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An experimental study of combined acid and sulfate attackof concrete

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Abstract

There is disagreement about the role of sulfuric acid in the thaumasite form of sulfate attack (TSA) of concrete. Some researchers suggest that thaumasite is formed only at pH above 10.5, whereas others report that the primary cause of deterioration in the affected M5 bridge foundations was sulfuric acid attack followed by neutral TSA. The aim of this work is to reconcile these conflicting views by undertaking parallel studies of concrete exposed to aggressive acid and sulfate solutions and concrete/clay interface work using weathered Lower Lias clay.

Concrete specimens have been exposed to BRE Digest 363 sulfate class solutions and acidic and acidic-sulfate solutions at 4.5 ± 0.5 °C. Selected samples are being characterised at intervals up to 5 years. At this stage, results are reported for 5-month samples. Various binders including Portland cement, Portland–limestone cement, blastfurnace slag cement, pulverized-fuel ash cement and sulfate-resisting Portland cement at water/binder ratios (w/b) from 0.35 to 0.5 have been studied.

Initial visual observations and X-ray diffraction analyses have identified thaumasite in some of the systems after 5 months immersion in solution.

An overview of the ongoing parallel concrete/clay interaction work is also presented to contextualise the concrete work.

Keywords: Sulfate attack; Acid attack; Ettringite; Thaumasite; X-ray diffraction

1. Introduction

The thaumasite form of sulfate attack (TSA) has recently emerged as a major concrete deterioration mechanism (especially in England) both in the field [1–5] and in laboratory studies [6–9]. Thaumasite has occasionally been found as deterioration product in various cement-based construction materials subjected to sulfate attack for around 30 years [10] but it is only relatively recently that its occurrence has been found to be widespread. Whilst thaumasite has been synthesised in the laboratory [11–13], very little is fully understood about the relative importance of the reactants, environment, rate of formation or the concomitant long-term effects on structures in the ground.

The Thaumasite Expert Group [1] concluded that the formation of thaumasite requires the presence of calcium silicate, sulfate ions, carbonate ions and a wet, cold (<15 °C) environment. However, the exact chemical conditions required are subject to some disagreement in the literature. Gaze and Crammond [6] believe that thaumasite does not form at pH less than 10.5 but, once formed, it can remain in contact with solutions with pH as low as 7, although there is evidence from the study reported in the following pages that pH values lower than this can be tolerated. On the other hand, Hobbs and Taylor [3] concluded that microstructural observations of concrete in TSA-affected bridge foundations were consistent with sulfuric acid attack being the primary cause of deterioration. They postulated that pyritic oxidation within the backfill led to the formation of sulfuric acid, reducing the pH of the groundwater and resulting in attack on the foundations.

This paper presents selected preliminary results from a study that aims to resolve these issues by characterising the products of combined acid and sulfate attack on concrete. The visual observation and X-ray diffraction results of concrete samples made with various binder combinations and subjected to a series of sulfate and acidic sulfate solutions for 5 months are reported and discussed.

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2. Laboratory studies

2.1. Cementitious binders and concrete mixes

Concrete mixes were prepared using Portland cement (OPC), Portland–limestone cement (PLC), sulfate-resisting Portland cement (SRPC), OPC/blastfurnace slag (GGBS) 65% and OPC/pulverized-fuel ash (PFA) 25% (Table 1). It should be noted that all cements, with the exception of PLC and SRPC, contain 5% limestone filler. Thames Valley gravel aggregate was used for both coarse and fine fractions.

2.2. Specimen preparation and exposure

Hundred millimeter concrete cubes were cast to BS 1881 [15], left for 18 h under wet hessian sheeting, demoulded and then individually double wrapped to simulate ground conditions. These were then placed in a mist room at around 95% RH and 21 °C for 28 days. After curing the cubes were unwrapped and transferred to their designated solutions (see Table 2) in exposure tanks maintained 4.5 ± 0.5 °C (Fig. 1). The "acidified solutions" quickly increased in pH through the release of alkalis and portlandite from the cubes. Acid was added every week to reduce the pH to below 4, while all the test solutions were renewed every three months.

2.3. Concrete testing

At the age of 6 months (5 months in solution) the samples were removed and individually photographed. Samples of any degradation product were removed and left to air-dry prior to grinding for powder X-ray diffraction.

