CEMENTITIOUS ACTIVITY OF CALCINED RED MUD

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Abstract

Red mud is a solid waste derived from the processing of bauxite ore to produce alumina. It is considered a hazardous waste due to its high pH. Since cementitious matrices are also strongly alkaline the incorporation of mud might be an interesting reuse solution. This paper describes the use of mud as collected and after calcination at distinct temperatures (450, 650, and 1000ºC) attempting to improve its reactivity. Materials with pozzolanic characteristics may partially replace the cement in mortars or concrete, with known benefits on the durability of products. Mortars containing up to 30 wt% red mud were prepared and characterized. Their pozzolanic activity index was evaluated based on physical and mechanical parameters (EN 4220) and on chemical analysis (EN 196-5). By comparing with a reference mixture without red mud, the obtained results confirm the potential of red mud as a pozzolanic additive to cementitious materials.

Keywords: Red mud, calcination, mortar; pozzolanic activity.

1. Introduction

World production of bauxite ore in 2009 reached 205 million tonnes. Brazil was ranked in 3rd position and produced 26.6 million tonnes. It also has the world's third largest bauxite ore reserves of around 3.5 billion tonnes, mainly concentrated in the north of the country in Pará state (IBRAM, 2009). Roughly 0.3 – 1.0 tonnes of red mud waste are generated for each tonne of produced aluminum, meaning that about 10.6 million tonnes of caustic red mud must be disposed annually. The world generation of red mud exceeds 117 million tonnes/year (Roskill Reports, 2008).

The red mud is a waste derived from the caustic soda digestion of bauxite ore, before calcination to generate alumina by the Bayer process. Its chemical and mineralogical composition is somewhat variable, depending on the characteristics of the bauxite ore and also on processing/technological conditions. The disposal of such large amounts of strongly alkaline waste is expensive, up to 1-2% of the alumina price. It also requires large landfill areas of about 0.2 km^2/year for a a plant that generates 1 Mtonnes/year of alumina. Its strong alkalinity creates environmental concerns and confinement conditions need to be strictly controlled (Singh et al., 1996; Glasser, 1997).

Several studies have evaluated the use of red mud directly as a component of clinker (Singh et al., 1996; Singh et al., 1997; Tsakirids et al., 2004), while its addition to mortar and concrete formulations has also been reported (Cabeza et al., 2003). The search for economically and environmentally viable recycling alternatives include applications of red mud as adsorbent for removal of cadmium, zinc and arsenic, fluoride, lead and chromium from aqueous solutions (Amritphale and Patel, 2007), as a component of ceramic bricks and tiles (Amritphale and Patel, 1987; Vincenzo et al., 2000), glazes (Yalcin and Sevnic, 2000), and in polymer-based composites (Asokan et al, 2005). The use in mortars and concrete was also tested (Gordon et al., 1996). However, there have been relatively little evaluation of the cementitious or pozzolanic activity of the red mud (Dow and Glasser, 2003).

Materials with pozzolanic characteristics may partially replace the cement in mortars or concrete, with known benefits on the durability of products (Yogananda and Jagadish, 1988; Cook et al., 1977; Pera et al., 1997; Mehta and Monteiro, 1994). A pozzolan is defined as a fine siliceous and/or aluminous powdered material that is able to react with lime (calcium hydroxide) in the presence of moisture and form stable cementitious compounds (Mehta and Monteiro, 1994). The research reported in this paper evaluates the pozzolanic activity of red mud in cementitious matrices, by using it as generated and after calcination at 450, 650 and 1000ºC.

2. Materials and Methods

2.1. Materials.

The mortars were produced with Portland cement 32.5, which is equivalent to ASTM C 596 (*Pozzolan-modified Portland cement*). The fine aggregate was natural siliceous sand.

The red mud (RM) was supplied by ALCOA Brazil, from Poços de Caldas-MG. It is a mixture containing about 60 wt% solids, collected immediately after alumina recovery from the digestion process (Bayer Process).

