

Sulphate corrosion behaviour of high volume slag concrete

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Abstract. Concrete mixes of water-cementitious ratio (w/c's) = 0.45, 0.5, 0.65 were used to prepare 100 mm cubes and 75 x 75 x 285 mm prisms. Moderately high alumina slag was incorporated in proportions of 50 or 70% and the specimens immersed in sodium sulphate or magnesium sulphate solutions of 50 g/L as SO₄. Emphasis in the study was to assess sulphate resistance using concrete samples and other non-conventional methods. Expansion measurements, mass loss and corrosion attack or physical deterioration of concrete were monitored for 69 weeks. It was found that the results of expansion, mass gain and corrosion were consistent for Na₂SO₄ solution, showing improved sulphate resistance with increase in ground granulated blast-furnace slag (GGBS) incorporation. The expansion observations under MgSO₄, while showing increased resistance with use of GGBS, gave conflicting results between expansion on one hand and, mass gain and corrosion on the other with the most severe corrosion occurring in concrete containing the high 70% GGBS. The corrosion test method appears to give a more realistic indicator of physical damage under MgSO₄ attack compared to expansion measurement.

Keywords. Sulphate resistance, high alumina slag, corrosion, mass loss, sodium sulphate, magnesium sulphate attack

Introduction

Past studies and field experiences with sulphate attack have generally established that the mechanism is associated with two processes of: (i) expansive chemical reactions within the pore structure of concrete resulting in ensuing pressures, that lead to the next process of (ii) physical degradation associated with cracking and delamination. Low alumina slags are considered to be those containing less than 11% Al₂O₃ in accordance ASTM C 989. Such slags are known to consistently increase sulphate resistance. High alumina slags have been found to show adverse effects and this understanding can be traced to an early South African study [1]. The South African slag used in the present study is of moderately high alumina content, being 13.4% Al₂O₃.

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1. Literature

1.1. Accelerated test methods

It is recognised that while accelerated test methods play an important role in determining early indications of potential long-term behaviour, their results may not provide confirmatory observations for various reasons: (a) the experimental conditions are typically severe than actual site environments, (b) the specimens are much smaller creating a different micro-climate and specimen responsiveness that may deviate widely from a finite element within the typically large-scale concrete element, (c) material characteristics of mortars used in the test may not adequately represent similar concrete properties, (d) overly severe tests may induce attack mechanisms different from those intended to develop in the deterioration process.

Sulphate attack in concrete is usually associated with ettringite formation within the cement paste matrix. It is generally observed that the attack increases with proportional growth in the amount of ettringite formed but there is no direct correlation between expansion observed in laboratory tests and the amount of ettringite formed. Infact, non-expansive systems may contain similar or more ettringite amounts as found in expansive systems [2]. In discussing sulphate attack, Idorn et al. [3] explained that the effect of ettringite formation, which usually causes expansions in laboratory tests, is not usually reflected with field concretes in form of expansions. In view of the range of experimental variations from real-life exposure conditions, it is typical to require that experimental results be related or calibrated against field observations to establish reliability of the accelerated test method. Often times, it is found that useful accelerated test methods provide a means for screening of potential material behaviour over short test time periods for which results must be obtained. But in many cases, the accelerated test methods typically tend towards severity and may fail materials that in real life exposure conditions would not exhibit failure under the mechanism of attack being examined. These fears have been recognised by researchers and in certain fields, confirmatory test methods conducted over relatively longer periods are devised to provide more reliable observations.

1.2. Some past studies on sulphate attack in concrete

In comparison to the mortar prism test of ASTM C 1012, relatively limited literature is available where sulphate resistance evaluation has been conducted using concretes. Khatri and Sirivivatnanon [4] used 75 x 75 x 285 mm prisms to monitor expansion in concrete of 35 MPa and 40 MPa strength grades made with ordinary Portland cement and sulphate resisting Portland cement, with or without 7% silica fume and 60% slag. In their study, mortar prism expansion tests were also conducted but emphasis in the study assessed the possibility of permeability playing a role in influencing sulphate resistance behaviour of the concretes. Specimens were stored in 5% sodium sulphate solution with a pH being maintained constant through automated addition of sulphuric acid. They found that the permeability property influenced expansion results in concretes but does not fully account for the observations made which they attributed to the chemical resistance in the cementitious systems. Some studies [5] along this approach recognise that a complete evaluation for sulphate resistance should adequately consider both the physical and chemical resistance properties of the

cementitious system. In this approach, permeability is favoured as a dominant parameter to represent physical ingress of sulphate into concrete and a method is proposed to rapidly measure sulphate permeability in a manner similar to the Rapid Chloride Permeability Test in accordance with ASTM C 1202.

