

Identification and Occurrence of Thaumasite in Concrete

A Discussion for the 1965 HRB Symposium on Aggressive Fluids

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•THE REACTIONS between components of concrete and aggressive solutions result in the formation of secondary compounds. Examples of the occurrences of such compounds are well documented in the literature and have also been commented on in this Symposium.

The purpose of this discussion is to bring to the attention of research personnel concerned with the chemistry of portland cement pastes the occurrence of a sulfate-bearing mineral known as thaumasite. Four interesting cases involving the alteration of portland cement concrete and a portland cement grout are investigated, and the means used to distinguish thaumasite from ettringite are described. A review of the literature has failed to disclose any comment on the occurrence of thaumasite in concrete or portland cement pastes, and we feel that it is of value to report our findings at this time.

The precise circumstances leading to the formation of thaumasite in the cases described herein have not been resolved. This may be attributed to the absence of the background information pertinent to the four specific cases investigated. In two of the cases presented, however, field and laboratory data indicate that sulfate was contributed to the concrete from an external source. The concrete environment in one of the two cases contained solutions sufficiently high in sulfate to merit classification as a moderate sulfate exposure. The occurrence of thaumasite, therefore, appears to represent situations involving attack by sulfate solutions.

The mineral thaumasite has the approximate composition $\text{CaSiO}_3 \cdot \text{CaSO}_4 \cdot \text{CaCO}_3 \cdot 14.5 \text{H}_2\text{O}$ and is usually found in metamorphosed rocks that have undergone hydrothermal alteration. Associated minerals in these zones commonly include ettringite ($3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{CaSO}_4 \cdot 31 \text{H}_2\text{O}$), aragonite and calcite (CaCO_3), portlandite (Ca(OH)_2), spurrite ($2 \text{Ca}_2\text{SiO}_4 \cdot \text{CaCO}_3$) and members of the tobermorite family (calcium silicate hydrates). Usually these minerals occur side by side in thin veinlets, but at Crestmore, Calif., Carpenter (1) found thaumasite as oriented overgrowths on ettringite and, in a few instances, as overgrowths inclosed by a second generation of ettringite. On the basis of analyses of crystallographic data and similarities in physical properties, McConnell and Murdoch (2) concluded that "the structures of ettringite and thaumasite must be closely related in several aspects." Later, McConnell and Verhoek (3) proposed that thaumasite is an intermediate isomorphic variant of a family containing ettringite and "calcium carboaluminate" as end members. Carpenter has suggested there may be a limited solid solution series between thaumasite and ettringite and points toward anomalies in refractive indices of the associated growths as evidence.

OCCURRENCES OF THAUMASITE IN CONCRETE

During the past 2 yr, four occurrences of thaumasite have been found; two were in sanitary sewer pipes, one was in a grout, and one was at the base of a core taken from a pavement. These occurrences were located in four different states, two in the northeastern portion of the United States and two in the midwest. Initial identification of thaumasite in the grout was made by Stark.

In Pavement

The bottom of one of a series of cores taken from an 11-yr-old highway pavement contained a soft, light gray material that represented cement paste extensively altered to thaumasite, ettringite, aragonite and calcite. Several horizontal fractures located in the bottom 1/4-in. of the core were also filled with thaumasite, aragonite and calcite. Thaumasite and ettringite often occurred as banded intergrowths normal to the long axis (c-axis) of the crystals (Fig. 1) and as overgrowths of thaumasite on ettringite (Fig. 2). Occasionally, intergrowths and overgrowths occurred in a single crystal. In microscopic examinations, the optical extinction positions of the intergrowths and overgrowths were parallel.

In Sewer Pipe

In the first such occurrence, thaumasite was identified as one component of a creamy, white substance filling blisters whose shells were composed of calcite and as a filling in thin veinlets located parallel and adjacent to the inside surface of a 5-yr-old sewer pipe. Associated compounds in both instances were calcite, gypsum and brucite.

The thaumasite occurred as long slender needles and as clusters and bundles of needles similar in morphology to the secondary ettringite often found in concrete.

An analysis of the sewage at the time the materials were submitted for examination indicated a sulfate content of 152.3 ppm and a pH of 8.3. A chemical analysis of material filling a blister, including aggregate, showed about 11.3 percent sulfate.

Interpretation of the petrographic microscopy data for the compound initially suggested that the material was ettringite, although the refractive index of the ordinary ray was considerably higher than normal. This may have resulted from substitution of iron for aluminum. Once positive identification of thaumasite in the grout was made, reinvestigation confirmed that the material was thaumasite.