2.2. Methods.

2.2.1. Materials Characterization

The red mud (RM) was characterized by X-ray diffraction (Rigaku Geirgeflex ME 210GF2 Diffractometer, configured with CuKα radiation, 40 KV voltage, 100 mA current, 2θ scanning and scanning speed 4º/min) and by X-ray fluorescence (Philips PW1480 X-ray Fluorescence Spectrometer), to evaluate phase and chemical composition respectively. Relevant physical parameters such as the specific surface area, estimated by BET, (using a Micrometrics Gemini 2370 V1.02 equipment) and specific gravity (Helium Pycnometer Accupyc 1330 V2.01 from Micrometrics) were determined.

TG/DTA analysis was carried out on Labsys Setaram equipment, with dry N2 as a stripping gas, to study the thermal behaviour of the mud and then define the calcination conditions. The heating rate was 10ºC/min and the samples were heated from 20ºC to 1100ºC.

2.2.2. Red Mud Calcination

The red mud was calcined using a Termolab BL 260/03 oven, with a heating rate of 10°C/min. Three distinct temperatures were selected (450, 650, and 1000°C). The dwell time was fixed at 2 hours.

2.2.3. Pozzolanic Activity

The pozzolanic activity of the red mud was evaluated by determining physical and chemical parameters of the mixtures. The physical determination follows the NP EN 4220 standard Pozzolans for Concrete by using mortars prepared as defined in Table

1. According to this standard, the water/binder (cement + pozzolan) and binder/aggregate ratios are constant and equal to 0.5 and 3.0 respectively. However, the water/cement ratio is higher (equal to 0.67) for mixtures containing 25 wt% RM.

After mixing, prismatic specimens 4x4x16 cm in size were moulded and after 24 hours immersed in water and placed in a climatic chamber at 38 ± 2ºC; 60% relative moisture for 28 days. After this curing period five specimens of each composition were tested by axial compression. According to the NP EN 4220 standard, the material is considered as a pozzolan if it develops an axial compressive strength that is higher than 0.85 of the sample prepared just with cement as binder. This defines the pozzolanic activity index.

Table 1. Material proportions

Composition	Cement (g)	Sand (g)	Red mud (g)	H_2O (g)
Standard mixture	450.0	1350.0	0.0	225.0
RM mortar	337.5	1350.0	112.5	225.0

The pozzolanic character of the red mud was evaluated by chemical tests according to NP EN 196-5. According to this standard, the pozzolanic index is determined by comparing the amount of calcium hydroxide present in the aqueous solution that contacts with the hydrated sample after a defined period of time, with the amount of calcium hydroxide required to saturate the environment with a similar alkalinity. The test is considered positive if the calcium hydroxide concentration in solution is lower than the saturation concentration.

A mixture of 20g cement to 100ml distilled water was used as the standard. The red mud mixture evaluated contained 15g cement and 5g RM per 100ml distilled water. Two replicas for each test were left in an climate chamber at 40 ± 2ºC; RH = 60% for 14 days.

3. Results and Discussion

3.1. Materials Characterization.

The Portland cement (32.5) used had a specific surface area of 0.93 m^2/g and a specific gravity of 3.11 kg/dm^3. The sand had a specific surface area of 0.68 m^2/g and a specific gravity of 2.70 kg/dm^3.

The red mud was received as a paste containing about 40% free water. It was dried and crushed to form a a powdered additive. TG/DTA curves of the red mud are presented in Figure 1 and were conducted to define suitable calcination temperatures.

