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Resistance of concrete containing ggbs to the thaumasite form of sulfate attack

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Abstract

A long-term laboratory study has investigated how cement-type, aggregate-type and curing, affect the susceptibility of concrete to the thaumasite form of sulfate attack (TSA). The cements were Portland cement (PC), sulfate-resisting Portland cement (SRPC) and a combination of 70% ground granulated blastfurnace slag (ggbs) with 30% PC. These were combined with various carbonate aggregates or a non-carbonate control. Initial curing was either in water or in air. Concrete cubes were immersed in four strengths of sulfate solution at 5 and 20 °C. This paper reports the results after up to six years of immersion in sulfate solution.

Deterioration, consistent with TSA, was observed on many of the PC and SRPC concretes that had been made with carbonate aggregate and stored in sulfate solutions at 5 °C, with SRPC providing no better resistance to TSA than PC. Good quality concretes made with 70%ggbs/30%PC showed high resistance to TSA and the presence of carbonate in the mix substantially improved their general sulfate resistance. An initial air-cure, proved beneficial against both the conventional and thaumasite form of sulfate attack. © 2003 Elsevier Ltd. All rights reserved.

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1. Introduction

Laboratory work carried out by BRE [1,2] in the early 1990s, suggested that incorporation of ground granulated blastfurnace slag (ggbs) could significantly improve the resistance of concrete to the thaumasite form of sulfate attack (TSA). The current study was initiated in 1994 to investigate in detail the performance of 70%ggbs/30%PC, compared with other types of cement. Concrete mixes were designed around the then current UK requirements for sulfate resistance: BRE Digest 363 [3]. The mixes contained various aggregates, with and without carbonate, and the cementitious materials were Portland cement (PC), sulfate-resisting Portland cement (SRPC) and 70\(^ggbs/30\)\(^pC\). The test specimens were concrete cubes, stored in sulfate solutions at 5 and 20 °C. The cubes have now been exposed to laboratory-prepared sulfate solutions for six years, with assessments carried out after 1, 2, 4.5, and 6 years. Some of the early results have been reported previously [4,5].

2. Materials

Table 1 gives the chemical analyses of the cementitious materials. The PC, SRPC and GGBS(1), are typical of current UK materials. GGBS(2) was specially produced, from a high-alumina granulated blastfurnace slag, to investigate how the alumina content of ggbs affects resistance to TSA. For the ggbs mixes, the ggbs was combined with the PC in the ratio 70/30.

Table 2 lists the aggregates used and their properties. The mixture of 'Thames Valley flint' coarse and fine aggregate, with a low carbonate content, would be classified as a range 'C' aggregate by the Thaumasite Expert Group Report [6] and was used in 'control' concretes, which were expected to be immune to TSA. A mixture of crushed Carboniferous limestone coarse, and Jurassic limestone fine aggregate, was used to produce all-carbonate aggregate concretes. A mixture of 'Thames Valley flint' coarse, and crushed Carboniferous limestone fine aggregate, was used to produce a concrete where only the fines were carbonate. Both these two latter aggregate mixtures would be classified as range 'A' aggregates and are referred to as 'normal carbonate aggregates'.

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Table 1 Composition (%) of cementitious materials

	SiO ₂	Al_2O_3	CaO	MgO	Fe ₂ O ₃	K ₂ O	Na ₂ O	SO_3	LOI	Free lime	C_3S	C_2S	C_3A	C ₄ AF
SRPC	22.2	3.47	64.1	0.93	5.57	0.69	0.11	2.05	0.48	0.65	52.6	24.0	0	16.9
PC	20.8	4.51	64.1	1.22	2.86	0.56	0.15	3.0	1.10	3.26	48.6	23.7	7.2	8.8
GGBS(1)	34.8	11.8	41.4	8.3	1.0	0.33	0.28							
GGBS(2)	32.1	16.9	35.8	10.5	0.75	0.46	0.36							

At the outset of the project, it was thought possible that only concrete made with low quality, very friable carbonate aggregates would suffer from TSA. Consequently two further aggregate combinations were included. These were materials, which would not normally be used in concrete because of their high absorptivity and low strength:

- (1) a mixture of poor-quality magnesian limestone (dolomite), coarse and fine aggregates;
- (2) a mixture of inferior oolitic limestone, coarse and fine aggregates.

