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Cement & Concrete Composites 22 (2000) 209–222

Cement &
Concrete
Composites

The formation of thaumasite in a cement:lime:sand mortar exposed to cold magnesium and potassium sulfate solutions

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Received 13 September 1999; accepted 20 December 1999

Abstract

This paper, which is presented in two parts, describes the performance of a laboratory-prepared masonry mortar after exposure to cold magnesium and potassium sulfate solutions. The objective of the study was to investigate the conditions under which the thaumasite form of sulfate attack can affect masonry mortars. This work was funded by the UK Department of the Environment, Transport and the Regions (DETR) and information contained in the following paper was included in the recently published DETR Report on the thaumasite form of sulfate attack (Department of the Environment, Transport and the Regions. The thaumasite form of sulfate attack: risks, diagnosis, remedial works and guidance on new construction. Report of the Thaumasite Expert Group, DETR, January 1999).

In Part I of the investigation, mortar tablets ($10 \times 28 \times 34$ mm^3) were prepared from a 1:1:5.5 cement:lime:sand, air entrained mortar to which powdered calcite had been added during mixing. Each mortar tablet was crushed before exposure in order to facilitate reaction and stored fully immersed in 200 ml of solution for several months. Two sets of storage conditions were used – one where the experiment was exposed to the atmosphere and the other where atmospheric exposure was prevented. The test material was sampled at intervals for analysis by X-ray diffraction to determine the nature of the products and the sequence of chemical events involved. Thaumasite was readily produced in both magnesium and potassium sulfate solution, following the prior formation of ettringite. It was not formed under conditions where ettringite was unstable, suggesting some involvement of the latter in the thaumasite forming process. It was also found that a rapid type of carbonation prevailed in potassium sulfate solution exposed to the atmosphere. This process, which has been called 'alkali carbonation', destroyed both ettringite and thaumasite.

In Part II of this investigation, the same mortar tablets were used but this time the performance of the whole tablets of uncrushed mortar was tested in the same sulfate solutions so that the physical effects of sulfate attack on hardened mortars could be assessed. The test method used was similar in principle to the BRE mortar durability test which combines the cyclic administration of sulfate solution with intermediate drying to simulate the processes occurring in practice in brickwork mortar. X-ray diffraction analysis of the tablets was carried out when first signs of sulfate attack were observed and also after severe damage had occurred. These showed that early damage appeared to be mainly due to ettringite formation but both ettringite and thaumasite were involved at the severe damage stage. Some non-calcite containing mortars were also examined during this phase of the investigation and results have found them to be slightly less durable than their added-calcite counterparts, particularly in weak magnesium sulfate solution. This was attributed to the improved impermeability of added-calcite mortars rather than any inherent chemical resistance to sulfate attack.

Even though Part I concentrated purely on the 'chemical' interactions between mortar and solution, the reaction products and sequences were found to be very similar to those discovered in Part II, where physical barriers to sulfate ingress had to be overcome prior to chemical attack. This provides confirmation that any masonry mortar can potentially deteriorate in the presence of excess sulfates providing the temperature is low, the mortar contains an available source of calcium carbonate, the brickwork is consistently wet and the pH of the reaction zone is maintained at 10.5 or above. Having said this, the extent of sulfate attack of brickwork in the field is small and should not become a major problem in practice, provided the current recommendations [Department of the Environment, Transport and the Regions. The thaumasite form of sulfate attack: risks, diagnosis, remedial works and guidance on new construction. Report of the Thaumasite Expert Group, DETR, January 1999] (especially the avoidance of using sulfate-bearing bricks in exposed situations) are adhered to. © 2000 The Building Research Establishment. Published by Elsevier Science Ltd. All rights reserved.

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PII: S0958-9465(00)00002-0

1. Part I

1.1. Introduction

Sulfate attack in mortars and concretes due to the expansive formation of ettringite is well known but, more recently, another type of sulfate attack has been identified [1]. This is caused by the formation of thaumasite, ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$), which requires the presence of both sulfate and carbonate ions and is associated with cold, wet conditions. In masonry construction, the source of sulfate ions is invariably sulfate-bearing clay bricks. Carbonate ions are always present to some extent in brickwork mortars as a result of atmospheric carbonation. The calcium carbonate content of a mortar can also be substantially increased by the incorporation of limestone fillers and aggregates. Thaumasite formation also requires silica, which is acquired via attack on the calcium silicate hydrates, (C–S–H), an action, which can ultimately reduce a mortar or concrete to a sludge. It is believed that the formation of thaumasite may require the prior formation of ettringite or the presence of a source of active alumina [2].

Part I of this investigation was carried out to ascertain whether thaumasite could be obtained when a crushed cement:lime:sand mortar was subjected to attack by magnesium and potassium sulfate solutions at a temperature of 5°C. A quantity of calcite was added to the mortar during mixing to serve as a source of carbonate ions. The material was sampled at intervals and subjected to X-ray diffraction analysis, (XRD), to determine the chemical changes occurring over a period of time. A related paper has recently been published which describes a similar experiment involving saturated calcium sulfate solutions [3].

1.2. Experimental

1.2.1. Mortar used

A 1:1:5.5 (designation iii mix as defined in BS4551:1980 [4]) air entrained cement:lime:sand mortar made from a Portland cement (PC) with a tricalcium aluminate (C_3A) content of 8.1%, a commercially available powdered lime ($Ca(OH)_2$) and a quartz-rich G sand [4] was used in this study. The chemical analysis of the cement is presented in Table 1 of Ref. [3]. High purity (Analar reagent grade) powdered calcite (25% by weight of the PC) was added as part of the aggregate. A proprietary air-entraining plasticiser containing a synthetic based surfactant was included as part of the mix. The dosage added was that recommended by the manufacturer. The air content was 11.1% and the water/cement (w/c) ratio, 1.1.

The mortar was prepared as for the BRE mortar durability test [5], i.e., it was laid between pairs of water saturated, surface dry bricks to produce 10 mm thick mortar beds, subjected to low suction during laying. The beds were separated from the bricks after 1 day's moist curing, returned to moist storage for a further 27 days, then cut to provide 28 × 34 mm tablets.

1.2.2. Test method

The prepared tablets were crushed and each separately stored and totally immersed in 200 mls of sulfate solution, kept at 5°C.

The solutions used were as follows:

- solution dilMg (0.42% SO_4), contains 10.8 g/l $MgSO_4 \cdot 7H_2O$,
- solution Mg (1.99% SO_4), contains 51.3 g/l $MgSO_4 \cdot 7H_2O$,
- solution dilK (0.42% SO_4), contains 7.6 g/l K_2SO_4,
- solution K (1.99% SO_4), contains 36.25 g/l K_2SO_4.

The pH of the solutions was measured by means of indicator papers to provide an approximate guide to changes in the availability of hydroxyl ions in the reacting material.

