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Thaumasite attack on concrete at Marbjerg Waterworks

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Abstract

Marbjerg Waterworks, run by 'Copenhagen Energy' and a supplier of drinking water for Copenhagen, was constructed 1932–1934. An inspection of the underside of the water oxidation stairs, only accessible when the waterworks is emptied of water, took place in 1997. The temperature at this part of the waterworks where the ground water enters the plant is 5–8 °C, all year round.

The concrete above the waterline, in the dome-shaped room below the oxidation stairs, showed an attack of an impressive character. The surface layer up to 10–12 mm depth was loose and easy to peel off, in some places like festoons. Further, the columns supporting the oxidation stairs showed an attack at and above the water table similar to a sulfate attack typical for the Middle East region.

Concrete samples were examined by thin section microscopy, identifying sulfuric acid and thaumasite as the causes of the spalling. Bacterial conversion of hydrogen sulfide to sulfuric acid was part of the proposed reaction mechanisms.

Attack on the concrete was noted only from the underside of the stairs, and above the water table, but no attack was seen on top of the oxidation stairs or other concrete parts permanently exposed to running water. Awareness is recommended to such hidden concrete attack under similar conditions.

Keywords: Waterworks; Sulfate attack; Sulfuric acid; Thaumasite; Case history

1. Introduction

In 1997 the waterworks in Marbjerg outside Copenhagen, run by 'Copenhagen Energy', was taken out of production in a short period for inspection purposes. Below the concrete oxidation stairs, in a space not accessible for inspection during the drinking water production, the concrete showed serious signs of surface attack. The attack was found on top of columns and on the underside of the concrete stairs, above the water table. Below the water table no attack was visible.

The oxidation of the groundwater is the first step in the series of treatments in the production of drinking water. Groundwater from borings is pumped into a circular concrete tank, 11 m in diameter and 4 m in height. Twelve concrete columns support the superstructure with three concrete oxidation stairs of varying diameter. Through a steel pipe in the middle of the tank, the water is pumped to the top level of the stairs and then runs freely down the stairs, continuing to two filtration units. A small amount of the oxidised water returns into the tank through small pressure equalising windows above the water level.

No information concerning concrete composition or possible earlier inspections or repairs was available. The composition of the ground water, analysed in 1997 and not necessarily representative of the past 65 years, showed no harmful content of aggressive components. An odour of hydrogen sulfide was noticed. The content of sulfide in the water was unquantifiable (limit of detection 0.02 mg/l). The degree of hardness was 21°dH (German degrees of hardness), no aggressive CO_2, pH 7.04, and a sulfate (SO_4^-) content of 96 mg/l.

2. Inspection

During the inspection of the empty water tank, columns and the underside of the oxidation stairs the following was observed:

- Extensive spalling/exfoliation from 5–6 to 10–12 mm depth below the original surface was noted on most concrete surfaces in the space above the normal water table, including top of columns.

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- The surface material was soft and greasy, whitish to brownish, and could easily be peeled off. The material contained sand and small aggregate particles with no adhesion to the binder. The material gave a colourless reaction to phenolphthalein.
- Beneath the loose surface material the concrete surface, with exposed coarse aggregate particles, was hard and had a sound appearance. The concrete gave an immediate red colour with phenolphthalein after removal of the loose surface material.
- No signs of reinforcement corrosion were noted, the reinforcement still being embedded in undamaged concrete.
- Spalling was not observed at places where water flowed back into the concrete tank, seeping down the walls from small pressure equalising windows.
- The concrete surface not showing attack was covered by a thin layer of red ochre from the ground water, e.g. on top of the oxidation stairs and on surfaces continuously exposed to water.

The surface attack was of a uniform appearance in the air-filled space below the oxidation stairs, e.g. in all places above the normal water level except where water was seeping down the walls. Figs. 1 and 2 show photos from the inspection.