1.3. Sulphate and magnesium sulphate attack processes

Studies have long established the difference in attack processes between the two different sulphate salts. In the case of external sulphate attack, ions from soils or water sources react with calcium hydroxide in concrete forming gypsum and soluble sodium hydroxide. The gypsum formed in turn converts calcium monosulphoaluminate hydrate into ettringite. The formation of ettringite structure results in large volume increase, leading to infilling of the existing pores and causing expansion in the hardened concrete with its continuous accumulation. In a similar manner, magnesium sulphate forms gypsum and magnesium hydroxide or brucite. But the difference arises from the insoluble nature of $Mg(OH)_2$. It has been reported that at advanced stages of the attack, brucite may replace the calcium component of the calcium silicate hydrate (C-S-H) forming a non-cementitious product M-S-H [6]. A combination of the expansive gypsum reactions to form ettringite and de-calcification of the C-S-H may be responsible for typically devastating physical attack by magnesium sulphate in comparison to sodium sulphate.

2. Experimental

2.1. Mixtures

The present study was conducted using concrete mixtures of w/c's = 0.45, 0.50, 0.65 made using CEM I 42.5N normal strength Portland cement and GGBS, as given in Tables 1 and 2. Ground granulated blast-furnace slag was incorporated as a cement extender in proportions of 50 or 70%. Concrete prisms 75 x 75 x 285 mm and 100 mm cubes were cast then water-cured for 28 days prior to immersion of the specimens in 50 g/L storage solutions of Na_2SO_4 and $MgSO_4$. No air entrainment or other chemical admixtures were used in the concrete mixtures.

Table 1. Chemical compositions of the cementitious materials

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	TiO ₃	Mn ₂ O ₃	Na ₂ O	SO ₃	Cl-	LOI
CEM1 42.5N	21.7	5.3	2.0	62.5	4.6	0.6	0.3	0.9	0.1	2.0	0.02	2.9
GGBS	38.3	13.4	0.8	35.3	7.5	1.0	0.9	1.1	0.3	12.4	0.02	0.7

2.2. Test methods

The test methods employed included conventional measurement of length change (expansion) of the prisms. Mass change was determined for prisms and cubes. In an attempt to quantify physical attack effects on the concretes, a method referred to as

corrosion assessment on cubes, was employed. The measurements were determined at intervals of 0, 2, 8, 13, 17, 25, 29 and 69 weeks.

Table 2. Concrete mixtures used to prepare specimens stored in Na₂SO₄ and MgSO₄ solutions (sg – slag)

Mix	Initial compressive strength upon immersion in sulphate solution (MPa)	GGBS (%)
0.45w/c-CEM I	52.4	0
0.45w/c-50sg	38.3	50
0.45w/c-70sg	28.6	70
0.5w/c-CEM I	48.3	0
0.5w/c-50sg	31.4	50
0.5w/c-70sg	24.0	70
0.65w/c-CEM I	36.5	0
0.65w/c-50sg	22.8	50
0.65w/c-70sg	20.0	70

Corrosion assessment was done by recording the cube diagonals at the top and bottom surfaces using a metric ruler. The ruler was placed on the diagonal across the face and the extent of loss of material or cracking at the corner was recorded in mm. A mean value (d) for each of these two corners was then calculated as:

$$d = (141 - D)/2 \quad (1)$$

Where, D is the length of “unattacked” area visible across the diagonal of the face measured.

The top and bottom faces of each cube as cast were measured in this way. The mean of the d values for the two faces of two cubes i.e. a total of 8 measurements was then considered the corrosion value for a particular mix and age of testing.

