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The role of carbon dioxide in the formation of thaumasite

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Abstract

The development of the thaumasite form of sulfate attack (TSA) has received considerable attention since its discovery in the foundations of motorway bridges in England in 1998. When TSA occurs in siliceous aggregate concrete and mortars, particularly in samples from the field, it is normally assumed that the carbonate source necessary for the formation of thaumasite was either present as a minor component in the aggregate, as a limestone filler in the binder, or from the groundwater. Recent laboratory studies carried out by the authors have identified a further source of carbonate ions, and that is from atmospheric carbonation. However, in other studies, it appears that an initial air cure can improve the resistance of concretes to TSA. This apparent dichotomy suggests that there is insufficient understanding of the relationship between atmospheric carbonation and TSA.

The performances of small mortar cubes made using fine aggregates of either high quality silica sand or limestone under different curing regimes have been compared. Detailed analyses of the nature of the thaumasite-ettringite solid solutions that formed have been carried out, and the mechanism of thaumasite formation, in particular, the role of calcium bicarbonate, is discussed in the light of the results obtained.

Keywords: X-ray diffraction; Carbonation; Sulfate attack; Thaumasite; Mortar

1. Introduction

Thaumasite as a naturally occurring, but rare, mineral has been known for over 100 years and, under suitable conditions, can be synthesised in the laboratory. Recently, it has become apparent that thaumasite will also form readily, with potentially serious degradation, in cementitious materials made with Portland cements, including both ordinary (OPC-ASTM Type I) and sulfate-resistant (SRPC ASTM Type V) Portland cements [1–3].

The thaumasite form of sulfate attack (TSA) in concretes and mortars has been found to occur most readily in situations where there is a plentiful supply of water and the temperature is normally less than 15 °C—conditions that are regularly found in the UK, particularly below ground level—and over 80 cases have been reported [3] in the last 15 years. More recently, thaumasite has also been reported in other countries where suitable conditions are found [4–6].

Thaumasite, $CaSiO_3.CaCO_3.CaSO_4.15H_2O$, is an unusual mineral because its structure incorporates three different anions: carbonate (CO_3^{2-}), sulfate (SO_4^{2-}) and silicate in the form $Si(OH)_6$, associated with the calcium cation, Ca^{2+}. A source of these ions is therefore also required for thaumasite to form. In cements, the silicate ion is derived from the bulk phase within the cement paste (the calcium silicate hydrate), which is the main reason why the cement loses its integrity during TSA. The source of the sulfate ion is generally considered to be external, normally derived from either the groundwater, where it can be associated with a number of different cations, principally magnesium, calcium and sodium (or a combination of these) or, for example, in the case of brickwork, from sulfate minerals present in the bricks used.

In a mortar or concrete containing either carbonate aggregates (calcareous or dolomitic limestone) or limestone filler as part of the cement, the carbonate ion will predominantly be derived from these sources. However, these cannot be the only source because TSA has been found in siliceous aggregate mortars and concretes made with cement not containing limestone filler [7]. So unless either the aggregate or binder is contaminated, the source of carbonate

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ions must be external. In these cases, it has been tacitly assumed that the carbonate ions have been supplied from the surrounding groundwater [3] or, possibly, from atmospheric carbonation during TSA, but this has not been proved.

Laboratory studies by the authors have investigated the role of calcium carbonate in the groundwater. However, during this work, a further important source of carbonate ions was identified, namely, that formed through atmospheric carbonation (i.e., the reaction between carbon dioxide and the portlandite present in the cement paste), during the curing of the cement or concrete (Eq. (1)).

$$Ca(OH)_2 + 2H_2O + 2CO_2 \rightleftharpoons Ca(HCO_3)_2 + 2H_2O \qquad (1)$$

1.1. The carbon cycle

The chemistry of carbon in the natural environment is often explained, in a very simple way, as the "carbon cycle", but to start understanding the role of carbon dioxide and mineral carbonates during the formation of thaumasite, it is necessary to understand some of the details of the carbon cycle, which, in fact, are far from simple. The most important aspect to be considered is associated with the dissolution of carbonate rocks by rainwater containing carbon dioxide. Significant scientific research has been carried out in this area, notably, under the generic heading of karst geomorphology and hydrology [8], although data have occasionally been reported in literature associated with cement and concrete, notably by Lea [9] and Cowie and Glasser [10]. It should be noted that karst also applies to the natural changes that occur in other minerals, notably, sulfates and silicates.

The reactions of carbon dioxide, water and calcite can be summarised as follows (e.g., Ref. [8]). Carbon dioxide dissolves in atmospheric water to form carbonic acid, a weak acid that dissociates into hydrogen and bicarbonate ions (Eq. 2).

$$CO_2 + H_2O \longleftarrow\!\rightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (2)$$

Calcium carbonate is only slightly soluble and dissociates in water, as shown in Eq. (3).

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad (3)$$

Rainwater, containing the carbonic acid, percolates through the ground and reacts with the limestone, providing an alternative mechanism for dissolution of calcite. Combining Eqs. (2) and (3) gives

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \qquad (4)$$

The formation of the calcium bicarbonate appears straightforward, but it is important to note that all these reactions are reversible, if or when the ambient conditions change. Several factors will affect these equilibria, namely, the temperature, the pH and the amount and nature of the carbon dioxide in solution.

1.1.1. Aggressive (CO_2^A) and stabilising carbon dioxide (CO_2^S)

The carbon dioxide in Eq. (4) is often referred to as being aggressive because it is available to react with the calcite. Rainwater therefore contains aggressive carbon dioxide before contacting the ground, which will remain aggressive until the water has dissolved sufficient calcite to reach an equilibrium in terms of Eq. (4). However, as the $CO_2{}^A$ is removed from the system during Reaction 4, more can dissolve, the amount depending on the partial pressure of the carbon dioxide in the surrounding atmosphere. This additional carbon dioxide is then available to bring about further dissolution of calcite. Due to organic activity, the partial pressure of CO_2 in the ground can be quite high, reported by Ford and Williams [8] to vary typically from 0.1% to 3.5%. The levels found are dependent on a number of factors [8], including "soil type, texture and horizon, depth, drainage and exposure, types of vegetation cover, soil flora and fauna, with seasonal and shorter period warming and wetting". These values are still much greater than the partial pressure of 0.03% present in the atmosphere so that the potential dissolution of CO_2 and, hence, calcite can be much higher than expected.

However, once calcium bicarbonate starts to form, any remaining carbon dioxide in the water is not all aggressive. A certain amount is also required to stabilise the calcium bicarbonate, and this amount varies nonlinearly with the amount of bicarbonate present. Lea [9] reports, using semiquantitative data, that when 44 mg/l of aggressive CO_2 is incorporated into the bicarbonate, it requires 0.32 mg/l of stabilising CO_2; but at 10 times the amount of CO_2 in the bicarbonate (440 mg/l), no less than 253 mg/l of stabilising CO_2 is required. This situation is complicated further by the presence of other ions in the water. For salts other than those of calcium, the effect will be to reduce the amount of stabilising CO_2 required, but for calcium salts, the converse is true: by extrapolation of curves given in Lea [9], when there is 440 mg/l CO_2 in the bicarbonate (as above), 580 mg/l of stabilising CO_2 is required in a saturated gypsum solution.

The concept of aggressive CO_2 and stabilising CO_2 is important in karst formation/groundwater chemistry. If two ground waters containing different levels of calcium bicarbonate are mixed together, the average new level of the calcium bicarbonate requires less stabilising CO_2 than the average level of the two original stabilising CO_2 values [8]. The excess CO_2 generated therefore becomes aggressive, and the water is capable of dissolving further calcite.

