ELSEVIER

Cement & Concrete Composites 25 (2003) 1119–1121

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

# Occurrence of thaumasite in deteriorated concrete

David C. Stark *

*Construction Technology Laboratories, Inc., 5420 Old Orchard Road, Skokie, IL 60077, USA*

**Abstract**

The first case histories of thaumasite in concrete products in the United States were identified by the writer in the 1960s. There included two underground sanitary pipes, a grout in an underground lead/zinc mine, and the bottom of a concrete pavement on grade. In these cases, thaumasite was first identified by optical properties in powder mounts in a petrographic microscope, then further confirmed by X-ray diffraction and characterized in an electron microscope. Morphological similarities and positive distinction between thaumasite and ettringite are considered.



*Keywords:* Case histories; Ettringite; Identification; Optical properties; Thaumasite; X-ray diffraction

## 1. Introduction

This paper describes four occurrences of thaumasite in the 1960s in Portland cement mortar or concrete and circumstances under which they appeared to have developed.

Thaumasite in these examples was initially identified in the petrographic microscope but can easily be misidentified as ettringite, both of which can be seen as fine acicular or needlelike crystals with a refractive index of about 1460. Also, the main peak for thaumasite and ettringite can be readily misidentified in X-ray diffraction (XRD).

## 2. Nature of thaumasite

The mineral thaumasite has the approximate composition $CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 14 \cdot 5H_2O$ and has been observed in metamorphosed rocks as a secondary mineral [1]. Associated minerals in these locations included ettringite, aragonite, calcite, portlandite, spurrite, and tobermorite. Carpenter [2] reported thaumasite as oriented overgrowths on ettringite and enclosed by a second generation on ettringite. He also suggested a limited solid solution series between thaumasite and ettringite and mentioned as evidence certain anomalies in refractive index of the two minerals.

## 3. Occurrences of thaumasite in concrete

These four occurrences of thaumasite were found in portland cement products; two in underground sanitary sewer pipes, one in a grout in a mine, and one in the base of a concrete pavement on grade. These are described below.

1. *Sewer pipe*: Thaumasite, calcite, and gypsum were observed as soft white substances partially filling voids and thin veinlets of a five-year old sewer pipe. Thaumasite appeared as clusters of needles similar in morphology to ettringite. Powder mounts in the petrographic microscope revealed the refractive index of the ordinary ray was in the range of 1.504, which was much greater than the 1.464 range for ettringite.
2. *Sewer pipe*: This sample was examined when it was 32 years of age. The cement paste matrix was severely deteriorated to depths up to about 50 mm (2 in.) along the interior surface of the pipe. The paste was converted to silica gel and gypsum along this surface but, between this, several deteriorated areas and the sound portions of the pipe were ettringite and thaumasite lining and filling entrapped air voids. The thaumasite occurred as discrete needlelike crystals and, occasionally, as overgrowths of ettringite crystals. In microscopical examination both thaumasite and ettringite were parallel to the optical extinction position.
3. *Non-setting grout*: Thaumasite, together with aragonite and calcite, was found as small clusters and disseminated crystals in a grout specimen that never

* Fax: +1-847-965-7500.
*E-mail address:* dstark@ctlgroup.com (D.C. Stark).

0958-9465/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0958-9465(03)00142-2

hardened. It was found in an abutment adjacent to a sodium chloride mine in which sulfate-bearing water had been passing.
4. *Slab-on-grade pavement*: This sample came from the bottom surface of a slab-on-grade pavement. It was severely altered cement paste that consisted of thaumasite, ettringite, aragonite, and calcite. This contained intergrowths of thaumasite and ettringite and occasionally, as overgrowths of thaumasite on ettringite.

## 4. Identification of thaumasite

Positive identification of thaumasite easily can be confused with ettringite. Morphologically, both appear as acicular and sometimes columnar crystals and as overgrowths of one with the other. Figs. 1 and 2 characterize common crystalline shapes seen in deteriorated concrete and also most like those reported in nature [1]. Table 1 compares the optical properties of thaumasite and ettringite. It is apparent that birefringence differs by about 0.03 but that can be confused by orientation and crystal thickness. Optically, the refractive index of the extraordinary ray may be similar and vary no more than about 0.006. The surest and least debatable index distinguishing whether particular crystalline material is thaumasite or ettringite is the ordinary ray, in which difference in refractive index is consistently about 0.038, which is about six times greater than that for the extraordinary ray of the two compounds.

Comparison of XRD patterns also shows some similarities between thaumasite and ettringite, particularly in the intensity of the primary Bragg angle peaks. These are shown in Fig. 3, where the primary peaks at about 8°–9° are almost identical, thus leading to uncertainty whether thaumasite or ettringite, or both, are present. Secondary XRD peaks provide better distinction between the two minerals and can be used to identify the mineral in question. However, several of the minor peaks for thaumasite were not present in the sample of grout in question.

