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Thaumasite formed by sulfate attack on mortar with limestone filler

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Abstract

Early evidence of thaumasite formation in mortar with limestone filler exposed to sulfate containing tunnel water in Norway is reviewed. The problem is discussed in light of the new European cement standard allowing cements containing up to 35% limestone (e.g. CEM II/B-L) rendering them prone to detrimental sulfate attack.

Experiments are performed where mortars with 20% limestone or quartz filler, respectively, are stored in 5% sodium sulfate solution saturated with gypsum at 5 °C. Length change, flexural strength and compressive strength are measured periodically for a year. The microstructure of the mortars is inspected by scanning electron microscopy and energy dispersive analyser of X-rays documenting the formation of sulfate containing species including ettringite and thaumasite.

Keywords: Limestone; Sulfate attack; Thaumasite; Deterioration

1. Introduction

The first Norwegian experience of thaumasite formation was probably the test programme exposing a number of mortar prisms in the sulfate laden water from alum shale in a dead-end tunnel under Oslo [1,2]. The water running through the alum shale is very aggressive towards concrete with a high sulfate content (in the range 200–300 mg SO_3/l) and rather low pH (3–4). At the time, the original concept of adding 20% limestone powder was that the sulfate would react with the limestone, rather than the C_3A of the cement to form the well-known detrimental ettringite. As can be seen in Fig. 1, the mortars with limestone filler (series 8) and crushed calcite (series 9) disintegrated and performed worse than reference mortar. The explanation at the time (1971) was that the acidic water decomposed limestone to yield CO_2 leading to a mechanical breakdown due to pressure build-up. Since the temperature in the tunnel is about 8 °C, it is likely with today's knowledge that it was due to thaumasite formation. This was also put forward by Hagelia et al. [3] in a recent paper, where they also reported on thaumasite formation in sprayed concrete in tunnels in the same alum shale area. Skjølsvold and Jensen [4] reported on sulfate attack on sprayed concrete in Norwegian sub-sea road tunnels in 1990. Jensen re-examined the thin sections in 1999 and found that it was thaumasite rather than ettringite formation.

As also recently pointed out by Bensted and Munn [5], the European standard for common cements ENV 197–1 allows up to 5% limestone as a minor additional constituent that can be ground into common cements. There are also two grades of Portland limestone cements that can contain respectively 6–20% and 21–35% limestone. Bensted and Munn [5] pointed out that Portland limestone cements are increasingly used across Western Europe, with two thirds of all construction cement produced in Italy being Portland limestone cement. In France three-fifths of current cement production is Portland limestone cement [5], but the French generally do not recommend this type of cement for underground concrete structures. Sweden recently launched a new building cement containing 12–15% limestone filler. With the present knowledge, e.g. [6], it is perhaps timely to put restrictions on the use of Portland limestone cement, not only in sulfate containing grounds, but perhaps also for marine structures exposed to sulfate containing sea water.

The objective of the present paper was to compare the behaviour of mortars containing limestone or quartz filler, respectively, when exposed for external sulfates at 5 °C.

