

Relative resistance of Portland and Pozzolanic cements to the thaumasite form of sulfate attack (TSA)

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Abstract

The development of TSA in concrete made with both limestone and siliceous aggregates that was immersed in three standard sulfate solutions of varying composition at 5°C for periods of 5, 11 and 23 months is reported. The concretes contained ordinary Portland cement (5% limestone filler), Portland-limestone cement (20% limestone filler), sulphate resisting cement (no limestone filler) and ordinary Portland cement with a) 25% pulverised fuel ash and b) 65% ground granulated blast furnace slag. Deterioration was assessed by visual inspection and X-ray diffraction, backed up by optical microscopy and scanning electron microscopy of selected samples. Thaumasite was readily identified in the degraded surface layers of all the cubes, except for those made from OPC/GGBS, which did not deteriorate during the investigation.

1. INTRODUCTION

Since the identification in 1998 of the thaumasite form of sulfate attack (TSA) in the concrete foundations to a number of bridges on the M5 motorway in southwest England, the phenomenon has been of serious interest to material specifiers and suppliers, consultants and contractors in the construction industry. A Thaumasite Expert Group (TEG) was set up by the UK government in 1999 to report on the causes, effects and possible solutions to these problems [1]. This Report was reviewed after one and three years [2, 3]. At least 50 new cases of TSA have been identified in the UK since the publication of the expert report and a further 30 have been added since the publication of the first review in 2001. The majority of these were discovered in the foundations of bridges constructed on Lower Lias Clay along the M5 motorway in southwest central England. Cases of TSA in USA, Canada, Denmark, Norway, Greece, Germany, Spain, Switzerland, Netherlands, Italy, Slovenia and South Africa were reported at the 1st International Conference on Thaumasite in Cementitious Materials, held at the Building Research Establishment (BRE), UK in 2002 [4]. The first case of TSA in China has been reported by Ma et al. [5].

More recently the Expert Group has published Special Digest 1 [6], which gives advice on the investigation and characterisation of the ground and

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the design of concrete suitable for the conditions found to be present. The recommended procedure entails classification of the ground into one of the 5 Design Sulfate (DS) classes, defined in Table 1, based on the determination of sulfate, pH and, where appropriate, the quantities of pyrite, Mg and Cl present. The Design Class of the concrete, which defines the 'quality' of concrete that will withstand attack in the particular situation, is then determined, depending on the DS class, pH and mobility of the groundwater, working life required for the concrete and the provision of measures designed to protect it from attack. A specific DC concrete is achieved by the use of an appropriate combination of water:cement ratio, minimum cement content, binder type, presence of additives to the binder and use of additional protective measures to the concrete.

Table 1 BRE Design sulfate classes and composition of test solutions

| BRE SD 1 Design sulfate classes | SOLUTIONS USED IN TESTS | LIMITS FOR SULFATE (mg/litre SO₄) | LIMITS FOR MAGNESIUM (mg/litre Mg) |
|--|---|---|---|
| Control | Saturated Ca(OH) ₂ solution | - | - |
| DS-1 | - | <500 | - |
| DS-2 | CaSO ₄ (1.4g/l SO ₄) | 500 -1500 | - |
| DS-3 | CaSO ₄ (1.4g/l SO ₄) + MgSO ₄ (1.6 g/l SO ₄) | 1600 – 3000 | - |
| DS-4 | - | 3100 – 6000 | <1200 |
| DS-4m | CaSO ₄ (1.4g/l SO ₄) + MgSO ₄ (4.6 g/l SO ₄) | 3100 – 6000 | >1200 |
| DS-5 | - | >6000 | <1200 |
| DS-5m | - | >6000 | >1200 |

This paper, which is the third in a series, reports on comparative studies of the incidence of thaumasite in concretes made with Portland and composite cements that were exposed to different levels of sulfate in controlled conditions for periods of up to 23 months. The first paper [7] re[ported the effect of pH on the performance of cubes that were immersed for 5 months in sulfate bearing solutions of varying pH. Thaumasite was identified in ordinary Portland cement (OPC) and Portland limestone cement (PLC), both with limestone filler, as well as in Sulfate resisting Portland cement (SRPC) where limestone was absent. Ettringite rather than thaumasite was formed in OPC with pulverised fuel ash (PFA), whereas OPC with ground granulated blastfurnace slag (GGBS) apparently resisted attack. In the second paper [8], a fuller account of the results up to 12 months was presented. In this it was firmly concluded that TSA occurs in OPC and PLC at high pH, but not in acidic conditions.

