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Incorporation of in Natura and Calcined Red Muds into Clay Ceramic

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Brazil is one of the world greatest aluminum producer and also comprises a large industrial sector dedicated to the production of alumina (Al_2O_3) by the traditional Bayer process. During this process an insoluble residue, known as red-mud, is generated and normally discarded. A possible use for the red mud is its incorporation into clay ceramics. Indeed, this has been a solution not only for the red mud but also for residues of different industrial segments. The common clay, like the kaolinite, versatility allows the incorporation of several types of residues. The red mud, in addition to compounds like silica and alumina that are compatible with clays, is also composed of iron, sodium, calcium and other elements that confer important characteristics to ceramic products. Thus, the present work investigated the incorporation of up 60 wt% of distinct red muds, one as processed, *in natura*, and the other calcined at 900 °C, into clay ceramics. Both red muds act as inert materials without improving the pure clay ceramic properties.

Keywords: *clay ceramic, calcined red mud, residue, technological properties*

1. Introduction

Brazil has the world third largest reverses of bauxite ores used in the production of alumina (Al_2O_3) and metallic aluminum (Al). Beginning with bauxite, the Bayer process produces Al_2O_3, which is the precursor to obtain the electrolitic Al as well as an insoluble residue known as red mud. In the Bayer process, developed in Germany by Karl Josef Bayer, more than 100 year ago, the bauxite is dissolved with NaOH and then filtered to separate the solid residue (red mud) from the liquid, which continues being processed until pure Al_2O_3 crystallization is attained[1].

The amount of generated red mud is directly conected to the quality of the bauxite ore deposit. However, there is no precise relationship between the red mud yield and the produced Al_2O_3. The literature indicates a ratio of about 1 to 2 ton of red mud for each ton of produced Al_2O_3. This would correspond in Brazil to millions ton per year of generated red mud, which corresponds to a significant environmental problem[2]. In past decades, the red mud was simply discarded in nearby rivers and ocean with the idea that dilution of a mud-like residue would not present a pollution problem. Today, specially designed containing ponds are required for red mud disposal. Even confined to a pond, the red mud can still represent an environmental problem in case of flood or underground penetration reaching the groundwater. In such case, toxic substances existing in the red mud, like NaOH and other chemicals from the Al_2O_3 processing operation[2], could eventually contaminate natural water bodies.

A relevant characteristic of the red mud is its high alkalinity with associated pH in the range of 10-13. This is due to the elevated content of of iron, sodium and calcium as well as other fluxing elements. Several works have investigated the incorporation of red mud into clay ceramics[2-7]. For the sintering (firing) process required to fabricate clay ceramics, fluxing raw materials that may exist in the red-mud add a market value to the products. Based on the aforementioned aspects, the objective of the present work was to investigate the effects of the incorporation of red mud on the technological properties of a kaolinitic clay ceramic. In order to evaluate the influence of previous thermal treatment, both as processed *in natura* and calcined at 900 °C red muds were individually incorporated. The aim of this investigation was to find sustainable destination to these red mud residues.

2. Material and Methods

The basic materials used in this work were a red mud residue, in two distinct conditions, and a common kaolinitic clay. The *in natura* red mud was collected in ia industry containing pond, Figure 1, after the processing line for aluminum production of the Brazilian firm CBA (Companhia Brasileira de Aluminio) located in the city of Sorocaba, state of São Paulo, Brazil. The yellow-type of kaolinitic

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clay, typically mined in the municipal area of Campos dos Goytacazes, north of the state of Rio de Janeiro, Brazil, was supplied by the Sardinha ceramic industry.

Both as-received precursor raw materials, were dried in a model EL-15 Odontobras stove at 110 °C until constant weight. The materials were then crushed and sieved to mesh 40 (0.42 mm).

A convenient amount of red mud residue was thermal treated by calcination in a model 7000 EDG electric furnace at 900 °C with a heating rate of 2 °C/min for 3 hours followed by cooling inside the turned-off furnace. This calcined mud is considered thermally inert for further firing temperatures used for clay ceramic production, normally from 600-900 °C, in the city of Campos dos Goytacazes[8].

