MECHANICAL BEHAVIOR OF A CLAY MATERIAL WITH GRANITE REJECT AND SINTERED BY NATURAL GAS

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Abstract. The use of industrial waste as additives in the brick and tile industries is becoming common practice. The heterogeneity of traditional clay-based materials accommodates a variety of waste products (e.g. paper and textile industries, urban waste), without to decrease the final product properties. The sintering of red ceramic in the ceramic industries has been causing a serious ambiental problem, due the use of wood as the mainly solid fuel. The State of Rio Grande do Norte has a great production of natural gas that can be used in the industries as principal fuel, preserving the ambient. This work has the objective to study the sintering and mechanical behavior of a clay material with granite reject and sintered by natural gas. The sintered materials were characterized by physical and mechanical properties. Water absorption and porosity values were calculated by Archimedes method in water. Flexural strength tests were carried out in three point bending. The results have showed that the addition of granite reject has a positive effect on the properties of the sintered materials and that the use of natural gas is a good alternative to wood material for the ceramic industries.

Keywords: clay material, granite reject, natural gas mechanical properties

1. INTRODUCTION

Actually, the industries are looking for alternative, new raw materials and have improved their manufactured processes in order to decrease the amount of waste and the ambiental problem There are various studies published in the literature that show the good effect caused by the incorporation of other industries rejects in the clay products (Anderson and Jackson, 1983; Perez et al.,1996; Domingues and Ulmann,1996; Acchar et al.,2005). The research works have shown that some wastes are similar in composition to the normally raw materials used in the ceramic industry, and often contain materials that are helpful to the sintering process of ceramics (Dondi et al., 1997; Silva et al.,1998; Caligaris et al.,2000; Hernadez and Rincón,2001; Souza and Mansur,2004; Segadaes et al., 2005; Monteiro et al.,2004). Thus, the use of industrial wastes to alternative ceramic raw materials is becoming common practice. The waste materials can be classified in three categories (Dondi et al., 1997) a) with high contents of organic or carbon-rich substances (fuel wastes), hence with high calorific added value), b) which improve the ceramics sinterability (fluxing wastes), and c) those likely to introduce changes in the green body preparation (plasticity-controlling wastes).

Marble and granite cutting rejects are inert, but are becoming a worrying factor for industry in Rio Grande do Norte, Brazil. An increasing amount of rejected mud is continuously discharged into rivers and lagoons, causing a serious environmental degradation. Granite and marble has, as major constituents, feldspar, quartz and mica, and calcite, respectively. Both rejects can be classified as fluxes, as they have the potential to acts as glassy phase formers during the sintering process, improving the quality of the clay products. The potential use of the incorporation of granite reject was investigated previously (Dondi et al., 1997; Acchar et al., 2005; Segadaes et al., 2005), and it was observed that the final properties of the fired products can be improved by the incorporation of granite sludge. The use of GLP or natural gas, as substitute to the wood, can change significantly the properties of the fired clay bodies. The state of Rio Grande do Norte, Brazil, exports a large amount of ornamental rocks and has a plentiful reserve of natural gas.

The objective of this work is to investigate the effect of an addition of granite reject in the production of red clay ceramics by a natural gas sintering atmosphere.

2. EXPERIMENTAL PROCEDURE

A commercial clay and a granite cutting reject were collected directly at industrial sites in the state of Rio Grande do Norte, Brazil, and used in this work. Specimens were obtained by extrusion process of clay and a mixture of clay with 30 wt. % granite reject. The samples were sintered in natural gas, for 1 hour, at 850, 950 and 1050 °C. The granite reject was not beneficiated in any way (used as collected from the industry). The chemical composition of the reject was obtained by X-ray fluorescence (Shimadzu EDX-700). The apparent density and porosity of the sintered samples were determined using the Archimedes water displacement method. Crystalline phases were identified by X-ray diffraction (Shimadzu XRD-600, 40 kW and 40 mA, in the range of 10 to 70 °). The mechanical strength of the sintered samples was determined as the average of four measurements for each composition, using a universal testing machine (Shimadzu Autograph, 250 kN) in a three-point bending geometry at a constant cross-head speed of 0.5 mm.min⁻¹. The microstructure of sintered samples was studied on fracture and polished surfaces, by Scanning Electron Microscopy (Hitachi S-4100, at 25 kV, after carbon coating) and EDS.