2. EXPERIMENTAL WORK

2.1 Specimen preparation

The concrete cubes (100mm) were cast to BS 1881:1998 [9] made with OPC (5% limestone filler), PLC (20% limestone filler) and SRPC (0% limestone filler), as well as OPC with a) 25% PFA (3.75% limestone filler) and b) 65% GGBS (1.75% limestone filler) as described elsewhere [7, 8]. Thames Valley gravel aggregate was used for both coarse and fine fractions, as representative of a siliceous, carbonate free aggregate. Some samples were prepared using limestone for the fine and coarse aggregate.

After casting the cubes were left for 18 hours under wet hessian, demoulded, individually double wrapped in Clingfilm and cured at 95% RH, 21°C for 28 days. Once cured, the unwrapped cubes were transferred to storage tanks containing standard sulfate solutions maintained at $4.5 \pm 0.5^\circ\text{C}$ for periods of 5, 11 and 23 months. The solutions were designed to simulate BRE Special Digest 1 [6] Design Sulfate classes DS-2, DS-3 and DS-4m, as shown in Table 1, where the Class DS-2 – DS-3 division is based on the solubility of calcium sulfate (1440mg/litre SO_4). Higher values of sulfate indicate the presence of highly soluble sulfates, such as those of Mg and Na. Control samples were placed in saturated $\text{Ca}(\text{OH})_2$ solution. The solutions were replaced every three months.

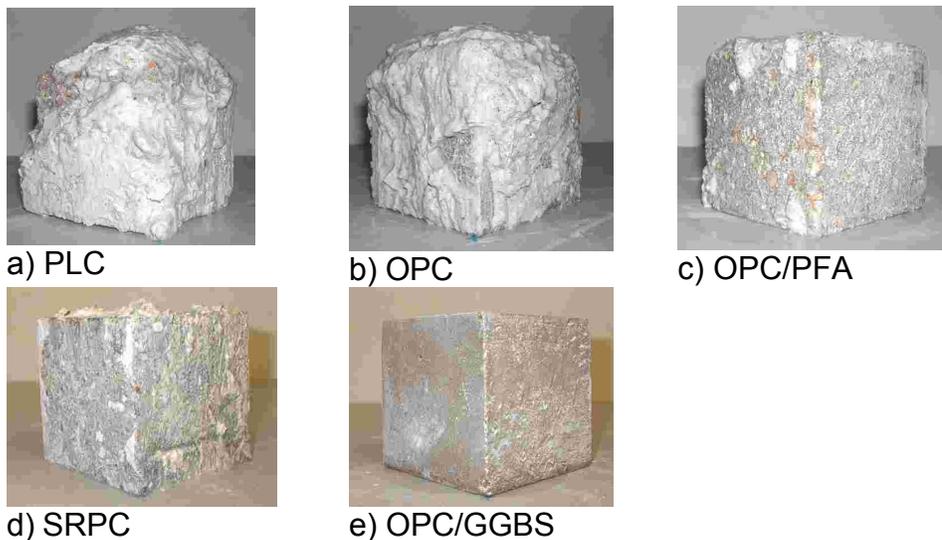


Figure 1. Cubes with limestone aggregate in DS-3 solution for 23 months

2.2 Concrete testing

Assessment of the cubes by visual inspection, X-ray diffraction (XRD) and optical microscopy (OM) was carried out at ages of 6, 12 and 24 months. Some samples were selected for further analysis using scanning electron

microscopy (SEM). Visual inspection included detailed description and each was photographed. Samples of degradation products as well as sound concrete were air-dried and ground for XRD analysis. Standard 30 μm thick petrographical thin sections were examined by optical microscopy to assist the identification of the mineral phases, including thaumasite, and also to record textural features.

Samples selected for scanning electron microscopy (SEM) were vacuum desiccated for 3 days, cold resin impregnated, ground and polished (6 μm down to 1/4 μm diamond paste) and finally carbon coated. A Camscan Series 2A AEM (Cambridge, UK) was used to produce both secondary and back scattered images.

