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Cement & Concrete Composites 25 (2003) 809–818

Cement & Concrete Composites

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The thaumasite form of sulfate attack in the UK

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Abstract

During the last 15 years, the thaumasite form of sulfate attack (TSA) has been found in over 80 UK field structures and buildings and is particularly prevalent in buried concrete. This form of sulfate attack completely destroys the cementitious binding ability of the concrete by transforming it into a mush. In 1998, the occurrence of several high profile cases in the foundations of UK motorway bridges initiated a rapid pan-industry response, culminating in a report by the UK Government's Thaumasite Expert Group. A brief account of the Group's findings, the diagnosis and risk factors needed for TSA and some postulated reasons for its apparent increase in recent years are discussed in this paper.

The Building Research Establishment has carried out extensive research since the early 1990s on the occurrence of TSA in the field and in laboratory concretes and mortars. Prior to this, a few other UK workers had been involved in more fundamental studies of the mineral thaumasite including its structural characterisation and its laboratory synthesis. Once the profile of TSA was raised in 1998, the number of government and industry funded research programmes increased significantly in the UK and the findings from many of these will be presented in this journal. Information gleaned from UK laboratory research is incorporated in the present paper along with the author's thoughts on a possible reaction mechanism for TSA.

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Keywords: Sulfate attack; Thaumasite; UK; Field cases; Laboratory studies; Diagnosis; Reaction mechanism

1. Introduction

Over the last 15 years, the Building Research Establishment (BRE) have carried out or have been aware of over 80 cases of sulfate attack of concretes and mortars in service in the UK [1–4]. The majority of these (over 95%) have been the result of the thaumasite form of sulfate attack (TSA). The conventional form of sulfate attack, in which the reaction product ettringite (±gypsum) is formed, may have occurred early on in the deterioration process but it was not the persistent mechanism. Even though there have been more reported cases of TSA in the UK than anywhere else, the occurrence of thaumasite in deteriorated building materials has been identified in a number of countries worldwide including USA, Canada, South Africa, France, Germany, Norway, Denmark, Switzerland, Italy and Slovenia. Probably the most severe case of TSA encountered so far was in the Canadian Arctic [5] so it is unlikely that this is mainly a UK phenomenon.

This paper provides a resume of the main findings from numerous field cases and laboratory studies carried out in the UK to date. Many of these are still ongoing and will be discussed in detail in this journal. The paper also includes a discussion on the risk factors, diagnosis and reaction mechanism of TSA along with some background information on the UK Government's Thaumasite Expert Group.

2. Thaumasite form of sulfate attack

In conventional sulfate attack incoming sulfate ions react with calcium aluminate phases and calcium hydroxide in hardened cement pastes to form either ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) or gypsum ($CaSO_4 \cdot 2H_2O$). The consequence is usually expansion and spalling of the attacked concrete or mortar. Over the years, the formulation of a sulfate resisting Portland cement (SRPC), in which the amount of aluminate hydrate is restricted, has combated damage of concretes or mortars from conventional sulfate attack. Unfortunately, this precautionary measure does not necessarily prevent the formation of thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$), in which the calcium silicate hydrates (CSH),

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0958-9465/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0958-9465(03)00106-9

not the aluminate phases, are attacked by external sulfates. The replacement of CSH by thaumasite results in the softening of the cement paste matrix into a white, mushy incohesive mass. It can be seen from the formula for thaumasite that carbonate ions are an additional necessary ingredient. Thaumasite preferentially forms under cold, wet conditions.

Thaumasite was first discovered as a product of sulfate attack in concretes in the USA in 1965 [6]. Its occurrence as a natural mineral in the form of white acicular crystals similar in appearance and structure to ettringite has been known about for much longer. Thaumasite is a hexagonal mineral with an '*a*' unit cell dimension of 11.054 angstroms and a '*c*' dimension of 10.410 angstroms. Its structure was characterised in 1969 by Edge and Taylor [7], who discovered that its silicon atoms occurred in the form of $[Si(OH)_6]^{2-}$ groups. This unusual mode of six co-ordinated silicon was later verified by Bensted [8] and others. This helps to explain the similarity in structure between thaumasite and ettringite, why one can grow epitaxially upon the other, and why there is a partial solid solution series between the two minerals. The extent of this solid solution series is currently being studied at Aberdeen University [9]. Thaumasite has also been successfully synthesised in the laboratory; the most notable UK experimenter being John Bensted, who discussed a variety of possible recipes in his 1988 review paper [10].

