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The thaumasite form of sulfate attack-breaking the rules

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Abstract

Following the discovery of advanced TSA in some motorway bridges, an emergency study under the chairmanship of Professor Clark culminated in national guidance being published in 1999 and reviewed in 2000. Four primary and four secondary risk factors controlling TSA were identified in the guidance and these are critically reviewed in this paper.

On the basis of these risk factors, a desk study screening exercise was undertaken, which has so far led to only a relatively small number of scientific investigations of structures deemed to be at risk. It is argued in this paper that the screening programme might have left some deteriorating structures uninvestigated and it is thought that even those investigations that have been carried out were sometimes too limited in scope.

By reference to practical experience with investigating structures in the UK and overseas, it is demonstrated that thaumasite formation (TF) or the thaumasite form of sulfate attack (TSA) can occur even when the four primary risk factors are not all obviously present. Anonymous examples are presented in summary form and, in some of the overseas cases, only one of the four primary risk factors was apparently satisfied. A source of external or internal sulfate was always present, but water was not always either abundant or mobile, there was not always a direct source of carbonate and temperatures were not always low. Possible alternative sources of carbonate are considered and the more destructive form of carbonation is highlighted.

The importance of differentiating TF from the early stages of TSA is emphasised and some preliminary guidance is suggested for identifying the 'incipient TSA' condition.

Keywords: Carbonate aggregate; Carbonation; Diagnosis; Petrography; Sulfate attack; Thaumasite

1. Introduction

Thaumasite is a rare naturally occurring mineral, usually found in metamorphic rocks and first identified in 1874. It is a complex sulfate-bearing mineral, structurally similar to ettringite, with the composition: $CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15\ H_2O$. Erlin and Stark [1] were the first to describe thaumasite occurrence in deteriorated concrete, since when it has been recognised by concrete petrographers as indicative of an unusual form of sulfate attack [2].

The thaumasite form of sulfate attack (TSA) is potentially more serious than the more common types of deterioration associated with sulfates, because the main calcium silicate cementing phases are affected, rather than only the portlandite and calcium aluminate phases, leading ultimately to complete loss of integrity and strength. A brief summary of TSA and the conditions that are conducive to its occurrence is given by Hartshorn and Sims [3].

Occasional reports of concrete deterioration caused by TSA have been published around the world since the mechanism was first recognised in 1966 and minor deposits of thaumasite have quite frequently been observed by petrographers during routine examinations. Research had also indicated that TSA might be a serious threat to durability in some circumstances [4]. However, in the UK, it was the well-publicised discovery of advanced TSA affecting buried concrete elements supporting some motorway bridges that raised concern and stimulated an emergency collation of information. This work, carried out by a 'Thaumasite Expert Group' (TEG) under the chairmanship of Professor Clark, culminated in the publication of national guidance [5,6], which *inter alia* scheduled the risk factors thought

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necessary for TSA to occur and generally provided reassurance that the mechanism was likely to be rare. The findings were also used to update the widely-used BRE guidance on sulfate ground conditions [7,8].

The advice of Clark's TEG was effective in reducing anxiety over the possibility that severely deteriorated buried concrete supporting structures might be widespread in the UK, although in some respects the guidance appeared to conflict with evidence from overseas. Since the TEG report was published, some structures have been investigated by the authors' laboratory and both anomalies and difficulties of interpretation have been encountered. Findings from some of these examples are summarised in this paper, but the work was carried out on a confidential basis and all the sites must therefore remain anonymous.

2. Factors controlling TSA

The TEG [5] recognises two levels of risk factor: four primary and four secondary. It was considered by the TEG that "*TSA will only occur in buried concretes when all the primary risk factors are present simultaneously and developed to a significant degree*". These primary risk factors, for any Portland cement-based material, may be summarised as follows:

- presence of a source of sulfate, including sulfide that may decay to sulfate,
- presence of mobile water (groundwater in the case of buried concrete),
- presence of carbonate (suggested by the TEG to be generally in the aggregate), and
- low temperatures (suggested by the TEG to be generally below 15 °C).

