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Thaumasite—direct, woodfordite and other possible formation routes

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Abstract

Two main formation routes for thaumasite exist below 15 °C. One is the direct route from C–S–H reacting with appropriate carbonate, sulfate, Ca^{2+} ions and excess water. The other route is the woodfordite route from ettringite reacting with C–S–H, carbonate, Ca^{2+} ions and excess water, in which thaumasite arises through the intermediate formation of the solid solution woodfordite. The woodfordite route for thaumasite formation appears to be relatively quicker (although still slow) than the direct route, presumably because with the former the ettringite already has the octahedral $[M(OH)_6]$ units that can facilitate the critical change from $[Al(OH)_6]^{3-}$ to $[Si(OH)_6]^{2-}$ groupings. Both routes are mutually dependent on each other. The presence of magnesium salts can modify the path to thaumasite formation. High pressure might be able to stabilise $[Si(OH)_6]^{2-}$ groupings and allow thaumasite to become formed above 15 °C. This possibility is discussed.

Keywords: Thaumasite; Woodfordite; Sulfate attack; 6-coordinated silicon; Birunite

1. Introduction

Thaumasite is an unusual mineral in that it contains silicon in 6-coordination with hydroxyl. Very few minerals contain silicon in 6-coordination with oxygen or hydroxyl and most of these are formed under pressure [1]. The pure mineral thaumasite contains $[Si(OH)_6]^{2-}$ groups which are very rare, only at present being known in the chromate analogue of thaumasite (chromate-thaumasite) [2]. Sodium silicate trihydrate Na_2SiO_3-$3H_2O$ was previously thought to contain silicon in 6-coordination with oxygen (hydroxyl), but was subsequently found by laser Raman spectroscopy to contain silicon in the normal 4-coordination state with oxygen [3]. Thaumasite can be represented chemically as $Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 24H_2O$, or more simply as $CaCO_3 \cdot CaSO_4 \cdot CaSiO_3 \cdot 15H_2O$, and would be known chemically as hexacalcium bis-hexahydroxosilicate dicarbonate disulfate tetracosahydrate in the pure state.

Where thaumasite is more unusual amongst the compounds containing silicon in 6-coordination with oxygen is that it is formed at atmospheric pressure. Some silicon phosphates containing silicon 6-coordinated by oxygen are formed at or near atmospheric pressure, but other minerals with this type of coordination are usually encountered at high temperatures and pressures, because of the strong polarisability of the Si^{4+} cation [1,4]. Germanium, the next chemical element in Group 4A of the periodic table after silicon, forms a wide range of germanates, most of which contain germanium in 4-coordination with oxygen [5]. However, there are more germanates than silicates with germanium in 6-coordination with oxygen/hydroxyl due to the greater size and thus lower polarisability of the Ge^{4+} cation. Indeed, there are many analogous silicates and germanates (with 4-coordinated oxygen/hydroxyl). It is possible that there could be a germanate analogue of thaumasite, of the type $Ca_6[Ge(OH)_6]_2(CO_3)_2(SO_4)_2$ x-H_2O (where x may be 24 or close to it) that could in theory form easier than thaumasite does, but this awaits discovery.

The reality is that thaumasite as a product of sulfate attack in cements, mortars and concretes, like the other cement-related mineral hydration products like C–S–H, ettringite and monosulfate-$C_4(A,F)H_{13}$ is not a pure phase and contains a range of impurities in solid solution [6].

2. Formation by the direct route

Thaumasite forms below 15 °C (ideally at 0–5 °C) by the general reaction of sulfate with carbonate (either CO_3^{2-} ions or atmospheric CO_2), silicate (including C–S–H)

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and excess water in the presence of calcium ions. Common reactants include gypsum, calcite and C–S–H. The reaction is very slow and normally takes several months to obtain a significant yield [6–8]. Both the alite phase C_3S and the belite C_2S can provide the binder C–S–H, which can react to form the non-binder thaumasite:

$$Ca_3Si_2O_73H_2O + 2\{CaSO_42H_2O\} + 2CaCO_3 + 24H_2O \rightarrow Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_224H_2O + Ca(OH)_2$$

$$Ca_3Si_2O_73H_2O + 2\{CaSO_42H_2O\} + CaCO_3 + CO_2 + 23H_2O \rightarrow Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_224H_2O$$

The calcium hydroxide formed would not stay as such – it would most likely carbonate by reaction with atmospheric carbon dioxide or CO_2 dissolved in the water to become a potential or actual reactant for forming more thaumasite:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Alternatively the calcium hydroxide could disappear by being a high lime reactant in the general form for producing thaumasite in a more direct manner.

