Pergamon

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Cement and Concrete Research 33 (2003) 1607–1611

CEMENT AND CONCRETE RESEARCH

Resistance of alkali-activated slag concrete to acid attack

T. Bakharev[a,*], J.G. Sanjayan[a], Y.-B. Cheng[b]

[a]*Department of Civil Engineering, Monash University, Clayton, Victoria 3800, Australia*
[b]*Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia*

Received 24 September 2002; accepted 31 March 2003

Abstract

This paper presents an investigation into the durability of alkali-activated slag (AAS) concrete exposed to acid attack. To study resistance of AAS concrete in acid environments, AAS concrete was immersed in an acetic acid solution of pH = 4. The main parameters studied were the evolution of compressive strength, products of degradation, and microstructural changes. It was found that AAS concrete of Grade 40 had a high resistance in acid environment, superior to the durability of OPC concrete of similar grade.

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

1. Introduction

There is a need in the development of chemically resistant materials for the use in the aggressive environment of food manufacturing, chemical, mining, mineral processing, and other industries. Acid resistance is one of the required properties for structural materials used in these applications. It is known that Portland cement concrete does not posses a high acid resistance due to its chemical composition that includes high-calcium compounds.

Durability of alkali-activated slag (AAS) concrete is being investigated because it was reported to have a superior durability in aggressive environments as compared to OPC [1–4]. It contains significantly less Ca in its composition and has a very low permeability, and thus is expected to be more durable than OPC in an acid environment. In the previous papers, the durability of AAS concrete when exposed to a sulfate environment and carbonation was studied [5,6]. AAS concrete had a superior durability to OPC in sulphate attack but was more exposed to carbonation. This paper presents the study of the durability of AAS concrete produced using Australian slag when exposed to low pH environment of acetic acid.

2. Experimental

2.1. Materials

The chemical composition and properties of slag are summarised 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 to 10 μm and is neutral with the basicity coefficient 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 ordinary Portland cement 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, weighted ratio of $SiO_2/Na_2O = 2$, percentage of $Na_2O = 14.7$, percentage of $SiO_2 = 29.4$) and sodium hydroxide solutions (Ajax Chemicals, 60% w/v water solution) were used 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 4% Na in the mixture with slag. Mix designs for concrete specimens were reported in Refs. [5,6]. 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. Performance of AAS concrete samples was compared to OPC samples with a nominal compressive strength of 40 MPa at 28 days and w/b = 0.5.

---

* Corresponding author.
E-mail address: bakharev@eng.monash.edu.au (T. Bakharev).

0008-8846/03/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00125-X

Table 1
Composition of slag

Oxide (%)	Slag[a]	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
Sulphide sulphur as S^{2-}	0.44	
Cl	80 ppm	
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] SteelCement, Port Melbourne, Australia.

[b] Type I/II, Geelong, Victoria, Australia.

2.2. Test procedures

Since there is no standard test for acid attack on concrete, the resistance to the acid attack in the present investigation was tested by immersion of concrete specimens in a solution of acetic acid of pH = 4. The media was replaced with the fresh solution monthly for the first 4 months and then at 6, 9, and 12 months of exposure. The compressive strength and the pH of concrete were measured before the test and at 1, 3, 4, 5, and 12 months of exposure. The deterioration was followed by a record of visual observations, SEM, and XRD for identification of degradation products.

A phenolphthalein method was used to monitor the pH of concrete in the experiment similar to pH measurements in carbonation experiments. In this method, phenolphthalein is used as an indicator of the pH change in the concrete pore solution. The usual method of studying reactions associated with changes in pH is to measure the depth of neutralisation as indicated by a phenolphthalein solution, which has been sprayed onto the fractured concrete surface. This indicator shows a magenta coloured region on the concrete where the pH value exceeds about 9 and a colourless region at the originally exposed surface where in the result of reaction with acid, the pH was reduced to below 9 [7]. At the time of measurement, a 50% phenolphthalein solution in alcohol was sprayed on a surface of the concrete cylinder freshly cut using a large concrete saw, with the orientation of the cylinder perpendicular to the longitudinal axis of symmetry.

2.2.1. Compressive strength

At predetermined intervals, the specimens were tested to find a strength reduction. Compressive strength testing was conducted on cylinders F($\varnothing$100 × 200 mm). Prior to the compressive strength test, concrete cylinders were taken from the solution, dried, caped by sulphur compound, and tested using a total of three cylinders for each data point. The companion specimens, cured in potable water, were also tested in compression. A reduction in a compressive strength was calculated as follows: reduction in compressive strength, $\%=[(A-B)/A]$x100, where A = the average compressive strength of three specimens cured in water, MPa; and B = the average compressive strength of three specimens cured in the test solution, MPa.

