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USE OF FINE STEEL SLUDGE WASTE AS A COMPONENT OF CLAYEY CERAMIC

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Abstract: The present paper has for objective to characterize and to evaluate the effect of fine steel sludge waste incorporation on the properties of a clayey body used to the fabrication of bricks and roofing tiles. Compositions were prepared with additions of waste of 0, 5 and 10 wt.% in a kaolinitic clay from the county of Campos dos Goytacazes, State of Rio de Janeiro, Brazil. To determine physical and mechanical properties such as linear shrinkage, water absorption and flexural strength, specimens were prepared by uniaxial pressure at 20 MPa and then fired in a laboratory furnace at 700ºC, 900ºC and 1100ºC. Environmental aspects of the incorporated ceramic were evaluated by solution test. The results showed that the incorporation up to 10 wt. % of fine steel sludge does not change the ceramic properties, specially, at low temperatures. Hence, the recycling of steel sludge into red ceramic fabrication can be considered as an environmentally correct solution for the final disposal of this type of waste.

Keywords: *Clayey Ceramic, Fine Steel Sludge, Recycling, Waste.*

INTRODUCTION

The incorporation into common red ceramics is nowadays a solution for the disposal of a wide range of solid wastes. The natural variability of the characteristics of clays [1], the use of relatively simple processing techniques, as well as the low technical performance required for the products, permit the presence of high amounts of impurities. The firing stage, fundamental to particle consolidation in red ceramics, also allows for: a) volatilization of dangerous compounds, b) changing in the chemical characteristics of materials and c) inertization of potentially toxic and dangerous compounds through its fixation in the vitreous phase. In addition, some types of wastes can also contribute to facilitate the red ceramic fabrication as well as to enhance the technical performance of the ceramic [2].

An integrated steel plant produces a wide variety of solid wastes, liquid effluents and gas emissions in its various processing stages [3,4]. Refining steel operations, such as the LD oxygen blow conversion of pig iron, contributes with 27 wt.% of the solid waste generated in the plant [5]. Among the solid wastes, about 650kg are generated per ton of steel produced. These wastes include slags, powders, sludges and scales. During the conversion from pig iron to steel, iron particles are released and ejected from the metallic bath at high temperatures as strong environment oxidants. These particles are collected at dust removal systems, generating the steel powders and sludges, coming from the LD converter. Although around 83 wt.% of this waste is recycled [5] and return to the process, the currently applied dust removal systems are no longer recommended due to the fine particles released into the atmosphere.

Therefore, the present paper has as its objective to characterize a fine steel sludge, from a integrated steel plant, and to evaluate the effect of its incorporation on the properties of a clayey ceramic at 700ºC, 900ºC and 1100ºC.

MATERIALS AND METHODS

The raw materials used in this work were: (a) a fine steel sludge waste obtained from the LD steel plant of a national integrated steel making plant; (b) a kaolinitic clayey body used for fabrication of bricks and roofing tiles in the country of Campos dos Goytacazes, State of Rio de Janeiro, Brazil.

The waste was initially characterized in terms of its mineralogical, chemical and physical composition as well as morphological aspects and firing behavior by thermo analysis. The qualitative mineralogical phase identification was performed by X-ray diffraction (XRD) in powder samples using a Seifert, model URD 65, diffractometer operating with Cu-K_{α} radiation and a scanning angle 2θ from 10 to 50º. The chemical composition was determined by X-ray fluorescence (XRF) in a Philips PW 2400 equipment. The particle size distribution was determined by both, sieving and sedimentation methods, following the norm [6]. The morphology of the waste powder was evaluated by scanning electron microscopy (SEM) in a Zeiss model DSM 962 equipment. The firing behavior of the waste was evaluated by thermogravimetric (TGA) and thermodifferential (DTA) analyses of a 25 mg powder sample, screened at 200 mesh (75 μm). These analyses were simultaneously conducted in a TA model SDT 2960 instrument operating under a flow of argon (100 $mL.min^{-1}$) and heating rate of $10^oC/min$ until the maximum temperature of 1300^oC.

Incorporations of 0, 5 and 10 wt. % of fine steel sludge into clayey body were performed in a pan mill. Test specimens (114.5x2.54x10mm) were obtained by uniaxial press molding at 20 MPa, dried at 110°C for 24h and then fired at 700°C, 900°C and 1100°C in a laboratory furnace. The heating rate was 3°C/minute with one hour soaking at the maximum temperature. Cooling occurred by natural convection inside the furnace after it was turned off. These specimens were tested for water absorption, linear shrinkage and three points bending flexural strength. The water absorption was determined according to standard procedure [7]. The linear shrinkage was obtained by measuring the length of the samples, before and after the firing stage, using a Mitutoyo caliper with ± 0.01 mm precision. The three point flexural rupture strength was determined in an Instron 5582 universal testing machine, using a cross head speed of 0.5 mm/min.

