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Rate of the thaumasite form of sulfate attack under laboratory conditions

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ABSTRACT

In order to give confidence to those responsible for the management of infrastructure, it is necessary to investigate the structural effects of the thaumasite form of sulfate attack (TSA) on buildings and structures. Whereas TSA is less common than other forms of structural concrete deterioration, its consequences can be quite serious.

To investigate TSA deterioration of concrete within a reasonable time scale, it is generally necessary to accelerate TSA in the laboratory. Using such an accelerated testing procedure, this paper is concerned with predicting the rate of TSA depending on varying mix designs and aggressive solutions. A methodology was developed to estimate the annual deterioration rate of TSA. It was shown that a combined carbonate and sulfate solution is less aggressive than a pure sulfate solution, and that deterioration rates of up to 1.8 mm/year are possible in commonly used concrete.

1. Introduction

Although the thaumasite form of sulfate attack (TSA) has been recognized for many years it did not receive any serious attention from either industry or the research community until the discovery of 10 cases of the thaumasite form of sulfate attack in the foundations of overbridges along the M5 motorway in Gloucestershire in 1998 [1]. The seriously attacked columns had been buried in backfilled Lower Lias Clay and were discovered during strengthening works.

TSA targets the calcium silicate hydrates (C–S–H), the main binding agent in all hydrated Portland cements, in contrast to the conventional sulfate attack which consumes calcium aluminate hydrates (CAHs) and causes expansion. TSA leads to a transformation of the cement matrix into a mush from the surface inwards. The Thaumasite Expert Group (TEG) [2] recognized two sets of conditions for the formation of TSA in buried Portland cement based concretes: these are four primary and four secondary risk factors. The primary risk factors are defined as [2]:

- A source of sulfates and/or sulfides in the ground.
- A source of carbonate.
- Presence of mobile groundwater.
- Low temperatures (<15 °C).

The four secondary risk factors are identified by the TEG as:

- Type and quantity of cement used in concrete.
- Quality of concrete mix, compaction.
- Changes to ground chemistry and water regime resulting from construction.
- Type, depth and geometry of buried concrete.

TSA takes place mainly in low temperatures (<15 °C: the optimum temperature is 5 °C), whereas conventional sulfate attack is predominantly at ambient temperatures of >15 °C. Deterioration due to TSA can be found in buried concretes such as concrete foundations [1,3,4], piles [5,6], tunnel linings [4,7,8], tunnel ventilation shafts [9], floor slabs [4,8,10], pavements [4,8,11] and lime stabilisations [4]. There also exist a few TSA cases of above ground structures such as in gypsum plaster and in brickwork in historical buildings [4,12–15].

Much of the research effort to date has concentrated very much on the formation mechanisms of TSA and the identification of concrete mixes capable of resisting it. However, structural consequences are less understood. Effects of TSA in buried concrete structures can be the loss of strength due to reduction of cross-sectional area, possible premature corrosion due to loss of cover concrete, loss of sliding resistance towards lateral movement and reduction in skin friction. Actual cases of loss of structural integrity in the field have not been found except for a structure in the Canadian Arctic, where the columns supporting a building had to be replaced after 2 years in an aggressive environment [16,17].

Data about the gradual loss of cross-sectional area of concrete elements have very rarely been found in the literature. Most of the time there only exist two data points, zero at the time of construction and the depth of deterioration when TSA was discovered. Based on these few data it has not been possible to obtain reliable rates of TSA. The TEG [2] suggested an average rate

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of about 1 mm/year over a long period and Erikson [18] estimated the rate of TSA of 0.2 mm/year. These estimates are based on field cases and do not include parameters such as environment, concrete mix and time of deterioration.

This paper presents a method to accelerate TSA on concrete samples in laboratory conditions to identify the time of TSA onset and to predict the annual deterioration rate. The effects of two aggressive solutions, a pure sulfate solution and a combined carbonate–sulfate solution, on varying mix design are discussed.

