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Sulfate attack on alkali-activated slag concrete

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Abstract

This paper presents an investigation into durability of alkali-activated slag (AAS) concrete in sulfate environment. Two tests were used to determine resistance of AAS concrete to sulfate attack. These tests involved immersion in 5% magnesium sulfate and 5% sodium sulfate solutions. The main parameters studied were evolution of compressive strength, products of degradation, and microstructural changes. After 12 months of exposure to the sodium sulfate solution, the strength decrease was up to 17% for AAS concrete and up to 25% for ordinary Portland cement (OPC) concrete. After the same period of exposure to the magnesium sulfate solution, the compressive strength decrease was more substantial, up to 37% for OPC and 23% for AAS. The main products of degradation were ettringite and gypsum in the case of Portland cement and gypsum in AAS. OPC samples had significant expansion, cracking, and loss of concrete, while AAS samples were not expanded but cracked in the test. During experiments with the sodium sulfate solution, some increase in strength of AAS concrete was recorded, likely due to continuing hydration.

Keywords: Ground granulated blast furnace slag; Alkali-activated cement; Durability; Sulfate attack

1. Introduction

Use of alkali-activated slag (AAS) in concrete manufacturing has environmental benefits as its production requires less energy than ordinary Portland cement (OPC) and it utilises industrial by-products [1]. AAS concrete was also reported to have a superior durability in aggressive environments as compared to OPC [2–4]. However, variability in chemical composition of slag may have an effect on its durability, and concretes prepared using different slags may have different resistance in aggressive media. This paper presents the study of the durability of AAS concrete produced using Australian slag in sulfate environment. Sulfate attack is known to produce significant degradation in concrete structures. Therefore, much attention was drawn to provide an adequate protection for concrete in contact with surroundings with high content of sulfate ions.

It was established that sulfate attack on OPC concrete is associated with the chemical reaction of sulfate ions as the aggressive substance and the aluminate component of hardened cement paste [5]. The reaction between these substances, if enough water is present, produces ettringite and gypsum and causes expansion of the OPC concrete, leading to cracking with an irregular pattern. These cracking gives easier access to further penetration of sulfates and the process continues up to complete disintegration. In 1930s, it was established that OPC concrete that was low in aluminium had a superior resistance in sulfate environment [6,7]. Later, it was found that slag concrete had good durability in sulfate environment and the mode of degradation of slag concrete was different from that of OPC concrete. This paper considers effect of sulfate attack on AAS concrete that was prepared using slag activated by alkaline activator as the only binder.

2. Experimental

2.1. Materials

The chemical composition of slag is shown in Table 1. The blast furnace slag is a granulated product ground to fineness of about 460 m^2/kg, with the particle size range of 1–10 μm, and is neutral with the basicity coefficient

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Table 1
Composition of slag

Oxide (wt.%)	Slag[a]	Portland cement[b]
SiO_2	35.04	19.9
Al_2O_3	13.91	4.62
Fe_2O_3	0.29	3.97
CaO	39.43	64.27
MgO	6.13	1.73
K_2O	0.39	0.57
Na_2O	0.34	
TiO_2	0.42	
P_2O_5	<0.1	
MnO	0.43	
SO_3	2.43	2.56
Sulfide sulfur as S^{2-}	0.44	
Cl (ppm)	80	
Loss on ignition	1.45	2.9
Bogue compounds (%)		
C_3S		64.2
C_2S		9.3
C_3A		5.7
C_4AF		12.2
Fineness (m^2/kg)	460	342

[a] Steel Cement, Port Melbourne, Australia.
[b] Type I/II, Geelong, Victoria, Australia.

$K_b = (CaO + MgO)/(SiO_2 + Al_2O_3)$ equal to 0.93. The slag is supplied with 2% blended gypsum. The chemical composition and properties of OPC used in OPC concrete preparations are also detailed in Table 1.