These two aggregate types are referred to as 'low-quality carbonate aggregates'.

All mixes were originally designed to have a free water/cement ratio of 0.50, and a cementitious content of 350 kg/m³. However with the low-quality carbonate aggregates, it was necessary to increase the cementitious content to 400 kg/m³ and use a water-reducing admixture, in order to achieve a compactable concrete at a w/c of 0.50. Even with these adjustments, the inferior oolitic mixes were of very low workability.

Table 3 gives details of the mixes, including their compacting factors and 28-day strengths. For the six 'core' mixes, triplicate specimens were exposed in each test condition, requiring 75 cubes per mix. For the 11 'smaller' mixes, duplicate specimens were used for each test condition with some of the test permutations being omitted, requiring only 36 cubes per mix. The total programme involved nearly 1000 cubes.

3. Preparation and storage of specimens

The concretes were vibrated into 100 mm cube moulds and stored for 24 h under damp hessian and polythene sheet. Then the cubes were de-moulded and numbered, before being cured for a further 27 days at 20 °C, either in water or else in air at 65% relative humidity. For both air and water storage, the cubes were stacked three high. Following curing, the cubes were immediately transferred into containers containing the test solutions. Five concentrations of solution were used.

1. Solution E: magnesium sulfate, of strength 1.8% as SO₄ (three times stronger than the maximum for 'Class 4b' in BRE Digest 363).

- 2. Solution C: magnesium sulfate, of strength 0.42% as SO₄ (in the middle of 'Class 4b' in BRE Digest 363)
- 3. Solution M: magnesium sulfate, of strength 0.14% as SO₄ (maximum for 'Class 2' in BRE Digest 363).
- 4. Solution I: sodium sulfate, of strength 1.8% as SO₄ (three times stronger than the maximum for 'Class 4a' in BRE Digest 363).
- 5. Tap water (as a control exposure).

Each container held four cubes, spaced apart in a single layer, and submerged in approximately 3.5 l of solution. The 'control' cubes were kept separate from cubes containing carbonate aggregate and generally, cubes made with the same binder type were stored together in the same container.

Two further variables were incorporated:

- The effect of temperature was investigated by storing the containers in rooms maintained at 5 and at 20 °C.
- Some of the containers were emptied and replenished with fresh solutions every three months (to simulate a mobile groundwater). In other containers, the solutions were left unchanged (to simulate 'static' groundwater), except where some cubes were removed for strength testing at two years, water was added to re-submerge the remaining cubes.

4. Monitoring and assessment

After 1, 2, 3.5, 4.5 and 6 years immersion in the test solutions, the cubes were visually assessed and photographs were taken of specimens that showed evidence of attack. At the same time, to provide a quantitative measure of attack, the 'wear rating' was measured. Previous experience at BRE [7] has found wear rating to be a useful measurement on specimens subject to conventional sulfate attack, where the initial damage is predominantly, cracking or erosion of the corners. It is the average depth of erosion or damage for one corner (in mm). Measurements are made on the struck face and the opposite face of the cubes. On each of these faces, two diagonal measurements are made of the distance from the edge of one corner damage to the edge of the diagonally opposite corner damage. Knowing the corresponding length on an undamaged cube, the wear

