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Increased sulfate resistance of ggbs concrete in the presence of carbonate

D.D. Higgins *

Cementitious Slag Makers Association, 4th Floor, Croudace House, Godstone Road, Caterham CR3 6XQ, UK

Abstract

Significant occurrence of the thaumasite form of sulfate attack (TSA) has only been identified in concrete containing carbonate aggregate, leading to a perception that the presence of calcium carbonate is undesirable in concrete exposed to sulfate attack. This paper reports on how the addition of a small percentage of calcium carbonate or calcium sulfate, affects the sulfate resistance of concrete containing ground granulated blastfurnace slag (ggbs). Three test methods were employed to assess sulfate resistance (all at 20 °C):

- Cubes were immersed in magnesium and sodium sulfate solutions and monitored for corner-loss and strength-loss, over six years.
- Mortar was sieved from fresh concrete and used to make prisms. These prisms were immersed in magnesium and sodium sulfate solutions and their expansions monitored for up to six years.
- In accordance with a draft of a European Standard for sulfate resistance, mortar prisms were prepared and monitored for expansion for one year.
- It was found that both calcium carbonate and calcium sulfate additions, had a consistent beneficial effect on the resistance of ggbs concrete to conventional sulfate attack, both in respect to expansion and in respect of disintegration. The paper discusses possible mechanisms for the improved resistance.

Keywords: Attack; Sulfate; Slag; Ggbs; Carbonate

1. Introduction

For more than a century, blastfurnace slag has been used as a cementitious material in concrete. It is either inter-ground with Portland cement clinker to produce bastfurnace cement, or added separately at the concrete mixer as ground granulated blastfurnace slag (ggbs) [1]. Blastfurnace cement and ggbs are well known to have good sulfate-resisting properties. Following cases in the UK of the thaumasite form of sulfate attack (TSA) on Portland cement and sulfate-resisting Portland cement concretes, two research projects at the Building Research Establishment investigated the effect of ggbs on TSA [2,3]. These projects included the testing of concrete cubes, made with carbonate and non-carbonate aggregates, in sulfate solutions at 5 and 20 °C. The ggbs concretes performed well and showed no evidence of attack by TSA. Additionally, an unexpected influence of aggregate type became apparent. At both 5 and 20 °C, the ggbs concretes, made with carbonate aggregate, were significantly more resistant to attack than equivalent concretes made with non-carbonate aggregate and it was concluded that the presence of carbonate in the aggregate was enhancing the resistance of ggbs concrete to conventional sulfate attack.

A literature search found no previous reports of aggregate-type having such an effect and there was no obvious explanation. By analogy with the reactions involved in TSA, it seemed possible that the carbonate aggregate was reacting with the cementitious hydrates and perhaps the sulfate solution. Due to the normally 'inert' role of such aggregate in concrete it was felt that any reaction could only be slight, and involve no more than a very small fraction of the carbonate in the aggregates.

Around the same time as this effect was identified, British Standards had changed to allow some cements

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[*] Fax: +44-188-333-1072.
E-mail address: denis.higgins@ukcsma.co.uk (D.D. Higgins).

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to contain small amounts (<5%) of 'minor additional constituents', such as calcium carbonate. While this is not yet permitted in the British Standard for ggbs, it was considered of interest to investigate whether adding calcium carbonate at the percentage permitted for 'minor additional constituents' would have the same effect on sulfate resistance as use of a carbonate aggregate. In parallel, the effect of adding calcium sulfate was also investigated, because of suggestions that a slightly increased level of sulfate in the cementitious materials can increase the sulfate resistance of ggbs concretes [4,5].

'Sulfate resistance' was measured by three methods, all of which involved immersing specimens in sulfate solutions at 20 °C.