3. RESULTS

3.1 Visual observations

Apart from the OPC/GGBS cubes, all the samples showed significant chemical attack. An acceleration in attack between 12 and 24 months was apparent in OPC and PLC stored in DS-2 solution, whereas the most significant changes in DS-3 and DS-4m solutions was after 12 months.

Fig. 1 shows concrete made with limestone aggregate after immersion in DS-3 solution for 23 months. Both PLC and OPC were badly deteriorated with classic grey-white mushy thaumasite coatings, respectively up to 21 and 14 mm thick, that was easily dislodged. OPC/PFA (Fig. 1c) was attacked but to a lesser extent than OPC, a result consistent with reported results [10]. In line with previous findings [7, 8], attack of SRPC was similar to that observed for OPC/PFA.

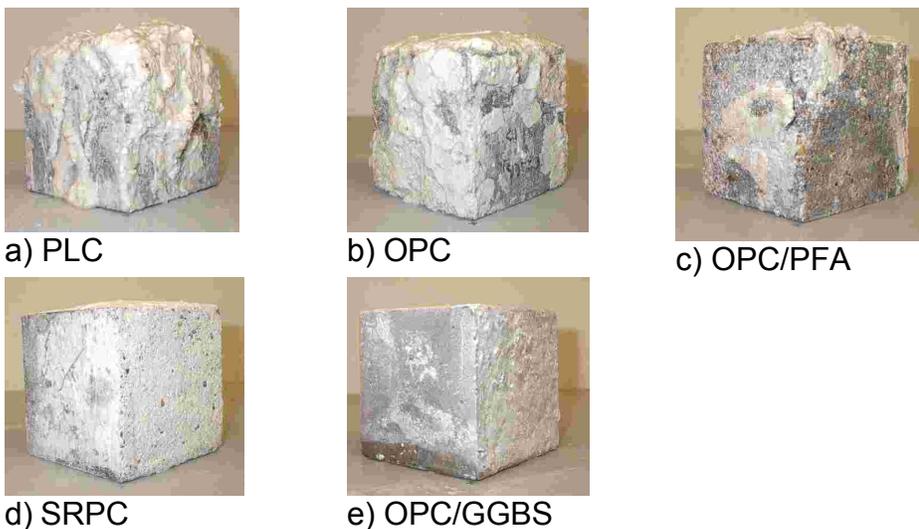


Figure 2. Cubes with siliceous aggregate in DS-3 solution for 23 months

Fig. 2 shows the deterioration of the concrete cubes made with gravel aggregate after immersion in Class DS-3 solution for 23 months. Although attack was similar to that in concretes made with limestone aggregates, in general the deterioration was less severe, although substantial damage had occurred to PLC and OPC and some attack of OPC/PFA and SRPC was apparent. With GGBS/OPC a white surface product was identified as gypsum (see discussion below) but there was no apparent deterioration. Fig. 3 shows OPC with siliceous aggregate in DS-3 solution after 5, 11 and 23 months, demonstrating progressive TSA attack with time.



Fig. 3 OPC with siliceous aggregate in DS-3 solution for 5, 11 and 23 months

3.2 X-ray diffraction

The results of the XRD analyses are summarised in Table 2. Fig. 4 shows the XRD traces for the limestone aggregate concretes exposed to Class DS-3 solution for 23 months. Thaumasite, along with calcium carbonate (calcite) and magnesium hydroxide (brucite) was readily identified in the PLC, OPC, OPC/PFA and SRPC samples. Gypsum was also present in OPC and SRPC. Gypsum, with traces of brucite, was the main product affecting OPC/GGBS but thaumasite was absent. As there was no clear sign of attack on these cubes, it is summarised that this gypsum was precipitated from the saturated solution rather than being formed as a degradation product. The XRD results for the siliceous aggregate concretes were similar to these for the limestone aggregates.

In Figure 5 the XRD traces for the surface products for the OPC/PFA concrete exposed to DS-3 solution for 5, 11 and 23 months, show a pattern of progressive degradation. Although some ettringite may have been present after 5 months, thaumasite rather than ettringite was clearly observed after 11 months, and an even greater amount, accompanied by gypsum, was present after 23 months. Crammond [13] reported that the results with binders containing PFA have been inconsistent, as such concretes were resistant in the field but did not always perform well under laboratory conditions.

