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# Structural ceramics made with clay and steel dust pollutants

A.T. Machado a,b, F.R. Valenzuela-Diaz b, C.A.C. de Souza a, L.R.P. de Andrade Lima a,\*

- <sup>a</sup> Department of Materials Science and Technology, Federal University of Bahia, Brazil
- <sup>b</sup> Department of Metallurgical and Materials Engineering, São Paulo University, Brazil

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#### ABSTRACT

Electric arc furnace steel dust is a by-product of the steelmaking process and contains high amounts of the iron and zinc and significant amounts of lead, chromium, and cadmium. Metal recycling however, is not always economically feasible, especially due to the complex mineralogical composition of this material. In this study an application of this material is presented. Ceramics were produced with clay and variable amounts of steel dust. The bulk material was fired between 800 and 1100 °C. The influence of the composition and the processing temperature on the mechanical strength, linear shrinkage, water absorption, apparent density and bending strength and metal leaching of the ceramic samples was investigated. A blend of clay with up to 20% dust yielded ceramics with limited metal contamination risk and may thus be used for structural ceramics production.

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#### 1. Introduction

Electric-arc furnace dust (EAFD) is one of the major by-products generated by the steel making industry, about 15–20 kg/ton of steel (Hagni et al., 1991). EAFD is a complex, fine-grained, high-density material, containing high amounts of zinc and iron and significant amounts of calcium, manganese, magnesium, lead and chromium depending on the steelmaking process. A small amount of EAFD is recycled for zinc recovery and a large amount is disposed in landfills despite the fact that EAFD cannot be disposed in regular landfills due to the leaching of potentially toxic elements that contaminate the environment (Domínguez and Ullmann, 1996; Hagni et al., 1991).

The chemical, physical and mineralogical characterization of the dust was reported in several studies (Dutra et al., 2006; Hagni et al., 1991; Pelino et al., 2002). In a typical EAFD, the particle size ranges from 0.1 to 100  $\mu$ m with a d<sub>50</sub> of about 0.5  $\mu$ m (Dutra et al., 2006). The major element contents of a typical EAFD are Fe: 30–42%, Zn: 5–13%, Ca: 2–10%, Cr: 1–11%, Mn: 1.7–1.9%, Si: 1.3–2.5%, Na: 1–2.7%, and Pb: 1.0–1.5%, depending on the raw materials (Dutra et al., 2006; Hagni et al., 1991; Pelino et al., 2002).

The recycling of zinc and iron of EAFD was addressed in several studies (Dutra et al., 2006; Nyirenda, 1991). The use of pyrometal-lurgical and hydrometallurgical processes for metal recovery depends on the physical and chemical characteristics of the EAFD and the production process. When the zinc content of EAFD is about 15–20% and the amount of EAFD processed is about 50,000 tons/year, pyrometallurgical processes may be used to recycle the metals

E-mail address: lelo@ufba.br (L.R.P. de Andrade Lima).

profitably (Dutra et al., 2006). However, finding a cost-effective and environmental-friendly process to recycle the metal content of the EADF is still a major challenge, and for this reason most recycling processes have never exceeded the pilot scale (Dutra et al., 2006).

The stabilization of the metals in the EAFD is the common option to treat this industrial residue (Domínguez and Ullmann, 1996; Mikhail et al., 1996; Pelino et al., 2002). In this study, EAFD was stabilized by mixing it with clay for the production of ceramics.

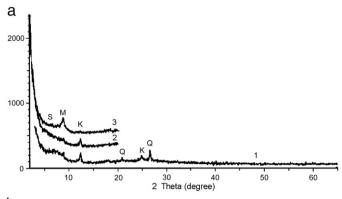
## 2. Materials and methods

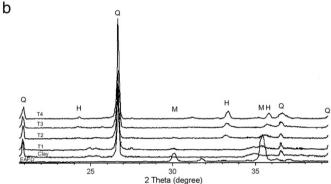
Samples of EAFD were collected at a carbon steel company in Bahia, Brazil (Usina Siderurgica da Bahia, USIBA) which processes iron ores from mines located in Minas Gerais State (Brazil) and scrap iron. About 20 kg of the EAFD were collected. The clay was collected from a factory of roofing tiles and hollow bricks (Cerâmica do Nordeste Ltda.) whose raw material comes from a clay mine located in the region of Feira de Santana, Bahia, Brazil.