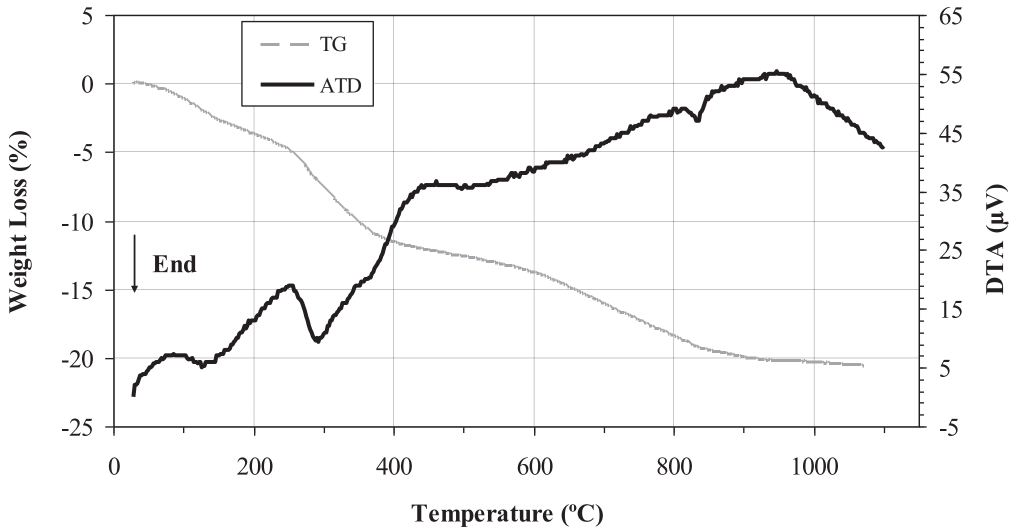

Figure 1. TG/DTA curves of the red mud as received

Up to 400ºC the material tends to show a continuous weight loss reaching about 12%. The endothermic character suggests decomposition reactions such as those involving removal of adsorbed water and dehydroxilation reactions (FeO(OH)).

Between 400ºC and 600ºC the material remains reasonably stable with a further 2% weight loss and no heat changes. Between 600ºC and 850ºC it tends to lose weight at a greater rate. Decarbonation ($CaCO_3$) and dehydroxilation reactions ($Al(OH)_3$ and muscovite) might occur, as suggested by the evolution of crystalline phases detected by XRD (see Figure 2). The weight loss tends to stop above 850ºC meaning that decomposition reactions are complete.

Based on these observations it was decided to calcine the red mud at 450ºC, 650ºC and 1000ºC. The material was then characterized, first in terms of crystalline phases as determined by XRD (see Figure 2). The red mud as received shows a complex mixture of crystalline phases. Aluminium hydroxide ($Al(OH)_3$), calcium carbonate ($CaCO_3$), iron oxide (Fe_2O_3) and hydroxide (FeO(OH)) SiO_2, muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$) and $Na_5Al_3CSi_3O_{15}$ are the detected compounds.

Calcination at 450ºC decomposes some hydrated compounds, with the destruction of the OH^- groups that are present in $Al(OH)_3$ and FeO(OH). So these compounds are not detected anymore. The evolution from 450 to 650°C is small, as denoted by the DTA/TG curves. The calcination at 1000°C tends to clean up the XRD spectrum of the material. Few phases remain stable (iron oxide and $Na_5Al_3CSi_3O_{15}$) while new ones are formed (nepheline) from the combination of existing reactive ones. Nepheline has the formula $K_{0.48}Na_{3.48}(AlSiO_4)_4$ and might result from the combination of quartz, muscovite and alumina. The formation of nepheline is reported by other authors (Usherov-Marshak et al., 1998; Wang et al., 2008; Wang and Scrivener, 1995; Liu et al., 2009; Moyd, 1959). The increasing crystallinity of the material, denoted by the sharpness of the peaks, might reduce its chemical reactivity.