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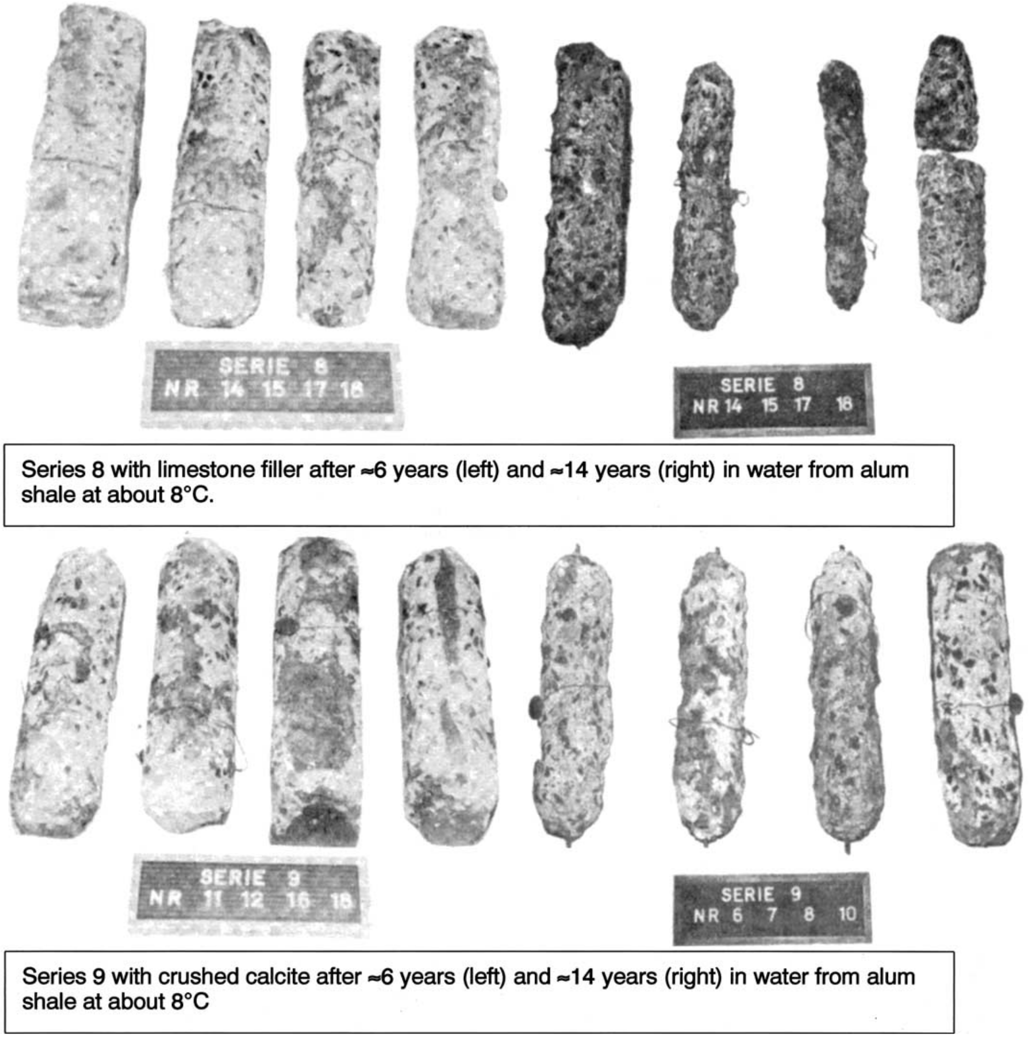

Fig. 1. Mortars with limestone filler (series 8 in upper part) and with crushed calcite (series 9 in lower part) after about 6 years (left part) and 14 years (right) exposure to water from alum shale at 8 °C as taken from Refs. [1] and [2].

2. Experimental

Mortars based on Norwegian Standard cement and 20% filler, one with limestone and one with quartz, were mixed and cast as 40 mm × 40 mm × 160 mm prisms. The cement/filler to sand ratio was 1:3 and w/c was 0.50. Three prisms from each mix had cast in studs in order to monitor the length change as a function of time. Sufficient prisms (12) were cast in order to be able to measure the flexural and compressive strength on three equivalent specimens at the same exposure period as for the length measurements.

The prisms were cured at 90% R.H. and 20 °C for 28 days prior to storage in two separate baths for the two mixes with 5% Na_2SO_4 and excess gypsum at 5 °C. After 10 months the deterioration of prisms with limestone filler appeared on a macro scale as rounded edges, and one half of one prism for each of the mixes were used to prepare 200 mm^2 plane polished specimens near the exposed surface for scanning electron microscopy (SEM) inspection. The SEM instrument was equipped with an energy dispersive analyser of X-rays (EDX) for determination of element distribution of selected details.

