

Thermodynamic Calculations on the Formation of Thaumasite and Validation by Experimental Investigations

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Abstract

Thermodynamic properties of thaumasite were measured at a temperature of 8°C. This data was used to investigate various chemical routes in the formation of thaumasite at this temperature. The obtained results were corroborated by experimental investigations. It was indicated by thermodynamic calculation that thaumasite can be formed from virtually all phase assemblages that can occur in hardened cement paste if gypsum acts as a source of sulfate. In contradiction to this, a reaction of ettringite with C-S-H phases to thaumasite without sulfate attack from the environment (Woodfordite route) does not proceed at 8°C. The minimum sulfate concentration in the aggressive environment that is required for the formation of thaumasite is very low, but can be increased by the addition of pozzolanic or latently hydraulic admixtures and the maintenance of a high pH in the pore solution. The carbonated surface layer of hardened cement paste is immune to a formation of thaumasite.

1. Introduction

Sulfate attack on concrete has been studied for some time. Until 1999, the destruction of concrete subjected to sulfate attack was attributed to the formation of ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$). This view has changed with the report of the Thaumasite Expert Group [1]. After investigations on bridges on a motorway in UK, it was considered that the formation of a third mineral can take place during sulfate attack. Thaumasite ($CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$) is structurally related to ettringite. It was reported that a series of solid solutions exists between the two minerals [2]. Thaumasite is preferentially formed during sulfate attack on concrete at low temperatures. The presence of water and a source of calcium carbonate are essential. Since the report of the Thaumasite Expert Group, many more cases of destruction of mortar and concrete due to a formation of thaumasite have been reported. The present study was set up to provide information on the chemical background of the formation of thaumasite. For this purpose, thermodynamic properties of this mineral were measured at 8°C. They were used for the calculation of different reaction routes that can be relevant in the formation of thaumasite in hardened concrete subjected to sulfate attack from the environment. The results were compared to the outcome of laboratory investigations reported in the literature.

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Thermophysical data for thaumasite has not yet been published. Solubility measurements were independently reported by Damidot et al. [3] and Blanco-Varela et al. [4] for a temperature of 25°C. However, the stability of thaumasite is strongly affected by temperature. It should be considered in thermodynamic calculations that the formation of this mineral is favored by low temperatures. Solubility data at a temperature of 5°C was reported by Macphee & Barnett [5] for the members of the solid solution series between thaumasite and ettringite. Because the pure end member thaumasite was not included, its solubility was measured in the present study at a temperature of 8°C. This temperature was used, because it is the median underground temperature in Central Europe. From the solubility product of thaumasite, a Gibbs free energy for the formation of this mineral from the constituting elements at 8°C was calculated. The obtained value was used to perform calculations on different reaction routes relevant in the formation of thaumasite.

2. Materials and Methods

Phase-pure thaumasite from a geological site in Norilsk, Russia was used for the solubility measurements. The mineral was ground and 5 samples were produced by mixing 1.0 g of thaumasite with 39.0 g of deionized water. The samples were stored in plastic tubes that had a cover with a small hole to allow an equilibration of the solution with the partial pressure of carbon dioxide in the atmosphere. The samples were stored for up to 30 weeks at a temperature of 8°C and were shaken twice a week.

After equilibration, the pH in the solutions was measured by a glass electrode. The electrode was calibrated using buffer solutions previously cooled to 8°C. After measurement of the pH, the solutions were filtered. The clear solutions were investigated by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) using an Optima 3000 (Perkin Elmer). The content of inorganic carbon in the solutions (TIC) was measured in a liquiTOC (Foss Heraeus). Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were used to characterize the solid residue of the filtration.

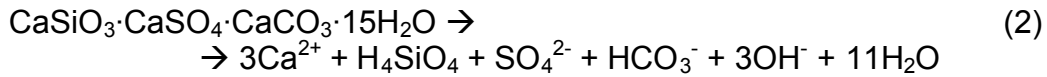
Details of the experimental procedures are given in [6]. In the thermodynamic calculations, data from Babuskin et al. [7] and Fujii & Kondo [8] was used.

