CHLORIDE DIFFUSION AND PORE STRUCTURE IN GEOPOLYMERS

I. Ismail (1,2), J.L. Provis (1), J.S.J. van Deventer (1,3) and S. Hamdan (4)

(1) Department of Chemical and Biomolecular Engineering, University of Melbourne, Victoria, Australia
(2) Department of Civil Engineering, Universiti Malaysia Sarawak, Sarawak, Malaysia
(3) Zeobond Pty. Ltd, Somerton, Victoria, Australia
(4) Department of Mechanical Engineering, Faculty of Engineering, Universiti Malaysia Sarawak, Sarawak, Malaysia

Abstract

Pore structure is the key factor that governs the mass transport of ions, fluids and gases in any concrete material, and thus directly relates to the behaviour of the material when exposed to aggressive environments. Chloride attack on reinforced concrete is a mechanism of deterioration which causes corrosion of steel reinforcement. However, detailed scientific and mechanistic information regarding the chloride resistance of alkali activated aluminosilicate materials, especially geopolymers synthesized from mixtures of fly ash and ground granulated blast furnace slag, is scarce. In this study, geopolymer mortars made from an alkali activated fly ash/slag system with varying water content were tested for non-steady state chloride migration using the standard NordTest 492 methodology. Mixtures of Australian class F fly ash and ground granulated blast furnace slag (GGBS) were activated by blending with water and solid sodium metasilicate. Water content was varied to produce a series of samples with water to binder ratios ranging from 0.40 to 0.60. Ordinary Portland cement (OPC) mortars with similar water to cement ratios were also prepared for direct comparison. Porosity and water absorption were measured, and correlated with the chloride diffusivity values. Although the porosity and water absorption of geopolymer are higher than the normal OPC mortars, chloride intrusion is lower in geopolymer system. This suggests that the differences in pore structure and gel chemistry between geopolymer and OPC system mean that the standard relationships between chloride penetration and porosity which apply to OPC systems cannot be directly applied to geopolymer binders. Scanning electron microscopy images with energy dispersive X-ray (EDX) analyzer and thermogravimetry analysis were performed at selected corroded sections of both sample types had shown some durability performance of geopolymer. In particular, geopolymers are seen to show higher resistance to chloride penetration than would be predicted based upon their high porosity.
1. INTRODUCTION

The fact that the production of one tonne of ordinary Portland cement (OPC) generates almost one tonne of carbon dioxide leads to urgency in finding alternative materials to supplement OPC usage in the future. Manufacturing of cement accounts for as much as 5% of global CO₂ emissions to the environment, making it one of the main contributors to global climate change [1]. Geopolymer is a potentially valuable new material for use in the concrete and construction industry. Made from industrial by-products or wastes from processes such as coal combustion (fly ash) and iron manufacture (slag), these low-CO₂ binders have proven to give comparable mechanical properties to normal Portland cement concrete, and ongoing work, including the study presented in this paper, is giving increased confidence in its likely durability in service. Geopolymer is synthesized from a combination of an alkaline solution with a reactive aluminosilicate powder such as metakaolin, fly ash and/or slag. The reaction of the aluminosilicate with the alkali results in the dissolution of the solid raw material, forming a disordered alkali aluminosilicate gel phase known as the geopolymeric gel binder, which also contains some embedded partially reacted solid precursor particles, and the water used in mixing [2].

Development of an understanding of the pore structure of cementitious materials is important in order to predict the behaviour and mechanisms of concrete deterioration in aggressive environments. Mass transport of ions, fluids and gases will be governed by the characteristics of the pore structure, mainly the pore size, tortuosity and connectivity. Deleterious reactions such as with chlorides, as well as the kinetics of the mechanisms, are affected by pore structure and are of wide interest among the concrete research community. The process of chloride attack on concrete is probably the most extensively observed and researched aspect of concrete durability worldwide. Corrosion of embedded steel bars is the main consequence when chloride penetrates into concrete. The application of de-icing salts, marine exposure, airborne salt or calcium chloride are the sources of chloride ions that can pose threats to concrete structures [3]. Steel embedded in concrete usually has a protective passive layer, which forms as an oxide layer while the pH of the pore solution is sufficiently high. However, when chloride ions are present, the protective layer will be destroyed, leading to corrosion of the steel reinforcement [4]. Chlorides may penetrate either by capillary absorption, hydrostatic pressure, and/or diffusion of ions. The formation of soluble iron chloride complexes leads to the deposition of loose iron rust and release of the chloride to continue the attack.

