Influence of red mud addition in alkali-activated mortars on corrosion resistance of steel

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Abstract. Alkali-activated materials (AAM) consist of a precursor, which is a source of aluminosilicates, and an alkali source. The precursors are usually waste materials from various industries such as fly ash from thermal power plants and slags from the metallurgical industry. Due to the increasing use of these materials in the cement industry and strategies for decommissioning coal-fired power plants, alternative raw materials from waste streams are increasingly being explored. One of these materials is waste from the aluminium industry, known as red mud. Due to its chemical composition, which is similar to that of other cementitious materials, red mud is suitable for use in the cement industry. It can also be used as a source of aluminosilicates in the synthesis of AAM. In this study, the corrosion behaviour of steel in chloride exposed AAMs based on fly ash and slag was investigated with and without the addition of red mud. During exposure of AAM to tap water and a 3.5 wt.% NaCl solution, the corrosion process was monitored by corrosion potential and polarisation resistance. AAM mixes containing red mud exhibited better corrosion resistivity and lower current density values compared to mixes without red mud, indicating a possible contribution of the red mud to chloride binding and improving the passivity of the steel.

1 Introduction

Cementless binders such as alkali-activated materials (AAM) are being researched as an alternative to Ordinary Portland cement, in the effort to reduce CO₂ emissions and landfiling of industrial by-products. AAMs are produced by the reaction of aluminosilicate, usually fly ash (FA) and blast furnace slag (BFS) with an alkaline activator, usually a concentrated aqueous solution of alkaline hydroxide, silicate, carbonate or sulphate. Due to the large exploitation of fly ash and slag in blended cements, availability of these precursors is decreasing, and therefore a need for alternatives is emerging [1]. Recently, much attention has been paid to bauxite residue, also called red mud. Red mud is a waste generated during the production of alumina, which involves dissolving bauxite ore in highly alkaline sodium hydroxide [2][3]. Due to the production process, red mud is a highly alkaline product with a pH of 10-13.5 and is pumped off for disposal, posing a major threat to the environment. For every ton of aluminium produced, about 0.3-1 tons of residue is generated [4]. Storage of this highly alkaline hazardous waste is expensive, requires large disposal areas, and can cause severe environmental problems. On the other hand, the high alkali content and chemical composition of red mud are attractive in the pretext of the corrosion resistance of reinforced concrete. It was previously hypothesised that red mud can prevent the corrosion of reinforcing bars by maintaining its passivity [5]. Furthermore, it was reported that in RM containing solutions, chloride binding activity of solution was increased [5] which could increase chloride threshold for corrosion initiation and further propagation. Present research is focused on observing the influence of locally available red mud used in alkali-activated binders on the corrosion parameters, such as open-circuit potential ($E_{corr}$), current density ($i_{corr}$) and total resistivity ($R_t$) of steel embedded in alkali-activated mortars exposed to tap water and NaCl 3.5 wt.% solution.

2 Materials and methods

Red mud was obtained from landfill in Dobro Selo near Mostar and fly ash originates from thermal power plant Kakanj, Bosnia and Herzegovina. Chemical composition of used materials is presented in Table 1, while Table 2 shows mix design of mortars used in this study. AAM mortars were prepared with w/b = 0.24, while binder to aggregate ratio was 0.33. OPC mortar was prepared according to standard [6]. Mix labelled FA 1 was based on fly ash as precursor, while mix labelled FARM 1 was based on the combination of fly ash and red mud.