A positive identification of thaumasite in a cement-based building material does not automatically indicate that a problem has occurred or, if it has, that thaumasite was the culprit. There are two distinct ways in which thaumasite can precipitate as a reaction product within concretes and mortars [1] and the following characteristics must be taken into account during diagnosis:

- *Thaumasite form of sulfate attack (TSA):* TSA is visually very distinctive. It is characterised by significant damage to the cement paste matrix of the concrete/mortar. The main hallmark of TSA is that the hardened cement paste becomes partially or totally replaced by thaumasite. As thaumasite does not possess any binding ability, the affected cement paste is ultimately transformed into an incohesive mass (mush) loosely holding the aggregate particles together. Other distinguishing features include subparallel cracks filled with thaumasite and white haloes of thaumasite occurring around aggregate particles. TSA causes gradual softening of the matrix of a buried concrete, starting from the concrete/ground interface and progressing inwards. It can sometimes be accompanied by expansive disruption.
- *Thaumasite formation (TF):* Thaumasite, like ettringite, can precipitate in voids and cracks without necessarily causing any disruption to the host concrete or mortar. This has been termed TF and it can be found in concretes/mortars showing no obvious visual signs of sulfate attack. TF can also be found in concretes already damaged by other deterioration mechanisms such as alkali silica reaction [11,12]. Although the presence of TF is more often than not innocuous, it can be a precursor to TSA, thereby indicating a potential future problem.

3. Primary risk factors for TSA

The following factors are all required for TSA to occur in cementitious-based building materials:

- *Source of* SO_4^{2-} *ions:* The principle sulfate source responsible for TSA in the UK is the groundwater in sulfate- and sulfide-bearing clay soils that occupy relatively large areas of England (for maps see Ref. [1]). This groundwater is usually saturated with respect to calcium sulfate and can contain soluble sulfates of magnesium and sodium. Re-working of unweathered sulfide-bearing clays can enhance sulfate content through oxidation. It has also been postulated that sulphuric acid from this oxidation process has contributed to concrete degradation as a result of acid attack [13,14]. Soluble sulfates can also be derived in ground throughout the UK from spoil from the mining of coal and oil shale and from industrial waste products and seawater. Other mostly above-ground sources contributing to TSA have included de-icing salts, sulfate-bearing bricks, gypsum plaster and contaminated aggregates or cements.
- *A source of* SiO_3*:* The main glue present in all hardened Portland cement pastes, including sulfate resisting Portland cement (SRPC), is CSH. This provides the main source of silicate needed to form thaumasite. Remnant unhydrated clinker grains of tri-calcium silicate (C_3S) and di-calcium silicate (C_2S) are a secondary source. The accessibility of these silicates to incoming sulfate ions depends on a number of factors including concrete/mortar quality and cement and aggregate type.
- *A source of* CO_3^{2-} *ions:* Evidence to date shows that the carbonate ions needed to fuel TSA can either be derived from particles of limestone used as aggregate or cement filler within the concrete or mortar itself, or can be supplied as carbonate or bicarbonate ions dissolved in the sulfate-bearing external water source. Smaller limestone particles are more reactive and it is possible that dolomitic limestone ($CaMg(CO_3)_2$) is more susceptible to TSA than $CaCO_3$ based limestones, but this is still not certain.
- *A source of water:* All forms of sulfate attack require a mobile water source. Such water often occurs naturally in the ground. Certain construction processes can make a site even wetter; for example the construc-

tion of concrete foundations in which groundwater is permanently contained within a sump formed by the original excavation.

- *Cold temperatures:* Thaumasite preferentially forms under cold temperatures below 15 °C, typical of the ground temperatures at foundation depth in the UK. Thaumasite can form at temperatures of up to 25 °C, but the rate is much slower [1,15]. The reasons postulated for accelerated TSA at cold temperatures are discussed in Section 7.5.