The powders of *in natura* and calcined red mud residue were individually mixed in amounts of 0, 20, 40 and 60 wt% with clay powder. These mixed formulations were moistened with 8 wt% water and then sieved to mesh 10 (2 mm). Prismatic 114×25×11 mm samples of red mud incorporated clay were press-molded under 20 MPa in a Schwing equipament. For each formulation, 7 samples were prepared and dried at 110 °C in a stove for 24 hours. After this drying stage, all samples were fired in the same above mentioned EDG furnace at 900 °C with a heating rate of 2 °C/min for one hour. Cooling occurred inside the turned off furnace until room temperature.

After firing and possessing a consistent ceramic structure, consolidated by sintering with partial melting of the fluxing phases at 900 °C, the samples were subjected to standard tests to determine the ceramic technical properties. The water absorption was performed by the boiling method. In this method, the fired ceramic samples were first dried in a stove for 24 hours, cooled by natural convection, and weighed in a model JH 2102 Bioprecisa scale. The dried samples with initial mass (m_q) were then immersed in boiling water during 2 hours. This boiling procedure was followed by submerging in water at ambient temperature. After cooling, the samples had their surface residual water eliminated before a final weigh to obtain the water saturated mass (m_a). The water absorption (WA) was calculated by the following equation according to the Brazilian norm[9].

$$WA = \left(\frac{m_a - m_q}{m_q}\right) * 100 \quad (1)$$

The linear shrinkage (LS) of the fired ceramic sample was measured with a digital Mitutoyo caliper using the following equation.

$$LS = \left(\frac{C_s - C_q}{C_S}\right) * 100 \quad (2)$$

where C_s is the length of the dried sample before firing and C_q the length after firing.

The mechanical strength of each sample was evaluated according to the norm[10] by means of three points bending test performed in a model 5582 Instron machine, operating at room temperature with deformation speed of 0.5 mm/min. The rupture flexural stress (σ) was determined by the following equation:

$$\sigma = \frac{3PL}{2be^2} \quad (3)$$

where P is the load , L the distance between support, b the specimen width and e the sample thickness. The experimental results of the above-described technical properties were evaluated through the Weibull statistical method. A precision parameter R^2 was obtained for each set of measured values.

3. Results and Discussion

Figure 2 shows the variation of linear shrinkage with the amount of incorporated red mud, both *in natura* and calcined. In this figure, it is important to notice that the *in natura* red mud incorporation continuously increases the clay ceramic linear shrinkage. By contrast, the calcined red mud incorporation reveals only a slight increase in the ceramic linear shrinkage. This distinct behavior may be attributed to the relatively greater volume of organic matter still existing in the *in natura* red mud. In the ceramic firing stage, the organic matter is burnt and CO_2 is released, which causes porosity[11-13]. The contraction of this porosity at 900 °C effectively contributes to the almost exponential increase in linear shrinkage shown in Figure 2. On the other hand, the

Figure 1. Containing pond of red mud at CBA.

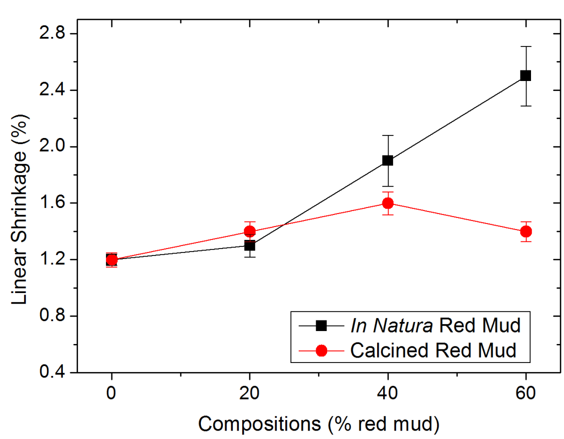

Figure 2. Linear shrinkage of clay ceramics as a function of the amount of incorporated red muds.

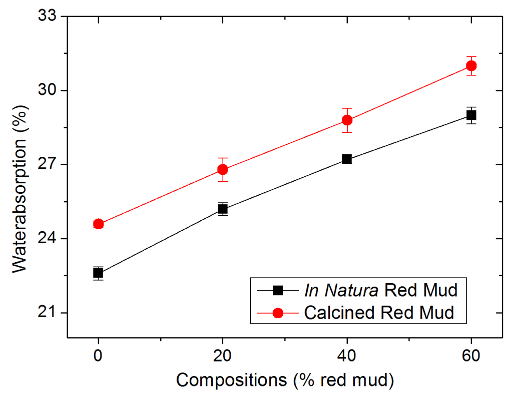

Figure 3. Water absorption of clay ceramics as a function of the amount of incorporated red muds.

