The Mechanism of Thaumasite Formation

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Thaumasite, Ca₆[Si(OH)₆.12H₂O]₂( SO₄)₂(CO₃)₂, is formed from external sulfate attack of Portland cement concrete at low temperatures. Its crystal structure is most unusual in that it contains silicon atoms that are surrounded by an octahedron of OH⁻ ions. This structure is closely related to that of ettringite, Ca₆[Al(OH)₆.12H₂O]₂( SO₄)₃(H₂O)₂, and the two minerals form a series of solid solutions, which have been the subject of several recent papers. Most emphasis has been given to the replacement of Al by Si, but the anions also have to change to compensate for the higher oxidation state of Si. The solid solution is therefore quite complex and might also involve sulfate-rich and carbonate-rich forms of thaumasite. These solid solutions probably form via a through solution mechanism involving dissolved ions and perhaps atmospheric carbon dioxide, accounting for the formation of thaumasite even in systems that do not incorporate limestone filler or aggregate.
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What is Thaumasite?

Greek Word:-

\[ \text{\textit{θαυμάζειν}} \]

The mineral thaumasite was named in 1878 from the Greek *thaumazein*, which means “to wonder at” or “to be surprised”.
Ettringite \( \text{Ca}_3\text{Al}_2\text{O}_6.3\text{CaSO}_4.32\text{H}_2\text{O} \)

Thaumasite \( \text{CaSiO}_3.\text{CaSO}_4.\text{CaCO}_3.15\text{H}_2\text{O} \)
Table I: Lattice Parameters for Thaumasite

<table>
<thead>
<tr>
<th>Reference</th>
<th>a (Å)</th>
<th>c (Å)</th>
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<tr>
<td>Edge and Taylor (1971)</td>
<td>11.04</td>
<td>10.39</td>
</tr>
<tr>
<td>Barnett et al. (1999)</td>
<td>11.054</td>
<td>10.410</td>
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<tr>
<td>Jacobsen et al. (2000)</td>
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<tr>
<td>Ettringite</td>
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<td>21.50</td>
</tr>
<tr>
<td>Tricarboaluminate</td>
<td>10.834</td>
<td>21.250</td>
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</tbody>
</table>
Chemical Composition of Thaumasite and Ettringite

Ettringite \[ \text{Ca}_3\text{Al}_2\text{O}_6 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \]

Thaumasite \[ \text{CaSiO}_3 \cdot \text{CaSO}_4 \cdot \text{CaCO}_3 \cdot 15\text{H}_2\text{O} \]

Ettringite \[ \text{Ca}_6[\text{Al(OH)}_6 \cdot 12\text{H}_2\text{O}]_2 (\text{SO}_4)_2 (\text{SO}_4) (\text{H}_2\text{O})_2 \]

Thaumasite \[ \text{Ca}_6[\text{Si(OH)}_6 \cdot 12\text{H}_2\text{O}]_2 (\text{SO}_4)_2 (\text{CO}_3)_2 \]
• Sandro Torres

*RS s/v by Prof Swamy and Dr Lynsdale also collaborating with Prof Sharp and Dr Kirk.*

An examination of some of Hartshorn’s samples that are now more than 5 years old.

Has deterioration worsened?

Is thaumasite present and if so, is in the form of a solid solution?
IR spectra of mortars containing different amounts of limestone filler replacement stored in magnesium sulfate solution at 5^o C for 5 years. (L = Limestone)
X-ray diffraction traces of the deteriorated surface material and the sound core material from a mortar prism made with Portland limestone cement (OPC/35% limestone) stored in 1.8% MgSO₄ solution at 5°C for 126 days (Hartshorn, Sharp and Swamy, 2002)
George Collett

*RS on the Foundation for the Built Environment scheme with BRE (s/v Crammond, Sharp and Swamy)*

Examination of concrete cubes buried 3 years ago by BRE. How do the field studies relate to complementary laboratory studies?

How is thaumasite formed if there is no limestone filler or aggregate present?
Condition of High Quality Quartz mortars immersed in sulfate solution (2400 mg/l)
Comparing HQS with time

Black 70 days
Red 98 days
Green 434 days
Exposure comparisons for hqs mortar

Key
- Black: No exposure to air
- Blue: Nitrogen mix: 24 hours nitrogen cure: 24 hours air cure: seal cure
- Red: Nitrogen mix: 24 hours nitrogen cure: 8 hours air cure: seal cure
- Brown: Air mix: 24 hours nitrogen cure: 24 hours air cure: seal cure
- Purple: Air mix: 24 hours nitrogen cure: 27 days air cure
- Green: Nitrogen mix: 24 hours nitrogen cure: 27 days air cure
Conclusions

• Portland cement pastes exposed to sulfate solutions at 5°C are readily susceptible to formation of thaumasite.

• Although TF is enhanced by the presence of limestone filler, it can occur even in the absence of limestone filler or aggregate.

• The thaumasite is often formed as solid solution with ettringite, involving some replacement of Si by Al and consequent adjustment of the anions.

• Atmospheric carbon dioxide may have an important role in the formation of thaumasite, perhaps via the intermediate formation of bicarbonate ions.

• Thaumasite (along with popcorn calcite and aragonite) almost certainly forms via a through solution mechanism.