3. Results and discussions

3.1. Expansion of prisms

Following 69 weeks of specimen storage in sulphate solutions, expansion occurred only in control prisms while the concretes containing extenders had not exhibited expansion, as seen in Table 3. The effect of water-cement ratio is notable, with mixes of high w/c's giving correspondingly higher expansions. In all cases, the expansion in Na₂SO₄ was always higher compared to the corresponding expansion in MgSO₄, as also seen in Figure 1 for 0.65 w/c concrete. Similar observations were exhibited in the 0.45 w/c and 0.50 w/c concretes, given in Figure 2. In all the blended cement mixes, the difference in expansion between the 50% and 70% slag concretes was small, but the surface deterioration of the 70% slag concrete was found to be quite severe, more especially for the specimen stored in MgSO₄ solution.

Table 3. Expansion of concrete prisms stored in Na₂SO₄ and MgSO₄ solutions

Mix	Expansion (%) after 69 weeks of storage in	
	Na ₂ SO ₄	MgSO ₄
0.45w/c-CEM I	0.06	0.03
0.45w/c-50sg	0.00	0.01
0.45w/c-70sg	0.00	0.00
0.5w/c-CEM I	0.05	0.04
0.5w/c-50sg	0.00	0.00
0.5w/c-70sg	0.00	0.00
0.65w/c-CEM I	1.25	0.30
0.65w/c-50sg	0.00	0.02
0.65w/c-70sg	0.00	0.00

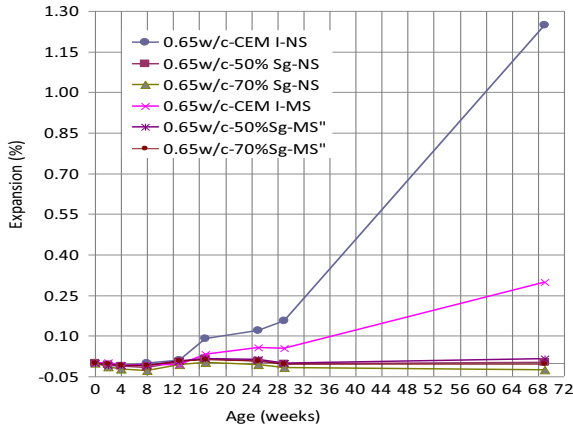


Figure 1. Expansion of 0.65 w/c concrete prisms in Na₂SO₄ and MgSO₄ solutions (NS-sodium sulphate, MS-magnesium sulphate, sg-slag)

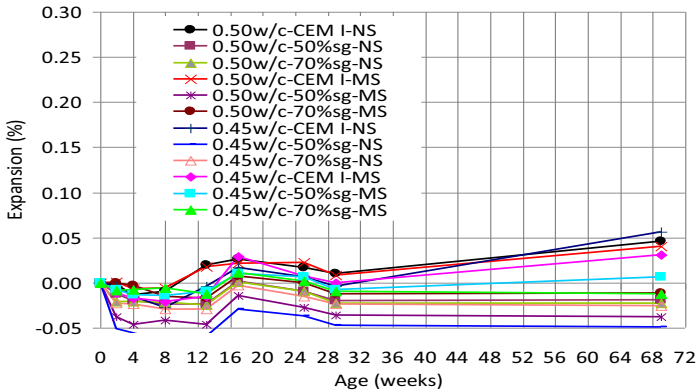


Figure 2. Expansion of 0.50 and 0.45 w/c concrete prisms in Na₂SO₄ and MgSO₄ solutions (NS-sodium sulphate, MS-magnesium sulphate, sg-slag)

3.2. Mass change

The graphs in Figure 3 show the mass gain trends of prisms stored in Na₂SO₄ and MgSO₄ solution for duration of 69 weeks. The mass gain is related to growth of reaction products responsible for deterioration. It can be seen that their deterioration is generally more severe in MgSO₄ solution than in Na₂SO₄ solution, contrary to observations in expansion results where the former shows lesser effect than the latter attack solution. Regardless of the lower values observed in sodium sulphate, CEM I mixes are the ones that gained more weight than the slag blended mixes. Comparing the prisms expansion rate and mass gain of the same prisms, it can be observed in Figures 1 and 4, that the rate of mass gain is initially faster than the expansion rate, this being presumably contributed by immediate water uptake upon immersion of prisms in solution.

