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The resistance of metakaolin (MK)–Portland cement (PC) concrete to the thaumasite-type of sulfate attack (TSA)—Programme of research and preliminary results

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Abstract

The thaumasite form of sulfate attack (TSA), is a deleterious physico-chemical attack of the calcium silicate hydrate (C–S–H), binding phase of concrete. Water:binder ratios (w:b), are known to control ingress of potentially deleterious ions by pore structure refinement at low (0.40) values. Equally, a physical–chemical barrier exists at about w:b ratio of 0.45 regardless of the binder type. The inclusion of ultra-fine pozzalans (e.g. metakaolin) in the binder has been shown to impart such properties through densification of the matrix and removal of calcium hydroxide.

A small-scale experimental design programme to establish the potential resistance of metakaolin–Portland cement (MK–PC), blended concrete to the thaumasite-type of attack is ongoing. Results are presented for concrete incorporating dolomitic limestone aggregate and with 0% and 7% metakaolin replacement of a high-C_3A PC binder at w:b ratios to 0.40 and 0.46. Exposure to three environments containing a sulfatic clay, sulfate solution and water has produced evidence of deleterious reactions within these samples. Visual data are quantified by a wear rating and supported by compressive strength and expansion values for up to 280 days of exposure. These results confirm the importance of low water binder ratios in the resistance of ion ingress and give an early indication of the desirable durability-enhancing properties of MK replacement of PC. Finally, the results also show that the two sulfatic environments of exposure produce marked differences in the degradation modes, which may be important in the methodologies used to determine TSA in the laboratory with reference to field observations.

Keywords: Durability; w:b ratios; Metakaolin; Thaumasite and resistance

1. Introduction

Sulfate attack including the thaumasite-type (TSA) is described by a complex physico-chemical system [1,2]. One approach to advancing knowledge and understanding of deleterious sulphatic processes is to seek to define the variables and mechanisms that contribute to a cementitious material's durability [3].

As a singular variable, durability is most dependent upon the water:binder ratio (w:b) and its associated relationship to porosity and pore structure [4,5]. Resistance to the ingress of ions is acquired where low permeability and porosity effectively create an impervious barrier. Capillary pores are known to contribute most to permeability for which a reduction in size and an associated segmentation of the connectivity occurs at a w:b ratio of 0.40. Critically for increasing w:b, the total pore structure must occupy a volume <40% of the total hydration volume for effective impermeability, achievable either by a decrease in free-water or an increase in binder content. For any binder type a physico-chemical threshold in the resistance to deleterious reactions also occurs around a w:b of 0.45. Below this value resistance is influenced principally by pore structure development and the hydrated binder's physical characteristics, whilst above 0.45 resistance becomes a function mainly of its' chemistry. This is critical in that to date most research work has been conducted at w:b ratios >0.45 [4].

Pozzalanic-Portland cement (PC) blends as binders in concrete are of increasing significance in producing durable cementitious materials [6–8]. Laboratory

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investigations [9] and field trials [10] of the pozzalan Metakaolin (MK) as a PC replacement, have established both enhanced physical and chemical properties associated with improved durability.

Physically, densification of the hydration products within the matrix occurs as a function of MK's finer particle size relative to that of PC, resulting in pore structure refinement. Though apparently contradictory, an increasing inclusion of a pozzalan increases the total pore volume with no apparent detriment to impermeability [5]. Resistance to the ingress of sulfate ions is reported, as is a decrease in ion diffusivity. Both reflect an associated suppression of the water absorption capacity of metakaolin blended materials demonstrated by their reduced sorptivity [11].

