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On the formation of thaumasite $CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$: Part II

F. Bellmann

Contribution by J. Bensted

[Affiliation of contributor to add]

Bellmann has produced an interesting theoretical study using thermodynamic data to discuss the formation of thaumasite,[8] which has followed on from an earlier more introductory contribution.[9] Bellmann's thesis is that according to thermodynamic calculations the formation of thaumasite is estimated to proceed from almost all mineral assemblages that can occur in concrete if gypsum acts as a sulphate source and only the carbonate zone might be immune against formation of thaumasite.[8] He then goes on to say that in contradiction to an earlier assumption,[2] ettringite and C–S–H are indicated to be stable in the presence of calcite, not giving way to thaumasite.

There are two issues here.

(*a*) There is no evidence that the presence of gypsum *per se* (as opposed to sulphate in general existing in the cementitious system) is the sole sulphate criterion necessary for thaumasite to form. After all, in a hardened Portland cement, some 60–70% of the sulphate normally ends up in the C–S–H phase, with little or no gypsum remaining. What is important here is the actual availablity of sulphate with the form of sulphate being very much a secondary issue in terms of thaumasite formation.

(*b*) If ettringite and C–S–H are stable in the presence of calcite as Bellmann infers,[8] then logic would dictate that thaumasite should not be formed via ettringite in the woodfordite route.[2] In fact, below 15°C thaumasite forms relatively *more easily* through the woodfordite route than through the direct route where ettringite is not actually involved.[10] The existence of the woodfordite route infers that the presence of ettringite in the hardened cement paste, which arises before thaumasite starts to form significantly, facilitates the actual production of thaumasite with the passage of time.

The greater facilitation for thaumasite formation via the woodfordite route can thus be explained on the basis that the presence of an octahedral framework for the $[Al(OH)_6]^{2-}$ groups within ettringite already has the basic skeletal structure for facilitating gradual replacement of Al by Si from C–S–H. This would allow a transition state intermediate of six OH^- groups surrounding the highly polarising Si^{4+} cations to remain stable long enough to allow the formation of stable $[Si(OH)_6]^{2-}$ groups by producing sufficient solid solution that can lead to displacement. Carbonate ions CO_3^{2-} are also very important here from the viewpoint of charge delocalisation with the silicate groups to allow $Si(OH)_6$ octahedra to become stabilised at ordin-

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ary pressures. Indeed, without the carbonate groups the silicate octahedra would not be stabilised.[10] Evidence for likely charge delocalisation comes from thaumasite, once having formed, being more stable than ettringite and undergoing sharp decomposition at *c.* 110°C.[10]

The low formation temperatures appear to be critical for thaumasite to be produced under ordinary pressure conditions. Indeed, apart from certain silicon phosphates, which are formed at or near atmospheric pressure, and the chromate analogue of thaumasite, octahedral co-ordination of silicon by oxygen is rare and mainly occurs for mineral assemblages under high pressure and high temperature conditions.[11] This is different from the situation with germanium, where 6-co-ordination of germanium by oxygen (hydroxyl) is much more common,[12,13] as a result of the lower polarisation of the larger Ge^{4+} cation compared with the smaller Si^{4+} one.

There are other criteria that need to be considered, since cementing reactions appear to be commonly thought of as proceeding to completion, when this is not necessarily the case in reality.

The reaction of the aluminate phase C_3A with gypsum to form ettringite only involves minority quantities of C_3A and SO_3 combined as ettringite at both initial and final set.[14] Indeed this reaction does not proceed to anything like completion, which can be readily ascertained by the quantities of sulphate found in the C–S–H phase. Similar comments can be made about the ferrite phase. This presents problems with the use of thermodynamic data for producing thermodynamic balances. Furthermore, the difficulties involved in producing pure ettringite from reacting C_3A with gypsum in excess water, because of the reaction not going to completion, in comparison with its ready formation by reacting aluminium sulphate with lime in excess water, need to be more fully appreciated.[14-16] They underline the problems that can arise in relying upon thermodynamic data for C_3A reacting with gypsum in water for cement studies. Nor must it be forgotten that the sulphoaluminate phases in real Portland cement systems are impure,[16,17] which also affects any equilibration in practice.