3. Investigations

'Copenhagen Energy' wanted to find out the cause of the observed damage before deciding on a repair method. The methods recommended for this purpose were thin section microscopy, preferably combined with scanning electron microscopy/X-ray analysis. As a start thin section investigations were decided upon.

Two concrete cores, one from a damaged part of a column and one from an undamaged part of the oxidation stair vertical surface, permanently exposed to running water, were drilled for macro description and preparation of a thin section from each. Further, a thin section with small pieces from the affected surface layer was prepared. The thin sections prepared from cores included the outer surface and the area perpendicular to the surface to a depth of 45 mm.

Fig. 1. Concrete "dome" with surface spalling, below the oxidation stairs.

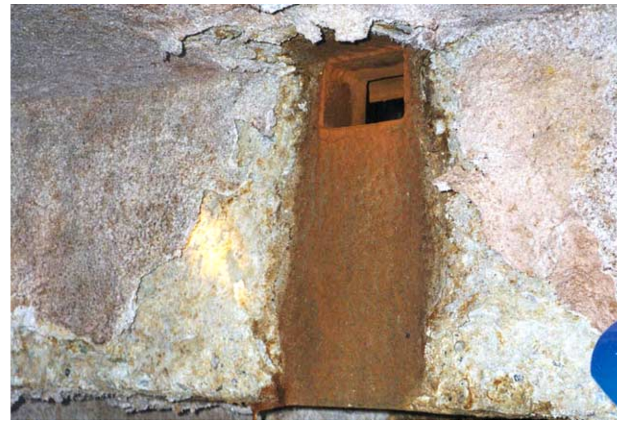

Fig. 2. No spalling observed below window where the concrete is continuously wet.

The thin sections were of dimensions 30×45 mm, thickness 0.020 mm, and the concrete was impregnated under vacuum with epoxy resin with a fluorescent dye before preparation took place. The thin sections were analysed by polarisation and fluorescence microscopy.

The results of the investigations were reported to 'Copenhagen Energy' in early 1998. Examinations by scanning electron microscopy or X-ray analysis were not performed.

4. Results

The concrete core without visible signs of attack shows a surface with a thin layer of calcium carbonate and ochre on the surface, and a leached paste of 1–3 mm thickness behind the 0.5–1 mm carbonated surface layer. A few air voids near the surface are filled with calcium carbonate crystals, indicating a weak carbonic acid attack.

The core from the column with surface attack does not contain the original surface layer. An estimated 7–8 mm of the outer surface is missing. An irregular, weak, and whitish/brownish surface layer is seen in the outermost 6–8 mm of the core, with several surface parallel cracks through paste and aggregate.

From the thin section of the damaged core the following is observed, from the surface inwards:

- In the outer 2–3 mm gypsum has formed in cracks around aggregate particles, in cracks through aggregate particles, and in cracks through the paste.

All the cracks run parallel to the surface. There is no calcium hydroxide left in the paste. The concrete is in a very bad condition due to acid attack and paste expansion; all cement particles have been more or less dissolved.

- At the border with the second layer, calcium carbonate crystals have been precipitated in a thin rim or as small 'islands'.
- The second layer, 4–5 mm in thickness, shows a high number of surface parallel cracks, through paste and aggregate. The cracks are partly filled with gypsum crystals, and partly fibrous to massive crystals with a very high birefringence. The high birefringence crystals are found in cracks in the paste, and the gypsum crystals are found in cracks in aggregate particles.
- In this second layer some cement paste is left, but calcium hydroxide is not visible. Other areas of the cement paste have been totally re-crystallised to mainly fibrous crystals, with only imprints of cement particles. The high birefringence crystals are assumed to be thaumasite, in cracks as well as in fully transformed paste. Near the bottom of this layer, ettringite crystals are noted in paste and voids, close to areas with gypsum and thaumasite.
- The second layer shows a distinct border to the underlying concrete, with unaffected cement paste and calcium hydroxide present. The cement paste contains an ordinary, coarse-grained Portland cement, and the water–cement ratio in the unaffected paste is close to 0.40. The fine aggregate consists mainly of quartz, feldspar and dense flint, and has a medium content of limestone particles and fossils. The coarse aggregate is mainly flint and granite.