Pozzalanic hydration reactions are described in the literature [12,13] in which calcium hydroxide (CH), from PC hydration is consumed in the formation of C–S–H gel. The significance of CH removal and the potential chemical durability of MK–PC blended materials where TSA may occur is highlighted by the recent work of Hartshorn et al. [14]. Bensted [15] describes the typical route of thaumasite formation by Si substitution of Al in ettringite by interaction with C–S–H gel in the presence of CO_3^{2-} within a cold, wet environment:

$$C_3A\cdot 3C\overline{S}\cdot H_{32} + C_3S_2H_3 + 2C\overline{C} + 4H$$
$$\Rightarrow 2(CS\cdot C\overline{C}\cdot C\overline{S}\cdot H_{15}) + C\overline{S}H_2 + AH_3 + 4CH$$

This mode of attack involves CH as a reaction product which Hartshorn's work disputes by proposing a necessary reactant role in the formation of delayed thaumasite in PC–limestone pastes. For samples incorporating fine limestone as a source of CO_3^{2-} ions and exposed to 1.8% SO_4^{2-} solution, thaumasite forms following C_3A conversion to ettringite, with secondary gypsum and brucite also formed by through solution reactions. This not only accounts for the reactant role for CH but also the suppression of the pH to destabilise the C–S–H gel necessary for TSA to follow. The complete reaction is described as:

$$C_3S_2H_3 + 3CH + 2C\overline{C} + 4M\overline{S} + 32H$$
$$\Rightarrow 2(CS\cdot C\overline{C}\cdot C\overline{S}\cdot H_{15}) + 2C\overline{S}H_2 + 4MH$$

At replacement levels of PC by MK in excess of 15% the availability of CH is severely restricted with a predicted associated increase in chemical resistance to TSA for MK–PC blended concrete [9].

In both conventional sulfate attack [16] and TSA [17] the associating cations are known to influence the severity of the distress to the exposed concretes, with Mg ions that may be sourced from dolomitic limestone aggregates being of concern. Significantly, such reactive aggregates also raise the potential for alkali-aggregate reactions (AAR) to occur, in which interaction with high pH alkali hydroxide pore solutions produce expansive reaction products including viscous gels. Classically, for argillaceous dolomitic limestones dedolomitisation occurs in which brucite, calcite and alkali carbonates are the products. Subsequent reaction of the carbonates with calcium hydroxide regenerates the alkali hydroxides to further the reaction as described below:

$$CaMg(CO_3)_2 + 2(Na,K)OH$$
$$\Rightarrow Mg(OH)_2 + CaCO_3 + (Na,K)_2CO_3$$
$$(Na,K)_2CO_3 + Ca(OH)_2 \Rightarrow CaCO_3 + 2(Na,K)OH$$

AAR is influenced by the alkali content of the pore solution primarily as a function of binder composition. Also the pore structure and volume control the water ingress and subsequent hydraulic regime, in which the ions and water interact. In addition external environmental factors including temperature and humidity also play an important role in AAR [18].

The objectives of the current research programme are:

- To establish the resistance of MK–PC blended concrete to TSA.
- To discern the physical and chemical resistance of cementitious materials at w:b above and below the theoretical threshold of 0.45.
- To contribute to the understanding and knowledge of the modes and mechanisms of TSA.

2. Materials

Table 1 gives the physical and chemical properties of the components of the concretes studied.

The incorporated aggregate is dolomitic limestone and the binders are PC, PC partially replaced with 7%, 14% and 21% MK and PC replaced with 80% ggbs by mass. The phase composition of the PC is 49% C_3S, 23% C_2S, 11% C_3A and 6% C_4AF, determined by the Bogue equations.

A sulfatic Lower Oxford clay (LOC), to which the various concretes are exposed has a potential total sulfate content of 6.12%. Its mineral composition is given in Table 2 and its sulfur and sulfate content, determined to BS 1047, are reported by Thomas [19] as respectively 2.45% and 0.97%. It should be noted that Thomas [19] reported a very rapid rise in sulfate content when the moist LOC was mixed with 2% lime, as a result of the rapid oxidation of the pyrite in an alkaline environment.