2.2.2. XRD

To perform XRD test, mortar was carefully removed from the surface region of the concrete sample. Each mortar sample was finely ground and then analysed using XRD. X-ray diffraction analyses were made using Rigaku Geigerflex D-max II automated diffractometer with the following conditions: 40 kV, 22.5 mA, and Cu-Kα radiation. The XRD patterns were obtained by scanning at 0.1° (2θ) per min and in steps of 0.01° (2θ).

2.2.3. SEM

Microstructures of samples exposed to tests were studied by an SEM (JEOL JSM-840 A) equipped with an EDS

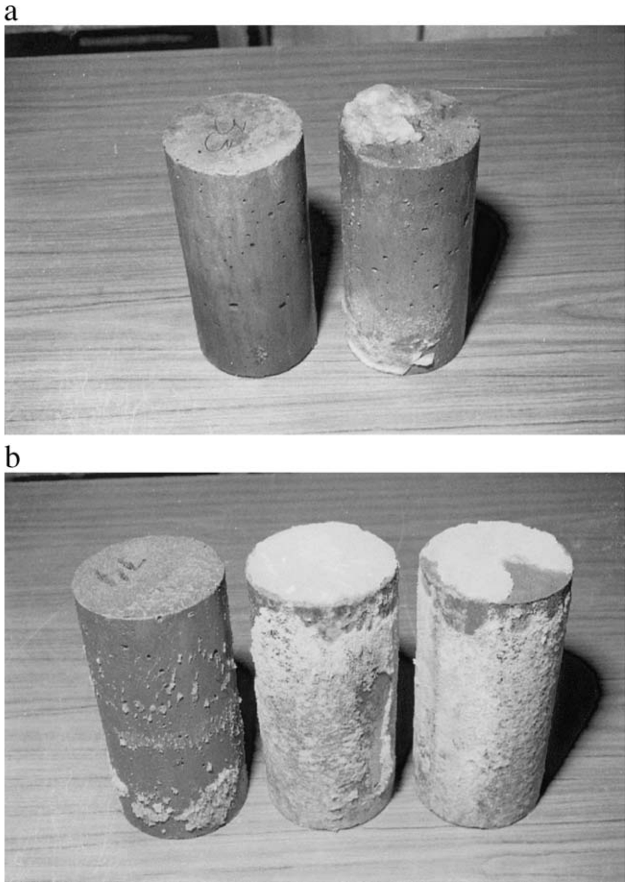

Fig.1. Concrete specimens exposed to acetic acid solution (pH = 4) for 2 months: (a) AAS and (b) OPC.

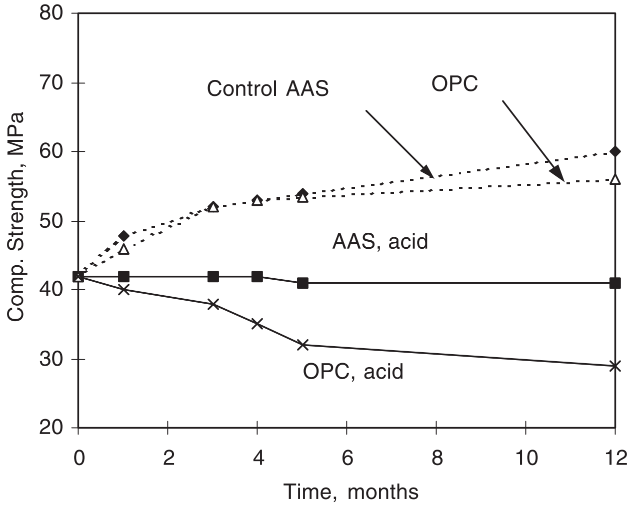

Fig. 2. Compressive strength of AAS concrete subjected to acid attack.

analyser (Oxford Image Analysis). The studies utilised backscattered electron imaging (BEI) of polished cross section. Specimens were cut from the concrete, impregnated in epoxy, and polished for examination of the surface and subsurface regions for evidence of deterioration. The samples were coated with a thin film of carbon before the SEM observation.