<table>
<thead>
<tr>
<th>Table 1. Chemical composition of used materials</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>FA</td>
</tr>
<tr>
<td>RM</td>
</tr>
</tbody>
</table>

Monitoring of steel corrosion in mortars was performed applying unconventional three-electrode cell suggested by Šoić et al. [7] and previously used by Runci et al. [8] with a PAR VMP2 potentiostat/galvanostat (Biologic, Seyssinet-Pariset, France). The scheme of the cell set-up is shown in Figure 1. After mixing, mortars were cast into plastic cylinders glued to polished steel plates and mortars were in contact with steel. Tap water and NaCl solution...
were poured on the mortar surface. A graphite stick was immersed in water as a counter electrode, and saturated calomel electrode was used as a reference. The open-circuit potential (OCP) and the linear polarisation resistance (LPR) were measured periodically. Steel was polarised to ±10 mV corrosion potential at a scan rate of 0.166 mV/s. Values of corrosion potential ($E_{corr}$), current density ($i_{corr}$) and total resistivity ($R_t$) of steel were used to analyse the corrosion behaviour of steel in mortars exposed to tap water and 3.5 wt.% NaCl solution.

### Table 2. Mix design of the mortars

<table>
<thead>
<tr>
<th>Mass (%)</th>
<th>OPC</th>
<th>FA 1</th>
<th>FARM 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Aggregate/binder</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>w/b</td>
<td>0.5</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>FA 1</td>
<td>0</td>
<td>66.1</td>
<td>52.9</td>
</tr>
<tr>
<td>RM</td>
<td>0</td>
<td>0</td>
<td>13.2</td>
</tr>
<tr>
<td>NaOH</td>
<td>0</td>
<td>9.4</td>
<td>9.4</td>
</tr>
<tr>
<td>Waterglass</td>
<td>0</td>
<td>24.5</td>
<td>24.5</td>
</tr>
</tbody>
</table>

In addition to corrosion parameters, the particle size distribution (PSD) of the red mud, fly ash and cement sample was determined using Mastersizer 2000 instrument with a wet laser diffraction method by dispersing the particles in different solvents.

### 3 Results and discussion

Particle size distribution of red mud, fly ash and cement sample is given in Figure 2. It is easy to see how red mud has a higher percentage of smaller particles than fly ash and cement. More than 50% of red mud particles is in range between 0.1 – 1μm. Higher percentage of smaller particles makes this material very fine which could be beneficial in terms of durability.

Figure 1. Particle size distribution of red mud, fly ash and cement sample

Figure 2. Particle size distribution of red mud, fly ash and cement sample

Figure 3 a) and 3 b) shows results obtained by measurement of the open-circuit potential ($E_{corr}$) of samples in tap water and 3.5% wt. NaCl solution, respectively. Results of $E_{corr}$ measured in NaCl are derived as an average value of three identical samples. In addition to alkali-activated mortars, OPC mortar was examined as reference. In tap water, Figure 3 a), OPC sample exhibited expected behaviour, potentials were quite stable and maintained around 0 and -100 mV during entire test period. Potentials in AAM samples were stabilised after 60 days. Potential in FA1 mortar was between -270 and -290 mV. Steel embedded in FARM 1 mortar exhibited lowest values of $E_{corr}$ in tap water. Mortars exposed to simulated sea water solution (3.5%wt. NaCl) are presented in Figure 3 b). After 60 days of monitoring, corrosion potential value in OPC started to decline, reaching value of -457 mV at the end of testing period. Steel embedded in FA 1 exhibited even more pronounced decline in values after 60 days. After 70 days in mix FARM 1 $E_{corr}$ started to decrease and reached – 363 mV by the end of the testing period. However, after 40 days of exposure and till the end of test period FARM 1 had higher $E_{corr}$ than the values in FA1 without RM and OPC sample.
Figure 3. Changes in potentials ($E_{corr}$) of samples exposed to a) tap water and b) NaCl 3.5 wt.% solution

Figure 4 a) and 4 b) show changes in current density ($i_{corr}$) of structural steel plates over time. It can be noted that the values of $i_{corr}$ in all samples are quite low and according to literature [9], there is a low risk of corrosion, probably due to the dense microstructure of the samples and the good quality of steel. Current density $i_{corr}$ values were stable in OPC and FA 1 samples and were around 0.02 and 0.04 μA/cm$^2$, respectively.