In all cases the amount of thaumasite formed increased with the duration of immersion in sulfate solution. In addition to the phases identified in

Figures 4 and 5, aragonite, a low-temperature form of calcium carbonate, was identified in some cubes made with limestone aggregate.

Table 2 Phases observed by XRD in attacked surfaces after immersion for 5, 11 and 23 months. (NA = no attack, NI = not investigated)

| Binder | Class | Siliceous | | | Limestone | | |
|--------------|-------|------------|---------------|------------------|---------------|------------------|------------------|
| | | 5 m | 11 m | 23 m | 5 m | 11 m | 23 m |
| PLC | DS-2 | T,C | T, C, Q | T, Q, C, G | NA | C, T, Q | C, T, Q |
| | DS-3 | T, C | T, C, Q | T, C, G, Q, B | T, C | C, T, Q, B | C, T, G, Q, B |
| OPC | DS-2 | C, T | T, C, Q | C, T, Q | NA | C, T, Q | C, T, Q |
| | DS-3 | C, T | T, C, Q | G, C, Q, T, B | T, C | C, T, Q | C, T, G, Q, B |
| SRPC | DS-3 | C, T | C, T, B | G, T, C, B | NA | T, C, B, A, G | G, T, C, Q, B |
| | DS-4m | G, T | G, C, T, Q | G, T, C | T, G, Q, C | | G, T |
| OPC/ PFA | DS-3 | T, C, Q | T, C, Q, B | G, C, T, Q, B | T, C | C, T, G, B, A | C, T, G, Q, B |
| | DS-4m | T, C | T, G, Q, C | G, T, C, B | T, C | G, C, T, B | G, C, T, B, A |
| OPC/ GGBS | DS-3 | NA | NA | G, A, B | NA | NA | G, B |
| | DS-4m | NA | NA | G, A | NA | C, A, G, B | G, A, B |