4. TSA field cases in the UK

In the UK, damage caused by TSA has been identified in:

- concrete foundations to 50 highway bridges exposed to sulfate and sulfide-bearing ground
- at least six concrete foundations to domestic homes and other buildings exposed to sulfate-bearing ground
- at least six ground floor slabs placed directly on sulfate-bearing ground
- over 20 cases in the mortar joints and renders of sulfate-bearing brickwork
- two cases in the tunnel linings to the London Underground system (one in a cement grout and the other in a brickwork mortar)
- one case of seawater attack on mortar from harbour steps

Details of these cases have been widely reported by the author and others [1,4,16–18]. The majority of the UK TSA field cases have been found in buried limestone aggregate concretes exposed to the sulfate-bearing Lower Lias Clay in the West of England. A major concern about this form of sulfate attack in some of the above field cases, is that it occurred in concrete which was correctly specified by contemporary guidance to provide adequate, if not good, sulfate resistance. Another interesting observation is that the majority of TSA-affected concretes in the UK have been found completely buried at depths of up to 5 m below ground. This contradicts the long thought theory that serious sulfate attack will only occur in well-compacted concretes which are only partially buried and where evaporation from an exposed surface can draw a continuous supply of sulfates through the concrete [19].

Over the past 15 years, the number of recorded field cases of TSA has grown significantly. However, in BRE's opinion, TSA is not a recent phenomenon. It is likely to have occurred in the past, but has not been recognised as such. There are several reasons for this, the main ones being:

- *Failure to detect thaumasite in standard sulfate resistance tests:* Thaumasite does not readily form under the typical conditions used in small-scale UK laboratory sulfate resistance tests [20]. This is also the case for the larger-scale concrete cube performance tests carried out at BRE and elsewhere [19]. The reasons are that the storage temperatures are too high (generally 20 °C) and usually the aggregate is carbonate-free. Long-term use of these standard cement and concrete tests at room temperature has failed to alert researchers to the existence of thaumasite as a possible sulfate-bearing reaction product. Consequently, they have not been expecting to find it in the field. Thaumasite was produced very readily under laboratory conditions once tests on concretes, mortars and cements were carried out at low temperatures (5–15 °C) and the ingredients included a source of carbonate ions.
- *Improved analytical techniques:* Advances in diagnostic techniques over the past 20 years has greatly improved information on the mineralogy and microstructure of deteriorated concretes. The identification of thaumasite is one notable example. Thaumasite has a very similar structure to ettringite and has been misdiagnosed as such in the past. Differentiation between the two minerals is not possible using chemical analysis alone and as sulfate determination was the traditional diagnostic tool used 20 years ago, many cases of TSA would have been reported simply as 'sulfate attack' with the assumption that deterioration was caused by ettringite formation. Differentiation between the two minerals has become increasingly easier over the last 20 years as the use of mineralogical analytical equipment such as modern X-ray diffractometers, optical microscopes and scanning electron microscopes have become much more refined and common place. These techniques are now routinely used in conjunction with chemical analysis.
- *Buried concretes rarely inspected:* Evidence of TSA is usually hidden below ground and cannot be detected by routine above-ground inspections. Once concrete foundations are buried and the structure is put into service, they are rarely excavated. The initial below-ground cases of TSA in the UK were all discovered during excavation for other purposes.
- *Post-construction enhancement of sulfate levels in the ground:* There are clays which, in their unweathered state, contain negligible amounts of sulfate-bearing phases but appreciable amounts of pyrite (FeS_2). Historically, in the UK, such clays have been classified as innocuous with respect to sulfate attack. However, if these clays are disturbed during construction such that they are exposed to air, water and bacteria, the sulfide in the pyrite can oxidise to sulfate. Under the latest UK guidance [21], the clay is re-classified as aggressive if concrete is to be placed adjacent to the disturbed clay or the clay is to be used as backfill. This was rarely, if ever, done in the past with the result

that some specified concrete has not been robust enough to withstand the increased level of sulfates.

- *Changes in composition of modern cements:* An increased occurrence of TSA could, in part, be the result of the amount of tri-calcium silicate (C_3S) having been significantly increased in modern Portland cements. Dimic and Drolic [22] postulated that for good sulfate resistance, the amount of C_3S in a PC should be less than 60%. It should be noted, however, that many of the recently discovered cases of TSA were found in 30-year-old bridge foundations and a 50-year-old ground floor slab. So, the contribution from this factor is not likely to be substantial.