Under both the Na₂SO₄ and MgSO₄ storage, the 70% slag replacement mixes expanded the least. The 70% GGBS concrete also gave the least mass gain under Na₂SO₄ but it exhibited the highest mass gain and most severe physical deterioration than all the other mixes when subjected to magnesium sulphate attack. This contrast in behaviour of magnesium sulphate relative to sodium sulphate is related to the formation of brucite in the former, as already explained in the foregone. At the age of 29 weeks of sample storage in MgSO₄, the 50% slag concrete of 0.45 w/c had 0.90% mass gain in comparison to 3.1% for 70% slag concrete and 1.31% mass gain for CEM I (see Figure 3). On the basis of mass gain and expansion alone, it would appear that the 50% slag concretes showed better performance in the magnesium sulphate solution than the CEM I or the 70% slag concretes. While in the Na₂SO₄ solution, performance improved with increase in proportion of slag incorporated into the mix.

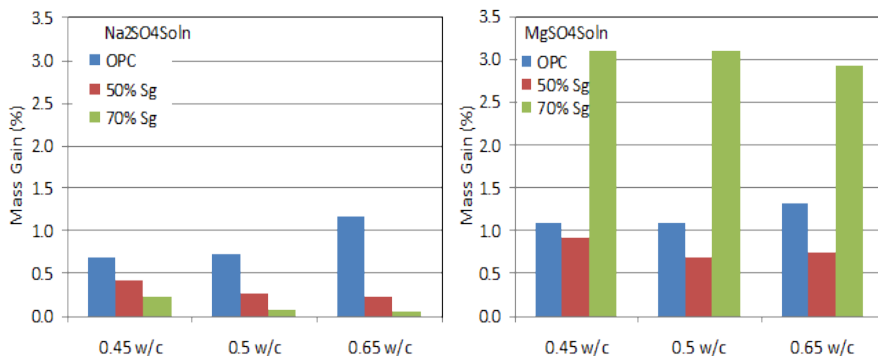


Figure 3. Mass change of concrete prisms after 29 weeks of storage in Na₂SO₄ and MgSO₄ solutions (OPC = CEM I Portland cement)

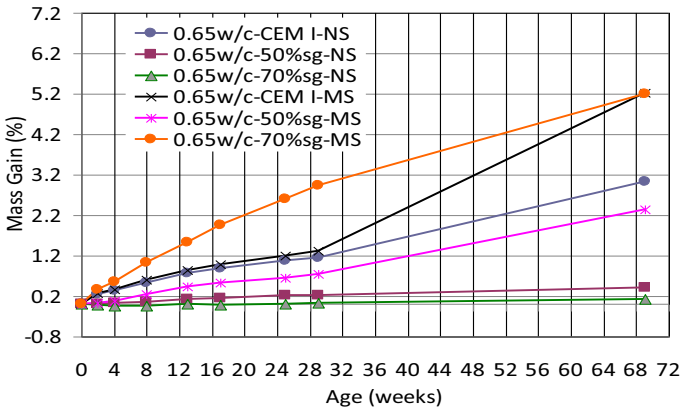


Figure 4. Mass change of 0.65 w/c concrete prisms after 29 weeks of storage in Na₂SO₄ and MgSO₄ solutions

3.3. Corrosion

The Figures 5 and 6 give the corrosion results for cubes that were exposed in Na₂SO₄ and MgSO₄ solutions for a period of 69 weeks. For specimens exposed to Na₂SO₄ solution, there is a clear separation between the corrosion results of CEM I mix samples on one hand, and the results of mixes containing GGBS extender, considering all the three w/c mixtures. It is evident that corrosion attack occurred only in the plain CEM I concrete cubes containing no extenders. The CEM I mixes of 0.45, 0.50, 0.65 w/c's gave respective corrosion values of 9.8%, 12%, 13.6% as compared to 2 to 3% corrosion in the mixes incorporating GGBS extender. There was no significant difference between the corrosion values of 50 % and 70% slag mixes.

