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Sulphate resistance of concrete made with moderately high alumina slag

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Abstract. This paper reports findings of ongoing investigation into the effect of high alumina ground granulated blast furnace slag (GGBS) on sulphate resistance of concrete. Slags used in most countries contain low alumina contents and provide high resistance to sulphate attack among other durability improvements. It is however known that slags of high alumina contents do not necessarily improve sulphate resistance but may otherwise adversely influence concrete performance. South African slags have moderately high alumina contents but hardly any studies have been conducted to determine its influence on sulphate resistance of concretes. In this investigation, commercially available slag widely used in South Africa was used. Mortar prisms 25 x 25 x 285 mm of 0.5 water-binder ratio incorporating 30%, 50%, 70% GGBS were prepared and immersed in sodium sulphate solutions of different concentrations of 28 g/L and 50 g/L as SO4.

Expansion and mass change of the cementitious systems were monitored. Variables examined were compressive strengths prior to immersion in Na_2SO_4 solution, slag replacement levels, concentrations of sulphate solutions. It was found that the moderately high alumina slag improved resistance to sulphate attack in correspondence with increase in the replacement levels of the extender. Mixtures that were not cured to develop 20 MPa initial strength prior to exposure in Na_2SO_4 solution, showed elevated early age expansion while their cured counterparts did not expand. The long-term expansions of mixtures that had not been cured were much higher than expansions of the respective cured mixes. Interestingly, the use of GGBS in proportions exceeding 50% mitigated the adverse effects of early age expansions giving no long-term expansions in any of the mixtures containing the extender.

Keywords. Sulphate resistance, mortar expansion, initial compressive strength, South African slag, sulphate concentration

Introduction

In South Africa, sulphate attack is not a dominant problem like other deterioration mechanisms such as alkali-silica reaction, and research towards sulphate attack has in the past not received much attention locally. However, sulphates do occur in soils and ground water in significant proportions in and around some brownfields, and naturally in some parts of the country, mostly in the western provinces. Besides natural sources of sulphate ions, urban occupancy, domestic lifestyles and industrial effluents also discharge sulphate laded wastes into existing infrastructure.

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Sulphate attack may therefore occur in sewer pipes and sewage storage tanks among other structures. As such, it is of interest to develop clear scientific understanding of the potentials and implications associated with use of extenders including local slag extenders in situations where sulphate attack is possible.

1. Background

1.1. An early South African study

This paper is first in a series of reports of an ongoing study of the effect of ground granulated blast-furnace slag produced in South Africa on sulphate resistance of concrete. The extender is widely used and typically incorporated in proportions of 50% but higher levels of up to 70% may also be used for special applications. It contributes significantly to the concrete industry due to major benefits ranging from its influence on engineering properties to environmental impact. While the contribution of the GGBS to engineering properties and durability of concrete are generally accepted to be significantly beneficial, little is known about their effect on sulphate resistance of concrete.

Emphasis in this investigation was placed on the potential ability of South African GGBS to mitigate sulphate attack in concrete. The practice of using GGBS to provide high sulphate resistance to concrete is well established for slags in Europe, North America and other countries where sulphate attack can be prevalent and an extensive body of knowledge in this regard has been accumulated. Research knowledge available in the mainstream literature may lead to the somehow erroneous view that GGBS does always provide improved sulphate resistance in concrete regardless of its source or type. Emerging research now appears to indicate that not all slags are capable of improving sulphate resistance of concrete.

1.2. High alumina slags

ASTM C 989 [1] recognises that there is an exception to contribution of high alumina slags to sulphate resistance. Alumina content of slags not exceeding 11% is considered to be low Al_2O_3 while high alumina contents can be as much as 18% Al_2O_3. However, the influence of alumina content is not necessarily an overriding factor in the different cementitious systems containing slags. Alumina affects sulphate resistance in conjunction with its interaction with the C_3A levels present in cement. ASTM C 989 stipulates that high replacement levels exceeding 60% slag should increase sulphate resistance irrespective of the composition of slag or cement while low Al_2O_3 content of slag should ensure improved sulphate resistance in cementitious systems.