Table 2 Properties of aggregates

Description	Aggregate	Source	10 min water	% pa	ssing si	eve size	(mm)							Mineralogical composition	
	size (mm)		absorption (%)	20	14	10	5	2.3	1.1	0.6	0.3	0.1	0.0		
Flint gravel	20–10	Thames	1.4	100	62	9								Mainly quartz, but trace of calcite	
	10-5	Valley	2.3			100	7							probably also present	
	<5		0.8				100	95	83	65	33	7	1		
Crushed Carboniferous	20-10	Somerset	0.4 100	77	20	0							Mainly calcite minor dolomite		
limestone	10-5		0.4			100	1							trace quartz	
	<5		0.5				100	76	46	30	20	12	5		
Jurassic limestone gravel	20-5	Upper	3.4	100	53	15	4							Mainly calcite, trace of quartz and	
	<5	Thames Valley	5.5				98	64	45	30	11	3	1	dolomite	
Crushed magnesian lime-	20–10	S. York-	6	NA	NA	NA	NA							Mainly dolomite (95%), trace	
stone	10-5	shire	6.3			NA	NA	NA						quartz and calcite	
	<5		2.0 ^a			- 111	100	96	61	35	19	10	5		
Crushed inferior oolitic limestone	20–10	Glouces-	~10	100	NA	NA								Mainly calcite, trace of quartz,	
	10-5	tershire	~10			100	NA	NA			20	0	0	and dolomite	
	<5		NA ^a			-00	100	85	70	45					

NA = not assessed.

^a The sand figure can often be much lower than the coarse aggregate absorption as it is difficult to determine and subject to large errors.

Table 3
Details of concrete mixes

Cement type	Coarse aggregate type	% coarse by weight	Fine aggregate type	% fines by weight	Compact- ing factor	Wet density (kg/m³)	Cement content (kg/m³)	Total w/c ratio	Free w/c ratio	28-day water-stored strength (N/mm ²)
Core mixes PC SRPC GGBS(1)/ PC	Carboniferous limestone	61 61 62	Jurassic limestone	39 39 38	0.94 0.94 0.93	2380 2400 2370	350 350 350	0.6 0.6 0.6	0.5 0.5 0.5	48.3 53.7 39.5
PC SRPC GGBS(1)/ PC	Flint gravel	59 59 59	Flint gravel	41 41 41	0.92 0.95 0.92	2330 2340 2320	350 350 350	0.6 0.6 0.6	0.5 0.5 0.5	45.5 44.3 34.2
Smaller mix PC SRPC GGBS(1)/ PC	Inferior oolitic limestone	57 57 59	Inferior oolitic limestone	43 43 41	0.86 0.85 0.87	2190 2200 2170	400 400 400	0.8 0.8 0.8	0.5 0.5 0.5	31.5 34.7 32.8
PC SRPC GGBS(1)/ PC	Magnesian limestone	58 58 59	Magne- sian lime- stone	42 42 41	0.97 0.97 0.97	2270 2280 2260	400 400 400	0.7 0.7 0.7	0.5 0.5 0.5	40.5 42.0 43.2
PC SRPC GGBS(1)/ PC	Flint gravel	55 55 55	Carbonif- erous limestone	45 45 45	0.92 0.91 0.91	2360 2370 2350	350 350 350	0.6 0.6 0.6	0.5 0.5 0.5	48.7 53.7 39.3
GGBS(2)/ PC GGBS(2)/ PC	Flint gravel Carboniferous limestone	59 62	Flint gravel Jurassic limestone	41 38	0.92 0.94	2310 2370	350 350	0.6 0.6	0.5 0.5	35.2 35.2

rating of a cube is calculated as 'the sum of the loss in millimetres of the four measured diagonals, divided by 8'.

5. Results

Two separate modes of sulfate deterioration had been expected to occur in the sulfate solutions:

- conventional sulfate attack which is primarily a reaction between sulfates and the alumina-containing phases of hydrated cement. The products of this reaction are expansive, and disrupt and spall the concrete, particularly at corners.
- TSA which is an attack on the calcium silicate hydrates that causes the cement paste to lose strength and turn to a 'mush'.

Knowing the conditions, which promote TSA, it was assumed that it could be distinguished from conventional sulfate attack by

• a tendency to occur much more at 5 °C than at 20 °C,

• only occurring in the test concretes made with carbonate aggregates.

From the visual observations, there was clear evidence of a mode of sulfate attack that was favoured with the concretes stored at the lower temperature and containing the carbonate aggregates. The characteristics exhibited by this mode of attack, were

- the initial symptoms could sometimes be quite dramatic (particularly in the strong magnesium sulfate solution) with the surface skin appearing to blow off as a result of a reaction occurring slightly under the surface: however more commonly, the first sign of deterioration was aggregate becoming visible as a result of erosion of the matrix;
- as the attack developed, softening and erosion of the cement paste matrix left the aggregate sticking well proud of the matrix;
- considerable quantities of a mushy white material were apparent on the cube and in the bottom of the container;
- the attack occurred evenly over a face with reduced tendency for removal of corners. Even when severely

attacked, the cube maintained a very 'square' appearance with distinct corners.

