THE EFFECT OF SLAG COMPOSITION ON ITS PERFORMANCE IN THE PRODUCTION OF ALKALI ACTIVATED SLAG BINDERS

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Introduction

Alkaline activated slag (AAS) binders are produced by the reaction of an aluminosilicate precursor and an alkaline solution1. Slags are ideal precursors for alkali-activation because of their high silicon and aluminium content and, when vitreous, can react in alkaline solutions. Tetronics International’s thermal DC plasma technology is used for various metal recovery and hazardous waste treatment processes for example; platinum group metal recovery from catalysts and the vitrification of air pollution control residue (APCr)2 and these processes produce slags of various compositions. Understanding the effect of variations of a slag’s composition on its behaviour during alkali-activation is an important factor in determining its suitability for producing alkali-activated binders.

Method and Materials

Slag derived from the plasma vitrification of APCr was obtained at Tetronics Trials Facility in Swindon, UK (slag sample S1). The composition of this slag was modified using Al2O3, CaO, SiO2 or TiO2 powders to resemble other plasma derived slags and re-melted in a muffle furnace at 1600°C before being quenched in air. X-ray diffraction (XRD) was used to ensure that the slag samples were vitreous before alkali activation. Alkali activated slag samples were made by mixing slag milled to a particle size less than 65 µm with 6M NaOH. The samples were cured in a controlled environment at 40°C for 28 days before their compression strength was determined. The compression tests were carried out using a Zwick Z030 Universal Testing Machine with a 50 kN load. Selective dissolution tests of the AAS concretes were performed to determine the extent of the slag reactivity following the method outlined by Luke and Glasser3.

Results

X-ray fluorescence (XRF) analysis of the slags in Table 1 show that the samples were mostly calcium-alumino-silicate slags with various levels of other oxides such as TiO2, Na2O, MgO and Fe2O3. Slag compositions can be described by their ‘basicity’ and there
are numerous equations to describe a slag’s basicity. Due to the complex multicomponent nature of these slags, their composition was characterised using the concept of ‘optical basicity’ introduced by Duffy. The optical basicity considers all the components of the slags and has been used by researchers in models to calculate slag viscosity, density and sulphide capacity which relies, to some extent, on the basicity of a slag.

The optical basicity can be calculated by Equation (1):

$$\Lambda = \frac{\sum x_i n_i \Lambda_i}{\sum x_i n_i}$$  \hspace{1cm} (1)

Where $x_i$ is the molar fraction of component $i$, $n$ is the number of oxygens in the component i.e. $n = 2$ for $\text{SiO}_2$, $3$ for $\text{Al}_2\text{O}_3$ etc. and $\Lambda_i$ is the optical basicity of component $i$.

The optical basicity for a component $\Lambda_i$ can be calculated for using Pauling’s electronegativity value $\chi_i$ for the metal in the component in Equation (2):

$$\Lambda_i = \frac{1}{1.36(\chi_i - 0.26)}$$  \hspace{1cm} (2)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
<th>S5</th>
<th>S6</th>
<th>S7</th>
<th>S8</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>43.7</td>
<td>43.8</td>
<td>38.6</td>
<td>32.7</td>
<td>34.3</td>
<td>37.3</td>
<td>40.3</td>
<td>42.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>9.8</td>
<td>10.6</td>
<td>9.1</td>
<td>27.8</td>
<td>17.7</td>
<td>19.5</td>
<td>16.3</td>
<td>9.9</td>
</tr>
<tr>
<td>CaO</td>
<td>41.7</td>
<td>38.0</td>
<td>33.5</td>
<td>32.8</td>
<td>37.1</td>
<td>28.4</td>
<td>35.6</td>
<td>42.2</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.2</td>
<td>5.4</td>
<td>16.6</td>
<td>1.2</td>
<td>1.1</td>
<td>1.3</td>
<td>1.4</td>
<td>1.9</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>1.2</td>
<td>5.2</td>
<td>8.1</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>MgO</td>
<td>1.5</td>
<td>1.3</td>
<td>1.1</td>
<td>1.4</td>
<td>1.4</td>
<td>1.5</td>
<td>2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1.2</td>
<td>0.3</td>
<td>0.4</td>
<td>2.0</td>
<td>2.6</td>
<td>2.8</td>
<td>2.3</td>
<td>0.4</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.7</td>
<td>0.4</td>
<td>0.8</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>99.8</td>
<td>99.8</td>
<td>99.6</td>
<td>99.8</td>
<td>99.8</td>
<td>99.7</td>
<td>99.7</td>
<td>99.4</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>0.630</td>
<td>0.620</td>
<td>0.614</td>
<td>0.629</td>
<td>0.652</td>
<td>0.629</td>
<td>0.620</td>
<td>0.634</td>
</tr>
</tbody>
</table>

