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Stability and reactivity of thaumasite at different pH levels

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Abstract

Thaumasite ($CaCO_3 \cdot CaSO_4 \cdot CaSiO_3 \cdot 15H_2O$) has been reported to form at low temperatures (below 15 °C) during sulfate attack. Reactions between calcium silicate hydrate (C-S-H) and Ca^{+2}, CO_3^{-2}, SO_4^{-2}, CO_2 and water, or between ettringite and C-S-H, CO_3^{-2} and/or CO_2 and water, result generally in the formation of thaumasite. In some instances, thaumasite may be affected by the presence of other chemicals in the surrounding environment (i.e., phosphates and ammonia in agricultural soil). There are insufficient data regarding the stability of thaumasite at different pH levels in the presence of other chemical ions. Understanding this issue might help in the detection of the thaumasite form of sulfate attack, and, therefore, in one's choice of the appropriate protection technique. This work reports the reactivity of thaumasite with phosphate, carbonate and bicarbonate ions at different pH levels ranging from 6.00 to 12.00, as well as the stability of thaumasite at high pH levels (greater than 12.00). Thaumasite was found to react with these ions at pH levels at and below 12.00; however, thaumasite was stable with minimal reactivity at pH levels greater than 12.00.

Keywords: pH; Reaction; Stability; X-ray diffraction; SEM

1. Introduction

Thaumasite ($CaCO_3 \cdot CaSO_4 \cdot CaSiO_3 \cdot 15H_2O$) is reported to form primarily at low temperatures (below 15 °C) during sulfate attack, when there is an available source of CO_3^{2-}, which could be either limestone dust, which is being increasingly used as filler, or limestone aggregate [1]. The thaumasite form of sulfate attack has been recognized to be particularly deleterious because the formation of thaumasite involves the destruction of calcium silicate hydrate (C-S-H) itself. The characteristic feature of its formation is to transform the surface of the concrete into a soft pulpy mass [2]. Traditional methods of protection against sulfate attack, such as the use of low C_3A cements, are not effective in this case.

The formation of thaumasite occurs in the near-surface regions of concrete attacked by sulfates. During the process of deterioration of the concrete, the surface regions often spall as a result of the expansion and softening associated with sulfate attack, leaving behind concrete that shows signs of conventional sulfate attack, i.e., the presence of gypsum and ettringite [3,4]. Thus, the traces of thaumasite get lost in the debris. In some instances, thaumasite may be affected by the presence of other chemicals in the surrounding environment (e.g., the presence of phosphates and ammonia in agricultural soil, etc.). In such cases, depending on the stability of thaumasite, it may maintain its form, or get converted to other compounds by reacting with these chemicals. There are insufficient data about the stability of thaumasite at different pH levels in the presence of other chemical ions. Understanding this issue might help in the detection of the thaumasite form of sulfate attack, and, therefore, in the choice of the appropriate protection techniques.

2. Experimental

Samples of natural thaumasite (Patterson, NJ) were obtained from Ward's Natural Science. Three groups of solutions including (i) mixtures of alkali phosphate solutions, (ii) sodium carbonate–bicarbonate or carbonate–

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Table 1
Solutions used at different pH levels

Solutions	Components in deionized water	pH
I. Mixtures of alkali phosphate solutions	potassium hydrogen phosphate (KH_2PO_4); sodium dihydrogen phosphate (Na_2HPO_4)	6.00 ± 0.02
	sodium dihydrogen phosphate, potassium hydrogen phosphate	7.00 ± 0.02
	sodium dihydrogen phosphate, potassium hydrogen phosphate	8.00 ± 0.02
	sodium phosphate, sodium dihydrogen phosphate	12.00 ± 0.10
II. Sodium carbonate–bicarbonate or carbonate–phosphate solutions	sodium bicarbonate ($NaHCO_3$); sodium carbonate (Na_2CO_3)	9.00 ± 0.02
	sodium carbonate; sodium bicarbonate	10.00 ± 0.02
	sodium phosphate (Na_3PO_4); sodium carbonate	11.00 ± 0.05
III. Sodium or calcium hydroxide solutions	aqueous calcium hydroxide solution	12.45
	aqueous sodium hydroxide solution	13.00

phosphate solutions and (iii) sodium or calcium hydroxide solutions (summarized in Table 1) were all obtained from VWR Scientific, except for the concentrated (1% w/v) sodium hydroxide solution, which was supplied by Fisher Scientific. Ten thaumasite samples, each piece weighing approximately 1 g, were completely immersed in each of the solutions (100 ml) were and stored in a temperature-controlled room at 25 ± 0.2 °C. The pH values of the solutions