5. The findings of the thaumasite expert group report

5.1. Background and main findings

Up until 1998, the BRE and other UK workers had published several journal and conference papers on TSA but it was only after its discovery in a highway structure in March 1998 that the subject reached the headlines of the UK construction press. The concrete foundations to a 30-year-old bridge over the M5 motorway in the west of England had been exposed in order to strengthen the bridge columns against vehicle impact. The supporting columns were found to be attacked near their bases, typically resulting in the outer 30–50 mm of the concrete being transformed into a soft white paste [1,18]. In places the steel reinforcement had corroded in the presence of chloride ions derived from run-off water contaminated with de-icing salts.

The UK Government convened the Thaumasite Expert Group (TEG) to investigate the problem, under the chairmanship of Professor Les Clark of Birmingham University. The Group comprised representatives from a wide range of construction industry stakeholders including BRE. The TEG Report on TSA was published in January 1999. It covers risks, diagnosis, remedial works and guidance on new construction. The report offered reassurance that the number of structures in the UK potentially at risk of TSA was relatively small. It also stated that the structural consequences for properly maintained structures would rarely be of serious concern in respect of public safety, as signs of structural deformation (e.g. cracking) would normally be evident well before there was a risk of collapse. Conversely, it warned the construction industry not to be complacent, as there could be a significant impairment of serviceability, which might be costly to remedy.

5.2. Guidance for new below-ground construction

The TEG Report contained guidance and interim recommendations aimed at minimising the risk of TSA in fully or partially buried concrete elements containing limestone aggregate in new construction. It also recommended revision of the UK's key guidance documents for buried concrete. Accordingly, BRE has just published Special Digest SD1 'Concrete in aggressive ground' [21], to replace its previous guidance (Digest 363). SD1 is not only based on the TEG interim recommendations but has also developed the guidance further to meet better the needs of material suppliers, concrete producers and users. Revisions have also been proposed for the British standards on concrete and aggregates.

The TEG also addressed the issue of acceptable carbonate levels permitted within a buried concrete as either aggregate or cement filler, although they had to base their guidance on the very limited laboratory evidence available at the time. Three key issues were considered. Firstly a system was devised in which aggregates containing a sufficient quantity of carbonate material to readily generate TSA in PC concretes exposed to moderate levels of sulfate were termed 'Range A' aggregates whilst those containing less carbonate material were termed 'Range B' (low carbonate) or 'Range C' (very low carbonate) aggregates. The second issue addressed was the use of Portland limestone cement (PLC). The TEG re-confirmed that the use of PLCs, in which the amount of limestone filler can range from 6% to 35%, should not be permitted in conditions where sulfate concentrations in the groundwater are in excess of 0.4 g/l (Design Sulfate Class 2 or above in SD1 [21]). The third main carbonate issue they had to resolve was the fact that European PCs can now contain up to 5% limestone filler [23]. Although in some research programmes published at the time [24,25], the addition of 5% limestone filler led to marginally worse sulfate resistance at cold temperatures compared with plain PCs, the TEG felt that there was not enough evidence to suggest that this would significantly affect the performance of concretes or mortars in the field. More work has been carried out on the topic of carbonate levels since publication of the TEG Report and opinions may change as details of these findings are announced.

5.3. Guidance for above-ground construction

In the UK, TSA has also been identified above ground in lime-gypsum plasters, sulfate-bearing brickwork, ground floor slabs and concretes contaminated with sulfates or sulfides [1,4]. All of these can be caused by failure to follow recommended good practice, either by using unsuitable materials for given service conditions, by poor workmanship on site, or by failure to keep structures dry. The TEG decided that sufficient recommendations were already in place to combat TSA in above-ground construction. Indeed the number of instances has decreased in new construction over the past few years, except for the case of sulfate-bearing brickwork. About two or three cases of TSA in rendered sulfate-bearing brickwork structures, some less than two years old, are reported to BRE every year. The message is not getting through to architects and builders that common sulfate-bearing bricks should not be used in exposed conditions, even if they are subsequently rendered. The main problem stems from the resultant structure not being sufficiently watertight either through poor detailing or defective rendering. Once water penetrates through to the brickwork, all the ingredients are present for TSA, which often proceeds at a relatively rapid rate at the render/brickwork interface and in mortar joints.

