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Nature of the thaumasite sulfate attack mechanism in field concrete

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Abstract

In the United Kingdom a number of cases of chemical attack on buried concrete bridge foundations have occurred, involving the sulfate-bearing mineral thaumasite. All of the affected concretes were in contact with a large volume of clay backfill. It is postulated that oxidation of pyrites within the backfill led to the formation of sulfuric acid, reducing the pH of the groundwater and resulting in attack on the foundations and in reactions that raised the groundwater sulfate level. It is shown that the observations made on thin sections taken from the affected bridge foundations are in accordance with sulfuric acid attack being the probable primary cause of deterioration. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: pH; $Ca(OH)_2$; Chloride; Ettringite; Thaumasite

1. Introduction

In March 1998 a form of chemical attack involving the formation of the sulfate-bearing mineral thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$) was diagnosed in the buried concrete elements of a number of 30-year-old M5 (motorway) overbridges near Cheltenham, Gloucestershire, west of England. This followed a similar diagnosis for the buried concrete foundations of two domestic properties also near Cheltenham. All of the concretes contained dolomitic or non-dolomitic carbonate coarse aggregate; the fine aggregate was either siliceous or limestone or a mixture of siliceous sand and limestone. In the case of the bridge foundations the concretes were—with one exception, when a sulfate-resisting Portland cement (SRPC) had been specified—Portland cement concretes and had been designed to meet the recommendations current at the time of construction for the sulfate level in groundwater in undisturbed soil [1]. The most severely affected foundation had a water-cement ratio of approximately 0.5 and was made using a Portland cement with a C_3A content of 11% by mass together with a dolomitic limestone coarse aggregate and a fine aggregate consisting of a mixture of siliceous sand and oolitic limestone. All of the affected bridge foundations were in contact with relatively large volumes of Lower Lias Clay as backfill, which had been excavated at depth to enable construction of the bridges. Prior to excavation the bulk of this clay would have been unweathered. No data exists on the pH and sulfate concentrations in the groundwater in the backfill during the early life of the bridge foundations.

Recently an Expert Group, set up in April 1998 by Mr. N. Raynsford (the UK Government Minister for London and Construction), issued a report dealing with thaumasite sulfate attack (TSA). The report explores the implications for existing structures and gives recommendations for new construction [2]. The Thaumasite Expert Group concluded that the overall structural integrity of the bridges and buildings was not seriously affected but where the bridge foundation concretes were exposed to deicing salt runoff, there was a reduction in effective cover to reinforcement caused by the attack, which considerably increased the risk of reinforcement corrosion resulting from chloride ion ingress. The Group recommended that disturbed ground should be classified by assuming that all the sulfide in disturbed ground is converted to sulfate. Such an approach could be very conservative and would allow for the effects of any acidity.

This work discusses a number of mechanisms for the formation of thaumasite, its physical effects on the host concrete, and its effect on chloride ion ingress.

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2. Petrographic observations on TSA-affected field concretes

Petrographic examination of thin sections taken from affected sections of the M5 overbridge foundations broadly indicated the following [2]:

- A zone at the concrete/clay backfill interface, where transformation of cement paste to thaumasite was complete (about 5 to 10 mm in thickness).
- A second zone where cracks filled or lined with thaumasite were present parallel to the concrete element's surface (generally 10 to 15 mm in thickness) and in which haloes of white thaumasite could be seen around the coarse and fine aggregate particles including the siliceous sand particles. In this zone there was an absence of other sulfate minerals, little calcium hydroxide, calcium carbonate was occasionally precipitated into cracks and voids (W.J. French, Geomaterials Research Services Ltd., personal communication, September, 1998) and the expansion of the original concrete was approximately 100%.
- A third, deeper zone with no visual evidence of attack but with voids occasionally lined with ettringite ($3CaO.Al_2O_3.3Ca\ SO_4.32H_2O$) and thaumasite (approximately 5 mm in thickness).

Petrographic examination of an attacked concrete strip foundation of a 12-year-old house garage of low cement content, possibly subject to a sulfate groundwater concentration in the range $1.4\ g/L < SO_4^{2-} < 3.0\ g/L$ [3], at a broadly neutral pH, namely UK sulfate Class 3 [4], indicated the following:

- A zone at the concrete/clay interface, where transformation of cement paste to thaumasite was complete.
- A zone of intact concrete with thaumasite and ettringite within voids.
- A zone with no visual evidence of attack but with ettringite within voids.

A concentration of 1.4 g/L of SO_4^{2-} corresponds to the maximum solubility of calcium sulfate in groundwater. The Portland cement content of the strip foundation ranged from 120 to 260 kg/m^3 [5] with the implication that the concrete was not of sufficient quality to resist conventional sulfate attack [6].

