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Field experiences in concrete deterioration by thaumasite formation: possibilities and problems in thaumasite analysis

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Abstract

In Germany, after testing two concretes deteriorated due to the formation of thaumasite, possibilities and problems in analysing thaumasite and ettringite-containing concrete samples will be discussed. The image of polished thin sections show, that thaumasite formation leads to microstructures similar to the microstructure of ettringite. It is recognisable in the microstructure that the formation of thaumasite happens as well via deterioration of CSH-phases as via the decomposition of ettringite. The identification of thaumasite using environmental scanning electron microscopy is possible without problems. Investigations using X-ray powder diffraction did show, that quantitative analysis of thaumasite and ettringite is possible by using the Rietveld method. The samples of deteriorated concrete (excluding coarse aggregate) contain 20–75% thaumasite.

Keywords: Concrete deterioration; Sulfate attack; Thaumasite; Ettringite; ESEM; Polarisation microscope; XRD; Rietveld refinement

1. Introduction

In connection with the durability of concrete thaumasite is thought to be a special kind of sulfate attack. The destruction of binding C–S–H phases leads to the total loss of concrete strength. Preconditions for the thaumasite formation are temperatures less than 10 °C, the contact with sulfate-containing water and the presence of $CaCO_3$ from limestone-dust-filler in cement, limestone- and dolomite-aggregate in concrete or $CaCO_3$ from carbonation of concrete. The formation of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) and thaumasite ($CaO \cdot SiO_2CaSO_4 \cdot CaCO_3 \cdot 15H_2O$) is dependent on the storage conditions. In the presence of sulfate- and carbonate-ions and at low temperatures thaumasite-formation is preferred [1–8].

Two examples of concrete deterioration by thaumasite and ettringite formation will be described. Both are examples of concrete damage in Germany. Using samples from this deteriorated concrete possibilities and problems shall be discussed in analysing thaumasite and ettringite using environmental scanning electron microscope (ESEM), polarisation microscope, and X-ray powder diffraction.

2. Examples for concrete deterioration in Germany

2.1. Concrete basin of a saltwater swimming bath

The swimming pool is 68 years old; the concrete formula is unknown. But it contains aggregates from microcrystalline partial biogenic limestone (mittlere Trias, shell-lime). The concrete from the pool-bottom shows no measurable strength. It can be broken by hand. After drying it disintegrates into small pieces. The concrete borders on gypsum and anhydrite containing layers (oberer Zechstein). Also it is in contact with sulfate-containing ground water. Sometimes the basin was used as a saltwater swimming pool. The saltwater contained sodium- and magnesium sulfate.

2.2. Concrete structures from a train-tunnel

The tunnel walls built from natural stone were stabilised by concrete structures in 1994. The concrete contains 330 kg/m^3 cement as portland-limestone-cement PKZ 35 F (CEM II/A-L). Under the tunnel bottom there is gypsum- and anhydrite-containing

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stone. Up to 550 mg/l Ca^{2+} and up to 1670 mg/l Mg^{2+} could be measured in groundwater. After six years the concrete structures in contact with the sulfate-containing water are totally destroyed on the surface (up to a depth of 5 cm). There are only small pieces or wet mush present.

In both examples perfect conditions are present for deterioration of concrete by formation of thaumasite. External sulfate attack from groundwater (sulfate from gypsum and anhydrite containing stone), low temperatures (seasonal variation on the bottom of the saltwater swimming pool, constant low in the tunnel), $CaCO_3$ proportion in concrete (limestone aggregate and progressive carbonation in example 1, ground limestone in example 2).

The following abbreviation "S1" will be used for the samples of deteriorated concrete described in Section 2.1 and "S2" will be used for the samples of deteriorated concrete described in Section 2.2.