3. Results

The ionic concentrations in the solutions equilibrated with thaumasite and carbon dioxide at 8°C were measured to calculate a solubility product for thaumasite. The results of the measurements are given in Table 1. Activities were calculated from the concentrations. These activities were

used to calculate the solubility product of thaumasite according to equation 1. The results of these calculations are included in Table 1. The Gibbs free energy for the formation of thaumasite from the elements at 8°C was computed following equation 2. Further details on the calculations are given in [6]. The value of $\Delta_f G^\circ = -7638$ kJ/mol for the formation of thaumasite from the elements at 8°C was adopted in the calculation of reaction routes relevant for the formation of thaumasite during sulfate attack on concrete.

$$IP_{\text{thaumasite}} = \{Ca^{2+}\}^3 \cdot \{H_4SiO_4\} \cdot \{SO_4^{2-}\} \cdot \{HCO_3^-\} \cdot \{OH^-\}^3 \quad (1)$$



Analyses of the solid residue of the filtration by SEM and XRD showed the presence of calcite and amorphous silicon dioxide beside undissolved thaumasite. These results were confirmed by the calculation of ionic products for these phases [6]. It can be concluded from the aforementioned observations that equilibrium between the solution, thaumasite, calcite, amorphous silicon dioxide and the actual partial pressure of carbon dioxide was achieved. Additional information on this issue can be obtained in an experiment in which thaumasite is not dissolved but precipitated. Such an experiment was not performed due to experimental difficulties.

Table 1: Results of solution analysis and calculation

Sample	1	2	3	4	5
Reaction time [weeks]	13	13	30	30	30
pH	8.14	8.19	8.13	8.20	8.16
Ca [mmol/l]	3.19	3.30	3.17	3.02	2.99
S [mmol/l]	2.85	2.87	3.03	2.78	2.85
Si [mmol/l]	2.54	2.40	2.25	2.20	2.22
K [mmol/l]	0.27	0.10	0.12	0.08	0.08
Na [mmol/l]	0.06	0.06	0.10	0.11	0.06
TIC [mmol/l]	0.75	0.75	0.58	0.60	0.60
$IP_{\text{thaumasite}}$	$7.9 \cdot 10^{-37}$	$9.6 \cdot 10^{-37}$	$6.1 \cdot 10^{-37}$	$8.4 \cdot 10^{-37}$	$6.4 \cdot 10^{-37}$

4. Discussion

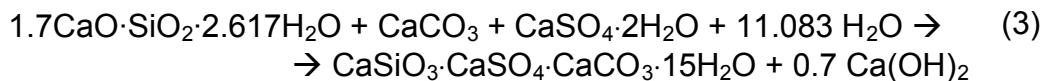
The value derived above for the Gibbs free energy for the formation of thaumasite from the elements was used to characterize different reaction routes that are relevant during sulfate attack on concrete. In the thermodynamic calculations, the Gibbs free energies of the educts and the

products in a specific reaction were compared. A reaction can proceed on its own if there is a decrease in Gibbs free energy at constant temperature and pressure. All calculations refer to a temperature of 8°C. Details of the computations were already given in [9].

The following situations were considered in the calculations:

- presence of gypsum: This mineral is contained in the cement as a set regulator. It is completely depleted within the first day of hydration. Therefore, gypsum is not a typical constituent of hardened cement paste. It may be present after sulfate attack on concrete.
- presence of ettringite: Ettringite is formed in the early stage of hydration. It is one of the major phases of hardened cement paste.
- completely carbonated surface layer: During the lifetime of concrete elements, carbon dioxide (CO₂) from the atmosphere can react with calcium-bearing phases to calcium carbonate (CaCO₃) after a diffusion of the gas in the hardened cement paste. There is an outer skin in which portlandite (Ca(OH)₂) and C-S-H phases have both reacted to calcium carbonate. Amorphous silicon dioxide (SiO₂) can be formed as a by-product. This outer skin is followed by a second layer in which C-S-H phases are not yet attacked. Only portlandite has been transformed into calcium carbonate. In the inner core of the concrete elements, C-S-H phases and portlandite are present, both being unaffected by carbon dioxide.
- attack by sulfate ions dissolved in an aggressive solution

In the first situation, gypsum was assumed as a source for the sulfate required during the formation of thaumasite. A reaction of gypsum with C-S-H phases and calcite is considered in equation 3.