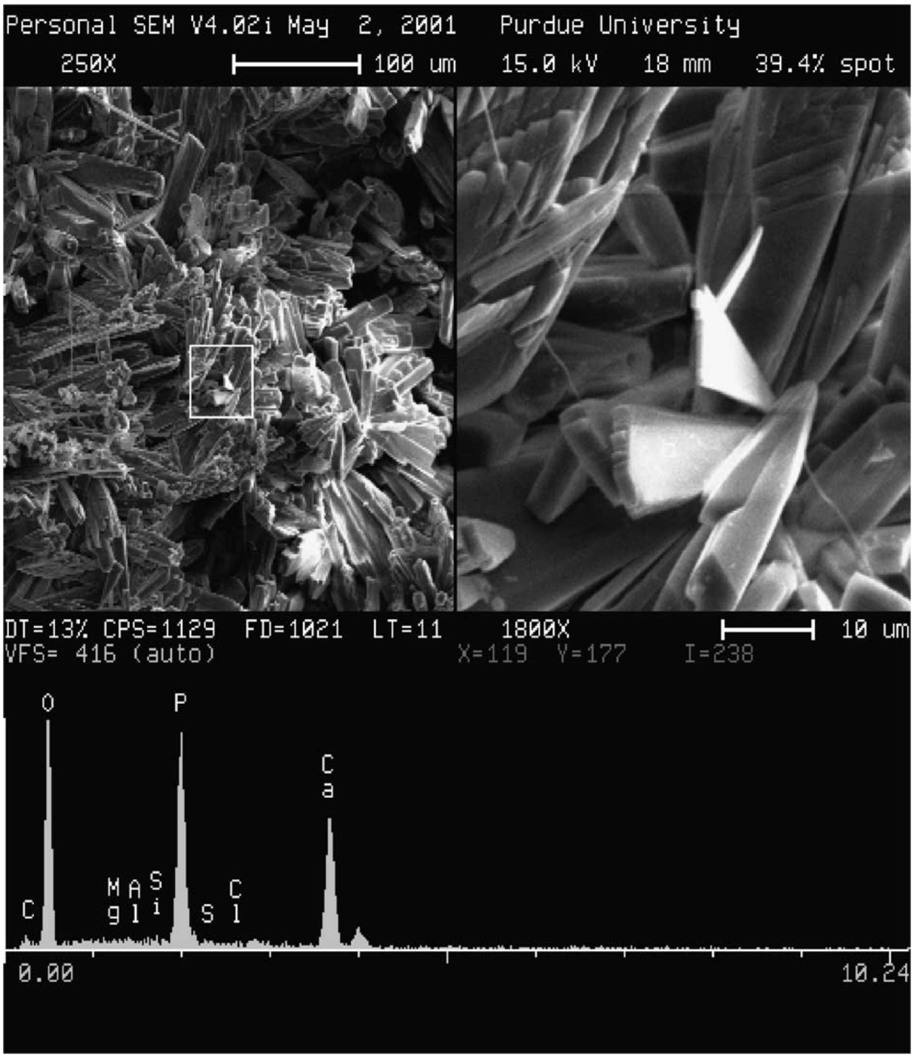

Fig. 1. SEM image of calcium phosphate formed.

were monitored using a digital pH-meter (calibrated vs. pH = 7.00 and pH = 10.00). After 30 days of immersion in the solutions, the solids were removed and dried in a CO_2-free desiccator to a constant mass (± 0.02 g) for 24 h. The specimens were further coated with a thin film (1–2 nm) of palladium–gold for SEM observation and energy-dispersive X-ray analysis, after which, the solids were finely crushed and prepared for X-ray diffraction (XRD) analysis.

3. Results and discussion

The SEM with energy-dispersive X-ray microanalysis observation of a thaumasite specimen immersed in alkali phosphate solutions at pH = 6.00 showed no sign of thaumasite; instead, only calcium phosphate (Fig. 1) (fine needle shaped crystals) appeared on the surface. In addition, the pH of the solution changed to 6.28 after 30 days. However, when the same salts were present in the solution at pH levels of 7.00, 8.00 and 12.00, SEM images showed thaumasite and calcium carbonate (hexagonal shaped crystals) (Fig. 2) to be present. There was no sign of calcium phosphate, and no change in the pH levels of the solutions used. However, when XRD was used, it detected thaumasite and brushite, *syn* ($Ca(HPO_4)\cdot 2(H_2O)$) (Fig. 3) at pH 6.00, thaumasite and aragonite ($CaCO_3$) at pHs 7.00 and 8.00, and only thaumasite at pH 12.00. This difference in results can be explained by the fact that the SEM images (penetration depth ≤ 2.0 μm; detection limit 0.1%) were taken randomly from three different spots on the sample's surface; while in the case of XRD (detection limit 10%) analysis, the samples were finely crushed resulting in a mixture where XRD intensities are proportional to phase concentrations.

