INFLUENCE OF POZZOLANIC PROPERTIES OF RED MUD WASTE AND HYDRATION PRODUCTS IN THE DURABILITY AND RETENTION OF HEAVY METALS IN MORTARS

Eliz P. Manfroi (1), Malik Cheriaf (2) and Janaíde C. Rocha (2)

(1, 2) Civil Engineering, University Federal of Santa Catarina, Brazil

Abstract
Red mud (RM) is a waste from alumina industry generated by the Bayer process. The large quantity of red mud produced and its disposal are currently a worldwide environmental problem. In the present research, the pozzolanic properties of dry and calcined red mud at 600, 700, 800 and 900°C were investigated by analyzing the consumption of calcium hydroxide, using differential thermal analysis and, using the methodology of Brazilian standard NBR 5752 of comparison of the compressive strength. The investigation of the compounds hydrated was carried out in pastes produced with 5 and 15% of red mud in replacing the cement, using X-ray diffraction and differential thermal analysis techniques. The assessment of the release of heavy metals from mortars produced with red mud and cement was investigated using non-destructive testing of leaching by diffusion based in the Dutch standard NEN 7345. Compressive strength test was carried in mortars constituted by 5, 10 and 15% red mud in replacement of cement. The results showed that the red mud calcined at 600 °C presents the best pozzolanic activity and, the compressive strength of mortars produced with this waste meet values in accordance with regulatory Brazilian standard. The analysis by X-ray diffraction and differential thermal analysis showed the formation of the hydration products CSH, hydrated silicates of aluminum and "hidrogarnets". In the mortars produced with calcined red mud at 600°C, that showed the best pozzolanic activity, there was the maximum retention of the chromium. The results showed that the pozzolanic reactions of the red mud with the cement compounds formed hydration products capable of encapsulating partly the heavy metals from red mud.

Keywords: red mud, waste, pozzolan, mortars.

1. INTRODUCTION
In 2009, the world production of primary aluminum reached the mark of 23.40 million tonnes. Therefore, by estimation, the aluminum industry generated approximately 14 million tonnes of red mud for high quality bauxite and 117 million tonnes for low quality bauxite. In spite of the merely illustrative purpose of the estimation, it demonstrates the size of the global environmental problem that red mud represents [1, 2].
In France, researches showed that French red mud presents good pozzolanic activity when calcined and can be used to produce mortars and concretes [3, 4]. In Brazil, studies evaluated the influence of the addition of dry red mud in the setting times of Portland cement through the Vicat apparatus and the pozzolanic index of the waste according to Brazilian standard NBR 5752 [5].

This article evaluates the pozzolanic property of red mud that has been dried and calcined at different temperatures through the procedure of calcium hydroxide consumption, and in comparison to Brazilian standard NBR 5752. In addition, this work seeks to analyze the hydrated compounds in pastes produced with red mud in substitution of cement. The evaluation of the compressive strength of mortars made with red mud are also presented in this work. Lastly, this paper aimed to contribute to the environmental assessment of red mud through leaching test described in Brazilian standard and to the environmental assessment of mortars produced with red mud according to the Dutch standard NEN 7345.

2. MATERIALS AND METHODS

The sample of red mud was collected in an alumina production industry in the state of Minas Gerais. For the production of the pastes and mortars the dry and calcined RM was used. It was dried in an oven at 105±5°C and later calcined at 600, 700, 800 and 900°C-1 hour. The red mud samples were ground and sieved to obtain a particle size of less than 0.15 mm. In order to obtain red mud chemical characteristics the chemical analysis test (EDX) and mineralogical analysis (XRD) were carried out. Fig.1 shows the mineralogical analysis of the dry red mud. The chemical composition of dry and calcined red mud’s is shown in Table 1.