3. Formation by the woodfordite route

The woodfordite route also arises below 15 °C, by reaction between ettringite, silicate (particularly C–S–H) and carbonate (either CO_3^{2-} ions or atmospheric CO_2) in the presence of excess water. Woodfordite is the name given to the solid solution whose end members are ettringite and thaumasite. Common reactants include C–S–H and calcite. This reaction is also very slow to begin, but once thaumasite has started to form the rate of reaction appears to rise significantly. Both alite C_3S and belite C_2S form the C–S–H binder, whilst aluminate C_3A and ferrite C_4AF with gypsum contribute to thaumasite formation via the woodfordite route. This reaction can be depicted as follows:

$$\begin{aligned}&Ca_6[Al_xFe_{(1-x)}(OH)_6]_2(SO_4)_326H_2O + Ca_3Si_2O_73H_2O \\ &\quad + 2CaCO_3 + 4H_2O \\ &\quad \rightarrow Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_224H_2O + CaSO_42H_2O \\ &\qquad + 2xAl(OH)_3 + 2(1-x)Fe(OH)_3 + 4Ca(OH)_2, \text{ or}\end{aligned}$$

$$\begin{aligned}&Ca_6[Al_xFe_{(1-x)}(OH)_6]_2(SO_4)_326H_2O + Ca_3Si_2O_73H_2O \\ &\quad + CaCO_3 + CO_2 + 3H_2O \\ &\quad \rightarrow Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_224H_2O + CaSO_42H_2O \\ &\qquad + 2xAl(OH)_3 + 2(1-x)Fe(OH)_3 + 3Ca(OH)_2\end{aligned}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The calcium hydroxide (portlandite) formed does not normally remain as an end-product, since it will readily react with carbon dioxide or CO_3^{2-} ions to form calcite and some water. The calcite formed is available to serve as a reactant for more thaumasite to be produced. As with the direct route, it is possible for portlandite also to become directly involved as a high lime reactant in the formation of thaumasite via the woodfordite route.

The solid solution between ettringite and thaumasite is not continuous. A likely discontinuity in this solid solution (woodfordite) has been found that is characterised by a gap at ca. 11.11–11.17 Å. This suggests that in practice an unstable range of compositions might exist within the solid solution series [9]. Such discontinuities, associated with large changes in surface energy, could be instrumental in the conversion of ettringite into thaumasite.

4. Comparisons between the direct and woodfordite routes

A qualitative study using DTA, infrared spectroscopy, optical microscopy and X-ray diffraction has shown that the woodfordite route is relatively quicker than the direct route (see Table 1). This has been established with the samples being examined every 6 months for 4 years.

More thaumasite was formed in consignment B in comparison with consignment A at all ages, although the differences were less marked at 6 months. Once

Table 1
Thaumasite formation by the direct and woodfordite routes

Consignment A[a]	6m vsl	12m vsl	18m sl	24m sl-m	30m sl-m	36m m	42m m	48m m
Consignment B[b]	6m vsl	12m sl	18m sl-m	24m sl-m	30m m	36m m-s	42m m-s	48m m-s

vsl: very slight, sl: slight, sl-m: slight to medium, m: medium.

[a] Consignment A: Thaumasite preparation from alite C_3S, calcite, gypsum and excess water at 2 °C with the minerals in stoichiometric proportions for thaumasite formation.