AAS concrete was prepared using sodium silicate glass (PQ Australia, sodium silicate solution Grade D, weight ratio $SiO_2/Na_2O = 2$, $\%Na_2O = 14.7$, $\%SiO_2 = 29.4$) and sodium hydroxide solutions (Ajax Chemicals, 60% w/v water solution) as activators. Liquid sodium silicate and sodium hydroxide were blended providing the modulus in solution (mass ratio of SiO_2 to Na_2O), M_s, equal to 0.75, and 5.4% Na_2O in mixture with slag. A previous investigation of Collins and Sanjayan [8] of AAS concrete utilised powdered sodium silicate and lime for slag activation. The current study does not include lime for slag activation.

Table 2 shows mix designs for concrete specimens. The AAS concrete had a nominal strength of 40 MPa at 28 days. The water-to-binder (w/b) ratio for AAS was fixed to 0.5 to enable direct comparison with OPC and to obtain reasonable concrete workability. OPC samples had a nominal compressive strength of 40 MPa at 28 days, and w/b = 0.5. Mixing of concrete was performed in a 70-l mixer. The sequence of mixing was as follows: mix for 2 min, rest for 2 min, and followed by remixing for 2 min. Activators were added in water, the chemical admixture was added in concrete mix.

2.2. Test procedures

ASTM C1012 *Test Method for Length Change of Hydraulic Cement Mortars Exposed to a Sulfate Solution* was used as a basis for the concrete sulfate resistance test. AAS concrete cylinders were cast and cured in a fog room for 28 days, after that the compressive strength was measured. The concrete specimens were then immersed in two solutions (a) containing 0.352 M of Na_2SO_4 (about 5% Na_2SO_4 solution) and (b) containing 0.352 M of $MgSO_4$ (about 5% $MgSO_4$ solution). The solutions in containers were replaced every 2 weeks for the first 3 months, and then at 4, 6, 9, and 12 months of exposure. The compressive strength was measured periodically over 12 months. The deterioration was followed by a record of visual observations and X-ray diffraction (XRD) for identification of degradation products.

At predetermined intervals, the specimens were tested to find a strength reduction. Compressive strength testing was conducted on cylinders ($\emptyset$ 100 × 200 mm). Prior to the compressive strength test, concrete cylinders were taken from the solution, dried, capped by sulfur compound, and tested. A total of three cylinders were tested for each datapoint. The companion specimens, cured in potable water, were also tested in compression. A reduction in compressive strength was calculated as follows:

$$\text{reduction in compressive strength } \% = [(A-B)/A] \times 100\%,$$

where A (in MPa) is the average compressive strength of three specimens cured in water and B (in MPa) is the average compressive strength of three specimens cured in the test solution.

To perform XRD analysis, mortar was carefully removed from the surface region of a concrete sample subjected to test. Each mortar sample was finely ground and then analysed using XRD. XRD analyses were made using Rigaku Geigerflex D-max II automated diffractometer with

Table 2
Mix proportions of concretes (kg/m^3)

Mix description	Added water	Cementitious	Sodium hydroxide solution	Sodium silicate solution	Total water[a]	Coarse aggregates[b]	Fine aggregates[c]
AAS	147.4	slag: 360	30.14	36.72	180	1130	830
OPC	180	cement: 360	–	–	180	1130	830

[a] Total water includes added water and water in sodium silicate and sodium hydroxide solutions.
[b] Old basalt 14/10 mm (Pakhenham, Victoria).
[c] Concrete sand, FM = 2.18 (Lydhurst, Victoria).

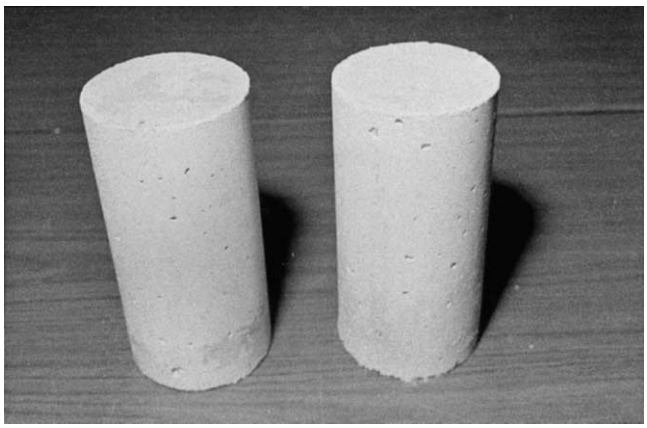

Fig. 1. AAS concrete cylinders exposed to sodium sulfate solution for 12 months showing no signs of deterioration.