This contrasted with the conventional form of sulfate attack that was predominant at 20 °C (or at 5 °C, with flint aggregate). Here the disintegration was more associated with spalling, than softening, and was concentrated on the corners and edges of the specimens, rather than spread across a face. As attack continued, the shape of the cube became more spherical than cubical.

The wear ratings measured after 1, 2, 4.5 and 6 years, for the specimens in solutions changed every three months, are presented in Table 4 (5 °C) and Table 5 (20 °C). Wear rating is a useful quantitative indication of the degree of conventional sulfate attack, but is unfortunately relatively insensitive for assessing TSA, where erosion occurs evenly across the face and is not concentrated on corners.

6. Discussion

6.1. Effect of initial curing

Osborne [8] has previously concluded that the surface carbonation, which results from an air-cure, produces an increased resistance to conventional sulfate attack. To investigate how the initial cure might influence the susceptibility to TSA, a limited number of the specimens were given an initial 27-day air-cure, instead of the standard water-cure. A particular interest was to determine whether with non-carbonate aggregates, this carbonation could provide a source of carbonate that would induce TSA. The investigation into air-curing was restricted to specimens subsequently immersed in sulfate solution at 5 °C.

It was found that the early symptoms of sulfate attack often showed across only one or two faces of a cube, whilst no distress was evident on the other faces. When two faces were affected, they were directly opposite faces. This was most obvious on the specimens showing TSA and was masked on the specimens subject to conventional sulfate attack, where corners were much more affected than the faces. This phenomenon of opposite faces being preferentially attacked, was attributed to the conditions during the initial water- or air-curing. Here the cubes were stacked three high, with some faces fully exposed, but other faces were in contact with other surfaces and consequently not fully-exposed. It became apparent that for the 'contact' faces, the degree of attack was generally similar irrespective of whether the specimens had been air- or water-cured and it was concluded that the surfaces in contact are effectively sealed against any effect caused by the initial curing environment. Subsequent investigation [9] by initial curing against plastic, has confirmed that preventing direct contact with air or water during the initial cure, results in increased TSA attack.

The 'non-contact' faces that had been fully exposed to water during the initial cure were slightly less susceptible to TSA than otherwise equivalent faces that had cured in direct contact with another surface. This might be attributable to carbon dioxide being present in the water, and slightly carbonating the fully exposed faces. However it is considered more likely to be due to the leaching of calcium hydroxide from the exposed surfaces, but not from the 'contact' surfaces. The greater concentration of calcium hydroxide in the 'contact' face could well increase the susceptibility to TSA.

The 'non-contact' faces that had been fully exposed to air during the initial cure appeared to be relatively immune to both the conventional and the thaumasite forms of sulfate attack. Interestingly, the air-cured specimens often had an unattacked 'picture frame', around the edge of the attacked face, indicating where some air had been able to diffuse in from the edges. At the 4.5-year assessment, no significant thaumasite-related attack was observed on those faces, which had been fully air-cured. After six years exposure, this was still the case, although some of the air-cured concretes containing PC and SRPC were now giving high wear ratings as a result of conventional and TSA attack on the faces that had not had the benefit of full exposure to

Air curing was remarkably beneficial for the ggbs/PC cubes. Indeed, all the air-cured ggbs/PC cubes are still in perfect condition, despite some of the equivalent watercured cubes showing significant corner attack in the stronger solutions. It was surprising that despite the stacking during air-curing, the contact faces of ggbs/PC cubes exhibited no tendency to be susceptible to attack. However this can be explained by the attack on ggbs/PC cubes in strong sulfate solutions being limited to the corners and not occurring on flat faces. Another investigation [10], involved immersion of specimens in similar sulfate solutions, and found that the extent of corner attack on ggbs/PC cubes was independent of specimen size, with disruption limited to a localised area around the corners. In the present study with the stacks used for initial curing, the localised areas round all of the corners could have received some exposure to air. With the ggbs/ PC cubes only vulnerable to corner attack, no 'contact face' effect would be expected.

