Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

Microstructure, mineralogy and environmental evaluation of cementitious composites produced with red mud waste

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ABSTRACT

Red mud (RM) is a by-product from alumina industry, and represents a renewed environmental problem due the significant annual throughput by the plants. In this study, the microstructure and mineralogical compositions of cement pastes constituted by until 15% of dry or calcined red mud (600-900ºC) were investigated by scanning electron microscopy, X-ray diffraction and differential thermal analysis techniques, respectively. The environmental evaluation of red mud was performed using TCLP procedures and diffusion tests in mortars. Water absorption by capillarity, wetting angle, compressive strength tests were realized on mortars constituted by until 15% red mud in replacement of cement. The compounds calcium silicate hydrate, AFm phase, CAH gel and ettringite were identified in the pastes produced with red mud. The results showed that the red mud waste can be used in replacement to cement to produce cementitious composites with microstructure, mechanical and hygroscopic properties suitable for their use in civil construction.

Keywords. Red mud, waste, cement, pastes, mortars.

INTRODUCTION

Red mud is a waste generated from the refining of bauxite during the Bayer process for the production of alumina and the posterior production of aluminum. In 2011, the world production of primary aluminum reached the mark of 25.63 million tonnes. Therefore, by estimation, the aluminum industry generated approximately 15 million tonnes of red mud for high quality bauxite and 128 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 (Wang et al., 2008; I.A.I, 2012).

The red mud contains silica, alumina and hematite in their chemical composition, compounds which confer pozzolanic property to red mud. The Brazilian red mud dry and calcined at 600, 700 and 800ºC has high pozzolanic activity, mainly when calcined at 600ºC. The red mud calcined at 900ºC shows low pozzolanic activity, however, it has filler effect (Manfroi, 2009).

This article evaluates the microstructure and the mineralogy of pastes produced with 5 and 15% of red mud in substitution of Portland cement. The evaluation of the compressive strength, water absorption by capillarity and wetting angle 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.

MATERIALS AND METHODS

Materials. 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 or 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 through a sieve with a mesh size of 150 μm.

The particles size distribution of the dry red mud obtained by laser granulometry method (Microtrac Flex) showed that 100% of its particles are smaller than 18 μm. The red mud dry and calcined at 600, 700, 800 and 900ºC show values of the specific area (Blaine method) about 6 to 9 times greater than the value of the specific area of the Portland cement CPII-F (3200 cm^2/g), ie the particles of the red mud are lower than the particles of the Portland cement. Moreover, the greater the calcination temperature, the lower is the specific area of the red mud. In order to obtain red mud chemical characteristics the chemical analysis test (EDX) was carried out. The chemical composition of dry and calcined red mud's is shown in Table 1.

Table 1. Chemical composition of dry and calcined red mud

Sample	Oxides (%)		
	Al_2O_3	Fe_2O_3	SiO_2
RM- Dry	32.220	23.977	21.904
RM- 600ºC	28.948	19.528	18.362
RM- 700ºC	28.639	19.033	18.496
RM- 800ºC	28.651	18.882	18.693
RM- 900ºC	29.645	18.924	18.248

Methods. 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. The pastes were molded with a water/binder ratio of 0.3 and 0.2 at 0.4% of 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. The microstructures of the pastes were investigated by scanning electron microscopy analysis (SEM).

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 additive was used. The cement CPII-F was replaced by 5, 10 and 15% of dry or calcined RM. The compressive strength test in mortars was carried out in accordance with the procedures described in Brazilian standard NBR 13279 (ABNT, 1995).

In order to evaluate the water absorption by capillarity of the mortars was used a procedure that consists in the measure of the height variation of a water column contained in a graduated Mariotte tube in function of time (Santos, 2006). The height variation of the water column is directly related with the amount of water absorbed by the sample. The volume of water absorbed by section of the sample was called absorption index (I = cm^3/cm^2). The inclination of the straight (absorption index versus square root of time) corresponds to sorptivity. The wetting angle test in mortars was carried out in accordance with an experimental procedure generally applied in soils (Santos, 2006). This procedure provides the determination of the apparent wetting angle by means of the evaluation of the capillary rise in test carried out in mortars.