1.1.2. Temperature

The solubility of carbon dioxide increases with decreasing temperature, with a twofold increase from 25 to 0 °C [8]. This change will allow about twice as much calcite to be dissolved at the lower temperature.

1.1.3. pH

The solubility of calcium carbonate is significantly affected by the pH of the solution. At a pH of about 7–7.5, typical of many groundwaters, the solubility of calcium carbonate (as calcium bicarbonate) can be high, as described in Section 1.1.1. However, as the pH increases, the solubility of calcium bicarbonate starts to decrease and that of the calcium carbonate starts to increase [11], until by a pH of about 12, the calcium carbonate predominates in the solution. This is shown graphically in Fig. 1 [11]. However, the absolute solubility of calcium carbonate, even at a pH of 12, is significantly less than the absolute solubility of the calcium bicarbonate at a pH of 7.5; thus, the increase in pH (e.g., as calcium hydroxide) is accompanied by the precipitation of solid calcium carbonate as follows

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightleftharpoons 2CaCO_3\downarrow + 2H_2O \qquad (5)$$

Cowie and Glasser [10] have developed a model for the interaction between dissolved calcium carbonate, aggressive CO_2 and the high pH encountered in cementitious materials. They used this model to consider what occurs in the case of “crack rehealing” in concrete and concluded that both dissolution and deposition of calcite can occur within a crack, dependent on the pH levels at different points within the crack.

1.2. Thaumasite

The chemical formula of thaumasite can be represented in two ways. The first, as given in the Introduction, shows the mineral make-up, but a better representation, which indicates the structural relationship between the various components, is $Ca_3[Si(OH)_6.12H_2O](SO_4)(CO_3)$. Thaumasite is structurally related to ettringite, $Ca_6[Al(OH)_6.12H_2O]_2(SO_4)_3.2H_2O$, which can occur naturally but is also found in hydrated Portland cements, formed by the reaction between sulfate ions and tricalcium aluminate.

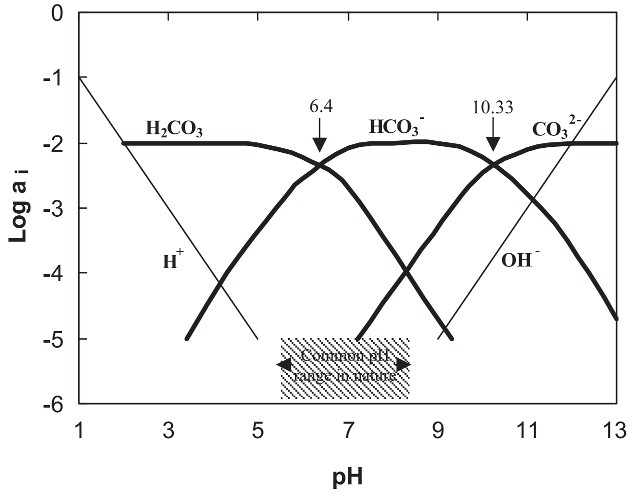

Fig. 1. Activities (a_i) of different species in the carbonate system as a function of pH, assuming low concentrations of the different species and temperature of 25 °C [11].

The similarity in the structures of thaumasite and ettringite can give rise to solid solutions between the two minerals, which have been investigated in detail in a series of publications by Barnett et al. [12–16], who, using pure chemicals, synthesised a series of samples between the thaumasite and ettringite end members. The samples were mainly characterised by the determination of lattice parameters using X-ray diffraction (XRD) and full pattern fitting techniques, and, as a result, they identified that there was a discontinuity in the solid solution series. Torres et al. [17,18], working with Portland limestone cement mortars, have demonstrated that similar solid solutions are obtained during TSA, including the presence of the discontinuity in the solid solution series. There still appears to be some uncertainty as to the exact location of this discontinuity. For example, the *a* dimension of the solid solution is variously quoted as ranging from either 11.08 or 11.11 to about 11.14 Å.

The curing of a Portland cement leads to the formation of a range of hydrated products that bind the aggregate particles together. A generic calcium silicate hydrate, $3CaO.2SiO_2.3H_2O$ or $C_3S_2H_3$ (although the composition is variable, and the C/S ratio can range from about 0.8 to about 2.0), portlandite, $Ca(OH)_2$ or CH, and ettringite, $C_3A.3C\check{S}.H_{32}$, all need to be considered.

There are a number of possible reactions, dependent on the exact chemical composition, that may occur when groundwater containing dissolved sulfate salts and calcium bicarbonate/carbon dioxide is in contact with a mortar or concrete surface. Under the appropriate conditions, it has been suggested [19] that when thaumasite forms, it may be via ettringite or directly from the compounds present.

When thaumasite ($C_3S\check{C}\check{S}H_{15}$) is formed, as a result of sulfate attack in the presence of magnesium ions, the following overall equation, to account for the observed formation of thaumasite, gypsum and brucite and the consumption of portlandite, has been advanced [20]

$$C_3S_2H_3 + 3CH + 2C\check{C} + 4M\check{S} + 32H \rightleftharpoons 2C_3S\check{C}\check{S}H_{15} + 2C\check{S}H_2 + 4MH\downarrow \qquad (6)$$

An alternative route [19], when magnesium ions are not present, might be

$$C_3S_2H_3 + 2C\check{S}H_2 + 2C\check{C} + 24H \rightleftharpoons 2C_3S\check{C}\check{S}H_{15} + CH \qquad (7)$$

with the portlandite produced reacting with any available CO_2 to form calcite. Why there may be CO_2 present is not specified.

If thaumasite also forms from ettringite, then, the following reaction (simplified) has been put forward [19]:

$$\mathrm{C_3A.3C\check{S}.H_{32} + C_3S_2H_3 + 2C\check{C} + 4H \rightleftharpoons 2C_3S\check{C}\check{S}H_{15} + C\check{S}H_2 + AH_3 + 4CH} \quad (8)$$

again with the portlandite formed as a reaction product reacting with any available CO_2 to form calcite.

The work of a number of authors, summarised by Crammond [3], suggests that thaumasite will generally only form at a pH >10.5, thus, it seems likely that the presence of $(OH)^-$ ions will be beneficial in TSA. The recent work of Zhou et al. [21] broadly confirms these observations, but also demonstrates that thaumasite does not form in acidic conditions.

Eqs. (6)–(8) suggest that in the formation of thaumasite, portlandite can be either a reactant or a product. It is conceivable that both situations may arise because different starting materials and chemical conditions can affect the course of a reaction, but this uncertainty indicates that the chemical reactions necessary to form thaumasite are not fully understood. The aim of this work was, therefore, to investigate the formation of thaumasite in small mortar samples, with particular reference to the role of carbon dioxide, calcium carbonate and calcium bicarbonate, and to try to determine whether one reaction is more likely than another, or whether they can all occur dependent on the prevailing conditions.

2. Initial experimental work and results

2.1. Experimental setup

Mortars were made with three aggregate types: a pure siliceous sand (S), Carboniferous limestone (L) and a mixture of Carboniferous limestone (8.3%) and Thames Valley sand (M). These were all mixed in the ratio three parts aggregate to one part cement using the same ordinary Portland cement (OPC) with a tricalcium aluminate content of 7%. The chemical and mineralogical analyses of the cement are given in Table 1. The cement did not contain any limestone filler, but, inevitably, some of the free lime may have carbonated. All the aggregates, except the pure siliceous sand, were < 5 mm and were mixed with a water-to-cement ratio of 0.53. The pure siliceous sand was very fine (< 0.42 mm), requiring a water-to-cement ratio of 0.83. This high water content will have resulted in a mortar with higher permeability, and of lower quality, than of the other mortars.