Solution test was performed in a selected incorporated following the Brazilian standard NBR 10006 [8]. The potentially toxic metals (Al, Ba, Cd, Cr, Cu, Fe, Mn, Na, Pb and Zn) determination in the solution extracts was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES).

RESULTS AND DISCUSSION

Table 1 shows the chemical composition of the raw materials, determined by X-ray fluorescence in a Philips PW 2400 equipment. The chemical composition of the clayey body indicates, as expected, a predominance of silica and alumina. This composition is typical of a kaolinite-based material with high alumina, Al_2O_3, and low amounts of alkaline oxides, such as K_2O and Na_2O. The percentage of 6.0 wt.% of Fe_2O_3 is responsible for the natural red color after firing. The high percentage of LoI is basically associated to constitution water of the kaolinite. The fine steel sludge is basically composed of high amounts, 73,95 wt.%, of iron compounds. Within this percentage, 60.30% correspond to oxides, such as wustite, FeO, and magnetite, Fe_3O_4. The balance is associated with metallic iron. The second major chemical constituent of the waste is the CaO, mainly in the form of calcite, $CaCO_3$, which is introduced in the LD converter operation to increase the slag basicity as well as to facilitate the sulfur and phosphorus removal from liquid metal.

TABLE 1 - CHEMICAL COMPOSITION OF THE RAW MATERIALS (WT. %).

Sludge waste	**SiO_2**	**Al_2O_3**	**Total Fe**	**TiO_2**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**ZnO**	**LoI**
	1.86	0.12	73.95	0.90	16.48	3.42	0.16	0.33	2.78	-
Clayey body	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**K_2O**	**P_2O_5**	**ZrO_2**	**LoI**
	50.20	27.88	6.00	1.06	0.24	0.74	1.24	0.18	0.03	12.43

Figure 1 shows the XRD pattern of the waste. The major crystalline phases identified are: free iron – Fe, wustite – FeO, magnetite – Fe_3O_4 and calcite – $CaCO_3$. The iron and iron oxides particles result from the untied and ejection of particles from the liquid metal during the oxygen injection in the LD steel conversor. The calcite is used to increase the basicity of the slag as well as to facilitate the removal of sulphur and phosphorus from the liquid metal.

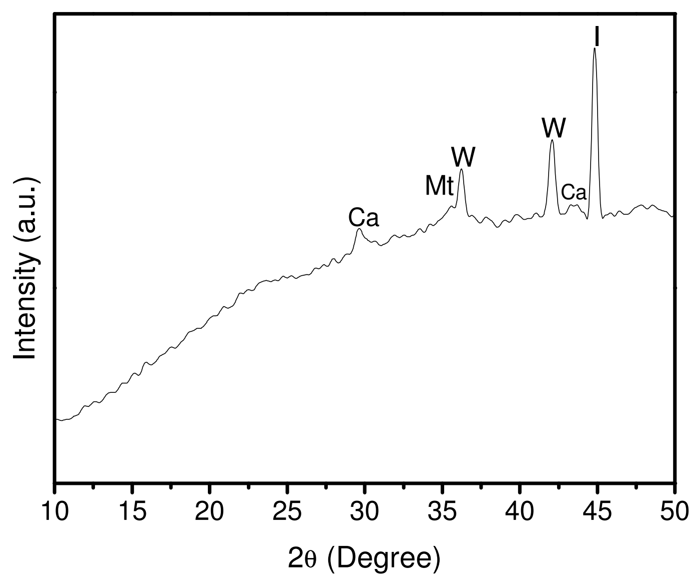

FIGURE 1. XRD PATTERN OF THE WASTE. **CA** = CALCITE; **I** = IRON; **MT** = MAGNETITE; **W** = WUSTITE.

According to Fig. 2, the waste shows a distribution of fine particles with equivalent spherical diameter smaller than 800 μm as well as a mean particle size of 35.6 μm. This characteristic of the waste is appropriate for red ceramic processing, that normally uses materials with particle size lower than 2000 μm. The real density of the waste, measured by picnometry, was found to be 4.96.cm^{-3}.