In the case of buried concrete, the source of sulfate is typically extraneous and derived from the surrounding ground. A major finding of the TEG was that the then conventional means of assessing sulfate ground conditions [7] sometimes produced misleading results. Sulfide-bearing clay ground that was disturbed, aerated and used as backfill during construction could yield low sulfate classes during site investigation, but gradually convert to a higher sulfate class owing to the decay on greater exposure of metastable sulfides. New procedures for ground assessment were recommended and these have now been incorporated into the latest BRE guidance [8].

However, in the case of buildings and cement-based materials that are above ground, TSA has been found to occur in respect of other types of sulfate source. These include internal sources associated with aggregate constituents or deriving from sulfate-based varieties of cement, and extraneous sources linked to sulfate-based or sulfate-bearing building materials or elements, such as conventional gypsum plaster, calcium sulfate types of render or screed and some forms of bricks and other clay-based masonry units.

The earliest studies into TSA identified the need for consistently wet conditions. Clark's TEG recognised that TSA on buried concretes would only be progressive, and thus be capable of serious damage, if there was a continuous flow of water to replenish the supply of extraneous sulfates. Hence the recommendation that only the presence of 'mobile' water represented a primary risk factor. However, this requirement for mobility might not apply to cases in which the sources of sulfate and the other ingredients needed for TSA (such as carbonate) were all internal, when continuous saturation or even intermittent wetting might suffice as a causal factor.

In view of the composition of thaumasite, it is self-evident that a source of carbonate is an essential requirement for TSA. The TEG considered that this "*will generally be carbonate present in coarse and/or fine concrete aggregates*", but conceded that "*carbonate may also rarely originate external to the concrete*" for which mechanism there was "*very little information*". Accordingly, the TEG report concentrates on aggregate-derived carbonates and presents a scheme for assessing aggregate combinations into three carbonate 'ranges', based on the overall content of calcium carbonate, plus an allowance for the greater reactivity of any carbonate contained within the sand component. Initially an unduly onerous method for measuring calcium carbonate content was envisaged, but the alternative use of petrography has since been recognised [6].

These decisions might have both introduced an unnecessary doubt over the suitability of limestone aggregates (some of which had ironically been preferred as a measure to minimise the risk of alkali-reactivity) and also, more importantly, unintentionally encouraged complacency over structures with concretes that were not made using limestone aggregates. Examples will be described later in this paper of TSA in cement-based materials, from the UK and overseas, that do not contain any significant amounts of carbonate in the aggregates.

Again, the earliest studies recognised that TSA tended to occur in conditions that were cold as well as wet. Clark's TEG advised that "*Fairly low temperatures, generally less than 15 °C, are needed for vigorous formation of thaumasite*". Although this is a correct statement, it should not be misconstrued as meaning that 15 °C can be regarded as a threshold in practice and particular note should be made of the use of the term 'vigorous'. It is certainly the case that TSA is greatly accelerated as temperature decreases; for example Bickley et al. [9] have described cases of rapid and serious deterioration of concrete in Arctic Canada.

However, it is clear from examples that TSA can and does occur at higher temperatures, including ambient temperatures in Mediterranean-type climatic regions. The rate of reaction may be slower in such cases, or possibly accelerated by factors other than temperature.

The secondary risk factors recognised by the TEG may be summarised as follows:

- type and quantity of cement used in concrete,
- quality of the concrete,
- changes to ground chemistry and water regime resulting from construction, and
- type, depth and geometry of buried concrete.