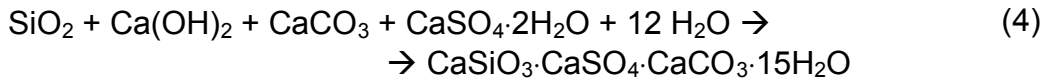


The change in Gibbs free energy during the reaction considered in equation 3 is calculated at 8°C to -19.0 kJ/mol. This value is negative, indicating that the reaction can proceed on its own. Therefore, according to thermodynamic calculations, a formation of thaumasite from gypsum, calcite and C-S-H phases is possible at 8°C.

This result is confirmed by experimental investigations in which a reaction of hardened cement pastes with gypsum and calcium carbonate to thaumasite was detected [10-13]. However, some ettringite may be required as a nucleation agent because the formation of thaumasite was not proven in the absence of this mineral [14]. It has to be noted that the formation of thaumasite from calcium-rich C-S-H phases, calcite and gypsum does not require the consumption of portlandite (equation 3). Therefore, a depletion of portlandite by a pozzolanic reaction seems to be unable to prevent the formation of thaumasite if gypsum acts as a source

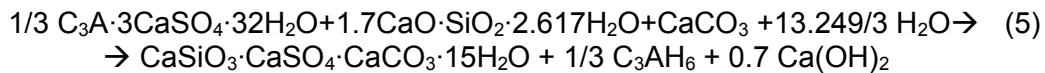
for sulfate. The influence of the calcium/silicon ratio of the C-S-H phases on the reaction with calcite and gypsum to thaumasite was not addressed by calculation.

Other than a consumption of C-S-H phases, a formation of thaumasite is possible by a reaction of amorphous silicon dioxide, portlandite, calcite and gypsum following equation 4.



In this case, the difference in Gibbs free energy was calculated to -61.1 kJ/mol and the reaction can proceed on its own. The formation of thaumasite from amorphous silicon dioxide, portlandite, gypsum and calcium carbonate was confirmed by experimental investigations at 5°C [15]. It is a concurrent reaction to the formation of C-S-H phases which themselves are prone to the formation of thaumasite.

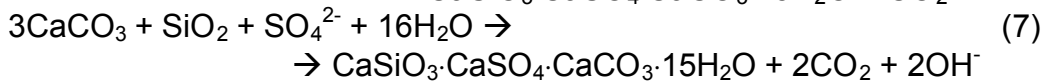
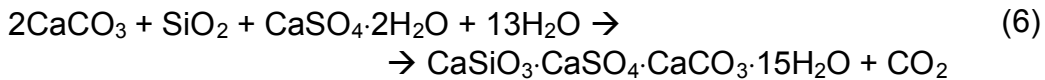
The second situation that was addressed is the formation of thaumasite when ettringite is assumed as a source for sulfate. Such a reaction is considered as the Woodfordite route in the formation of thaumasite [16]. It has to be investigated if ettringite can react with C-S-H phases and calcite to thaumasite following equation 5.



In equation 5, a reaction of phases is considered that are contained in most hardened cement pastes. If this reaction can proceed, the formation of thaumasite without sulfate attack would be possible. Only cooling to low temperatures would be required for a disintegration of concrete due to the formation of thaumasite. The change in Gibbs free energy during reaction 5 was calculated to +3.2 kJ/mol. Formally, this result indicates that reaction 5 can not proceed on its own, because the computed value is positive. However, it needs to be considered that the obtained value is smaller than the errors in the underlying database and it has to be investigated by experimental means if reaction 5 can take place. It was shown that the reaction can proceed at a temperature of 2°C [17], whereas ettringite and C-S-H phases were not transformed into thaumasite at 8°C [18]. Additionally, also the reverse reaction of equation 5 did not take place at 8°C. These results have led to the interpretation that both sides of equation 5 might be at or close to equilibrium at 8°C [18]. Nevertheless, the formation of thaumasite by a reaction of ettringite and C-S-H phases without sulfate attack was not detected during the examination of field cases. It is concluded that the Woodfordite route does not play a vital role when concrete is exposed to sulfate attack. Its occurrence under some specific laboratory conditions is still a matter of

current investigations.