2.4. X-ray diffraction

The dried samples were ground by hand to a fine powder of <63 μm using an agate mortar and pestle. The powder was packed into back-filled sample holders (to minimise preferred orientation) for use in a Philips 1710 X-ray diffractometer using monochromatic CuKα radiation operating at a voltage of 50 kV and current of 30 mA. A scanning speed of $2° \ 2\theta \ \mathrm{min}^{-1}$ and a step size of 0.02° were used to examine the samples in the range of $5–65° \ 2\theta$ to cover the phases under investigation.

Table 2
Test solutions

BRE Digest 363 [14] class	Solution
Control	Saturated $Ca(OH)_2$ solution
Class 2	$CaSO_4$ (1.4 g/l SO_4)
Class 3	$CaSO_4$ (1.4 g/l SO_4) + $MgSO_4$ (1.6 g/l SO_4)
Class 4B	$CaSO_4$ (1.4 g/l SO_4) + $MgSO_4$ (4.6 g/l SO_4)
Class 3 acid	$CaSO_4$ (1.4 g/l SO_4) + $MgSO_4$ (1.6 g/l SO_4) + H_2SO_4 (to pH 4)
Acid	H_2SO_4 (to pH 4)

Fig. 1. One of the four sulfate/acid solution exposure tanks maintained at 4.5 °C.

3. Results and discussion

3.1. Visual observations

The most extreme visual examples of attack observed in each solution are shown in Fig. 2.

Table 1
Concrete mixes, w/b ratios and test solutions

Cement type	Aggregate	Free w/b	Limestone filler (%)	BRE Digest 363 [14] class solutions
OPC	Gravel	0.50	5	Control, 2, 3, acid
PLC	Gravel	0.45	20	Control, 2, 3, acid
PC/GGBS 65%	Gravel	0.45	5	Control, 2, 3, 4B, 3 acid, acid
	Gravel	0.35	5	3 acid
PC/PFA 25%	Gravel	0.45	5	Control, 2, 3, 4B, 3 acid, acid
SRPC	Gravel	0.45	0	Control, 2, 3, 4B, 3 acid, acid
	Gravel	0.35	0	3 acid

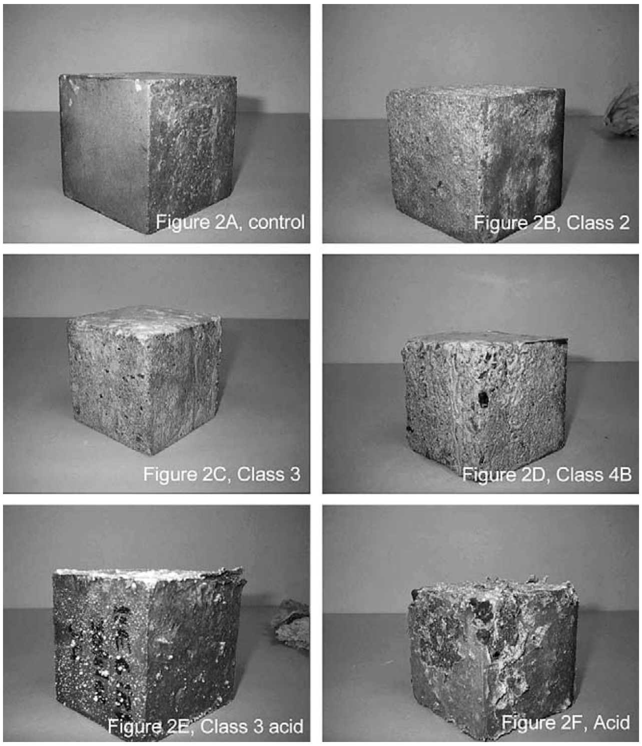

Fig. 2. Worst case examples of concrete degradation observed with a range of binder types in various test solutions after 5 months.

3.1.1. Control

There were no signs of attack upon any of the concrete specimens stored in saturated $Ca(OH)_2$. Fig. 2A is indicative of all the concrete samples stored in this solution.

3.1.2. Class 2

On both OPC and PLC concrete cubes a white mushy substance was evident on most faces, indicating slight attack. Also, in the PLC sample (Fig. 2B), aggregate was exposed on most faces.

3.1.3. Class 3

OPC, PLC, PFA and SRPC concretes had a white mushy substance on the top surface of the cubes and exposed aggregate on all faces, whereas GGBS concrete showed no signs of any attack. An OPC sample is shown in Fig. 2C. SRPC concrete was less affected than OPC and PLC concrete in that the mushy layer was not as thick and the aggregate was less exposed.