From the reactions:

$$Ca(OH)_2 + MgSO_4 = CaSO_4 + Mg(OH)_2$$
$$Ca(OH)_2 + K_2SO_4 = CaSO_4 + 2KOH$$

it can be calculated that 200 ml of dilute solution (0.84 g SO_4) are required to react with 0.65 g $Ca(OH)_2$ and 200 ml of strong solution (3.98 g SO_4) to react with 3.07 g $Ca(OH)_2$.

Each tablet contained approximately 1.8 g cement (the hydration of which would produce a small amount of lime [1]) and 0.7 g added lime. Thus the sulfate present in 200 ml of a dilute solution would be roughly equivalent to a tablet's lime content. The same quantity of strong solution would be more than equivalent to both the free lime content plus all that combined in the cement.

Two types of storage container were used:

1. Plastic beakers covered with glass petri dishes to reduce evaporation without preventing atmospheric carbonation. Samples so stored are referred to as 'exposed'.
2. Plastic bottles with tight fitting lids so as to reduce exposure to atmospheric CO_2 to a minimum – only three of the solutions (dilMg, dilK, K) involved this type of storage. These samples are referred to as 'non-exposed'.

1.3. Results and discussion

The XRD results for the samples stored in magnesium sulfate solutions are given in Tables 1 and 2 and

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[1] Fully hydrated PC $\Rightarrow\sim$ 15–20% $Ca(OH)_2$ $\Rightarrow\sim 0.3$ g $Ca(OH)_2$ in 1.8 g of cement.

Table 1
XRD results for magnesium Sulfate samples exposed to the atmosphere

Age days	Solution dilMg			Solution Mg		
6				Calcite	(s)	pH 10.0
				Gypsum	(ms)	
				Ettringite	(t)	
				Brucite	(w)	
14	Calcite	(s)	pH 12.3	Calcite	(s)	pH 9.5
	Portlandite	(w)				
	Gypsum	(s)		Gypsum	(vs)	
	Ettringite	(mw)		Ettringite	(vw)	
	Brucite	(w)		Brucite	(w)	
20	Calcite	(s)	pH 12.0	Calcite	(s)	pH 8.7
	Gypsum	(s)		Gypsum	(vs)	
	Ettringite	(mw)		Ettringite	(w)	
	Brucite	(t)		Brucite	(w)	
29	Calcite	(s)	pH 11.8			
	Gypsum	(s)				
	Ettringite	(mw)				
	Thaumasite	(w)				
	Brucite	(w)				
33				Calcite	(s)	pH 7.7
				Gypsum	(vs)	
				Ettringite	(t)	
				Brucite	(w)	
40	Calcite	(s)	pH 11.5			
	Gypsum	(ms)				
	Ettringite	(vw)				
	Thaumasite	(ms)				
	Brucite	(w)				
48				Calcite	(s)	pH 7.7
				Aragonite	(t)	
				Gypsum	(vs)	
				Brucite	(w)	
63				Calcite	(s)	pH 7.7
				Aragonite	(mw)	
				Gypsum	(vvs)	
				Brucite	(w)	
141	Calcite	(vs)	pH 6.5			
	Gypsum	(mw)				
	Thaumasite	(ms)				
	Brucite	(w)				
197	Calcite	(vs)	pH 6.5			
	Gypsum	(mw)				
	Thaumasite	(ms)				
	Brucite	(w)				

Figs. 1–3, those for potassium sulfate solutions in Tables 3 and 4 and Figs. 4–7. The pH values in Figs. 1–7 can be read directly off the '*y*' axes. However, the '*y*' axis units for the mineral concentrations are only semi-quantitative and relate to the relative strength of the XRD peaks denoted in Tables 1–4 (trace to very very strong). Two actual XRD traces are presented in Figs. 8 and 9.

1.3.1. Results for magnesium sulfate solutions (Tables 1 and 2 and Figs. 1–3)

Initially, the dilMg solution containing material exposed to the atmosphere, (Table 1 and Fig. 1), produced gypsum and ettringite but a small amount of thaumasite was also detectable by day 29. Subsequently, there was a rather ill-defined change in the ettringite XRD pattern

Table 2
XRD results for non-exposed solution dilMg sample[a]

Age days	Solution dilMg		
40	Calcite	(s)	pH 12.5
	Portlandite	(vw)	
	Gypsum	(vs)	
	Ettringite	(m)	
	Thaumasite	(vw)	
	Brucite	(mw)	
63	Calcite	(s)	pH 12.3
	Gypsum	(vs)	
	Ettringite	(m)	
	Thaumasite	(mw)	
	Brucite	(mw)	
90	Calcite	(s)	pH 12.5
	Gypsum	(s)	
	Ettringite	(ms)	
	Thaumasite	(ms)	
	Brucite	(mw)	

[a] *Key to tables*: t = trace, vw = very weak, w = weak, mw = moderately weak, m = moderate, ms = moderately strong, s = strong, vs = very strong, vvs = very very strong.

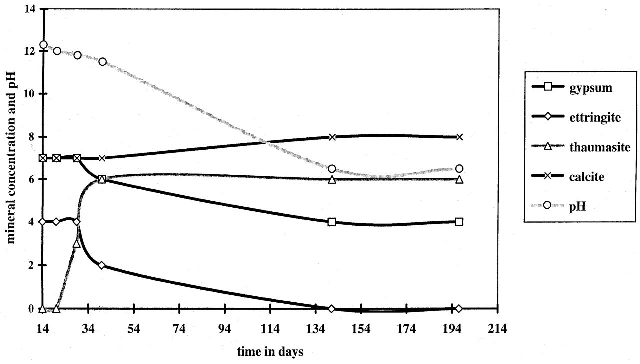

Fig. 1. Graph showing mineral concentration and pH changes with time for solution dilMg sample exposed to the atmosphere (see Table 1).

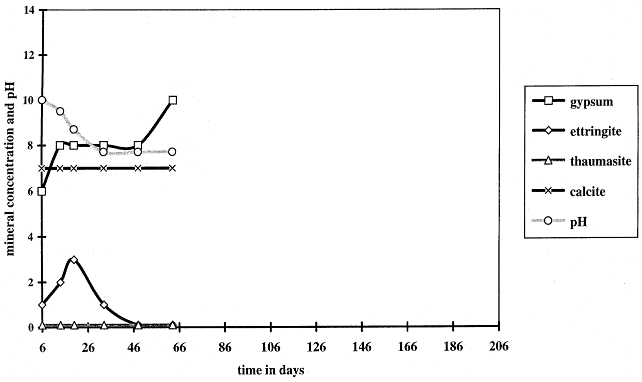

Fig. 2. Graph showing mineral concentration and pH changes with time for solution Mg sample exposed to the atmosphere (see Table 1).