The second occurrence of this type was in a sewer pipe over 32 years of age at the time of examination. Paste along the inside surface of the pipe was severely deteriorated to depths of about 1/2 in. and converted to gypsum and silica gel. Between the severely deteriorated and sound portions of the pipe were deposits of thaumasite, ettringite, gypsum and traces of calcite. In sound portions of the pipe, tuffs and rosettes of ettringite and thaumasite lined or filled entrapped air voids. In these voids, thaumasite occurred as discrete long slender needles, occasionally as overgrowths incasing ettringite, and as petal overgrowths on bundles of ettringite crystals. In microscopic examinations, the optical extinction positions of the overgrowths were parallel with ettringite.

In Grout

Thaumasite occurred in small clusters and as disseminated crystals in a moist, granulated grout specimen. Associated materials were aragonite, calcite and fine aggregate.

The grout was taken from a pressure pointed abutment in an area adjacent to sodium chloride mines where sulfate-bearing waters could have been.

IDENTIFICATION OF THAUMASITE

The identification of thaumasite and ettringite in the cases discussed was initially and principally by petrographic microscopy. Although this means provided positive identification, failure to find mention of thaumasite in literature pertaining to concrete prompted further investigation by X-ray and electron diffraction, electron microscopy, and chemical analysis. The thaumasite used for these studies was handpicked from the grout and separated from the material filling a blister in the sewer pipe by sedimentation in water.

Light Microscopy

Optical data for naturally occurring thaumasite and for the compound found in all

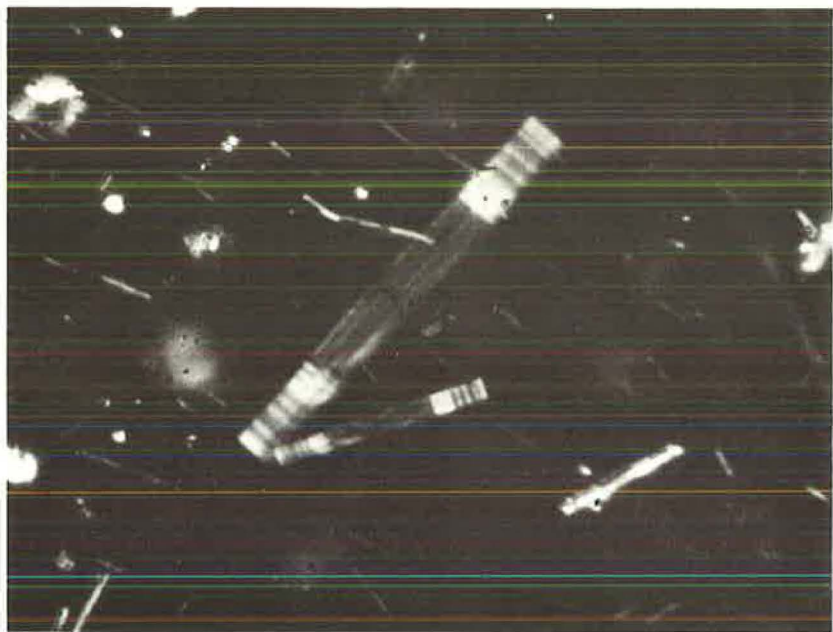


Figure 1. Photomicrograph showing bands of thaumasite and ettringite oriented normal to c-axis of crystal; crossed nicols (magnification 1,360X).