To date, there have been limited investigations on the effects of chloride ingress in geopolymer concrete. The rapid chloride permeability test (RCPT), ASTM C1202, is frequently used, but it measures the ability of concrete specimen to transmit direct current, not its physical ability to restrict the movement of chloride ions [5]. For geopolymer materials, alkali mobility in the pore network will complicate chloride diffusion testing by measurement of charge passed, as the actual diffusion of chloride will be affected by alkali movement, and the charges of the mobile alkali cations will also register in the test, contributing to the measured charge [6].

It is well known that higher porosity structures in concrete matrices will lead to higher permeability and absorption when exposed to damaging environments, reducing the durability of the material. Geopolymer mortar has a higher porosity compared to normal OPC mortar...
when measured using a direct drying technique [7]. However, the discussion of durability and its relation to porosity parameters has yet to arrive at a consensus for geopolymer materials. In OPC concrete, the main component that affects pore structure is water. Water, and in particular how it relates to pore structure, has yet to be the focus of the study of geopolymer materials. Therefore, the main objective of this study is to understand the effect of water content on the durability of geopolymer mortar exposed to a chloride medium.

2. EXPERIMENTAL METHODS

2.1 Material

The cementitious materials used in this study were ordinary Portland cement (OPC), class F fly ash and ground granulated blast furnace slag (GGBS). OPC was produced and supplied by CMS Cement Pty. Ltd. from Sarawak, Malaysia, and the fly ash and GGBS were supplied by Zeobond Pty Ltd, Australia. The chemical compositions of the raw materials are given in Table 1. Geopolymer mortars were prepared using equal amounts (by mass) of fly ash and GGBS as the main binder components. Sodium silicate granules (anhydrous Na₂SiO₃) were used as the activator for geopolymers. Tap water was used to dissolve the activator prior to mixing with the solid aluminosilicates, at water to fly ash and slag ratio (w/b) of 0.4, 0.5 and 0.6. The fine aggregate was natural sand with fineness modulus of 3.6 and a specific gravity of 2.5. For control samples, OPC was used to produce mortar samples with the same water to cement ratios (w/c). Table 2 summarises the mix design of the mortars.

Table 1: Chemical composition of raw materials from X-ray fluorescence; LOI is loss on ignition at 1000°C

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Fly Ash</th>
<th>GGBS</th>
<th>OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>62.93</td>
<td>33.80</td>
<td>20.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>24.91</td>
<td>13.68</td>
<td>5.94</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.22</td>
<td>0.4</td>
<td>3.62</td>
</tr>
<tr>
<td>CaO</td>
<td>0</td>
<td>42.56</td>
<td>64.53</td>
</tr>
<tr>
<td>MgO</td>
<td>1.01</td>
<td>5.34</td>
<td>0.58</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.23</td>
<td>0.83</td>
<td>2.5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.16</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.31</td>
<td>0.36</td>
<td>0.45</td>
</tr>
<tr>
<td>LOI</td>
<td>2.64</td>
<td>1.81</td>
<td>1.66</td>
</tr>
</tbody>
</table>