3. Experimental

A small-scale, laboratory experimental design was devised to facilitate a large number of mix design combinations and sample points. Both visual assessment and

Table 1
Physical and chemical properties of the component materials

Material	% Analysis													
	SiO_2	Al_2O_3	Fe_2O_3	Mn_2O_3	TiO_2	CaO	MgO	SO_3 total	CO_2	K_2O	Na_2O	LOI	IR	s.s. (m^2/kg)[e]
Dolomite l/st[a]	2.0	0.7	1.4	–	–	29.9	20.4	–	–	–	–	–	–	–
PC[b]	20.9	5.5	2.1	0.04	0.26	64.9	0.9	3.0	0.9	0.54	0.19	1.3	0. 45	350
MK[c]	52.1	41.0	4.32	–	0.81	0.07	0.19	–	–	0.63	0.26	0.6		12 000
ggbs[d]	35.5	12.0	0.4	8.0	–	42.0	8.0	1.2	0.2	–	–	–	0.3	450

[a] Provided by Hanson Aggregate, Aberdare.
[b] Provided by Blue Circle Technical Centre.
[c] Provided by Imerys Ltd., St. Austell.
[d] Provided by Civil and Marine Slag cement UK.
[e] Specific surface.

Table 2
Mineralogy of Lower Oxford clay

Mineral	Quartz	Illite	Kaolinite	Calcite	Feldspar	Chlorite	Organic	Pyrite	Gypsum
% Content[a]	29	23	10	10	8	7	7	4	2

[a] Provided by Hanson Brick Co., Stewartby.

analytical tests have been carried out on concrete samples with w:b ratios of 0.40 and 0.46 and exposed to water, sulfate solution and the sulfatic LOC at 5 °C, and these tests are ongoing. Sample sizes and the associated data determinations are given in Table 3.

Trial mixes with a minimum binder content of 450 kg/m^3 as recommended by the Thaumasite Expert Group [17] were conducted and the final mix composition selected (based upon satisfactory workability to give full compaction on a vibrating table using no superplasticiser) was 1 binder:1 coarse aggregate (6.3 mm):0.5 medium aggregate (5.0 mm):1 fine aggregate (<2.36 mm). Mixing and casting of the samples was carried out to BS 1881 part 125 [20]. After 24 h they were demoulded, wrapped in clingfilm and moist cured for 14 days prior to placing in the three different environments of exposure. The European prestandard for sulfate exposure, pr ENV 196-X [21], was modified to include 're-seeding' of the sulfate ions to the original concentration at 100 day intervals, which reduces the disturbance of the chemical system thus allowing potential secondary reactions to proceed unhindered. Samples exposed to clay were kept in a saturated environment by inclusion of a small reservoir of deionised water at the base of and in contact with the clay mass, whilst the control samples in water were left undisturbed.

All the samples were placed in appropriate sealable containers at 5 ± 5 °C which enabled a 'unit' volume of exposure equivalent to 0.005 ml of solution to 1 mm^3 of concrete for those placed in water and sulfate solution. Similarly, in the clay a 'cell' volume of exposure of between 3–5 mm^3 per mm^3 of the concrete sample was achieved. At 28, 56, 112, 196 and 280 days of exposure samples were assessed as described in Table 3. The wearing value, $W = \sum$ loss of diagonals $(mm)/8$ is determined after Harrison who used the value of W to assess the degree of sulfate resistance [22]. The criteria are; $W \geqslant 5$ poor sulfate resistance, $W \geqslant 2$ but <5 satisfactory resistance and $W < 2$ good sulfate resistance for one year of exposure. Compressive strength values for 25 mm cubes were determined on a Instron 8502 with a loading rate of 11.2 kN/min, equivalent to the BS 1881 part 116 loading rate of 0.3 N/(mm^2 sec), and expansion of the 20×20×160 bars was determined to 0.002 mm