2. Methodology

2.1. General

To produce thaumasite in the laboratory, in addition to creating an external environment that is conducive to the development of thaumasite, the concrete mix must be susceptible to attack. The main factor governing susceptibility and, incidentally, strength of concrete is the water–cement (w/c) ratio. BRE Special Digest 1 [19] gives maximum free water/cement ratios for prevention of sulfate attack of 0.35 for the most aggressive environments and 0.55 for slightly aggressive conditions. It can be inferred from this guidance that to encourage and accelerate attack the w/c-ratio should be greater than 0.55.

All binders based on Portland cement are susceptible to the thaumasite form of sulfate attack as thaumasite consumes the calcium silicate hydrates that are the main strength giving agents in all of these binders. The time of onset of deterioration can be influenced by the type of filler used as this has physical as well as chemical effects on the cement paste. The most vulnerable binders in laboratory based experiments are Portland cement (PC) [20] and Portland limestone cement (PLC) [21,22].

To accelerate TSA in laboratory conditions it is appropriate to provide the highest source of carbonate ions possible, i.e. the aggregate should contain of up to 100% of calcite. The type of curing also affects the TSA resistance and seal-curing was found to be the most reactive type [20,23]. In seal curing, specimens are wrapped in three layers of cling film and then put in a polythene bag immediately after demolding for 27 days at 20 °C.

TSA can occur within a few years of exposure to aggressive environments and progress quickly or gradually depending on the environment. Initial ‘dormant’ periods of low activity have been observed before deterioration started which could last up to 15 years [24].

2.2. Sample parameters

To accelerate and investigate the rate of progress of TSA of Portland cement based concrete samples in laboratory conditions five different mixes immersed in two aggressive solutions were chosen. Cement contents (CEM I 42.5N, C_3A = 8%) of 290 kg/m^3 and 320 kg/m^3 and water/cement ratios of 0.55, 0.65 and 0.75 were used (see Table 1). To allow comparison with work undertaken by the Building Research Establishment (BRE) two of the mixes conformed to mixes used at the Shipston-on-Stour field trial [20,25]. The fine (0–4 mm) and coarse (4–20 mm) aggregate fractions consisted of Jurassic Oolitic limestone.

Table 1
Mix parameter.

Mix	1	2	3 (BRE)	4 (BRE)	5
Cement content (kg/m^3)	290	290	290	320	320
Water/cement ratio	0.55	0.65	0.75	0.55	0.75
Aggregate content (kg/m^3)	1890	1820	1740	1830	1660

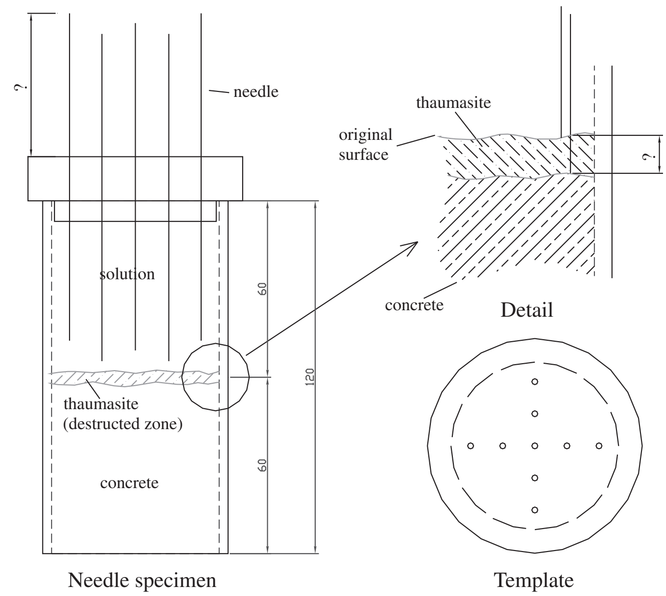

Fig. 1. ‘Needle’-test apparatus.