- The first method followed the procedures normally employed by the UK Building Research Establishment for investigating sulfate resistance. Concrete cubes were used as the specimens and sulfate attack was measured as loss of dimension [6].
- A second method was based on the 'Sandberg' method [7], which measures the expansion of flat mortar prisms. To align the flat prisms as closely as possible with the concrete cubes, the mortar for the prisms was obtained by sieving it out of a similar concrete to that used to manufacture the cubes.
- The third method followed a draft European Standard Test Method for sulfate resistance [8]. This is similar to the Sandberg method, in that it measures the expansion of mortar prisms, but differs in detail. The mortars used for the specimens for the European draft method were mixed conventionally, as opposed to being sieved from concrete.

2. Materials

Details of the materials used are given in Table 1. The aggregates were chosen to be non-carbonate-containing, with silica sand as the fine aggregate and 'Glensanda' granite as the coarse. The Portland cement had the highest C_3A content (11.8%) that could be sourced in the UK, so that it would have relatively low sulfate resistance. Many UK Portland cements have C_3A contents well below 10% and although not specifically manufactured as such, can exhibit moderate sulfate resistance. The ggbs was typical of that produced in the UK. The calcium carbonate was a commercially available limestone powder. The calcium sulfate was a commercially available synthetic anhydrite. This anhydrous form of calcium sulfate was chosen rather than gypsum, because it was felt that it might be the preferred option for full-scale addition of sulfate to ggbs. In cement manufacture, excessively high temperatures in the grinding mills can reputedly dehydrate gypsum to the hemi-hydrate form and cause 'false set' problems [9]. Theoretically, the temperatures involved in the drying and grinding of ggbs might have a similar effect.

3. Concrete mixtures

The main programme compared six concrete mixtures:

- Portland cement control
- 40% Portland cement: 60% ggbs (the SO_3 content was 1.3% percent by mass of cementitious)
- 30% Portland cement: 70% ggbs (the SO_3 content was 1.0% percent by mass of cementitious)
- 40% Portland cement: 60% ggbs with calcium carbonate added at 4% by mass of the ggbs
- 40% Portland cement: 60% ggbs with anhydrite added to increase SO_3 percent of cementitious to 2%
- 40% Portland cement: 60% ggbs with anhydrite added to increase SO_3 percent of cementitious to 3%

The calcium carbonate and the anhydrite were counted as part of the cementitious content. The mixtures all had

Table 1
Chemical composition of materials used

	For cubes, and Sandberg prisms		For draft European Standard prisms		For all cubes and prisms	
	Portland cement	ggbs	Portland cement	ggbs	Calcium carbonate (LS)	Anhydrite
Silica (SiO_2)	n/d	34.8%	20.1%	35.5%	n/d	n/d
Calcium (CaO)	n/d	41.4%	64.9%	40.5%	55.8%	40.6%
Alumina (Al_2O_3)	6.09%	11.8%	5.4%	12.5%	n/d	n/d
Magnesia (MgO)	n/d	8.3%	1.0%	8%	n/d	n/d
Iron (Fe_2O_3)	2.55%	1.0%	2.3%	0.5%	n/d	n/d
Acid soluble sulfate (as SO_3)	3.22%	0.05%	3.2%	0.1%	0.03%	54.2%
Sulfide	n/d	1.0%	n/d	0.8%	n/d	n/d
C_3A	11.8%	n/a	10%	n/a	n/d	n/d
Surface area	n/d	440 m^2/kg	353 m^2/kg	410 m^2/kg	n/d	n/d
<45 μm	n/d	95%	85%	n/d	80%	95%

n/d = not determined.

a water/cementitious ratio of 0.5 and a total cementitious content of 350 kg/m^3.

4. Testing

Hundred millimeter concrete cubes manufactured from each mixture, were tested for compressive strength after storage in water at 20 °C for periods of: 3-days, 7-days, 28-days, 1-year, 2-years and 6-years.

