Chloride ingress through alkali activated slag concretes

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ABSTRACT: Alkali activated slag (AAS) is a credible alternative to Portland cement (PC) based binder systems. The superior strength gain and low embodied carbon make it a potential binder for next generation concretes. However there is little known about the long term durability of AAS systems, especially the chloride transport and subsequent corrosion of reinforcing steel. In this study, chloride transport through 12 AAS concretes with different alkali concentrations (Na2O% of mass of slag) and different modulus (Ms) of sodium silicate solution activator was investigated. A non-steady state chloride diffusion test was used for this study due to its similarity to the real exposure environment in terms of chloride transport through concrete. The results showed that the chloride concentration at the surface (Cs) of AAS concretes was higher than that for PC concrete. However, lower non-steady state chloride diffusion coefficient (Dnssd) was obtained for the AAS concretes. The Dnssd of the AAS concretes decreased with the increase of Na2O% and Ms of 1.50 gave the lowest Dnssd. The results are encouraging and it can be concluded that AAS concrete offers a superior performance in terms of chloride transport.

KEY WORDS: AAS; chloride diffusion; anionic exchange; pore structure; chloride binding.

1 INTRODUCTION

Slag, which is a by-product from steel industry, is activated by using alkali activator to produce AAS. Compared to PC, AAS is an environmentally friendly cementitious material. Besides, it has higher strength and superior durability [1]. As a result, there is a global increase in research in this area to determine if such materials have the potential to compete with PC based concretes.

Chloride induced corrosion of steel in reinforced concrete is a major cause of deterioration for structures in the U.K. and Ireland. [2]. Besides the surface chloride concentration, the pore structure and pore solution chemistry of concrete have significant influence on controlling the transport of chloride ions [3]. As a novel cementing material, the pore structure and pore solution chemistry of AAS are different from those of PC [4, 5]. They will vary largely based on the Na2O% and Ms when sodium silicate solution is used as the activator. With a change in Na2O% and Ms, the resultant concretes will not only have a different pore structure, but it will also have significantly different ionic structure. The influence of the above factors on chloride transport is not clearly known and therefore, an experimental programme was developed to address this shortcoming in knowledge.

2 EXPERIMENTAL PROGRAMME

Pore structure and pore solution of the AAS concretes was characterized and expressed with an attempt to identify their effect on chloride transport. Furthermore, the effect of Na2O% of slag and Ms of activator on chloride transport in AAS concretes was also investigated. Details of which are explained in the following sections.

2.1 Materials

Sodium silicate solution (or commonly known as water glass), which is available as ‘Crystal 0503’ from Tennants Distribution Ltd., UK was used as the activator for Ground Granulated Blastfurnace Slag (GGBS). Industrial grade sodium hydroxide powder with a purity of 99% was used to modulate the modulus of the sodium silicate solution to the required values. The GGBS was provided by Civil and Marine Ltd., UK. A commercial retarder ‘YP-1®’ [6] was used to retard the setting of the AAS concretes. Portland cement (CEM I) used in PC control mix was supplied by QUINN Cement. Superplasticiser used in the PC mix was CHEMCRETE HP3 provided by Larsen. The chemical composition and physical properties of the GGBS, the sodium silicate solution and the Portland cement are reported in Table 1.

Crushed basalt with specific gravity of 2.75 and size fractions of 20mm and 10mm combined in a ratio of 1:1 was used as the coarse aggregate. Natural sand with specific gravity of 2.73 and fineness modulus of 3.68 was used as the fine aggregate. Mixing water was from the mains water supply.