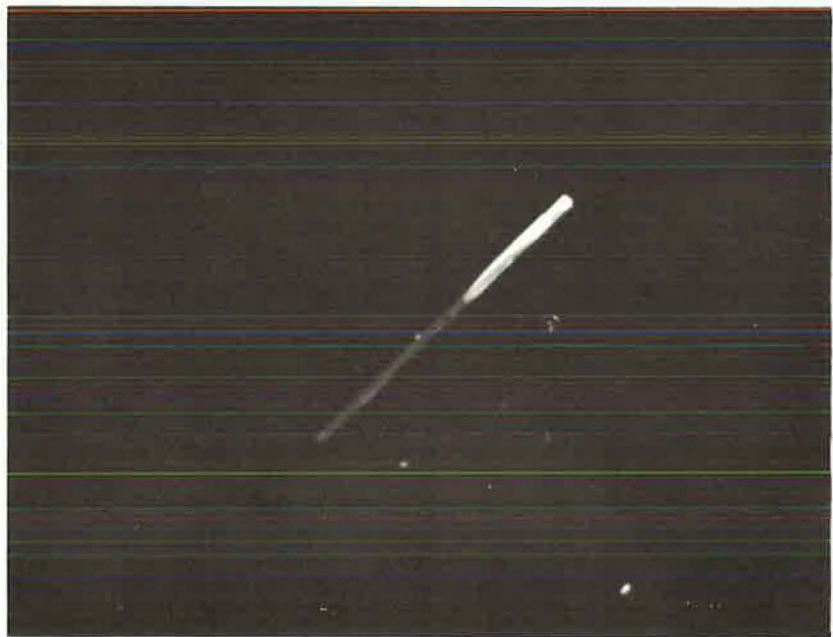


Figure 2. Photomicrograph showing overgrowths of thaumasite on ettringite; crossed nicols (magnification 1,090X).

TABLE 1
COMPARISON OF REFRACTIVE INDICES
FOR THAUMASITE

Source	E	O
Crestmore, Calif.	1.470 ± 0.002	1.492 ± .002
	1.468 ± 0.002	1.507 ± .002
Great Notch, N. J.	1.468	1.505
Co. Down, N. Ireland	1.470	1.504
Sewer pipe, grout, pavement	1.468 ± 0.002	1.504

TABLE 2
CHEMICAL ANALYSES OF THAUMASITE

Source	Percentage by Weight						
	CaO	SO ₃	R ₂ O ₃	SiO ₂	H ₂ O + CO ₂	Na ₂ O + K ₂ O	MgO
Crestmore, Calif.	27.6	13.0	0.8	9.1	49.5	-	-
Areskuta, Sweden	27.4	13.1	0.2	9.6	49.1	0.3	-
PCA	24.7	10.1	3.6	10.8	43.6	0.01	5.1

a Analysis totals 97.9 percent which probably resulted from presence of undetermined oxides and separate ignition loss determination.

four of the concretes investigated are compared in Table 1. These indices are in sufficient agreement for positive identification of the compound as thaumasite.

X-Ray Diffractometry

X-ray diffraction data for naturally occurring thaumasite and for the compound from the grout and sewer were identical. A few of the minor peaks reported for naturally occurring thaumasite were not present in the diffraction pattern obtained from the compound in the grout.

Electron Microscopy and Diffractometry

Specimens identified under the petrographic microscope as thaumasite were taken from the grout and the sewer and studied by electron microscopy and electron diffraction. Unit cell dimensions calculated from the electron diffraction patterns are in close agreement with those determined from X-ray diffraction data reported by other investigators for naturally occurring thaumasite. Although the precise orientation of the crystals in these studies was not known, their preferred orientation noted under the petrographic microscope was also observed in the electron microscope. In addition, close examination of the diffraction pattern showed that the c-axis of the crystal was, within several degrees, oriented normal to the electron beam (Fig. 3).

Chemical Analysis

A chemical analysis of thaumasite from the sewer pipe is given in Table 2 and com-

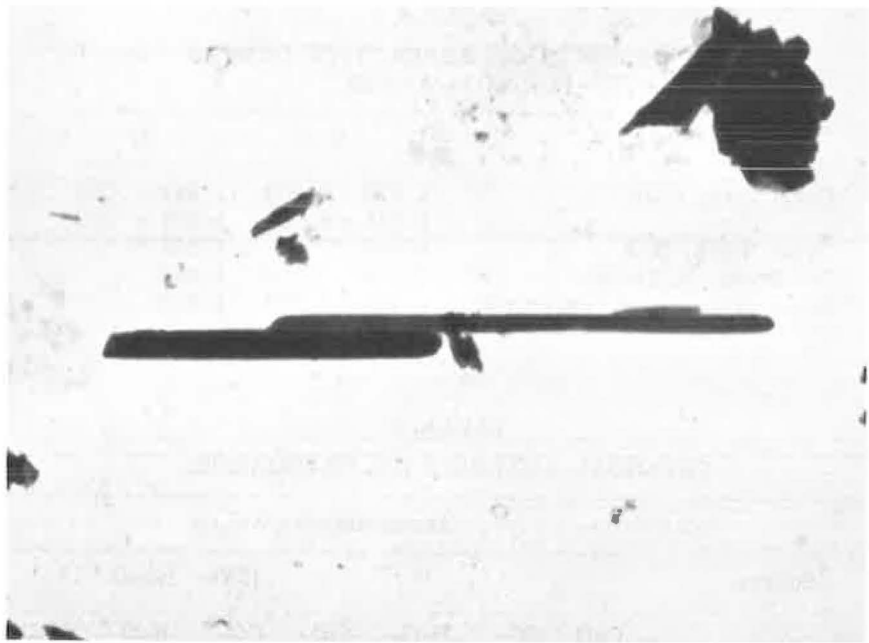


Figure 3. Electron micrograph showing crystals of thaumasite from which electron diffraction patterns were obtained (magnification 13,750X).