Further 100 mm cubes were given an initial 28-days cure in water at 20 °C, before being immersed in sulfate solutions. The solutions were either sodium sulfate or magnesium sulfate, containing 1.5% by mass of sulfate as SO_3. The sulfate solutions were maintained at 20 °C and changed every 6 months. The dimensional changes of cubes in sulfate solution were determined annually up to 6 years. In addition, cubes were removed after 1, 2 and 6 years and tested for compressive strength. The compressive strength was calculated from the crushing strength without any correction for loss of section and is a measure of degree of attack rather than a true compressive strength.

Mortar fractions were sieved from the concrete mixtures and used to make 40 × 10 × 160 mm flat prisms for 'Sandberg' flat-prism testing [7]. The prisms were cured for 14 days in water and then immersed in one of four solutions maintained at 20 °C:

- Sodium sulfate or magnesium sulfate at 1.5% SO_3, i.e. the same solutions as used for the concrete cubes.
- Sodium sulfate at 2.4% SO_3, which is the solution previously used for Sandberg flat-prism testing.
- water.

The length changes of the specimens in water and in sulfate solution were measured up to 6 years and expansion calculated as the expansion in sulfate solution less the expansion of water-stored controls.

Testing was also carried out in accordance with the draft European Standard for measuring sulfate resistance, which was current at the time [8]. The specimens were 20 × 20 × 160 mm prisms of w/c ratio 0.5 and the test solution was sodium sulfate of concentration 1.3% SO_3. The same proportions of cementitious mixtures as used for making the concrete specimens were used as the 'cement' in this test, except that the mix with 'anhydrite added to increase SO_3 content of cementitious to 2%', was omitted.

5. Results

Table 2 shows the compressive strength of the cubes stored in water and in the sulfate solutions. The strengths in the sulfate solutions are expressed as a percentage of the strength of equivalent concretes stored in water for the same age. Table 3 shows the 'wear ratings' of the cubes, measured annually. 'Wear rating' is a measure of the attack on the corners of a cube. Measurements were made on the four vertical as-cast, faces of the cubes. On each of these faces, two diagonal measurements were 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 rating of a cube is calculated as: "the sum of the loss in millimetres of the eight measured diagonals, divided by 16". It is the average depth of erosion or damage for one corner (in

Table 2
Compressive strength in water and in sulfate solutions

	Compressive strength in water (N/mm^2)						% strength in Na_2SO_4			% strength in $MgSO_4$		
	3-day	7-day	28-day	1-year	2-year	6-year	1-year	2-year	6-year	1-year	2-year	6-year
Portland cement	34	41	53	66	68	69	97	87	0	85	74	28
60% ggbs	17	31	48	65	69	73	106	97	62	95	75	18
70% ggbs	13	28	49	63	66	71	105	89	90	94	77	28
60% ggbs + LS	15	28	45	67	69	76	99	97	84	96	83	41
60% ggbs 2% SO_3	19	29	47	68	67	72	97	99	33	94	81	19
60% ggbs 3% SO_3	18	32	50	62	69	75	102	99	80	94	88	50

Table 3
Wear rating in sulfate solutions

	Wear rating in Na_2SO_4 solution						Wear rating in $MgSO_4$ solution					
	1-year	2-year	3-year	4-year	5-year	6-year	1-year	2-year	3-year	4-year	5-year	6-year
Portland cement	1	1	1	3	10	71	1	1	1	0	0	2
60% ggbs	2	2	3	5	9	12	4	6	7	10	15	23
70% ggbs	2	3	3	3	2	3	5	4	6	6	7	6
60% ggbs + LS	0	2	2	2	2	3	1	2	4	4	7	9
60% ggbs 2% SO_3	1	4	12	11	15	22	1	4	8	9	14	20
60% ggbs 3% SO_3	1	2	2	1	1	3	1	2	4	2	2	5

millimetres). The sulfate solutions are about five times stronger than concrete is likely to be exposed to in a natural environment, and by 6 years there is considerable attack of the cubes.