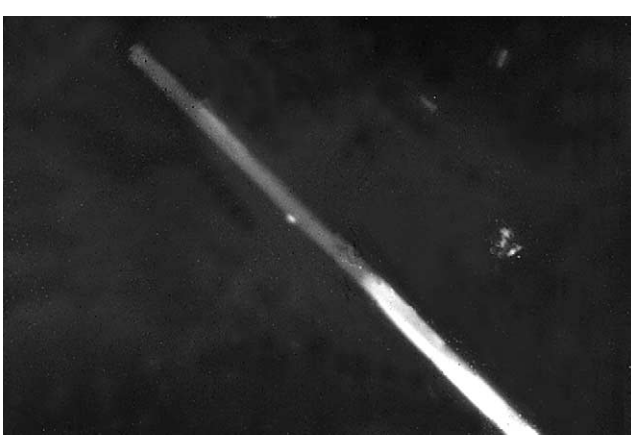

Fig. 1. Overgrowth of needlelike crystal of thaumasite on ettringite. The brighter portion of the growth in thaumasite as indicated by the greater birefringence of thaumasite, as opposed to the darker grey colour of ettringite. Magnification ×1100.

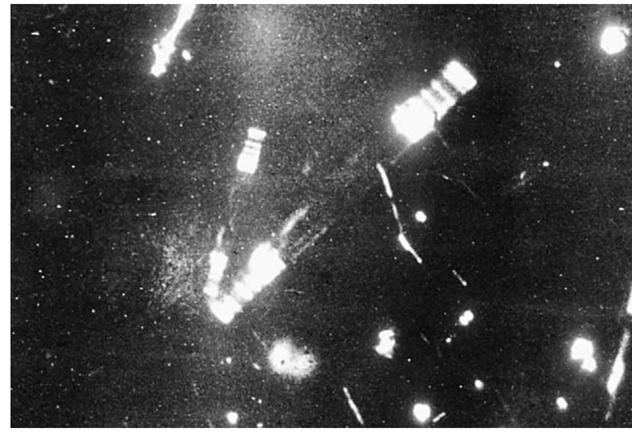

Fig. 2. Layered intergrowth of thaumasite and ettringite, as reflected by the bonded darker and lighter reflection of differences in birefringence. Brighter crystal portions are thaumasite. Magnification ×1360.

Table 1
Optical properties for thaumasite and ettringite

| Property | Thaumasite | Ettringite |
|---|---|---|
| Crystal system | Hexagonal | Hexagonal |
| Optical elongation and sign | Negative | Negative |
| O-ray | 1.504 | $1.464 \pm 0.002$ |
| E-ray | $1.468 \pm 0.002$ | $1.458 \pm 0.002$ |
| Birefringence | 0.036 | 0.006 |

Chemical analyses of the grout sample mentioned above and two naturally occurring thaumasite samples are given in Table 2. Laboratory prepared ettringite is included for comparison. Compositions of the natural and the grout samples of thaumasite are similar, but the ettringite contains alumina instead of silica. Also, the carbonate ion is an integral component of thaumasite but not of ettringite.

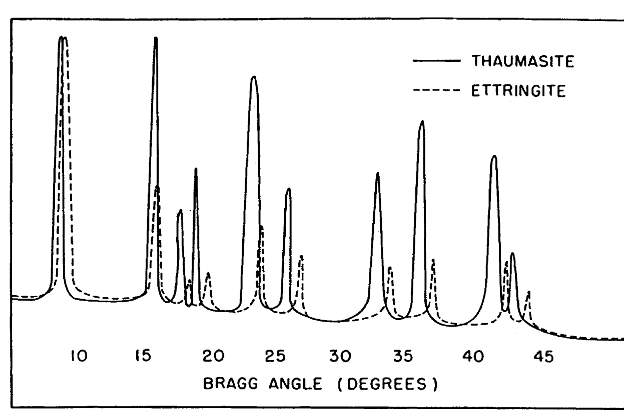


Fig. 3. XRD patterns for thaumasite and ettringite.

Table 2
Chemical analyses of thaumasite and ettringite

| Sample source | Percentage by mass | | | | |
|---|---|---|---|---|---|
| | CaO | $SO_3$ | $SiO_2$ | $Al_2O_3$ | $H_2O + CO_2$ |
| Thaumasite, Crestmore, California | 27.6 | 13.0 | 9.1 | 0.0 | 49.5 |
| Thaumasite, cement grout | 24.7 | 10.1 | 10.8 | 0.0 | 43.6 |
| Ettringite, laboratory preparation | 27.2 | 19.3 | 0.0 | 8.24 | 45.3 |

Scanning election microscopy (SEM), including electron diffraction X-ray (EDX), has been used to identify or characterize the possible presence of thaumasite and ettringite. It was observed in these samples that crystal morphology was similar for thaumasite and ettringite and therefore did not clearly distinguish the two. Elemental differences revealed the major presence of sulfur, silica, and calcium but the absence of alumina, thus the absence of ettringite.

## 5. Summary

Thaumasite as a component of deteriorated concrete was first identified in the structures described here. It was first detected in the grout sample by petrographic microscopy followed by XRD by the writer, in 1962. Later, thaumasite was initially misidentified as ettringite, then reexamined and found to be present as both thaumasite and ettringite by the same techniques. These examples demonstrate the petrographic microscope can definitively identify thaumasite in Portland cement products as distinct from the presence of ettringite.

## References

[1] Winchell AN, Winchell H. Elements of optical mineralogy, part II, descriptions of minerals. 4th ed. John Wiley & Sons, Inc.; 1956. p. 179.

[2] Carpenter AB. Oriented overgrowths of thaumasite on ettringite. Am Miner 1963;48(11 and 12):1394–6.