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 NBR 10005 (ABNT, 2004). 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 NEN 7345 (NNI, 1995). After 64 days, the leachate extract obtained was filtered and analyzed using energy dispersive X-ray fluorescence spectrometry (EDX).

RESULTS AND DISCUSSION

Investigation of Hydrated Compounds. 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), indicating that the incorporation of RM in the blends did not change the types of compounds normally hydrated in a cement paste. Figure 1 shows the diffractograms of the pastes with 15% of RM calcined at 600ºC. The presence of calcite (C) in the pastes comes from the chemical composition of red mud and from the type of cement (CPII-F), which is composed by 6 to 10% of limestone.

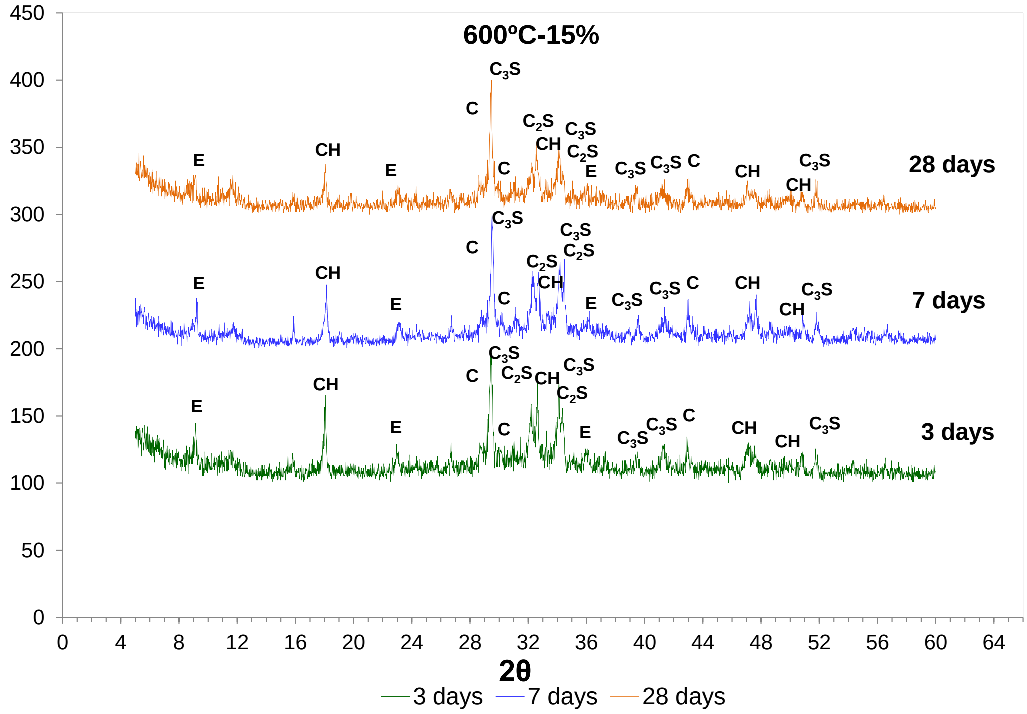


Figure 1. Diffractograms of the pastes with 15% of red mud calcined at 600ºC

The differential thermal analyses in the pastes with 5 and 15% of RM showed the formation of calcium silicate hydrate (CSH) and the existence of a new hydrated compound, the Afm phase and CAH gel, which in fact do not exist in the reference pastes (only cement). Figure 2 shows the thermograms of the pastes with 15% of red mud and of the reference paste. The presence of the small peak at 300ºC, in the pastes produced with dry and calcined red mud at 600, 700 and 800ºC is correspondent the residual presence of gibbsite. The peak between 500 and 600°C is associated to portlandite (CH).