In sodium sulfate solution, the PC-only concrete had almost completely disintegrated by 6 years, while the ggbs concretes were generally showing only minor strength- and corner-loss. As would be expected, 70% ggbs was more resistant to attack than 60% ggbs. The lower level of addition of calcium sulfate (to increase the SO_3 level of the cementitious to 2%), significantly increased the degree of attack. However at the higher level of addition of calcium sulfate (to increase the SO_3 level of the cementitious to 3%) the degree of attack was reduced, as was also the case with the addition of calcium carbonate.

In magnesium sulfate solution, the PC-only concrete performed somewhat better, whereas the ggbs concretes performed distinctly less well in the magnesium than the sodium solution. This is what is normally observed [6] with ggbs concrete generally more susceptible to attack by magnesium sulfate than sodium sulfate. Once again 70% ggbs is more resistant than 60% and the lower level of addition of calcium sulfate gave no advantage. The higher level of addition of calcium sulfate and the addition of calcium carbonate both reduced the degree of attack.

Figs. 1–3 show the expansion results for mortar sieved from the concrete. Because of the differences in the rate and extent of expansion, the graph for magnesium sulfate solution is plotted with an expansion axis 20 times larger than for sodium sulfate. For PC-only the expansion is rapid, reaching 1% after about 9 months in all three solutions (off the scale in Figs. 2 and 3). In the two sodium sulfate solutions the 60% ggbs specimens disintegrated at a relatively low expansion of less than 0.1%. As would be expected, expansion and disintegration were somewhat faster in the stronger solution. The 70% ggbs and the specimens with additions of calcium sulfate or carbonate, all survived with low expansions, although the lower level of calcium sulfate addition is showing signs of more rapid expansion at 72 months. In magnesium sulfate, expansion is more rapid and severe. All the specimens had disintegrated by 48 months. Once again the higher level of addition of calcium sulfate and the addition of calcium carbonate, proved particularly beneficial.

Fig. 4 shows the expansion in the draft European Standard method. Within the 52-week time-scale of monitoring required by this test, only the OPC-only and the 60% ggbs specimens have expanded to a significant extent. The ranking of the specimens is the same as found with the Sandberg prisms in sodium sulfate solution, with the extent of expansion tending to be greater in the European Standard test despite the slightly weaker solution. This may be due to a different Portland cement with a slightly lower C_3A content having been used for the series of mixtures for the European Standard test.

6. Discussion

The present study has found that addition of either calcium carbonate or calcium sulfate to ggbs concrete produced a consistent increase in sulfate resistance, across a range of tests that measure either expansion or disintegration. Cement hydration and sulfate attack are complex reactions, still far from fully understood. Sul-