The strengths of the alkali-activated binders change as the composition of the slag changes as shown in Figure 1. Figure 2 shows a close relationship shown between the compression strength of the binder with the % of reacted slag indicating the reactivity of the slag changes with composition. The effect of the titanium addition on the compression strength can clearly be seen. As the TiO$_2$ content increases in the slag, the compression strength and the reactivity of the binder is reduced.

Figure 3 shows that there is a good relationship between the optical basicity of a slag’s composition and the compression strength of the binder which is produced. It suggests
that as the optical basicity of the slag increases, the reactivity of the slag in an alkaline environment increases which, in turn, increases the strength of the alkali-activated binder which is formed.

**Figure 1:** Compressive strength of the alkali-activated slag binders

**Figure 2:** Extent of reactivity of slag in the alkali-activated binders

**Figure 3:** Compression strength vs optical basicity

**Discussion**

The basicity of vitreous slag indicates the degree of polymerisation of the silicate chain network which forms the glass structure. The polymerisation is increased by network forming oxides SiO$_2$, TiO$_2$ and P$_2$O$_5$ and depolymerised by the network modifying oxides are CaO, Na$_2$O, MgO and FeO. Al$_2$O$_3$ and Fe$_2$O$_3$ are amphoteric oxides which can act as either network formers or modifiers in the slag system. An increased optical basicity indicates greater depolymerisation of the network. The addition of TiO$_2$, a network former, to the slag system causes a decrease in the optical basicity of the composition and the reactivity of the slag. In the slag system, TiO$_2$ stabilises the silicate network because metal ions such as Na$^+$ or Ca$^{2+}$ which would otherwise act as network modifying oxides preferably co-ordinate with titanate ions rather than silicate ions allowing for a greater polymerisation of the silicate network. A greater amount of
polymerisation of the silicate network causes an increased stability of the slag and a reduction in its reactivity during alkali-activation by reducing its dissolution at a high pH. -O-Si-O- bonds are more stable than -Si-O-Al-O- bonds or -Si-O-Ca- bonds in the slag. A decrease in the number -O-Si-O- bonds in the slag increases the dissolution of Si and Al species into solution which are required for the formation of the binding gel’s network structure. However, depolymerisation of the slag is not wholly compositionally dependant and can be affected by the quench rate of the slag during cooling. A faster quench rate can cause a greater depolymerisation and possible the cause of S7 being an anomaly of having a high compression strength but a low optical basicity.

The dissolution of the slag in the alkaline material can also be enhanced by reducing the particle size of the slag, a finer particle size creates a greater surface area for dissolution and the effect of curing temperature also effects the dissolution rate due to increased kinetics at higher temperatures. Therefore, although compositional variations can affect the strength of the slag, changing processing conditions can help to alleviate this and allow for the formation of a high strength material.

Conclusions

The dissolution of slag in the alkaline activating solution is an important factor in determining the strength of the alkali-activated binders which are produced from alkali-activation. The dissolution of the slag is related to the stability of the glass structure and the extent of the polymerisation of the silicate network structure. Greater concentrations of network formers in the slag composition, for example TiO$_2$, reduce the reactivity of the slag which can be indicated by the calculated optical basicity. However, the strength of the alkali-activated slag binder can be increased by processing conditions such as curing temperature particle size which can compensate for variations in strength due to slag composition.

References