6.2. Effect of regularly changing the solutions

For the present paper, limitations on space, preclude the inclusion of tabulated results for specimens where the solutions were not changed. Irrespective of whether the solutions were changed or left undisturbed, the general trends were very similar. As would be expected, the degree of attack was somewhat greater when the

Table 4
Wear rating assessments for cubes stored in 5 °C sulfate solutions (three monthly change)

	Solution E			Solution	on I			Solution	on C		Solution	on M				
	1 yr	2 yr	4.5 yr	6 yr	1 yr	2 yr	4.5 yr	6 yr	1 yr	2 yr	4.5 yr	6 yr	1 yr	2 yr	4.5 yr	6 yı
Water cured																
OPC + flint/flint	3	11	40	67	8.5	13	23	36	4	9	26	41	0	0.5	1	3
SRPC + flint/flint	2	4	5	8	2	7	12	13	0	2.5	1	2	0	0	1	1
GGBS(1)/PC + flint/flint	4.5	14	26	39	4.5	10	16	16	0	5.5	13	17	0	0	2	3
GGBS(2)/PC + flint/flint	19	25	36	57	4	5	23	28	3	13	21	25	0	1.5	0	13
OPC + Carb/Jur	8.5	18	20	38	7	8	13	29	9	9	16	27	2	3	5	9
SRPC + Carb/Jur	2.5	9	16	39	0	5.5	10	15	0	8	14	31	0	4	8	12
GGBS(1)/PC + Carb/Jur	3	3.5	4	12	0	0.5	5	16	0	0	1	1	0	0	3	4
GGBS(2)/PC + Carb/Jur	4	7	5	13	1	1	3	3	0	0	0	1	0	1.5	2	1
OPC + flint/Carb	10.5	17	20	34	5	8	8	19	10	8	NA	NA	3.5	4	5	10
SRPC + flint/Carb	2	2.5	10	21	3	3	12	19	0	1.5	9	27	0	0.5	2	6
GGBS(1)/PC + flint/Carb	3	2.5	5	11	0	1	1	1	0	0	1	2	0	0	1	1
OPC + Ool/Ool	18	18	NA	70	9.5	10	30	70	10.5	10	NA	44	0	2	5	7
SRPC + Ool/Ool	3	12	29	61	2	4	24	31	0	9	11	20	0	0	2	5
GGBS(1)/PC + Ool/Ool	26	29	>40	70	21	24	>40	70	16	15	22	34	0	0	11	22
OPC + Mg/Mg	13	13	X	70	11	11	25	40	10	8	18	57	4	4	7	14
SRPC + Mg/Mg	4	12	31	70	3.5	4.5	37	65	0	10	15	27	2.5	4.5	11	14
GGBS(1)/PC + Mg/Mg	11	15	34	70	4	13	29	61	11	11	20	30	0	0	14	30
Air cured																
OPC + flint/flint	0	1.5	9	23	0	1	11	21	Not in	programi	me		0	1	4	8
SRPC + flint/flint	0	5.5	7	12	1.5	4.5	10	12		r	-		0	0	2	2
GGBS(1)/PC + flint/flint	0	0	1	3	0	0	2	1					0	0	8	4
OPC + Carb/Jur	0	14	29	54	0	6	15	27					0	2	3	11
SRPC + Carb/Jur	0	0	5	16	0	3.5	8	13					0	0	9	17
GGBS(1)/PC + Carb/Jur	0	0	1	3	0	0	1	2					0	0	1	1

Table 5 Wear rating assessments for water cured, cubes stored in 20 °C sulfate solutions (three monthly change)