5.4. Recommended further research

The TEG Report included recommendations for further research on the subject of TSA. This has encouraged the initiation of several new research programmes, funded by UK Government and industry, including:

- thermodynamic studies
- identification of TSA-resistant concretes
- review of acceptable carbonate levels in aggregates and cements
- role of carbonate ions from groundwater
- improvement of ground assessment and its contribution to TSA
- structural engineering effects of TSA
- study of protective coatings to prevent TSA
- development of effective repair techniques

BRE is extensively involved in many of these projects. Other bodies carrying out this research in the UK include the Universities of Aberdeen, Sheffield, Birmingham, Glamorgan, Staffordshire and Leeds. Industrial support has been supplied by the Cementitious Slag Makers Association (CSMA), Quarry Products Association (QPA), British Cement Association (BCA), UK Quality Ash Association (UKQAA), Highways Agency (HA), Halcrow Group and Concrete Pipe Association (CPA). A collaborative research programme has also been set up between BRE and the Norwegian Public Roads Administration (NPRA). Information from all the laboratory studies carried out at BRE is reported in Section 6 of this paper.

5.5. TEG Report reviews

The TEG Report was reviewed by the Thaumasite Expert Group in Spring 2000 after one year [2] and at the end of 2001 after three years [3]. Both reviews contained important new information on the occurrence of TSA in laboratory test concretes made using siliceous aggregates. Overall the two reviews have not reported any findings, which would suggest that the guidance and interim recommendations provided in the original TEG Report is not robust.

6. Investigative work at BRE

6.1. Introduction

BRE has carried out numerous TSA laboratory performance tests on concretes and mortars over the last ten years [25–31]. It has also initiated the first TSA field trial, in which concretes of known composition were buried at a sulfate-bearing clay site at Shipston on Stour (Shipston) in central England. This work has been funded primarily by the UK Government, but there has been significant input from industry including CSMA, QPA, BCA, UKQAA and CPA. A great deal of information has been gleaned from these experiments and the major findings so far are discussed below. This information has already been incorporated into the TEG Report and its subsequent reviews.

6.2. Avoidance of TSA in buried concrete containing limestone aggregate

A logical way to avoid TSA in buried concrete is to prevent sulfate-bearing groundwater actually getting into the concrete. This is often not a practical solution. So, assuming that the groundwater reaches the concrete, there are three main ways of preventing or slowing down TSA in limestone aggregate concrete:

- The use of slag cement (70% ground granulated blastfurnace slag (ggbs) + 30% PC) is very good at resisting TSA in concretes containing commonly used limestone aggregates. Similar results have been found for BRECEM (50% calcium aluminate cement + 50% ggbs) but this cement is not commercially available.
- The amount of TSA is reduced as the concrete quality is improved by lowering water/cement ratios, increasing cement content and ensuring good compaction.
- An initial air-cure prevents the onset of TSA in laboratory concretes. This fact was corroborated in the field trial where pre-cast concretes have performed much better than those cast-in-situ.

6.3. Effect of curing

Curing has proven to be a crucial parameter in determining the TSA-resistance of test concretes made using either PC or SRPC and limestone aggregate. An initial air-cure was found to be very beneficial as already noted. When concretes were water-cured, TSA developed to a significant level within two-year-old laboratory-stored specimens tested at 5 °C. However, the development of TSA was most noticeable in concretes, which had been wrapped in plastic film (seal-cured) for a period of 28 days prior to sulfate exposure. The main difference experienced by the surfaces of the test concretes as a result of these three types of curing is the level of alkalinity in the pore solutions. With seal-curing, maximum pH values in excess of 13 would be attained, whereas progressively lower pH values would be found after water-curing and air-curing. It follows that a very high pH pore solution at the concrete surface exposed to sulfates will encourage the onset of TSA, even though actual deterioration does not happen for some months. The reason for this is still unclear although it may help to explain the superior TSA-resistance of slag cements, which produce lower pH pore solutions than Portland cements.

6.4. Effect of aggregate

One of the first TSA experiments carried out at BRE was to determine whether or not the source of carbonate ions could be derived solely from the aggregate [27]. This was achieved by immersing a specimen of good quality SRPC concrete containing an all-in limestone aggregate in a strong Mg SO_4 (1.8% as SO_4^{2-}) solution made with de-ionised water. The specimen and solution were stored in a sealed container at 5 °C and the solution was never replenished. The only viable source of carbonate ions in this closed system had to be the limestone aggregate. After eight months the concrete had started to crack and after 18 months about a quarter of the specimen had eroded away as a result of TSA, to form a sludge at the bottom of the storage container. The degradation process continued at a rapid rate and after three years it became possible to 'pour' the deteriorated concrete from one container to another. This experiment proved conclusively that the limestone aggregate supplied all the carbonate ions needed to fuel TSA. Initially it was thought that only very fine limestone aggregate particles were involved in TSA, but this was soon found not to be the case. TSA was found in concretes containing good quality carbonate aggregates, in which the amount of limestone dust was small and it was even found in cases where limestone was only present as coarse aggregate.