2.2 Test procedures

All mortar samples were mixed in a pan mixer following the standard for mortar mixing recommended by ASTM C 109. The mixes were cast in 50 mm tri-gang cube moulds and 100 mm (diameter) x 200 mm (height) cylinders after a vibration period of approximately two minutes. All samples were cured in sealed plastic bags at ambient temperature (28±5°C). Six mortar cubes were used for compressive strength test at 28 days of age. After 28 days, the cylindrical mortar samples were sliced at approximately 25 mm thickness and tested for the volume of permeable voids (VPV) following ASTM C 642, and non-steady state chloride migration following NT Build 492 (NordTest) as shown in the schematic diagram in Figure 1.
The sliced mortars were then tested for chloride content using the acid-soluble titration method and the chloride-exposed parts were imaged in a scanning electron microscope (SEM) to analyse morphology and chloride content. Thermogravimetry (TGA) and derivative thermogravimetry (DTG) were performed to compare the possible formation of crystalline and amorphous phases in the corroded parts of both mortars, using a Mettler Toledo TGA/SDTA 851 with an isothermal hold at 40°C for 60 minutes prior to heating from 40°C to 1000°C at 10°C/min in a nitrogen atmosphere.

3. RESULTS AND ANALYSIS

3.1 Compressive strength

The 28-day compressive strengths of both types of mortars are shown in Figure 2. Compressive strength declines for OPC mortars as the water/cement ratio increases, as expected, because water increases porosity and hence reduces binder strength. For geopolymer mortars, the strength is highest at a water/binder ratio of 0.5. The compressive strength of a geopolymer depends on many factors, such as composition ratios in the raw material blend, the concentration and type of the activator, and curing conditions (time, temperature and humidity). Water and activator dosage are among the most influential factors in determining the strength and reaction products of geopolymers [8, 9].
Calcium released from the reaction of slag with the alkali can form Al-substituted calcium silicate hydrate (C-(A)-S-H) as a hydration product that can contribute to the strength of geopolymer, in addition to the alkali aluminosilicate gel formed through the reaction of fly ash; with the right water and activator dosage to give desirable gel formation, optimum strength can be achieved. For water/binder ratios of 0.4 and 0.6, the amount of water in these ratios may have affected activator concentration by giving either insufficient alkalinity (excessive water) or insufficient workability to enable full compaction (low water). Lower workability and difficulty in compaction was also observed for water/binder ratio of 0.4 that could affect the value obtained in the compressive strength test.

3.2 Volume of permeable voids (VPV)
A comparison of the volume of permeable voids (VPV) data between the two sample types is shown in Figure 3. The trend in the VPV plot can be correlated with the findings from compressive strength analysis. In OPC mortar, the trend here shows a higher VPV with increasing water/binder ratio, which is an expected outcome based on the understanding of higher pore volume as the water content increases. Contrary to the compressive strength results, OPC in general has a lower VPV than the geopolymer samples, except at very high water content. This indicates that the total pore volume of a geopolymer may not be directly related to compressive strength per se, in the same way as in OPC. The VPV of the geopolymer mixes does not show a significant trend with respect to water/binder ratio. Again, it can be assumed that the optimum alkali concentration plays important role in controlling the reaction products, strength and pore structure of geopolymer; this parameter was not analysed here.

![Figure 3: Volume of permeable voids](image)

3.3 Chloride content and diffusion coefficient
The amount of chloride which becomes incorporated into the binder phases in both types of mortars, as measured by titration, is presented in Figure 4a. The extent of chloride incorporation into the binder during the chloride migration test shows a strong relationship with w/b for both sample sets, and appears to decrease for samples with increasing strength within each sample set. The chloride content of OPC samples is significantly higher than that of the geopolymer samples, although the VPV of the geopolymer samples was much higher. In OPC, a higher water/binder ratio gives higher chloride content at the end of the test, while the highest chloride content in a geopolymer is shown in the sample with w/b of 0.4, which...
also shows the highest VPV value. It is important to note that the values obtained are averages of the data points obtained from three samples and, for the case of water/binder of 0.4, the higher average values resulted from one sample showing much higher chloride ingress than the other two. This may be related to the workability and compaction difficulties as noted in the discussion of the compressive strength data. The other two samples from this set gave a much lower value (lower than 0.1%) than the average shown in Figure 4(a). Geopolymer shows good performance in this test; for water/binder ratios of 0.5 and 0.6, also less than 0.1% chloride content was observed.