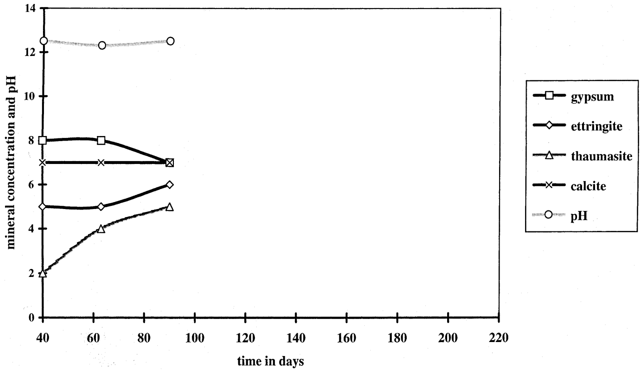

Fig. 3. Graph showing mineral concentration and pH changes with time for non-exposed solution dilMg sample (see Table 2).

towards that of thaumasite. Ettringite was probably still present by day 40, but only thaumasite was found at later ages. Portlandite disappeared early on but gypsum was always present, although the amount appeared to decrease with time. The pH started at a high value of around 12 but by day 141, it had decreased to 6.5.

A similar sequence was observed in the non-exposed solution dilMg sample, (Table 2 and Fig. 3), but thaumasite formation was much slower and only just detectable by day 40. However, as can be seen from Fig. 8, it was well developed by day 90 together with significant amounts of ettringite and gypsum. Portlandite lasted longer in this sample, being detectable up to day 40 and the pH was still measuring 12.5 on the last day data were collected (day 90).

The results for the solution Mg sample, which was exposed to the atmosphere (Table 1 and Fig. 2) were quite different. Ettringite appeared briefly between days 6–33, but only in trace or very small amounts. No thaumasite or portlandite were found at any age. The major feature appeared to be the production of gypsum. During the experiment, the deposition of increased amounts of a white powder were observed. Separately analysed this was found to be mainly gypsum but it was also found to contain significant amounts of aragonite. By day 63, the pH of the mixture had dropped from 10 to 7.7.

Reaction between lime and magnesium sulfate

$$Ca(OH)_2 + MgSO_4 = CaSO_4 + Mg(OH)_2 \qquad (1)$$

results in the formation of brucite, $Mg(OH)_2$, a sparingly soluble salt whose saturated solution has a pH of about 10.5. This is too low to maintain C–S–H stability, which requires a pH of about 12.5. Once the pH drops below this point the C–S–H starts to decompose, releasing lime which reacts to form more brucite, causing further lime release. Continuous attack ultimately results in complete C–S–H breakdown as the pH drops towards 10.5.

Table 3
XRD results for non-exposed potassium sulfate samples

Age days	Solution dilK			Solution K		
50	Calcite	(s)	pH 13.0	Calcite	(s)	pH 13.0
	Portlandite	(ms)		Portlandite	(mw)	
	Gypsum	(w)		Gypsum	(mw)	
	Ettringite	(ms)		Ettringite	(ms)	
	Thaumasite	(t)		Thaumasite	(ms)	
65	Calcite	(s)	pH 13.0	Calcite	(s)	pH 13.0
	Portlandite	(ms)		Portlandite	(mw)	
	Ettringite	(s)		Ettringite	(ms)	
	Thaumasite	(w)		Syngenite	(ms)	
79	Calcite	(s)	pH 13.0	Calcite	(s)	pH 13.0
	Portlandite	(ms)		Portlandite	(mw)	
	Ettringite	(s)		Ettringite	(ms)	
	Thaumasite	(mw)		Syngenite	(s)	
100	Calcite	(s)	pH 13.0	Calcite	(s)	pH 13.0
	Portlandite	(ms)		Portlandite	(mw)	
	Ettringite	(s)		Ettringite	(s)	
	Thaumasite	(mw)		Thaumasite	(w)	
				Syngenite	(vs)	
135	Calcite	(s)	pH 13.0	Calcite	(s)	pH 13.0
	Portlandite	(ms)		Portlandite	(w)	
	Ettringite	(s)		Ettringite	(ms)	
	Thaumasite	(s)		Thaumasite	(m)	
				Syngenite	(mw)	
170	Calcite	(s)	pH 13.0	Calcite	(s)	pH 13.0
	Portlandite	(ms)		Portlandite	(w)	
	Ettringite	(s)		Ettringite	(ms)	
	Thaumasite	(s)		Thaumasite	(s)	
				Syngenite	(mw)	
249	Calcite	(s)	pH 13.0	Calcite	(s)	pH 13.0
	Portlandite	(m)		Portlandite	(vw)	
				Ettringite	(ms)	
	Thaumasite	(vs)		Thaumasite	(vs)	
				Syngenite	(mw)	

Ettringite is reportedly decomposed when the pH falls below 10.7 [6]. The differences in the amount of ettringite formation obtained can thus be related to differences in the solution's sulfate content. For solution Mg, sufficient sulfate was present to react with all the free and combined lime. Consequently only lower pH values unsuitable for ettringite stability were achievable. For the much weaker solution dilMg, modest lime removal resulted in higher pH values.

Although a high pH was maintained in the non-exposed solution dilMg for a period of up to 90 days, values fell continuously in the exposed one. This was due to the additional effects of carbonation, which also reduces pH. Nevertheless values were maintained above 10.7 for a while so that ettringite was produced in both samples. However, production was more marked in the non-exposed sample.

The conditions for thaumasite formation were found to be similar to those for ettringite. Where ettringite was stable, thaumasite formed later on, but none was produced where ettringite was unstable. This did not seem to be due to thaumasite being similarly unstable at lower pH, as demonstrated by the 141-day and 197-day results for the exposed solution dilMg sample (Table 1, Fig. 1). These showed long term contact between thaumasite and a lower pH solution, so, in this respect, thaumasite appeared to be more stable than ettringite.

There were obvious differences between the formation of thaumasite in the two solution dilMg samples. In particular the rate was much faster in the exposed sample. However there were no obvious reasons for this difference.

The combination of ettringite decrease with thaumasite increase was exhibited by the exposed solution dilMg sample. This might have been due to entry into a pH region where ettringite was decomposing whilst thaumasite remained stable – except that a similar feature was found for the non-exposed dilK sample (see

Table 4
XRD results for exposed potassium sulfate samples

Age days	Solution dilK			Solution K		
6	Calcite	(s)	pH 12.3	Calcite	(s)	pH 13.0
	Portlandite	(s)		Portlandite	(mw)	
	Gypsum	(s)		Gypsum	(vs)	
	Ettringite	(w)		Ettringite	(w)	
				Syngenite	(w)	
13	Calcite	(s)	pH 12.8	Calcite	(s)	pH 13.0
	Portlandite	(ms)		Portlandite	(t)	
	Gypsum	(s)		Gypsum	(vs)	
	Ettringite	(mw)		Ettringite	(w)	
20	Calcite	(s)	pH 12.0	Calcite	(s)	pH 13.0
	Portlandite	(mw)				
	Gypsum	(ms)		Gypsum	(vs)	
	Ettringite	(mw)		Ettringite	(w)	
27	Calcite	(vs)	pH 12.5	Calcite	(vs)	pH 13.0
	Portlandite	(w)				
	Gypsum	(s)		Gypsum	(s)	
	Ettringite	(m)		Ettringite	(mw)	
34	Calcite	(vs)	pH 12.5	Calcite	(vs)	pH 13.0
	Gypsum	(s)		Gypsum	(ms)	
	Ettringite	(m)		Ettringite	(mw)	
41	Calcite	(vs)	pH 12.5	Calcite	(vs)	pH 12.8
	Ettringite	(m)		Ettringite	(mw)	
	Thaumasite	(t)		Syngenite	(w)	
48	Calcite	(vs)	pH 12.3	Calcite	(vs)	pH 12.5
	Ettringite	(m)		Ettringite	(mw)	
	Thaumasite	(t)				
53	Calcite	(vs)	pH 12.0			
	Ettringite	(m)				
	Thaumasite	(vw)				
62	Calcite	(vs)	pH 10.5	Calcite	(vs)	pH 7.7
	Thaumasite	(vw)		Ettringite	(vw)	
77	Calcite	(vs)	pH 9.0	Calcite	(vvs)	9.0
97	Calcite	(vvs)	pH 8.1	Calcite	(vvs)	8.1