Portland cements are susceptible to TSA, which destroys the essential calcium silicate phases (both hydrated and residual unhydrated). 'Sulfate-resisting' types of Portland cement are formulated to be low in calcium aluminate, as a measure to inhibit the more common form of sulfate attack, but still contain similar calcium silicate phases and are thus not immune to TSA. Modern UK and European Portland cements are permitted to contain up to 5% limestone filler as a minor addition (i.e. not 'Portland limestone cement' with 6–20% powdered limestone) and the presence of finely divided carbonate in intimate mixture with Portland cement clinker might be expected possibly to enhance TSA, given the importance of carbonate content as a primary factor. However, the TEG advised that "*this relatively low level of carbonate material will not adversely affect the PC's* (sic) *performance in concretes containing either siliceous or carbonate aggregates*".

This advice might have been pragmatic, in view of the apparently growing using of Portland cement with a small proportion of limestone filler, but the presence of a finely divided and intimately intermixed carbonate constituent might sometimes represent a critical factor in otherwise marginal circumstances. Hartshorn et al. [10] and Torres et al. [11] have confirmed experimentally that thaumasite can form in pastes made with Portland cement containing only 5% fine limestone.

3. Practical investigations

3.1. Procedures

Guidance on the inspection of structures and the diagnosis of TSA is included in Clark's TEG report [5]. A practical scheme for surveying and sampling concrete units, and for their subsequent investigation in the laboratory, was described by Sims and Hartshorn [12]. Basically, samples are obtained, taking care to recover any incompetent deteriorated surface concrete, to represent the range of surface appearances (or conditions) that are apparent on site. These samples are then subjected in the laboratory to a programme of examination and analysis, aimed at identifying any evidence of thaumasite and any micro-textures indicative of TSA. Petrographic examination, involving thin-sections and high-power petrological microscopy, is the key diagnostic technique, but ancillary analytical methods are sometimes necessary and/or usefully corroborative.

Following publication of the TEG report in 1999, regional engineers in the UK undertook desk study risk assessments in order to identify structures that might contain buried concrete exposed to *all* of the primary risk factors identified by the TEG. This theoretical survey would automatically have removed from further scrutiny any structure that was deemed to be subjected to only low sulfate ground exposure, or only dry or immobile wet conditions, or temperatures that were not less than 15 °C, or which were constructed using a concrete thought likely to contain only a safely low amount of carbonate. Inevitably, perhaps, it seems that this screening exercise eliminated most structures and left only a relatively small overall proportion that were considered to be at risk, those being concentrated into certain regions and areas. Of those deemed to be at risk, a small number of sample structures were selected for physical investigation. As a consequence of this desk study screening, it seems that comparatively few structures were scientifically investigated, doubtless enabling administrators to feel that economies had been achieved. However, as the desk study criteria were provisional and will certainly be refined and amended as experience grows, it seems probable that some structures that are actually at risk were eliminated from the investigation during the screening process.

Furthermore, in the authors' experience, the degree of investigation of the selected sample structures was decidedly limited. Commonly, large bridge and fly-over structures were 'represented' by just a few cores taken from just one, or possibly two, units. Sims and Hartshorn [12] had recommended that "*It is imperative that the* '*laboratory*' *investigation commences on site, with the construction materials scientist conducting condition mapping of the units in question, identifying the most appropriate sampling locations and, if necessary, hand-sampling the most severely attacked areas of concrete surface*". This advice was not always heeded; samples of uncertain provenance or site significance being taken by others and then delivered to the materials specialists' laboratory. Although the advice was accepted in most of the cases in which the authors have been involved, the numbers of locations and samples was usually strictly limited by clients and structure owners, presumably on a cost-control basis.

Clark's TEG made distinction between TSA, in which "*there is significant damage to the matrix of a concrete or mortar as a consequence of replacement of cement hydrates by thaumasite*" and 'thaumasite formation' (TF) where "*thaumasite may also be found in pre-existing voids and cracks but without necessarily causing deterioration*". Although this seems to be a sensible approach and is intended to ensure that the significance of only minor occurrences of thaumasite is not over-emphasised, it also presents the investigator with interpretative difficulties. Whilst unambiguously clear examples of TSA and TF might be distinguished without dispute, this is not the case with more marginal cases. In particular, it is unclear how to differentiate TF from an early stage of TSA, which could be a crucial distinction when advising on prognosis. It is also likely that, in some circumstances, conditions giving rise to TF might be a precursor of those liable to cause TSA over a longer period.