After mixing, each composition was cast into clean steel moulds to produce bars of 25 × 25 × 250 mm, vibrated and trowelled level to the top of the mould. The bars were allowed to set and were moist cured in air at 20 °C for 24 h before demoulding and seal curing, which consisted of wrapping the bars in a minimum of three layers of cling film [3]. The bars were then held at 20 °C for a further 27 days, when they were unwrapped and cut into eight separate 25-mm cubes before immersion in sulfate solution. The samples and solutions were held in polythene containers with tight-fitting lids at 5 °C. For consistency, each trial started with four cubes per litre of solution, but the relative volumes changed slightly as the trials progressed, dependent on the rate of sample removal and the number of cubes remaining.

To provide a link to the field trial samples at Shipston on Stour [7], the initial sulfate content of the various solutions was in line with the measured levels made at the field site [Sulfate Class 3 (1.4–3.0 g/l SO_4)]. This is shown in Table 2. During the course of the work, 25% of the solution was replaced at a nominal concentration to return to the initial sulfate composition, every three months.

Five different water types were used to make the sulfate solutions: deionised and boiled (DB), deionised (D), tap (T), deionised and boiled with 310 mg/l of added calcium carbonate (DBC) and solution DBC with additional carbon dioxide (DBCC). The measured calcium carbonate content of the tap water at BRE was about 270 mg/l, while, nominally, the deionised and boiled water contained neither dissolved solids nor gases. The deionised water contained no dissolved solids but would have contained dissolved gases, including carbon dioxide.

The experimental matrix is shown in Table 3. It was intended that the control for the investigation was the mortar made with the silica sand immersed in the sulfate solution made with DB water; that is, there were no carbonate ions in the system, either from the mortar or the pseudogroundwater.

Table 1
Cement composition

	Silica	Alumina	Ferric oxide	Lime	Sulfur trioxide	Free lime
%	21.11	4.66	2.69	64.47	3.27	1.55[a]
Phase	C_3S	C_2S	C_4AF	C_3A		
%	54.8	18.0	8.1	7.6		

[a] Supplier's result.

Table 2
Sulfate solution composition

Material	$CaSO_4.2H_2O$	$MgSO_4.7H_2O$	Na_2SO_4	K_2SO_4	Total sulfate
Weight (g/l)	1.53	2.56	0.772	0.045	2.4

Table 3
Experimental matrix

Aggregate	Solution				
	DB	D	T	DBC	DBCC
S	X	X	X		
L	X	X	X		
M	X	X	X	X	X

The cubes were examined on a weekly basis and removed at intervals. Photographs were taken of the cubes, and small samples, removed from the cube surface and dried on absorptive paper, in air at room temperature, were removed for XRD analysis when thought to be appropriate. This technique for sample collection was used consistently, and cross checks with samples dried under nitrogen indicated that little carbonation after the removal from the solutions had occurred.

The XRD analysis consisted of grinding the sample to pass a 53-micron sieve and dispersing it, using methyl alcohol, on a silicon wafer. The sample was then mounted in a Siemens Kristalloflex diffractometer and was scanned at a slow rate (step size $0.02^\circ 2\theta$ with a 14-s count per step) using copper K-alpha radiation. Quartz, as either part of the aggregate or added during the grinding process for the limestone aggregate specimens, has been used as an internal standard for zero point error calibration.

2.2. Results

2.2.1. Visual observations

The following applies to all but the DBCC, which is described at the end of the section.

The initial pH of all the solutions was in the range 7.0–7.5. After about 28 days of immersion, examination of the specimens indicated that the pH of all the solutions was in excess of 11. At this time, a white precipitate was present in all the sample containers, particularly on the top surface of the samples. After 49 days, the pH had risen to above 12 and was still at this level after 586 days.

The first sign of attack was fine cracking on the top surface, normally running parallel and close to the cube edges. For the mixed aggregate specimens, cracking started after about 42 days, followed by the pure siliceous aggregate mortars after about 56 days and the limestone mortars from about 70 days. The cracks appeared to be in a hard outer layer, or skin, with the gradual formation of white degraded material under this layer.

As time increased, the cracking became more extensive, and the amount of degraded material increased until the outer layer was more or less consumed, leaving a soft, white layer on the surface (Fig. 2), which appeared to be similar for all the mortars, regardless of aggregate type or the water used to make the sulfate solutions.

The side faces of the cubes did not show signs of attack until several weeks after the top surfaces. The visual mode of attack differed with that observed on the top face, with the faces in contact with the mould also behaving differently to the cut faces. The mould faces started showing signs of attack first, exhibiting fine blistering together with development of an efflorescence, while the cut faces showed little sign of attack for several months. Eventually, all the faces became badly eroded (Fig. 2).

The initial pH of the DBCC was less than 6, rising to about 7 after 28 days of immersion. The pH after 427 days had risen slightly to 7.5 but subsequently increased to 10.7 after 586 days. The appearance of the cube during the entire period showed little change, with no sign of attack (Fig. 2), although the surface had a slight yellow colour.

2.2.2. X-ray diffraction

The XRD results of the precipitates found on top of the cubes during the first few weeks of exposure to sulfate solution indicated the presence, to varying degrees, of

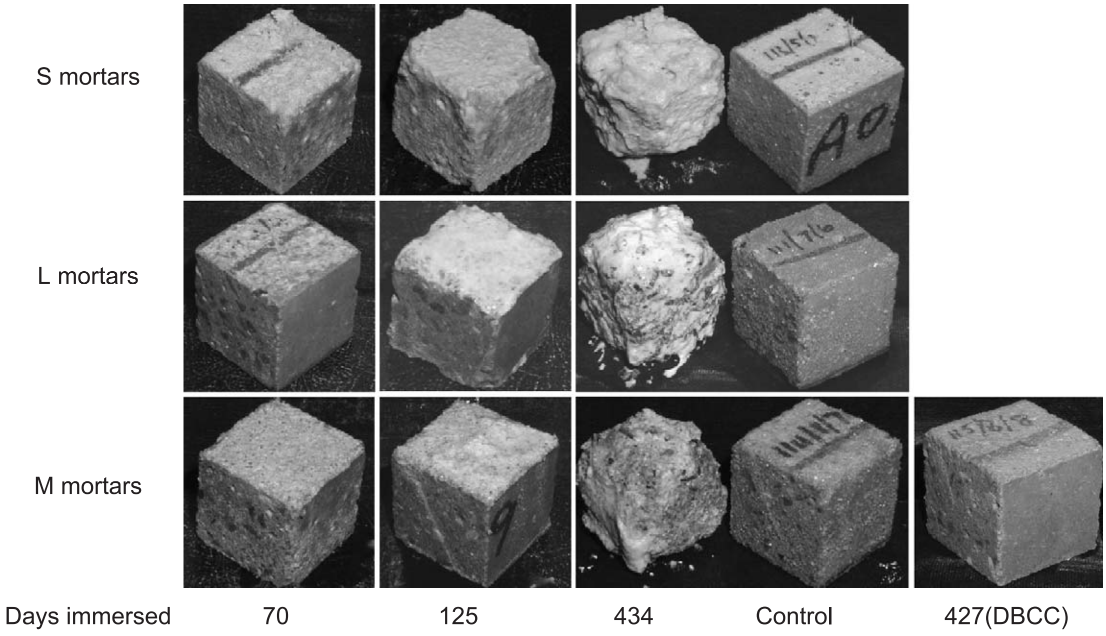

Fig. 2. Aggregate comparisons (NB controls stored in DB water only).

several minerals including quartz, calcite, brucite, gypsum and, occasionally, anhydrite.