In order to evaluate the pozzolanic potential of red mud the calcium hydroxide consumption method, established by reference [6], adapted by reference [7] was used. The pastes with red mud and reference paste were molded with a water/solid ratio of 0.60. After the hydration periods, 3, 7 and 28 days, the samples were dried in an oven, ground and submitted to differential thermal analysis. The evaluation of pozzolanic activity was also carried out according to procedure requirements established by Brazilian standard NBR 5752 [8].

Figure 1: Diffractogram of the dry red mud
Table 1: Chemical composition of red mud

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxides (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>RM- 600°C</td>
<td>28.948</td>
</tr>
<tr>
<td>RM- 800°C</td>
<td>28.651</td>
</tr>
</tbody>
</table>

The investigation of the hydrated compounds was carried out in pastes composed by 5 and 15% of dry and calcined red mud, in a mass substitution of the cement CPII-F-32. The pastes were molded with a water/binder ratio of 0.3 and a superplasticizer additive. After the hydration periods (3, 7 and 28 days), samples were dried in an oven, ground and submitted to X-ray diffraction and differential thermal analysis tests. Mortars were produced in the 1:3 trace with a water/cement ratio of 0.53. In the mortars with 10 and 15% of red mud the superplasticizer was used. The cement CPII-F-32 was replaced by 5, 10 and 15% of dry or calcined RM.

The samples of dry and calcined red mud at 600, 700, 800 and 900°C with a particle size of less than 0.15 mm were submitted to the leaching test in accordance with the procedures described in Brazilian standard [9]. In order to evaluate the release of heavy metals from mortars the leaching test was performed in accordance with the procedure established by Dutch standard [10]. After 64 days, the leachate extract obtained was filtered and analyzed using energy dispersive X-ray fluorescence spectrometry (EDX).

3. RESULTS AND DISCUSSION

3.1 Evaluation of the pozzolanic activity of red mud - Method of calcium hydroxide consumption

The thermograms of the pastes with calcined red mud at 600 and 900°C and reference paste (3, 7 and 28 days) are shown in Fig. 2 at Fig. 4. The results obtained show the presence of an endothermic peak at 115 and 125°C, which indicates the presence of calcium silicate hydrate (CSH) and possibly CAH gel.

The Afm phase is evidenced by the endothermic peak at 200°C. The peak around 320°C is attributed to the dehydroxylation of gibbsite - Al(OH)$_3$. The peak between 500 and 550°C represents the residual Ca(OH)$_2$. In pastes with calcined RM at 700°C and 800°C the same peaks found in pastes with calcined RM at 600°C were identified, with a variation regarding only the size of the peak.

Differently from the other samples, the paste with calcined red mud at 900°C did not present gibbsite attributed to its complete and irreversible dehydroxylation, thus becoming forms of alpha alumina ($\alpha$Al$_2$O$_3$). For the pastes produced with dry and calcined red mud, the bigger the age, the smaller the peak area of Ca(OH)$_2$. Consequently, the greater is the consumption of calcium hydroxide and the greater is the pozzolanic activity.
Figure 2: Thermograms of the pastes with calcined red mud at 600°C

Figure 3: Thermograms of the pastes with calcined red mud at 900°C

Figure 4: Thermograms of the reference pastes
3.2 Evaluation of the pozzolanic activity of red mud – Brazilian standard NBR 5752

The results of the pozzolanic activity indexes show that the samples of dry and calcined red mud do not present the 75% minimum pozzolanic activity index when evaluated by the methodology of Brazilian standard NBR 5752 [8], as shown in Fig. 5.

![Figure 5: Index of pozzolanic activity of red mud with cement within 28 days](image)

3.3 Investigation of hydrated compounds

Fig. 6 shows the thermograms of the pastes with 15% of red mud and of the reference paste, respectively. The differential thermal analyses in the pastes with 15% of RM showed the formation of calcium silicate hydrate (CSH) and the existence of a new hydrated compound, the Afm phase and possibly CAH gel, which in fact do not exist in the reference pastes (only cement). The presence of the small peak at 300°C, in the pastes produced with dry and calcined red mud at 600, 700 and 800°C is correspondent the residual presence of gibbsite. The peak between 500 and 600°C is associated to portlandite (CH). In pastes with 5% of RM the same peaks found in pastes with 15% of RM were identified, with a variation regarding only the size of the peak.