The specimens were cast in cylindrical molds with an internal diameter of 57 mm and a height of 120 mm which were filled with concrete to about 60 mm and, after 28 days seal curing, were immersed by filling the top approximately 60 mm of the mold with a solution of either 1.8% sulfate, as magnesium sulfate, or carbonate–sulfate solution (370 mg CO_3/l + 1.8% SO_4/l). The solutions were renewed every 3 months. The specimens were stored in an environmental chamber at a temperature of 5 °C.

2.3. Progress measurement

Manual measurement of the depth of attack was performed using a needle test rig where the depth of the deterioration was measured with a needle at nine defined points on the specimen’s surface. Formation of thaumasite causes the cement matrix to change into a soft white paste which, in the initial stages, causes the surface of the concrete to heave. The depth of deterioration was determined by pushing the needle into the concrete until solid concrete was reached and measuring the movement relative to a zero measurement describing the distance between template and needle end taken at the start of the investigation period. An illustration of the test rig is shown in Fig. 1.

3. Results of TSA progress

3.1. Effect of mix design

The deterioration of the five concrete mixes immersed in a 1.8% SO_4-solution was observed over a period of 27 months. To determine the TSA progress the top cast surface was investigated. The measurements made using the needle test assess the pure structural effects of the deterioration caused by TSA because the actual loss of cement matrix is measured. The deterioration progress is represented in Fig. 2. From the figure it can be seen that after an initial period of 6 months of very little activity deterioration was observed. This dormant period of 6 months was also observed by Crammond and Nixon [26] in TSA laboratory investigations. Monteiro [24] also observed dormant periods during sulfate attack in specimens with low water–cement ratio which could last up to 15 years. In the majority of cases a reduction in w/c-ratio and increase in cement content resulted in an increase in resistance to TSA.

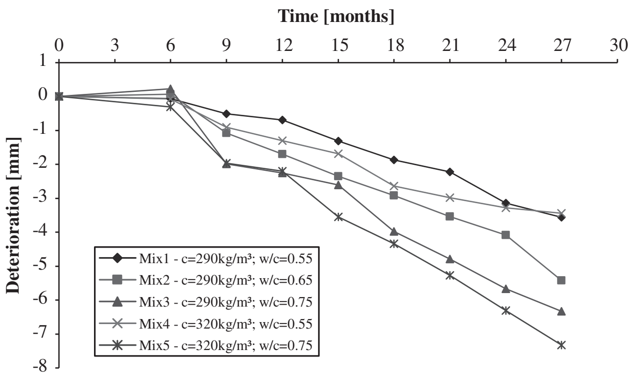

Fig. 2. TSA progress in 1.8% SO_4-solution.

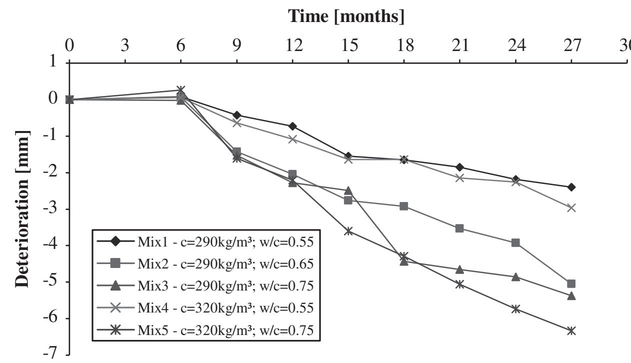

Fig. 5. TSA progress in combined sulfate–carbonate solution.

Fig. 3. Carbonated crust, 9 months.

Fig. 4. Layer of deteriorated TSA affected concrete, 27 months.

Table 2
Deterioration progress in the two aggressive solutions.