Generally, the results of the XRD analysis of the degraded material from the top faces of the cubes indicated the presence of thaumasite and/or ettringite (or their solid solutions), together with other mineral types, notably, gypsum and, occasionally, brucite, with quartz or calcite from the aggregate. XRD traces for S mortars at 84 and 434 days are given in Fig. 3. More detailed traces, at approximately 16°2θ, for S and L mortars are presented in Fig. 4. These figures will be discussed in detail later in this section.

In the mixed aggregate mortars in the sulfate solutions made from DB, D, T and DBC water, the degraded material exhibited similar XRD traces to those reported above for the single aggregate mortars and are therefore not reported here.

Although the mixed aggregate sample in DBCC showed no visual signs of degradation, material was scraped from the top surface for XRD analysis. Aragonite was the only phase detected, apart from calcite and quartz from the original aggregate, but the intensities of the peaks due to both these phases were weaker than those attributable to aragonite.

For the limestone aggregate mortars in all three sulfate solutions, the degraded material consisted principally of a thaumasite form of solid solution because there were strong peaks in the XRD patterns at about 9.2°, 15.9°, 18.5°, 19.3°, 25.1° and 28.0°2θ. The peaks at the higher angles (>25°), which are better than those at lower angles to differentiate between thaumasite and ettringite, clearly showed the absence of any strong peaks associated with ettringite. The peaks present, however, were displaced towards lower values of 2θ (higher d-spacings) than pure thaumasite, indicating a thaumasite form of solid solution, although with time (>26 weeks), there was a slight shift towards lower d-spacings. Gypsum and calcite were also detected in the XRD traces.

In the pure quartz sand aggregate mortars in all three solution types, an ettringite–thaumasite solid solution formed on the top surface. In the case of the sulfate solution made with DB water, the degraded material was initially (from 56 to 70 days immersion) an ettringite form of solid solution followed by a period (from about 70 to 112 days) when a thaumasite form of solid solution was the major phase (see Fig. 3). Beyond 112 days, the pore solution composition was such that an ettringite solid solution began to predominate again. To form, thaumasite needs a source of carbonate ions, and in this system, it was concluded that the only source of carbonate ions had to have originated from atmospheric carbon dioxide during carbonation. This is confirmed by the size of the calcite peak at about 29.5°2θ, which was very large after 84 days, when little reaction had taken place, but had virtually disappeared after 434 days when the carbonate ions had been consumed in the formation of thaumasite (Fig. 3). The main exposure to CO_2 would have occurred during the 24-h air cure that took place after casting, but could also have arisen during the cutting of the mortar bars and the labelling of the cubes before immersion in the sulfate solution.

The XRD patterns for degraded material from both the limestone and silica sand mortars in DB water have been examined up to 585 days immersion in sulfate solution. Comparative traces for the (110) peak at about 16°2θ for both mortar types, after 84 and 434 days, are shown in Fig. 4. In the S mortars, as described above, there was a broad

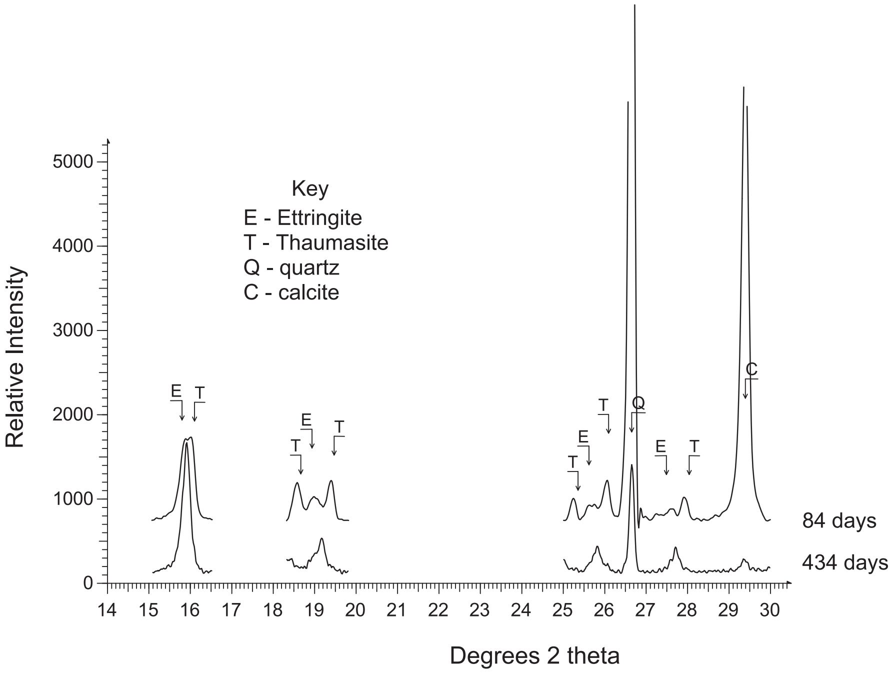

Fig. 3. XRD traces for S mortars immersed in sulfate solution made with DB water.

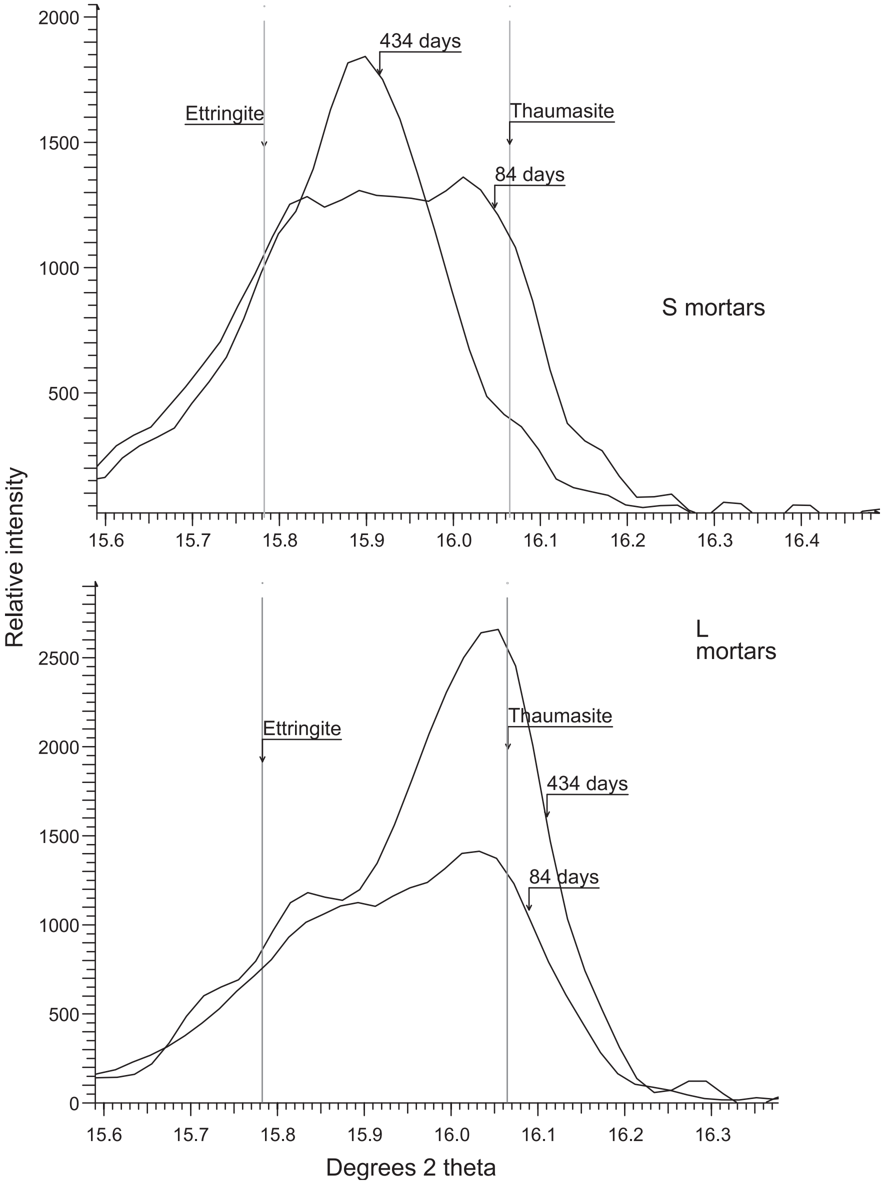

Fig. 4. Development of thaumasite in different aggregate mortars immersed in sulfate solution made with DB water for the periods indicated.