3. Results

The photographs of the AAS and OPC concrete cylinders exposed to the acid solution for 2 months are found in Fig. 1a and b. The AAS specimens had no change of their appearance and had a small increase in mass. The OPC samples, on the contrary, had soft white depositions on the surface, softening of concrete, a significant increase in the mass of samples if measured with the white deposits (up to 20 g/kg), and a loss of mass (about 8 g/kg) if measured with the deposits removed.

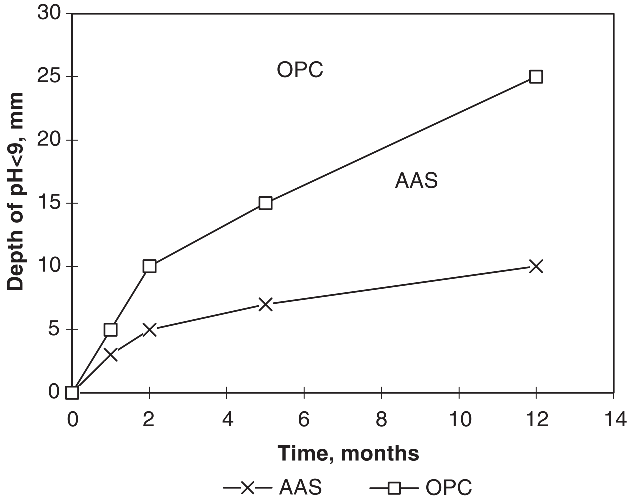

Fig. 3. Evolution of pH in OPC and AAS concrete exposed to the acetic acid solution (depth of pH below 9).

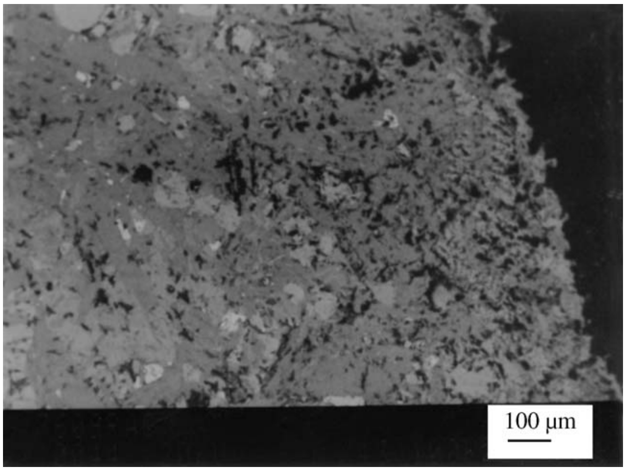

Fig. 4. BEI of the surface region of AAS concrete exposed to the acetic acid solution (pH = 4) showing deterioration of the aggregate.

The compressive strength evolution during the experiment is shown in Fig. 2. If compared to specimens stored in water, OPC samples had about 47% and AAS about 33% strength reduction when stored in the acid solution for 12 months. Fig. 3 presents the evolution of the pH in AAS and OPC concretes. After 12 months of exposure, OPC had a pH reduction below 9 to a depth of 22 mm, while AAS concrete had a pH reduction below 9 to a depth of 16 mm. Thus, AAS concrete performed better than OPC concrete when exposed to the acid solution.

3.1. SEM and XRD

Two specimens of AAS concrete exposed to acid solution (pH = 4) for 6 months were examined using SEM (BEI). The specimens were taken from the cross section perpendicular to the surface exposed to deterioration. The samples showed dissolution and loss of aggregates and paste (Fig. 4) from the concrete surface to a depth of up to 5 mm. The deteriorated surface layer became soft and could be removed exposing interior concrete to further deterioration. The EDS analysis of the paste in the deteriorated area showed the presence of Si, Ca, Al, Mg, C, and O and a small amount of Na. The Si/Ca ratio in the deteriorated regions of paste was about 3.5 (Fig. 6). The XRD analysis of the paste from the deteriorated surface layer was similar to a nondeteriorated sample. It is possible that the product of degradation could not be observed in the XRD traces because of its high solubility and insignificant amount in the matrix.