Van Aardt and Visser [2] while conducting a study of South African slags in sulphate solutions, were among the first to show that alumina content of slags played an important role in determining the influence of the extender on sulphate resistance. Their study was conducted using mortars cured in water for 28 days prior to immersion in 5% magnesium sulphate or 5% sodium sulphate solutions. Expansion and the dynamic modulus of specimens were monitored. The cementitious materials used were ordinary Portland cements of 0, 6.6, 6.9% C_3A contents; milled GGBS of 10.1, 15.5, 18.4% Al_2O_3; and one sulphate resisting Portland cement (SRPC). Cement /slag blends used in the experiment consisted of 30%, 50% and 70% slag. They found that the performance of the blends was dependent on the Al_2O_3 of the slags. The slag with 10.1% Al_2O_3 increased sulphate resistance of the mixture. Increase in the Al_2O_3 content of slags reduced sulphate resistance with the slag containing a high 18.4% Al_2O_3 giving results poorer than Portland cement alone. Use of higher slag contents led to relatively improved sulphate resistance but in all cases, worse than results of control mix. These NBRI findings somehow disagree with ASTM C 1012 which stipulates that use of high replacement levels exceeding 60% should, by implication improve sulphate resistance even for high Al_2O_3 slags.

The findings of the National Building Research Institute (NBRI) study were mentioned in the earlier edition of Fulton's Concrete Technology [3]. Later, an independent Australian study [4] made reference to these NBRI findings, pointing out that some of the Australian slags also had similarly high Al_2O_3 contents in the range of 17%, and so an investigation into their performance was conducted. In their experiment, cylindrical specimens 31.5 mm dia x 63 mm long were prepared using mortars of 1: 3 cement to sand, and water-cement ratio (w/c) of 0.5. Specimens were cured in water for 28 days before immersion in 5% sodium sulphate solution. Length change was monitored. The slag studied contained 17% Al_2O_3 and was blended in proportions of 50% with Portland cements of 3.8% and 8% C_3A contents. Their results showed the cement/slag blends to be highly expansive in sulphate solutions than the control mix containing Portland cement alone, confirming the findings of Van Aardt and Visser [2].

The current scientific understanding appears to suggest that slags with low Al_2O_3 contents significantly increase sulphate resistance when used as extender in concrete. North American slags have low alumina contents of 8 to 11%, and are used to mitigate sulphate attack in concrete but in the pacific rim, slags of high Al_2O_3 of 12 to 18% have been reported. While these slags are known to provide high durability improvement against deterioration due to attack mechanisms such as corrosion and alkali-silica reaction, they generally show poor resistance to sulphate attack. Their high Al_2O_3 content is clearly the main influential factor, but it has also been suggested that this alone does not fully account for the observed behaviour [5]. Further research is needed to establish fully the critical factors responsible for the differing behaviours between high and low alumina slags under sulphate environments.

The objective of this investigation was to assess the performance of proprietary cementitious materials incorporating South Africa slags under sulphate environments. This was done against the background of the early NBRI study [2]. Experimental details of the investigation, results, discussion of findings and conclusions are presented in the subsequent sections.

2. Experimental

2.1. Mixtures

CEM I 42.5N normal strength Portland cement was used in the study with normal cured mortars. The extender used was a commercially available slag incorporated in cement in varied proportions of 30%, 50%, and 70%. Table 1 shows the composition of the cementitious materials used. Mortar bars 25 x 25 x 285 mm were prepared according to ASTM C 1012 and either moist-cured in water for 21 days or immersed immediately in sulphate solutions. Mortar mixtures consisting of 1: 2.25: 0.5 cement to sand to water were made using South African silica sand. No air entrainment or admixtures were used in the mortar mixtures.

2.2. Curing and storage

ASTM C 1012 requires attainment of 20 MPa compressive strength prior to immersion of specimens in sulphate solution. In this study, two sets of mortar mixtures were cast for each mixture. One set designated with *'X'*, was allowed to develop minimum required strength which was achieved at around 21 days of curing in water. The other set of mortar mixes designated with *'i'* were those immersed in sulphate solutions immediately after demoulding of specimens i.e. without curing. Two different concentrations of sodium sulphate solution of 28 g/L and 50 g/L as SO_4 were used. Length change measurements were monitored at regular intervals. In Table 2 are given the mix combinations used including the initial compressive strengths at time of immersion of the mortar specimens in sulphate storage solutions, binder proportions, and the concentrations of the storage solutions for each mix.