The third thin section, prepared from small pieces of scaled material anticipated to include the original concrete surface, shows from the outside a severe acid attack with precipitation of gypsum in cracks and at the surface. The cement paste is more or less dissolved with only imprints of former cement particles. A limestone particle near the surface is half dissolved due to acid attack, and deeper precipitation of calcium carbonate is seen in narrow strips. Deeper again, thaumasite is identified in cracks and in larger areas of former cement paste.

Examples of the microstructure at the surface in the damaged core, with gypsum crystals in the outer 2–3 mm, are shown in Fig. 3. Presence of gypsum, thaumasite and ettringite in paste and cracks in the following 4–5 mm inwards is presented in Figs. 4–7.

5. Discussion and conclusion

From the macro observations as well as the microscopic investigations presence of thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) as part of the attack were considered most likely under the prevailing conditions: cold, humid surroundings, presence of sulfates (or sulfide),

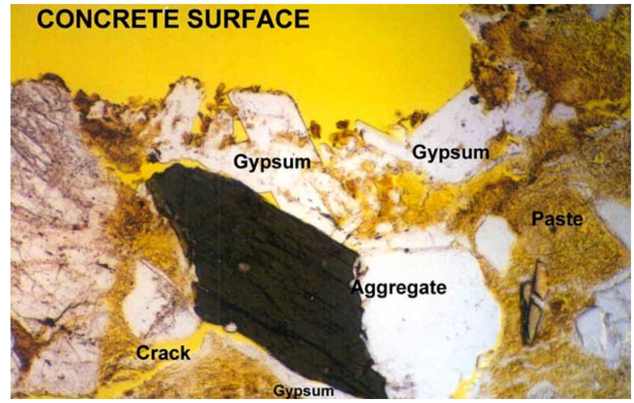

Fig. 3. Concrete surface with gypsum crystals in paste and in cracks. Photo size 1 × 1.5 mm.

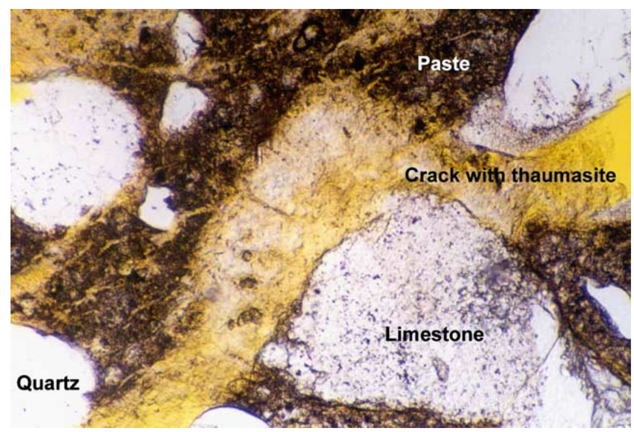

Fig. 4. Crack filled with thaumasite crystals, ≈4 mm below the surface. Photo size 0.6 × 0.9 mm.

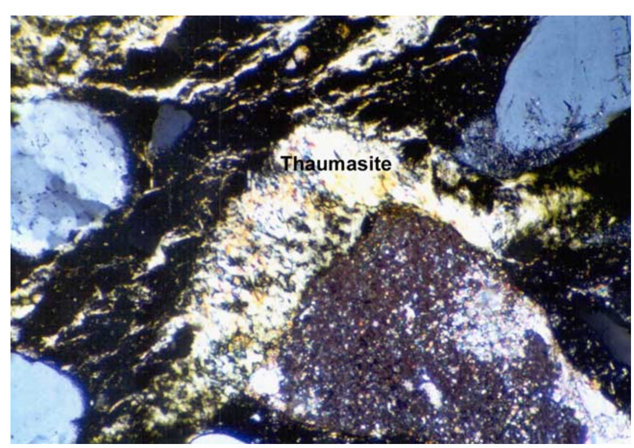

Fig. 5. Same as photo 4, crossed nicols. High birefringence of thaumasite is seen in coarse crack and also in fine veins through the cement paste.