In addition, the likelihood of incomplete cementitious reactions, side reactions and interactive effects cannot be disregarded when considering the value of thermodynamic data in making predictions about particular cement-related chemical reactions. Under such conditions the reliability of thermodynamic data used may at times be questionable where complex reactions are concerned. As well as contemporary thermodynamic data, there is also much older data in current use. Much of the older data has been obtained from the technical literature published many years ago and was based upon procedures prevalent at the time, which have not always been as well documented as they should have been. As a result, thermodynamic data[18] utilised to obtain thermodynamic balances during cementitious reactions may be satisfactory, but not always. Such a situation arises for a variety of reasons. These include the question of accuracy of older data obtained by cruder experiments than are normally undertaken today, the possibility of unreported side reactions, the lack of complete reaction taking place in some instances, and ignoring the fact that most sulphate actually ends up in the C–S–H phase (Mchedlov-Petrossyan O. P. 1997, personal communication). Therefore, even with accurate thermodynamic data utilised on a theoretical basis, predictions may not necessarily correspond precisely to what happens in practice in the field.

One particular area where there have been problems with lack of equilibrium in cementitious reactions is the hydrothermal situation for Portland cements.[19] As a consequence, there are situations, for instance, where a phase like the crystalline calcium silicate hydrate tobermorite, which theoretically should not be stable above 150°C, may in real cementitious systems remain stable indefinitely at 200°C. What this means is that the application of thermodynamic data to cementitious systems must be applied with caution, in order to have proper validity in connection with the actualities of the experimentally observed phenomena, including the possibility of side reactions.

Overall, this can suggest that the observation of the woodfordite (incomplete ettringite–thaumasite solid solution) route for the formation of thaumasite,[2,10] which has been observed practically in numerous instances, cannot be denied upon the simple basis of quoting thermodynamic data relating to pure systems in isolated scenarios.[8] Studies of the incomplete solid solution in woodfordite have been made by Barnett *et al.*[5,20] Their experiments have shown that ettringite can be replaced by up to 50% of its Al by Si and thaumasite can be substituted by up to 12% of its Si by Al. As a result, when ettringite effectively reacts with C–S–H to form thaumasite, the route involves proceeding via an increasing solid solution of Si in ettringite. This is then followed by a decreasing solid solution of Al in ettringite when the points of discontinuity of the ettringite–thaumasite solid solutions are moved through in the presence of C–S–H in the reacting media. The mechanism of reaction is complex and involves the stereochemical arrangement for having six OH^- ions surrounding a highly polarising Si^{4+} cation with the $CO_3{}^{2-}$ groups in close proximity to help delocalise the negative charge of the OH^- ions away from the Si^{4+} cations, so as to give a stable (although obviously distorted) molecular arrangement of $Si(OH)_6{}^{2-}$ groups at ordinary pressure.[10]

Furthermore, the work undertaken at Sheffield University should also be considered.[21] This work has shown that Portland-limestone cement pastes containing fine limestone additions (water/solids ratio 0·5% with 0, 5, 15 and 35% limestone additions) are susceptible to thaumasite formation after only a few months exposure to sulphate additions. Indeed, the extent of

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thaumasite formation was greater with increasing limestone additions and when magnesium sulphate was present in the solutions. Furthermore, C–S–H gel was consumed in these reactions. Such observations do not appear to be compatible with the idea of C–S–H not reacting with calcite in the presence of sulphate to form thaumasite. In addition, the view that only the carbonate *might* be immune against the formation of thaumasite[8] does not appear to be compatible with the results of the Sheffield work.[21] These experiments clearly showed that the greater the ground limestone addition in Portland-limestone cement composition, the greater the quantity of thaumasite produced.

Caution needs to be taken in seeking to translate results obtained in isolated modelling systems to real situations involved with practical cementitious systems.