When thaumasite specimens were immersed in solutions containing sodium carbonate and sodium bicarbonate at pH levels of 9.00 and 10.00, SEM observations showed no sign of thaumasite; only a calcium carbonate (hexagonal crystals) was present. In addition to a calcium carbonate, a calcium

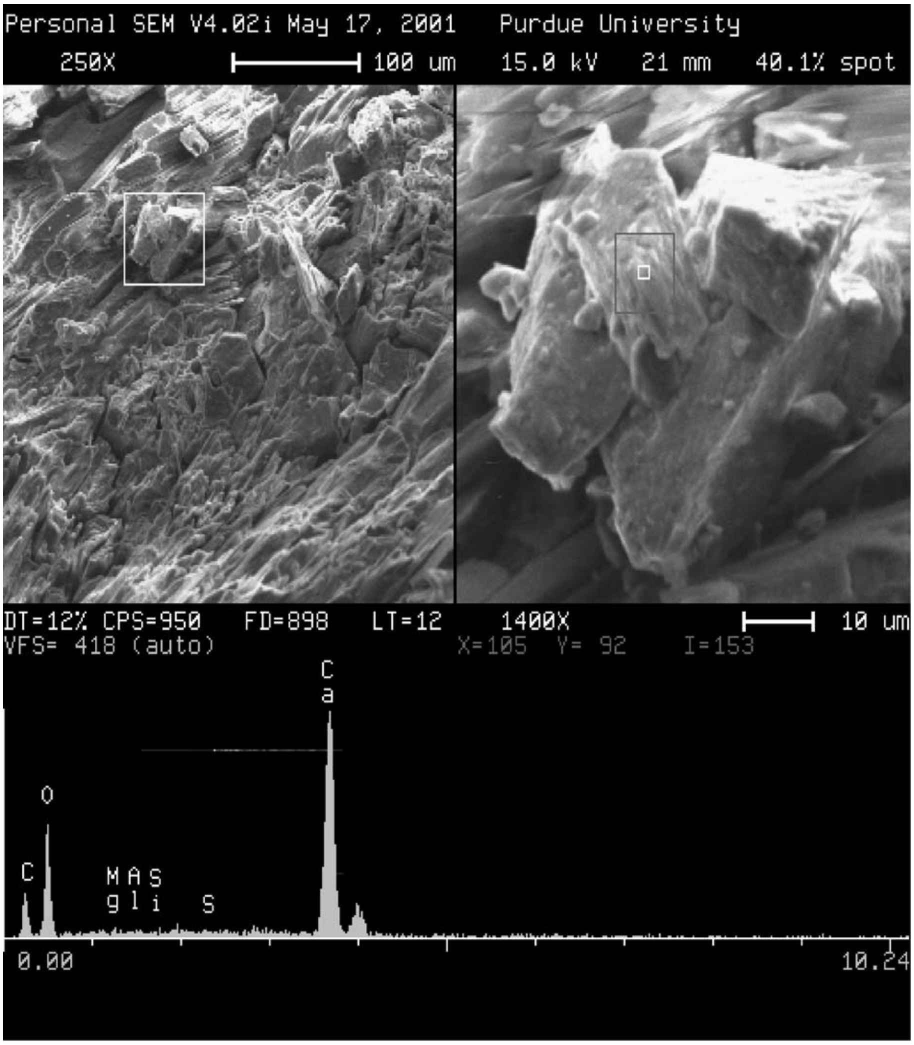

Fig. 2. SEM image of calcium carbonate formed.