Even though limestone aggregate is the main source of carbonate ions, TSA has been found in some concretes made with siliceous (Range B) aggregates that were exposed to sulfate solutions in the laboratory. This surprising observation only occurred in concretes that had been seal-cured and made of PC (it was not found in SRPC concretes). The same effect was found in the siliceous aggregate PC concretes from the field trial. Both results provide experimental evidence to support the discovery by French [1,32] of TSA in field structures, in which the concrete contained siliceous aggregate. As there would have been insufficient carbonate material in the aggregate, additional, if not all of the carbonate ions must have come from the immersion solution (made with tap water) or from the groundwater. Fortunately, the use of PC concretes is only permitted in ground where the concentration of sulfate ions is less than 1.4 g/l [1,4] but this is a development which needs to be monitored.

6.5. Relative performance of cements (binders)

The relative performances of the cements (binders) used in the BRE laboratory and field trial studies are listed below [25–31]. These results are based on the use of the various cements in concretes containing commonly used limestone aggregates (except for PLC concretes, which contained siliceous aggregate) maintained at temperatures below 15 °C.

- *PLC:* Portland limestone cement can contain between 6% and 35% limestone filler and is more susceptible to TSA the greater the amount of filler. This is the least TSA-resistant binder type investigated by BRE.
- *PC:* Portland cement with tri-calcium aluminate values of between 7% and 10% is not resistant to TSA either under laboratory conditions or in the field.
- *SRPC:* In one of the larger programmes of work, sulfate resisting Portland cement shows superior sulfate resistance compared with PC up to a period of about two years exposure to laboratory sulfate solutions [29,30]. However, after four [31] and six years exposure, the amount of deterioration caused by TSA in the SRPC concretes was very similar to that of the PC concretes. SRPC concretes made with limestone aggregate were not resistant to TSA after three years exposure to sulfate-bearing groundwater at the BRE Shipston field trial site.
- *Binders containing pulverised fuel ash (pfa):* A variety of concretes containing between 25% and 40% cement replacement with pfa have been investigated. The results have been inconsistent as the concretes were very resistant to TSA in the field but did not always perform well under laboratory conditions.
- *Binders containing microsilica and metakaolin:* Portland microsilica (silica fume) cement and Portland metakaolin cement were both very resistant to TSA in the field trial. These binder types have not been investigated by BRE in the laboratory.
- *Binders containing ground granulated blastfurnace slag (ggbs):* Concretes containing either slag cement (70%ggbs + 30%PC) or BRECEM (50%ggbs + 50% CAC) were found to be very resistant to TSA under both field and laboratory conditions.

6.6. Effect of storage temperature

TSA occurs more rapidly in laboratory experiments carried out at temperatures below 15 °C. The optimum temperature appears to be in the region of 5 °C. Reasons for this are postulated under Section 7.5.

6.7. Rate of deterioration

Determination of the rate of deterioration as a result of TSA will always be a complicated procedure. This is because it is influenced by a number of factors. These include the availability and concentration of both sulfate and carbonate ions, the quality and type of concrete, and whether or not the temperature is below 15 °C. In the laboratory tests carried out at BRE, significant signs of TSA were always present in susceptible concrete mixes after a period of one to two years, increasing to substantial levels after six years.

On the whole, a good correlation was found between the performances of the BRE field trial concretes and the parallel laboratory-stored specimens after the three-year field trial assessment. The depth of attack had reached several millimetres in some of the field trial concretes, but it must be borne in mind that these concretes failed to satisfy the current requirements of SD1 [21]. There must also have been carbonate or bicarbonate ions available in the groundwater, as significant TSA was found in siliceous aggregate concretes. Consequently, the rate of deterioration would probably be faster at the Shipston field trial site than in other parts of the country, for example in the BRE North London field trial site [19], where siliceous aggregate concretes did not undergo TSA.