Table 1. Chemical compositions of the cementitious materials

	CEM1 42.5N	**GGBS**	**50/50 CEM/GGBS**
SiO_2	21.7	38.3	30.1
Al_2O_3	5.3	13.4	9.4
Fe_2O_3	2.0	0.8	1.4
CaO	62.5	35.3	48.4
MgO	4.6	7.5	6.1
K_2O	0.6	1.0	0.8
TiO3	0.3	0.9	0.6
Mn2O3	0.9	1.1	1.0
Na_2O	0.1	0.3	0.2
SO_3	2.0	12.4	2.3
Cl-	0.02	0.02	0.02
LOI	2.9	0.7	1.1
C_3A	10.7		
C_3S	45.3		
C_2S	28.3		
C_4AF	6.1		
Blaine fineness (m^2/kg)	337.5	384.1	364.1
45 μm sieve residue (%)	14.9	14.8	14.7

3. Results

Expansion results were examined on the basis of variables consisting of the initial compressive prior to exposure of specimens to sulphate solutions, concentrations of Na_2SO_4 solution, and the replacement levels of GGBS. All the samples were made of CEM 1N 42.5 of 10.7% C_3A and GGBS of 13.4% Al_2O_3 (see Table 1). Figures 1 to 3 give the results of expansion measurements observed for the various mixtures and storage conditions.

Table 2. Mortar mixtures, binders and storage solutions

Description	Mix	Initial compressive strength (MPa)	GGBS (%)	Na_2SO_4 (g/L)
Mortars immersed in sulphate solutions immediately i.e. at one day, without water curing (i-mixes)	0-28g/L-i	11.5	0	28
	0-50g/L-i	11.5	0	50
	50%-28g/L-i	6.4	50	28
	50%-50g/L-i	6.4	50	50
	70%-28g/L-i	4.2	70	28
	70%-50g/L-i	4.2	70	50
Mortars immersed in sulphate solutions after 21 days of curing in water (x-mixes)	0-28g/L-x	29.3	0	28
	0-50g/L-x	29.3	0	50
	30%-28g/L-x	26.3	30	28
	50%-28g/L-x	22.8	50	28
	50%-50g/L-x	22.8	50	50
	70%-28g/L-x	17.3	70	28
	70%-50g/L-x	17.3	70	50

3.1. Effect of minimum compressive strength at immersion of mortars in sulphate solution:

The compressive strengths at one day and at 21 days are shown in Table 2 for mixtures containing varied replacement proportions of GGBS. As expected, the mixtures incorporating GGBS developed lower early strengths with increase in the proportion of the extender. Mixtures containing 70% GGBS were able to achieved only 17 MPa after 21 days. However, this was considered substantial enough to relatively avoid or significantly minimize undue effects of low early strengths. The significance of 20 MPa as a requirement in conduct of the ASTM C 1012 compressive strength is intended to allow adequate initial tensile strength to develop within the cementitious matrix for resistance of expansive pressures. The requirement is considered important with regard to the relatively slower early strength development in the mixtures containing extenders. Without adequate strength development it has been argued that the dilution effect of using extenders can result in undue penalization of mixtures incorporating extenders, resulting in poorer results.

Figure 3 gives the initial development of expansions in the cured and non-cured prisms. It can be seen that the non-cured specimens of low strengths prior to immersion in Na_2SO_4 solution exhibited relatively elevated early-age expansion values in the range of 0.05% compared to 0.0% expansion for their water-cured counterparts. Despite the initial ‘shock effect’ due to low early strengths in non-cured specimens, resulting in their early-age elevated expansions, the long-term results indicate that the mitigating effect of GGBS against sulphate expansion was not affected as mixes containing 50 or 70% GGBS showed no expansion whatsoever (Figure 1). In fact, it is evident that after about 3 months of storage, the use of GGBS caused a reversal of the early age elevated expansions in the non-cured mixtures, reducing the early age expansion of 0.05% to a level of 0% in the long-term.

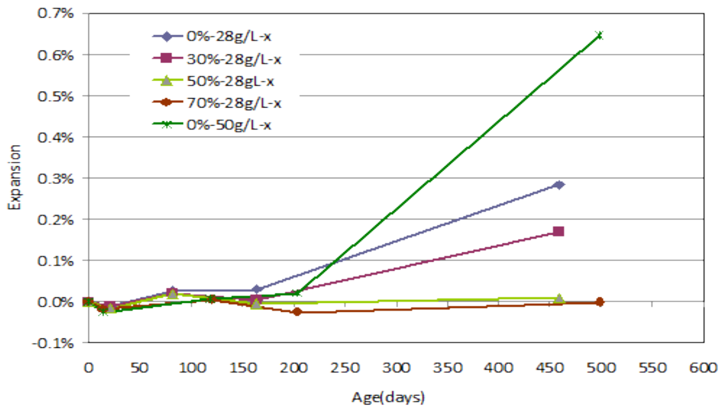

Figure 1. Expansion of mortar prisms not cured prior to storage in 28 g/L and 50 g/L Na_2SO_4 solutions i.e. immersed at the low one-day compressive strengths