later results, Table 3 and Fig. 4) where conditions remained very alkaline. Consequently some connection between ettringite and thaumasite formation was indicated.

1.3.2. Results from potassium sulfate solutions

In contrast to the magnesium sulfate results, those obtained for potassium sulfate were quite similar for solutions of different concentration. Major differences, in this case, were however found to occur between the two storage conditions.

1.3.2.1. Non-exposed samples (results in Table 3 and Figs. 4 and 5). When first sampled at age 50 days, both samples contained gypsum, portlandite and ettringite. The dilK sample contained only a trace of thaumasite at this age but both ettringite and thaumasite were strongly present by day 170. Later on, (day 245), ettringite was no longer detectable but the strength of the thaumasite XRD pattern was much increased as shown in Fig. 9. The pH values remained at 13.0 throughout the duration of the experiment.

Initial thaumasite formation occurred much later in solution K, with only a minor amount present by day 100. It was strongly present by day 245 together with ettringite.

Reaction between potassium sulfate and calcium hydroxide can be represented as

$$K_2SO_4 + Ca(OH)_2 = CaSO_4 + 2KOH \qquad (2)$$

The formaton of KOH, and consequent high pH, should have preserved the C–S–H. However, the formation

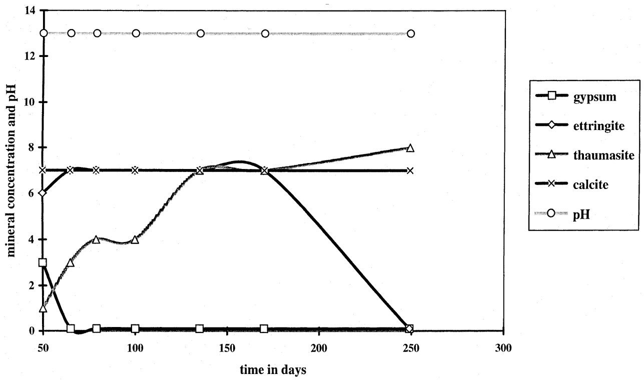

Fig. 4. Graph showing mineral concentration and pH changes with time for non-exposed solution dilK sample (see Table 3).

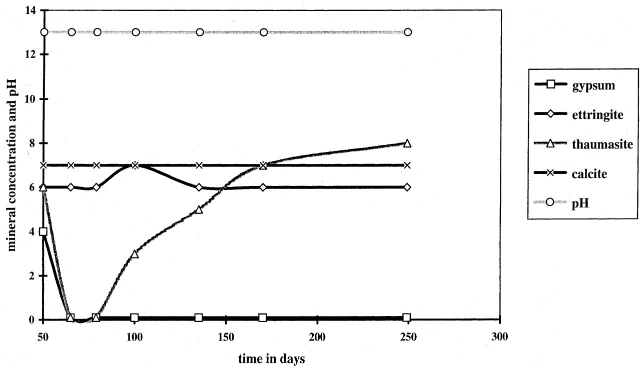

Fig. 5. Graph showing mineral concentration and pH changes with time for non-exposed solution K sample (see Table 3).

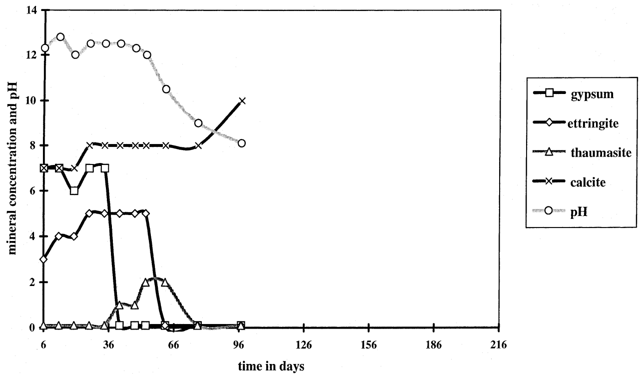

Fig. 6. Graph showing mineral concentration and pH changes with time for solution DilK sample exposed to the atmosphere (Table 4).

of thaumasite showed that some decomposition of the C–S–H must have occurred as the latter is the source of the former's silica.

Portlandite was always present in these samples, in contrast to its relatively early disappearance from the samples exposed to magnesium sulfate. This could be

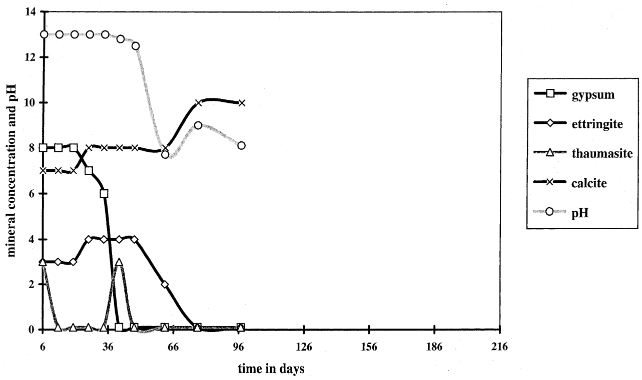

Fig. 7.Graph showing mineral concentration and pH changes with time for solution K sample exposed to the atmosphere (Table 4).

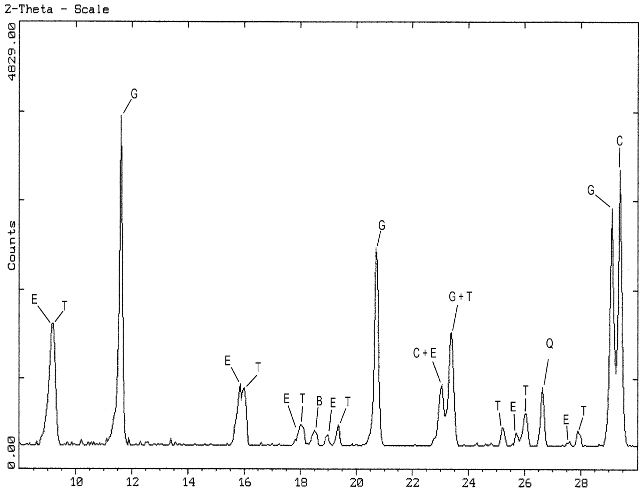

Fig. 8. XRD trace for non-exposed solution dilMg sample at age 90 days (G – gypsum (s), C – calcite (s), E – ettringite (ms), T – thaumasite (ms), B – brucite (w) and Q – quartz (from sand)).