Table 3
Sample sizes with appropriate visual and/or analytical determinations

Sample size (mm)	Visual assessments and analytical determinations
20×20×160 bar	Expansion, mass and qualitative visual assessment
50×50×50 cube	Qualitative visual assessment, wearing value, mass, density and surface voids
25×25×25 cube	Qualitative visual assessment, compressive strength, mass and density
20×20×18 tablet	Qualitative visual assessment and dried at 40 °C over silica gel to constant mass wrapped in cling film and stored in airtight containers as reserve samples. Samples for TG, SEM, XRD and petrographic analysis are taken from all samples as appropriate

using a comparator. Each expansion value and each strength value is the average for three separate specimens. Data are presented for concretes with 100% PC and 93% PC–7% MK as binders and with w:b ratios of 0.40 and 0.46 as it is these samples that are currently showing significant physical and chemical responses to the environments of exposure. Another three concretes with binders containing respectively 14% MK, 21% MK and 80% ggbs, also with w:b ratios of 0.40 and 0.46 are not yet showing evidence of deleterious reactions.

4. Results and discussion

The visual assessments are summarised in Table 4. For those cubes exposed to water, physically there is no loss of external integrity, though significantly there is evidence of deleterious reaction(s) manifest by the presence of a 'gel' on the cube surfaces. The development of this 'gel' (as shown in Fig. 1) is substantial in the 25 mm cube size samples for concrete with PC binder and PC–7% MK binder and particularly for the concretes with w:b 0.40 where extrusion is a function of a smaller pore volume. Similar evidence for gel development is not apparent in 14% MK, 21% MK and 80% ggbs concretes. Thermogravimetric analysis and transmission electron microscopy with EDAX analysis shows that the gel is essentially an alkali carbonate gel. The percentage mean cation composition of the dried gel (from six separate particle analyses) is 79.5% Ca, 14.3% K, 2.7% Na, 1.8% Al, 1.3% Si with negligible amounts of Mg. Values varied between 66–99% for Ca, 4–22% for K, 1–5% for Na, 1–3% for Al and 1–2% for Si.

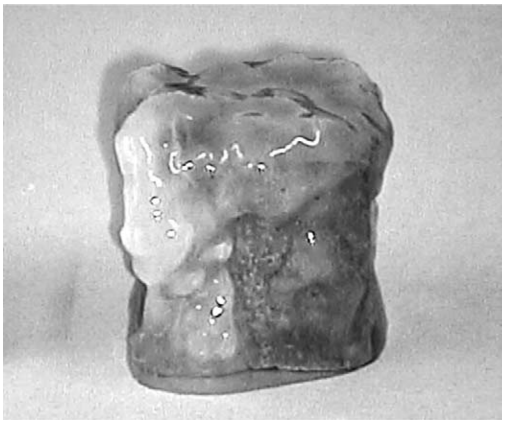

Fig. 1. 196 day 25 mm cube 7% MK at w:b 0.40 exposed to water with extruded 'gel'.

In sulfate solution the 100% PC binder samples at both w:b ratios show significant 'physical' removal of material at the concrete–solution interface exposing the matrix to further attack. In contrast, for 7% MK at both w:b ratios the loss of material occurs where reactions below the finished surface (indicated by blistering) isolate the surface material which separates by exfoliation. These two different material loss mechanisms are illustrated in Figs. 2 and 3. For samples placed in sulfatic clay the mode of attack is similar for all samples in that corners and edges deteriorate into a white, pulpy mush. This is followed by the reaction front migrating across the faces as illustrated in Fig. 4. The degree of attack appears to be controlled by the w:b ratio. For both 100% PC concrete and 7% MK concrete at w:b 0.46 there is a greater loss of material than for the equivalent concretes at w:b 0.40.