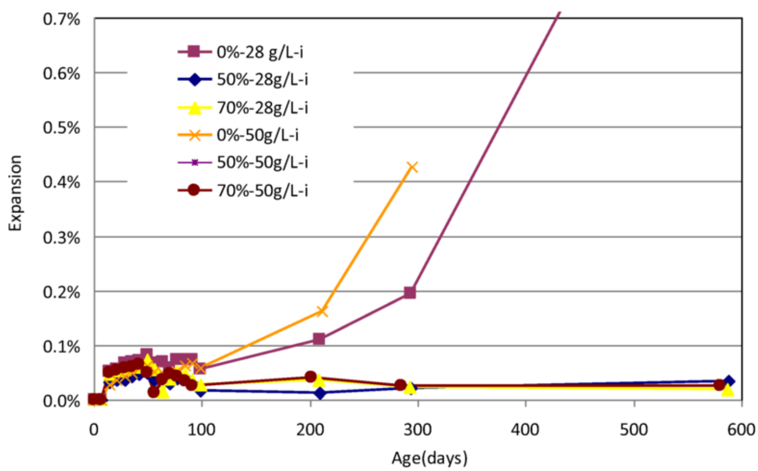

Figure 2. Expansion of mortar prisms cured in water to attain high compressive strengths prior to storage in 28 g/L and 50 g/L Na_2SO_4 solutions

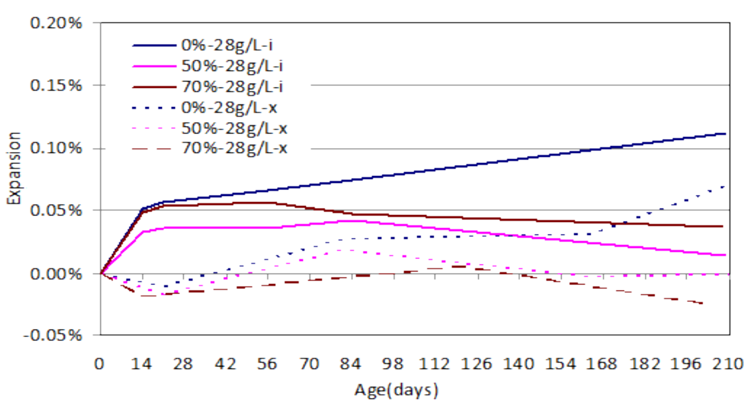

Figure 3. Early – age expansion results for cured and non-cured mortar prisms stored in 28 g/L Na_2SO_4 solution

For plain /control mixtures (not incorporating GGBS), the long-term expansions were much greater in the non-cured mixes i.e. of lower initial compressive strengths compared to their water-cured counterparts. At the age of 500 days, the expansions of non-cured and water-cured prisms were 1.29% and 0.28% respectively for specimens stored in 28 g/L Na_2SO_4. Similar results were observed for 50 g/L Na_2SO_4 storage solution (see also Table 3).

The mass change results of the cured mortar mixes are given in Figure 4, showing similar tendency as the expansion results (Figure 2) with the plain mortars giving greater mass gain relative to the mortars containing extenders. Generally, the mass gain decreased with increase in proportion of GGBS incorporated. Expansive mortars broke after about 2 to 6 % mass increase.

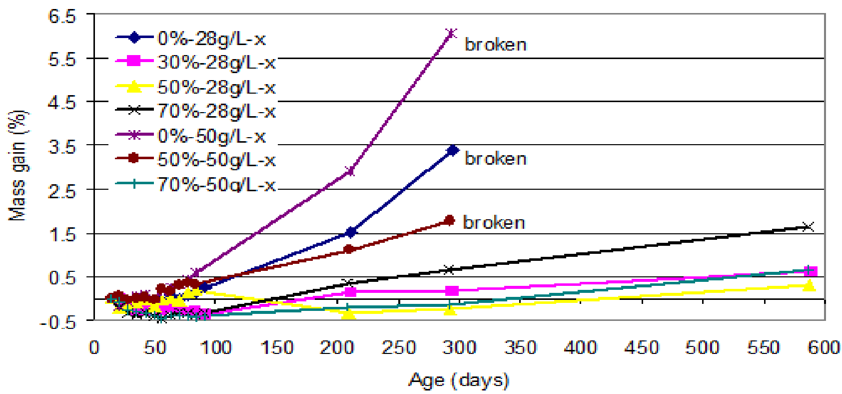

Figure 4. Mass change results for the cured mortar prisms stored in 28 g/L or 50 g/L Na_2SO_4 solution

3.2. Effect of the concentration of Na_2SO_4 storage solution

Two solution concentrations of 28 g/L and 50 g/L Na_2SO_4 were used in the study. Some past studies [6] have reported that higher Na_2SO_4 concentrations may give lower expansions than lower Na_2SO_4 concentrations. In this study, the effect of solution concentration can be seen from Table 3, showing that the expansions observed were greater the higher the Na_2SO_4 concentration, also plotted in Figure 5 for the ages of 300 and 500 days. The graph does not include mixtures containing GGBS as no expansions resulted from these specimens.