![Figure 6: Thermograms of the pastes produced with 15% of red mud and of the reference](image)
Fig. 7 shows the diffractograms of the pastes with 15% of RM calcined at 600°C. Pastes produced with 15% of red mud calcined at 600 and 900°C and reference pastes presented the hydration products: ettringite (E) and portlandite (CH). The presence of calcite (C) in the pastes comes from the chemical composition of red mud and from the type of cement (CPII-F-32), which is composed by 6 to 10% of limestone.

Differently from the reference paste (only cement), the pastes with 15% of red mud showed the Afm phase and CAH gel, which are products resulting from pozzolanic reactions of the red mud with the cement compounds.

![Figure 7: Diffractograms of the pastes with 15% of red mud calcined at 600°C](image)

**3.4 Evaluation of compressive strength**

The mortars produced with 5% of calcined and dry red mud at 600, 700 and 800°C showed compressive strength values within 28 days which were on average equal to the compressive strength values of the reference mortar (Fig. 8). The mortars produced through substitutions of cement by 10 and 15% of dry or calcined red mud at 600, 700 and 800°C showed lower compressive strength values than the reference sample; however, they can be used for the laying and covering of the walls and roof, where high compressive strength is not necessary. Only the calcined RM at 900°C can replace up to 15% of cement mass increasing the compressive strength of the mortars.
3.5 Environmental assessment

The concentrations of the metals leached from dry and calcined red mud and from cement CPII-F are shown in Fig. 9. The results show that the red mud of this study, either dry or calcined, is classified as hazardous waste (class I), because in all cases it presented higher concentrations of chromium and selenium than the limits defined in annex F of the Brazilian standard NBR 10004 [11].

The elements leached from mortars with 5 and 10% of red mud and the reference mortar are shown in Fig. 10 and Fig. 11. The mortars produced without RM showed concentrations of cadmium higher than the limits values defined in annex F of the Brazilian standard NBR 10004 [11]. The mortars with 5 and 10% of RM showed concentrations of cadmium leached lower than the concentrations leached from the reference mortar.

The mortars produced with 10% of calcined red mud at 700, 800 and 900°C showed a higher concentration of heavy metals leached when compared with the mortars produced with 5% of RM. In general, the mortars produced with 10% of calcined RM at 600°C showed the
lowest concentrations of heavy metals leached. All samples produced with 5 and 10% of red mud showed concentrations of chromium leached higher than the limits values defined in the Brazilian standard NBR 10004 [11].

Figure 10: Concentrations of elements leached from mortars with 5% of red mud

Figure 11: Concentrations of elements leached from mortars with 10% of red mud

4. CONCLUSIONS

The analyses carried out in the dry and calcined red mud demonstrated that they have silica and alumina in their chemical composition, compounds which confer pozzolanic characteristics to RM. The dry and calcined red mud at 600, 700, 800 and 900°C presents pozzolanic activity in the presence of calcium hydroxide. Although the evaluation of the pozzolanic activity of RM through the procedure of Brazilian regulation NBR 5752 has classified RM as non-pozzolanic material, in the study of the consumption of calcium hydroxide with the differential thermal analysis the samples of dry and calcined red mud at 600, 700 and 800°C present high consumption of calcium hydroxide, the largest being the consumption measured at 600°C. Furthermore, there was a formation of hydration products, hydrated calcium silicates (C-S-H), Afm phase and possibly CAH gel, thus showing
pozzolanic activity. The calcined red mud at 900°C presents the lowest consumption of calcium hydroxide; however, it has the highest compressive strength, and therefore shows a greater filler effect. The results regarding compressive strength and the release of heavy metals from the mortars show that the most appropriate substitution is red mud calcined at 600°C.

REFERENCES