7. Possible TSA reaction mechanism

7.1. Introduction

Theories on the mechanism of TSA have evolved and will continue to develop as results from fundamental studies materialise and more laboratory and field evidence unfolds. If rules and predictive models are to be imposed, they must take into account variations in pore fluid composition with time. These will be influenced by an array of parameters including temperature, alkalinity, composition of incoming water (in particular the relative quantities of sulfate, magnesium, sodium, carbonate and bicarbonate ions), cement type, aggregate type and concrete quality. The following mechanism for TSA is suggested by the author.

7.2. Possible topochemical replacement of ettringite by thaumasite

The synthesis of thaumasite is encouraged when a small amount of alumina (at least 0.4%) is present among the reactants [10,15,33]. It is commonly thought that this is because the formation of ettringite is a precursor to that of thaumasite. They both have very similar structures and the topochemical interchange of [Si] for [Al] and [$CO_3^{2-} + SO_4^{2-}$] for [$SO_4^{2-} + H_2O$] results in a solid solution series between the two minerals. After being replaced by silicon, aluminium would be released back into solution, where it would react to form more ettringite, thereby regenerating the sequence of thaumasite production. For thaumasite to form in this way the solid solution would need to be continuous, but current evidence suggests that this is not the case [9]. If more thought is applied to the mode of deterioration that would be expected from topochemical replacement, then the whole idea becomes less appealing. In TSA, thaumasite does not only form in the areas of cement paste previously occupied by ettringite, but it forms continuously throughout the paste. Thaumasite is much more likely, therefore, to have formed through solution. A better scenario, which still explains why some alumina is beneficial, would be for thaumasite to use ettringite only as a template for its initial nucleation and that once nucleated, additional thaumasite would continue to form directly from solution. The catalytic influence of ettringite on the formation of thaumasite has been confirmed by Lachaud [33].

7.3. Through solution mechanism

The pore solution in a recently hydrated PC concrete or mortar is saturated with respect to $Ca(OH)_2$ and the presence of additional soluble alkalis gives it a pH of about 13 or over. Any interaction between hardened concrete/mortar during its service life and an influx of external sulfates and associated cations (notably Mg, Na and Ca) will alter the composition of the pore fluid and the solid phases in equilibrium with it. During an episode of sulfate attack, there will always be a range of cementitious materials, including sulfate-bearing reaction products, competing for common ions in the pore solution. Incoming sulfate ions will react with any available calcium aluminate hydrates to form ettringite and as soon as the alumina is used up, ettringite precipitation will stop [34]. Once ettringite ceases to form, any further ingress of sulfate ions will be forced to find a new sulfate-bearing host. Portlandite ($Ca(OH)_2$) will have been reacting with sulfate ions to form gypsum but in the presence of available carbonate or bicarbonate ions, thaumasite forms instead. Gaze and Crammond [35] have already shown that thaumasite forms at pH values from 13 down to 10.5. Any magnesium ions present in the pore fluid will precipitate out as brucite ($Mg(OH)_2$). Whether or not a particular reaction product precipitates will depend heavily on the relative solubilities of the competing species with the more insoluble phases tending to precipitate preferentially. Thaumasite is very insoluble, especially at cold temperatures [36]. This means that slightly less insoluble phases like CSH will dissolve more readily in order to maintain equilibrium when in the presence of a more insoluble phase like thaumasite. Once initiated, TSA is very persistent because it feeds off the large reservoir of calcium silicates present in the cement paste and its formation will continue to completion provided the sources of sulfate and carbonate ions are not depleted and the alkalinity of the pore fluid remains above 10.5. Evidence has shown that any alumina present will be incorporated into the thaumasite structure [37,38] and remnant clinker grains of C_3S, C_2S and even ferrite can be broken down during TSA [38,39].