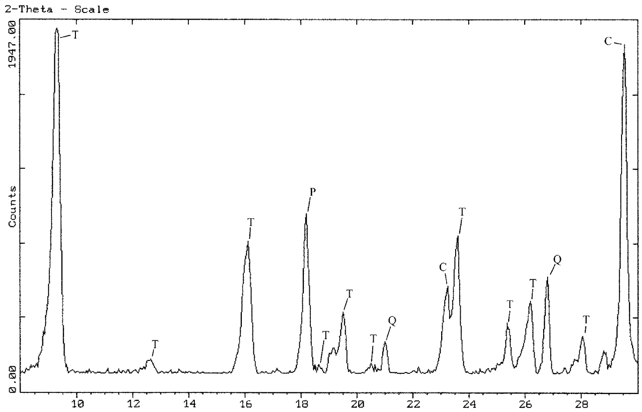

Fig. 9. XRD trace for non-exposed solution dilK sample at age 249 days (T – thaumasite (vs), C – calcite (s), P – portlandite (m) and Q – quartz (from sand)).

indicative of partial reaction since the latter results showed that sufficient sulfate was present to convert all the free portlandite to gypsum. According to Lea [7], reaction between alkali metal sulfates and lime only goes to completion where the resultant alkali hydroxide is continuously removed.

Syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$, formed in significant amounts in the solution K samples. It was quite strongly present on first sampling, when it was found that the originally granular material had solidified into a mat, interlaced with a mass of tiny, needlelike crystals. Syngenite appeared to increase up to day 100, but subsequently decreased. (It also occurred in the exposed solution K material but only weakly and sporadically.)

1.3.2.2. Exposed samples (results in Table 4 and Figs. 6 and 7). These results were dominated by the effects of carbonation. Similar results to those for the non-exposed samples were obtained at early ages, but by day 77 only calcite was detectable. It seems probable that this rapid rate of carbonation, which has been called 'alkali carbonation' was due to the generation of alkali in the lime/sulfate reaction, Eq. (2). Alkali metal hydroxides readily absorb carbon dioxide, i.e.,

$$2KOH + CO_2 = K_2CO_3 + H_2O \tag{3}$$

The presence of potassium carbonate would allow further KOH production via the carbonation of lime, i.e.,

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH \tag{4}$$

It would also allow the removal of calcium sulfate and regeneration of the original alkali sulfate, i.e.,

$$K_2CO_3 + CaSO_4 = CaCO_3 + K_2SO_4 \tag{5}$$

It may be of interest that the above reaction was cited by Skoulikidis and Papakonstantinou [8], who used applications of K_2CO_3 solution to remove gypsum crystals from limestone statues damaged by acid rain.

Alkali carbonation resulted in the removal of both ettringite and thaumasite, which had formed in the exposed dilK sample. The latter result was thus the only indication that thaumasite itself could be attacked.

The exposed sample results suggest that sulfate attack by alkali metal sulfates in the field may well be accompanied by an accelerated rate of carbonation. Normally, carbonation (via the dissolution of CO_2 in water) is inhibited by very dry, or very wet conditions where the pores become filled with water. However, in the case of alkali carbonation, since (a) alkali metal hydroxides are hygroscopic and (b) their solutions have a strong affinity for CO_2 it seems unlikely that inhibition would apply to the same extent.

Additionally, if ettringite forms, causes damage and is then partially removed, it may appear that a great deal of damage has been caused by only a small amount of ettringite. Complete carbonation combined with washout of the regenerated alkali sulfate could lead to what might be termed 'fossilised sulfate attack', where only the physical effects are preserved. This effect (apart from removal of the alkali sulfate) has been demonstrated in Part II.

1.4. Conclusions

1.4.1.

The conditions for thaumasite formation in the above experiment were found to be similar to those required for ettringite formation and these included a high pH of around 10.5 and above. Ettringite was always formed first but, at late ages, increase in thaumasite correlated with decrease and disappearance of ettringite. This has confirmed previous findings [1,3] that in brickwork mortars made with a high C_3A PC, ettringite formation precedes the formation of thaumasite.

1.4.2.

Thaumasite was readily formed in both types of dilute magnesium sulfate solution. In the case of the exposed dilute solution, it appeared to form at high pH and be preserved at low pH. In the strong magnesium sulfate solution, a rapid reduction in pH was effected and no thaumasite was obtained.

1.4.3.

Thaumasite also formed in both strong and dilute potassium sulfate solutions protected from the atmosphere. However exposure to the atmosphere resulted in rapid carbonation and destruction of all the solid sulfate-containing phases. This has been called 'alkali carbonation'. In this case thaumasite appeared only briefly in the dilute solution. This was the only instance found where thaumasite itself was attacked.

2. Part II

2.1. Introduction

The experiment depicted in Part I of this report examined the development of thaumasite in crushed mortar tablets exposed to magnesium and potassium sulfate solutions at 5°C. The work presented in Part II examines the effects of the same solutions in a more practical situation using whole mortar tablets. The test method used was similar in principle to the BRE mortar durability test [5,9], which combines the cyclic administration of sulfate solution with intermediate drying to simulate the processes occurring in practice. The method involves solution uptake via capillary action, thus relating uptake to a mortar's capacity to draw dissolved sulfate salts out of the bricks. This is in contrast to continuous full immersion in a sulfate solution where the same amount of sulfate would be applied to different mortars, regardless of their structure.

XRD analysis of the tablets was carried out when first signs of sulfate attack were observed and also after severe damage had occurred.

2.2. Experimental

2.2.1. Mortars used

Two designation (iii), 1:1:5:5, air entrained cement:lime:sand mortars were made from a PC, (C_3A 8.9%), a commercially available powdered lime, ($Ca(OH)_2$), and a quartz-rich G sand. One mortar, the 'added-calcite mortar', also contained high purity powdered calcite (25% by weight of the PC) which was added as part of the aggregate to keep the cement content of both mortars as close as possible. Air contents and w/c ratios were similar with mean values of 11.1% and 1.2, respectively.

The test specimens were mortar tablets, ($10 \times 28 \times 34$ mm), cut from 10 mm thick mortar beds which had been cured for 28 days after laying between pairs of water saturated bricks, as for the BRE mortar durability test [5,9].

2.2.2. Solutions

The same four solutions were used in Part II of the experiment as were used in Part I. Solution K was the same solution used in the BRE mortar durability test [5,9].

2.2.3. Test method

1. The tablets were weighed and then fully immersed in a small amount of sulfate solution for 10 min. They were then re-weighed to obtain the amount of solution taken up.
2. The tablets were stored in a desiccator over water for 5 days at 5°C, to allow time for reaction and to provide the cold, damp conditions suitable for thaumasite formation. The tap of the desiccator was left open so that contact with atmospheric CO_2 could occur.
3. The tablets were removed from the desiccator and left exposed to the atmosphere, again at 5°C, for a further 2 days. Generally, this removed 60–80% of the absorbed water. After this the cycle was repeated.