Reply by F. Bellmann

A solubility product and a Gibbs free energy have been reported for pure thaumasite.[9] The obtained values served as a basis for the calculation of possible reaction paths for the formation of thaumasite in hardened cement paste at risk of sulphate attack.[8] These investigations and calculations referred to a temperature of 8°C which is commonly encountered in underground structures.

Some of the obtained results are the subject of a discussion by Professor Bensted. He raises three main points in his contribution.

(1) The question of use (or misuse) of thermodynamic calculations and the interpretation of the obtained results.
(2) The existence of a woodfordite route in the formation of thaumasite, which is not indicated by calculation.
(3) Hardened cement paste containing calcium carbonate is susceptible to the formation of thaumasite whereas completely carbonated cement pastes seem to be immune against the formation of this mineral.

Responses to these points are presented in the following paragraphs.

(1) The use of thermodynamic data and the interpretation of the results obtained by calculation.

As already stated,[8] all results obtained by thermodynamic calculation have to be considered in terms of their derivation. As with all methods, thermodynamic calculations have their power and their limitations. The important limitations are listed here.

(*a*) In the present case, the calculations refer to the mere formation of the mineral thaumasite (TF), not to the damage of a concrete structure by its conversion into thaumasite (TSA).
(*b*) Since kinetic aspects are not included, deviations from equilibrium are possible.
(*c*) A close mixture of the considered phases is assumed in the calculations but not present in hardened concrete.
(*d*) Thermodynamic data may not be accurate enough to obtain the correct results.

Given these uncertainties, Professor Bensted correctly concludes that 'caution needs to be taken in seeking to translate results obtained in isolated modelling systems to real situations involved with practical cementitious systems'.

However, such a translation is indeed possible and a deep insight into the chemical inter-relations of thaumasite formation can be gained by thermodynamic calculation. Translation can be performed by a careful comparison of the results obtained by calculation with those derived from experiments. Thermodynamic calculations are a powerful method to categorise the knowledge of chemical interaction but they require confirmation by experimental evidence. In contrast to experimental investigations which are a direct proof, thermodynamic calculations are only a more or less strong indication that a reaction can proceed. This was already outlined in ref. 9, where it is stated that the results of the calculations presented in ref. 8 will be compared with experimental evidence in a separate paper. Since these experiments are complicated and require a long experimental period, only preliminary data has been published up to now.[22,23]

Nevertheless, the available data from the author's observations and experiments reported in the literature confirm the results of the calculations. Some still unpublished results will be given below for the woodfordite route discussed by Professor Bensted.

In conclusion, validation of the results obtained by thermodynamic calculation is achieved by experimental investigations.

(2) The existence of a woodfordite route in the formation of thaumasite

General considerations

In his discussion, Professor Bensted demonstrates the stabilisation of the 6-co-ordination of silicon in thaumasite by carbonate ions and low temperatures. According to his view, '$[Al(OH)_6]^{2-}$' groups present in ettringite can be replaced by $[Si(OH)_6]^{2-}$ units in thaumasite. However, this refers to the arrangement of the ions in the crystal and not to the way by which thaumasite is formed. The displacement of '$[Al(OH)_6]^{2-}$' by the migration of such a group through a crystal is not likely. The binding energies are stronger than the thermal vibrations needed to allow such a temporary defect. Furthermore, such a group seems to be too big to 'travel'

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through a crystal. For this reason, the discussion of a substitution of ionic groups is helpful with regard to structural details but not relevant for the way the reaction actually progresses.

As stated for the formation of ettringite,[24] chemical reactions such as the hydration of cement in general, and the formation of thaumasite from ettringite in particular, proceed as a process of dissolution of an educt in the pore solution and the following precipitation of the product from the supersaturated solution.

A further point is that a progressing reaction is not allowed to violate the second law of thermodynamics. This law applies to all chemical reactions and the replacement of an ion in a crystal by another ion is not an exception. Reactions in isolated systems at constant temperature and pressure can only run spontaneously if there is a decrease in Gibbs free energy.