T thaumasite, G gypsum, C calcite, Q quartz, B brucite, A aragonite

PLC, OPC - Control: NA; DS-4m: NI

SRPC, OPC/PFA, OPC/GGGBS - Control: NA; DS-2: NI

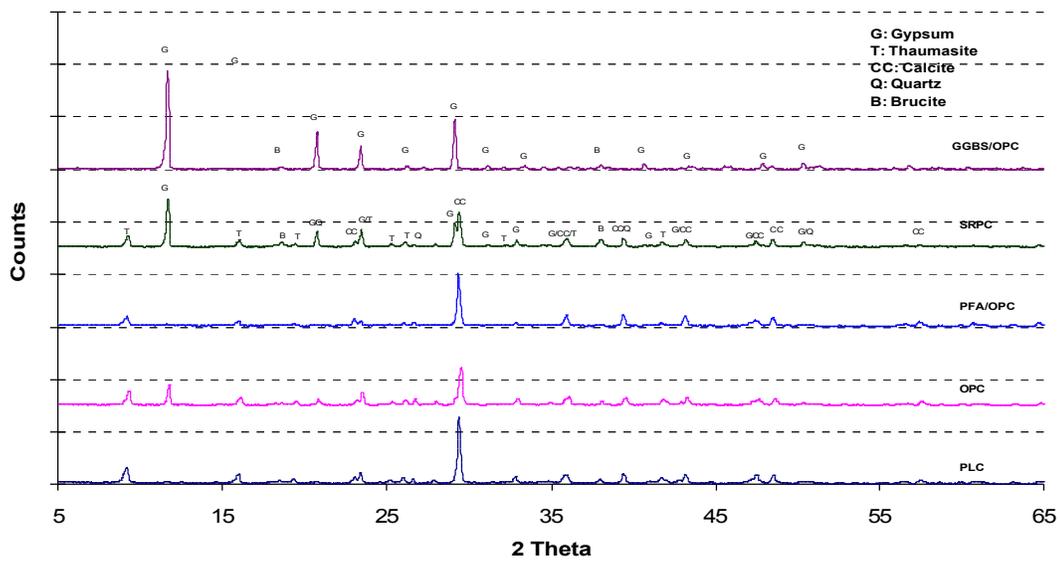


Fig. 4. XRD traces for surface products for DS-3 solution after 23 months

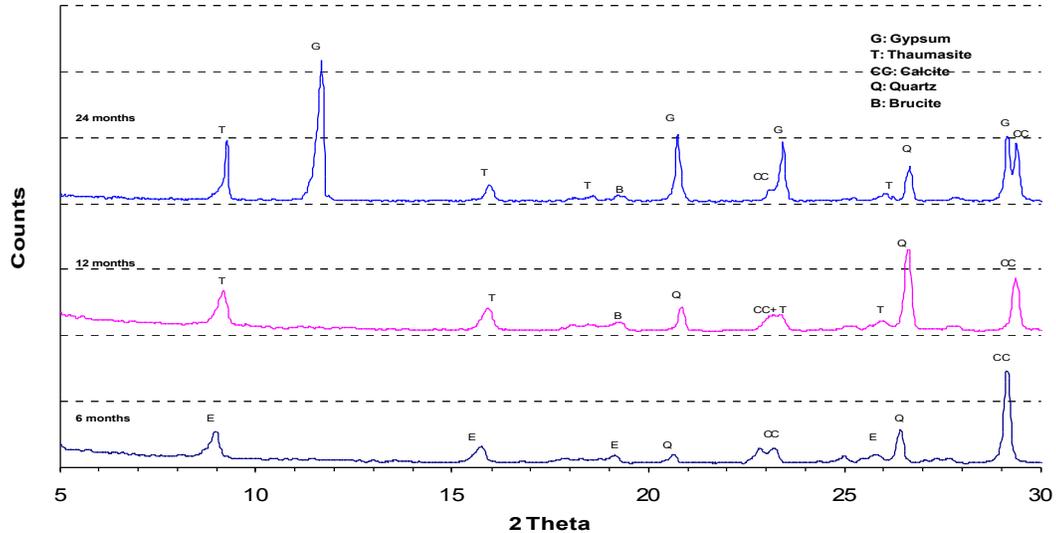


Fig. 5. XRD traces for surface products for OPC/PFA with siliceous aggregate in DS-3 solution for 5, 11 and 23 months.

3.3 Scanning Electronic Microscopy and Optical Microscopy

SEM and OM examinations of OPC/PFA with gravel aggregate in DS-3 solution for 11 months are shown respectively in Figs 6 and 7. SEM analysis (Fig. 6) shows progressive replacement of cement paste between the fine aggregate particles by thaumasite as the attack front advanced inwards, giving a 2-layer zone. Analysis for S, Si and Mg by EPS confirmed that both layers contained thaumasite and brucite.

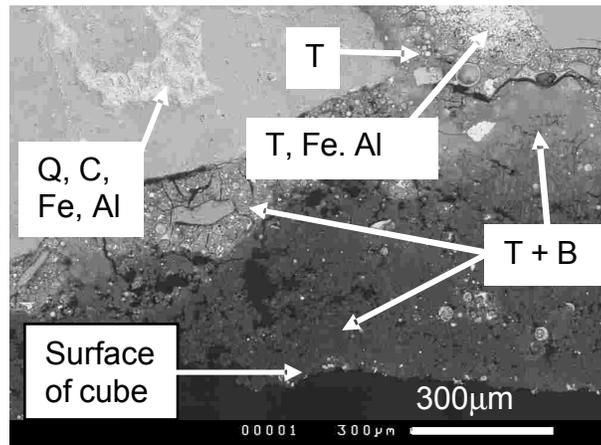
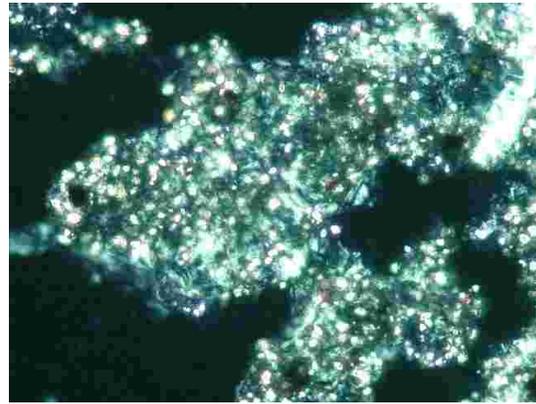
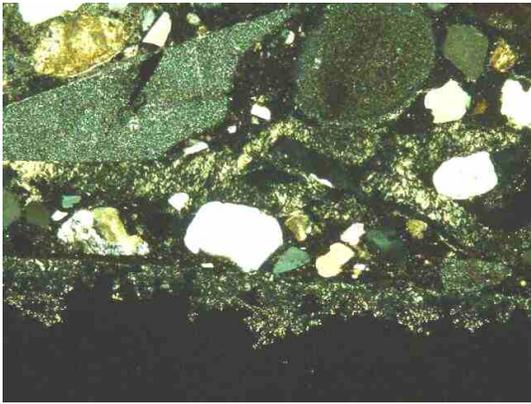