It follows that the form of attack on the concrete bridge foundations in contact with the backfill is dissimilar to the form of attack on the concrete strip foundation, indicating that the mechanism of attack is likely to be different.

3. Observations on TSA-affected laboratory concretes

Examinations by X-ray diffraction and scanning electron microscopy on TSA-affected laboratory concretes stored at 5°C in "neutral" sulfate solutions indicates that ahead of the thaumasite front, conventional products of sulfate attack (namely gypsum and ettringite) are present [7]. These observations accord more closely with the examinations made on the affected concrete strip foundation than those made on the affected concrete bridge foundations. In addition, the laboratory studies showed that storage in a magnesium sulfate solution results in greater attack than storage in a sodium sulfate solution [7,8]. In the case of companion concretes stored in similar solutions at 20°C, visual deterioration due to thaumasite attack was not observed [7].

4. Hypothesis: Mechanism of TSA in field concrete

The hardened cement paste fraction (the result of hydration of Portland cement) in a concrete consists primarily of calcium silicate hydrates, calcium hydroxide, and lower proportions of calcium sulfoaluminate hydrate either as ettringite or monosulfate. Approximately 20% of the hardened cement paste volume is calcium hydroxide. The pore solution is normally a saturated solution of calcium hydroxide within which high concentrations of potassium and sodium hydroxides are present.

All conventional concretes are vulnerable in varying degrees to attack by inorganic salts and inorganic/organic acids present in groundwaters. In soil and natural groundwater, sulfates of sodium, potassium, magnesium, and calcium are common. Sulfuric acid, when present in natural groundwater, forms from the oxidation of iron sulfide (pyrites) minerals in soil.

In concretes exposed to aggressive groundwater, the thaumasite form of sulfate attack can result from "neutral" sulfate ion ingress into concrete [9] or sulfuric acid attack on concrete [10]. From the petrographic observations on thin sections reported above, attack occurs within the surface region largely depleted of calcium hydroxide. This latter observation indicates that a pH below about 12.5 (i.e., the pH corresponding with a saturated solution of calcium hydroxide) is probably required for thaumasite to form and also, because the solubility of calcium hydroxide is inversely related to temperature [11], that the rate of attack is likely to be inversely related to temperature.

In the case of the M5 bridge foundations all of the affected sections were in contact with a large volume of a clay backfill ($\sim$ 200 m^3) containing pyrites (possibly up to 5% by mass of clay [2]). Prior to excavation the bulk of this clay would have been unweathered given that the excavations were up to 4 m in depth. Within undisturbed unweathered clay the groundwater conditions are likely to be UK Class 1 or 2 ($SO_4^{2-} < 1.4\ g/L$) resulting from the presence of calcium sulfate [2,4]. This calcium sulfate may be present in the clay as selenite or gypsum or may be formed in a two-stage reaction as follows: slow oxidation of pyrites giving either $4Fe\ S_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4$ [2] or $2Fe\ S_2 + 2H_2O + 7O\ _2 > 2FeSO_4 + 2H_2SO_4$

[12], followed by neutralisation of the sulfuric acid primarily with calcium carbonate in the clay, $Ca\ CO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO_2 \uparrow$.

Where the M5 foundations are in contact with undisturbed and unweathered clay negligible deterioration has occurred, indicating that the concretes have performed well under UK Class 2 sulfate exposure [2,4]. This is to be expected since the mobility of the groundwater in undisturbed clay is low and little depletion of hydroxides from the concrete and little ingress of calcium sulfate into the concrete would have occurred.

According to the Thaumasite Expert Group, much of the formerly unweathered blue-grey coloured Lower Lias Clay is now, within the backfill, weathered olive brown material. This indicates that relatively rapid oxidation of the pyritic iron compounds in the clay could have occurred, favouring the formation of ferric oxide (brown) and sulfuric acid [2] rather than ferrous sulfate and sulfuric acid, which would have resulted ultimately in a yellow colouration of the backfill as the ferrous ion would have oxidised to give ferric sulfate (yellow). It should be noted that only limited reaction between ferric oxide and sulfuric acid would have occurred since ferric oxide is relatively insoluble in dilute mineral acid and would again have resulted in a yellow colouration of the backfill.