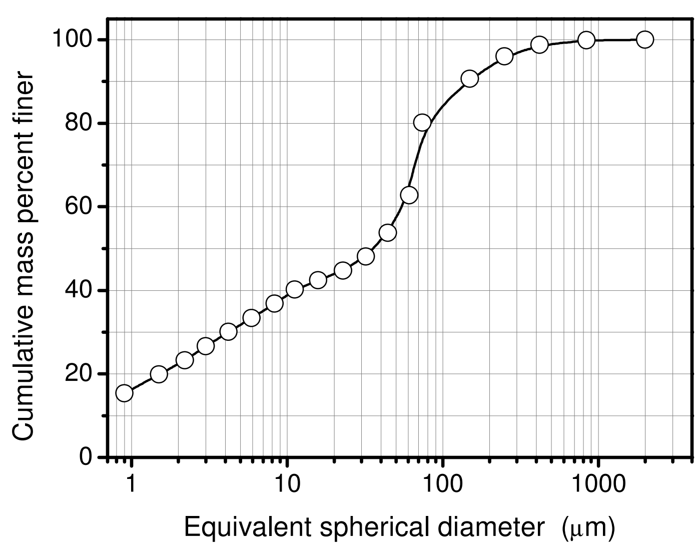

FIGURE 2. PARTICLE SIZE DISTRIBUTION OF THE WASTE.

Figure 3 shows different aspects of the waste particle morphology. In this figure it is observed not only fine individual particles but also large porous agglomerates. with rounded morphology. The porous agglomerates are probably formed by iron oxides. On the other hand, the finer particles are metallic iron.

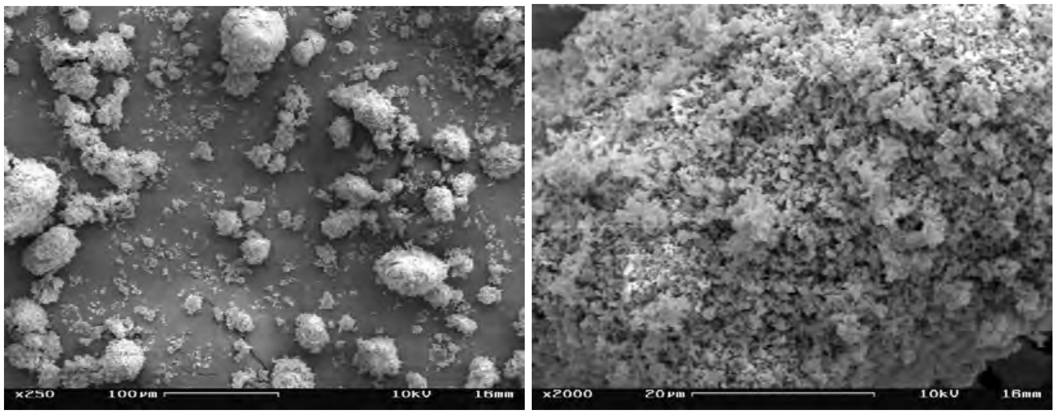

FIGURE 3. SEM PHOTOMICROGRAHS OF THE WASTE POWDER.

The thermal behavior of the waste was analyzed by thermogravimetry (TGA), differential thermogravimetry (DTG) and thermodifferential analysis (DTA) as shown in Figure 4. The fundamental aspects of the thermal behavior of the waste is an exothermic peak at 40.3ºC, which is associated with a weight gain of 8.6%. This is probably due to the oxidation of iron oxides such as magnetite and wustite. At 691^{o}C an endothermic peak occur with a weight loss of 4.2% that can be associated with calcium carbonate, calcite, decomposition. Finally, at 875.3^{o}C an exothermic peak revels another weight gain of 4.2%. The thermal behavior of the waste indicates a relative stability with practically no weight loss, which is another favourable condition to red ceramic processing.