The two following sections present some summarised and simplified examples of actual investigations, including some of those commercially undertaken by the authors, which illustrate the issues raised in the foregoing sections.

3.2. UK examples

In some cases details of the concrete composition was not known to the engineer undertaking the desk screening study. The following examples represent bridge structures in which the concrete aggregates were not usually found on investigation to contain significant amounts of carbonate, but the occurrence of TF and/or TSA varied. It is emphasised that the authors' involvement was typically restricted to inspection and sampling of very limited amounts of already-excavated concrete, followed by a restricted programme of laboratory investigation of the concrete samples. In some cases localised sampling of the ground and groundwater was also permitted. Structure ages were not usually advised, but none was recent.

- *Fly-over and bridge* (*foundations*). Concrete: flint gravel 14/20 mm aggregate, quartz/flint sand (up to 20% shell in the sand only, or about 7% overall), carbonate range C, or B worst-case; Portland cement, no additions; 0.5% excess voidage; maximum carbonation depth 6 mm; minor micro-cracking; ASR gel traces; surface leaching and secondary sulfates in voids, probably ettringite. Soil: only Class 1, but excluding >2 mm brick debris. Overview: no TSA, possible early stage of TF; risk of future TF or possibly TSA.
- *Bridge* (*piles, pile cap and superstructure*). Concrete: flint gravel 20 mm aggregate, quartz/flint sand (up to 30% shell in the sand only, or about 10% overall), carbonate range A/B; Portland cement (SRPC in pile cap), no additions; 1% maximum excess voidage, high water/cement ratio in piles and pile cap; maximum carbonation depths 2 mm (pile cap) and 6 mm (superstructure); rare micro-cracking; ASR gel traces (pile cap only); leaching and secondary ettringite in piles and pile cap. Soil: only Class 1. Overview: no TF or TSA; no risk of future TF or TSA.
- *Bridge* (*piles and pile cap*). Concrete: flint gravel 14/20 mm aggregate, quartz/flint sand, carbonate range C; Portland (SRPC), no additions; 1% maximum excess voidage (but honeycombed zone in pile); maximum carbonation 1mm; cracking in piles, occasional micro-cracking; leaching and secondary coarse portlandite and ettringite. Soil: only Class 1. Overview: no TF or TSA; no risk of future TF or TSA.
- *Bridge* (*piles, pile cap and superstructure*)*—70 years' old*. Concrete: flint gravel 10/14mm aggregate, quartz/flint sand (up to 10% Chalk in the sand only, or about 3% overall), carbonate range C, or B worst case; Portland cement, no additions; maximum excess voidage 3% (piles) or 5% (superstructure); maximum carbonation depths <1 mm piles and pile cap (except for patches of coarse 'aggressive' carbonation near pile cap surface) or up to 22 mm (superstructure); sporadic cracking and minor micro-cracking; minor leaching and softening with TF and possibly incipient TSA in piles and pile cap. Soil: only Class 1. Groundwater: Class 3, plus high Mg, high Cl and $pH = 8$. Overview: TF and early stages of TSA in buried concrete; significant risk of further TSA; groundwater gave very different sulfate class to soil.
- *Bridge* (*ground beams*). Concrete: flint gravel 20 mm aggregate, quartz/flint sand, carbonate range C; Portland cement, no additions; 1% maximum excess voidage; maximum carbonation depth 6 mm; frequent micro-cracking; ASR gel traces; minor leaching with secondary portlandite and ettringite. Analysis: cement content 465–470 kg/m^3; 3% (by mass of cement) maximum sulfate. Soil: only Class 1; no groundwater encountered. Overview: no TF or TSA; no risk of future TF or TSA.
- *Bridge* (*strip foundations*, *piles*, *pile cap*)*—early 1900s*, *widened 1950s*. Concrete: flint gravel 20 mm aggregate; quartz/flint sand, carbonate range C; Portland cement, no additions; maximum excess voidage 5% (strip foundations, but 15% in honeycombed patches), <1% piles and 4% pile cap; maximum carbonation depth (strip foundation) up to 45 mm; no cracking; ettringite in some voids. Analysis: 3% (by mass of cement) maximum sulfate; 0.5% (by mass of cement) maximum chloride. Soil: only Class 1. Overview: no TF or TSA; no risk of future TF or TSA.