Fig. 3. OPC concrete cylinders exposed to sodium sulfate solution for 12 months. Some expansion and cracking on the surface of concrete specimens are evident.

the following conditions: 40 kV, 22.5 mA, Cu–Kα radiation. The XRD patterns were obtained by scanning at 0.1° (2θ)/min and in steps of 0.01° (2θ).

3. Results

Visual examination of AAS concrete subjected to sulfate test for a period of 12 months showed (a) no signs of deterioration of the specimens of AAS concrete in Na_2SO_4 solution (Fig. 1) and (b) cracking of concrete at the corners of specimens immersed in $MgSO_4$ solution (Fig. 2). After 2-month exposure to magnesium sulfate solution, elongated needle-like crystals grew on the AAS concrete surface and clustered at the capillary pores. Through XRD analysis, the crystals appeared to be gypsum. AAS concrete cylinders exposed to the magnesium sulfate solution for 12 months had some cracking started to develop at the cylinders' corners.

Visual examination of OPC concrete subjected to sulfate test for a period of 12 months showed (a) expansion and cracking of the specimens of in Na_2SO_4 solution (Fig. 3) and (b) an expansion, cracking, and loss of concrete at the corners of OPC concrete specimens immersed in $MgSO_4$ solution (Fig. 4). OPC concrete experienced greater expansion in sodium sulfate than in magnesium sulfate solution, but the cracking and loss of concrete was more significant in the latter.

3.1. Compressive strength

The evolution of the compressive strength of concrete specimens placed in sodium sulfate and magnesium sulfate solutions is shown in Figs. 5 and 6, respectively. The data on strength reduction for the same specimens are shown in Figs. 7 and 8, respectively. Up to 60 days, strength reduction was the same for AAS and OPC concretes in both environments. After that time, the strength reduction in OPC was higher than that in AAS samples in both environments. For example, after 12 months, the strength reduction for OPC concrete was 25% in sodium sulfate and 37% in magnesium

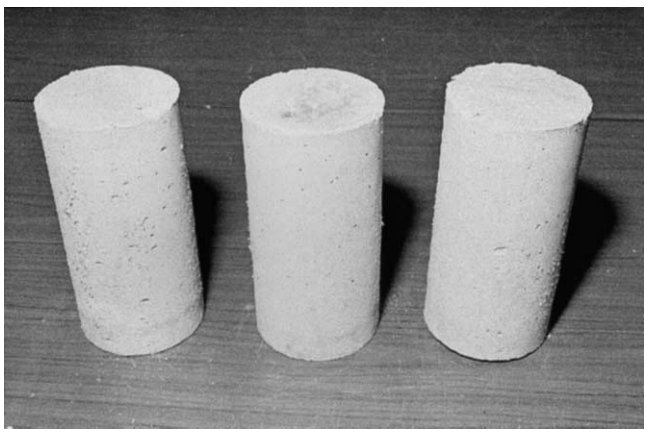

Fig. 2. AAS concrete cylinders exposed to magnesium sulfate solution for 12 months. Cracking on the corners of some specimens is observed.

Fig. 4. OPC concrete cylinders exposed to sodium sulfate solution for 12 months. Some expansion, cracking, and loss of concrete at the corners were observed.

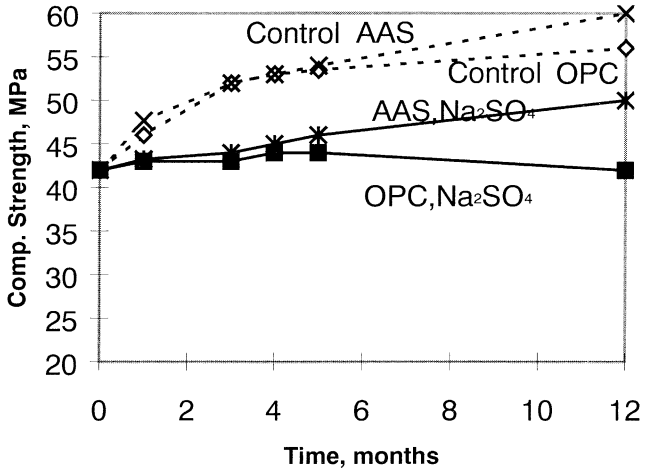

Fig. 5. Compressive strength of AAS concrete subjected to 5% Na_2SO_4 solution.