3. Possibilities and problems in analysing thaumasite and ettringite

3.1. Microstructure under polarisation microscope, polished thin section investigations

There are two polished thin sections (thickness = 20 μm) of deteriorated concrete parts from the first case of deterioration (Section 2.1). Analysis with polarisation microscope (instrument: POLIM JENALAB; ZEISS) shows the following results:

Distinction between the crystallographic characteristics of thaumasite and ettringite is not possible because of the quit similar habit and density (ettringite $\rho = 1.75$ g/cm^3, thaumasite $\rho = 1.83$ g/cm^3) and the nearly identical value for refraction index respectively the *Doppelbrechung* (ettringite: $\mu = 0.026$, thaumasite $\mu = 0.027$). That means, that the detection and proof of thaumasite must be done by X-ray diffraction or electron microscopy (REM/ESEM).

Formation of thaumasite in small or large pores leads to a similar appearance than formation of secondary ettringite. Small pores are completely filled; larger pores are occupied on the edges or completely filled with thaumasite needles (Fig. 1). Thaumasite crystal needles seem always to be shorter than ettringite crystal needles.

Progress of thaumasite formation is like a front line (Fig. 2). This concrete sample mainly contains coarse aggregate (quartz), with less C_4AF (calcium ferroaluminate) and thaumasite. Also not hydrated rests of C_3S (tricalcium silicate), (normally existing in small amounts in old concrete) are much less than expected. The result of these observations is, that CS- and CSH-phases are consumed during the formation of thaumasite [3].

In large hollows new formed thaumasite and gypsum can be seen (Fig. 3). Both minerals are connected. In this part of the structure thaumasite seems to be formed by consuming decomposition products of ettringite. A second indication is, that gypsum appears only in limited districts and only in small amounts. Gypsum was not found in the X-ray powder diffraction pattern. Also simple crystallisation of infiltrating sulfate-containing solution (groundwater) is improbable.

The edges of the numerous limestone aggregates do not show any special features, which can be detected

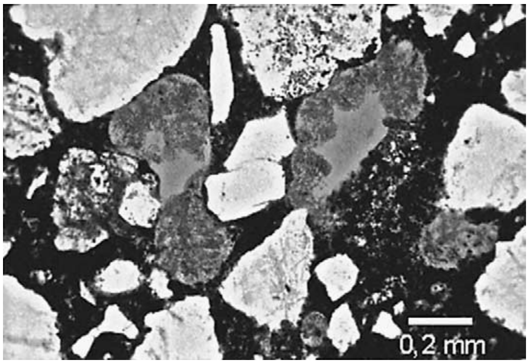

Fig. 1. Sample S1: short needles of new formed thaumasite.

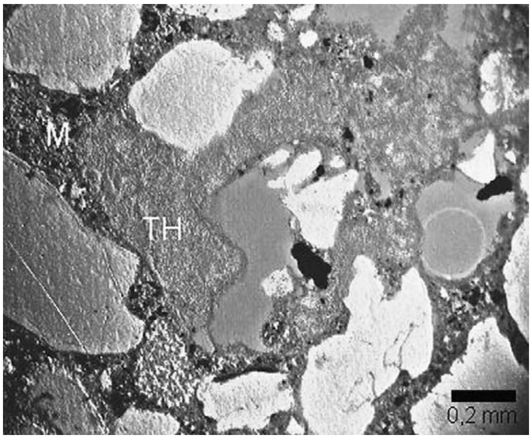

Fig. 2. Sample S1: intact matrix (M), new formed thaumasite (Th).

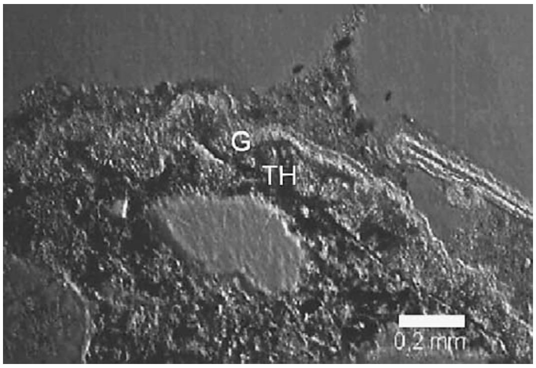

Fig. 3. Sample S1: concrete structure with gypsum (G) and thaumasite (Th).

under a microscope. The question whether limestone aggregate is attacked on the surface cannot be answered by this way. Indeed the concrete is intensely carbonated. On one side there is a layer of calcite formed with a thickness of 200 μm. Calcite respectively portlandite (form fine particles in concrete) must be dissolved and calcite precipitation occurred. If the calcium- and carbonate-ion content becomes large enough thaumasite formation occurs.