3.1.4. Class 4B

No OPC or PLC concrete was stored in this solution since these cements are considered to be susceptible to this environment [14]. The PFA (Fig. 2D) and SRPC samples showed similar but greater levels of attack compared to those stored in Class 3 solution. Again, and notably, the GGBS concrete did not show any signs of attack.

3.1.5. Class 3 acid

All samples stored in this environment (GGBS, PFA, SRPC) showed some signs of attack, which was of a different form to that observed for cubes stored in Classes 2, 3 and 4B. Blistering, spalling and aggregate exposure occurred to some extent in all these samples, but the cubes remained essentially intact. GGBS concrete was least affected, but the samples containing PFA (Fig. 2E) and SRPC showed blistering on all faces. Some of these blisters were deep and a white substance was present within. Spalling appeared to start at the corners and edges of the cubes.

3.1.6. Acid

The OPC and PLC concretes showed quite severe blistering with a white substance within the blisters, which was most severe with PLC concrete (Fig. 2F). The form of attack in the acid solution was similar to that observed in Solution E, but greater differences between the different concretes were observed in this solution. Similar attack was seen in the PFA concrete but was not as severe as was found with Class 3 with added sulfuric acid). Both the SRPC and GGBS samples were intact, although the SRPC concrete showed signs of slight attack starting along the edges. Uniquely to the GGBS concrete, yellow crystals were observed forming on the cube faces, but not yet in sufficient quantity to analyse.

There were two features common to all the samples stored in acidic solutions. The samples were orange/brown as opposed to grey as with other solutions, and gypsum crystals (which looked like very fine hairs) were observed on the intact surfaces of all cubes.

3.1.7. Summary

It was observed that GGBS concrete, followed by SRPC concrete, suffered less degradation than concrete made with other binders. All other samples had been attacked sufficiently to expose the aggregate on the cube faces, except in the control solution. The worst attack appeared to occur in the acid solutions. The X-ray diffraction (XRD) study, discussed below, was carried out to characterise the products formed as a result of sulfate and acid–sulfate attack.

3.2. X-ray diffraction

It should be noted that the preliminary results discussed below were obtained from samples exposed to aggressive solutions for only 5 months. The material from the core of the cubes was comprised primarily of quartz, calcite, gypsum, portlandite and ettringite. The XRD patterns, shown in Figs. 3–7, were obtained from samples scraped from the surface of the cube or from

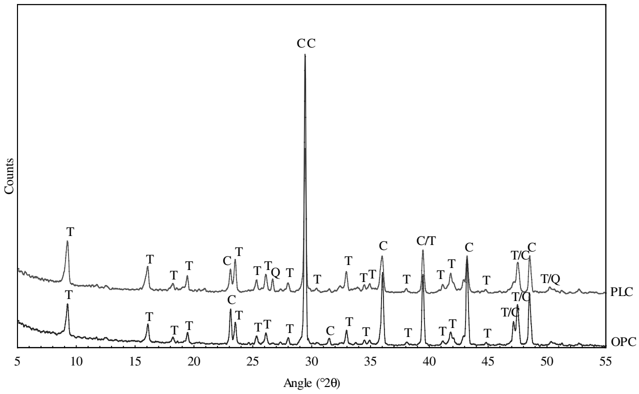

Fig. 3. XRD traces of surface products observed in concrete exposed to Class 2 conditions.

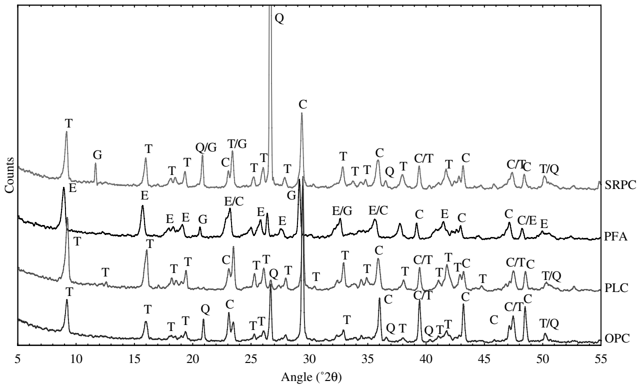

Fig. 4. XRD traces of surface products observed in concrete exposed to Class 3 conditions.