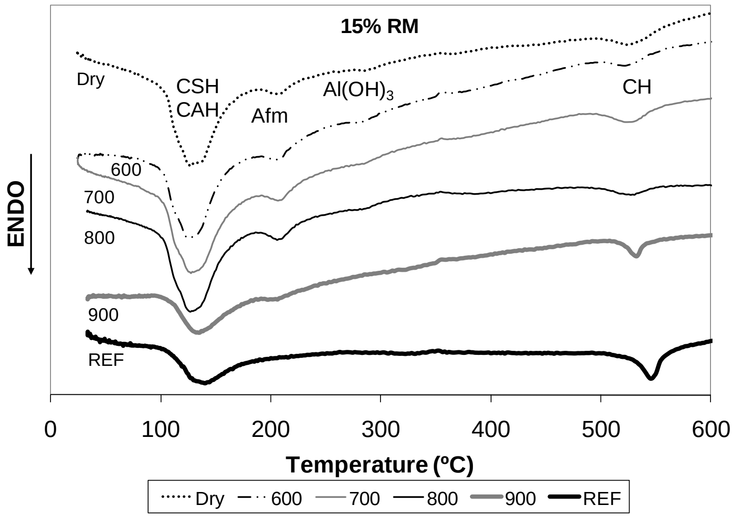


Figure 2. Thermograms of the pastes produced with 15% of red mud and of the reference paste

The image of the microstructure of the reference paste shows the presence of the hydration products calcium silicate hydrate (CSH), monosulfate, portlandite (CH) and gehlenite (Figure 3). The hydrated compounds calcium silicate hydrate and portlandite were also identified by differential thermal analysis and X-ray diffraction techniques.

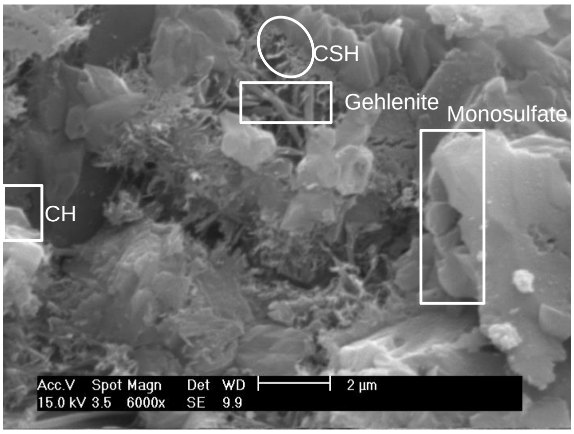
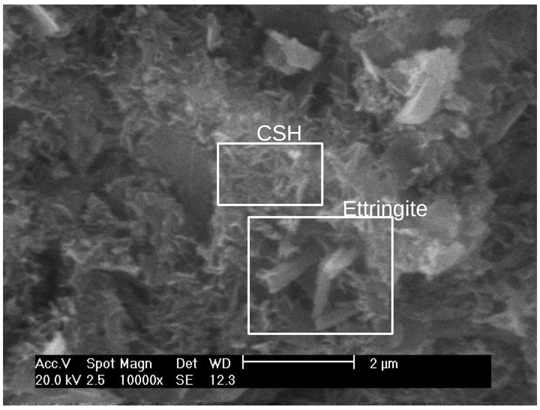
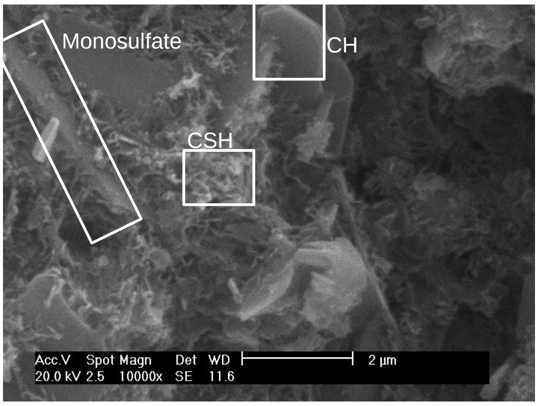