peak after 84 days, showing the presence of both ettringite and thaumasite solid solutions, but with time, the thaumasite solid solution disappeared, leaving a single strong ettringite solid solution peak. Over the same time scale, the dominant peak in the L mortars remained as a thaumasite form of solid solution, although a lesser amount of an ettringite form of solid solution was also observed.

In addition, the *a* dimension of the unit cell has been estimated from this peak for the two mortars and plotted against time (Fig. 5). The variation of *a* with time and the final values determined after 585 days are different. With a minimum measurement interval on the X-ray diffractometer of $0.02^\circ 2\theta$, it is estimated that the error in the determination of the *a* dimension is about ± 0.007 Å. The results have been compared with the *a* dimensions reported in the literature [12–18]. The observed differences in the two mortar types are significant and are discussed in Section 4.2.

XRD analysis of the mould faces of the pure quartz aggregate mortars indicated the presence of a broad solid solution of thaumasite and ettringite together with gypsum and, to a lesser extent, brucite. For thaumasite to form here again requires the availability of calcite, but the small quantity, together with only a very fine surface skin (blistering), would suggest a much lower level of carbonation compared with the top surface, consistent with a limited amount of exposure to air, i.e., exposure only occurring after the initial 24-h cure.

The cut faces would have had an even lower exposure to carbon dioxide than the mould faces, which could explain the absence of attack on these surfaces.

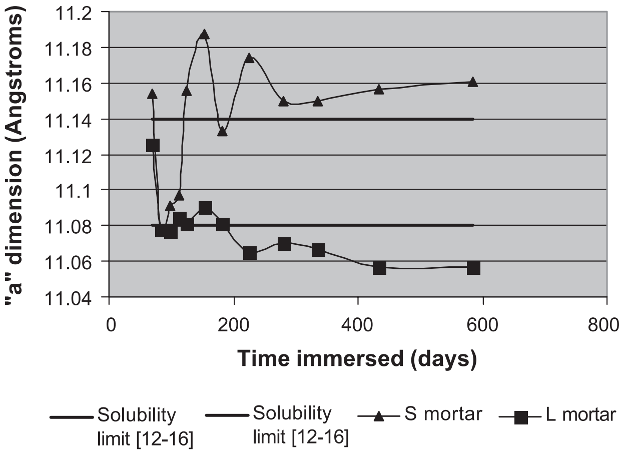

Fig. 5. Change in *a* dimension with time for S and L mortars using (110) peak (For thaumasite a = ca.11.05 and for ettringite a = ca.11.23 Angstroms).

The extent of TSA observed in the "control experiment" was unexpected, and further work was undertaken to ascertain the extent of attack under different carbonation conditions.

3. Further experimental work and results

3.1. Experimental setup

Further experiments were devised to investigate the role of carbonation in the development of TSA. These included using similar conditions to some of the original experiments but introducing mixing and curing in a carefully controlled nitrogen atmosphere.

To provide a better physical comparison between mortars made with the high-quality sand and those made with limestone aggregates, the limestone was ground and graded to a similar grain size distribution as the high purity quartz sand (99% falling between 0.425 and 0.075 mm). The same OPC and cement-to-aggregate ratio were used as before with a water-to-cement ratio of 0.82, adjusted to suit the fineness of the aggregate. The mixing and casting were carried out by hand in a glove box with a flowing nitrogen atmosphere, and after casting, the samples were left under nitrogen for the first 24 h of curing. Individual polythene moulds, about 22 × 22 × 22 mm, shaped like partially truncated cubes, were used to avoid exposure to the air, which had occurred previously when the mortar bars were cut into cubes. After 24 h, the samples were not demoulded but were seal cured to 27 days, and the cling film was removed (see Section 2.1). The samples were retained in the moulds, to limit sulfate exposure to the top surface of the sample only, and then immersed in sulfate solution, made with DB water, with the same chemical composition used previously. At all times, contact with the air was minimised by working in the glove box and, after immersion, by keeping the samples and solutions in polythene containers with tight-fitting lids. All the samples in these experiments were held at 5 °C.

3.2. Results

3.2.1. Visual observations

The samples were examined and removed as before, with significantly different visual results. Initially, the samples appeared similar, with both the high-quality quartz sand and limestone aggregate mortars being rapidly coated with a 2- to 3-mm thick white precipitate. The limestone aggregate samples again started to crack between about 70 and 90 days immersion (i.e., similar to that observed previously), but degradation of the exposed surface was observed to be in two parts: a soft white material, which, by 143 days, was about 3 mm thick, covered with a thin and relatively hard, dark layer (about 1–2 mm thick).

The silica sand mortar, however, showed no signs of cracking or other attack after 186 days immersion. This is in marked contrast to the original samples that had been exposed to air during the first days' curing, which had started to crack after 56 days. The visual appearance of both mortar types is shown in Fig. 6.

3.2.2. X-ray diffraction

XRD traces for samples from both the high-purity silica sand (scraped from the top surface) and limestone (both light and dark material) mortars after 186 days are given in Fig. 7. These results, together with those obtained on earlier samples, are discussed below.

The XRD analysis of the white precipitate on both the pure sand and limestone aggregate mortars showed similar results up to 186 days, with the major crystalline phase present being brucite. Significant amounts of calcite and, to a lesser extent, aragonite were also detected, and their presence was believed to be a result of the exposure of the XRD samples to air during the sampling process or possibly due to the slow ingress of air into the "sealed" containers during the course of the experiment. This is because calcite was not detected in the sample between the end of the seal cure period and before immersion.

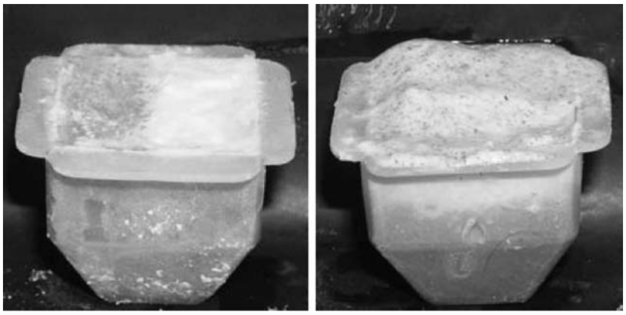
S mortar L mortar

Fig. 6. Aggregate comparisons with no carbonation, after 186 days immersion in sulfate solution.