	Solutio	n E			Solutio	n I			Solutio	on C		Solution M				
	1 yr	2 yr	4.5 yr	6 yr	1 yr	2 yr	4.5 yr	6 yr	1 yr	2 yr	4.5 yr	6 yr	1 yr	2 yr	4.5 yr	6 yr
OPC + flint/flint	2	3.5	5	11	0	5.5	6	7	0	0	0	1	0	0	1	1
SRPC + flint/flint	0	2.5	2	3	0	0	2	1	0	0	0	3	0	0	1	1
GGBS(1)/	7.5	11.5	27	47	0	2	16	23	0	1	1	5	0	0	1	1
PC + flint/flint																
GGBS(2)/	15	20	>40	70	2.5	4	18	25	0	0	4	16	0	0	1	1
PC + flint/flint																
OPC + Carb/Jur	1.5	3	5	8	0	2	4	4	0	2	7	8	0	0	0	1
SRPC + Carb/Jur	0	1.5	2	3	0	0	1	1	0	0	0	1	0	0	0	1
GGBS(1)/	3.5	5	4	9	0	0	1	1	0	0	0	1	0	0	1	2
PC + Carb/Jur																
GGBS(2)/	1.5	4	5	15	0	0	1	2	0	0	1	2	0	0	0	1
PC + Carb/Jur																
OPC + flint/Carb	2.5	3	8	12	0	4.5	7	5	0	2	8	9	0	0	2	4
SRPC + flint/Carb	2.5	2.5	3	4	0	0	0	1	0	0	0	1	0	0	0	2
GGBS(1)/	4.5	6.5	8	14	0	0	1	1	0	0	0	1	0	0	0	2
PC + flint/Carb																
OPC + Ool/Ool	2	11.5	22	55	0	1.5	1	1	0	0.5	9	27	0	0	1	1
SRPC + Ool/Ool	3	3	5	8	0	0	0	1	0	0	0	2	0	0	0	1
GGBS(1)/	4	23	>40	70	3.5	11	>40	70	6	13	22	41	1	1	0	2
PC + Ool/Ool																
OPC + Mg/Mg	3	8	13	42	0	0	3	17	0	0	0	3	0	0	1	1
SRPC + Mg/Mg	4	4	5	11	0	0	1	2	0	0	1.5	2	0	0	0	2
GGBS(1)/	2	7	26	35	1	6	10	13	3.5	3.5	5	10	1	1	0	1
PC + Mg/Mg																

solutions were regularly changed. Less predictably, the deterioration in the unchanged solutions continued to increase with time and even at six years, there was little evidence of deterioration ceasing due to depletion of the sulfate.

6.3. Effect of test temperature

The storage temperature had a large effect on both the mode and extent of deterioration. For PC with all the aggregate types, the deterioration was significantly worse at 5 °C. The lower temperature appeared to increase the susceptibility of concretes made with PC to both conventional sulfate attack and to TSA. The SRPC mixes performed very well at 20 °C, and with all-flint aggregate at 5 °C. However at 5 °C, in the mixes with carbonate aggregates, SRPC was susceptible to TSA. The ggbs/PC mixes contrasted with those made with PC and SRPC, in that their performance was little affected by temperature.

6.4. Effect of cement and aggregate type

From the visual observations and the wear ratings it was apparent that

- at 5 °C, the PC and SRPC specimens, made with carbonate aggregates, consistently exhibited symptoms of deterioration due to TSA. There was slight attack even in the weakest solution M, which equates to the top of 'Class 2' in BRE Digest 363 (Design Class 2 in Special Digest 1, the new BRE guidance for buried concrete in sulfate-bearing ground [11]). The degree of attack increased with the strength of the solution;
- the SRPC specimens were extremely resistant to conventional sulfate attack but showed no better resistance against TSA, than those made with PC. This indicates that a low C₃A content does not necessarily increase the resistance of a cement to TSA. As pointed out by Alksnis and Alksne [12], consideration must be given to the other components such as tricalcium silicate content:
- in ggbs/PC concretes made with flint aggregates, the ggbs of high alumina content showed an increased susceptibility to conventional sulfate attack, compared with the normal alumina ggbs. Apart from this there did not appear to be much difference in performance between concretes made with the two types of ggbs;
- there was no evidence of TSA on any of the ggbs/PC specimens made with the good quality limestone aggregates, with either ggbs;
- at both temperatures, the ggbs/PC mixes, with carbonate aggregates performed much better than those made with all-flint aggregates. The presence of car-