4. Discussion

AAS concrete samples had some softening of the surface layer when exposed to the acid solution, but the damage was

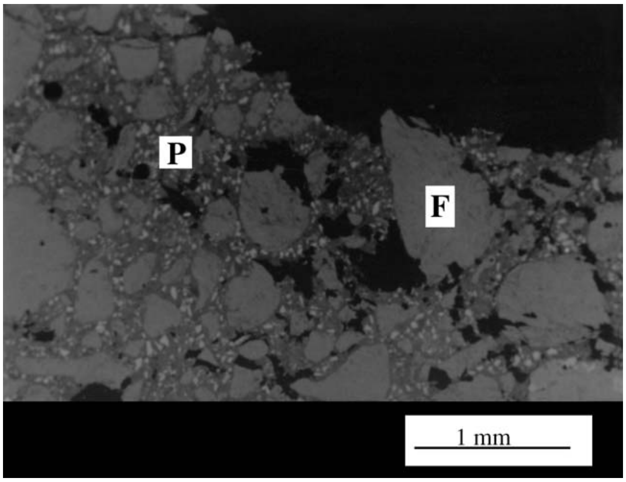

Fig. 5. BEI of the surface region of AAS concrete exposed to the acetic acid solution (pH = 4) showing deterioration of the paste. P—AAS paste, F—fine aggregates.

significantly less than in OPC concrete. AAS concrete had less strength loss and depth of concrete layer with the pH reduction and also less visible signs of deterioration than OPC concrete. Therefore, AAS concrete performed better than OPC concrete when exposed to acid solution.

The action of acids on cement paste consists in an attack on the components of the hardened cement paste. It is believed that this action leads to a conversion of all the calcium compounds, unreacted residue of C_3S and C_2S in cement grains, calcium hydroxide, calcium silicate hydrate, and calcium aluminate hydrate to the calcium salt of the attacking acid [8]. As a result of the conversion, the binding capacity of the hardened cement is destroyed. It is accepted that the rate of attack would depend on quality of the concrete and also on the solubility of the resulting calcium salt and the permeability of precipitates [9].

It is possible that OPC concrete is more vulnerable than slag concrete to acid attack due to difference in chemical and phase composition. The cement paste in OPC concrete is rich in calcium due to presence of residues of C_2S and C_3S, portlandite [$Ca(OH)_2$], and C-S-H with average Ca/Si ratio of 1.7 [10]. These calcium-containing compounds in the cement paste react with the acetic acid producing a gel-like white cover, which contains calcium acetate, the product of chemical reaction of OPC paste with the acetic acid solution. Calcium acetate is soluble and leaves the cement paste. Decalcified C-S-H and silica gel, another reaction product, have no structural properties. As a result of this, OPC concrete surface becomes soft and could be removed, thus, exposing the interior concrete layers to deterioration.

Good performance of AAS concrete when exposed to the acid solution was attributed to low content of Ca in slag paste if compared with OPC paste. In the AAS paste, slag particles and low-Ca C-S-H with average Ca/Si ratio of 1 [11] were more stable in the acid solution than constituents of the OPC paste.

The SEM micrographs showed deterioration of both AAS paste and some of the aggregates in acid solution. It is possible that there were some limestone aggregates in AAS concrete that reacted with acetic acid (Fig. 4). In addition, parts of the slag paste were lost as the surface of the AAS concrete softened (Fig. 5). The EDS analysis (Fig. 6) showed that the deteriorated paste became rich in Si and depleted in Ca. This evidence provides a support for the proposed mechanism of deterioration being the decalcification of C-S-H. It appears that the decalcified C-S-H and calcium acetate replace C-S-H in the result of the reaction. Because calcium acetate is very soluble, structural properties of the decalcified C-S-H degraded, and the surface of AAS concrete became soft, though deterioration in AAS material was at a much slower rate than that in OPC concrete.

The results of the investigation reported by Glukhovsky [3] show that AAS mortar continued to gain flexural strength in the solutions of hydrochloric and lactic acids of pH = 3, although at a slower pace than in water. In acetic acid solution, the strength increase was very small. This result correlates well with the present study, although the specimens used had significantly higher compressive strength than in the present study. Jiang et al. [12] reported the results of exposure of AAS mortar over a 6-month period to 5% solutions of acids. In the solution of citric acid, only slight changes were observed, in hydrochloric acid and nitric acid solutions, there were moderate changes, while in sulphuric acid solution, severe degradation was observed. Therefore, results of the experiment depended on type of acid, and sulphuric acid had the greatest deteriorating effect.

In previous investigations, it was pointed out that concrete containing less free lime performs better in the acidic environment [9,12–14]. This is consistent with the observations in the present investigation. For the durability of concrete in an acidic environment, the production of a high-quality, dense, impervious, and well-compacted concrete was found of paramount importance.