Fig. 6. SEM image of OPC/PFA with gravel aggregate in SD-3 solution for 11 months. (T = thaumasite, B = brucite, C = calcite)

Figure 7a is an OM photomicrograph of OPC/ PFA in which thaumasite appears as colourless to straw-yellow, needle shaped crystal on the attacked surface and between the aggregate particles which appear as uniform white or grey areas. Figure 7(b) shows “popcorn” calcite in which massive, coarse grains of calcite have formed by the precipitation around nuclei. A similar feature has been described by Sibbick and Crammond et al. [11]. Rosette-like calcite crystals are formed in a highly porous arrangement, thus making a friable cement paste matrix.



a) Thaumasite around aggregate grains and replacing cement paste b) Popcorn calcium carbonate (calcite) under cross polarised light

Figure 7 Optical photomicrographs (x 25 magnification) of TSA-affected OPC/PFA with siliceous aggregate in SD-3 solution for 11 months.

4. DISCUSSION

4.1 Portland limestone cement and ordinary Portland cement

TSA was particularly severe in PLC (20% limestone filler) such that at 24 months, a thick layer of reaction products was present. The exposed aggregate would provide an additional source of silica in gravel aggregate concretes, so an acceleration of the rate of reaction could be expected. Thus it was confirmed that of the binders tested, PLC possessed the least resistance to TSA at low temperature. Accordingly, great caution should be exercised in its use in sub-surface applications where sulfate bearing groundwaters are possible. In fact SD1 [6] advises against its use in these conditions. It was observed that OPC (5% limestone) also performed poorly with respect to TSA, although it was better than PLC. In view of this, as discussed by Torres et al. [12] and in spite of the assurance of the TEG report [1] that 5% limestone would not adversely affect the performance of OPC in concrete containing either siliceous or carbonate aggregate, OPC should be used cautiously in buried concrete liable to come into contact with groundwater as aggressive as the solutions used in these tests. This is important because European cement manufactures are not obliged to declare the presence of up to 5% filler in OPC and, although limestone filler can have advantages in concrete used above ground, the possibility of buried concrete being subject to aggressive conditions should be borne in mind.

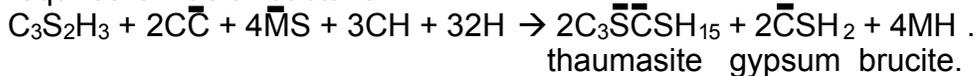
4.2 Portland cement with 25% PFA replacement

As indicated in Fig. 5, thaumasite had undoubtedly formed after 12 and 24 months without co-existing ettringite being detected by XRD and while

25% PFA provided a degree of short-term protection, TSA was not prevented.

“Popcorn” calcite was observed in OPC/PFA. This, and the presence of aragonite (Table 2), provides evidence for thaumasite formation via the through solution mechanism [13]. As discussed by Hartshorn et al. and Zhou et al. [8,14, 15], solid phases partially dissolve in the pore water providing the Ca, Si, CO₃ and SO₄ ions required for thaumasite formation. When the activities of these ions in solution reach the requisite levels, thaumasite can precipitate accompanied by gypsum, brucite (in the presence of Mg), and, sometimes, popcorn calcite or aragonite.

The protection against TSA afforded by the addition of PFA may be a dilution effect or it may have been associated with competing reactions to consume the portlandite produced – the pozzolanic reaction of PFA to form more C-S-H gel or the chemical reaction to form thaumasite which requires CH as a reactant:



4.3 Sulfate resisting Portland cement (SRPC)

The performance of SRPC warrants special attention as this is specifically designed for use in high-sulfate conditions. However, as TSA results from attack on the C-S-H gel as opposed to ettringite formation from the C-A-H and C-A-S-H phases present in the hydrated cement, SRPC is vulnerable. The formation of ettringite becomes more important at higher temperatures of around 20°C. In fact, Taylor [23], p374 states “Since the attack is on the silicate and not the aluminate constituents of the cement paste, sulphate-resisting Portland cement does not offer any special protection”. It is not surprising, therefore, that this study confirmed the vulnerability of SRPC to TSA, although less so than that for OPC. This observation is in line with BRE’s findings [13]. The greater resistance of SRPC may be related to the absence of any limestone, rather than to any chemical change in the base cement.