Mix	1.8% SO_4-solution (mm/year)	Correlation coefficient R^2	Combined SO_4–CO_3-solution (mm/year)	Correlation coefficient R^2
1	2.1	0.9824	1.3	0.9423
2	2.7	0.9797	2.2	0.9711
3	3.1	0.9721	2.7	0.9226
4	1.8	0.9591	1.4	0.9618
5	3.7	0.9889	3.2	0.9855

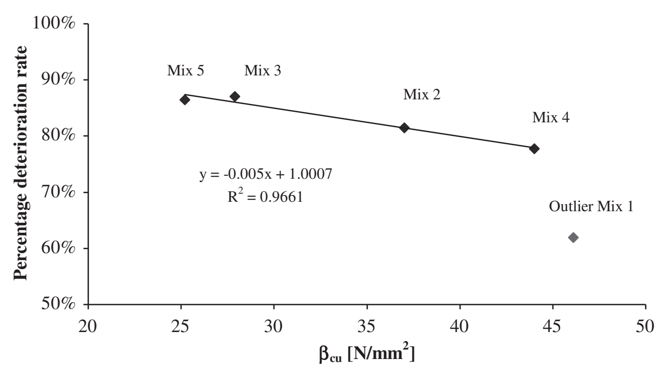

Fig. 6. Percentage rate of deterioration in SO_4–CO_3-solution compared to the SO_4-solution.

Gradually breakdown of the matrix inwards occurred after the tensile strength of a 'sound' concrete crust was exceeded. This crust was identified as carbonated and is shown in Fig. 3. The volume change of the TSA affected zone under unrestrained conditions was assessed with an average of 290% in respect to the actual deterioration (see Fig. 4).

3.2. Effect of aggressive solution

The effect of aggressive solution on the TSA progress of five different mixes was investigated on a second set of specimens immersed in a combined sulfate–carbonate solution (1.8% SO_4 + 370mgCO_3/l) under equivalent conditions. The deterioration progress is shown in Fig. 5 and similar features as seen in the pure sulfate solution were observed, with deterioration increasing with an increase in water–cement ratio. The dormant period was found to be similar in both the sulfate–carbonate solution and the pure sulfate solution; however, the rate of deterioration in the sulfate–carbonate solution was slower. Results for both solution types are compared in Table 2. It should be noted that even for Mix 4, which is a commonly used concrete mix, a deterioration rate of 1.8 mm/year was achieved.

The effect of mix design is the same as for specimens immersed in the pure sulfate solution; however, in Fig. 6 it can be seen that the deterioration rate was reduced to 60–90% of the rate measured in the 1.8% sulfate solution. The figure represents the percentage deterioration in the combined sulfate–carbonate solution compared to the pure sulfate solution. The percentage deterioration is compared using the 28 day concrete cube compressive strength (β_{cu}). The highest reduction to 60% occurred in the Mix 1 specimens, this reduction is considered as an outlier which is clearly shown based on the regression. On the other hand Mix 1 could also show the trend of a curve. Excluding the Mix 1 value there was a clear linear dependency of the deterioration rate in the combined sulfate–carbonate solution on the compressive strength. Specimens in the combined sulfate–carbonate solution deteriorated 5% per 10 N/mm^2 increasing strength slower than specimens in the pure sulfate solution, i.e. the additional carbonate decelerated the deterioration in concretes with less permeability. It is suggested that excess supply of carbonate favoured the precipitation of calcite in the concrete pores hence the density of the cement matrix increased and the transportation of aggressive sulfate ions was reduced. A lower amount of additional carbonate in solution may enhance the rate of deterioration. The optimum carbonate content in solution for the acceleration of TSA should be investigated in future work.

4. Discussion

The rate of concrete deterioration (mm/year) due to TSA was found to be dependent on the mix design and the type of solution; however, the onset of TSA was found to be independent and occurred after a dormant period of 6 months for all parameters investigated. The mix design combines two separate parameters: the water–cement ratio and cement content. As the concrete strength increases with decreasing w/c-ratio and, generally, the durability improves with increasing cement/binder content and decreasing water–cement ratio, the concrete compressive strength was used as a single parameter to assess the rate of deterioration in the two aggressive solutions used during this investigation. The effects of the water–cement ratio and cement content are apparent in Figs. 2 and 5. The concrete compressive strength results were obtained by using the 28 day strength of cubes cast with the specimens.