Notes on test method: In the BRE mortar durability test, solution uptake is achieved by standing a tablet on a glass plate covered to a depth of 1 mm with solution K for 20 min. Total solution uptake tends to be small but, in the present case, larger uptakes were required to ensure significant sulfate attack using the weaker solutions. Tests carried out showed that greater solution uptake could be achieved by a longer time on the plate, up to a maximum limit. However, this could take a long time and, since it was found that the same maximum could be achieved by a short period of full immersion, this method was adopted instead. Further tests showed that the maximum uptake was still not exceeded even when full immersion was continued for up to 3 days so that, at least up to this age, only capillary space was filled. This method also had the advantage that magnesium sulfate solutions, whose uptake is negligible using the BRE mortar durability method, could also be tested.

2.2.4. Damage assessment and XRD analysis

Two tablets were used for each solution and were examined under a low power microscope after each cycle. One tablet was removed for XRD analysis when initial hair-line cracking was first observed to determine whether ettringite, thaumasite, or both were involved at this early stage of attack.

Cycling was continued with the second tablet to a state of 'severe damage' when it too was subjected to XRD analysis. This involved a subjective judgement but the state was quite well defined for most of the tablets. These exhibited increasingly severe cracking then failed quite abruptly over only one or two cycles with large, relatively hard pieces of outer coat falling off from a soft powdery inside. In these cases, separate analysis of the inner and outer portions was possible. The exception was the solution K tablet which became very badly cracked but remained hard and in one piece, even though cycling was continued for far longer than the others. Since there was no obvious point of failure for the solution K tablets, a compromise method of analysis was adopted with a repeat added-calcite tablet being cycled until it had absorbed the same amount of solution as the corresponding solution Mg tablet.

2.3. Results and discussions

Table 5 gives the mean solution uptakes per cycle. XRD results are given in Table 6. A summary of previous results is given below for purposes of comparison.

2.3.1. Summary of the results obtained in Part I

In the experiment depicted in Part I of this paper, each tablet was crushed and the resultant powder was immersed in 200 ml of a particular solution and kept, at 5°C, under conditions where atmospheric carbonation could occur. Duplicate samples were additionally stored under non-carbonating conditions.

Two types of results were identified for magnesium sulfate solutions. The first occurred in solution dilMg where sufficient portlandite was left over after initial reaction to keep the pH relatively high. This showed

Table 5
Solution uptakes per cycle

Mortar	Solution	Number	1st cycle uptake (ml)	Mean uptakes/cycle (ml)		Solution	Number	1st cycle uptake (ml)	Mean uptakes/cycle (ml)	
				To initial hair-line cracking	From hlc to severe damage				To initial hair-line cracking	From hlc to severe damage
Non-calcite	dilMg	1	2.35	1.91	2.05	dil K	1	2.30	1.94	2.03
		2	2.34	1.94			2	2.28	1.90	
Added-calcite	dilMg	1	1.99	1.34	1.44	dil K	1	1.95	1.49	1.59
		2	1.98	1.33			2	1.95	1.46	
Non-calcite	Mg	1	2.39	1.72	1.96	K	1	2.35	1.93	2.01
		2	2.40	1.72			2	2.42	1.94	
Added-calcite	Mg	1	1.81	1.07	1.48	K	1	2.00	1.46	1.70
		2	1.84	1.09			2	1.99	1.46	1.70

early ettringite production followed later on by the formation of thaumasite. The second type was found in solution Mg, where all the portlandite was removed. This resulted in a decrease in solution pH to a level where ettringite became unstable and decomposition of the C–S–H occurred. This sample produced only a little short-lived ettringite and large amounts of gypsum.

Two types of results were also found for the potassium sulfate solutions but these were more related to atmospheric exposure than sulfate concentration. Samples protected from carbonation produced ettringite followed by thaumasite. Samples exposed to the atmosphere initially produced ettringite with, later on, a little thaumasite in solution dilK. Subsequently, all the sulfate containing phases disappeared, leaving only calcite. It was proposed that this was due to 'alkali carbonation', the results of CO_2 absorption by the KOH produced in the lime/sulfate reaction – essentially the formation of potassium carbonate. This was able to carbonate calcium sulfate as well as portlandite and so eventually resulted in destruction of the complex sulfates.

2.3.2. Exposure of whole tablets to magnesium sulfate solutions

Both sets of tablets were severely damaged by total solution uptakes considerably smaller than the 200 ml used in Part I. Thus, even for solution Mg, too little sulfate was present to lower the pH to a value which triggered C–S–H decomposition. Consequently, the XRD results for both sets accorded with those previously obtained for the crushed tablets in solution dilMg. It appeared that the non-calcite mortar had acquired significant amounts of calcite via atmospheric carbonation resulting in similar phase assemblages for both types of mortar.

Ettringite was the predominant expansive phase present when hair-line cracking occurred but significant amounts of thaumasite were additionally present at the severe damage stage. Separate analyses at the latter stage indicated a greater concentration of expansive products in the inner portion which correlated with its powdery state. The outer coat appeared to be more carbonated which probably contributed to its better physical condition.

Gypsum was much less in evidence, the portlandite lasted longer and the overall level of carbonation appeared to be greater than previously obtained in Part I. This is probably related to the present lower sulfate content since less portlandite will react to form gypsum. Consequently, a greater quantity of portlandite would be available for ultimate carbonation. However, the present method provides opportunities for carbonation between the successive small sulfate uptakes and so would allow for a more even distribution between sulphation and carbonation, in any case.

Table 6
XRD analyses[a]