Figure 3. Image of the microstructure of the reference paste at 28 days

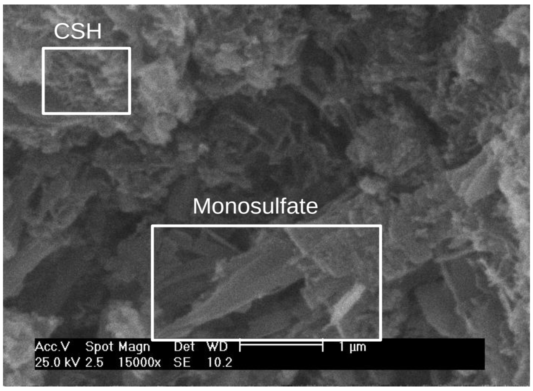
The images of the microstructures of the pastes made with 15% of red mud dry and calcined at 600, 700, 800 e 900°C at 28 days are shown in Figure 4. The scanning electron microscopy analysis in the pastes produced with dry and calcined red mud at 600, 700, 800 e 900º confirmed the formation of the hydration products calcium silicate hydrate (CSH), AFm phase (monosulfate), ettringite and portlandite (CH). These hydrated compounds were also detected by means of the analysis of X-ray diffraction and differential thermal analysis.



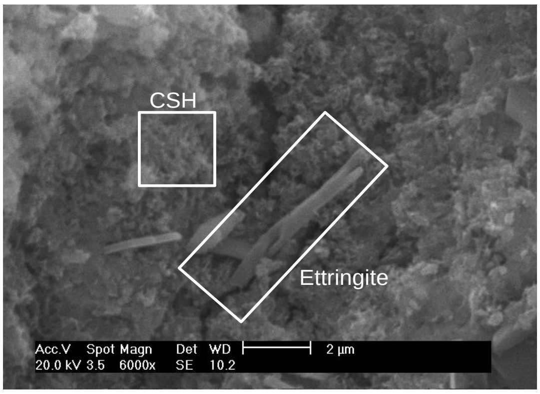
a) Paste with dry RM



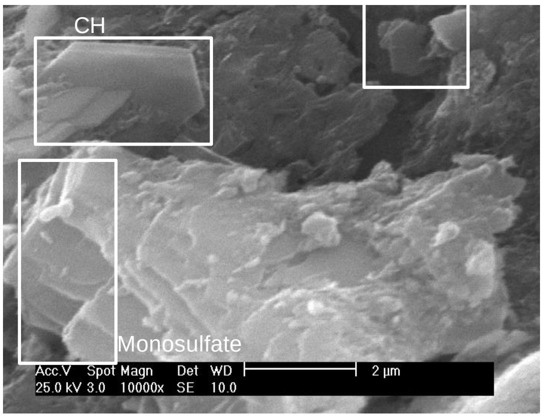
b) Paste with calcined RM at 600ºC



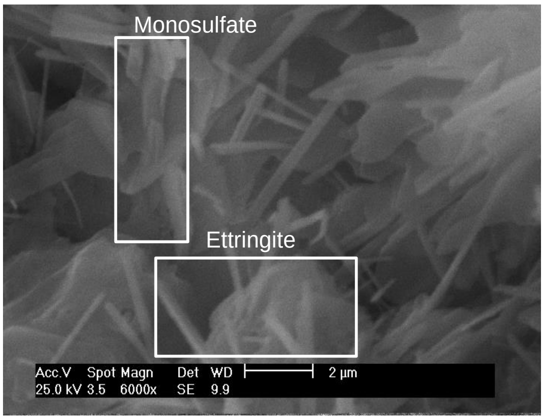
c) Paste with calcined RM at 700ºC



d) Paste with calcined red mud at 800ºC



e) Paste with calcined RM at 900ºC- Section 1



f) Paste with calcined RM at 900ºC- Section 2

Figura 4. Images of the microstructure of the pastes produced with 15% of RM at 28 days

The compound calcium silicate hydrate can be seen in the sections of the pastes produced with 15% of the red mud dry and calcined at 600, 700 and 800ºC. In the sections of the pastes with 15% of red mud calcined at 900º the calcium silicate hydrate can not be viewed clearly as in the other pastes produced with red mud. Furthermore, the section of the paste with 15% of the red mud calcined at 900ºC (Figure 14 e) presents hexagonal crystals (CH) well defined, confirming the low pozzolanic activity of the calcined red mud at 900 ºC. Monosulfate plates can be seen in the sections of the pastes produced with 15% of the red mud calcined at 600, 700 and 900ºC. The needles in the images of the pastes with dry and calcined red at 800 and 900° C (Figures 14 a, d, e) correspond to ettringite.