sulfate solutions, while for AAS concrete it was 17% and 23%, respectively. For both concretes, the strength reduction was higher in magnesium sulfate than in sodium sulfate solution. After 12 months of exposure, the strength reduction in AAS specimens placed in magnesium sulfate was about 1.35 times that in sodium sulfate solution, while in OPC samples this ratio was about 1.5 times. In AAS concrete, some loss of strength was observed by comparing samples stored in water with samples under $MgSO_4$ and Na_2SO_4 attack. However, in AAS samples, the loss of strength was less than in corresponding OPC samples.

In summary, AAS concrete performed better than OPC concrete of a similar grade when exposed to sulfate attack. In fact, AAS concrete had some increase in strength with time in sodium sulfate solution and no significant strength loss in magnesium sulfate solution. However, OPC concrete of a similar grade had more significant loss of strength in both solutions and had visual signs of susceptibility to sulfate attack such as expansion, cracking, and concrete loss.

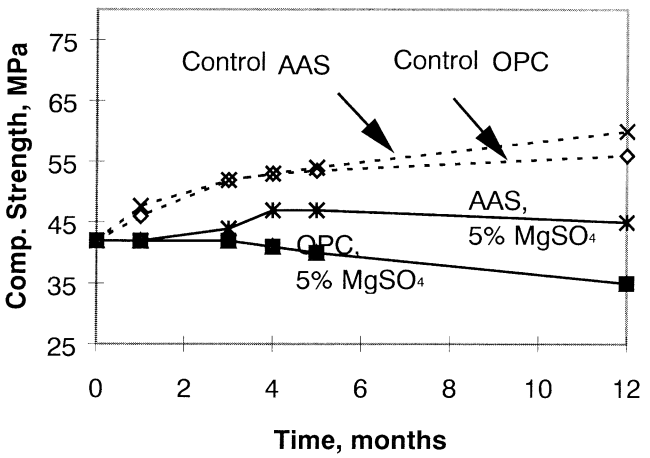

Fig. 6. Compressive strength of AAS concrete subjected to 5% $MgSO_4$ solution.

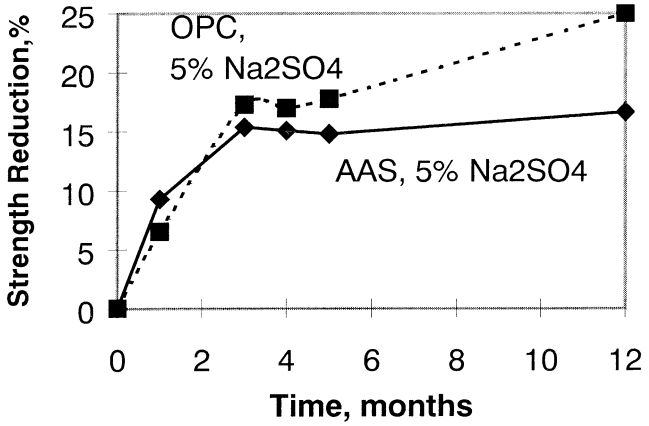

Fig. 7. Compressive strength reduction of AAS and OPC samples subjected to sulfate attack in 5% Na_2SO_4 solution.

3.2. XRD

The XRD analysis of the mortar from the surface of AAS and OPC samples showed different degradation products in AAS and OPC concretes (Fig. 9). In AAS samples after 2 months of exposure, no gypsum or ettringite was present in the sample exposed to Na_2SO_4 solution, while a considerable amount of gypsum was present in samples exposed to $MgSO_4$ solution. Meanwhile, in OPC samples, ettringite was present in the sample exposed to Na_2SO_4 solution, and considerable amounts of ettringite and gypsum were found in the sample exposed to $MgSO_4$.