None of these examples involved concrete containing discretely carbonate aggregate, indeed they all contained a combination of flint gravel coarse aggregate and natural sand dominated by quartz, with flint forming the coarser particles. Mostly the combinations were clearly carbonate range C materials, although in some examples those individual 'worst-case' samples with the highest proportions of shell (or in one case Chalk) in the sand could possibly fall into range B. Notwithstanding these generally low levels of carbonate, two of the six examples exhibited some evidence of current TF or TSA and a risk of future TF or TSA. One of these two cases, which exhibited TF and the early stages of TSA, was 70 years old and the ground sulfate conditions were found to be Class 3 when assessed from the groundwater.

The following example was typical of the cases that were difficult to interpret:

- *Bridge* (*foundations*). Concrete: natural gravel (60% limestone, 25% chert, 15% quartzite) 20 mm aggregate, natural sand (45% quartz/quartzite, 35% limestone, 15% chert); carbonate range A; Portland cement, no additions; 0.5% excess voidage; carbonation depth <1%; rare micro-cracking; ASR gel traces; some leaching and softened areas, with soft material and deposits being a mixture of gypsum, ettringite and thaumasite. Analysis: cement content 320–335 kg/m^3; 3% (by mass of cement) maximum sulfate; Overview: TF, probably incipient TSA; risk of future TSA.

The concrete core samples were drilled by the client and sent to the authors' laboratory, without any soil or groundwater samples, but it was advised that the ground conditions were considered conducive to TSA. Investigations, variously using optical microscopy, scanning electron microscopy, X-ray diffraction and infrared spectrophotometry, clearly demonstrated some patchy alteration of the matrix and the presence of a mixture of secondary sulfates, including but not exclusively thaumasite. Generalised chemical analysis for sulfate yielded normal levels (3% by mass of Portland cement), suggesting that the quantity of attacked matrix was currently limited. It was concluded that the sample exhibited more than TF, but not yet well-developed TSA, possibly best described as 'incipient TSA'. It must be important to make this distinction, because 'TF' implies no future risk, whereas 'incipient TSA' clearly implies a risk of more serious deterioration over a period of continued exposure. However, at present there are no clear guidelines for making this distinction, which thus depends on the expertise of the investigator, but also on the thoroughness of the permitted investigation.