Mortar	Initial hair-line crack stage		Severe damage stage		
	XRD analysis	M1s solution (no cycles)	XRD analysis		M1s solution (no cycles)
			Outer	Inner	
Magnesium sulphate solutions					
Non-calcite	Calcite (vvs) Portlandite (m) Ettringite (m) Thaumasite (t)	25 ml solution dilMg 13 cycles	Calcite (vvs) Gypsum (t) Ettringite (mw) Thaumasite (mw)	Calcite (s) Gypsum (t) Ettringite (s) Thaumasite (s)	40 ml solution dilMg 20 cycles
Added-calcite	Calcite (vvs) Portlandite (m) Ettringite (m) Thaumasite (t)	23 ml solution dilMg 17 cycles	Calcite (vvs) Thaumasite (mw)	Calcite (s) Ettringite (ms) Thaumasite (ms)	36 ml solution dilMg 26 cycles
Non-calcite	Calcite (ms) Portlandite (ms) Gypsum (mW) Ettringite (m)	13 ml solution Mg (60)[*] 7 cycles	Calcite (vs) Gypsum (mW) Ettringite (ms) Thaumasite (mW)	Calcite (m) Portlandite (ms) Gypsum (mW) Ettringite (s) Thaumasite (ms)	21 mls solution Mg (100) 11 cycles
Added-calcite	Calcite (vs) Portlandite (ms) Gypsum (w) Ettringite (mw)	10 mils solution Mg (50) 9 cycles	Calcite (vs) Gypsum (mW) Ettringite (m) Thaumasite (m)	Calcite (vs) Portlandite (m) Gypsum (mW) Ettringite (ms) Thaumasite (ms)	22 mls solution Mg (106) 17 cycles
Potassium sulphate solutions					
Non-calcite	Calcite (vvs) Portlandite (m) Ettringite (mw)	20 mls solution dil K 10 cycles	Calcite (vvs) Ettringite (w) Thaumasite (W)	Calcite (m) Portlandite (mw) Gypsum (mW) Ettringite (s) Thaumasite (m)	34 mls solution dil K 17 cycles
Added-calcite	Calcite (vvs) Portlandite (m) Ettringite (mw)	18 mls solution dil K 12 cycles	Calcite (vvs) Thaumasite (t)	Calcite (vs) Portlandite (mw) Gypsum (mw) Ettringite (s)	29 mls solution dil K 19 cycles
Non-calcite	Calcite (vvs) Portlandite (mw) Ettringite (w)	14 mls solution K (66) 7 cycles	Calcite (vvs) syngenite (w)		56 mls solution K (267) 28 cycles
Added-calcite	Calcite (vvs) Portlandite (mw) Ettringite (w)	12 mls solution K (58) 8 cycles	Calcite (vvs) Syngenite (vw)		46 mls solution K (218) 28 cycles
Added-calcite (repeat)	–	–	Calcite (vvs)		21 mls solution K (101) 15 cycles

[a] *Key*: t = trace, w = weak to moderate, m = moderate, ms = moderate to strong, s = strong, vs = very strong.

[*] Figures in brackets are dilute solution equivalents.

It would even be possible to allow carbonation to predominate by lengthening the cycles and/or using weaker solutions.

Comparison of the solution uptakes shows that similar amounts of the same solution dilMg caused similar degrees of damage in both the non- and added-calcite mortars. However, more cycles were needed to achieve that uptake for the latter, particularly for the solution dilMg tablets. This appears to be due to its lower average solution uptake per cycle, (Table 5), which could indicate a difference in capillary structure. Thus, although the added calcite mortar lasted longer and would thus be designated the more durable, the results suggest a physical cause, not a greater chemical resistance to sulfate attack. Barker and Hobbs [10] have also investigated the performance in cold sulfate solutions (magnesium sulfate – 0.42% as SO_4 and sodium sulfate – 0.42% as SO_4) of laboratory-prepared mortar prisms made with and without limestone filler additions. The PC used had a C_3A content of about 10% by mass, the Portland limestone cement (PLC) contained 15% limestone filler by mass and all the mortars were made with a w/c ratio of either 0.5 or 0.75. It was concluded from this mortar prism work that the vulnerability to sulfate attack of the PC mortars was broadly similar to that of the 15% PLC mortars, although the mode of attack was different.

Solution Mg was much stronger than solution dilMg. Consequently, sulfate uptake per cycle was greater for the solution Mg tablets and fewer cycles were required to achieve a given degree of damage. Nevertheless, solution dilMg appeared to be the most efficient in sulfate attack terms. For instance, 40 ml of solution dilMg are equivalent in sulfate content to 8 ml solution Mg. Application of the former caused severe damage to the added calcite mortar, whereas application of the latter did not even cause hair-line cracking (Table 6). This seems surprising, even granting that some disparity between solutions of such different strengths might be expected. It could suggest that the amount of reaction which can occur in a given time increases with increase in solution strength but only up to a limit. After this there is simply a build-up of unused sulfate in the tablet which requires much more time to react. Future work might include a repeat of this experiment using longer cycle times.

2.3.3. Exposure of whole tablets to potassium sulfate solutions

Overall, the tablets exhibited many of the features found for the magnesium sulfate tablets, i.e., ettringite appeared to be the cause of hair-line cracking, there was not much difference in the phases produced by corresponding non- and added-calcite mortars and the added-calcite tablet was the longer lasting, although only marginally so, in this case.

Ettringite was present in the solution K tablets at the hair-line crack stage, but had disappeared at the later ages when more or less complete calcification had occurred. It seems probable that this calcification caused the cracked tablet to remain intact and hard. The dilK tablets, on the other hand, disintegrated in the same way as the solution dilMg and Mg tablets and produced similar reaction products.

Comparison of the later stage results for the repeat added-calcite tablet in solution K with those for solution Mg also showed a different type of physical damage and different reaction products, even though both tablets had taken up similar amounts of their respective strong solutions in a similar number of cycles. Two of the solution K tablets contained traces of syngenite but the repeat added calcite tablet was completely carbonated. These results were thus very similar to those previously obtained in Part I for carbonating conditions.

Sulfate attack in the field may be expected to show evidence of both physical damage and elevated levels of the expansive sulfates. The results for the solution K tablets, though, show that this is not necessarily the case. These tablets were severely cracked during earlier cycles, when ettringite was formed. However, the onset of alkali carbonation resulted in the disappearance of the ettringite leaving only the physical damage preserved. Under the present experimental conditions, chemical analysis would reveal the presence of sulfate ion, but, in the field, even this evidence could be washed away.

Similar physical results were not obtained for the solution dilK tablets. In this case it is assumed that the smaller sulfate uptake did not generate sufficient alkali for alkali carbonation to predominate in the experimental time allowed. However, the fact that the mortar crumbled does not mean that the chemical processes had ceased. If alkali carbonation were to continue (as it did in Part I), then the resultant calcite mass would present a quite different physical appearance to that obtained for the solution K tablets. This would seem to merit further investigation since such a result might well accord better with what is found in practice, where lower sulfate levels are more likely.

2.3.4. General comment

The test method employed in Part II of this investigation resulted in considerable reductions in the amounts of solution applied to the tablets but good correlation was still obtained with the reaction products and sequences found in Part I. Perhaps more importantly, previous features reported in Part I such as the formation of thaumasite and alkali carbonation, have been shown to have effects in a much more practical situation.

All the solutions, except solution K, produced thaumasite. This was present at the later ages, but early damage appeared to be caused by ettringite. It seems likely that this will usually be the case for Portland cements with high C_3A contents because these cements have the potential to produce a lot of ettringite whose formation apparently always precedes that of thaumasite. The situation could well be different for sulfate resisting Portland cements where, even though ettringite still forms first, the amount may be too small to cause any expansion. In such a case, the later formation of thaumasite might be required before any damage occurs.

The present method seems well suited to determine whether this is so since it enables damage to be determined at a very early stage and provides a way of correlating damage with the sulfate phases produced. It also seems suited for the examination of the vagaries of sulfate attack in general, since it is very flexible. Cycles may be lengthened or shortened, temperatures and solutions altered and reaction and drying times could be carried out under non-carbonating conditions, if required.