These XRD results correlate quite well with visual observations. AAS concrete exposed to sodium sulfate solution had no signs of deterioration, and no degradation products such as gypsum or ettringite were observed by XRD in these samples. In AAS specimens immersed in $MgSO_4$ solution, there were some cracks on the corners, and gypsum was present in the sample. Meanwhile, in OPC concrete, there were expansion, cracking, and loss of concrete on the corners in specimens subjected to $MgSO_4$ solution, where considerable amounts of gypsum and ettrin-

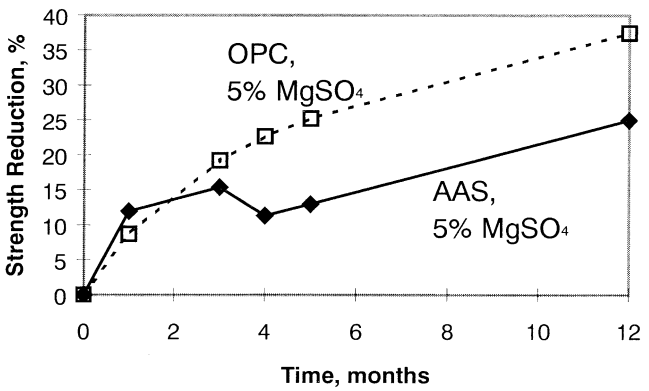

Fig. 8. Compressive strength reduction of AAS and OPC samples subjected to sulfate attack in 5% $MgSO_4$ solution.

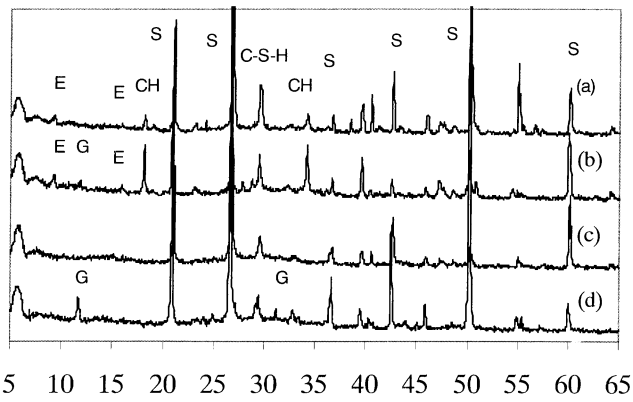

Fig. 9. XRD spectra of mortar from the surface of concrete specimens exposed to sulfate attack: (a) OPC concrete in 5% Na_2SO_4 solution; (b) OPC concrete in 5% MgSO4 solution; (c) AAS concrete in 5% Na_2SO_4 solution; (d) AAS concrete in 5% MgSO4 solution. E = Ettringite, G = gypsum, CH = portlandite, S = silica (quartz), C-S-H = calcium silicate hydrate.

gite were observed. In OPC specimens exposed to sodium sulfate solution, some expansion was observed and the specimens contained ettringite having expansive properties.

4. Discussion

Sulfate attack on OPC concrete is characterised by the chemical reaction of sulfate ions as the aggressive substance and the aluminate component of hardened cement paste [5,9–12]. The reaction between these substances, if enough water is present, produces ettringite and gypsum and causes expansion of the OPC concrete, leading to cracking. At the same time as the sulfate attack, the attack of magnesium ions and, to a lesser extent, the sodium ions on C-S-H starts when CH is depleted [5,9,10,13–15]. This attack leads to gypsum precipitation and decalcification of C-S-H. The decalcification of C-S-H destroys the binding capacity of C-S-H and leads to a loss of adhesion and strength in concrete.

Thus, previous studies of external sulfate attack on OPC concrete show that reactions involve C-S-H and the aluminate component of hardened cement paste [5,11,12]. As a result of these reactions, expansion and cracking are caused, directly or indirectly, by ettringite and gypsum formation, while softening and disintegration are caused by destruction of C-S-H. The deterioration in the case of magnesium sulfate attack was reported to be more severe than in the case of sodium sulfate attack. Therefore, it was important to study the performance of AAS concrete in the solutions of sodium and magnesium sulfate.