The third situation that was addressed was the carbonated surface layer of concrete. In the outer layer, where only calcite and amorphous silicon dioxide are present instead of portlandite and C-S-H phases, a reaction of these phases with gypsum to thaumasite can proceed according to equation 6. For carbon dioxide appearing in this equation, a partial pressure of $3.5 \cdot 10^{-4}$ atm was assumed. The change in Gibbs free energy during reaction 6 was calculated to -2.9 kJ/mol at a temperature of 8°C. This result suggests that both sides of equation 6 are close to equilibrium at the temperature of interest. If sulfate ions are assumed to attack the carbonated surface layer, the formation of thaumasite can follow equation 7.



The change in Gibbs free energy during reaction 7 is calculated to +57.5 kJ/mol. This value refers to the standard states of the compounds appearing in equation 7. For sulfate ions and hydroxide ions, this standard state is a concentration of 1.0 mol/kg and ideal behavior. It is evident that such conditions are not relevant here and an equilibrium constant (K_{SP}) has to be calculated from the difference in Gibbs free energy using equation 8. In equation 8, the molar gas constant is denoted as R, the temperature as T. The result of this computation leads to equation 9.

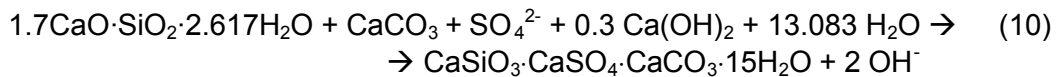
$$\Delta_r G^\circ = -R \cdot T \cdot \ln 10 \cdot \log K_{\text{SP}} \quad (8)$$

$$\{\text{SO}_4^{2-}\} = 4.9 \cdot 10^{10} \cdot \{\text{OH}^-\}^2 \quad (9)$$

Equation 9 gives the minimum sulfate ion activity that is required for the formation of thaumasite following equation 7. Activities are concentrations that are corrected using activity coefficients. Activity coefficients are exactly calculated if the concentrations of all ionic species in the solution are known. In the present discussion, where the composition of the solution can have a very broad range, activity coefficients can only be estimated. For solutions with low concentrations they lie typically between 0.2 and 0.7. Therefore, the sulfate ion concentration required for a reaction of calcite and amorphous SiO_2 to thaumasite depends on the activity coefficient of the sulfate ions and the hydroxide ion activity. Hydroxide ion activity is a direct measure of the pH-value of the solution. Inspection of equation 9 shows that very high sulfate concentrations beyond that occurring under most field conditions would be required for a reaction of the sulfate ions with calcite and amorphous silicon dioxide. This result, that the completely carbonated surface layer is immune against sulfate

solutions is supported by investigations in which the surface skin of concrete was not affected by sulfate attack. The formation of thaumasite took place behind the completely carbonated surface layer [1]. In contrast to this, a formation of thaumasite can proceed if C-S-H phases are still present as occurs if the process of carbonation is not completed.

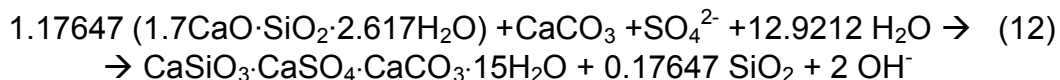
The last situation that was addressed by thermodynamic calculation is the ingress of sulfate ions from the environment. A reaction of sulfate ions with calcite, portlandite and calcium-rich C-S-H phases to thaumasite is considered in equation 10.



The difference in Gibbs free energy for equation 10 at 8°C is calculated to -16.8 kJ/mol. The calculation of an equilibrium constant following equation 8 to predict the minimum sulfate ion concentration required for the formation of thaumasite leads to equation 11.