2.2 Mix proportion

Twelve AAS mixes with different Na2O% of 4, 6 and 8 and different Ms of 0.75, 1.00, 1.50 and 2.00 were studied. One PC mix was studied as well as reference. For the AAS concretes, the total binder content, which was considered as the sum of the GGBS and the solid component in the activator, and the water-binder ratio (w/b) were kept the same at 400kg/m³ and 0.47, respectively. The water content in the sodium silicate solution was considered in the calculation of w/b. This w/b was determined in order to make the AAS
mixes to achieve the minimum requirement of slump class S2 specified in BS EN 206-1. The content of retarder was 0.3% of the mass of the GGBS for all AAS mixes. The binder content (400kg/m³) was kept the same for the PC concrete. The w/b of 0.42 was used for the PC concrete, which was considered to allow the PC concrete to meet the requirement of maximum w/b and minimum compressive strength under the exposure class XS3 specified in BS EN 206-1. 0.5% (by the mass of cement) superplasticiser was added for the PC concrete to achieve a workability that meets the minimum requirement for S2 slump class. The water content (40%) in the superplasticiser was also considered in the calculation of w/b for the PC mix. A ratio of 36% between fine aggregate and total aggregates was used for both the AAS and the PC concretes. The mix design of PC mix was based on the DoE method. The mix proportions are given in Table 2.

Table 1. Chemical composition and physical properties of the raw materials.

<table>
<thead>
<tr>
<th></th>
<th>GGBS (CEM I)</th>
<th>PC</th>
<th>Sodium silicate solution 'Crystal 0503'</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO%</td>
<td>39.4</td>
<td>61.3</td>
<td>Ms</td>
</tr>
<tr>
<td>SiO₂%</td>
<td>34.3</td>
<td>23</td>
<td>Na₂O%</td>
</tr>
<tr>
<td>Al₂O₃%</td>
<td>15</td>
<td>6.15</td>
<td>SiO₂%</td>
</tr>
<tr>
<td>MgO%</td>
<td>8</td>
<td>1.8</td>
<td>Water content%</td>
</tr>
<tr>
<td>Sulfide%</td>
<td>0.8</td>
<td>2.5</td>
<td>Viscosity (20°C) poises</td>
</tr>
<tr>
<td>Na₂O%</td>
<td>0.45</td>
<td>0.22</td>
<td>Specific gravity</td>
</tr>
<tr>
<td>Fe₂O₃%</td>
<td>0.4</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td>K₂O%</td>
<td>0.38</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>LOI%</td>
<td>0.7</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>Specific surface area</td>
<td>527</td>
<td>386</td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.89</td>
<td>3.13</td>
<td></td>
</tr>
</tbody>
</table>

2.3 Casting, curing test specimens

Three 250×250×110mm slabs and nine 100×100×100mm cubes per mix were cast for the tests to be detailed in the section 2.4.

After casting, the specimens were covered with thin polythene sheets to minimise the evaporation of water from the surface of concrete. Approximately 1 hour after the concrete surface became stiff, the moulds were covered with layers of previously wetted hessian and polythene sheets. The specimens were stored in this condition for three days. The moisture condition of the hessian was maintained every six hours. After demoulding, the concrete specimens were covered with wet hessian and wrapped in plastic bags, storing in constant temperature room at 20±1°C until testing. The moisture condition of the hessian was checked every two weeks.

2.4 Test methods

2.4.1 Tests for slump and compressive strength

Slump test specified in BS EN 12350-2 was carried out on the fresh concretes. The compressive strength test according to BS EN 12390-3 was carried out on the 100mm cubes at 3, 28 and 91 days of age. The strength to be reported is an average of three values.

<table>
<thead>
<tr>
<th>Mix</th>
<th>S</th>
<th>C</th>
<th>WG</th>
<th>NaOH</th>
<th>CA</th>
<th>FA</th>
<th>W</th>
<th>SP</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td>371</td>
<td>34.6</td>
<td>13.6</td>
<td>1163</td>
<td>654</td>
<td>199</td>
<td></td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>4%</td>
<td>368</td>
<td>45.8</td>
<td>11.6</td>
<td>1164</td>
<td>655</td>
<td>192</td>
<td></td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>4%</td>
<td>362</td>
<td>67.7</td>
<td>7.8</td>
<td>1167</td>
<td>656</td>
<td>180</td>
<td></td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>4%</td>
<td>357</td>
<td>88.9</td>
<td>4.2</td>
<td>1170</td>
<td>658</td>
<td>168</td>
<td></td>
<td></td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 2. Concrete mix proportions (kg/m³).