Thus the term 'replacement' can be used when comparing the crystal structures of ettringite and thaumasite, but is not appropriate when discussing a conversion of the first into the second. Other concepts have to be considered to characterise such a reaction. This will be done here. First, the results of thermodynamic calculations[8] will be repeated and then the experimental observations will be presented to validate these results. In this way it is possible to characterise the woodfordite route in the formation of thaumasite.

Initially the conditions have to be defined very carefully. There is no agreement on the equation that can be attributed to the woodfordite route. The original equation given by Professor Bensted[2] is shown below.

$$\begin{aligned}&C_3A{\cdot}3CaSO_4{\cdot}32H_2O + C_3S_2H_3 + 2CaCO_3\\&+ 4H_2O \rightarrow 2CaSiO_3{\cdot}CaSO_4{\cdot}CaCO_3{\cdot}15H_2O\\&+ CaSO_4{\cdot}2H_2O + 2Al(OH)_3 + 4Ca(OH)_2\end{aligned}$$

The formation of gypsum as a by-product is not likely since this phase can react with portlandite and aluminium hydroxide to ettringite. Subsequently, the formation of gypsum was not reported when the existence of the woodfordite route was demonstrated on pure phases at a temperature of 2°C.[10] Furthermore, aluminium hydroxide and calcium hydroxide should react to form calcium aluminate hydrate. Thermodynamic calculations show that the reaction given above can not proceed on its own at 8°C because there is no decrease in Gibbs free energy ($\Delta_rG = +43{\cdot}5$ kJ/mol). A more appropriate equation for the woodfordite route is given below.

Thermodynamic calculations

First, the reaction of ettringite to thaumasite or vice-versa depends on the presence of other phases which can be involved in this reaction. A reaction can proceed if there is a decrease in Gibbs free energy during this particular reaction. For further discussion, equation (12) from ref. 8 is recalled. The same educts are used as in the equation given by Professor Bensted[2] and the products were chosen to obtain a stable phase assemblage.

$$\begin{aligned}&1/3\ C_3A{\cdot}3CaSO_4{\cdot}32H_2O + 1{\cdot}7CaO{\cdot}SiO_2{\cdot}2{\cdot}617H_2O\\&+ CaCO_3 + 13{\cdot}249/3\,H_20\\&\rightarrow CaSiO_3{\cdot}CaSO_4{\cdot}CaCO_3{\cdot}15H_2O\\&+ 1/3\,C_3AH_6 + 0{\cdot}7\,Ca(OH)_2\end{aligned}$$

This equation describes a reaction of ettringite with C–S–H phases and calcium carbonate to thaumasite. The aluminium that is released during this reaction is assumed to be present in the form of hydrogarnet. The change in Gibbs free energy in this reaction was calculated to be +3·2 kJ/mol.[2] Formally, this would indicate that a formation of thaumasite from ettringite, calcite and C–S–H is not possible at the temperature of calculation (8°C), but the computed value is below the error margins in the thermodynamic data used here.

Experimental observations

The woodfordite route states a reaction of ettringite with C–S–H phases and calcium carbonate to thaumasite. Ettringite and C–S–H phases are present in virtually all cement pastes and calcium carbonate is also contained in many cases. For this reason, thaumasite could be formed via the woodfordite route in almost every hardened cement paste and also in almost every concrete. In such a case, no sulphate attack from the environment would be required and there would be an 'autogeneous' formation of thaumasite. There is overwhelming evidence that such a reaction does not take place in normal concrete at room temperature. Ettringite, calcite and C–S–H phases are a stable phase assemblage and do not react to thaumasite. This shows that thaumasite can not be formed via the woodfordite route at room temperature. In contrast to this, the mineral can be formed by the woodfordite route at a very low temperature (2°C) according to data published by Professor Bensted.[10] In this study, C–S–H phases from C_3S hydration were mixed with ettringite and calcium carbonate. After 6 months storage at 2°C, thaumasite was identified by X-ray diffraction (XRD). There was a steady increase of the amount of thaumasite reported up to 4 years. This is in contrast to the situation at room temperature at which thaumasite can not be formed via the woodfordite route. It therefore suggests that there is a point of inflection between these temperatures.