Evaluation of Compressive Strength. The mortars produced with 5% of dry and calcined 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 (Figure 5). 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. Only the calcined RM at 900ºC can replace up to15% of cement mass increasing the compressive strength of the mortars. Although the red mud calcined at 900ºC has low pozzolanic activity, it has a greater filler effect improving the compressive strength of the mortars.

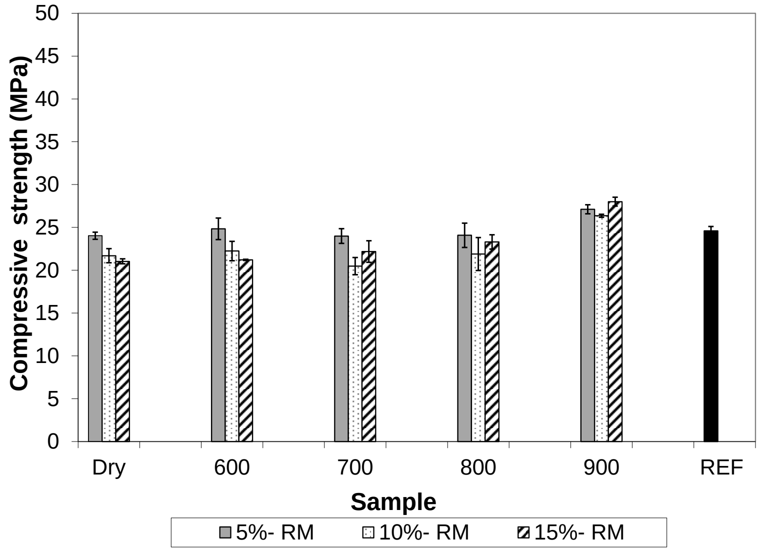


Figura 5. Average compressive strength of the mortars

Water Absorption by Capillarity. The substitutions of cement by 5% of dry or calcined red mud decreased the sorptivity of the mortars, this when compared to reference mortar (Figure 6). The lower sorptivity of the mortars produced with 5% of dry and calcined red mud at 600, 700 and 800ºC is related to property pozzolanic of red mud, where the large crystals and oriented of the $Ca(OH)_2$ are replaced by several smaller crystals and less oriented, reducing the pore connectivity and the amount of water absorbed. However, the lower sorptivity of the mortar with 5% of red mud calcined at 900ºC is related to filler effect of the red mud when calcined in this temperature. The filler effect of the red mud calcined at 900ºC promoted the filling of the empty capillaries, consequently, reducing the quantity of water absorbed.

The mortars with 10% of red mud (Figure 7) showed greater sorptivity than the mortars produced with 5% red mud. In the replacements of the cement by 10% of red mud, only the mortars produced with red mud calcined at 700, 800 and 900 °C showed sorptivity lower than the reference mortar.