3.2. ESEM

The identification of thaumasite using electron microscopy (instrument HITACHI S 2700 LB) respectively ESEM (instrument PHILIPS environmental scanning electron microscope XL-30) is possible without problems. Examples of ESEM-pictures from both deterioration cases are shown in Figs. 4 and 5. Comparison of a few EDX data belonging to it are shown in Table 1.

In the first case of deterioration it is noteworthy that the relationship between SiO_2 and SO_3 (0.63...0.73) is near to the theoretical value for thaumasite (0.75). On the other hand the relationship between CaO and SiO_2 and the relationship between Ca and SO_3 is much higher than expected for thaumasite. The reason for this is the presence of calcite crystals between the thaumasite crystals. Chloride and Na_2O components from saltwater are detected because of the formation of monochloride (friedels salt). In the second case of deterioration alkalies and chlorine have not been found. All other results are similar to those in the first case of deterioration.

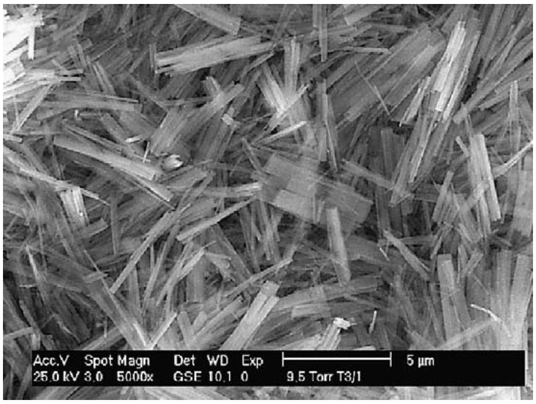

Fig. 5. Sample S2: new formed thaumasite—ESEM image.

Table 1
EDX analysis of new formed thaumasite from case 1 (S1, bath) and case 2 (S2, tunnel)

	S1/1	S1/2	S1/3	S2/1 integr.	S2/1 detail
SiO_2	15.40	17.19	17.95	15.52	20.13
Al_2O_3	1.47	3.23	2.23	2.23	0.00
Fe_2O_3	1.52	0.87	1.11	2.83	0.00
CaO	55.31	52.75	51.74	52.84	50.44
MgO	2.70	1.38	0.55	2.56	0.00
K_2O	0.07	0.16	0.00	0.00	0.00
Na_2O	0.23	0.21	0.09	0.00	0.00
SO_3	22.14	23.49	26.05	24.02	29.43
Cl^-	0.87	0.31	0.19	0.00	0.00

3.3. XRD investigations, using Rietveld refinement

Simultaneous qualitative and quantitative analysis of thaumasite and ettringite can be problematical. Fig. 6 is an XRD pattern of one sample from the first case (Section 2.1; instrument Siemens D5000). In this pattern the simultaneous analysis of ettringite and thaumasite is possible. In the region of 16° 2θ thaumasite and ettringite can be detected definitely.

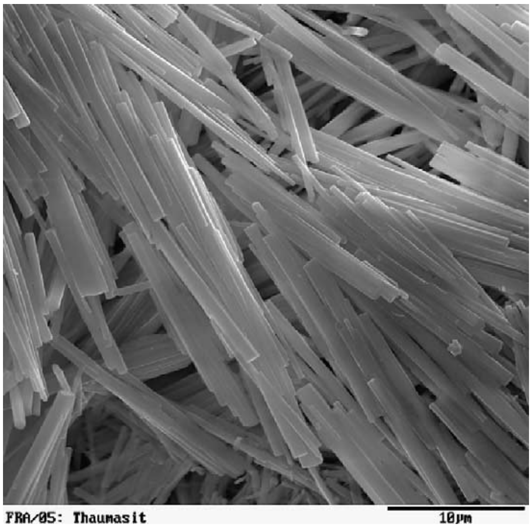

Fig. 4. Sample S2: New thaumasite formation—REM image.