In Fig. 7 the rate of deterioration is plotted against concrete compressive strength for each aggressive solution. The difference in the rate of deterioration for each solution and the linear dependency on the compressive strength are clearly visible. Based on the linear regression equation it was found to be possible to determine the minimum concrete compressive strength, i.e. the intercept with the *x*-axis via extrapolation, where the rate of deterioration due to TSA is likely to be zero. It is reasonable to assume that the rate of deterioration should approach zero the higher is the strength and the quality of the surface zone.

This threshold, where TSA deterioration rate would be zero, was found to be at concrete compressive strengths above 61 N/mm^2 and 70 N/mm^2 when stored under equivalent laboratory conditions in a combined sulfate–carbonate and sulfate solution, respectively. However, it is recognized that the results of this investigation are limited to a maximum concrete compressive strength of 46 N/mm^2, and, hence, that the proposed thresholds are theoretical and it is possible that TSA will be able to occur at compressive strengths greater than the above stated threshold values. Therefore the possibility of TSA occurring at high strength, and low water–cement ratios, cannot be excluded. However, it would appear that high quality concrete is able to decrease the rate of deterioration to such an extent that the depth of deterioration can be considered to be negligible despite attack occurring after an initial dormant period. The concrete surface usually forms a weaker barrier to the ingress of media than does the concrete bulk, as the surface zone has an increased water–cement ratio and higher percentage of fines, when cast against conventional formwork, causing a higher porosity. Although it appears that the onset of attack cannot be prevented in carbonate-containing concrete, the severity of deterioration can be reduced by, for example, the use of controlled permeability formwork (CPF) liners which can achieve a reduced water–cement ratio in the surface zone.

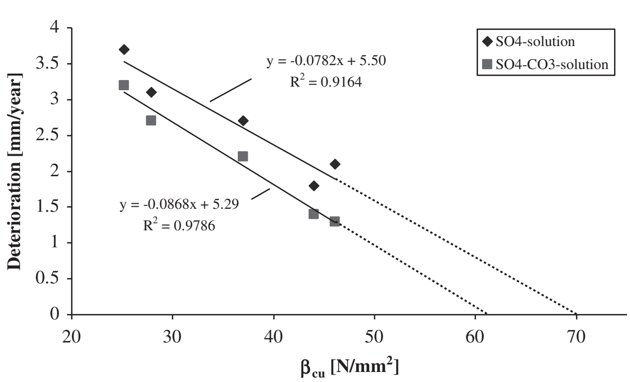

Fig. 7. Relationship between compressive strength and annual deterioration.

5. Conclusions

The investigation on the effects of TSA on pure structural effects showed that TSA deterioration rates of up to 1.8 mm/year are possible for a commonly used concrete with a w/c-ratio of 0.55 and a cement content of 320 kg/m^3. The findings in respect to the progress of TSA are based on unrestrained laboratory conditions and listed below:

- Deterioration consisted of two stages – an initial dormant period and subsequent measurable deterioration.
- A crust of ‘sound’ concrete formed in the unrestrained specimens.
- TSA formed as an uncohesive loose mass when immersed in solution. The TSA reaction product layer was three times the thickness of the actual depth of concrete deterioration
- The length of the dormant period was found to be independent of the mix design
- The severity of thaumasite deterioration, i.e. the rate of deterioration, was directly dependent on the mix design, i.e. water–cement ratio and cement content, and decreased with an increase in concrete strength.
- TSA is very likely to be insignificant in concrete with a compressive strength above about 70 N/mm^2.
- An additional source of carbonate in solution did not accelerate TSA, i.e. a combined sulfate–carbonate solution was less aggressive than a sulfate solution.

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