Table 3. Influence on Na_2SO_4 concentration on expansion of control mixes

Specimen	Age (days)	Expansion (%)
0%-28g/L-i	300	0.19
0%-28g/L-i	500	1.29
0%-28g/L-x	500	0.28
0%-50g/L-i	300	0.43
0%-50g/L-i	500	broken
0%-50g/L-x	500	0.65

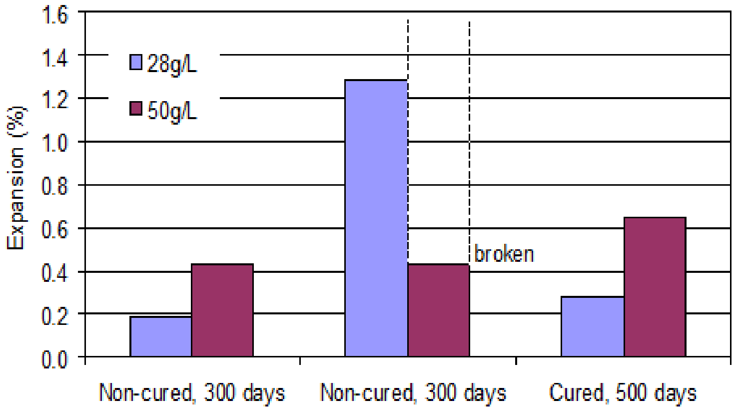

Figure 5. Influence of initial compressive strengths and storage solution concentrations on long-term expansion

3.3. Effect of GGBS content on sulphate resistance

It is evident in Figure 2, that the sulphate resistance of the mixtures increased with increase in the proportion of GGBS incorporated. For specimens stored in 28 g/L Na_2SO_4 solution, the expansions at 460 days for mixes incorporating 0%, 30%, 50, 70% were 0.28%, 0.17%, 0.01%, 0.00% respectively. The results showed some expansion at 30% GGBS but no expansions were observed for 50 or 70% GGBS. The results are consistent with the well established understanding in the literature, that higher GGBS proportions are required to effectively control sulphate resistance.

4. Conclusions

The effectiveness of South African slag of moderately high alumina content of 10.7% C_3A and 13.4% Al_2O_3, was investigated along with the influence of initial strength requirements and solution concentrations.

Basing on the observations of up to 600 days, it was found that the moderately high alumina slag was effective in increasing the sulphate resistance of cementitious systems. Incorporation of at least 50% GGBS was effective in preventing sulphate expansion. The results that did not meet the initial compressive strength requirement of 20 MPa gave relatively high long-term expansion measurements, in those mixtures not containing GGBS. For mixtures containing ≥50%, the low initial strength had no effect on the long-term results as no expansion resulted. But in all cases, the non-cured specimens with low initial strengths showed relatively elevated early age expansion measurements compared to their water-cured counterparts. For the limited Na_2SO_4 solution concentrations used, mortar expansions increased with increase in sulphate concentration of the storage solution.

Acknowledgement

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References

[1] American Society for Testing and Materials, Standard specification for ground granulated blast-furnace slag for use in concrete and mortars, *Annual Book of ASTM Standards, ASTM C989*, 2006.
[2] Aardt and Visser., The behaviour of mixtures of milled granulated blast-furnace slag and Portland cement in sulphate solutions, *National Building Research Institute (NBRI),* Bulletin **47,** 1967, USA.
[3] Fulton., *Fulton's Concrete Technology*, Second edition, Portland Cement Institute, Midrand, South Africa, 1974, pp. 956.
[4] Heaton B.S., Down F.W. and Emery J.J., Properties of ground granulated slag in cement blends, *National Slag Association* (NSA), pp. 181 – 12.
[5] Hooton, R.D., A review of different forms of sulphate attack, *Dept of Civil Engineering, University of Toronto,* 35 St George Str., Toronto, Canada.
[6] Hooton R.D. and Emery J.J., Sulfate resistance of a Canadian slag cement, ACI Materials Journal, V. 87, No. 6**,** 1990, pp. 547-555.