Table 4
Wearing values (*W*) for 50 cm^3 exposed for 280 days

Sample description[a]	Wearing value (*W*) 0–280 days	Observations
0.40-00W	0–0 good	No visible erosion, evidence of 'gel' coating
0.46-00W	<1–<1 good	No visible erosion, evidence of 'gel' coating
0.40-07W	<1–<1 good	No visible erosion, evidence of 'gel' coating
0.46-07W	<1–<1 good	No visible erosion, evidence of 'gel' coating
0.40-00S	0–4 satisfactory	Loss of exterior material by physical removal, <0.46-00S
0.46-00S	1–4 satisfactory	Loss of surface integrity, exposure of aggregate and matrix
0.40-07S	<1–<1 good	Below surface reactions producing exfoliation
0.46-07S	0–1 good	Loss of edges and corners with blistering
0.40-00C	0–0 good	No loss of material, evidence of surface reaction zones
0.46-00C	<1–<3 satisfactory	Reaction zones notable at corners with loss of material
0.40-07C	<1–1 good	Reaction zones notable at corners with some loss of material
0.46-07C	<1–<3 satisfactory	Reaction zones notable at corners with loss of material

[a] 0.40-00W where 0.40 and 0.46 denotes the w:b ratios, -00 = 0% and 07 = 7% replacement of PC by MK and W = water, S = sulfate and C = clay environments of exposure.

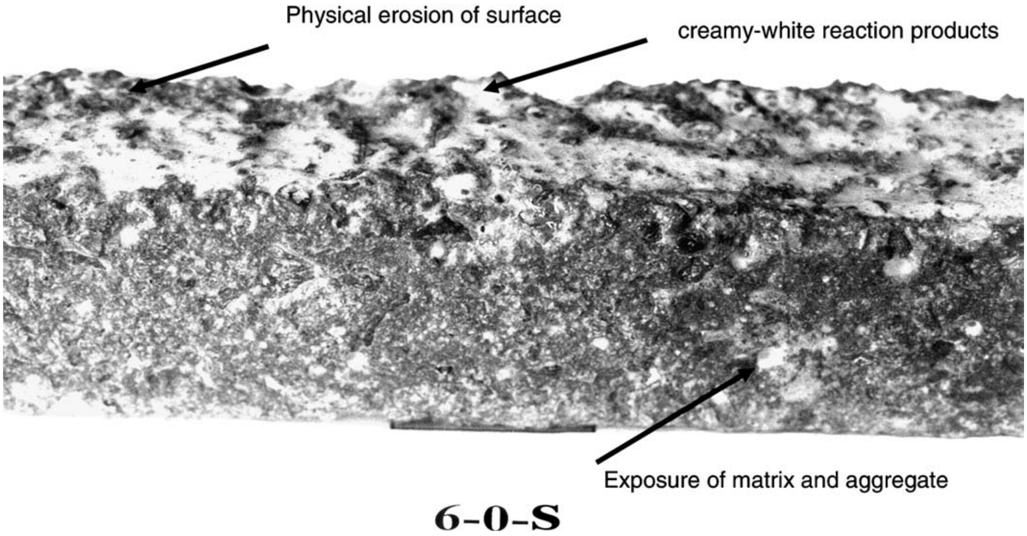

Fig. 2. 196 day 20×20×160 mm bar 100% PC at w:b 0.46 exposed to sulfate solution.