- bonate in the aggregate in these mixes increased significantly the resistance to conventional sulfate attack. Further evidence of this effect, together with a discussion of the likely mechanisms, is reported elsewhere in this Conference [13];
- the cubes made with ggbs/PC and the very weak, porous, oolitic limestone performed relatively poorly and at 20 °C lost a lot of material, especially in the stronger solutions. The PC and SRPC specimens made with this aggregate performed relatively well, with only the PC cubes in solutions 'E' and 'C', showing significant signs of attack. At 5 °C with this aggregate, the ggbs/PC performed equally poorly, but no worse than at 20 °C, while the PC and SRPC specimens were significantly more attacked at the lower temperature. For this aggregate, the cement types showed different modes of deterioration. On the ggbs/PC cubes, the deteriorated faces were relatively smooth, and cleaved faces of coarse aggregate ran flush with the surface. For the PC and SRPC specimens at 5 °C, there was little sign of aggregate fracture on deteriorated faces and coarse aggregate poked out proud of the surface; only at 20 °C, on the deteriorated PC mix in solution 'E', was fracture of aggregate, predominant. The mode of deterioration and the independence of temperature would suggest that TSA could probably be discounted for the ggbs/PC specimens. However the exact mode of deterioration is still unclear;
- the specimens made with poor-quality magnesian limestone showed similar trends to those made with inferior oolitic limestone, but to a lesser extent. Once again the ggbs/PC specimens showed cleavage of the aggregate particles, while in the PC and SRPC specimens the particles were unbroken and stuck out proud of the matrix. It would appear that the poorquality magnesian limestone aggregate had an adverse effect on the sulfate resistance of the ggbs/PC mixes, but to a lesser extent than the inferior oolitic limestone:
- overall, concretes made with PC had deteriorated more than those made with the other binders. This would be expected, from cubes made with a non-sulfate resisting cement type. However at 20 °C and with flint aggregates, the PC cubes showed somewhat less attack than the ggbs/PC cubes, suggesting that with its relatively low C₃A content of 7.2%, the PC may have had some sulfate-resisting properties.

6.5. Rates of deterioration

Conventional sulfate attack predominantly results in spalling of corners and the wear ratings provide a good measure of its extent. The change in wear ratings with time (shown in Tables 4 and 5), suggest that the dete-

rioration due to conventional attack is increasing approximately linearly with time.

TSA attack produces a gradual loss of strength and softening prior to visible disruption. For fear of disturbing the surface of the specimens in a way that would affect their future deterioration, no attempt has been made to quantitatively estimate the extent and depth of TSA attack. From the visual observations it can be qualitatively concluded that the degree of attack by TSA is increasing with time, possibly at an approximately constant rate.

7. Conclusions

- 1. Deterioration, consistent with TSA was found to occur on all of the PC and SRPC concretes that had been made with carbonate aggregate and stored in sulfate solutions at 5 °C.
- 2. The degree of TSA increased with the sulfate concentration of the test solution and with time.
- At 5 °C, there was no discernible difference between the performance of SRPC concretes containing carbonate aggregates and those made with PC, indicating that the SRPC was no more resistant to TSA than the PC.
- 4. Concretes made with 70%ggbs/30%PC and normal quality carbonate aggregates performed extremely well and showed no evidence of TSA in any of the solutions, with either normal or high-alumina ggbs.
- 5. However concretes made with 70%ggbs/30%PC and inferior quality carbonate aggregates did not perform well at either 5 or 20 °C.
- 6. An initial air-cure proved beneficial against both conventional sulfate attack and TSA. After six years, the air-cured 70%ggbs concretes show no evidence of attack, even in the strongest sulfate solution.
- 7. The presence of carbonate in the mix substantially improved the resistance of 70%ggbs/30%PC concretes to conventional sulfate attack.
- 8. Overall, the worst performers were concretes made with PC. However, the concretes made with PC, appeared slightly less susceptible to conventional sulfate attack than those made with 70%ggbs/30% PC and it would appear that the low C₃A PC used in the present study, had some sulfate-resisting properties.

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