Further data was obtained at 8°C, the temperature of the thermodynamic calculations. Both directions of the woodfordite route have been studied in as yet unpublished investigations. In the first investigation, mortar bars made from Portland-limestone cement were stored for about 5·5 years in water at 8°C. As ettringite, C–S–H phases and calcite were all present they should have

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reacted to thaumasite if the woodfordite route can proceed at 8°C. Instead, investigations by XRD and electron microscopy showed that ettringite was still present and had not given way to thaumasite. This result is in agreement with field observations. A formation of thaumasite just by exposing the concrete to low temperatures was not reported.

In another experimental investigation, the reverse reaction of the woodfordite route was studied. Phase pure thaumasite from a geological source was mixed with portlandite, hydrogarnet and water. The phase development was controlled by XRD until 2·5 years. After this period, thaumasite was still present and had not reacted to ettringite.

At first glance these two investigations show conflicting results. No reaction was detected at 8°C for either of the sides of the woodfordite route. A closer inspection shows that they are in agreement with the thermodynamic calculations since they indicate that thaumasite is in equilibrium or close to equilibrium with ettringite and the C–S–H phases at 8°C. This is exactly the result of the thermodynamic calculations because a value close to zero indicates that both sides of the equation are in equilibrium. There is further support from the fact that the woodfordite route can proceed at 2°C (which is below 8°C) and can not proceed at room temperature (which is higher than 8°C). Between these temperatures there has to be a point of inflection which might be at or close to 8°C.

Nevertheless, ettringite plays an important role in the formation of thaumasite by being a nucleus for this mineral.

In conclusion, the thermodynamic calculations and experimental investigations indicate that the formation of thaumasite via the woodfordite route can only proceed at very low temperatures (2°C) that are below the ones commonly encountered in underground structures in Central Europe (6–10°C). It seems to be reasonable to conclude that any damage of a concrete structure by TSA is due to the interaction of the hardened cement paste with sulphate ions from an aggressive environment. The conversion of concrete into thaumasite just by cooling it to low temperatures (woodfordite route) has not been reported from field cases.

(3) Completely carbonated cement pastes seem to be immune to the formation of thaumasite

A completely carbonated cement paste does not contain C–S–H phases or portlandite since these phases have reacted with carbon dioxide from the atmosphere. All calcium is present in the form of calcium carbonate. The formation of thaumasite from calcium carbonate has been investigated by thermodynamic calculation.[8] It is indicated that a reaction of calcium carbonate with sulphate to thaumasite can not proceed in the absence of C–S–H phases and portlandite. This is confirmed by the results of investigations on damaged concrete structures.[3] The formation of thaumasite does not start at the surface of the concrete structure, but behind the completely carbonated surface layer. In contrast to this, the addition of calcium carbonate facilitates the formation of thaumasite in the presence of portlandite and C–S–H phases.

Both situations are different and shall not be confused. The experiments reported by Hartshorn *et al.*[21] are in agreement with the thermodynamic calculations.

In conclusion, the addition of limestone or other carbonates to cement or concrete increases the risk of thaumasite formation because calcium carbonate can react with the C–S–H phases and portlandite to thaumasite. In contradiction to this, the carbonated surface layer of concrete which does not contain portlandite or C–S–H phases seems to be immune against a formation of thaumasite.

Concluding remarks

In this reply it was shown that both results of thermodynamic calculation discussed by Professor Bensted can be confirmed by experimental observations. The following conclusions can be drawn.

(*a*) The formation of thaumasite without sulphate attack via the woodfordite route is not relevant at temperatures commonly encountered in underground structures in Central Europe (6–10°C).
(*b*) The completely carbonated surface layer that does not contain portlandite or C–S–H phases appears to be immune to the formation of thaumasite.

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