3. Results and discussion

The flexural and compressive strength developments of the mortars are listed in Table 1, while the relative length change after the same exposure period is given in Table 2. The strength of the prisms with limestone filler was higher than the prisms with quartz filler until 6 months, going through a maximum at 3 months storage. This can be explained by a pore filling reaction that eventually will start degrading the binder. It is interesting to see that the prisms with limestone filler have a significant mass increase until 6 months and a mass decrease from 10 months that means that material is

Table 1
Relative mass change, Δm (g), from 7 days curing until testing of compressive, σ_c (MPa), and flexural, σ_f (MPa), strength for mortars with different fillers as a function of exposure time in 5% sodium sulfate solution with excess gypsum at 5 °C

Filler	Limestone			Quartz		
Time (months)	Δm (g)	σ_c (MPa)	σ_f (MPa)	Δm (g)	σ_c (MPa)	σ_f (MPa)
1	1.1 ± 0.1	40 ± 1	7.8 ± 0.5	1.3 ± 0.1	34 ± 1	7.6 ± 0.2
3	3.0 ± 0.1	46 ± 1	8.5 ± 0.3	2.8 ± 0.1	40 ± 1	7.5 ± 0.2
6	6.2 ± 0.1	43 ± 3	8.1 ± 0.3	4.7 ± 0.1	39 ± 1	7.4 ± 0.2
10	−9 ± 2	38 ± 3	6.7 ± 0.2	3 ± 1	37 ± 1	6.6 ± 0.5

Table 2
Relative mass change, Δm (g), and length change, Δl (0/00), from 7 days until exposure time in 5% sodium sulfate solution with excess gypsum at 5 °C

Filler	Limestone		Quartz	
Time (months)	Δm (g)	Δl (0/00)	Δm (g)	Δl (0/00)
1	0.9 ± 0.1	−0.059 ± 0.003	0.9 ± 0.1	−0.057 ± 0.005
3	2.7 ± 0.1	0.005 ± 0.002	2.7 ± 0.2	0.016 ± 0.008
6	5.5 ± 0.1	0.32 ± 0.08	5.0 ± 0.3	0.142 ± 0.009
10	−8 ± 1	0.62 ± 0.06	5.0 ± 0.9	0.44 ± 0.01
12	−21.4 ± 0.8	0.69 ± 0.07	0.4 ± 0.7	0.83 ± 0.13

falling off as can be seen from the photos in Fig. 2. The prisms with quartz filler have a mass gain at all ages due to gypsum formation and potential ettringite formation. The results in Table 2 show that the mass gain is associated with an expansion that is particularly visible between 3 and 6 months of exposure. The expansion takes place for both series, with about a 50% higher value for the mortar with limestone filler compared with the mortar with quartz filler after 10 months of exposure to 5% sodium sulfate solution with excess gypsum at 5 °C. Sodium sulfate will form gypsum in contact with calcium hydroxide, leading to a net expansion of 224% for the solid particles

$$\begin{aligned} &\mathrm{Na_2SO_4(aq) + 2H_2O + Ca(OH)_2(s)} \\ &\quad = \mathrm{CaSO_4 \cdot 2H_2O(s) + 2NaOH(aq)} \qquad (1) \end{aligned}$$