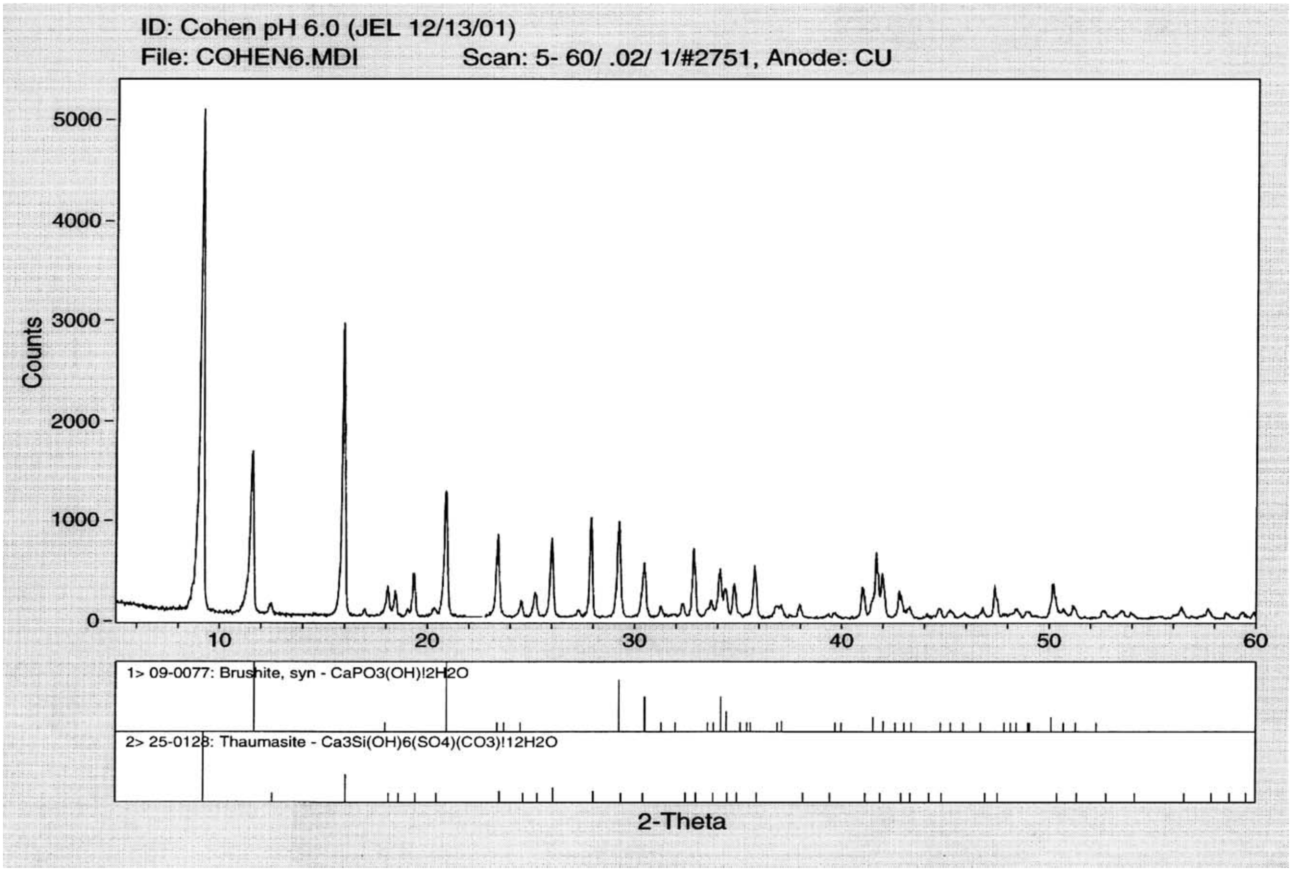

Fig. 3. XRD spectrum of a mixture shown to be of thaumasite and brushite, with those of the pure phases for comparison.

silicate (Fig. 4) was detected in the case of the solution with pH 10.00. The detection of C-S-H at pH 10.00 is possible because pH 10.00 is the absolute minimum for forming this phase. A noticeable change in pH = 9.00 solution occurred (final pH = 9.38), while the other solution maintained its pH at 10.00. XRD measurements detected both thaumasite and calcite, *syn* ($CaCO_3$) at pHs 9.00 and 10.00. In addition, a trace of afwillite, $Ca_3(HSiO_4)_2 \cdot 2H_2O$, was detected at pH 10.00.

A solution containing both sodium phosphate and sodium carbonate salt was used to test the reactivity of thaumasite at a pH of 11.00. Energy-dispersive X-ray microanalysis showed the presence of thaumasite, a calcium carbonate, a calcium phosphate and a silicate without any recorded change in the pH of the solution. XRD spectra revealed the presence of thaumasite and traces of calcite and afwillite; however, no trace of a calcium phosphate was detected.

Finally, thaumasite specimens were tested for stability in two solutions containing calcium hydroxide and sodium hydroxide bases at pH levels of 12.45 and 13.00, respectively. In addition to thaumasite, calcium carbonate was detected in the case of the solution with pH 12.00. However, the SEM observations showed that thaumasite preserved its chemical identity in the case of the solution with pH 13.00. The pH of the solutions changed during the course of the experiment. The final pH decreased from 12.45 to 12.24 and from 13.00 to 12.84. XRD findings showed the presence of thuamasite in both cases with no detectable traces of other crystalline phases.