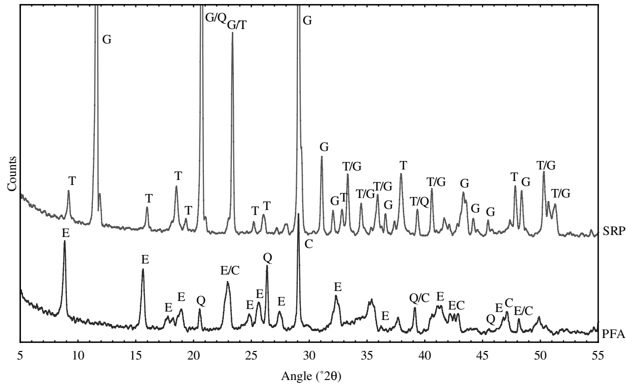

Fig. 5. XRD traces of surface products observed in concrete exposed to Class 4B solution.

material in surface blisters. Although most of the reaction products are likely to remain the same, it is possible that new or modified products may be observed as the project progresses. There are, for example, no XRD patterns available yet for cubes stored in the control solution as there has been no degradation of the cube.

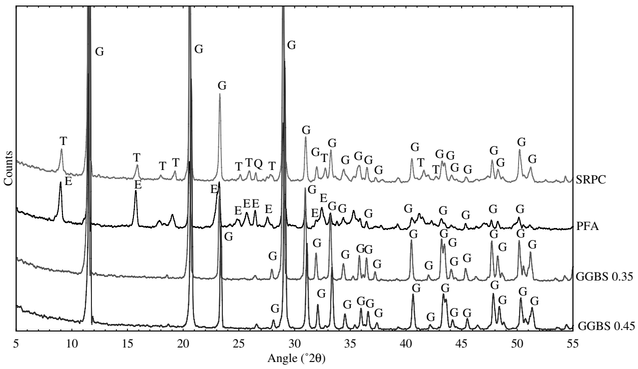

Fig. 6. XRD traces of surface products observed in concrete exposed to Class 3 (acid).

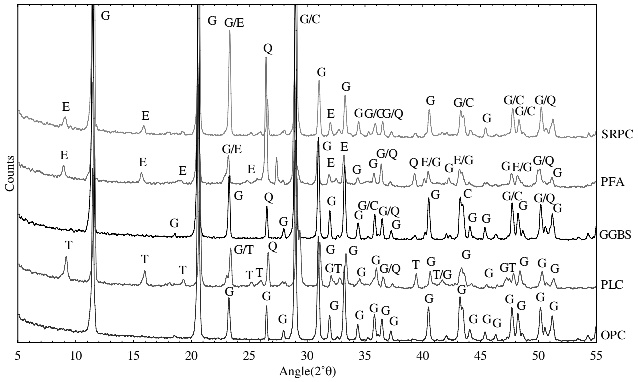

Fig. 7. XRD traces of surface products observed in concrete exposed to acid.

The XRD patterns obtained from the degradation products of the OPC and PLC concrete cubes after 5 months storage in Class 2 conditions containing $CaSO_4$ are shown in Fig. 3 (T = thaumasite, E = ettringite, G = gypsum, C = calcite, Q = quartz). Both samples consisted primarily of thaumasite and calcite. The same result can be seen for these samples when stored in Class 3 solution (Fig. 4). The SRPC concrete not only contained thaumasite and calcite, but also some gypsum and quartz, the latter from the fine aggregate. The relatively high quartz peak at around 26.5° 2θ is due to more aggregate being incorporated into this particular XRD sample. The PFA concrete contained ettringite, not thaumasite, as illustrated by the *d*-spacings of the peaks shown in Fig. 4, especially between 18° and 29° 2θ. The *d*-spacing values of the strongest peaks for ettringite and thaumasite are very close (9.73 and 9.59 Å respectively) and can lead to misidentification. It is clear, however, that ettringite and thaumasite do not co-exist in any results reported here.

GGBS concrete showed no deterioration in Classes 3 and 4B. It can be seen from Fig. 5 that, as with Class 3, PFA concrete stored in Class 4B showed ettringite, not thaumasite, formation. Although there was no detectable amount of thaumasite present, the concrete was quite deteriorated. Hence the XRD specimen unavoidably contained some fine aggregate, identified as quartz. The SRPC concrete contained thaumasite and also strong peaks attributable to gypsum.

The results of the samples stored in Class 3 acid are shown in Fig. 6. With GGBS very little attack had taken place and neither ettringite nor thaumasite observed, only gypsum. The PFA concrete contained only ettringite and gypsum, whereas the SRPC concrete contained thaumasite and gypsum. The most notable observation is that there is much more gypsum present in these samples than had been observed in those stored in Class 2, 3 and 4b conditions.