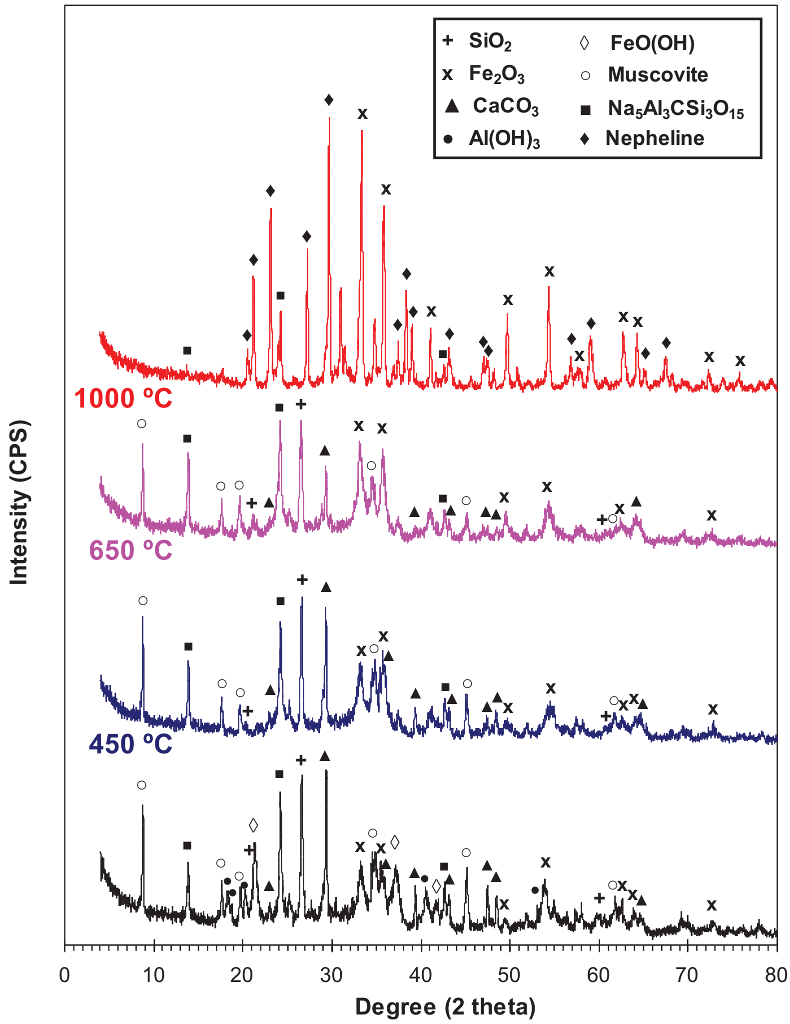

Figure 2. X-ray diffraction patterns of the red mud as received (lowest curve) and after calcination at 450, 650 and 1000ºC

Calcination also changes some physical characteristics of the powder that might then affect its reactivity. The values of specific surface area, specific gravity and unit weight are given in Table 2. The evolution of grain size distribution is shown in Figure 3.

Table 2. Effect of calcination temperature on the main physical properties.

Calcination Temperature	Specific surface area (m^2/g)	Specific gravity (g/cm^3)	Unitary mass (g/cm^3)
-	21.9	2.90	0.64
450ºC	21.6	2.91	0.62
650ºC	20.9	3.00	0.59
1000ºC	3.60	3.27	0.56