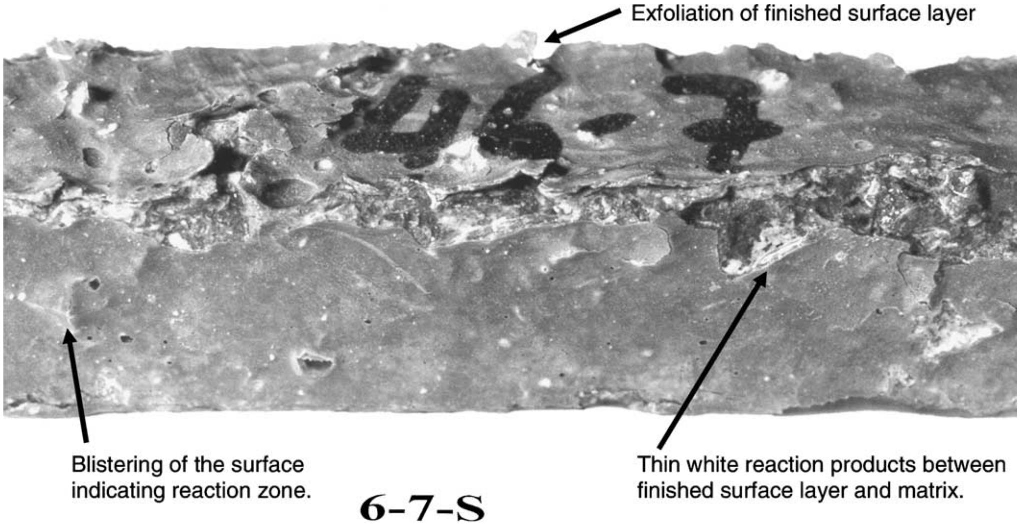

Fig. 3. 196 day 20×20×160 mm bar 7% MK replacement at w:b 0.46 exposed to sulfate solution.

Fig. 5 shows the strength development (up to 280 days) of the concretes with w/b ratios of 0.40 and 0.46, and with the PC partially replaced with 0% and 7% MK, in the three exposure environments of water, sulfate solution and Lower Oxford clay. For specimens without MK the strength, as might be expected is higher at the lower w:b ratio. The effect of partial replacement of PC with 7% MK is to generally enhance the strengths although this effect is more consistent for the concretes of w:b ratio 0.46 and is less consistent for concretes of w:b 0.40, particularly at extended ages.

Strength development clearly shows consistently different behaviours in the three exposure environments. In water, near maximum strength is achieved by about 28 days and subsequently there are relatively small changes in strength up to at least 280 days. In sulfate solution maximum strength is attained at about 28 days and there is then a general decline in strength up to at least 280 days. In Lower Oxford clay, for three of the samples near maximum strength is achieved at 28 days, then after about 150 days strength begins to show a significant decline. For the sample with w/b 0.46 and no MK strength is not maintained after 28 days and shows continual decline.

Fig. 6 shows the expansion of these concretes in the three different exposure conditions, and it is clear that their behaviour in clay is qualitatively different from that in either water or sulfate solution. In water expansion is very small (<0.2%) and occurs within the first 28 days of soaking. The specimens without MK show the greatest expansion, which increases with increase in w:b ratio. In sulfate solution expansion also occurs within the first 28 days of soaking but then continues to increase systematically with exposure time. As in water, expansion

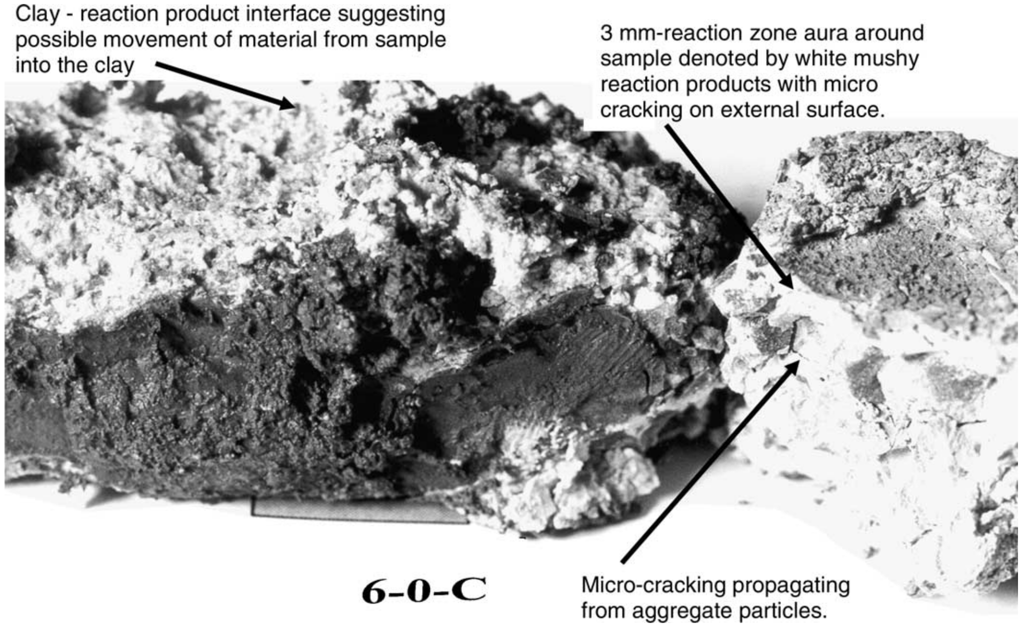

Fig. 4. 196 day 20×20×160 mm bar 100% PC at w:b 0.46 exposed to sulfatic clay.