A full set of results for samples stored in sulfuric acid is shown in Fig. 7. As for Class 3 acid, gypsum was abundant at the expense of calcite in all the samples. Quartz was also present in some of the samples but there was no evidence of either thaumasite or ettringite in either the OPC or GGBS concrete samples. The PLC concrete, however, showed evidence of thaumasite but no ettringite, whereas both the PFA and SRPC concretes contained ettringite but no thaumasite.

The phases identified in the degraded surface layers in the various test solutions, arranged in order from alkaline to acid conditions, are summarised in Table 3. The clear trend is that thaumasite and calcite are dominant in Classes 2 and 3, whereas gypsum is dominant in Class 3 acid and the acid solution and is more likely to be accompanied by ettringite than by thaumasite. Thus ettringite was observed in only one concrete (that made with PFA) out of the seven stored in alkaline sulfate-rich solutions, Classes 2 and 3, while thaumasite was observed in only two out of the nine systems stored in the acidic solutions (neither ettringite nor thaumasite was detected in four of these systems). Except for these four systems, which will be closely monitored as the project progresses, thaumasite was detected when ettringite was not, and vice-versa. In no system was there evidence for the presence of both ettringite and thaumasite, although that possibility is not entirely ruled out, nor is the possible presence of solid solutions based on thaumasite–ettringite as reported recently by Barnett and coworkers [9,13].

4. Further discussion

The evidence obtained to date does not support the hypothesis [3] that thaumasite formation is favoured by the combination of acid and sulfate in the storage solution. The dominant reaction that takes place in the presence of sulfuric acid is the conversion of calcite to gypsum according to the equation:

$$CaCO_3 + H_2SO_4 + H_2O = CaSO_4 \cdot 2H_2O + CO_2$$

This is a standard acid–base reaction and leads to the observation of large amounts of gypsum as observed in both acid solutions. The only instance of thaumasite formation observed to date in acid solution is in PLC

Table 3
Summary of the phases identified by XRD

Solution	Cement	w/b	Ettringite	Thaumasite	Gypsum	Calcite
Control	OPC	0.5	–	–	–	–
	PLC	0.5	–	–	–	–
Class 2	OPC	0.5	×	✓	×	✓✓✓
	PLC	0.45	×	✓	×	✓✓✓
Class 3	OPC	0.5	×	✓	×	✓✓
	PLC	0.45	×	✓	×	✓✓
	SRPC	0.45	×	✓	✓	✓
	PFA	0.45	✓	×	×	✓
	GGBS	0.45	–	–	–	–
Class 4B	SRPC	0.45	×	✓	✓✓✓	×
	PFA	0.45	✓	×	×	✓
	GGBS	0.45	–	–	–	–
Class 3 acid	SRPC	0.45	×	✓	✓✓✓	×
	PFA	0.45	✓	×	✓✓✓	×
	GGBS	0.45	×	×	✓✓✓	×
	GGBS	0.35	×	×	✓✓✓	×
Acid	OPC	0.5	×	×	✓✓✓	×
	PLC	0.45	×	✓	✓✓✓	×
	SRPC	0.45	✓	×	✓✓✓	×
	PFA	0.45	✓	×	✓✓✓	×
	GGBS	0.45	×	×	✓✓✓	×

Peak intensity: ✓✓✓ = strong, ✓✓ = medium, ✓ = weak, – = no degradation, × = not identified.

concrete, which presumably has sufficient limestone to maintain enough carbonate ions in solution to form thaumasite by a through solution mechanism. In Class 3 acid (which contains sulfuric acid, calcium sulfate and magnesium sulfate) thaumasite was identified in SRPC concrete, which suggests that this form of cement is particularly vulnerable to TSA. The concrete cubes on which this tentative conclusion is based will also be monitored particularly carefully. The instability of thaumasite in acid solution has been suggested previously by Gaze and Crammond [6] and is hardly surprising since thaumasite itself may be a weak base that could react with sulfuric acid according to the equation:

$$\begin{aligned}&CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O + 2H_2SO_4\\&\quad = 3CaSO_4 \cdot 2H_2O + SiO_2 + CO_2 + 11H_2O\end{aligned}$$