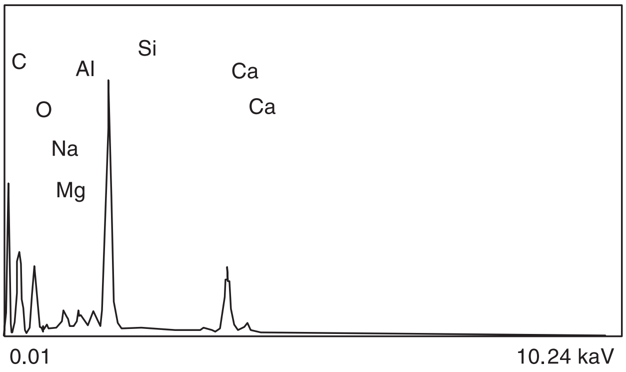

Fig. 6. EDS spectrum of a surface region of deteriorated AAS concrete exposed to the acetic acid solution (pH = 4).

5. Conclusions

The investigation of durability of AAS concrete examined the performance of AAS concrete exposed to acetic acid solution. It was found that AAS concrete of Grade 40 has a superior durability to OPC concrete of similar grade under acid attack. The mechanism of deterioration involves decalcification of C-S-H and formation of soluble salt calcium acetate. Slag paste was found more resistant to deterioration in acid solution than OPC paste.

Acknowledgements

The financial support for this project was provided by Independent Cement and Lime, Blue Circle Southern Cement, and Australian Steel Mill Services. The efforts and assistance with the laboratory work provided by Jeoff Doddrell. Roger Doulis and Peter Dunbar are also gratefully acknowledged.

References

[1] D.M. Roy, G.M. Idorn, Hydration, structure, and properties of blast furnace slag cements, mortars, and concrete, ACI Mater. J. 79 (12) (1982) 444–457.

[2] X.C. Pu, C.C. Gan, S.D. Wang, C.H. Yang, Summary Reports of Research on Alkali-Activated Slag Cement and Concrete, vol. 1–6, Chongqing Institute of Architecture and Engineering, Chongqing, 1988.

[3] V.D. Glukhovsky, Slag–Alkali Concretes Produced from Fine-Grained Aggregate, Vishcha Shkola, Kiev, USSR, 1981, in Russian.

[4] V.D. Glukhovsky, V.A. Pakhomov, Slag–Alkali Cements and Concretes, Budivelnik Publishers, Kiev, 1978, in Russian.

[5] T. Bakharev, J.G. Sanjayan, Y.-B. Cheng, Sulfate attack on alkali activated slag concrete, Cem. Concr. Res. 32 (2002) 211–216.

[6] T. Bakharev, J.G. Sanjayan, Y.-B. Cheng, Resistance of alkali activated slag concrete to carbonation, Cem. Concr. Res. 31 (2001) 1277–1283.

[7] L.J. Parrott, A review of carbonation in reinforced concrete, Cem. Concr. Assoc. (1987) 126 (Report C/1-0987).

[8] CEB Bulletin No. 172, CEB-RILEM, in: S. Rostam (Ed.), International Workshop. Durability of Concrete Structures (1983, Copenhagen, Denmark), Technical University of Denmark, Copenhagen, 1984, p. 67.

[9] W.H. Harrison, Durability of concrete in acidic soils and waters, Concrete 1 (2) (1987) 18–24.

[10] I. Jawed, J. Skalny, J.F. Young, Hydration of Portland cement, in: P. Barnes (Ed.), Structure and Performance of Cements, Applied Science, London, 1983, pp. 237–317.

[11] T. Bakharev, J.G. Sanjayan, Y.-B. Cheng, Hydration of Alkali Activated Slag Cements, submitted to C&CR for publication.

[12] W. Jiang, M.R. Silsbee, E. Breval, D.M. Roy, Alkali activated cementitious materials in chemically aggressive environments, in: K.L Scrivener, J.F. Young (Eds.), Mechanisms of Chemical Degradation of Cement-Based Systems, E & FN Spon, London, 1997, pp. 289–296.

[13] D.M. Roy, P. Arjunan, M.R. Silsbee, Effect of silica fume, matakaolin, and low-calcium fly ash on chemical resistance of concrete, Cem. Concr. Res. 31 (2001) 1809–1813.

[14] M.A. Ward, Hardened mortar and concrete with fly ash. Chemical resistance, in: K. Wesche (Ed.), Fly Ash in Concrete. Properties and Performance, RILEM Report No. 7, E & FN Spon/Chapman & Hall, 1991, pp. 133–135.