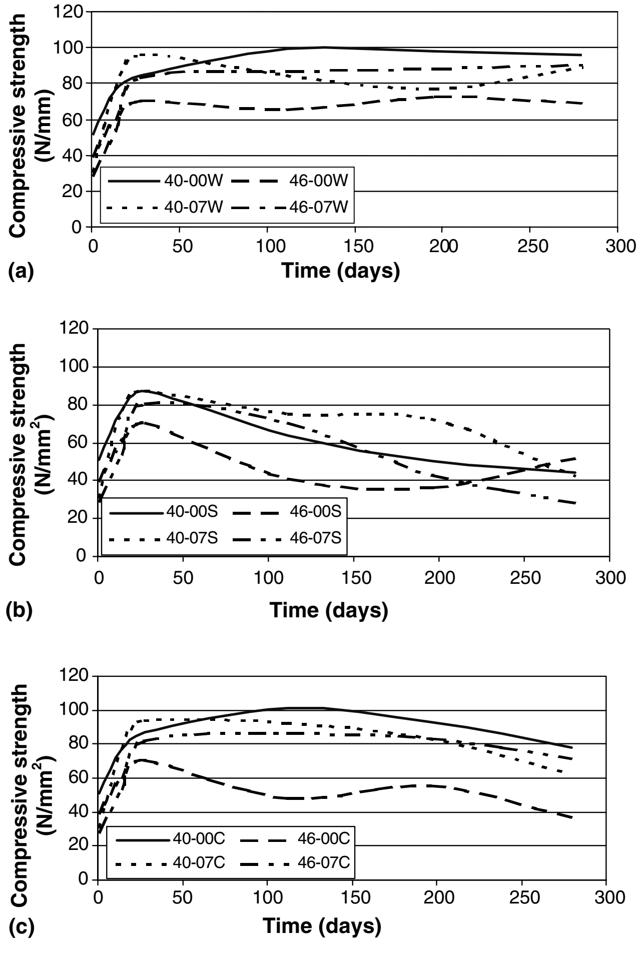

Fig. 5. Compressive strength values for samples exposed to water, sulfate solution and sulfatic clay: (a) exposure to water, (b) exposure to sulfate solution and (c) exposure to sulfatic clay.