In view of the extensive use of SRPC in high sulfate conditions, this has important implications in the case of existing buried concrete structures. According to these results, the allocation of SRPC to Class SD1 DS-3, implying high resistance to TSA, would appear to be inappropriate.

4.4 Portland cement with 65% GGBS replacement

It has been confirmed by this investigation and other researchers [13, 16, 17] that incorporation of blastfurnace slag substantially improves the resistance of OPC to TSA. In the present study, even after two years

immersion in a highly aggressive solution, the only apparent effect was a white coating of gypsum, which might have precipitated from the storage solution. Four explanations for the excellent performance of OPC/GGBS have been advanced, although the phenomenon is not fully understood:

a. Lower permeability. Various studies have demonstrated that GGBS substitution lowers the permeability of concrete [10, 13, 18] which by restricting migration of reaction products, would reduce the rate of TSA. These observations conform with the well-accepted view [19, 20] that lowering permeability is more important than composition control in achieving sulfate resistance.

b. Lower pH With 65% replacement of GGBS, a lower pH of pore solution will result than for OPC alone. Although thaumasite should form if pH is above 10.5 [1, 13, 21, 22]; it does not form at low pH [7, 8].

c. Dilution Replacement of OPC by GGBS would provide less C-S-H gel and less limestone filler for reaction with sulfate.

d. Lack of portlandite A number of authors [12, 14, 21] have noted that portlandite is required as a reactant in thaumasite formation. The pozzolanic reaction in OPC/GGBS ensures that the level of CH is very much lower than that in OPC or PLC.

It is probable that a combination of these reasons is responsible for the good resistance to TSA.

4.5 Relative resistance to TSA of the various cements investigated

It is immediately evident from Figs 1 and 2 that PLC and OPC are highly vulnerable to TSA when immersed in Class DS-3 sulfate solution at 5°C. The XRD data (Fig. 3) establish that thaumasite is a major component of the degraded layers. The observation is similar to those made in several recent studies based at BRE, the University of Sheffield and elsewhere. However, the principal aim of the work was to investigate whether concretes made with other cements were less susceptible to TSA when cured and stored under identical conditions.

Overall, the deterioration decreased in the following sequence:

Limestone aggregate: PLC > OPC >> OPC/PFA ~ SRPC >> OPC/GGBS

Siliceous aggregate: PLC > OPC >> OPC/PFA > SRPC >> OPC/GGBS

Thus it is clear that OPC/PFA and SRPC are also vulnerable to attack in low-temperature, DS-3 conditions. The OPC/GGBS was apparently unchanged after immersion in Class DS-3 sulfate solution for 2 years (Figs 1 and 2) and examination by XRD failed to detect any thaumasite. As noted in Section 4.4, other workers [16, 17] have reported similar excellent resistance to TSA.

5. Conclusions

The main conclusions of this study are summarised below:

- PLC, OPC, SRPC and OPC/PFA all showed signs of significant chemical attack after 23 months exposure to DS-3 solution at 5°C.
- OPC/GGBS was effectively resistant to attack after 23 months exposure to DS-4m solution at 5°C.
- Overall, the deterioration of the cubes decreased as follows:
Limestone aggregate: PLC>OPC>>OPC/PFA ~ SRPC >>OPC/GGBS
- The results for the siliceous aggregate were similar to those for limestone aggregate, although the attack was less.
- Whereas the Expert Group specifically stated that 5% limestone would not adversely affect the performance of OPC in concrete containing either siliceous or carbonate aggregates, these results indicate high vulnerability at 5°C even for DS-2.
- It would appear to be inappropriate to use SRPC in buried concrete, especially if sulfate ions might be present at low temperatures.
- It is concluded that TSA occurs via a through solution mechanism due to high sulfate concentration (activity) and low-temperature.
- Portlandite is a reactant in the formation of thaumasite, which may partly explain why OPC/GGBS composite cement is resistant to TSA.

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