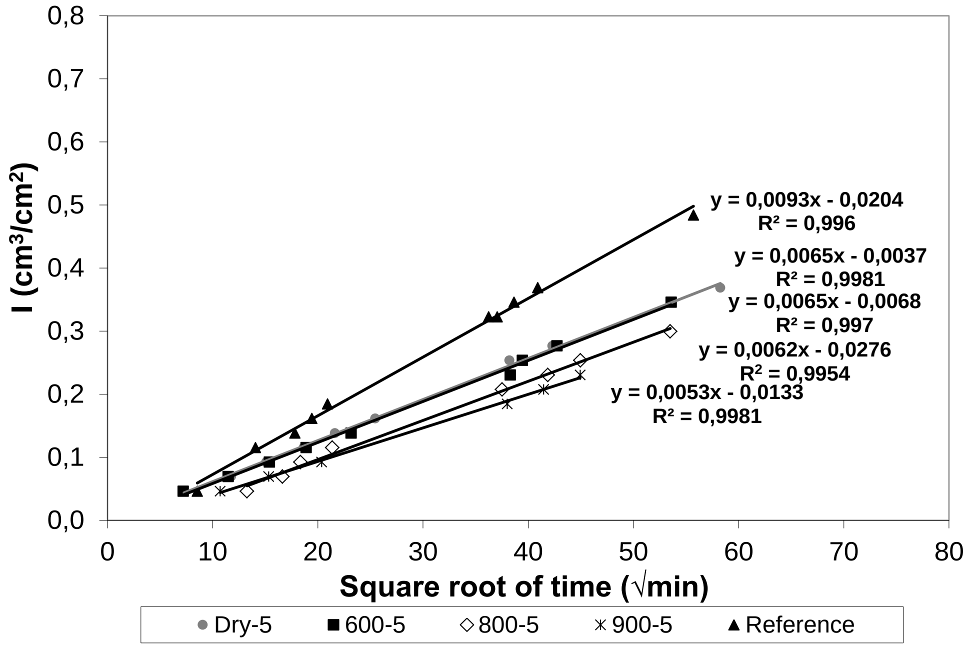


Figure 6. Volume of water by section of the sample x square root of time – Mortars with 5% of RM and reference

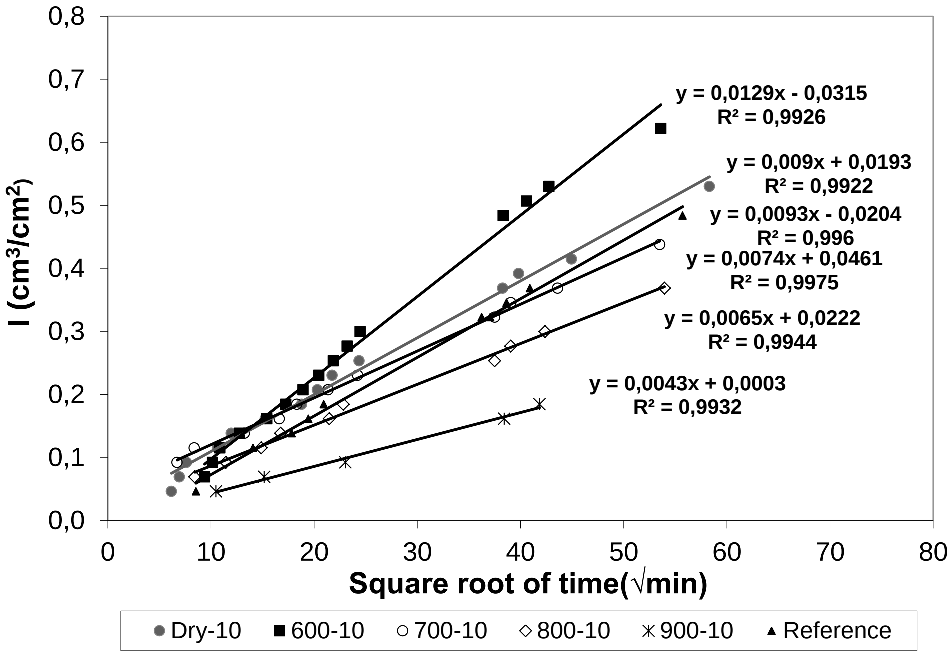


Figure 7. Volume of water by section of the sample x square root of time – Mortars with 10% of RM and reference

Apparent Wetting Angle. The mortars with 5% of red mud showed apparent wetting angle greater than the mortar without RM (Figure 8), therefore it has lower wettability. The greater wetting angle in the mortars produced with 5% of RM were expected, because this mortars showed sorptivity lower than the reference sample. The mortars produced with 10% of red mud showed wetting angle lower than the mortars produced with 5% red mud, i.e. greater the wettability, except for the sample with RM calcined at 900ºC. The mortars with red mud calcined at 900ºC showed wetting angle greater and wettability lower than the others mortars. This reduction of wettability is related to greater filler effect of red mud when calcined at 900ºC.