3.3. International examples

- *Structural concrete—Canada* [9]. TSA was reported as the cause of severe deterioration of structural concrete columns and a slab, discovered within two years of casting, in the Canadian Arctic. Carbonates dominated the aggregates, which comprised a dolomite/dolomitic limestone sand and gravel, with a proportion of shelly material in the finer fraction. Sulfate concentrations within the soil around the columns were very high. Comment: Three of the four primary risk factors were satisfied, but it is unclear whether the ground conditions included mobile water; ground in the Arctic is permanently frozen beneath a shallow depth.
- *Tunnel lining—Italy* [13]. A case of TSA, with an internal source of sulfate was discovered in a concrete tunnel lining in the Formazzo Valley. Severe deterioration was reported in a concrete containing a main aggregate that was similar to the local bedrock. This was a sulfide-bearing gneissic quartzite, with some carbon-bearing mylonite produced by movements along the numerous geological faults in the region. Deterioration was so severe that, in places, the entire 300 mm thickness of the tunnel lining was becoming detached. Comment: Again, three of the four primary risk factors were probably satisfied, but there is no direct source of carbonate indicated.
- *Concrete blocks—Europe* [14]. Cracking and fragmentation was occurring with standard concrete building blocks used in masonry walls above ground level. Investigation found that the aggregate was wholly crushed limestone, with a high proportion of fines, and that thaumasite was visible infilling cracks and voids; additionally, gypsum was observed surrounding pyritic aggregate particles. It was found that pyrite accounted for 8% by mass of the concrete and that the sulfate content was up to around 10% by mass of cement. The pyrite was a constituent within the limestone outcrop, variously forming nodules and seams, from which the aggregate was quarried. It was concluded that the internal source of sulfate was gradual decay of the pyritic constituent within the aggregate. Comment: Only two of the primary risk factors are clearly satisfied; an internal source of sulfate and an internal source of carbonate. However, in above-ground masonry walls, it is not clear that water would be mobile, though the blocks were used in a wet region of Europe and might frequently be saturated. Nor was it likely that very low temperatures would be experienced other than occasionally, although these might be less than 15 °C quite frequently during winter months.
- *Concrete bricks—South Africa* [15]. In the Eastern Transvaal, several houses showed severe expansion and cracking only two years after being built, with the white, powdery deterioration products predominantly composed of thaumasite. The thaumasite was found in the concrete brickwork made with a carbonaceous, sulfide-bearing cummingtonite slate aggregate. A laboratory investigation to try to duplicate the deterioration successfully reproduced the expansion, but the expansive product was found to be ettringite, not thaumasite. Comment: Only one

of the primary risk factors was satisfied in this unusual example: there was an internal source of sulfates, from the decay of sulfides in the aggregate. However, any water would not be mobile, there was no direct source of carbonate and the ambient temperatures are unlikely to be as low as 15 °C.

- *Render and Mortar—Southern Italy* [16]. Thaumasite has been identified as a reaction product in deteriorated masonry walls and renders, in a region where temperatures are typically in excess of 20 °C. Many of the examples of TSA were associated with repair materials which were shown to be incompatible with the historical mortars and renders. Comment: The nature of the aggregate is uncertain and might be a source of carbonate, but otherwise only one of the primary risk factors is satisfied, assuming that the incompatible historic fabric is gypsum-based and thus a source of sulfate. The masonry is unlikely to be subject to mobile water and, in Southern Italy, will rarely be either saturated or at temperatures as low as 15 °C.
- *Mortar—Mediterranean* (*authors*). High-rise brick buildings situated on the coast were exhibiting rapid deterioration of the jointing mortars, thought initially to be caused by a lack of cement and/or airborne salt weathering. However, chemical analysis found relatively high cement contents (mix proportions typically about 1:3 or 1:$3\frac{1}{2}$), though the material was highly voided, and only modest levels of chloride. Microscopy found evidence of sulfate attack, including separate developments of both ettringite and thaumasite. The degree of attack varied, with the highest sulfate contents in the mortar corresponding with the greatest microscopic evidence of attack and the lowest levels of sulfate in the immediately adjacent brick. Various mortars were made with either crushed limestone/dolomite sand or natural quartz sand and the sulfate attack appeared to occur irrespective of the sand type (in fact more of the quartz sand mortar samples were affected than the limestone sand samples). The mortars were all completely carbonated. Comment: Again, only one of the four primary risk factors was invariably satisfied: a source of sulfate in the adjacent clay bricks. Only some of the affected mortars potentially had an internal direct source of carbonate. The brickwork masonry is unlikely to be subject to mobile water and, on the Mediterranean coast, will rarely be either saturated or at temperatures as low as 15 °C.

4. Discussion

4.1. Carbonate source

It is apparent from many of the foregoing examples, variously from the UK and overseas, that TF and TSA can and do occur in concretes which do not contain any significant amount of carbonate in the aggregate. This is an important finding in the UK context, because it is thought that the desk study screening exercise will have eliminated from further investigation many structures made with concrete containing non-carbonate aggregates, which may otherwise have been assessed as being at risk of TSA. It is also necessary to try to identify the source of carbonate in these cases.