Comparison of degree 2θ values from JCPDF for thaumasite (25–128) and ettringite (41–1451) is shown in Table 2. There it is pointed out, that the simultaneous analysis of thaumasite and ettringite is possible in principal. In practice it is important that the amount of these substances is large enough. Unavoidable deviation in peak position must be corrected by orientation on other peaks present (quartz, calcite) or by using an internal standard.

If there are low concentrations of thaumasite and ettringite analysis is very difficult. In this case selective solution with Na_2CO_3 solution is recommended [1] to dissolve ettringite completely before making XRD.

Recent research shows the possibility of quantitative analysis of thaumasite and ettringite by using Rietveld method. This research was carried out at the F.A. Finger institute using the computer-program TOPAS from Bruker AXS. The first results are represented and discussed as follows.

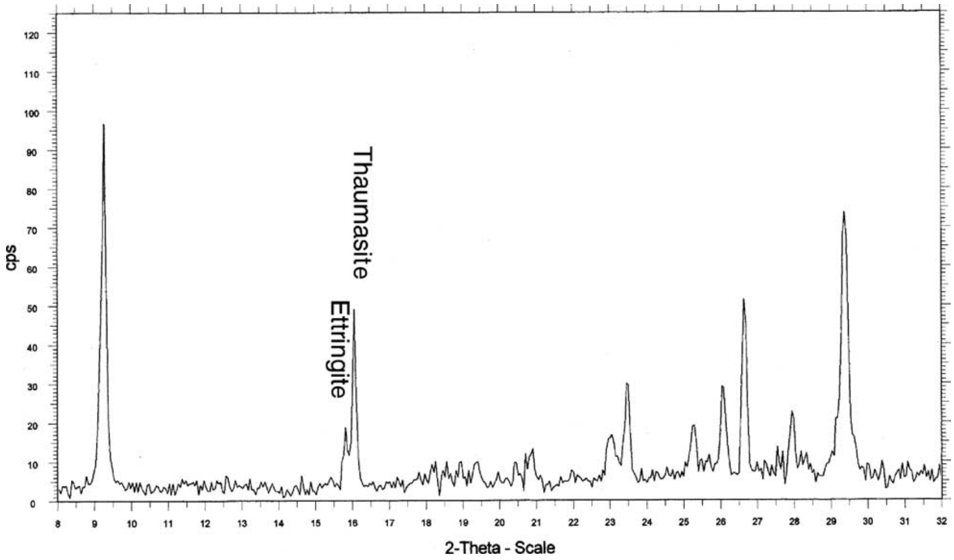

Fig. 6. XRD pattern of a thaumasite and ettringite containing mixture.

Table 2
Intensities, *d* values and indices of thaumasite and ettringite (JCPDF data)

Intensity		*d* values		*hkl*	
Thaumasite	Ettringite	Thaumasite	Ettringite	Thaumasite	Ettringite
100	100	9.72	9.56	1 0 0	1 0 0
76	40	5.61	5.51	1 1 0	1 1 0
6	5	4.859	4.76	2 0 0	2 0 0
31	16	3.873	3.78	1 1 4	1 1 2
23	20	3.475	3.41	2 1 2	2 1 1
21	16	3.240	3.18	3 0 0	3 0 0
25	16	2.772	2.71	3 0 4	3 0 2

Firstly quantitative investigations on standard samples of known composition have been needed to have the basis for analysing technical samples (from deterioration case—Sections 2.1 and 2.2).