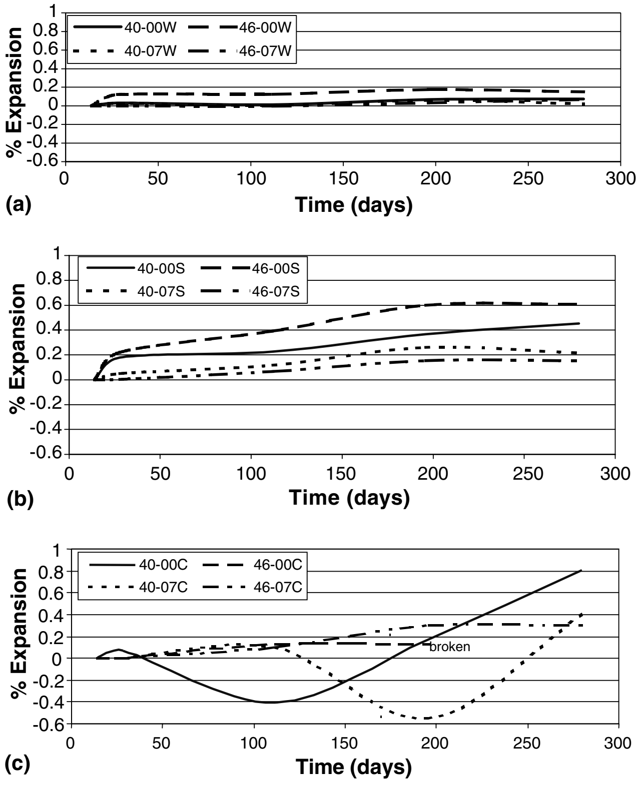

Fig. 6. Expansion values for samples exposed to water, sulfate solution and sulfatic clay: (a) exposure to water, (b) exposure to sulfate solution and (c) exposure to sulfatic clay.

is greatest for specimens without MK and is higher at higher w:b ratio. By 280 days, although the samples show spalling of surface reaction products, they remain intact. For concrete exposed to saturated clay, specimens with w:b 0.40 show a different pattern of length change from that with w:b 0.46. After small initial expansion both concretes (with and without MK) show significant contraction followed by sharp expansion, the expansion of the bar with MK occurring at a later time than that without MK. Also the concrete prisms are still intact at 280 days. The contraction at low w:b ratio is attributed to autogenous shrinkage, where (unlike concrete fully immersed in water/sulfate solution) the movement of water into the concrete is inhibited by the restricted availability of water at the clay–concrete interface. A similar pattern of initial expansion followed by shrinkage has previously been reported by Wild et al. [23] for PC–MK pastes. Surprisingly, although the concretes with w:b 0.40 subsequently show marked expansion, they are still intact at 280 days, whereas the concretes with w:b ratio 0.46 fractured in a number of places at periods between 112 and 196 days for the concrete without MK and between 196 and 280 days for the concrete with MK.

Currently there is no visual evidence of sulfate attack in the 14% MK, 21% MK and 80% ggbs concretes and the expansion of these concretes is negligible. It may be significant that these concretes do not show the extensive development of surface gel coatings when exposed to water as do the PC control and 7% MK concretes, suggesting that the formation of this gel may be indirectly associated with TSA.

5. Conclusions

The investigation is ongoing and therefore the results reported here are of a preliminary nature. The visual evidence accumulated of concrete degradation is typical of TSA although this has yet to be confirmed by the planned analytical programme. From the observations made it may be concluded that:

- Expansion of concrete exposed to sulfate solution at 5 °C is reduced by reducing the w:b ratio and by partially replacing the binder with 7% MK. The expansion of the concrete is accompanied by corresponding reductions in concrete compressive strength.
- Concrete with low w:b ratio (0.40) exposed to LOC at 5 °C experiences initial autogenous shrinkage followed by marked expansion, whereas concrete at the higher w:b ratio (0.46) shows negligible shrinkage and reduced expansion, but specimens fracture within the current exposure period of 280 days. Replacing the binder with 7% MK tends to delay these processes. Also compared to concrete in sulfate solution the onset of the fall in compressive strength is substantially delayed.
- The form of degradation of the concrete exposed to sulfate solution at 5 °C is very different from that exposed to sulfatic clay at 5 °C. In the former case, material resulting from chemical reaction continually spalls away from the outer surfaces leaving them continuously exposed to the aggressive solution. In the latter case the vulnerable surface regions transform into a white pulpy ‘mush’. Clearly diffusion rates and concentration gradients of aggressive species at the concrete–exposure-medium interface are going to be very different in the two different exposure environments and the former may not be appropriate for investigating reaction mechanisms under field conditions.

Although monitoring is continuing, the preliminary evidence (not all reported here in detail) does confirm that both MK and ggbs inhibit TSA in the short term and may therefore have potential application for preventing TSA in concrete. In addition the observation of extrusion of gel, particularly extreme for the concrete with w:b ratio 0.40 and with 7% MK, suggests that alkali carbonate reaction may be associated with the TSA in the particular system under investigation. It is anticipated that planned detailed analytical work will answer some of these questions.

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