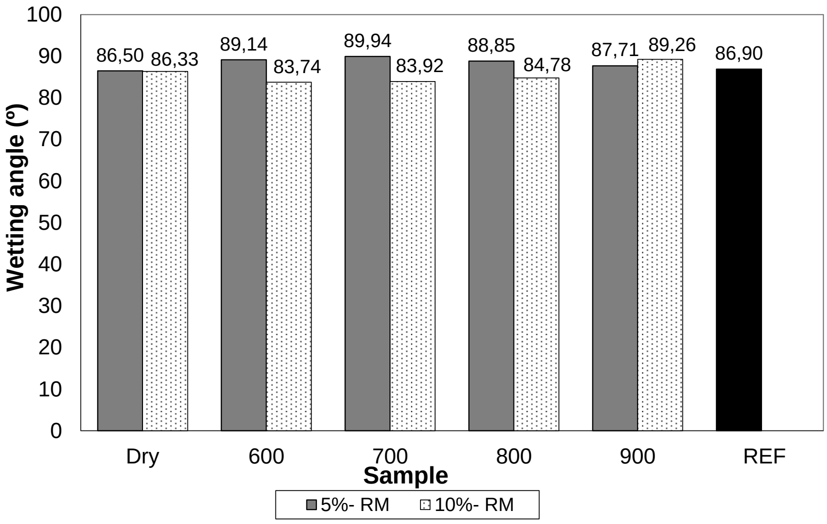


Figure 8. Apparent wetting angle of the mortars

Environmental Assessment. The concentrations of the metals leached from dry and calcined red mud and from cement CPII-F are shown in Figure 9. The results show that RM, 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 (ABNT, 20004).

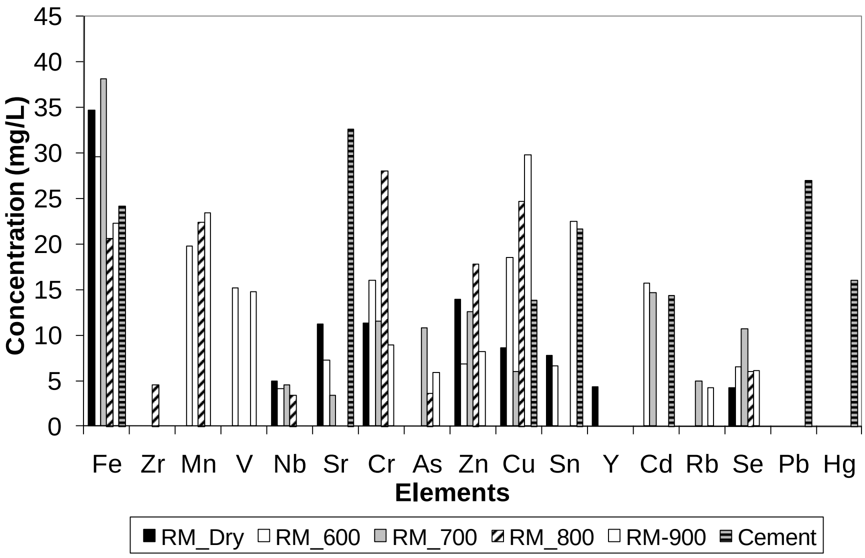


Figure 9. Concentrations of elements leached from samples of red mud and of the cement CPII-F

The elements leached from mortars with 5 and 10% of red mud and the reference mortar are shown in Figure 10 and Figure 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 (ABNT, 2004). The results show that mortars with 5 and 10% of RM release more heavy metals than mortar without RM. However, the mortars with 5 and 10% of RM showed concentrations of cadmium leached lower than the concentrations leached from the reference mortar.