In agreement with previous investigations, visual examination of concrete cylinders exposed to sodium and magnesium sulfate solutions and their compressive strength reduction showed that attack by magnesium sulfate was more aggressive in its action on AAS and OPC concrete than sodium sulfate attack. In sodium sulfate attack, AAS performed better than OPC, as no visual signs of degradation were observed in AAS, while OPC samples expanded significantly. The compressive strength reduction was also less in AAS concrete than in OPC concrete. In magnesium sulfate solution, AAS showed some signs of deterioration, such as the formation of gypsum crystals on the surface and some cracking. However, the deterioration of OPC samples in magnesium sulfate solution with loss of concrete and large cracks was more significant, which was evident from visual observations and compressive strength reduction.

In these tests, XRD traces showed that different products of degradation had formed in OPC and in AAS concretes in the sulfate attack. In both experiments, with sodium and magnesium sulfate solutions, ettringite formation was the dominant effect in Portland cement concrete exposed to sulfate attack. This observation is in agreement with the findings of Taylor and Gollop [5] and Gollop and Taylor [11] who concluded that ettringite formation was the main mechanism of deterioration in Portland cement paste that was high in C_3A or in blends with small amount of slag. These researchers also noted that the ettringite formation in OPC was minimal with sulfate-resistant Portland cements due to low C_3A content [5,12]. Similarly, the ettringite formation is low with blends high in slag because slag is rich in the aluminium that is not in the form available for reaction [5].

On the other hand, gypsum appeared to be the main reaction product in AAS cement in magnesium sulfate attack. The present investigation has observed cracks at the corners of AAS concrete specimens where some softening of the concrete occurred when exposed to magnesium sulfate solution. Other reports also indicated that slag cements failed in the sulfate test due to weakening and disintegration before expansion took place [9,10]. Thus, deterioration has mainly been observed in slag cements exposed to sulfate and magnesium ions containing environments.

It is possible that the mechanisms of deterioration in the sulfate attack in Portland cement paste and in slag cement are different due to the different chemical and phase compositions of these cements. It appears that destruction of C-S-H is an important deterioration mechanism in the case of attack by magnesium sulfate solution for cements high in slag. Previously, it was found that the destruction of C-S-H was an important result in the case of attack by magnesium sulfate solution for Portland cements and sulfate-resistant Portland cements [9,10, 13–15]. It was reported that in this reaction, gypsum, hydrous silica, brucite, and magnesium silicate hydrate were produced [12–15]. In the present investigation, it was observed that in the magnesium sulfate attack, gypsum precipitated in the surface layers of AAS and OPC in the process of destruction or decalcification of C-S-H. Decalcification of C-S-H destroys the binding capacity of the paste and causes concrete softening that is apparent

due to cracks developed in the AAS samples. Decalcification of C-S-H is also important in Portland cement as significant gypsum precipitation and loss of concrete were observed in the surface layers under magnesium sulfate attack. In addition, significant gypsum was observed in OPC samples in the case of sodium sulfate and magnesium sulfate attacks that contributed to expansion of OPC samples. Thus, it appears that in OPC, both mechanisms of ettringite and gypsum formation are important, while in AAS concrete, deterioration under sulfate attack is associated with precipitation of gypsum.

Among properties that influence the resistance to sulfate attack, chemical composition, and permeability of cement paste are the most important. It was pointed out that as compared to AAS, OPC paste has an additional supply of Ca from calcium hydroxide, one of the products of cement hydration, which has to be depleted before decalcification of C-S-H takes place [5]. This additional supply of calcium in OPC may help to reduce decalcification of C-S-H in sulfate attack. As compared to OPC, AAS paste has almost no calcium hydroxide [16]. On the other hand, AAS paste was reported to have pores of smaller size than OPC [17] and consequently, compared to OPC, AAS paste has lower permeability that protects AAS from the ingress of deleterious ions.

5. Conclusions

Two tests were used to determine resistance of AAS concrete to sulfate attack. These tests involved immersion in 5% magnesium sulfate and 5% sodium sulfate solutions. The compressive strength measurements showed that the strength of AAS concrete decreased by up to 17% for AAS concrete and up to 25% for OPC concrete in the case of sodium sulfate solution. In the case of the magnesium sulfate solution, the compressive strength decrease was more substantial, up to 37% for OPC, and 23% for AAS. The main products of degradation in sulfate attack are gypsum and ettringite in the case OPC concrete and gypsum in the case of AAS concrete.

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