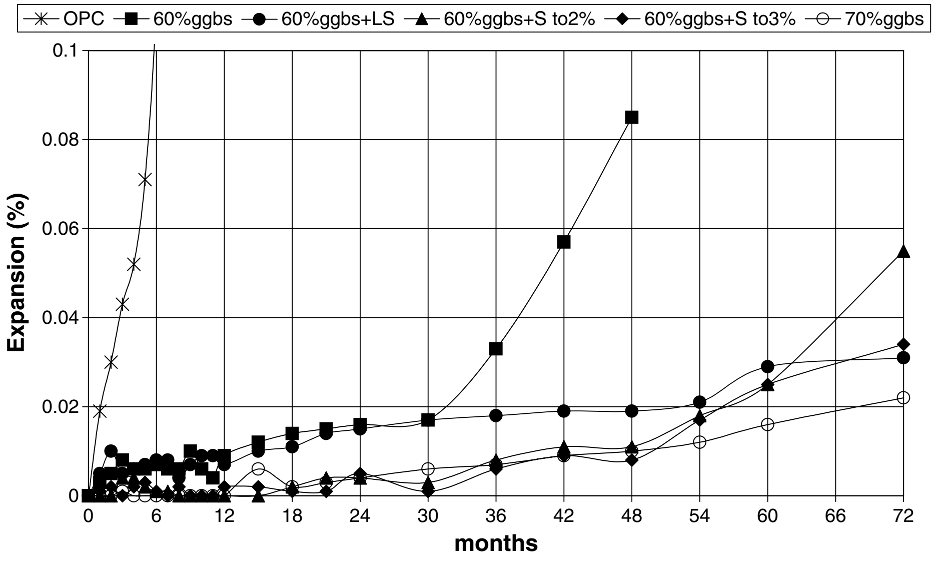

Fig. 1. Expansion of Sandberg prisms in Na_2SO_4 solution (1.5% SO_3).

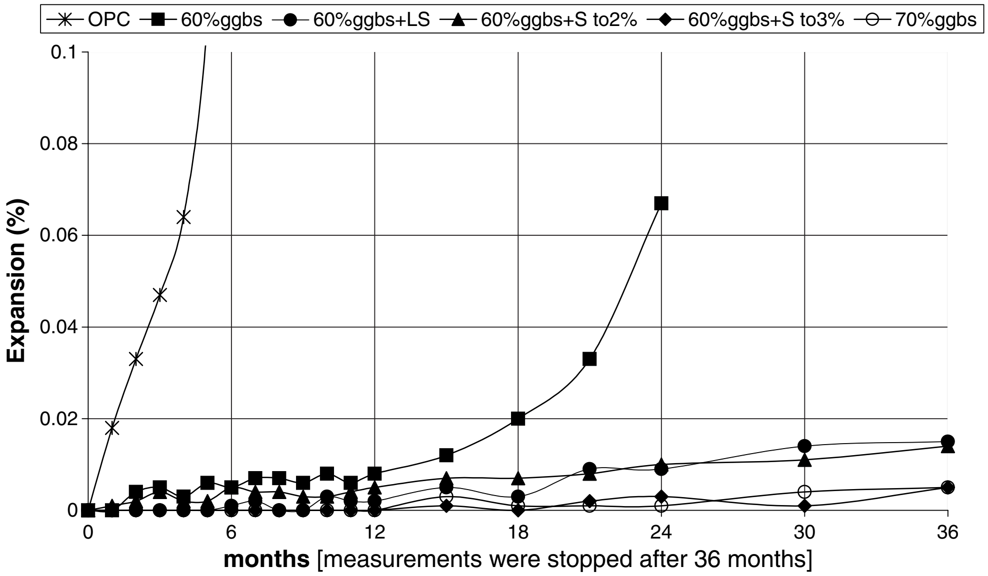

Fig. 2. Expansion of Sandberg prisms in Na_2SO_4 solution (at higher (2.4%) SO_3).