Figure 5. Changes in total resistivity ($R_t$) of mortars exposed to a) tap water and b) NaCl 3.5 wt.% solution

The results of the total resistivity $R_t$ of steel embedded in mortar exposed to tap water and 3.5 wt.% NaCl solution are shown in Figures 5 a) and 5 b) respectively. In tap water, the resistivity values of most samples were stable throughout the entire testing period. The resistivity values of steel were higher in AAM mortars compared to OPC, however, all mortar samples showed quite high resistivity values. In an aggressive environment simulated with 3.5 wt.% NaCl (Figure 5 b), the resistivity of most samples was stable over time except for the mixture FA 1, where a significant decrease in resistivity was observed after 60 days and by the end of test period resistivity reach 209 kΩ cm$^2$. Although resistivity of FARM 1 sample started to slightly decrease after 60 days, still it showed highest values and by the end of testing it was 3000 kΩ cm$^2$ which is significantly more than its equivalent without red mud. From the presented results it can be observed that red mud in an aggressive environment contributes to the passivation of steel in alkali-activated mortar. It can be assumed that addition of RM favours steel passivation due to joint action of several mechanisms which have been proven in other studies. Since RM originates from bauxite ore, iron oxide dominates in its composition. Hematite ($Fe_2O_3$) has a great influence on corrosion, since certain degree of redox activity on the steel surface can be indicated in the presence of Fe$^{3+}$ ions thus favouring steel passivation [10]. As detected by XRD, hematite is the most represented mineral in used RM [11] which can be source of passivating Fe$^{3+}$ ions. One of the most important properties of red mud is the fineness of the particles. Figure 2 shows the particle size distribution (PSD) of red mud fly ash and cement sample. In the Figure 2 it can be seen that most of the red mud particles are between 0.1 - 1 μm, while fly ash and cement particles are larger and most particles are between 10-100 μm, meaning that RM
is extremely fine. Fineness of red mud particles can contribute enhancement of microstructure acting as a filler thus preventing transport of aggressive substances such as chlorides through the matrix. Additionally, red mud has higher amount of alkalis in its composition which can also affects higher pH value of concrete in contact with rebar. Furthermore, in comprehensive study by Koleva et al. [5] the passivation of steel was attributed to the combined effect of Al\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} from RM and other waste materials. The presence of Al\textsubscript{2}O\textsubscript{3} enhanced steel passivity by its adsorbing mechanism and thus steel electrodes immersed in solutions with RM showed increased corrosion resistivity. Also, presence of Al\textsubscript{2}O\textsubscript{3} has effect on chloride binding and with higher amounts of Al\textsubscript{2}O\textsubscript{3}, higher chloride binding capacity can be expected. In AAM mortars, waste materials with relatively high amount of Al\textsubscript{2}O\textsubscript{3} were used and according to above mentioned, combined use of such materials can be beneficial in terms of corrosion protection.

4 Conclusion

This study investigated the corrosion behaviour of steel embedded in alkali-activated fly ash mortar and in mortar in which 20\% of the fly ash have been replaced by red mud. The mortars were exposed to tap water and 3.5 wt\% NaCl solution and the following corrosion parameters were monitored: open circuit potential (E\textsubscript{corr}), current density (i\textsubscript{corr}) and total resistivity (R\textsubscript{t}). The values of current densities measured in all samples were relatively low and would normally be considered a low corrosion risk. When the mortars were exposed to a NaCl solution, the sample with red mud had lower i\textsubscript{corr} values compared to the sample without substitution and OPC. In addition, the resistivity of mortar with red mud in a corrosion cell was higher than that of mortar without red mud. Although the causes of this beneficial effect need to be further investigated, based on previous studies with red mud, it can be hypothesised that this positive effect of red mud may be due to the presence of Fe\textsuperscript{3+} ions, which promote the passivation of steel. Furthermore, the presence of Al\textsubscript{2}O\textsubscript{3} also affects chloride bonding, which may be another reason why sample with red mud in NaCl solution showed more beneficial results. In addition, the fineness of the red mud may help to fill up the microstructure and thus prevent chloride penetration.

Acknowledgment

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References

[1] European Coal Combustion Products Association (ECOBA), Production and utilisation of CCPs in 2008 in Europe (EU 15)