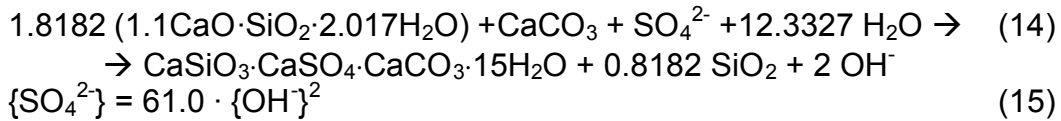
$$\{\text{SO}_4^{2-}\} = 7.5\cdot 10^{-4} \cdot \{\text{OH}^-\}^2 \quad (11)$$

This calculation was repeated for the absence of portlandite which can be consumed during a pozzolanic reaction. In this case, the formation of amorphous silicon dioxide as a by-product was assumed (equation 12). The change in Gibbs free energy is calculated to -9.3 kJ/mol. The corresponding equation for the prediction of the minimum sulfate ion concentration for the formation of thaumasite is given in equation 13.



$$\{\text{SO}_4^{2-}\} = 0.019 \cdot \{\text{OH}^-\}^2 \quad (13)$$

In a pozzolanic reaction, not only portlandite is consumed. If the reaction proceeds further, the calcium/silicon ratio of the C-S-H phases is lowered. In the presence of portlandite, C-S-H phases are rich in calcium and have a calcium/silicon ratio of about 1.7. The calcium/silicon ratio of silicon-rich C-S-H phases that are formed if a sufficient amount of pozzolanic or latently hydraulic admixtures is added is around 1.1 [19]. Equation 14 details a reaction of sulfate ions with calcite and silicon-rich C-S-H phases. The difference in Gibbs free energy calculated for a temperature of 8°C is +9.6 kJ/mol. The equilibrium constant for the prediction of the minimum sulfate ion concentration required for the formation of thaumasite is presented in equation 15.



For a discussion of the resistance of different C-S-H phases against a reaction with sulfate ions and calcite to thaumasite, equations 11, 13 and 15 are compared. In all three equations, the minimum sulfate ion concentration required for the formation of thaumasite depends on the pH-value. However, the calculated equilibrium constants vary between these equations. The lowest sulfate ion concentration is required if calcium-rich C-S-H phases are attacked in the presence of portlandite. Less sensitive