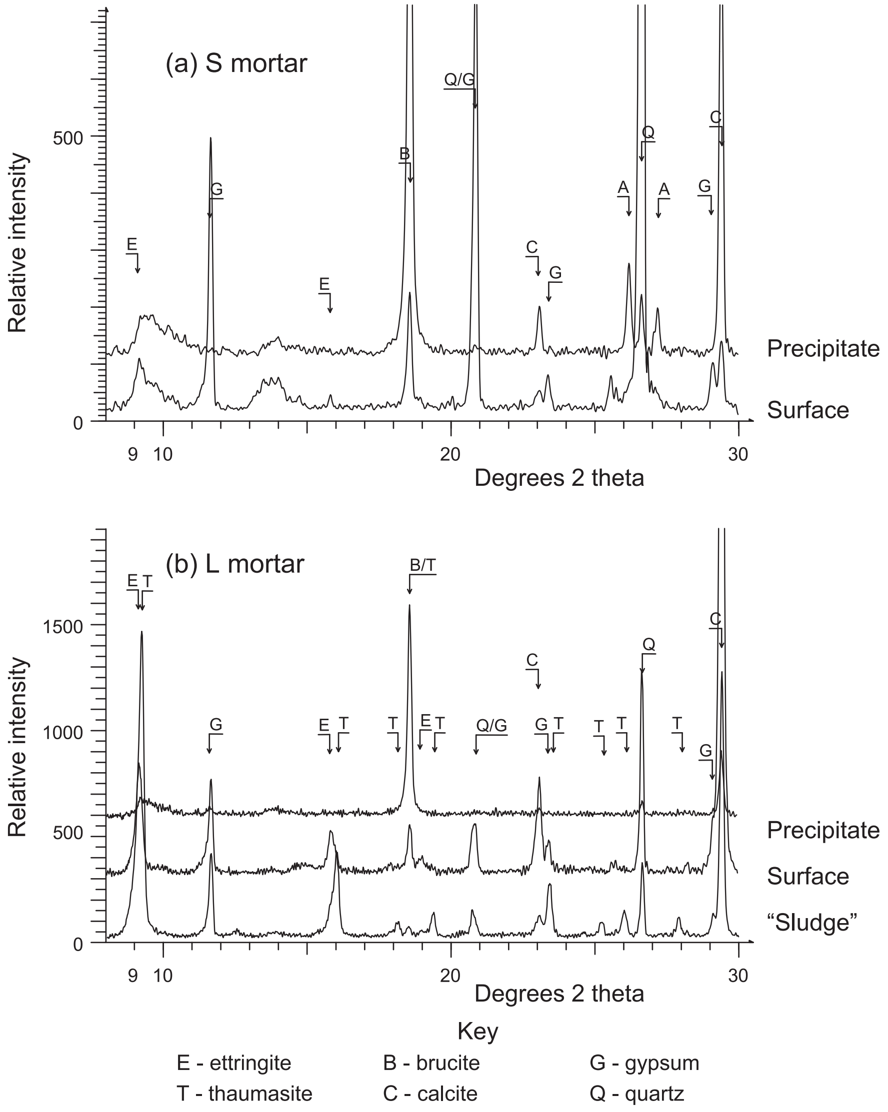

Fig. 7. XRD of precipitate and cube for (a) S and (b) L mortars after 186 days immersion in sulfate solution.

Before any attack was observed on the samples, material was scraped from the surface below the precipitate. The major reaction product present in this material for both aggregate types was gypsum together with small amounts of brucite. In the case of the pure silica sand mortars, a small amount of (secondary) calcite was also detected. The XRD analysis of the surface layer of the S mortar remained the same up to 186 days, but because of the attack on the L mortars, further analysis was required.

Once the limestone aggregate mortars had started to be attacked, it was possible to separate the dark surface layer from the soft white material, or sludge, underneath for separate XRD analysis. The soft white layer consisted of well-developed thaumasite (or thaumasite solid solution) together with gypsum and limestone, but no brucite. The dark surface layer was markedly different, with little or no thaumasite or thaumasite solid solution but (relatively weak peaks) of an ettringite form of solid solution together with strong gypsum peaks, a small amount of brucite and calcite from the aggregate.

4. Discussion

The visual observations reported in Sections 2 and 3 clearly demonstrate that to understand the mechanism of thaumasite formation and, hence, TSA, the role of carbon dioxide must be thoroughly understood.

In the initial experimental work, carbon dioxide was excluded from the systems immersed in DB water, except for 24-h exposure during mixing and initial curing, and a much lower level of exposure after 28 days curing. Under these conditions, the development of TSA was expected in the mortars containing limestone aggregates, but significant TSA was also observed in the silica sand aggregate mortars. The carbonate ions necessary for thaumasite to form had to have been derived from the formation of calcite from atmospheric carbonation.

In the second series of experiments, carbon dioxide was excluded during mixing and curing, even if small quantities entered the system at a later stage, because there was no detectable calcite in the silica sand aggregate (S) mortar immediately before immersion in solution. This obviously cannot be proved in the case of the limestone aggregate (L) mortar, but as that mortar was made under the same conditions, it is unlikely to have been carbonated. These samples are discussed first.

4.1. No carbon dioxide exposure

Both the uncarbonated S and L aggregate mortars initially appeared to react in the same way, precipitating significant quantities of brucite (Section 3.2.2), and, at the same time, high levels of gypsum were also detected in the top surface of the mortars. Eq. (9) would appear to be in line with these observations, except that it does not explain why the gypsum appeared within the surface layers of the mortar in preference to co-precipitating with the brucite (Fig. 7).

$$M\check{S} + CH + 2H \rightleftharpoons MH \downarrow + C\check{S}H_2 \tag{9}$$

Under the initial experimental conditions, the sulfate solution was saturated with gypsum and, thus, cannot dissolve anymore. Hence, the gypsum from the reaction did not co-precipitate with the brucite (Fig. 7) but, instead, was observed to have entered the surface pores. The reason for this is not clear, but it may be that the pore water initially has a low, or zero, gypsum concentration, and, with interconnected pores, calcium and sulfate ions can flow into the mortar under the concentration gradient created.

In the case of the S mortar, high sulfate levels did not give rise to visible signs of sulfate attack up to 186 days. Without calcite present, thaumasite cannot form, but it would also appear that ettringite did not develop either in sufficient quantities to cause cracking.

In the L mortar, significant TSA occurred in the sludge under a surface layer of mortar, but not in the surface layer itself. It may be that this layer was not conducive to sulfate attack because the pH was too low due to the removal of portlandite during the formation of the brucite [9]. Although, according to Eqs. (7) and (8), all the ingredients in the limestone mortar were present in this surface layer to form thaumasite, it did not form. A possible explanation is given later.

The presence of magnesium sulfate and the precipitation of brucite have therefore resulted in a high concentration of gypsum in the mortar, which, if other conditions are suitable, must favour sulfate attack and could help to explain why the presence of magnesium sulfate leads to the most aggressive sulfate attack.

In the body of the L mortar cube, there will be a high pH (>12) due to the presence of unreacted portlandite and both limestone and calcium silicate hydrates, but no gypsum, so thaumasite cannot form, except possibly via ettringite (Eq. (8)). However, there must be an interface or reaction zone, shown in Fig. 8, between the outer, low-pH (7.0–7.5) surface layer and the high-pH interior, and it appears that at this junction, the conditions are appropriate for TSA to occur.

4.2. With carbon dioxide exposure (carbonation)

The observations and XRD analysis on the samples with no air cure, as described above, are significantly different from those with an initial air cure (Section 2.2). In the latter, for both the S and L mortars, the first sign of attack was cracking of the top surface. This was followed by TSA under a top outer skin, although the skin was eventually consumed. The precipitation of brucite was very limited compared with the samples not air cured. Can these differences be explained and therefore help to explain what is happening in the formation of thaumasite?