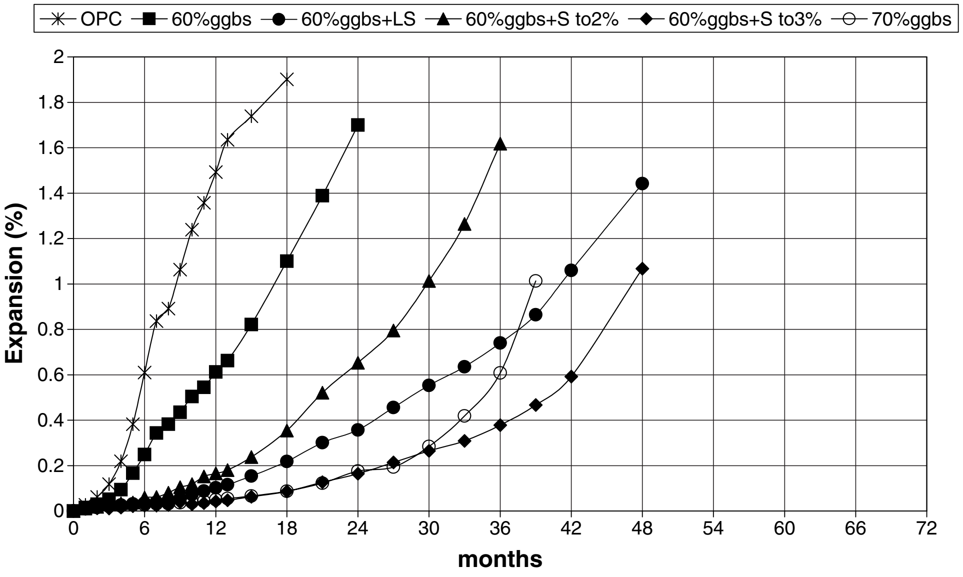

Fig. 3. Expansion of Sandberg prisms in $MgSO_4$ solution (1.5% SO_3).

fate attack involves a mixture of two associated destructive mechanisms:

1. *Expansion and cracking*: This is generally attributed to expansive forces generated by sulfate reacting with the calcium aluminium hydrates to form ettringite.
2. *Loss of adhesion and strength*: This is generally attributed to reactions where sulfate attacks and breaks down the calcium silicate hydrate (C–S–H), which is the main binding component of hardened cement.

Several authors [4,5] have reported that an increased calcium sulfate content increases the sulfate resistance of concrete made with ggbs. Gollop and Taylor [10] have discussed possible mechanisms for this and attribute it to "formation and retention of ettringite formed at an early stage of hydration before sulfate attack had begun". They note that a higher alumina content in the slag tends to make concrete more susceptible to sulfate attack and associate severity of attack with the quantity of alumina that is available to form disruptive ettringite. Increasing the gypsum content would be expected to result in more alumina from the slag reacting with gypsum during the early stage where the concrete is still plastic. Ettringite formed while the concrete is still plastic, should have no disruptive effect and the alumina tied up in this initially formed ettringite would not be available to react at later stages to cause disruptive

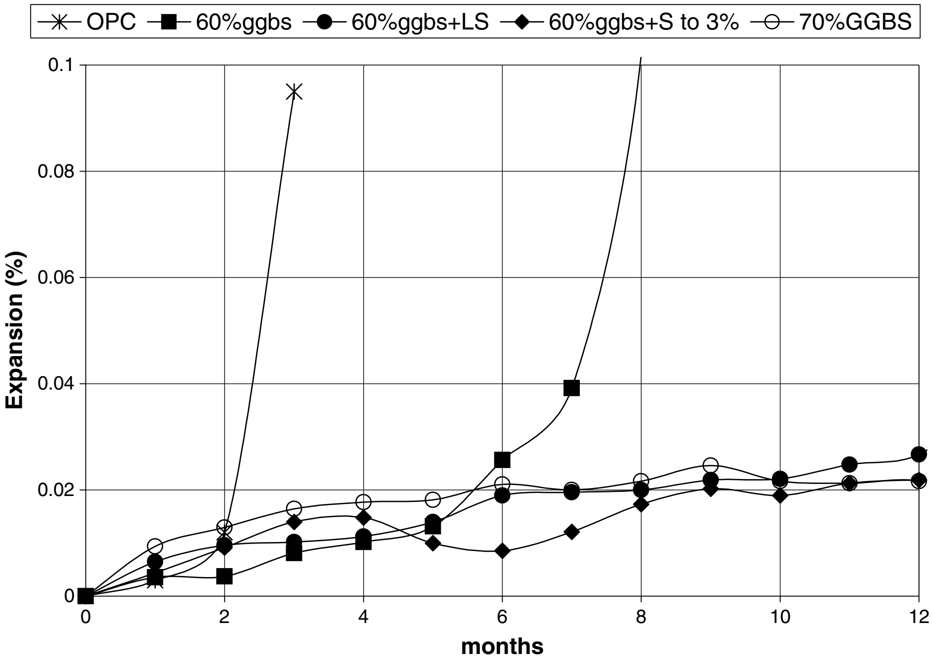

Fig. 4. Expansion by draft European test in sodium sulfate solution (1.3% SO_3).

expansion. The difficulty with this explanation is the fact that sulfate resistance increases with higher proportions of ggbs, where more alumina should be available. Gollop and Taylor attempt to account for this by suggesting that at high slag levels, an increase in the silica/calcium ratio of the C–S–H results in more alumina being bound up in the C–S–H and unavailable to form ettringite. They also propose that as the content of slag increases, the proportion which reacts decreases and this limits the quantity of alumina released at high slag contents.