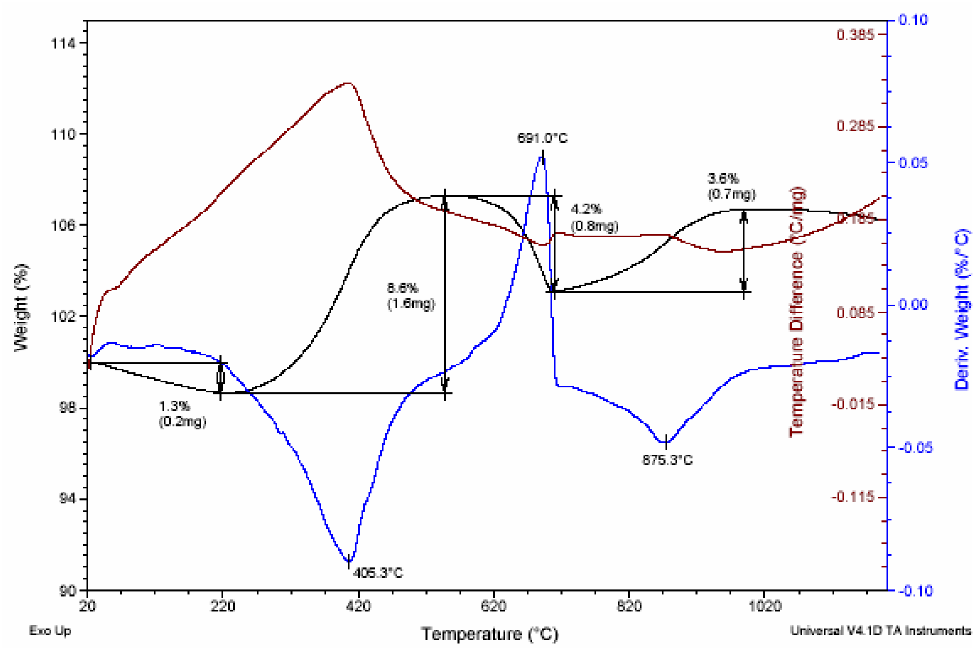

FIGURE 4. DTA/TGA/DTG CURVES OF THE WASTE.

Figure 5 presents the linear shrinkage of the clayey body, fired at 700, 900 and 1100^{o}C, as a function of the amount of steel sludge incorporated. As can be seen, the linear shrinkage of all compositions increases with the firing temperature. This is more significant at 1100ºC, due to the more effective sintering process. At 700ºC and 900ºC no significant changes occur in the linear shrinkage with the steel sludge incorporation. On the other hand, at 1100ºC, one should notice that the linear shrinkage decreases with additions of steel sludge. This behavior can be attributed to the inert characteristic of the waste, which does not contribute to the sintering mechanisms, mainly by a viscous type flux vitrification.

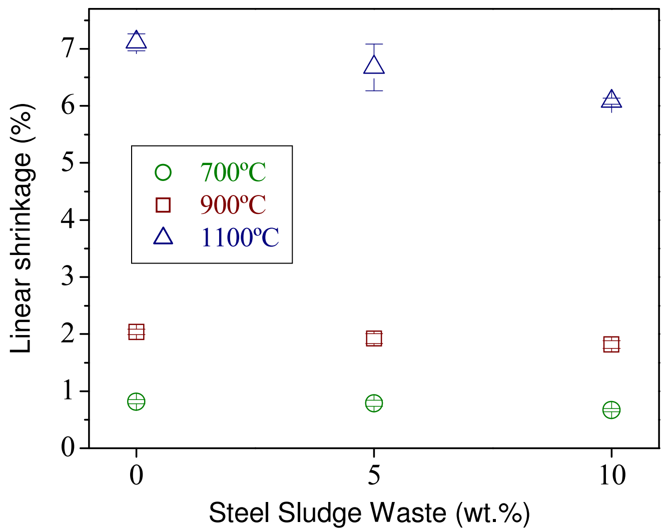

FIGURE 5. LINEAR SHRINKAGE OF THE CLAYEY BODY AS A FUNCTION OF THE AMOUNT OF STEEL SLUDGE INCORPORATED.

Figure 6 presents the water absorption of the clayey body, fired at 700, 900 and 1100°C, as a function of the amount of steel sludge incorporated. According to this figure, the water absorption does not change at 700 and 900°C for all compositions. By contrast, at 1100°C the water absorption abruptly decreases. At lower temperatures sintering mechanisms, based on liquid phase formation and solid-state diffusion, occur gradually and make no significant changes on the open porosity of the ceramics. Therefore, at 1100°C, the clayey ceramics from Campos dos Goytacazes display a sharp decrease in the porosity as a consequence of the vitrification process [9]. A small increase on this property with addition of incorporated waste is also observed in the clayey body fired at 1100ºC. This behavior can be attributed to the inert characteristic of the waste. It is expected that the steel sludge will be mainly constituted of hematite, Fe_2O_3, in the range of 700 to 1100°C. The hematite is considered as a refractory material that difficult the sintering mechanisms [10].