![Graph showing chloride content and coefficient of chloride diffusion](image)

Figure 4. (a) Chloride content obtained by titration after the Nordtest procedure, and (b) Coefficient of chloride diffusion obtained from the Nordtest method.

The test also allowed calculation of chloride migration diffusion coefficients, as shown in Figure 4(b), which can give better perception of performance. The results show that geopolymer has a much better performance in controlling chloride migration compared to OPC. This is strongly contradictory to the VPV results, which would lead to a prediction of very high migration rates through geopolymers on the basis of higher porosity. Further analysis is required to understand how geopolymer behaves in chloride environment, and in particular the reasons why porosity and permeability correlate poorly. It may be that this is due to the three-dimensional structure of the pore network, or it may be related to gel chemistry and sorption effects.

The chloride binding capacity has been reported to be controlled by C-S-H gel composition, regardless of water content [10], and from the data at water/binder ratios of 0.5 and 0.6, this could also be true for geopolymers. Another explanation for chloride durability in geopolymer can be relate to chloride activity as a function of pH in the pore solution [11], and also influences related to sorption on the aluminosilicate-type gels present. The pore solution extractions of geopolymers conducted by Lloyd et al. [12] indicate that geopolymer is rich in alkali cations, with a pH greater than 13. This is a good starting point for geopolymer to give lower and desirable Cl/OH ratio, although there may also be other prominent factors that could explain the mechanism of chloride migration in geopolymer.
3.4 Scanning electron microscopy (SEM) and derivative thermogravimetry (DTG)

Figure 5 shows SEM images from both sample types with water/binder ratios of 0.6, where samples were taken from the regions which had been intruded by chloride. Precipitation of crystalline needles is clearly seen in the OPC sample; analysis of the needles using an energy dispersive X-ray analyzer (EDX) showed a composition of Ca-Al-S-Cl. There is no visible new crystal formation found in the geopolymer in Figure 5b. The corroded parts of both samples were crushed and sieved and analyzed using derivative thermogravimetry, as shown in Figure 6. There is a peak at 130°C, consistent with the presence of ettringite or calcium monosulphoaluminate; the latter of these phases can react with chloride ions to produce C₃A-CaCl₂·10H₂O, Friedel’s salt [13]. The coexistence of the AFm phase and Friedel’s salt in OPC mortars in chloride environment is a common phenomenon. This is also supported by the DTG peak at 370°C in Figure 6, suggesting the presence of Friedel’s salt in the OPC mortar [13, 14]. The DTG of geopolymer showed no apparent peaks that relate to any of these phases formation due to chloride intrusion. The reaction products are not similar for OPC and geopolymer, and this may control the binding of chloride and/or deposition of crystalline products during the chloride test.

Figure 5: SEM images of chloride-exposed mortars; (a) OPC, and (b) geopolymer

Figure 6: DTG analysis of corroded parts of the OPC and geopolymer samples with w/b=0.6
4. CONCLUSIONS

The influence of water content, porosity and the reaction in chloride migration test between OPC and geopolymer mortars are compared. Despite being high in porosity and permeable voids, geopolymer shows good performance in the NordTest protocol for chloride penetration based on migration coefficient calculation, direct measurement of the penetration depth, SEM and DTG analysis. This may also suggest that the pore structure and/or gel chemistry of geopolymer is somewhat different from that of OPC, meaning that they behave differently in chloride environment. Either the pore structure or gel chemistry of the geopolymer binder may be leading to high resistance to chloride penetration, which is beneficial for durability.

ACKNOWLEDGEMENT

The authors would like to thank Jimmy Ling from Department of Civil Engineering UNIMAS for his assistance in data collection of the NordTest. Thank you also to Faculty of Science and Resource Technology, UNIMAS for providing the SEM facility.

REFERENCES