An increased rate of formation of sulfuric acid would lower the pH of the groundwater and the sulfuric acid would be depleted by neutralisation reactions within the backfill and with any concrete surface in contact with the backfill and also to some degree by washout. Within a clay, depending upon the carbonates present, sulfates of calcium, magnesium, sodium, and potassium could form, for example $Mg\ CO_3 + H_2SO_4 + H_2O \rightarrow MgSO_4 + 2H_2O + CO_2 \uparrow$. Magnesium sulfate, sodium sulfate, and potassium sulfate are very soluble and their formation, resulting from the more rapid production of sulfuric acid in disturbed clay, could maintain the groundwater sulfate level above Class 2.

The above speculation regarding the effect of oxidation of pyritic iron compounds upon the aggressivity of groundwater is supported by observation. Monitoring of the runoff water from a sulfide-bearing shale quarry by one UK cement manufacturer has shown that the water is acidic with its pH occasionally falling as low as 4.0 (G.K. Moir, Blue Circle Industries, personal communication, 1998). This means that the reactions within a disturbed shale or clay are not necessarily sufficient to neutralise all the acid formed. Several investigators have observed that sulfides, particularly pyrites, in soils can oxidise, resulting in acidity and/or an enhancement in the sulfate level, for example granular soils [13], clays [14], black shales [15], and Lias Clay [16]. Additionally, a UK guidance document, published by the Building Research Establishment [17], points out that rapid oxidation can occur of pyrite exposed by soil excavation.

Ingress of magnesium sulfate (and sodium sulfate) into concrete or sulfuric acid attack on concrete containing a carbonate aggregate could result in gypsum formation in the concrete as follows: $Ca\ (OH)_2 + MgSO_4 + 2H_2O \rightarrow CaSO_4.2H_2O + Mg\ (OH)_2$; $Ca\ CO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO_2 \uparrow$; $Ca\ (OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O$.

These reactions would occur primarily in the surface region of the concrete where calcium ions from leaching of calcium hydroxide and decalcification of C-S-H would meet high concentrations of $SO_4{}^{2}-$ ions. In the case of dolomitic limestone aggregate, sulfuric acid attack could result in the further formation of magnesium sulfate within the concrete, which could react with calcium hydroxide forming brucite, $Mg\ (OH)_2$, and gypsum.

Depending on the available space left by leaching and decalcification, the formation of crystalline gypsum could be an expansive reaction and the remaining sulfate ions in solution would be available for further reaction or to diffuse more deeply into the concrete.

The carbon dioxide gas evolved during sulfuric acid attack on carbonate aggregate within the concrete would tend to dissolve in the pore solution and react with any calcium ions in solution, precipitating calcium carbonate preferentially into cracks and pores within the concrete. Such precipitation has been noted in the affected concrete of the M5 overbridge foundations (W.J. French, Geomaterials Research Services Ltd, personal communication, September, 1998).

When the calcium hydroxide (and potassium and sodium hydroxides) became largely depleted by conversion to sulfate and leaching, the formation of the insoluble mineral brucite would also reduce the pH, increasing the degree of chemical attack on the calcium silicate hydrates, while the soluble sodium hydroxide, resulting from ingress of sodium sulfate, would increase the pH, resulting in a lower rate of chemical attack on the calcium silicate hydrates. It should be noted here that in concrete exposed to mobile groundwater, a large proportion of the potassium and sodium hydroxides normally present in the surface region would be likely to leach out into the groundwater.

In saturated concrete some or all of the crystalline gypsum formed could react with the hydrated calcium aluminates to form ettringite (conventional sulfate attack). Alternatively, as a consequence of the observation that little calcium hydroxide is present in the region of the concretes affected by thaumasite formation, it can be postulated that as the pH drops to about 12.5 and below, the gypsum could react with calcium silicate hydrates and calcium carbonate to form thaumasite. The formation of thaumasite would then be more likely to occur when concrete has been exposed to magnesium sulfate in groundwater than to concrete exposed to sodium sulfate.

The formation of both ettringite and thaumasite are expansive reactions and restraint of this expansion by the unaffected "heart" concrete results in fine cracks parallel to the face of a concrete element. It should be noted that ettringite is a normal hydration product and it can be found