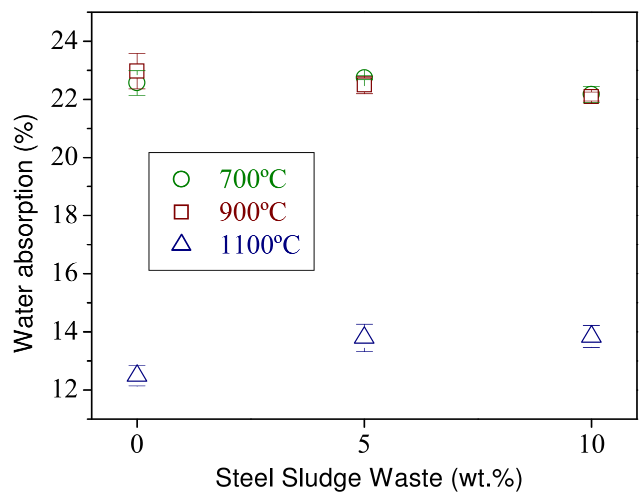

FIGURE 6. WATER ABSORPTION OF THE CLAYEY BODY AS A FUNCTION OF THE AMOUNT OF STEEL SLUDGE INCORPORATED.

Figure 7 presents the variation of the flexural rupture strength of the compositions as a function of the amount of waste. In this figure, it is observed an increase in the mechanical strength of the compositions with the firing temperature. This is due to the sintering processes that promote microstructural consolidation between the particles. One should notice that the additions of 5 and 10 wt.% of steel sludge waste do not statistically change this property at all investigated temperatures. Since the mechanical strength is strongly dependent on the microstructural characteristics of the fired ceramic, mainly the intrinsic flaw size, the obtained results indicate that additions up to 10 wt.% do not introduce pore or cracks into the clayey microstructure.

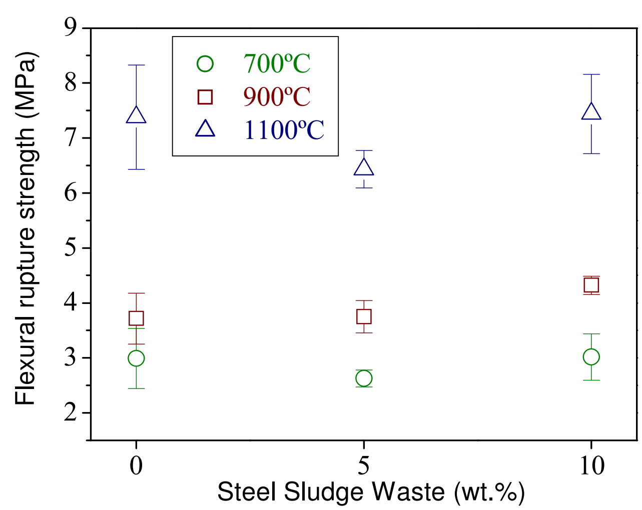

FIGURE 7. FLEXURAL RUPTURE STRENGTH OF THE CLAYEY BODY AS A FUNCTION OF THE AMOUNT OF STEEL SLUDGE INCORPORATED.

The solution results associated with potentially toxic metals in the extracts of the clayey ceramic incorporated with 5 wt.% of waste fired at 900^{o}C are shown in Table 2. According to these results, the ceramics fulfil the NBR 10004 standard [11] requirements for most elements. For all analysed samples, only the values for Al content are above that recommended by norm [11]. Here, it must be emphasized that the pure clay, which is a natural materials in equilibrium with the earth environment, has an Al content above the norm.

TABLE 2 - POTENTIALLY TOXIC METALS IN THE SOLUTION EXTRACTS OF THE CLAYEY BODY WITH 5 WT.% OF INCORPORATED WASTE.

Element	Solution extract (mg/L)	Limits (mg/L)
Al	1.8	0.2
Ba	0.06	0.7
Cd	< 0.003	0.005
Cr (total)	< 0.02	0.05
Cu	0.004	2.0
Fe	0.02	0.3
Mn	0.02	0.1
Na	10	200
Pb	< 0.06	0.1
Zn	0.02	5.0

CONCLUSIONS

In this work, the results of characterization of a fine steel sludge waste, generated during the steel refining LD process, and its incorporation into clayey body used for red ceramic fabrication, showed that the waste is predominantly composed by Fe metalic, Fe oxides – magnetite and wustite, and calcium carbonate - calcite. This waste shows a fine particle size, that is appropriate for incorporation into red ceramics. The evaluated clayey ceramic properties, such as linear shrinkage, water absorption and flexural rupture strength, practically were not changed with waste additions up to 10 wt.%. The inertization of the potentially toxic metals in the ceramic with waste addition was satisfactory, with the exception of Al, according to solution test. The proper industrial clay ceramic body is rich in Al, that is presents in the clay mineral structure (kaolinite), aluminossilicate (mica muscovite) and hidroxide (gibbsite). This indicated that the ash addition did not cause environmental problems. The excessive Al observed in the solution test, which is attributed to the clay, is apparently a natural environmental situation.

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