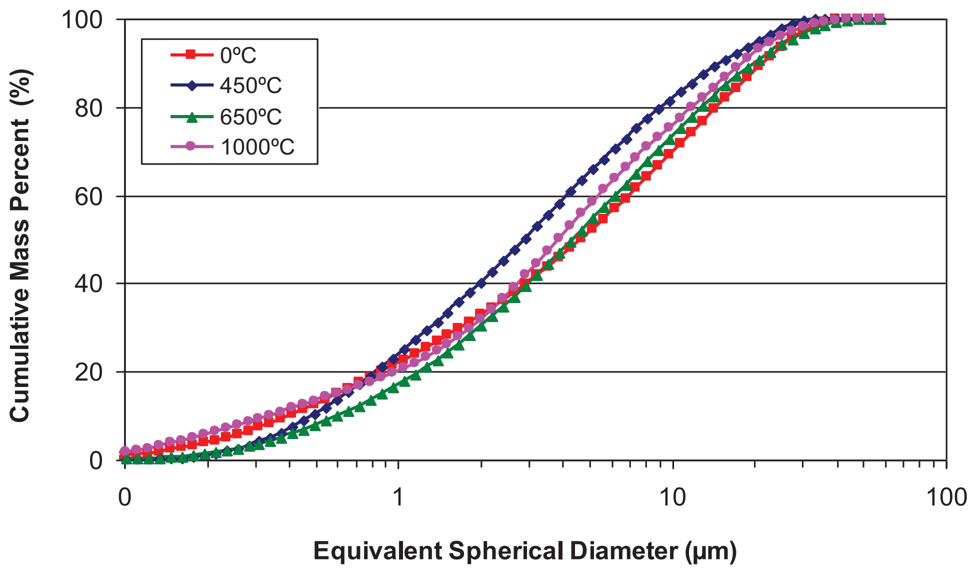

Figure 3. Particle size distribution of the red mud as received and after calcination at 450, 650 and 1000ºC

The increase of calcination temperature tends to increase density due to organic matter and water removal. Surface area tends to reduce particularly from 650 to 1000°C as a result of combination of components. The reduction in surface area is directly related to the decrease of unitary mass. However, the grain size distribution of each powder remained almost unchanged.

3.2. Verification of Pozzolanic Activity by Physical Test Method.

Mechanical properties are holistic indicators of the microstructure development of cement matrices upon hydration. In addition to chemical effects, values are mainly controlled by physical parameters such as porosity and compactness. Grain size distribution of components and the water/binder ratio are relevant parameters that control workability of the mixtures in the fresh state, with obvious effects on the mechanical strength of hardened bodies. Hence, the effect of a single component such as the red mud is difficult to evaluate just by determination of the mechanical strength of the mortar. The comparison of results presented in Table 3 is difficult to interpret. It is observed that the use of red mud generates mixtures showing acceptable values of pozzolanic activity indexes in all situations. Optimal behaviour is achieved by the use of RM calcined at 1000ºC.

Table 3. Axial compressive strength and pozzolanic activity index of mortars after 28 days curing

Mixture	Axial compressive mechanical strength after 28 days (MPa)	Pozzolanic activity index
Standard	27.54 ± 1.02	-
RM as received	23.47 ± 0.11	0.85
450ºC	24.53 ± 0.41	0.89
650ºC	24.13 ± 0.65	0.88
1000ºC	27.31± 0.64	0.99

Dow and Glasser (2003) found that the amounts of SiO_2 and Al_2O_3 dissolved in calcined red mud (500-700ºC) are much larger than those found in the sample in natura. This factor could be decisive in increasing the cementitious activity of the material. Furthermore, the hydration reaction of cement is favoured by the high alkalinity environment characteristic of red mud (Gordon et al., 1996).

The red mud calcined at 1000 ºC results are very positive with pozzolanic activity index equal to 0.99. The new phase present in this material is nepheline. According to Usherov-Marshak et al. (1998), the increase in share of low-basic compounds in the products of hardening of the cements with mineral additives such as nepheline results in quick and early occurrence of maximum strength gain. The XRD analysis indicates that the main mineral phase transformed from nepheline ($NaAlSiO_4$) in alumosilicate phase is gehlenite ($Ca_2Al_2SiO_7$), according to Equation 1 (Liu et al., 2009).

$$2Na(AlSiO_4) + 2Ca(OH)2 \rightarrow Ca_2Al_2SiO_7 + Na_2SiO_3 + 2H_2O \quad (1)$$

These results are very promising and indicate the possibility of using this material in addition to Portland cement without significant loss of performance. However, this test in isolation is not indicative of material reactivity and can only be a consequence of improvements in physical appearance, with better packing of particles and filled voids due to high fineness of the material i.e. filler effect.