When concretes and mortars made with Portland cement and either siliceous or calcareous aggregates are exposed to air during curing, the portlandite formed during the hydration process reacts with the CO_2 in the air to form calcium bicarbonate (Eq. (1)), which may convert to calcium carbonate (Eq. (5)), dependent on the pH levels. The formation of calcium bicarbonate will occur rapidly to begin with while the surface is wet, but because water must also be present for the reaction, it will slow down as the surface layer dries out and the CO_2 has to diffuse through the pore structure. As this drying takes place, the calcium bicarbonate will be converted to calcite and deposit on the outer surface and in the pores. An interface or reaction zone, where the carbon dioxide is reacting with the portlandite, will therefore move into the concrete/mortar, the depth being dependent on the porosity/permeability of the material, and on time. The latter parameter will be influenced by two factors: the drying time and how long the sample is exposed to carbon dioxide. The interface on a seal-cured item (i.e., exposed to the air for the first 24 h only) will be closer to the surface than one cured in air for 28 days. Similarly, the lower the permeability, the closer the interface will be to the surface.

If hydration in the surface layers is complete, the potential amount of portlandite that could form in this layer is about 25% of the initial cement content, which in a 3 parts aggregate–1 part cement equates to just over 6% in the test mortar. If all this portlandite reacts with carbon dioxide, then, there could be about 8% calcite, compared with the original solid material content, in the carbonated surface layer. If this calcite seals the surface/pores of the mortar, it will prevent the ingress of aggressive species into the interior of the mortar and therefore increase the resistance of the material to attack, including TSA. This would only happen in a good-quality mortar: If the mortar is of poorer quality and remains permeable, the converse will apply.

If the test mortar is now placed in a mixed sulfate solution, as previously described, and as can occur in the field, what occurs will depend on the conditions given above. If the surface has become impermeable, there will be a layer of calcite on the surface, which will not readily allow the ingress of the sulfate solution or the escape of portlandite to occur. With no portlandite, the pH at the surface will be stable at about 7–7.5, thus, brucite cannot form, and there will be no deposition of gypsum in the surface layers. The only place, therefore, that thaumasite could form would be at the surface, where all the ingredients shown in Eqs. (6)–(8) will be present. However, thaumasite has not been observed to form at these pH levels.

Conversely, if the surface remains permeable, some portlandite will diffuse outwards and, in doing so, will react with either the magnesium sulfate to form brucite and gypsum (Eq. (9)) or with the calcium bicarbonate, if present, to form either calcite or aragonite (Eq. (5)). The former reaction is more likely to occur because brucite is less soluble than calcium carbonate. As portlandite is consumed in both of these reactions, the availability of $(OH)^-$ ions is low, and the pH is unlikely to increase very much. Again, the formation of thaumasite is unlikely. Although the surface carbonated layer will remain at a pH of 7/7.5, the reaction to form brucite and gypsum (Eq. (9)) will continue, thus increasing the amount of gypsum that could react to form thaumasite. It is only when the Ca^{2+} and SO_4^{2-} ions reach the interface between the carbonated layer and the sound mortar below that conditions start to change with an increase in pH, together with the presence of calcium carbonate or calcium bicarbonate. All the ingredients are now present in close proximity for the formation of thaumasite, and this is in line with what has been observed for both the carbonated S and L mortars.

However, the subsequent development of the thaumasite–ettringite solid solutions in the two mortar types varied, as indicated in Fig. 5. The *a* dimension of the solid solution for the L mortars consistently indicated a thaumasite form of solid solution, while the S mortar only indicated a thaumasite form of solid solution over an initial time interval of about 4 weeks. This observation is consistent with sufficient calcite being available for a short time to form a thaumasite solid solution, and the only source of this calcite was from carbonation during the one-day air cure. Obviously, there was only a limited amount of calcite present (compare the amount of calcite shown in the two traces at 84 and 434 days shown in Fig. 3), and once this had been consumed, thaumasite could no longer form, although the reaction appears to continue, but with the formation of an ettringite form of solid solution. It is not clear, however, whether the disappearance of the calcite simply stops the thaumasite solid solution forming or whether the thaumasite solid solution formed dissociates to form the ettringite form of solid solution.

In previously reported work [3], a degree of carbonation has often been considered beneficial in preventing TSA, but it has been shown in this work that under certain conditions, the formation of calcite during carbonation can also act as a significant source of carbonate ions. It can therefore explain why TSA occurs in siliceous aggregate concrete or mortars, particularly as the thaumasite formed is normally observed to be close to the surface or in surface cracks [7] and, where the carbonation history is unknown, may also provide explanations of other unexpected results.

4.3. Mixed aggregate mortar in DBCC

Mixed aggregate mortar cubes, cured in air for 24 h and placed in the sulfate solution made with deionised and boiled water and 310 mg/l added calcium carbonate (DBC), reacted in a similar way with the equivalent samples immersed in the other water compositions (Section 2.2). The addition of carbon dioxide to the solution (DBCC) effectively produced a groundwater composition with aggressive CO_2 present. This carbonic acid must have reacted with the portlandite to form aragonite, as in Eqs. (1) and (5), in preference to the magnesium sulfate, and either sealed the pores with aragonite and/or calcite, thus preventing the egress of any more portlandite, or was present in sufficient quantity to continue reacting with the portlandite.

These observations have some parallels with the work by Zhou et al. [21] and Hill et al. [22], who, by adding sulfuric acid, attempted to maintain their sulfate solutions at a pH of about 4. To maintain this low pH, acid was regularly added to neutralise the alkalis produced from the concrete samples used, and thaumasite was shown not to form. In the present study the DBCC solution was initially acidic because of the presence of carbonic acid, and its pH increased only slowly, reaching 7.5 after 427 days. Thereafter, the pH increased more rapidly, reaching 10.7 after 586 days. The deposition of the calcium carbonate, more specifically aragonite (Section 2.2.2), must therefore have sealed, or nearly sealed, the surface of the mortar samples, suppressing the release of portlandite and further reaction.

4.4. Overall observations

This work has confirmed at least three general observations made in the literature [1], namely,

(a) a high pH, probably ≥ 10.5, is required for TSA to occur,
(b) thaumasite can occur in mortars with siliceous as well as carbonate aggregates, although it is likely that the attack will be confined to the surface and in surface cracks,
(c) magnesium sulfate is a particularly aggressive solution,

but it also helps to explain why this is so. Can it also be used to understand the mechanism of thaumasite formation and confirm, or otherwise, the validity of Eqs. (6)–(8)?

Hartshorn et al. [20] proposed Eq. (6) to explain the formation of thaumasite, gypsum and brucite. They concluded that portlandite is a reactant in the formation of thaumasite when magnesium sulfate is present [20] and cannot, therefore, simultaneously be a reaction product. It also assumes that magnesium sulfate takes part in the reaction to form thaumasite. The current work shows that in conditions where carbonation during curing did not occur, brucite formed very rapidly (Eq. (9)), and it is unlikely that any magnesium sulfate would be left in the static experimental conditions of this work to be a reactant, as in Eq. (6).

Where carbonation has occurred during the first day exposure to air, the egress of portlandite will have been reduced, as indicated by the lower levels of brucite observed in the XRD traces. However, although slower, it is probable that the reactions indicated above for the non-carbonated samples will be the same.

The sulfate concentrations used in this current work were intentionally chosen to be representative of groundwater found in the field trial at Shipston on Stour [7]. At these sulfate levels, it appears that brucite only forms on the surface of the mortar samples and is not associated with the formation of thaumasite that has formed under a skin of unreacted mortar. The formation of this brucite has, however, resulted in a high concentration of gypsum in this skin and will therefore help promote the formation of thaumasite. If the magnesium sulfate does not take part directly in the reaction to form thaumasite, then, Eq. (6), proposed by Hartshorn et al. [20], in a study which used significantly higher sulfate concentrations, may require further investigation.