Carbonate is most likely to affect the susceptibility of concrete to TSA when it is in a finely divided state and present in a high concentration. Many of the examples of TSA in concrete in the UK appeared to have resulted from the reaction of incorporated limestone aggregate and, indeed, in some cases it was possible to demonstrate the consumption of limestone (see Fig. 5 in [3]). Apparent reactions have sometimes been associated with dusty limestone coarse aggregate, although it has been acknowledged in the TEG report that carbonate fine aggregates are likely to render a concrete more susceptible to TSA. In several of the UK examples summarised earlier, there was a minor potential source of carbonate in the sand, mainly shell but sometimes Chalk, but it was unclear whether these small scattered amounts of carbonate could be an adequate source for the TF and TSA that was detected. It should be emphasised that these structures were scheduled for investigation by a cautious screening engineer, only in the absence of any documentary information on the original concrete mix; otherwise they would quite possibly have been excluded from further investigation on the grounds of not containing carbonate in the aggregate.

In the Italian tunnel lining and South African brick examples described above, there was no apparent presence of any carbonate component, either internally or in the vicinity. However, in both cases there was a source of carbon. In the Italian tunnel lining concrete, both the crushed rock (gneissic quartzite) aggregate and the similar surrounding bedrock were found to contain graphite-bearing mylonite. In the South African concrete bricks, the aggregate comprised a carbon-bearing slate. Is it possible that graphite (naturally-occurring crystalline carbon) can oxidise in the acidic solution derived from decay of the sulfides that were also reported to be present in both the quartzite and slate rocks involved?

Carbonation of concretes and mortars is a normal part of the concrete ageing process and typically increases resistance to external sulfate attack. Carbon dioxide from the atmosphere reacts with both portlandite and the calcium silicate hydrates in the cement paste forming a finely or poorly crystalline variety of calcite. In some relatively porous renders and mortars, this metastable calcite, in the presence of high concentrations of sulfates from adjacent bricks, could contribute to TSA in favourable environmental conditions [17].

A more destructive form of carbonation has recently been recognised, in which coarser and weaker carbonated 'popcorn' micro-textures are created in certain circumstances. Thaulow and Jakobsen [18] termed this 'bicarbonation' and Thaulow et al. [19] have explained that types of low quality, high water/cement ratio concretes are particularly vulnerable. French and Crammond [20] have reported some apparently similar examples in the UK, involving concretes buried in wet conditions variously in the London Clay and the Mercia Mudstone, whose groundwaters are typically rich in Ca, HCO_3 and SO_3 ions. French and Crammond have termed this 'sub-aqueous carbonation' and shown that this can occur in combination with the formation of thaumasite in concretes that do not contain any significant amounts of carbonate in the aggregate. Although clearly further research is needed, it would appear likely that, in some circumstances at least, the carbonation of concretes, including buried concretes, can provide the carbonate source needed for the generation of thaumasite.

It has been shown that a content of carbonate aggregate is not an invariable prerequisite for TF or TSA to occur. Similarly, it is important to record that concretes containing carbonate aggregate do not necessarily exhibit evidence of TF or TSA, even when the other primary risk factors are all present. It is interesting to note that, in parts of France for example, where limestone aggregate concretes have been used in concrete structures for many decades, apparently little evidence of TF or TSA has been reported, even in circumstances that would normally be considered conducive to thaumasite development. In a large number of these cases the cements contained a high proportion of blast-furnace slag.

4.2. Temperature

There is strong evidence that lower (<15 °C) temperatures contribute greatly towards rapid deterioration of concretes in susceptible environments [10]. However, it cannot be denied that concrete deterioration as a result of the development of thaumasite has been reported in several cases at higher temperatures, especially overseas, some examples of which were summarised earlier. Moreover, experimentally, Hartshorn et al. [10] produced thaumasite in the laboratory at 20 °C as well as at 5 °C. Bensted [21] argues thermodynamically, using Kleber's rule, that a decrease in temperature leads to an increase in co-ordination number, so that low temperatures allow the formation of $Si(OH)_6$. Thus, whilst thaumasite formation is accelerated at lower temperatures, it is not necessarily precluded at higher temperatures.