[b] Consignment B: Thaumasite preparation from pure ettringite, calcite and C–S–H at 2 °C in the proportions for thaumasite formation. (The C–S–H was obtained from C_3S having hydrated for 2 years with water beforehand under nitrogen to stop carbonation.)

thaumasite had slowly formed in detectable quantities, with the progression of time the relative rates of reaction to form thaumasite had increased in both consignments. The likely reasons for this are given later in the reaction mechanism.

In real cementitious systems being subjected to sulfate attack the direct and woodfordite routes are interdependent. This arises because the key difference between the two routes is the presence of ettringite as a starting material for the woodfordite route. Thaumasite formation in the direct route A affects the alite C_3S and belite C_2S phases, whilst thaumasite formation in the woodfordite route B affects all four principal Portland cement phases, alite and belite for the C–S–H which gradually engulfs the ettringite, and aluminate C_3A and ferrite C_4AF for forming the ettringite in the first place. Thus, when close to ettringite in the hardened cementitious paste, the C–S–H is likely to react preferentially to form thaumasite by first forming the intermediate solid solution woodfordite. Conversely, in areas of the hardened cement paste where there is a dearth of ettringite, C–S–H is more likely to react with CO_2 and/or calcite and sulfate from gypsum to form thaumasite. Although C–S–H in real hardening cements contains sulfate, which can assist in forming thaumasite, unlike that in ettringite it is not already present in the basic pseudohexagonal structure for easier transformation into woodfordite and thence into thaumasite (see below).

It should be remembered that in real cementitious systems none of the reacting phases is pure and nor consequently are the products. This means that thaumasite, as found in sulfate attack situations is impure, like ettringite and contains other ions in solid solution in its structure. This means that it is unlikely that any reliable differentiation could be found in practice for thaumasite formed by the woodfordite route as compared with that produced by the direct route. Also, the presence of significant and variable amounts of impurities in solid solution means that equilibrium conditions are likely to be non-existent in real thaumasite sulfate attack situations.

5. Mechanistic considerations

The reluctance of thaumasite to form above ca. 15 °C in confirmed sulfate attack situations, coupled with the stability of the mineral up to 110 °C (higher than ettringite) suggests that special conditions are necessary for its formation. After all, thaumasite is unusual in having silicon in 6-coordination with hydroxyl and being formed at atmospheric pressure. Most structures containing silicon in 6-coordination with oxygen are formed at high temperatures and pressures, on account of the highly polarising nature of the small Si^{4+} cation. The related element germanium, which also has an extensive cement chemistry, mostly forms compounds containing the germanium in 4-coordination with oxygen (or hydroxyl) like silicon. However, germanium does form stable compounds in 6-coordination with oxygen (or hydroxyl) since the Ge^{4+} cation is larger than that of silicon and is accordingly less polarisable and more able to accommodate 6-coordinated compounds.

For thaumasite to be produced, the conditions must be such as to favour its formation. There needs to be a transition state intermediate to permit an octahedral arrangement of OH^- ions around the highly polarising Si^{4+} ions which can last long enough for stable bonding to take place (see Fig. 1). This can arise more readily at lower temperatures where atomic and molecular vibrations are relatively slower. Furthermore, bearing in mind the highly polarising nature of the Si^{4+} cations, the presence of the planar tetra-atomic CO_3^{2-} ions would be able to spread or delocalise the charge from the silicon cations away from the hydroxyl groups sufficiently to permit a stable octahedral arrangement of the latter to assemble and allow bonding to take place. The $[Si(OH)_6]^{2-}$ groups thus formed would be very distorted octahedra and this is borne out from Raman spectral investigations of thaumasite.

