots analysed; one MgO outlier (Grubb's ESD, $\alpha = 0.05$) removed from statistics.

[b] 15 spots analysed; one Al_2O_3 and one SiO_2 outlier (both $\alpha = 0.01$) removed.

1 g of cementitious material were made with additions of 0%, 1% or 2% w/w of alumina and 100% w/w calcium carbonate, allowed to harden and then ground to pass a 600 μm sieve. The samples were then placed into 60 ml of $MgSO_4$ solution at a concentration of 0.42% SO_4^{2-}. The samples were maintained at 5 °C and permanently agitated for a period of 100 days. After this period, approximately 8 ml of the resultant slurry was dried at BRE and used to form a thin film on a silica slice suitable for XRD analysis (5–50° 2θ, $\lambda = 1.5406$ Å). Phases of interest were calcite, gypsum, ettringite and thaumasite and standard JCPDS masks were used to help analyse the traces.

3. Results

The results of the XRD analysis (i.e. the requisite portions of the XRD traces) for the type A and type B slurries are shown in Figs. 1 and 2 respectively, the percentage figure referring to the amount of alumina addition w/w cementitious material. Masks have been added to the traces, indicated by the vertical lines. In Fig. 1, the masks correspond to ettringite and thaumasite (solid/dashed lines respectively); in Fig. 2, the mask indicates gypsum. No residual unhydrated type A or type B cementitious material was detected indicating complete hydration.

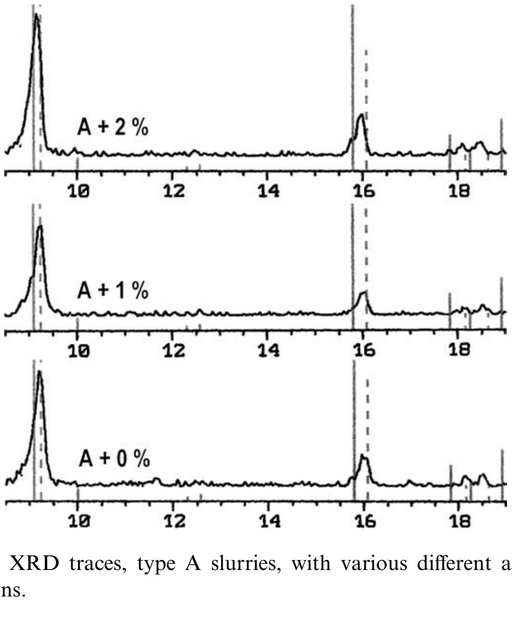

Fig. 1. XRD traces, type A slurries, with various different alumina additions.

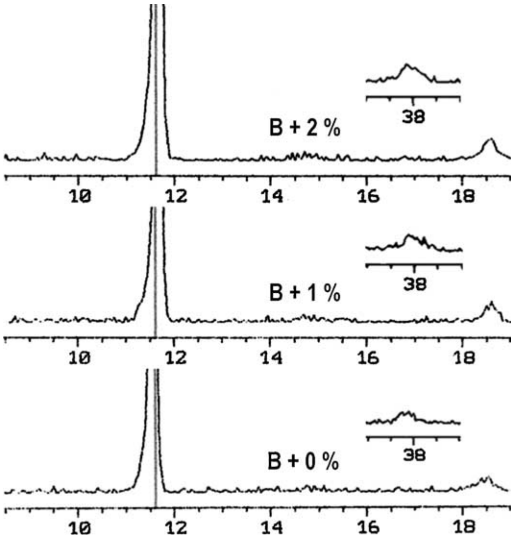

Fig. 2. XRD traces, type B slurries, with various different alumina additions.

In type A slurries with no added alumina, thaumasite was detected. With an addition of 1% alumina, thaumasite with small amounts of ettringite were detected, as signified by the shoulder on the left of the peak at ~9°. With an addition of 2% alumina, the main peaks at both ~9° and ~16° appeared to have shifted markedly to the left and the peak at ~16° showed a clear ettringite shoulder. Thus both ettringite and a phase probably consisting of either a mixture or a solid solution of thaumasite and ettringite were present. In all cases, residual calcite was also readily detected which interfered with the most convenient peaks for thaumasite/ettringite distinction, hence the concentration on the ~9° and ~16° 2θ areas of the diffractograms. No residual alumina or secondary gypsum was detected.