The significance for the UK is that the primary risk factor concerning low temperature is generally taken to imply that only deeply buried concrete is likely to be susceptible to TSA. In the case of relatively shallow building foundations, the TEG report even suggests that heating within occupied buildings may reduce the susceptibility of their concrete foundations to TSA; reference is made to a single example. Again, as with the carbonate risk factor, it is likely that the desk study screening will have eliminated structures at risk on the basis that the concrete in question will not have been subjected to low temperatures.

4.3. Interpretation of anomalies

The reliability of pre-selecting structures for detailed investigation on the basis of a desk study screening exercise has been placed in doubt by the finding of cases of TF and TSA in which not all of the four primary risk factors are present. In some of the overseas cases, as few as just one of the four factors was apparently satisfied. It must therefore be a real possibility that some concrete structures in the UK are gradually deteriorating, often in buried units that are not available for routine inspection, but have not yet been identified and scheduled for any level of scientific investigation.

Few of the structures that have been short-listed for further investigation have shown any immediate signs of distress and the degree of deterioration found by detailed laboratory examination has often been negligible or limited. However, in some cases there has been minor evidence of chemical attack, including the generation of secondary sulfates, including thaumasite, sometimes in association with leaching and moderately destructive carbonation. Some examples appear to comprise sound concrete, apart from the presence of some secondary sulfates merely infilling voids and other pre-existing spaces, and might be reasonably and hopefully safely described as TF. The dilemma occurs with other examples in which none of the textures considered characteristic of well-developed TSA are present, but there is nonetheless some limited evidence of matrix alteration and the minor occurrence of secondary sulfates including thaumasite. In these cases the authors consider that the term TF would be misleading and unsafe, preferring and recommending the term 'incipient TSA'.

The importance of this distinction cannot be overstated. A finding of TF will be regarded as benign and the concrete structure will probably not be monitored or scheduled for periodic re-inspection. However, a finding of incipient TSA should properly lead to further corroborative investigation and the structure in question also being subjected to occasional re-inspection during its continued service. Further research and experience will be needed to enable the incipient TSA condition to be prognostically evaluated.

5. Conclusions

- Experience in the UK and overseas has shown that the four primary risk factors identified by the TEG in the UK do not always have to be obviously present for TF or TSA to occur in concrete. In some overseas cases, apparently as few as one of the four factors was satisfied.
- Of the four primary risk factors, there is always a source of sulfates, although it is sometimes internal, rather than external. Water does not always need to be mobile, especially when the sources of sulfate and carbonate are both internal. TSA is not exclusively associated with concretes containing carbonate aggregates. It is established that TSA is accelerated at lower temperatures, but does occur at higher temperatures.
- Although these potential variations from the common situation were recognised within the detailed text of the TEG report, it is thought possible that the desk study screening exercise, undertaken in the UK to identify structures warranting scientific investigation, might have been unreliable. Some structures at risk of TSA will not have been identified and have not been investigated.
- Even those scientific investigations that were carried out were often very limited in scope, on a cost-restricting basis.
- TF and TSA can occur in the absence of any significant content of carbonate in the aggregate. Alternative sources of carbonate seem likely to be associated with normal carbonation, or particularly with the more destructive 'bicarbonation' (or 'sub-aqueous carbonation'), or possibly even the oxidation of carbon in the form of graphite that is sometimes present in aggregates and/or surrounding bedrock.
- It is important to differentiate between TF and incipient TSA. It is suggested that the former should be restricted to cases where the concrete material is wholly sound and the deposits of secondary thaumasite are merely infilling voids and other pre-existing spaces.

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