Note: S—slag, C—cement, WG—sodium silicate solution, CA—coarse aggregate, FA—fine aggregate, W—water, SP—superplasticiser, R—retarder

2.4.2 Test for chloride diffusion

The non-steady state chloride diffusion test for the concretes was carried out by following the procedure given in NT BUILD 443 [7] and the samples were tested at an age of 91 days. The testing specimens were three Ø100×60mm cores taken from the three 250×250×110mm slabs for each concrete mix. The vacuum saturation regime similar to that of NT BUILD 492 [8] was used to precondition the cores. In NT BUILD 492 after the application of the vacuum, saturated Ca(OH)₂ solution is introduced into the container. However this is likely to lead to leaching of ions from the samples. Therefore, in this research, after the application of the vacuum, the vacuum was released, samples were wrapped in deionised water saturated hessian and placed back in the container. The vacuum was again applied. The purpose of this change was to prevent calcium hydroxide solution used for saturation affecting the pore solution chemistry of the concrete samples and minimise the loss of ions from the concrete samples. The mould finish face of the specimens was exposed to the salt solution. The duration of immersion was 3 months. After the immersion, the cores were ground in layers to obtain sufficient concrete dust from different depths; at an increment of 3mm and up to a depth of 30mm. RILEM TC 178-TMC recommendations [9, 10] was
followed to dissolve the dust in acid and water, respectively, to obtain the chloride containing solutions. A pre-calibrated potentiometric titration was carried out on the acid dissolved samples to determine the total chloride content in the solution. A non-linear regression analysis based on Fick’s second law was performed to determine the $D_{nssd}$ and the $C_s$ of the concrete cores once the chloride profile was obtained. The $D_{nssd}$ and the $C_s$ to be reported are an average of three values.

The pH of the water dissolved solution was measured in order to monitor the change of alkalinity in the concretes due to the chloride transport.

2.4.3 Test for pore structure indication
Before the chloride diffusion test, bulk electrical resistivity of the concrete cores was measured according to the literature [11] in order to indicate the pore structure of the concretes. Under the consideration of the effect of pore solution on the bulk electrical resistivity measurement, pore solution conductivity of the concretes was also measured (details in the next section) and the pore solution resistivity to be reported with the bulk electrical resistivity is the reciprocal of the pore solution conductivity.

2.4.4 Test for pore solution expression
Concrete cores with size of Ø60×100mm were taken from the 250×250×110mm slabs to be used for extracting pore solution at an age of 91 days. The sample preparation regime was similar to that of the chloride diffusion test. Pore solution of the cores was extracted by using a specialist pore fluid extraction device which compressed the specimen under pressures up to 1000MPa. pH and conductivity of the pore solution collected were measured immediately after the extraction by using a pH meter and a conductivity meter, respectively. Concentration of Na⁺ in the pore solution was measured subsequently by using Inductively Coupled Plasma-Optical Emission Spectrometer technique.

3 RESULTS AND DISCUSSION

3.1 Slump
The slump results of the concretes are presented in Figure 1. The mix design principle for the AAS concretes was to use a fixed w/b allowing all of them to meet the minimum slump requirement for its use in chloride environments, such as S2 in marine environments as specified in BS 8500-1. The mix design for the PC reference concrete also followed the same principle. Therefore, the slump results of all 13 mixes met the minimum requirement of S2 which is 50mm. It is also found that the slump of the AAS concretes increased with Na₂O%. The plasticizing effect provided by Na₂O component in the activator may be responsible for this [12].

3.2 Compressive strength
Figure 2 presents the compressive strength of the concretes at the ages of 3d, 28d and 91d. Due to the presence of retarder in the AAS concretes, some of them showed an unfavourable compressive strength at the age of 3d. The mix design for the PC reference concrete was to meet the requirement for XS3 and XD3 exposure environments specified in BS 8500-1. From the compressive strength results at the age of 28d it can be seen that not all the AAS concretes achieved the required strength (58MPa) for the two exposure classes. However, most of the AAS concretes met the strength requirement of 50MPa for the exposure classes XS1, XD1 and XD2. It should be noted that the w/b used for the AAS concretes (0.47) was higher than that for the PC concrete (0.42). Therefore, an improved compressive strength could be expected if a lower w/b was used for the AAS concretes. An AAS superplasticiser may be required in those instances.