In type B slurries, no ettringite or thaumasite were detected regardless of alumina addition, the only sulfate phase detected was gypsum and there were no significant differences in gypsum content between the three traces. In samples with added alumina, small, broad peaks were evident at ~18.5° and ~38° which may indicate the presence of poorly crystalline gibbsite or partially ordered AH_3 gel and, if so, explain the fate of the alumina. There appeared to be stronger residual calcite traces compared to those found in the type A samples.

4. Discussion

The finding that the different cement minerals behaved so very differently under thaumasite-inducing conditions was unexpected. However a number of hypotheses may be advanced to account for the behaviour. One would be simply that thaumasite formation (TF) cannot be initiated by triclinic C_3S but this seems implausible for two main reasons. First, according to a recent chemical model [2] the necessary pre-cursors for TF are C–S–H gel and CH (plus sources of carbonate, sulfate and water) rather than unhydrated C_3S. It would not be expected that the hydration products of the triclinic form of C_3S are sufficiently different from those of the monoclinic form such that the TF reaction is effectively suppressed. Similar arguments would also seem to preclude the hypothesis that only C_2S, as present in type A samples, can initiate TF since it is generally accepted that C_2S hydration produces similar C–S–H gel to C_3S hydration although markedly less CH is produced. However, it is known [7] that a small proportion of the CH produced in hydrating cement pastes is cryptocrystalline and intimately mixed with the C–S–H gel; this is not the case when hydrating pure triclinic C_3S. If CH is a reactant phase in TF, then Portland cement pastes (closer to type A) might be more susceptible than pure triclinic C_3S pastes (type B). Secondly, XRD suggests that in fact some monoclinic C_3S was present in type B samples and some TF might thus have been expected even if the triclinic form were unreactive.

A more defensible argument would concern the aluminate content of the two cementitious materials. The role of aluminium in thaumasite formation is still debated. Hartshorn et al. [2] have surmised that, in sulfate-exposed pastes containing calcium carbonate, TF can only begin once all the C_3A has been exhausted during conversion to ettringite and/or monosulfate, in effect citing an alumino-sulfate as a necessary pre-cursor phase for TF. Taylor [8] suggested that 0.4–1.0% 'reactive alumina' in addition to the appropriate ions may be an important component of mixtures in which TF occurs readily at 4 °C, noting that 'a little Al^{3+} may be essential'. Benstead [9] stated that at 0–5 °C, the starting materials for TF should include hydraulic calcium silicates, a source of calcium sulphate and a source of calcium carbonate; no mention was made of aluminates. Barnett & Macphee [10] showed that when preparing thaumasite from calcium oxide with sodium silicate, sulfate and carbonate TF was increased 5-fold by the use of soluble sodium aluminate cf. Al_2O_3. The EDXA analysis of the anhydrous materials used in this study revealed that the A:C ratios of type A and B powders were approximately 0.016 and 0.002 respectively or, expressed as percentages by weight of alumina, around 1.7% and 0.3%. These figures suggest that it is not sufficient to have reactive alumina available as an additive (as evidenced by the non-reaction of type B samples). Aluminium ions appear to have to be present within a hydraulic phase and thus be available within the hydrated C–S–H structure (substituting for Si in bridging tetrahedra [11]). Exactly how the Al facilitates the thaumasite reaction is still unclear. It may be that ettringite is a necessary pre-cursor or perhaps Al^{3+} ions somehow promote the formation of the unusual $[Si(OH)_6]$ octahedra central to the thaumasite structure? This latter thesis is surprising to researchers in other fields concerned with six-coordinated silicon, who find that alumina is detrimental to its formation [12].

It should be noted here that it is perfectly possible that thaumasite might be formed in type B slurries after sufficient time. Ironically, thaumasite formation, despite being slow even by cement chemistry standards, is actually among the faster geological reactions; the formation of thaumasite in the volcanoclastic sediments of the Upper Tonga Trench is thought to have taken "... a short period of time e.g. ⩽1000 years" [13].

5. Conclusions

In slurries prepared from either pure predominantly triclinic-C_3S or from monoclinic-alite/belite mixtures, with various additions of alumina, exposure to conditions known to initiate thaumasite formation in cement pastes caused only the alite/belite samples to form thaumasite within 100 days. Ettringite was also formed in these samples when alumina had been added. In the pure C_3S samples, only gypsum was produced. It is suggested that the alumina content of the pure C_3S was insufficient to catalyse thaumasite formation over this timescale and the added alumina had no effect. Thus it appears that aluminium ions must be present within the structure of the anhydrous calcium silicate minerals if thaumasite is to be formed readily.

Acknowledgements

We extend our thanks to M. Halliwell, N. Crammond and K. Quillin at the BRE and A. Brough at Leeds University for their help during this project.

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