3.3.1. Finding out good crystal models for refinement using XRD pattern of the pure substances thaumasite and ettringite

Thaumasite was a natural mineral; ettringite was synthesised in the laboratory.

Ettringite:
Starting model—ICSD 16045;
Refined model—ettringite P31c, $a = 11.25$, $b = 21.49$.
Thaumasite:
Starting model—ICSD 9057 appropriate for quantitative analysis.

3.3.2. Quantitative analysis of binary mixture of thaumasite and ettringite

Results are shown in Table 3. Fig. 7 shows that in binary mixtures the peaks of thaumasite and ettringite are separated well enough to distinguish them. There are also no problems relating to peaks being superposed by other peaks. The accuracy of the analytical results is very good.

3.3.3. Mixtures from thaumasite and calcite respectively ettringite and calcite

(In concrete samples there is always calcite from carbonated parts, filler or abrasion of aggregate.) The results are shown in Table 4.

In the presence of calcite accuracy like this in binary mixtures cannot be reached until now. Especially it is conspicuous that the quantitative value for calcite is always too large and the calculated value for ettringite is always too small.

3.3.4. Five components mixtures of thaumasite and ettringite (with gypsum, calcite and quartz) and six components mixtures of thaumasite and ettringite (with gypsum, calcite, quartz and aragonite)

Results are in Tables 5 and 6. Quartz from ground aggregate is often present in samples of old concrete. After 6–12 months storage it could be seen, that

Table 3
Quantitative analysis of binary thaumasite–ettringite mixtures

	Mixture 1		Mixture 2	
	Weighted %	Calculated %	Weighted %	Calculated %
Thaumasite	65	66.44	35	33.77
Ettringite	35	33.56	65	66.23

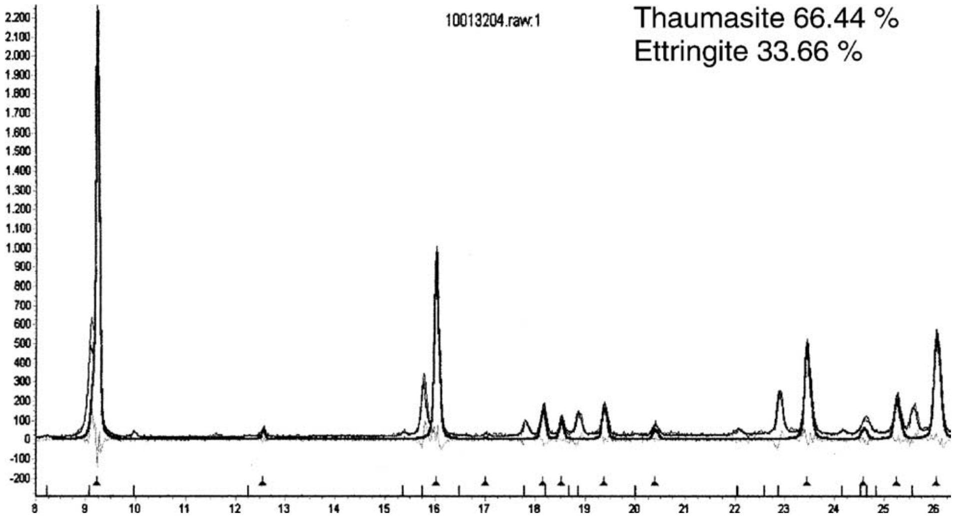

Fig. 7. XRD pattern of a binary mixture of thaumasite and ettringite.

Table 4
Quantitative analysis of thaumasite–ettringite mixtures with calcite

	Mixture 1		Mixture 2		Mixture 3		Mixture 4	
	Weighted %	Calculated %	Weighted %	Calculated %	Weighted %	Calculated %	Weighted %	Calculated %
Thaumasite	65	61.33	35	33.77	0	0	0	0
Ettringite	0	0	0	0	65	55.47	35	25.39
Calcite	35	38.94	65	66.23	35	44.53	65	74.61

Table 5
Quantitative analysis of thaumasite and ettringite in a five component mixture

	Mixture 1		Mixture 2		Mixture 3	
	Weighted %	Calculated %	Weighted %	Calculated %	Weighted %	Calculated %
Thaumasite	50	46.35	30	29.83	10	11.07
Ettringite	10	11.26	30	24.03	50	42.21
Gypsum	10	8.28	10	9.99	10	11.25
Quartz	10	11.07	10	12.42	10	10.88
Calcite	20	23.04	20	23.78	20	24.59

thaumasite has been carbonated and new formation of aragonite has occurred.