When magnesium sulfate is not present, Bensted [19] has proposed Eqs. (7) and (8), which both have portlandite as a product of reaction. The current work has confirmed the need for a high pH (generally, >10.5 [1]) for the formation of thaumasite. This high pH may be due, initially, to the presence of both potassium and sodium hydroxide in the pore solution, but it is more likely that the pH of 10.5+ is maintained by the continued dissolution of portlandite from the cement hydration products, again suggesting a requirement for portlandite to be present as a reactant. If this is the case, then, Eqs. (7) and (8) may not be valid.

A better understanding of the reaction mechanism is provided by considering calcium bicarbonate, instead of calcium carbonate, as the source of carbonate ions required for thaumasite formation. The calcium bicarbonate cannot exist at the high pH present inside the reaction interface (i.e., in the core of the material) but can be present at a high concentration in the outer, lower pH layer. Somewhere within the interface layer, therefore, will be an intermediate pH where calcium bicarbonate will still be present following carbonation, and here, thaumasite can form. The pH of 10.5, mentioned above, may be significant in this reaction because it is a value very close to the crossover point (pH 10.33) on the solubility curves of the carbonate ions and bicarbonate ions, shown in Fig. 1. A schematic representation of the reactions taking place in the top surface of a carbonated mortar sample is shown in Fig. 8.

If the reacting species is calcium bicarbonate and not calcium carbonate, there are now additional driving forces for the formation of thaumasite. The first is that it effectively introduces additional carbonate ions into the system, which, as the pH increases, want to precipitate, as per Eq. (5). However, more importantly, as they precipitate, there is the generation of aggressive CO_2 (CO_2^A or $\check{C}^A$), which is then available to dissolve more calcite elsewhere in the sample. The CO_2^A is derived from the stabilising CO_2 (CO_2^S or $\check{C}^S$), which is no longer required to maintain the calcium bicarbonate in the solution.

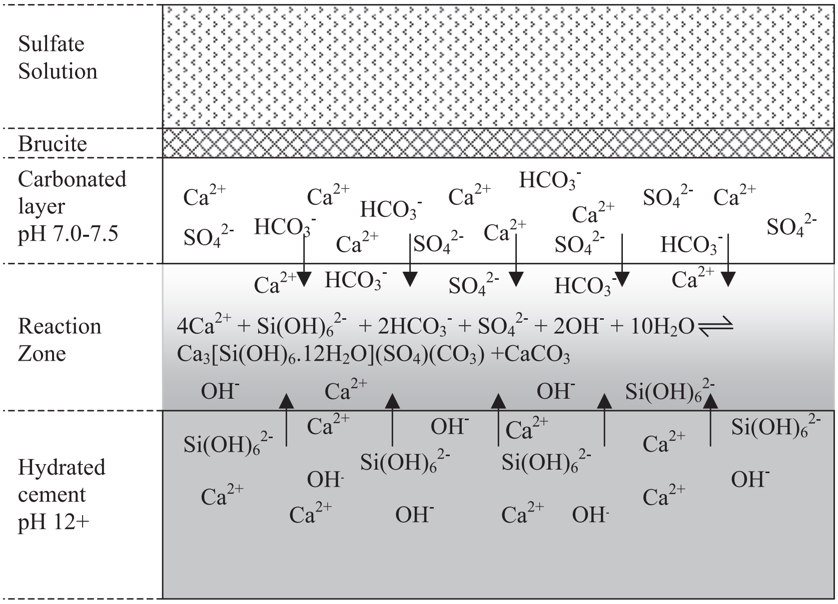

Fig. 8. Schematic of the top surface of a carbonated mortar showing the movement of chemical species into the reaction zone.

The possible equations for thaumasite formation, involving calcium bicarbonate as $\mathrm{CH\check{C}_2}$, now become

$$\begin{aligned}&\mathrm{C_3S_2H_3 + 2C\check{S}H_2 + 2[CH\check{C}_2(+\check{C}^S)] + CH}\\&\quad\mathrm{+ 20H \rightleftharpoons 2C_3S\check{C}\check{S}H_{15}}\\&\quad\mathrm{\downarrow +2C\check{C} \downarrow +2\check{C}^A}\end{aligned}\tag{10}$$

$$\begin{aligned}&\mathrm{2C_3S_2H_3 + C_3A.3C\check{S}.H_{32} + 6[CH\check{C}_2(+\check{C}^S)] + CH + C\check{S}H_2}\\&\quad\mathrm{+16H \rightleftharpoons 4C_3S\check{C}\check{S}H_{15} \downarrow +8C\check{C} \downarrow +AH_3 + 6\check{C}^A}\end{aligned}\tag{11}$$

The amount of aggressive CO_2 derived from the stabilising CO_2 will depend on the initial concentration of the calcium bicarbonate in solution, and could be very significant indeed if the partial pressure of CO_2 is high and high concentrations of gypsum are present [6], leading to further rapid dissolution of calcite. Such circumstances are known to be important in karst geomorphology [8], and there may be a good correlation with thaumasite formation.

The concentration of the calcium bicarbonate will be increased still further at 5 °C compared with 20 °C because the solubility of carbon dioxide approximately doubles as the temperature drops from 25 to 0 °C [8]. This must be one of the main reasons why thaumasite forms more readily at 5 °C.

In a closed system, the calcium bicarbonate and aggressive CO_2 will be consumed, thus, it is likely that both the reactions will slow down and eventually terminate if solutions are not replenished with suitable water. Conversely, once established, the dissolution of calcite present in the concrete/mortar may be sufficient to maintain the reaction. Certainly thaumasite has appeared to form readily in this work with a plentiful supply of limestone and when the samples were not intentionally exposed to air, so the above equations do not fully explain what has happened in that system. In a system open to the air or exposed to slowly changing groundwater conditions, the reaction can continue as above.

Eqs. (10) and (11) appear to give a good representation of what is observed during TSA, including the formation of secondary calcium carbonate, normally in the form of calcite or, more unusually, aragonite, which is often observed to co-precipitate with thaumasite. Both equations include portlandite as a reactant as opposed to a product in the reaction to form thaumasite.

This mechanism suggests that for TSA to occur, there is a need for an interconnected pore system, which can act as pathways for reacting species but, at the same time, can isolate different reactions that could not otherwise take place in such close proximity.

5. Conclusions

This work has demonstrated that the role of carbon dioxide is very important in the development of thaumasite in both carbonated and uncarbonated mortar samples, made using OPC and different aggregates and immersed in sulfate solutions at 5 °C. The conclusions can be summarised as follows:

- TSA can occur in systems without the addition of limestone filler or aggregate if exposed to atmospheric carbon dioxide.
- The required carbonate is provided by atmospheric carbon dioxide via the intermediate formation of bicarbonate ions.
- Thaumasite can only form when all the chemical species are present, and this has been shown to occur at a reaction interface below the outer surface of the sample mortars.
- The reaction interface coincides with the depth of atmospheric carbonation, where bicarbonate ions are present and sulfate ions are being supplied from the surrounding solution and hydroxyl ions from the inner core of the mortar.
- A suitable pore structure is therefore required to promote the optimum development of thaumasite.
- The presence of bicarbonate ions, instead of carbonate ions, appears to represent better what is observed to occur in the reaction to form thaumasite, as given in Eqs. (10) and (11).
- The reaction of magnesium sulfate with portlandite produces high concentrations of calcium and sulfate ions in the outer layers of the mortar, which helps to explain why magnesium sulfate appears to be the most aggressive sulfate solution in the occurrence of TSA.
- The doubling in solubility of carbon dioxide in water, as the temperature falls from 25 to 0 °C, helps to explain why thaumasite forms more readily at low temperatures.

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