2.4. Conclusions

In Part II of this investigation, good correlation was obtained with the reaction products and sequences found in the purely 'chemical' scenario of the Part I experiment where the mortar tablets were crushed to a powder prior to sulfate exposure. Features such as thaumasite formation and alkali carbonation have been shown to have effects in the more practical Part II situation, where the mortar tablets had to physically absorb the solutions before reaction could occur. Any difference in the results between Parts I and II appears to be due to smaller amounts of solution uptake in the latter case.

This work has shown that physical damage of a mortar tablet as a result of sulfate attack can be preserved during alkali carbonation at the same time as the residual ettringite or thaumasite is being destroyed. Care must therefore be taken when diagnosing such samples in the field, where the agent responsible for inflicting damage may no longer be in evidence.

All the solutions, except solution K, produced thaumasite which was present at the severe damage state, together with ettringite. In all cases, earlier hairline cracking appeared to be mainly due to ettringite formation.

Sulfate attack was obtained more quickly using the stronger solutions but the weaker solutions were more efficient, comparable damage being achieved with smaller amounts of sulfate.

There was not much difference between the results for the non-and added-calcite mortar, although the latter appeared to be more durable, particularly for solution dilMg. These results agree with those of Barker and Hobbs [10]. It was concluded that the slightly increased durability of the added-calcite mortar was due to its lower solution uptake per cycle rather than any inherent chemical resistance to sulfate attack.

2.5. Overall conclusions and future work

Even though Part I concentrated purely on the 'chemical' interactions between mortar and solution, the reaction products and sequences were found to be very similar to those discovered in Part II, where physical barriers to sulfate ingress had to be overcome prior to chemical attack. This provides confirmation that any masonry mortar can potentially deteriorate in the presence of excess sulfates providing the temperature is low, the mortar contains an available source of calcium carbonate, the brickwork is consistently wet and the pH of the reaction zone is maintained at 10.5 or above. Having said this, the extent of sulfate attack of brickwork in the field is small and should not become a major problem in practice, provided the current recommendations [1] (especially the avoidance of using sulfate-bearing bricks in exposed situations) are adhered to. The work has also confirmed previous findings [1,3] that in brickwork mortars made with a high C_3A PC, ettringite formation precedes the formation of thaumasite.

Some non-calcite containing mortars were also examined during Part II of this investigation and results have found them to be slightly less durable than their added-calcite counterparts, particularly in weak magnesium sulfate solution. This was attributed to the improved impermeability of added-calcite mortars rather than any inherent chemical resistance to sulfate attack.

The information obtained from both parts of this investigation has helped a great deal with the understanding of reaction sequences and conditions necessary for the production and long term stability of thaumasite in one example of a brickwork mortar. Any information of this kind is essential in the quest of finding a solution for avoiding damage caused by the formation of thaumasite in the field and the results from this study have already been incorporated into the Thaumasite Expert Group Report published in January 1999 [1]. The next stage will be to establish at what point the physical robustness of mortar starts to slow down the rate of chemical interaction by experimenting with changing the mortar constituents and mix design. Future work will also need to incorporate concrete specimens.

The relationship between pH and the formation of thaumasite in magnesium-rich sulfate solutions has already been discussed in the literature [11,12]. In both these studies, the evidence pointed to thaumasite forming in pH conditions below a value of about 10.5, when brucite and magnesium silicate hydrate were formed and CSH was no longer stable. The current series of experiments shows a complicated relationship between pH and thaumasite stability. Thaumasite does not appear to form at a pH of below 10.5 (e.g., Figs. 2–5) and in fact readily forms at a pH of 13 (Figs. 4 and 5). However, once formed, it can remain in contact with pH solutions as low as 7 (Fig. 1), perhaps giving the impression that these were the conditions under which it formed. More work is needed in this area of research in order to verify these findings.

Sulfate attack in the field may be expected to show evidence of both physical damage and elevated levels of sulfate reaction products. However, the two following sets of results from the present study have shown that this is not necessarily the case:

- Sulfate attack was obtained more quickly in whole mortar tablets exposed to the stronger sulfate solutions. However, the weaker solutions were more efficient, with comparable damage being achieved with smaller amounts of sulfate.
- In the situation where a bout of sulfate attack is followed by alkali carbonation, two circumstances arise. The first is that any damage caused by the sulfate attack can be preserved and the second is that any ettringite or thaumasite formed can be destroyed. So in this situation there is no longer any evidence that sulfate attack was involved in the deterioration process.

The concept of 'alkali carbonation' is new. There have been a few examples of disintegration of concrete products in the field, which could have been attributable to this process. Two such examples have been discussed in the literature, in which crumbling of a concrete block in service [13] and crumbling of mass concrete exposed to cold sodium sulfate solutions [12] occurred as a result of cement paste replacement by coarsely crystalline calcite. More field and laboratory studies are therefore needed in order to understand fully both the chemical and physical implications of alkali carbonation.

References

[1] Department of the Environment, Transport and the Regions. The thaumasite form of sulfate attack: risks, diagnosis, remedial works and guidance on new construction. Report of the Thaumasite Expert Group, DETR, January 1999.

[2] Taylor HFW. Cement chemistry, Second ed. London: Academic Press, 1997, pp. 401–402.

[3] Gaze ME. The effects of varying gypsum content on thaumasite formation in a cement:lime:sand mortar at 5°C. Cement Concrete Res 1997;27(2):259–65.

[4] British Standard Institution, BS 4551:1980 Methods of testing mortars, screeds and plasters, 1980.

[5] Harrison WH, Gaze ME. Lab-scale tests on building mortars for durability and related properties. Masonry Int 1989;3(1):35.

[6] Gabrisova A, Havlica J. Stability of calcium sulphoaluminate hydrates in water solutions with various pH values. Cement Concrete Res 1989;21(6):1023–7.

[7] Lea FM. The Chemistry of Cement and Concrete, Third ed. London: Arnold, 1970, pp. 345–347.

[8] Skoulikidis T, Papakonstantinou P. Stone cleaning by the inversion of gypsum back into calcium carbonate. In: Proceedings International Conference on Stone Cleaning, Edinburgh, UK, 14–16 April 1992, pp. 155–158.

[9] Harrison WH. Durability tests on building mortars – effect of sand grading. Mag Conc Res 1986;38(135).

[10] Barker AP, Hobbs DW. Performance of Portland limestone cements in mortar prisms immersed in sulfate solutions at 5°C. Cement Conc Comp 1999;21(2):129–38.

[11] Hartshorn SA, Sharp JH, Swamy RN. Thaumasite formation in Portland limestone cement pastes. Cement Conc Res 1999;29:1331–40.

[12] Crammond NJ, Nixon PJ. Deterioration of concrete foundation piles as a result of thaumasite formation. In: Sixth International Conference on the Durability of Building Materials, vol. 1, Japan, 1993, pp. 295–305.

[13] Bromley A, Pettifer K. Sulfide-related degradation of concrete in southwest England (The mundic problem). Construction Research Communications (CRC), BRE Lab Report, BR325, 1997.