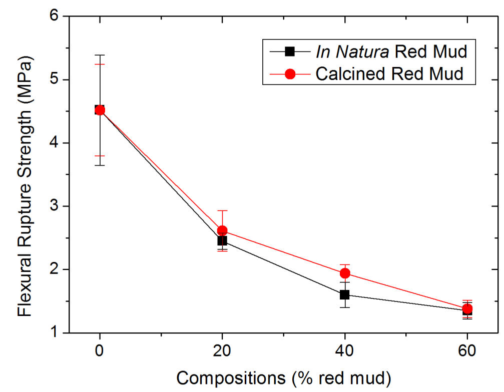

Figure 4. Flexural rupture strength of clay ceramics as a function of the amount of incorporated red muds.

calcined red mud no longer possess organic matter and thus caused only a small effect on the ceramic linear shrinkage.

Figure 3 presents the variation of the water absorption with the amount of incorporated red mud, both *in natura* and calcined. A sensible increase in water absorption is seen in this figure with slightly higher values for the calcined red mud incorporated ceramics. The water absorption is directly related to the existence of open porosity in the ceramic. The results in Figure 3 indicate that, even after firing at 900 °C, the incorporated red mud still has open pores. The fact that the calcined red mud has slightly higher water absorption, Figure 3, apparently reveals that its previous exposition to a 900 °C calcination treatment contributes to consolidate the open pores. On the other hand, the open porosity of the *in natura* red mud could undergo further reduction by interactions within the clay ceramic structure being fired at 900 °C. An alternative interpretation might be due a systematic error in the evaluation of the water absorption as a consequence of the difference in moisture adsorbed at the surface of both red muds. In practice, these almost similar results in Figure 3 could be considered technically negligible.

Figure 4 depicts the variation of the flexural strength of the fired ceramic with the amount of incorporated red mud, both *in natura* and calcined. In this figure the main result to be noted is the significant decrease in strength from 4.5 to 1.5 MPa for the 60 wt% incorporated red mud ceramic. This is certainly a consequence of the relatively higher porosity existing in both red muds as already discussed. Indeed, the results in Figures 2 and 3 confirm that due to more porosity in both red muds, the linear shrinkage and the water absorption are increased in comparison with the neat clay ceramic. The existence of pores is a well know mechanism for nucleation and propagation of cracks responsible for the rupture of brittle ceramics[14]. In Figure 4, within the error bars (standard deviation) there is no sensible difference in the strength between the incorporation of distinct red muds.

Finally, it is worth mentioning that, as an environmental solution, the incorporation of the red mud is a viable alternative. However, the effects caused in a clay ceramic will determined the possible practical use and the right amount of red mud in terms of the specification required by the norms for each class of ceramic product.

As for the calcination treatment of the red mud, only the linear shrinkage was improved above 20 wt% incorporation. Since no advantage was found for the water absorption, Figure 3, and mechanical strength, Figure 4, the use of calcined form of the red mud may not be recommended due to additional thermal treatment. As for the *in natura* red mud, in spite of the negative results on the technical properties, Figures 2 and 4, its incorporation into ceramic products would save clay, reduce cost and constitute an environmentally correct solution for this Al_2O_3 processing waste.

4. Conclusions

- The incorporation of red mud residue, generated by the Bayer process in the Al_2O_3 / aluminum industries, into common clay ceramic for civil construction products caused significant changes is the linear shrinkage, water absorption and flexural strength.
- In principle these changes impair the ceramic properties. However, as an environmentally correct solution they could be justified for incorporations in amounts that still attend the technical norm required for a given clay ceramic product.
- The primary calcination of the red mud, at the same 900 °C temperature of the final ceramic firing, provided a relative improvement in the linear shrinkage above 20 wt% incorporation. However, the additional costs of this treatment might not compensate the previous thermal treatment of the residue.
- The as-processed, *in natura*, red mud could be of practical interest despite negative effects on the clay ceramic properties. Its incorporation saves non-renewable clay mineral and reduces the cost of the ceramic product. More important, the incorporation is an environmentally correct solution for the red mud final destination.

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