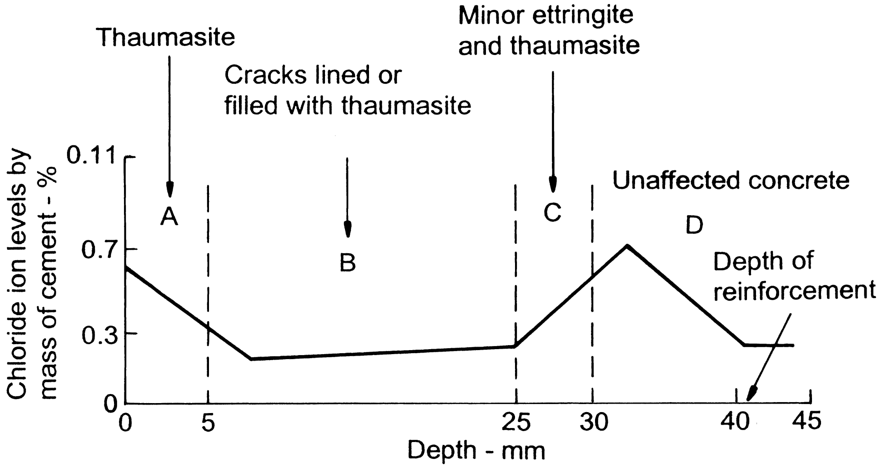

Fig. 1. Chloride profile in the surface region of an affected concrete reported by the Thaumasite Expert Group.

in both sound and deteriorating concrete. Ettringite formation only leads to distress when excessive quantities of ettringite are formed at late ages, which cannot be accommodated in the available microstructure.

5. Hypothesis: Explanation for the observed chloride ion distribution in field concrete

The Thaumasite Expert Group concluded that where reinforced concrete affected by thaumasite formation was exposed to external chlorides, there was an increased risk of steel corrosion [2]. A chloride profile in the surface region of an affected concrete reported by the Thaumasite Expert Group is shown in Fig. 1 [2]. In this section, a hypothesis is developed to explain the form of this chloride profile.

The chloride profile shown in Fig. 1 indicates that zones A and B offer little resistance to chloride ion ingress [2] and that in zones C and D chloride binding by calcium silicate hydrates, as expected, is occurring. The following assumptions lead to the idealized chloride profile, normalized for the effects of expansion, shown in Fig. 2 for the same surface region of concrete depicted in Fig. 1, during the winter (deicing salt application) months.

1. Zones A and B offer no resistance to chloride ion ingress [2].
2. During the winter months the chloride ion concentration by mass of cement at the interface between zones B and C is around 0.25% (after Fig. 1).
3. The proportion of bound chlorides by mass of total chlorides ranges from zero in zones A and B [2] and at the interface between zones B and C to two thirds at the interface between zones C and D. This latter proportion is higher than that measured on concretes exposed from an age of 1 to 29 days to external chlorides, namely approximately one half [18].
4. The expansion in zones B and A is 100% [2] and 200%, respectively, giving cement contents per unit volume in zones A, B, C, and D in the ratio 1:2:3:3.

In the winter months these assumptions lead to total chloride ion levels by mass of cement in zones A and B of 0.75 and 0.50%, respectively. With partial washout of

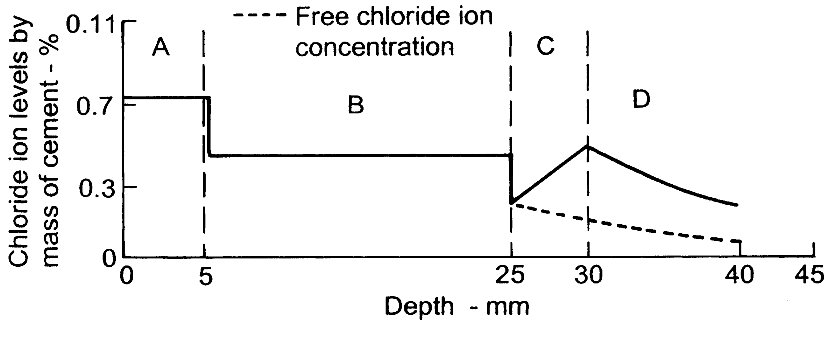

Fig. 2. Idealized chloride profile normalized for the effects of expansion for the same surface region of concrete depicted in Fig. 1, during the winter (deicing salt application) months.

chlorides from the groundwater occurring in the nonwinter months, the chloride concentrations in zones A and B would fall, giving a range of possible chloride profiles in zones A and B including profiles similar to that measured and shown in Fig. 1. So the chloride profiles reported are not unexpected and are predictable if it is assumed that the region of concrete showing deterioration due to thaumasite formation offers no resistance to chloride ion ingress.

6. Conclusions

In the case of the M5 overbridge foundations it is not entirely clear to what extent thaumasite sulfate attack is due either to "neutral" sulfates or sulfuric acid or a combination of both. However, the observations on thin sections are in accordance with the hypothesis that sulfuric acid is mainly responsible for the attack.

In the case of the affected garage strip foundation, which was made using poor quality concrete, the main mechanisms involved are more likely to be loss of calcium hydroxide by leaching and ingress of calcium sulfate leading to "neutral" sulfate ion attack.

Acknowledgments

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