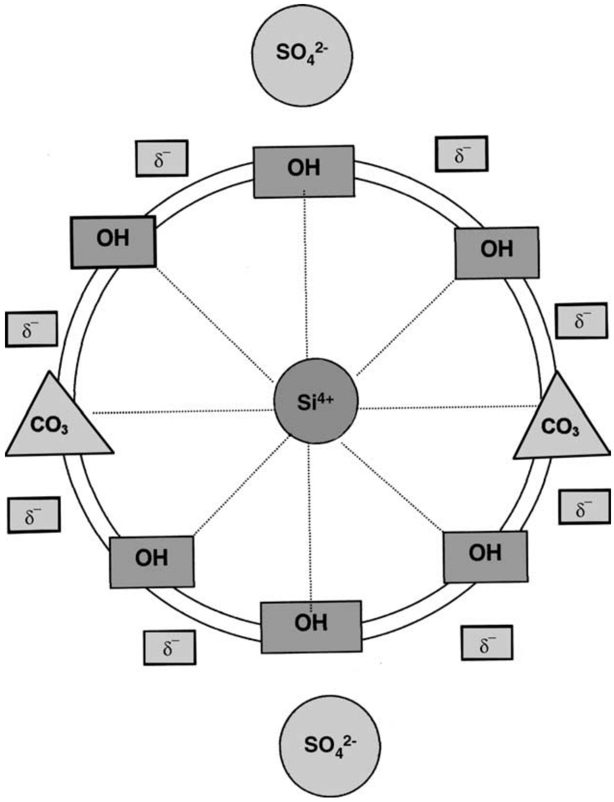

Fig. 1. Simplified presentation of charge delocalisation that stabilises the thaumasite structure (δ^- indicates delocalised spread of the negative anionic charge).

6. Effects of magnesium salts

Magnesium sulfate attack reinforces thaumasite sulfate attack and makes the overall deterioration worse. There is a *direct route method*, which has been delineated as follows, when excess water is present, with both thaumasite and brucite being formed as products [10]:

$$\begin{aligned}&Ca_3Si_2O_7 3H_2O + Ca(OH)_2 + 2CaCO_3 + 2MgSO_4\\&\quad + 28H_2O\\&\quad \rightarrow Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 24H_2O + 2Mg(OH)_2.\end{aligned}$$

The C–S–H and $Ca(OH)_2$ would also be undergoing carbonation and some direct sulfate attack, but sufficient of these materials would remain, or in the case of $Ca(OH)_2$ be formed during cement hydration to replenish some of the 'stock' lost and produce thaumasite at a slow rate because of the need for the $[Si(OH)_6]^{2-}$ ions to form from a stabilised transition state intermediate, as discussed above.

Thaumasite formation is a fairly general type of reaction at low temperatures and could indeed, contrary to what has been said [10], also be a product, as shown in the aforementioned mechanism, which can readily carbonate to form calcite, which can then participate as a reactant in a kind of 'recycling exercise'. The thaumasite forming reaction is modified somewhat in the presence of magnesium salts in that brucite $Mg(OH)_2$, which has a lower solubility than portlandite $Ca(OH)_2$, is also normally produced alongside thaumasite as a deterioration product.

Thaumasite can also be produced by the *woodfordite route* in the presence of magnesium sulfate. Such formation may also have taken place in the work done by Hartshorn et al. [10], since they report that the delay in the formation of thaumasite seems to have been associated with the reaction of C_3A to form ettringite. Some of the ettringite would also arise from C_4AF in Portland cement systems. It would be the case for thaumasite to be formed via the *woodfordite route* for sufficient thaumasite to form first of all due to the slow nature of thaumasite formation. There would need to be sufficient ettringite form that could be engulfed by C–S–H and calcium hydroxide from cement hydration and by calcium carbonate (or atmospheric CO_2 in the presence of Ca^{2+} ions) and magnesium sulfate with excess water around. Not too much C–S–H and CH would be directly carbonated in real Portland cement situations, so thaumasite and brucite can be formed by the two main routes mentioned.

Again the *woodfordite route* should be relatively faster than the *direct route*, because of the presence of the aluminate (and ferrite) octahedral skeleton in the ettringite formed already. This should better facilitate the transition state intermediate whereby Si replaces Al in the hexagonal arrangement of OH^- ions with the neighbouring CO_3^{2-} ions being able to delocalise the high charge of the small polarising Si^{4+} cations.

7. Possible thaumasite formation at elevated temperatures

In more recent times the question of whether or not thaumasite can be formed at more elevated temperatures, and if so how, has arisen periodically.