3.3 Non-steady state chloride diffusion coefficient ($D_{nssd}$)
Figure 3 presents the $D_{nssd}$ of the concretes. It can be seen that the $D_{nssd}$ of the AAS concretes was much smaller than the corresponding value obtained for the PC concrete despite the higher w/b of the AAS concretes.
was also measured and its reciprocal (pore solution resistivity) was reported in Figure 4 as well for comparison.

As shown in Figure 4, the AAS concretes had lower pore solution resistivity than the PC concrete owing to its highly ionic nature. Therefore, according to the model proposed by Whittington et al. [14], the reason for the higher bulk electrical resistivity of the AAS concretes could be attributed to they had denser pore structure and/or their binder matrix was less conductive. When the pore solution is highly ionic and conductive, the conductivity of binder matrix will be insignificant (under normal circumstances). Suggesting that more ionic flow will take place through the pore solution and the binder will play insignificant role in the overall electrical resistivity. This would also mean the higher bulk electrical resistivity shown in Figure 4 and the lower chloride diffusivity shown in Figure 3 is a result of the denser pore structure.

The hydration products of AAS, such as C-S-H(I), C-A-S-H and hydrotalcite [15] have much potential to bind alkali cations [16]. During the transport of chloride ions, the binding of the accompany cations could retard the further ingress of chloride anions [3]. At the beginning of the mixing, large amount of sodium cations was introduced in the AAS concretes (refer to AAS with N₂O₅% of 4 was used by Puertas et al. [5], concentration of sodium ions of 60000ppm was observed in AAS at the age of 3 hours). However, after three months of curing, a dramatic reduction in the concentration of sodium ions was observed in the AAS concretes as reported in Table 3. This suggests that the matrix is capable of binding sodium ions in high proportion. It is assumed that this binding nature will also continue during the chloride ingress phase. This could further retard the movement of chloride ions and reduce their overall chloride diffusivity.

<table>
<thead>
<tr>
<th>Mix</th>
<th>pH</th>
<th>Na⁺ (ppm)</th>
<th>Mix</th>
<th>pH</th>
<th>Na⁺ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%-0.75</td>
<td>11.7</td>
<td>2154</td>
<td>6%-2.00</td>
<td>9.9</td>
<td>18.20</td>
</tr>
<tr>
<td>4%-1.00</td>
<td>11.9</td>
<td>4740</td>
<td>8%-0.75</td>
<td>12.4</td>
<td>202.0</td>
</tr>
<tr>
<td>4%-1.50</td>
<td>10.5</td>
<td>58.96</td>
<td>8%-1.00</td>
<td>12.2</td>
<td>244.0</td>
</tr>
<tr>
<td>4%-2.00</td>
<td>9.9</td>
<td>121.2</td>
<td>8%-1.50</td>
<td>10.8</td>
<td>185.3</td>
</tr>
<tr>
<td>6%-0.75</td>
<td>11.9</td>
<td>96.26</td>
<td>8%-2.00</td>
<td>11.9</td>
<td>64.34</td>
</tr>
<tr>
<td>6%-1.00</td>
<td>11.9</td>
<td>69.19</td>
<td>PC</td>
<td>12.5</td>
<td>1234</td>
</tr>
<tr>
<td>6%-1.50</td>
<td>11.4</td>
<td>42.81</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Chloride binding may be enhanced when the concrete is less alkaline [17]. As reported in Table 3, the AAS concretes had a lower alkalinity than the PC concrete. Therefore, it is anticipated that more chlorides might have been bound by the hydration products of the AAS concretes delaying their further ingress. This may also explain the lower Dₙ₉₉₉ obtained for the AAS concretes.