3.3. Verification of Pozzolanic Activity by Chemical Test Method.

European Standard NP EN 196-5 compares the quantity of calcium hydroxide present in the aqueous solution in contact with cement hydrated after 14 days with the amount of calcium hydroxide required to saturate the environment of equal alkalinity. The material is considered pozzolanic if the calcium hydroxide concentration in solution is lower than the saturation concentration. The results are shown in Figure 4.

The pozzolanic effect is denoted by a decrease of CaO concentration in the liquid phase, since calcium hydroxide generated by cement hydration is sequestered and combined by the pozzolan.

There is a decrease of CaO concentration in the solution when red mud is added and a simultaneous increase of $[OH^-]$ ion concentration. When red mud *in natura* and calcined at 450ºC are used the values are close to the saturation limit. However a clear pozzolanic action is observed for mixtures containing red mud calcined at 650ºC and 1000°C.

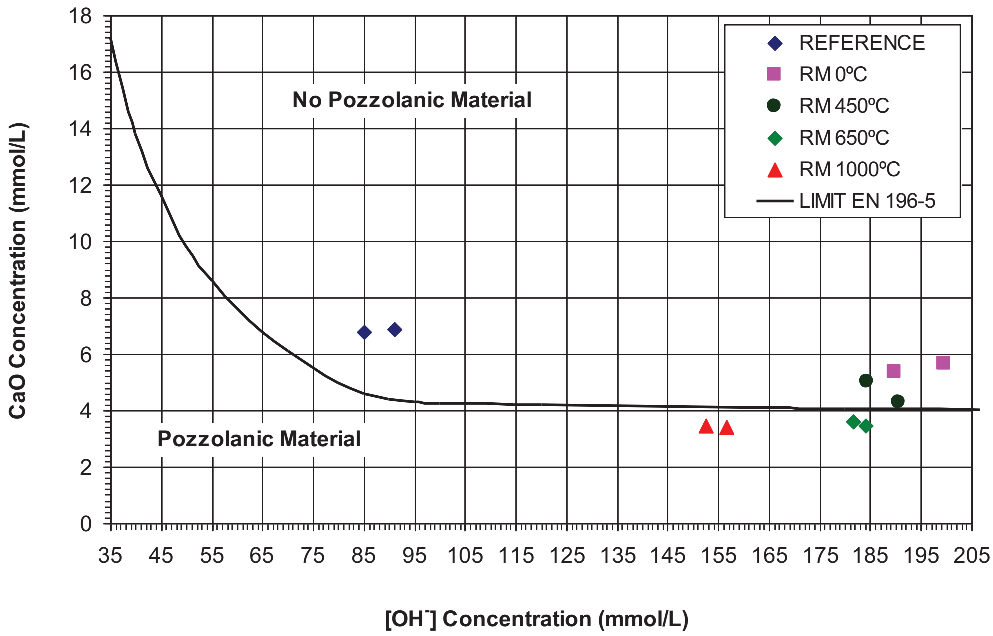

Figure 4. Diagram for determining the pozzolanicity according to NP EN 196-5 standard

4. Conclusions

Based on an analysis of the results, the following conclusions can be drawn:

- The red mud seems to be active specially if pre-calcined at temperatures between 650 and 1000°C;
- This thermal treatment changes the phase composition of the material, mainly by promoting the elimination of hydrated phases and improves its amorphous character;
- Physical parameters of red mud are affected by calcination process: the surface area and the unitary mass decrease and the specific gravity increases;
- The results of pozzolanic activity by chemical and physical methods were very satisfactory and indicate the feasibility of red mud use as a pozzolan, in addition to Portland cement;
- Satisfactory results are probably a consequence of the nepheline ($NaAlSiO_4$) presence after calcination and its transformation in alumosilicate phase gehlenite ($Ca_2Al_2SiO_7$).

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