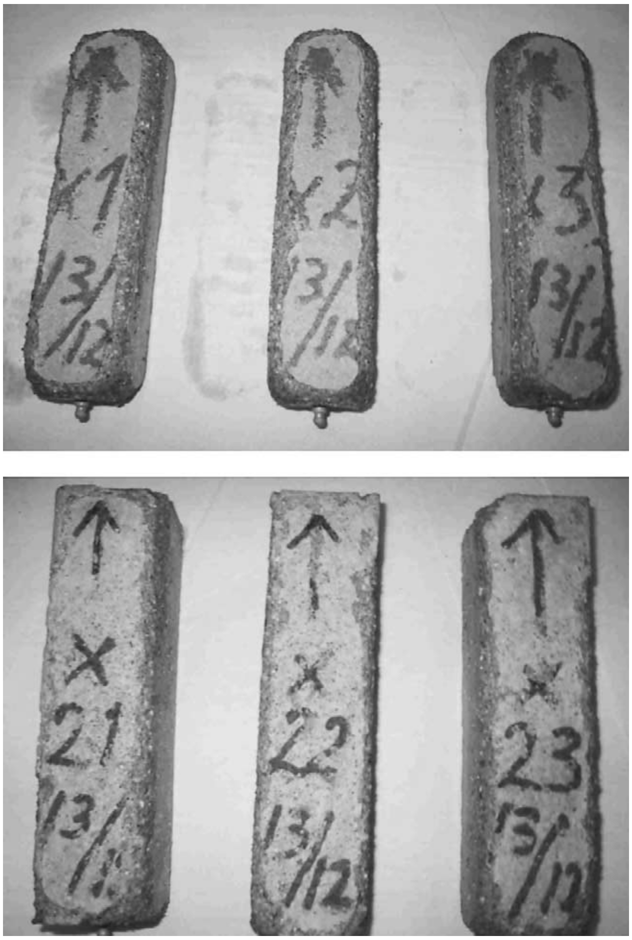

Fig. 2. Storage of mortar prisms with 20% limestone filler (upper) and 20% quartz filler (lower) in 5% sodium sulfate solutions with excess gypsum at 5 °C. Pictures are from the 12 month terminus.

It is well known that sulfate attack of mortar or concrete with calcareous aggregate or limestone filler may form thaumasite; $\mathrm{Ca_3Si(OH)_6(SO_4)(CO_3) \times 12H_2O}$, at moist conditions below 15 °C taking the silica part from the CSH gel [7]. Thaumasite is non-hydraulic and the binder will lose strength as the replacement takes place, as seen by the strength retrogression in Table 1. The backscattered electron images (BEI) by SEM on mortars with limestone filler, as in Figs. 3–5, reveal thaumasite as a dark, amorphous mass with lighter grey crystals of gypsum embedded in it. Actually, analysing random spots of the binder in the outer 0.5 mm of these mortars seems to yield element distributions close to that of thaumasite (i.e. molar Ca:S:Si = 3:1:1), indicating that the whole binder is deteriorating.

In the SEM inspection of the mortars with quartz filler, there was a greater number of unreacted cement grains (not as much reacted through as for the mortar with limestone filler). The quartz filler grains sometimes looked reacted with clear rims, or channels running into defects. This may be caused by the high pH created by

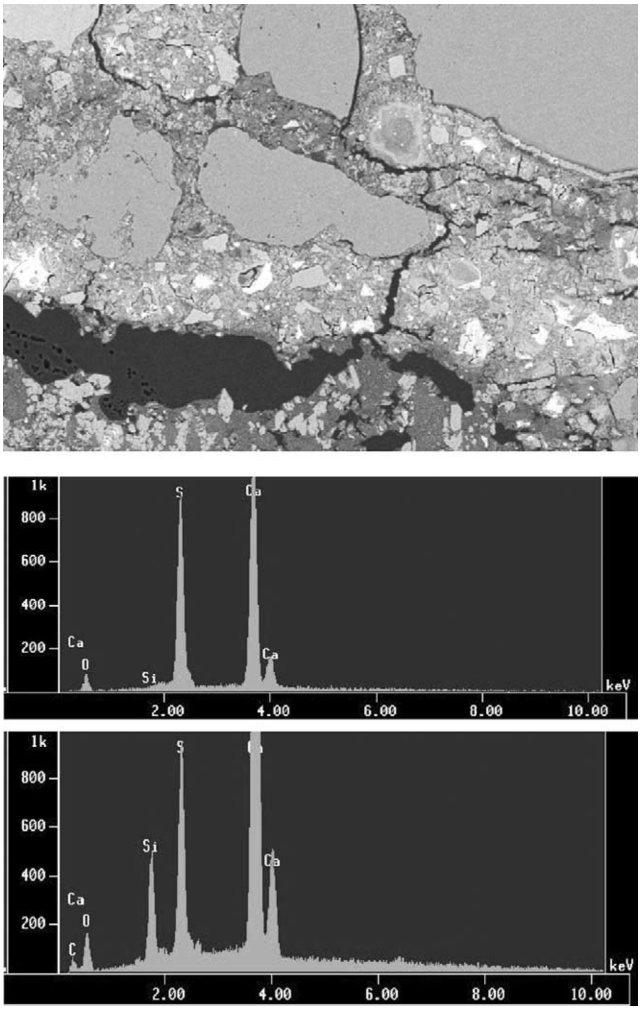

Fig. 3. Back scattered electrons image (BEI) of mortar with limestone filler exposed for sulfates at 5 °C for 10 months (200× magnification). The light grey crystals in the dark mass below the gap (black area) are gypsum as revealed by the upper element spectrum (EDX), while darker area is composed of thaumasite as seen from the element distribution in the lower EDX.