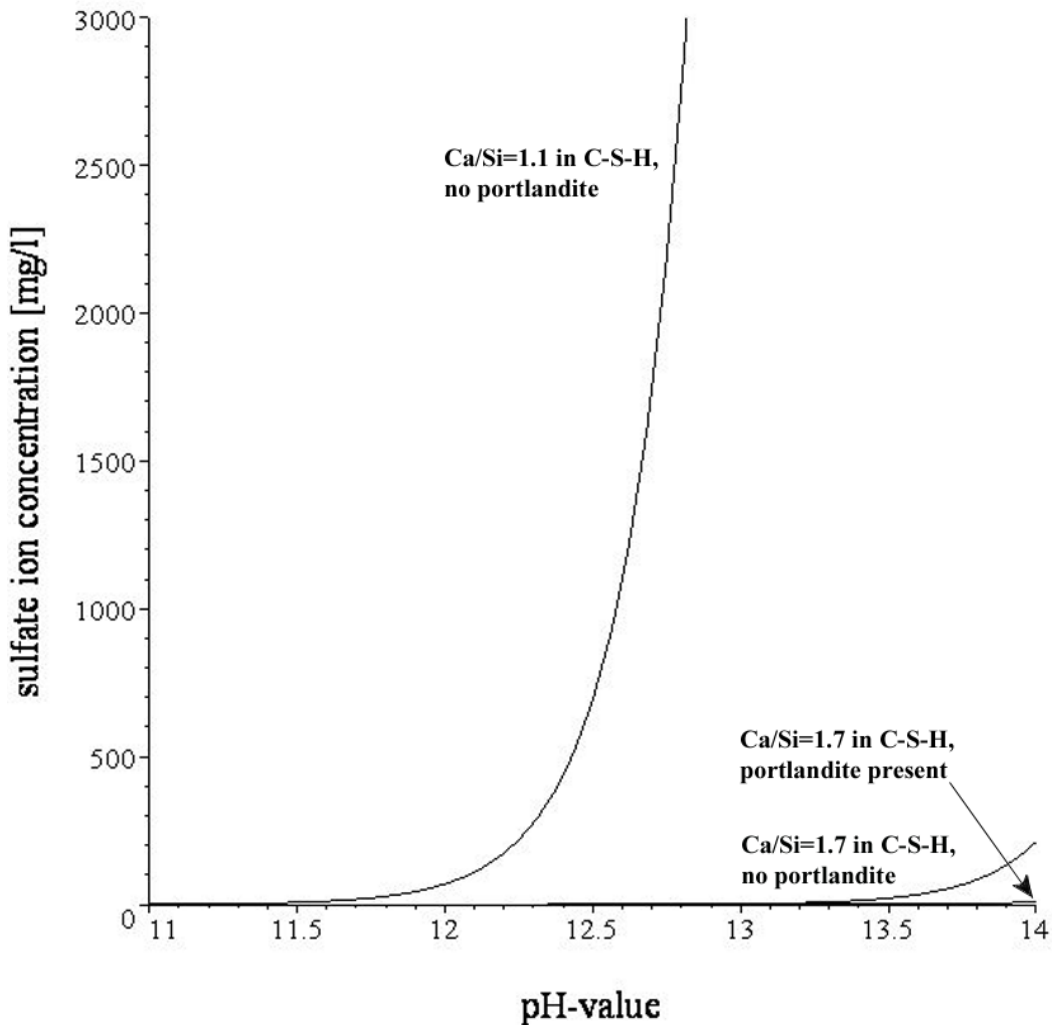


Figure 1: Sulfate ion concentration calculated for the transformation of C-S-H phases into thaumasite
 are calcium-rich C-S-H phases if no portlandite can be consumed. Silicon-rich C-S-H phases are indicated to have the highest resistance against a transformation into thaumasite. These inter-relations are visualized in Figure 1, where the minimum sulfate ion concentration required for the formation of thaumasite is plotted against the pH-value at the place of

reaction. Activity coefficients had to be estimated for this purpose. It can be concluded that the resistance of concrete against the formation of thaumasite during sulfate attack can be increased by the addition of pozzolanic and latently hydraulic admixtures. The amount and reactivity of these materials needs to be high enough to transform virtually all of the portlandite released during the hydration of the Portland cement clinker into C-S-H and other cementitious phases and to lower the calcium-silicon ratio of the C-S-H phases. This conclusion is supported by the outcome of experimental investigations. It was shown that the formation of thaumasite is possible at low sulfate concentrations [14,20,21]. It can be suppressed at a sulfate ion concentration of 3000 mg/l and temperatures of 5°C and 10°C by the addition of a sufficient amount of silica fume to lower the calcium/silicon ratio in the binders from 3.0 to 1.0 [14]. In another study, mortar bars stored at 8°C were damaged by sodium sulfate solution having a sulfate ion concentration as low as 1500 mg/l. The deterioration was avoided by the addition of high amounts of coal fly ash and blast furnace slag. Details of this investigation can not be included here due to limitations in space. More information are available in [21].

5. Conclusions

Thermodynamic calculations can be used to systemize the knowledge on the chemical resistance against the formation of thaumasite. The following results were obtained by calculation and compared to the outcome of experimental studies reported in the literature:

- The transformation of cementitious systems into thaumasite is possible if they are in contact with gypsum.
- A reaction of ettringite with C-S-H phases and calcite to thaumasite without sulfate attack (Woodfordite route) is not likely. The formation of thaumasite at temperatures occurring in undergrounds in Central Europe (6-10°C) requires sulfate attack.
- The completely carbonated surface layer that contains neither portlandite nor C-S-H phases seems to be immune against the formation of thaumasite.
- C-S-H phases are prone to the formation of thaumasite in the presence of portlandite. The resistance can be increased by the addition of high amounts of pozzolanic and latently hydraulic admixtures. Upon a reaction of these materials, portlandite is consumed and the calcium/silicon ratio of the C-S-H phases is lowered.
- It is suggested to use pozzolanic and latently hydraulic admixtures to increase the resistance of concrete against the formation of thaumasite.

The aforementioned conclusions were derived for "plain" sulfate attack at low temperatures. A modification of the results is possible if additional reactions occur such as the formation of brucite ($\text{Mg}(\text{OH})_2$).

Acknowledgment

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