7.4. Effect of pH

TSA will continue forming as long as the pore solution at the reaction front is supplied with the necessary ions, is kept cold and is maintained at a pH of above 10.5. In fact, the evidence already discussed in Section 6.3 suggests that the higher the pH, the greater the likelihood of TSA. However, recent evidence from BRE and Norway [16,40] has shown that deterioration of the cement paste can still continue even if the pH drops below 10.5. An explanation for this is as follows:

During sulfate attack, extra calcium is needed to form either ettringite or thaumasite and this is obtained directly from portlandite in the first instance followed by de-calcification of the CSH phase. De-calcification has the effect of reducing the pH of pore fluids from 13 towards the neutral value of 7. If the pH drops below 10.5 as a result of prolonged de-calcification, action of magnesium ions on CSH or the action of alkali carbonation as described by Gaze and Crammond [35], then thaumasite will stop forming. Evidence of de-calcification has been observed in TSA field cases [16,27,38]. As the pH drops even further towards 7, thaumasite becomes unstable and the only stable calcium-bearing phase, which can form is calcite [35]. This calcite has been found to comprise clusters of coarse crystals in the order of a hundred microns or less in diameter. Like thaumasite, it does not possess any binding properties, it forms under wet conditions and it forms in areas of a deteriorated concrete previously occupied by cement paste. This mode of calcite precipitation has been termed cornflake calcite by BRE [16], popcorn calcite by Thaulow [41] and secondary calcite precipitating as a result of sub-aqueous carbonation by French [32]. It is important to adopt only one of these terms and the author acknowledges that 'popcorn calcite' is the term which should be used from now on as the crystals are present in the form of irregular-shaped spheres and not as two-dimensional flakes. The occurrence of popcorn calcite can therefore be the final degradation process associated with TSA. During its formation, sulfate ions will be released back into the pore solution to start the sequence all over again in a sound part of the concrete, where the pH is still high. An important observation to note is that care must be taken when diagnosing the reaction sequence responsible for forming popcorn calcite, as the sulfate ions, which played a major role, are no longer present.

7.5. Effect of temperature

The optimum temperature conditions under which thaumasite forms is a very interesting issue. In laboratory studies, time and again thaumasite forms more readily at low temperatures of around 5 °C [1,10,15,25,28,29,33,42]. BRE have found the cut off point to be between 15 and 20 °C [25]. This temperature dependency is because at cold temperatures:

- thaumasite is much more insoluble
- six co-ordinated $Si(OH)_6$ groups are more stable [10]
- solubility of CO_2 in water increases
- portlandite is more soluble

It should be noted, however, that TSA has been found in floor slabs and interior walls of buildings [4,16], which for the majority of their lives have probably been at temperatures of 20 °C or above.

7.6. Further ideas on reaction mechanisms

Several researchers are now working specifically on the reaction mechanisms of TSA with three notable groups being Aberdeen University, Aalborg Portland in Denmark and BRE [9,43]. Subjects such as the effect of temperature, pH and carbonate sources have become topical issues along with the close relationship between TSA and popcorn calcite.

8. Concluding remarks

The extent of TSA in the UK and on a global scale is still unknown. Despite the fact that TSA can occur below ground without resulting in hazardous consequences, it should not be ignored in existing structures where public safety and longevity are paramount. The UK Highways Agency has initiated a TSA assessment programme in which they actively search for potential cases of TSA in highway sub-structures. Their predictive model is based on the fact that all five primary risk factors (Section 3) must co-exist for TSA to occur. So far, their hit rate in Gloucestershire has been high with TSA being found in the majority of structures investigated. Dealing with TSA in existing buried concretes will always be difficult but at least its occurrence can be controlled in new construction. The UK has already taken steps to protect its future structures by revising its guidance documents.

It is the author's opinion that our whole approach to researching sulfate attack should be re-addressed and our standard sulfate resistance tests updated. Sulfate attack has been known about since the early twentieth century but years of detailed laboratory research failed to identify TSA. This form of sulfate attack was only discovered relatively recently when experimental temperatures were reduced from 20 °C to around 5 °C. As soon as this step was taken and the necessary ingredients were in place, TSA was reproduced very easily in laboratory-stored cements, mortars and concretes.

The word thaumasite is derived from the Greek 'to be surprised' [1]. It is the author's opinion that no-one should be surprised at the discovery of thaumasite forming as a product of sulfate attack in concretes and mortars. After all, it comprises $CaSiO_3$, $CaSO_4$, $CaCO_3$ and water, which are four very common constituents in and around cementitious-based materials in service. Furthermore, thaumasite preferentially forms under the cold, wet, alkaline conditions typically experienced by buried concrete structures.

Acknowledgements

The author would like to thank the UK Government's Construction Directorate for funding the BRE work on TSA, the BRE thaumasite team for all their advice and support and other thaumasite researchers throughout the world for some very interesting technical discussions.

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