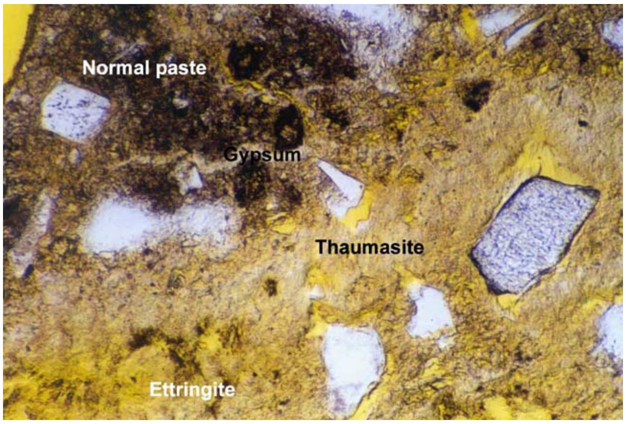

Fig. 6. Gypsum in finer cracks, thaumasite in large and finer cracks, and ettringite in porous paste. Photo size 0.6×0.9 mm.

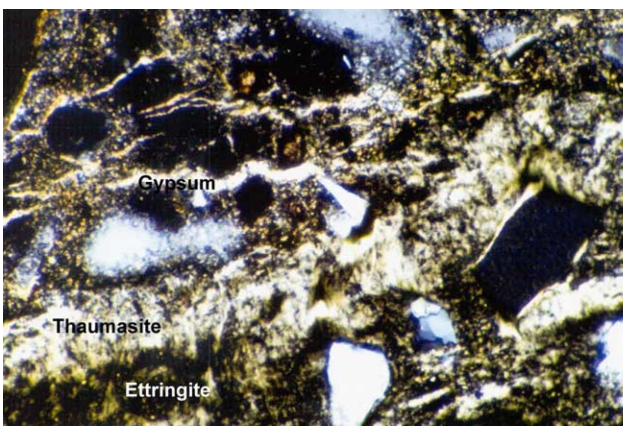

Fig. 7. Same as Fig. 6, crossed nicols.

and presence of carbonates. In the Concrete Petrography handbook by St John et al. [1] photos of thaumasite in thin sections were found with high resemblance to the present case. The microphotos of thaumasite later published in the Report of the Thaumasite Expert Group [2] also support the assumed identification of thaumasite in Marbjerg Waterworks in 1997–1998.

The sulfuric acid attack at the surface is the first part of the attack. A probable explanation to this attack was considered to be oxidation of hydrogen sulfide, absorbed in the moist film on surfaces, and converted to sulfuric acid by help of aerobic bacterial action, see Biczók [3]. A similar attack is typical for sewer systems, just above the water level.

In Denmark, thaumasite had not earlier been identified as a part of similar concrete attacks. However, similar cases of damage had earlier been observed in other waterworks, according to 'Copenhagen Energy'. The repair method had been to remove all loose material and to spray a new mortar layer onto the cleaned surface. As this specific part of the waterworks is not easily accessible no follow-up inspections had been performed.

As the Marbjerg structure was 65 years old at the time of investigation it is concluded that the rate of attack has been low, ~0.2 mm/year. The exposure conditions are assumed to have been rather steady with time at the investigated site.

A repair solution with a new sacrificial mortar layer of low w/c-ratio was decided for the next 65 years—combined with regular inspections.

At other waterworks conditions may be different, worse or better depending on water composition and presence of hydrogen sulfide. A general recommendation to waterworks is to inspect similar structural parts where an attack may have taken place and developed unnoticed over time, the concrete seemingly in a good condition inspected from the outside.

Acknowledgement

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