3. RESULTS AND DISCUSSION

"Table 1" gives the chemical composition of the clay and the granite reject used in this work. The clay material shows the expected typical composition: rich in silica and alumina with minor content of Ng, Ti ,Ca ,Na and K oxides. The iron content shows a significant amount (12.07 wt. %), which will cause a dark colour of the fired samples. The loss on ignition (8.48) is within the usual range for red clay material, and is most likely associated with volatile component, organic matter burn-off and/or carbonate decomposition. The granite reject consisted basically of SiO₂, Al₂O₃ and CaO, (8.71 wt. %) with minor contents of MgO, K₂O, Na₂O, Fe₂O₃ and TiO₂.

Table 1. Chemical compositions of the used raw materials, as determined by XRF (wt. %).

	Al_2O_3	SiO ₂	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	TiO ₂	MnO	Lol
Clay	27.02	40.61	12.07	1.42	0.80	4.40	2.88	1.41	0.18	8.48
Granite reject	22.38	44.21	9.86	8.71	2.71	4.13	3.51	2.33	0.15	0.43

"Fig. 1" shows the X-ray diffraction patterns of the clay with 30 wt. % granite reject. It can seen that the sintered material consisted basically on quartz and minor amounts of hematite and anorthite, This crystalline phase analyze is in agreement with the chemical composition presented in "Table 1".

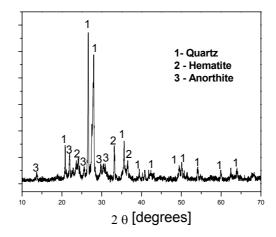


Figure 1. X-ray diffraction patterns of the clay with 30 wt. % granite reject.

"Fig. 2" shows the dependence of the porosity and water absorption values on sintering temperature and the presence of granite reject. The results show an increase of the porosity values by increasing the sintering temperature that can be associated with the mass loss, caused by the decomposition of the carbonate and volatilization of organic elements (8 LoL, "Tab. 1"). The presence of the granite reject increases the porosity values of the sintered material. This behavior can be attributed to higher degree of calcite decomposition that takes place with the addition of the granite reject. The reject has a significant higher CaO content as compared to the clay material ("Tab. 1"). The water absorption follows the same behavior, an increasing of the values by higher sintering temperature and by the presence of the granite reject.

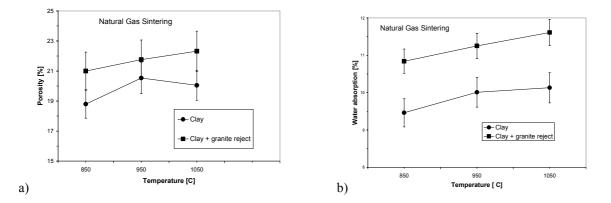


Figure 2. Porosity (a) and water absorption (b) values as a function of the sintering temperature.

"Fig. 3" shows the variation of the flexural strength as a function of the sintering temperature. The results shows clearly that the addition of granite reject decreases the mechanical resistance of the clay material, regardless the sintering temperature, what is in agreement with the values observed for porosity and water absorption showed in "Fig. 2". The effect caused by the incorporation of granite reject observed in this work are contrary to the published in the literature to clay with granite reject uniaxially pressed and sintered in normal atmosphere (Acchar et al.,2005; Segadaes et al., 2005). This divergence of the effect of the incorporation of granite in the clay material observed in this work can be explained basically by two factors: a) Higher degree of carbonate decomposition of the granite reject (high CaO content, "Tab. 1") and b) Gas evolution during the early sintering stages caused by the natural gas sintering, restraining the densification of the material.

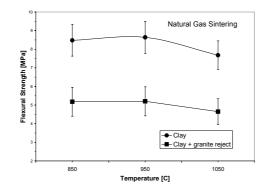


Figure 3. Flexural strength values as a function of the sintering temperature.

"Figs. 4 and 5" illustrate the fracture surface of sintered samples, as observed by SEM. The sintered clay material display large quartz grain (strong peak in the XRD in "Fig. 1") and a significant amount of porosity, even in the highest firing temperature. The clay with granite reject shows a similar microstructure, but also clear signs of vitrification, due the presence of a liquid phase during the sintering process.



Figure 4. SEM micrograph of clay material sintered at: a) 850 °C , b) 950 °C and b) 1050 °C.

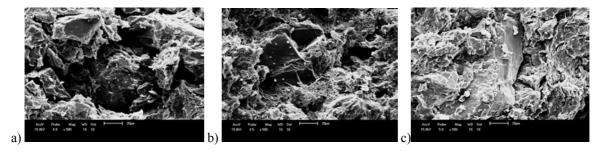


Figure 5. SEM micrograph of clay with granite reject sintered at: a) 850 °C , b) 950 °C and b) 1050 °C.

4. CONCLUSIONS

The results obtained in this work have showed that the addition of granite reject has a positive effect on the properties of the sintered materials and that the use of natural gas is a good alternative to wood material for the ceramic industries.

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