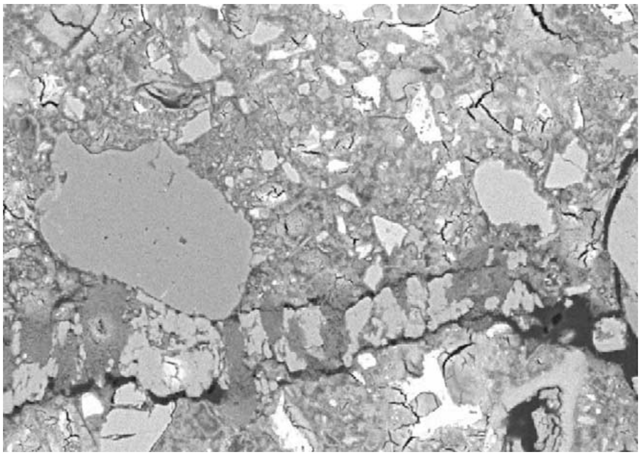

Fig. 4. The band crossing the lower part of this BEI consists of bright gypsum crystals embedded in darker thaumasite as proven by EDX (600× magnification).

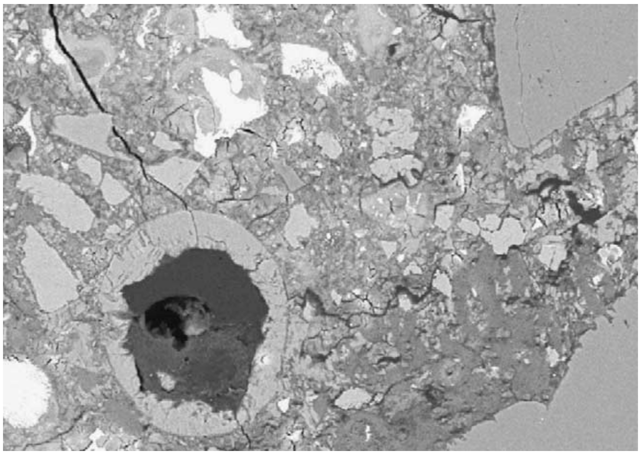

Fig. 5. BEI of mortar with limestone filler exposed for sulfates at 5 °C for 10 months. An air void has precipitated gypsum crystals around the wall, while the dark area to the right is thaumasite as identified by EDX (400× magnification).