The corrosion results for mixes stored in MgSO₄ solution gave a different and contrary behavior from that observed under Na₂SO₄ storage. Figure 6 shows that for the cube samples stored in MgSO₄ solution, plain CEM I concretes gave better corrosion performance than slag blended mixes. The corrosion increased with increase in the proportion of GGBS incorporated and with increase in w/c ratio. After 69 weeks of storage, the corrosion in the plain CEM I mixes was in the range of 3 to 5% compared to 7 to 17% in slag blended mixes, depending on the w/c and slag proportion. The disintegration of concrete was already excessive just in five months of exposure of the 70% slag mix in MgSO₄, while the corresponding CEM I mixes showed no significant deterioration over the same period. In comparison of expansion results and the corrosion observations under Na₂SO₄ storage, it is quite interesting to note that both methods were in good agreement, showing the same tendencies in behavior of the mixes. Only the plain CEM I mixes showed expansion and also showed corrosion attack. The blended mixes showed neither expansion nor corrosion. But under the MgSO₄ attack, it was found that the expansion results showed a different behavior from the corrosion results. The expansion of prisms in the magnesium sulphate solution was less compared to corresponding expansions in sodium sulphate, but the reverse was true for corrosion, with deterioration being severe in magnesium sulphate than in

sodium sulphate solution. The behaviour of the two solutions emphasizes the need to know the type of sulphate present in the soil, groundwater or the exposure environment before deciding on the suitable mix design.

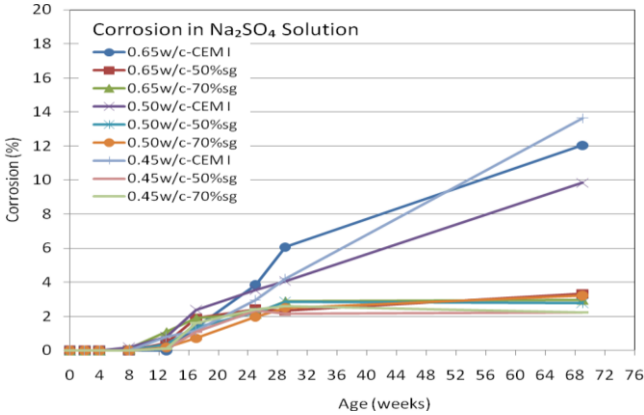


Figure 5. Corrosion of concrete cubes stored in Na₂SO₄ solution

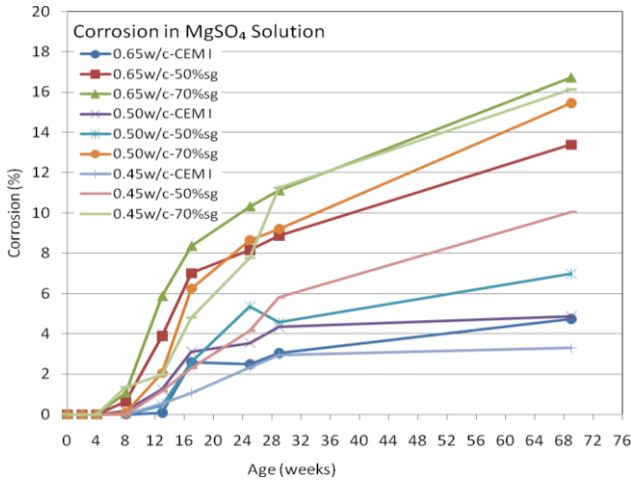


Figure 6. Corrosion of concrete cubes stored in MgSO₄ solution

4. Conclusions

In the foregone investigation, both conventional and some non-conventional methods were used to assess the sulphate corrosion behavior of high volume slag concrete subjected to two different forms of sulphate solutions namely, Na₂SO₄ and MgSO₄ solutions.

Basing on the expansion measurements conducted up to 29 weeks, it was found that the moderately high alumina slag was effective in increasing the resistance of cementitious systems against both magnesium and sodium sulphate attack but the expansions under sodium sulphate were far greater than corresponding results under magnesium sulphate solution.

For sodium sulphate attack, the corrosion results were in agreement with expansion results. However, for magnesium sulphate attack, the corrosion and mass change results contradict expansion results with systems containing slag exhibiting greater corrosion in proportion to the amount of slag incorporated. The 70% slag extender was found to be especially vulnerable to significant physical deterioration from magnesium sulphate attack. The use of 50% slag blend in conjunction with a low water-cementitious ratio ≤ 0.5 , appears to exhibit a combination of generally good chemical and physical resistance to both sodium and magnesium sulphate attack processes. It can be concluded that the expansion method alone is not capable of representing the physical resistance of concretes under magnesium sulphate attack.

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