As shown, the major product of this reaction is again gypsum, explaining why this phase totally dominates the XRD patterns shown in Figs. 6 and 7. Some of these patterns, such as those from samples obtained from the GGBS concrete, show only XRD peaks attributable to gypsum. There is, of course, a high concentration of sulfate ions in these solutions. So it would appear that it is neither acidic conditions nor high concentration of sulfate ions *alone* that brings about the formation of thaumasite, but the combination of relatively high sulfate levels and neutral or alkaline conditions. The equation predicts the formation of silica, presumably in the form of an amorphous silica gel. Such a phase has not previously been reported as a product of sulfate attack, and evidence for its presence will be investigated in future work. Interestingly, however, some very recent results from cubes exposed to acidic solutions for 12 months (not shown here) also show the continuing presence of some thaumasite and this phenomenon, as well as the rate at which thaumasite decomposes in acidic conditions, also needs to be investigated in order to fully explain the reactions taking place.

The differences between the behaviour of the individual cements were fairly predictable. Concrete cubes made from PLC formed thaumasite in all the solutions in which they were placed, including the one containing acid. Cubes made using OPC (incorporating 5% limestone filler) and SRPC (with no added limestone) also readily gave rise to thaumasite formation, except in acid solution. In contrast, the cubes containing PFA and GGBS did not produce thaumasite. Instead PFA concrete formed ettringite, while GGBS concrete formed neither ettringite nor thaumasite in solutions containing acid (GGBS concrete had not deteriorated enough for samples to be taken in neutral or alkaline conditions). The observed behaviour of the GGBS concrete may be attributed to the dilution effect brought about by the high (65%) replacement level. That of the PFA concrete (with only 25% replacement) is tentatively attributed to a competition for hydroxyl ions between the pozzolanic reaction of the PFA especially during the first 28 days curing at 20 °C, and the reaction to form thaumasite which Hartshorn et al. [7] have shown consumes portlandite. If this hypothesis is correct, the behaviour of PFA concrete would be different (i.e. more likely to form thaumasite) if it was cured for only 24 h before being placed in the sulfate-containing environment at 5 °C.

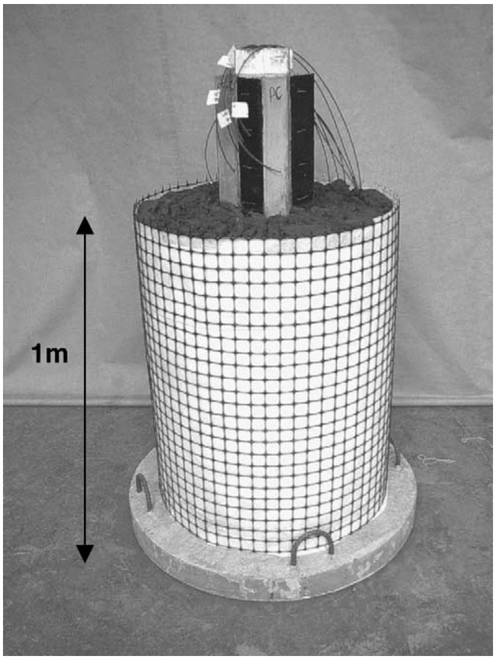

Fig. 8. Weathered Lower Lias clay concrete foundation simulation prior to being immersed in chilled water tank.

5. Parallel concrete/clay interaction studies

Unique large-scale clay/concrete interface experimental tests using weathered Lower Lias clay in direct contact with plain and bitumen-coated PC, SRPC, PLC and PC/PFA concrete at 4.5 °C are also being carried out at the Centre for Cement and Concrete (Fig. 8). Measurements of the types of compounds formed at the concrete surface and radial changes in clay pH and chemical composition are being made.

The results from this study will be published elsewhere and will be used to understand the significance of the early-age concrete immersion study reported in this paper to the site scenario.

6. Conclusions

1. Sulfate and acid attack of the cubes appeared to start at the edges and corners in all solutions.

2. Visually, acid solutions appeared to cause the greatest amount of deterioration of the surface of the cubes.
3. Thaumasite has been identified in samples with only 5% limestone filler present and also in SRPC where there was no limestone filler present in all solutions except acid.
4. The presence of gypsum increased and, conversely, calcium carbonate decreased, when acid was present.
5. Visual observations indicated that PFA concrete was attacked but ettringite, rather than thaumasite, was formed.
6. GGBS concrete appeared to resist attack in all solutions and did not form detectable amounts of thaumasite.
7. Initial results suggested that the presence of acid does not seem to promote the formation of thaumasite.

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