Firstly the possibility is seen to distinguish thaumasite and ettringite in complex mixtures and it is principally possible to analyse them quantitatively. For testing the efficiency of the program TOPAS on XRD pattern, a mixture without ettringite was used. An ettringite starting model too was given for refinement. The calculated result for the portion of ettringite was clearly 0%.

In Tables 5 and 6, the composition of complex mixtures from thaumasite gypsum, quartz and aragonite can be calculated with an error of 5%. The fact, that the calculated values for ettringite are always too small and the calculated values for calcite are always too large point out that perhaps there is a systematic error.

Table 6
Quantitative analysis of thaumasite and ettringite in a six-component mixture

	Mixture 1		Mixture 2		Mixture 3	
	Weighted %	Calculated %	Weighted %	Calculated %	Weighted %	Calculated %
Thaumasite	25	24.60	20	20.67	20	20.32
Ettringite	25	19.65	35	26.66	60	54.32
Calcite	10	11.90	15	18.63	0	0
Gypsum	10	11.16	10	11.21	10	11.53
Quartz	10	12.33	10	11.67	10	13.83
Aragonite	20	20.35	10	11.66	0	0

Table 7
Quantitative analysis of samples S1 (bath) and S2 (tunnel)

	S1/3	S2/1	S2/3	S 2/4	S2/5.1	S2/5.2
Thaumasite	75.72	39.20	67.23	31.12	25.76	20.92
Ettringite	0.00	0.00		trace	0.00	0.00
Calcite	9.99	38.94	10.54	55.97	66.93	65.35
Quartz	6.54	3.59	2.02	4.08	3.37	4.30
Gypsum	1.86	7.25	7.95	1.50	0.18	5.08
Bassanite	3.86	7.02	8.22	4.15	3.00	2.98
Aragonite	2.03	4.01	3.99	1.92	0.76	1.38
C3S	0.00	0.00	0.00	1.25	0.00	0.00

Coupling between calcite and ettringite is not assumed because of the fact that calculated ettringite values are also too small in absence of calcite (Table 6). Results may become better by using better starting models. Testing and refining models for quantitative Rietveld analysis is part of the investigations at the F.A. Finger Institute. Besides, the preparation of powder samples containing thaumasite and ettringite is difficult and less homogeneous samples lead to wrong quantitative results.

Using the results and starting models from the pure ettringite and thaumasite standards respectively, quantitative Rietveld analysis was done from concrete samples (grain size <63 μm) of the two cases of deterioration. The samples had been stored more than two months, so aragonite and bassanite are present in the samples. The results are shown in Table 7.

It is recognisable that S2 samples from concrete with ground limestone have high amounts of calcite. In all samples some correlation between aragonite and bassanite is recognisable. That means, during the storage time thaumasite carbonation and simultaneous formation of aragonite and bassanite occurs.

The thaumasite content is between 20% and 75% in samples from totally deteriorated concrete.

4. Conclusions

It is recognisable in the microstructure that the formation of thaumasite happens as well via deterioration of CSH phases as via the decomposition of ettringite. The identification of thaumasite using ESEM is possible without problems. It is too possible to distinguish thaumasite and ettringite using X-ray powder diffraction. Also quantitative analysis is possible with Rietveld refinement in the case that the amount of thaumasite and ettringite is high enough.

The samples of deteriorated concrete from the cases examined in Sections 2.1 and 2.2 (excluding coarse aggregate) contain 20–75% thaumasite.

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