TABLE 3
COMPARISON OF OPTICAL DATA FOR
ETTRINGITE AND THAUMASITE

Property	Thaumasite	Ettringite
Crystal system	Hexagonal	Hexagonal
Crystal habit	Acicular	Acicular
Elongation and sign	Negative	Negative
O - Ray	1.504	1.464 ± 0.002
E - Ray	1.468 ± 0.002	1.458 ± 0.002
Birefringence	0.036	0.006

pared with data reported for two natural occurrences. The water plus carbon dioxide content reported for the PCA analysis is the weight loss on ignition of another portion of the specimen used for the analysis. Our data are close to those reported but deviate slightly, possibly because other phases of the concrete may have been present in the analyzed material.

Comparison of Optical and X-Ray Properties of Thaumasite and Ettringite

Although thaumasite may be identified by means of X-ray diffractometry and optical microscopy, some difficulties may arise in distinguishing it from ettringite in portland cement concrete. The optical data for the two compounds are similar (Table 3); the only appreciable differences are in the birefringence and refractive index of the ordinary ray. With the exception of the sign of elongation, which is identical for both compounds, the extremely small crystal sizes of thaumasite and ettringite encountered

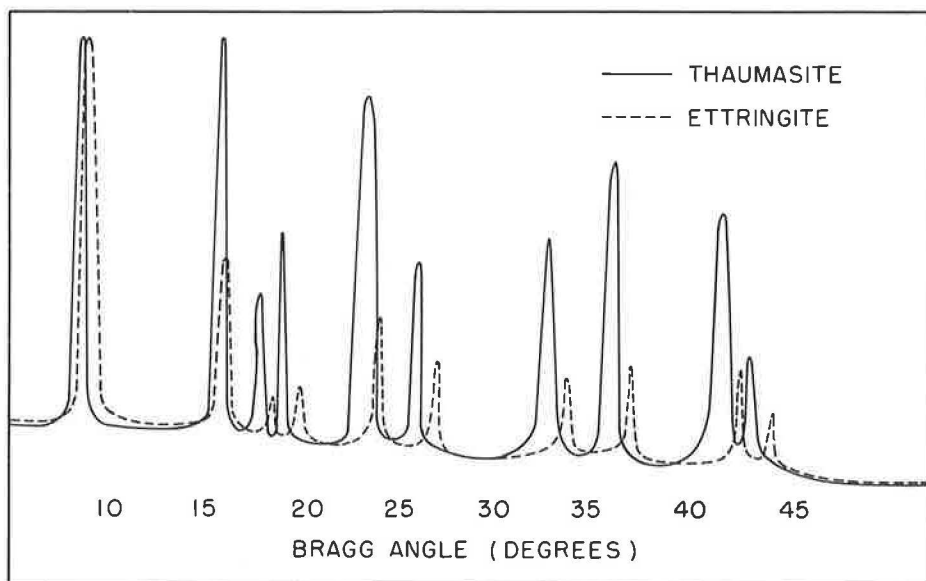


Figure 4. X-ray diffraction patterns for thaumasite and ettringite.

in concrete and the similarity in refractive index of the extraordinary ray require the determination of the ordinary ray to distinguish between the two compounds.

X-ray diffraction patterns for thaumasite and ettringite are likewise similar, as shown in Figure 4. These patterns were obtained on thaumasite removed from the sewer pipe and on ettringite synthesized at our laboratories. The greatest differences occur at the higher Bragg angles where, in impure specimens, the peaks are of relatively low intensity and, in some instances, may be obscured by peaks produced by other compounds.

CONCLUSION

The four occurrences of thaumasite described cannot represent the only cases where the compound has formed in deteriorated concrete. Difficulties may be encountered in identifying the compound by petrographic microscopy and X-ray diffractometry. These difficulties may explain the absence of reports in the published literature describing the presence of secondary thaumasite in portland cement concrete.

REFERENCES

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