In one instance the remnants of a hardened Class G oilwell cement were removed from the downhole annulus in a Canadian wellbore at a bottom hole static temperature of 40 °C and a pressure of ca. 20 MPa. An absence of both C–S–H and ettringite was observed, although there was extensive calcite. No thaumasite was found, but the total absence of bonded material indicated that thaumasite might have arisen as a fine powder and could have dropped out of position to points lower down the annulus that were not examined at the time. Alternatively, flowing brines in the rock formation might have contained dissolved CO_2 that could have carbonated the C–S–H binder, and this would not have involved thaumasite formation. It did not prove to be possible to retrieve any further material from this particular well, so the likelihood of thaumasite formation under the specific well conditions remained possible, but unproven [11].

Interestingly the mineral birunite was reported to occur with numerous other minerals in efflorescent mineral assemblages associated with cracked and degraded residential concrete foundations in Southern California. These were primarily examined by X-ray diffraction [12]. Birunite was discovered in Uzbekistan and reported to be a mineral of the thaumasite group. It has the composition $17CaSiO_3 \cdot 17CaCO_3 \cdot 2CaSO_4 \cdot 30H_2O$ [13,14]. So far, birunite does not appear to have been synthesised. Hence it is not known whether birunite is of significance in sulfate attack or not, or whether it has associations with thaumasite as an intermediary in its formation or a subsequential product thereof. There have been no recent X-ray crystallographic studies undertaken on birunite with modern equipment that has greater resolution than the older instrumentation, so many questions remain about the mineral, including whether it contains at least some of its silicon content in 6-coordination with hydroxyl. Based on the original formula, birunite might have a structure of the type $Ca_{34}H_{34}(SiO_4)_{13}[Si(OH)_6]_4(CO_3)_{17}(SO_4)_2H_2O$ [15].

Also more recent reports have been made of both birunite and thaumasite having been found in concrete subjected to sulfate attack. However, these claims concerning sulfate attack are not yet confirmed, because the prime tests were carried out by scanning electron microscopy using energy dispersive X-ray analysis, which is not *per se* a confirmatory investigative technique [16].

A range of suitable techniques is required to confirm whether these minerals are definitely present or not. Such techniques are likely to include optical microscopy in the petrographic examinations.

Nevertheless, it might be possible for thaumasite to form in Southern California at higher temperatures than found hitherto because of the high crystallisation pressures generated by some of the salts present. Salts such as thenardite, mirabilite and halite can achieve crystallisation pressures for supersaturated solutions of 970, 234 and 1845 atmospheres respectively at 0 °C, which increase with temperature rise [12]. In theory $[Si(OH)_6]^{2-}$ groups could possibly form at higher temperatures than 15 °C by the application of pressure, which could force the stability of such octahedral groupings in a transition state intermediate and hence allow the bonding to develop that could produce thaumasite.

Clearly these situations need to be carefully investigated with a wide range of tests in order to show clearly if thaumasite can be formed above 15 °C under pressure.

8. Conclusion

Methods of forming thaumasite during sulfate attack upon Portland cement based compositions have been discussed. Thaumasite can form below 15 °C by two different but closely related routes. These are the direct route from calcium silicate hydrate C–S–H formed during hydration of the siliceous phases alite C_3S and belite C_2S, and the woodfordite route from ettringite produced during hydration of the aluminate C_3A and ferrite C_4AF phases in the presence of calcium sulfate The woodfordite route proceeds by way of the woodfordite (the discontinuous solid solution between ettringite and thaumasite). Thus all the main phases can ultimately give rise to the non-binder thaumasite. Thaumasite is slow to appear, but ultimately the reaction can increase significantly. The key factor for forming thaumasite is the assembly of 6 OH^- ions around an Si^{4+} cation to give $[Si(OH)_6]^{2-}$ groups in a stable environment. Such an environment exists below ca. 15 °C, where CO_3^{2-} groups are also present to delocalise the high charge of the strongly polarising Si^{4+} cation. Although not yet confirmed to exist at more elevated temperatures, such an existence could be possible on theoretical grounds under pressure, if that pressure were sufficient to stabilise the presence of the $[Si(OH)_6]^{2-}$ anionic groupings.

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