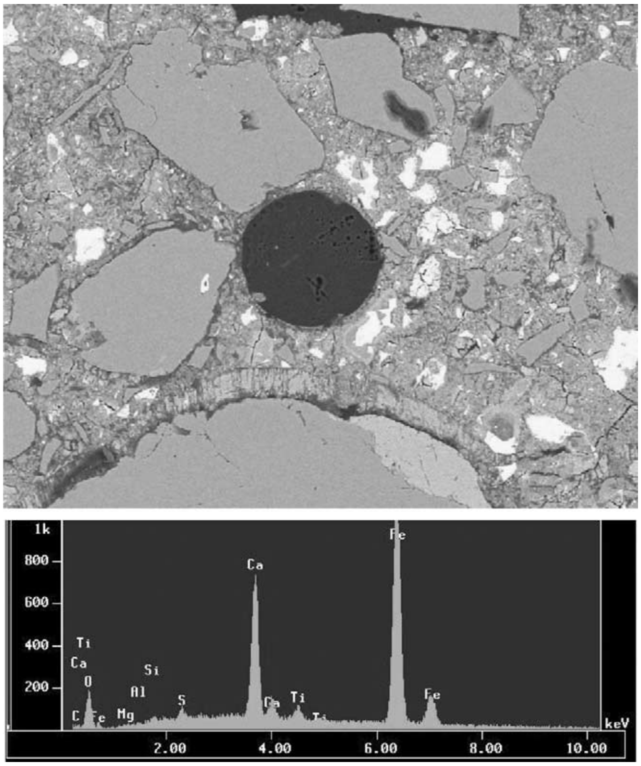

Fig. 6. BEI taken 0.5 mm from the exposed surface of mortar with quartz filler. The crystalline band along the interface of the lower aggregate consists entirely of gypsum. The solid white particles are unreacted cement grains that seems less reacted through than in the case of mortar with limestone filler. The two cracked, white phases to the left of the circular air void in the centre consist actually of calcium and iron (oxides) only as seen from the EDX below the BEI. Note that the evenly grey quartz grains in some cases seems to have reacted (e.g. two grains in to the upper right), and there seems in general to be a rim around the grains (200× magnification).

Eq. (1) in the pores as also in this case gypsum precipitation was observed (see Fig. 6). Reacted quartz filler

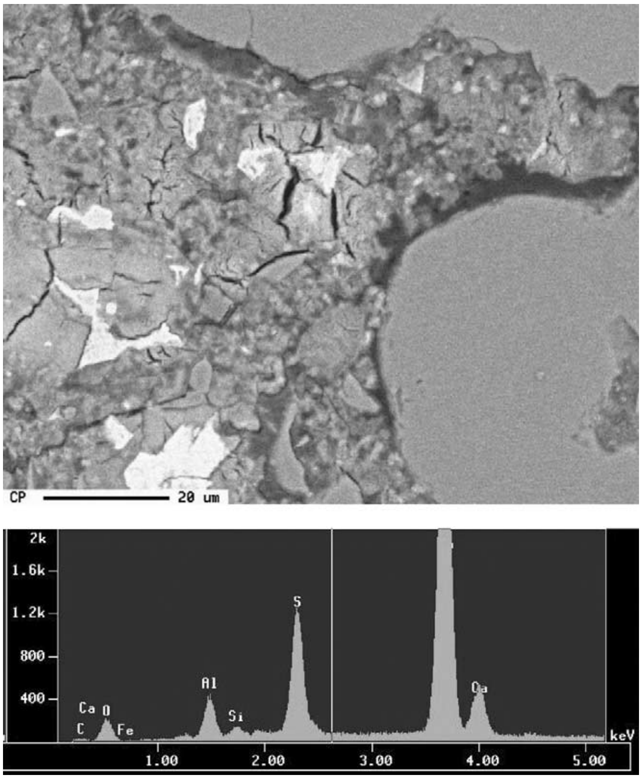

Fig. 7. BEI of the mortar with quartz filler. Ettringite was hard to find, but the crazed crystals in the middle of the BEI have an EDX (below the BEI) that corresponds to ettringite. Other areas of sulfate and aluminate was often contaminated with silicate, either through substitution from reacted quartz or from solid solution with thaumasite since the standard cement was delivered with 4% interground limestone from the producer (1000× magnification).

could explain why it was very difficult to find phases with aluminate and sulfate (i.e. ettringite, as in Fig. 7) without (according to EDX) significant contribution of silicate. This could simply be due to partly substitution (i.e. contamination) by silicon in the ettringite lattice or by solid solution with minor thaumasite since it turned out that the standard cement used contained 4% interground limestone by the producer. An unusual phase consisting of calcium and iron oxide only was detected (see Fig. 6), which could be due to a de-alumination of C_4AF by the potential high pH of the pore water according to Eq. (1). Considering the high pH created in the pore water in this sulfate test, one should in the future perhaps find a less reactive filler than quartz as an "inert filler" for reference.

4. Conclusion

Mortars with 20% limestone filler by weight of cement subjected to 5% sodium sulfate solution with excess gypsum at 5 °C form excessive thaumasite in the binder within 10 months exposure with resulting mass loss, expansion and strength retrogression.

Mortars with 20% quartz filler subjected to the same storage conditions also expand to a certain extent due to gypsum crystallisation in the matrix and possibly some ettringite formation. Minor thaumasite formation cannot be excluded since the cement used contained 4% limestone interground with the clinker by the producer.

In the light of present findings and today's knowledge, the filler cements allowed according to the new European standard with up to 6–20% and 21–35% limestone, respectively, should be restricted in their use to environments where sulfates are not present.

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