3.4 Effect of Na₂O% and Ms on the Dₙ₉₉₉ of the AAS concretes

Effects of Na₂O% and Ms on the Dₙ₉₉₉ of the AAS concretes are presented in Figures 5 and 6, respectively.

From Figure 5 it can be seen that the Dₙ₉₉₉ of the AAS concretes decreased with the increase of Na₂O% from 4 to 8. As reported by Karahan and Yakupoglu [18], porosity of AAS is reduced with the increase of Na₂O%. This could be one of the primary reasons for the reduction in Dₙ₉₉₉ with the increase of Na₂O% for the AAS concretes.

Besides, hydration degree of AAS increases with the increase of Na₂O% [19]. As a result, more hydration products such as C-S-H gel and hydrotalcite would be formed in the AAS with a higher Na₂O%. Such hydration products show potential to bind chlorides during their transport in AAS. Therefore, chloride binding in the AAS concretes might have been enhanced with the increase of Na₂O% delaying further ingress of chlorides. This could be also responsible for the reduced Dₙ₉₉₉ of the AAS concretes with the increase of Na₂O% in Figure 5.

Ms around 1.50 is optimum for the hydration of AAS [20, 21]. Therefore, as a result of the possibly reduced porosity and improved chloride binding, the AAS concretes with Ms of 1.50 gave the lowest Dₙ₉₉₉ as shown in Figure 6.

3.5 Chloride concentration at the surface (Cₛ)

Figure 7 presents the estimated total Cₛ of the concretes by using Fick’s second law based curve fitting. It can be seen that the Cₛ of the AAS concretes was higher than that obtained from the PC concrete.

As stated by Buenfield et al. [22], for sake of electron-neutrality, the transport of chloride anions in concrete should be balanced by an outward transport of other anions (such as hydroxyl anions) from the concrete.
Figure 5. Effect of Na₂O% on the Dₚₐₚ of the AAS concretes at different Ms.

Figure 6. Effect of Ms on the Dₚₐₚ of the AAS concretes at different Na₂O%.

Figure 8 presents the pH profiles of concretes after chloride immersion test. It is clear to see that the pH values drop dramatically in the near surface zone of AAS concretes.

When the outward diffusion of hydroxyl ions occurs in PC concrete, Ca(OH)₂ would dissolve in the pore solution to buffer its alkalinity [23]. This may have explained the constant pH values in the PC concrete with depth as shown in Figure 8. However, Ca(OH)₂ is not one of the hydration products of AAS [15]. Without the buffering effect, the loss of alkalinity would be more severe in the case of the AAS concretes as shown in Figure 8. This is particularly significant in the near surface zone.

As a result of the outward diffusion of hydroxyl ions, chloride ions of the same charge penetrated into the concretes to take the sites originally occupied by hydroxyl ions [22]. The AAS concretes lose hydroxyl ions from the near surface zone and there no further hydroxides generated by the binder, more chlorides from outside will migrate and occupy the sites. This may explain the higher chloride content observed at the surface of the AAS concretes as presented in Figure 7. The reduction of alkalinity in such concretes will enhance the binding capacity as discussed earlier. This could also be a contributing factor for the increase in Cₛ as shown in Figure 7.

4 CONCLUSION

- Surface chloride concentration (Cₛ) for the AAS concretes was found to be higher than that of the PC concrete. Severe loss of hydroxyl ions and subsequent improvement in chloride binding could explain the increased Cₛ values.
• Chloride diffusivity, $D_{\text{nssd}}$, of the AAS concretes was lower than that of the PC concrete. Based on the analysis and interpretation, the AAS concretes were found to have (1) denser pore structure, (2) higher binding capacity of alkali cations and (3) possibly improved chloride binding capacity. All of the above factors individually or collectively help to explain the lower $D_{\text{nssd}}$ observed for AAS concrete.

• The $D_{\text{nssd}}$ of the AAS concretes decreased with the increase of Na$_2$O% from 4 to 8, and the AAS concretes with Ms of 1.50 had the lowest $D_{\text{nssd}}$. These are cohesive with the effect of Na$_2$O% and Ms on the hydration of AAS.

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