An increase in sulfate resistance due to added calcium carbonate does not appear to have been previously identified. Osborne [6] did report an effect of carbonation, where exposing concrete to air before immersion in sulfate solution, increased the resistance to sulfate attack. He linked this to the formation of calcium carbonate in the surface layer of the concrete and proposed that the calcium carbonate had a 'pore blocking' effect, restricting ingress of sulfate. Osborne found that the air-cure effect applied to both slag and PC-only concretes. However the effect of added calcium carbonate does not appear to apply to non-ggbs concretes. Matthews [11] studied the effect of added calcium carbonate on the sulfate resistance of Portland cement, using the same 'cube' test method, as employed in the present study. He found no consistent, significant change in sulfate resistance with either 5% or 25% addition of limestone by weight of cement. Hooton [12] used both ASTM C452 and ASTM C1012 to assess the sulfate resistance of commercially available Canadian Portland cements, with and without additions of calcium carbonate up to 5%. He concluded that "for commercial cements, sulfate resistance appears to be unaffected by carbonate additions". Other studies related to TSA have tested concretes of various cement types with carbonate and with non-carbonate aggregates [3]. Only slag concretes seem to show enhanced sulfate resistance with added calcium carbonate.

An explanation for the effect of added calcium carbonate on ggbs concretes is suggested by detailed scanning electron microscopy and X-ray diffraction studies of 69% ggbs concrete cubes, stored in sodium and magnesium sulfate solutions, carried out by Gollop and Taylor [13]. They found that decalcification and decomposition of the C–S–H was a dominant effect, particularly in magnesium sulfate solution. Brown and Taylor [14] state that in sulfate attack on PC and SRPC concretes, ettringite and gypsum are formed. Formation of both requires a supply of calcium, which is initially obtained by dissolution of calcium hydroxide. When no more calcium hydroxide is readily available, decalcification of C–S–H begins. Calcium hydroxide contents are low or even zero in hardened concretes that are high in ggbs. ggbs concretes tend to fail through disintegration and softening, rather than through expansion and cracking [15] and for them, decalcification may be more destructive than ettringite expansion. This being the case, if the added calcium carbonate was available as a source of calcium for ettringite and gypsum formation, then there would be a reduced need for decalcification of the C–S–H. The reactivity of calcium carbonate and its ability to take part in the reactions associated with sulfate attack, are convincingly demonstrated by the occurrence of TSA. Hence the beneficial effect of the calcium carbonate can be attributed to it being an alternative source of calcium, whose presence reduces the extent of decalcification of the C–S–H.

Further investigation is necessary to resolve the exact mechanisms. Gollop and Taylor's proposed mechanism of reaction of alumina from the ggbs with sulfate to cause 'formation of ettringite at an early stage of hydration', could plausibly account for the effect of calcium sulfate. However the evidence is circumstantial rather than totally conclusive and such a mechanism could not occur with calcium carbonate. The present study demonstrated similar improvements in sulfate resistance with additions of both calcium carbonate and calcium sulfate and it is tempting to suggest that there could be a common mechanism operating, namely that addition of 'calcium ions' reduces the susceptibility to decalcification of the C–S–H.

7. Conclusions

1. Addition of small percentages of either calcium carbonate or calcium sulfate, to ggbs concrete improved the resistance to sulfate attack.
2. Mechanisms can be suggested to account for the increase in sulfate resistance but further investigation is required into this aspect.

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