These experiments showed thaumasite to react with different inorganic salts at pH levels at and below 12.45 yielding chemical products that might give a negative detection of thaumasite when concrete is present in a groundwater environment rich in ions other than sulfate ions. However, when the pH is greater than 12.45, thaumasite reactivity is minimal and will not affect detection at sites where concrete has been subjected to sulfate attack in the presence of other inorganic salts in the medium. In addition, the reactions seemed to be pH dependent, because phosphate ions reacted with thaumasite at pHs 6.00, 7.00 and 8.00; however, no reaction took place between these ions and thaumasite at pH 12.00. In addition, a phase of C-S-H was only detected at pHs 10.00 and 11.00.

4. Conclusion

The stability of thaumasite was affected by the pH of the surrounding environment. At low pH levels (≤ 11.00),

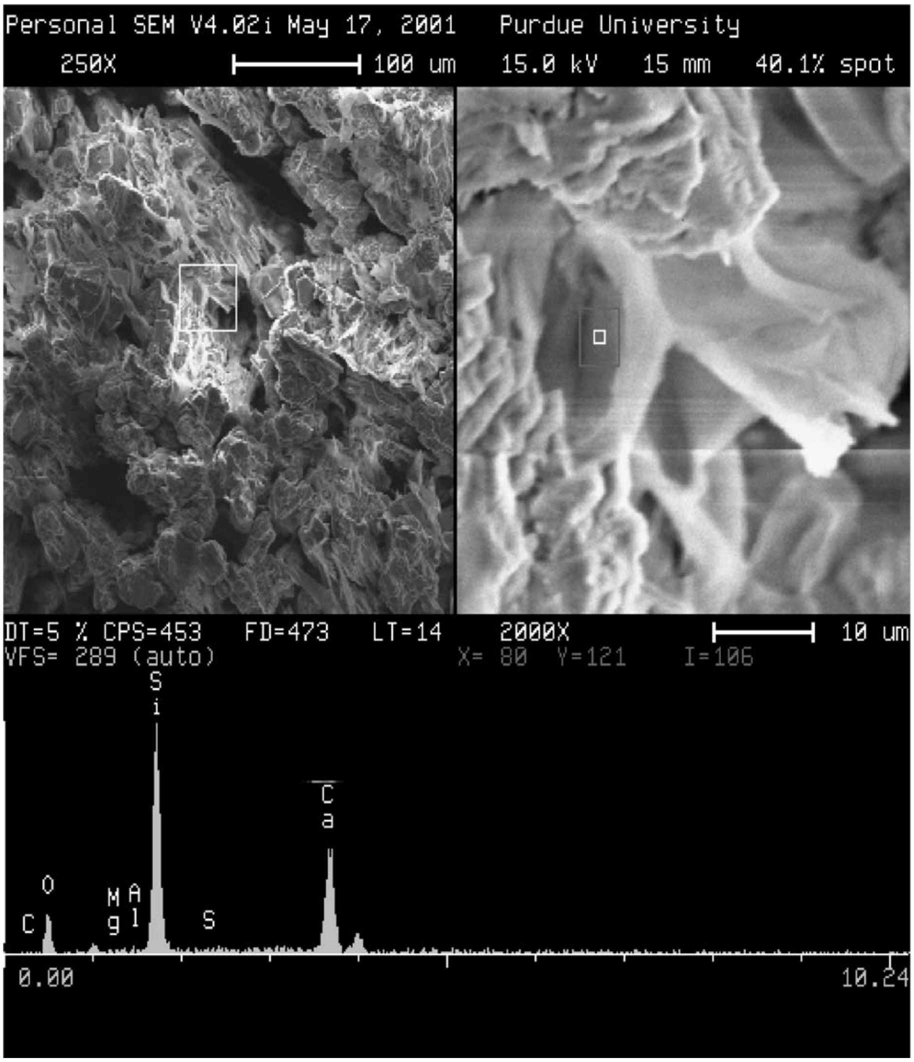

Fig. 4. SEM image of calcium silicate formed.

thaumasite reacted with the ions present in the solutions, and some conversion to calcium phosphate, calcium silicate and calcium carbonate was detected. At pH levels >11.00, minor amounts of calcium carbonate were detected, while in highly basic conditions (pH = 13.00), thaumasite was stable.

Acknowledgements

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