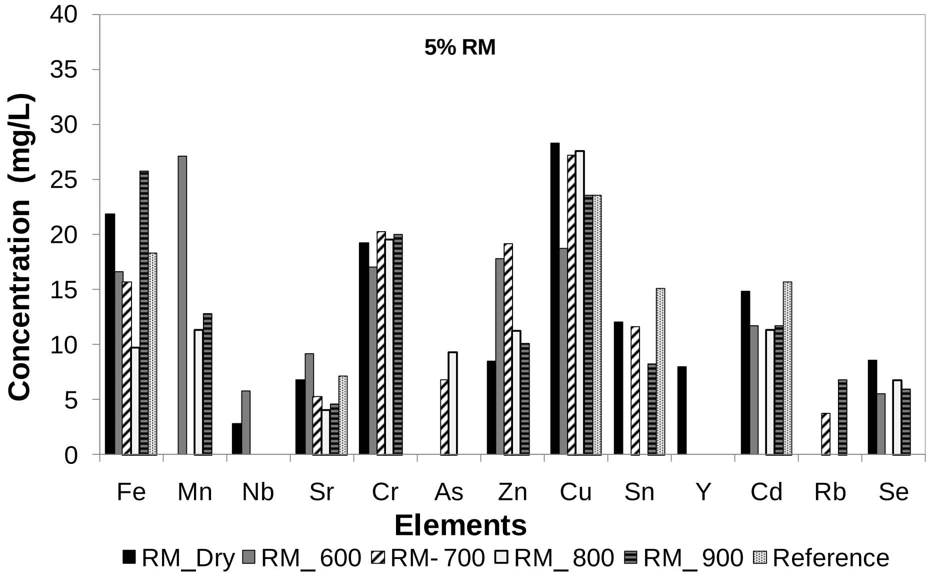


Figure 10. Concentrations of elements leached from mortars with 5% of RM

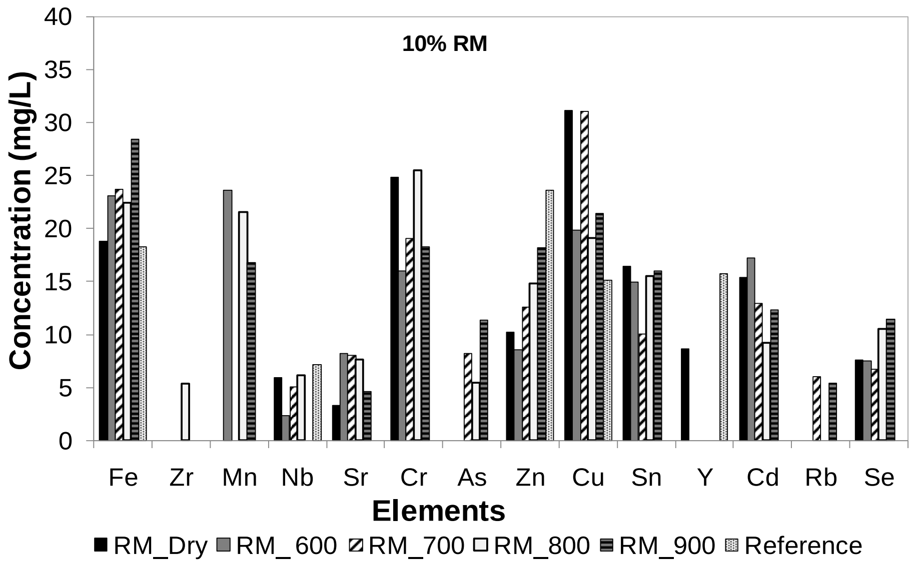


Figure 11. Concentrations of elements leached from mortars with 10% of RM

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 600ºC 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 (ABNT, 2004). In leachate extracts from mortars produced with 5 and 10% red mud was not detected the presence of vanadium, indicating that this element from the chemical composition of red mud is in stable chemical compounds.

CONCLUSIONS

The pastes produced with until 15% of red mud showed the hydration products: calcium silicate hydrate (CSH), ettringite, AFm phase (monosulfate) and CAH gel, confirming the pozzolanic activity of the dry and calcined red mud at 600, 700 e 800ºC.

Despite the Portland cement CPII-F be replaced by until 15% of red mud, the pastes produced with red mud showed the hydrated compounds calcium silicate hydrate (CSH) and ettringite, indicating that silica and the alumina contained in the red mud reacted with the compounds of the cement. Furthermore, the presence of the AFm phase and CAH gel in the pastes produced with red mud is justified by larger amount of the red mud added, and consequently a higher F_2O_3 and Al_2O_3 content available for formation of the AFm phase and CAH gel.

As the red mud calcined at 900ºC has low pozzolanic activity, the pastes produced with the same showed hexagonal crystals of portlandite well defined. Furthermore, the compound calcium silicate hydrate cannot be seen clearly in these pastes.

The results regarding investigation of hydrated compounds in pastes, compressive strength, water absorption by capillarity, wetting angle and the release of heavy metals from the mortars show that the most appropriate substitution is of until 5% of red mud calcined at 600ºC.

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