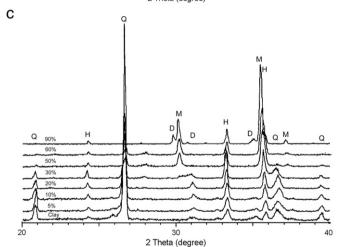
The clay was blended with 5, 10, 20, 30, 50, 60, and 90% of EAFD. Samples were prepared with a total mass of 12 g of the blend in a prismatic mold of  $6.0\times2.0\times0.5$  cm. The powder was compressed in the mold at 204 kPa using a Forney Model QC-200 DR compression tester. A total of 35 samples were produced for each EAFD content. Most samples were dried at room temperature for five days. Five samples were dried at 110 °C. Thirty dried samples were fired in an electric furnace at 800, 950 and 1100 °C (ten samples at each temperature). In this case, the heating rate was 10 °C/min and the firing time was two hours. The cooling rate was not automatically controlled.

The raw materials and the ceramic samples were analyzed at the University of São Paulo (Brazil). Scanning electronic microscopy

<sup>\*</sup> Corresponding author at: Rua Aristides Novis, 2, Salvador, Bahia, Brazil, 40210-630. Tel.: +55 71 3283 9514; fax: +55 71 3283 9837.







**Fig. 1.** a) XRD patterns of the raw clay (1) and the clay treated with ethylene glycol (2) and fired at  $500\,^{\circ}\text{C}$  for  $4\,\text{h}$  (3). Q quartz, K kaolinite, M muscovite, S smectite. b) XRD patterns of the raw clay (T1), dried at  $110\,^{\circ}\text{C}$  (T2), and fired at  $800\,^{\circ}\text{C}$  (T3),  $950\,^{\circ}\text{C}$  (T4), and  $1100\,^{\circ}\text{C}$  (T5). c) XRD patterns of EAFD, raw clay, clay dried at  $110\,^{\circ}\text{C}$  (T1), and the  $5\%\,^{\circ}\text{EAFD}$  blend fired at  $800\,^{\circ}\text{C}$  (T2),  $950\,^{\circ}\text{C}$  (T4), and  $1100\,^{\circ}\text{C}$  (T4). Q quartz, H hematite, M magnetite, D diopside.

(SEM) images were taken with the Philips XL–30 with an EDAX. X-ray diffraction patterns were obtained with CuK $\alpha$  radiation using the Philips X'Pert MPD and the software EVA. The chemical analysis of the clay and the EAFD were performed with the ICP Spectro Co Ciros CCD and X-ray fluorescence Philips PW 2404.

Five ceramic samples of each firing temperature were used to measure linear shrinkages, water absorption, apparent porosity, and apparent density. The other five samples were used to measure the bending strengths. These tests were performed according to the Brazilian Standards (NBR, 2005).

The Brazilian leaching test was established by NBR (1987a,b) and uses 50 g of the solid waste, finer than 9.5 mm, and 1000 mL of an extraction solution composed of 5.7 mL of glacial acetic acid, 64.3 mL of a 1 M NaOH, and 930 mL of ultra pure water (conductivity < 1.0 mS/

cm) in a closed polyethylene bottle. After agitation at 30 rpm for  $18\pm2~h$  at room temperature the sample was filtered with a  $0.45~\mu m$  membrane filter, and the solution was analyzed by atomic absorption spectrometry (AAS) or inductively coupled plasma optical emission spectroscopy (ICP). The Brazilian solubilization test was established by NBR (1987a,c) and uses 250 g of the solid waste and 1000 mL of ultra pure water in a closed polyethylene bottle. After agitation at 30 rpm for 5 min at room temperature, the sample was left for seven days. The sample was then filtered with a 0.45  $\mu m$  membrane filter, and the solution was analyzed by AAS or ICP. The leaching and the stabilization tests were performed with the raw materials (clay and EAFD) and the ceramic samples.

#### 3. Results and discussion

#### 3.1. Characterization

The chemical analysis showed a large amount of Si, Al and Fe in the clay (SiO $_2$  69.08%, Al $_2$ O $_3$  14.82%, Fe $_2$ O $_3$  5.19%, TiO $_2$  1.47%, K $_2$ O 1.37%, MgO 1.13%, CaO 0.43%, P $_2$ O $_5$  0.07%, MnO 0.07%, and Na $_2$ O 0.05%); the total amount of these oxides was 93.4%. EAFD contains large amounts of Fe and Zn (Fe $_2$ O $_3$  60.72%, ZnO 11.59%, SiO $_2$  4.31%, CaO 3.68%, Al $_2$ O 3.08%, MgO 2.03%, K $_2$ O 1.91%, MnO 1.35%, Na $_2$ O 1.30%, PbO 1.23%, P $_2$ O 5.71%, and TiO $_2$  0.06%); total of 91.0%. Among the major and trace elements of the EAFD, the Pb and Cd content (194 mg/kg) potential toxicity.

The mineralogical analysis of the clay using X-ray diffraction for the raw clay and the clay reacted with ethylene glycol and heated at 500 °C for four hours indicated the presence of large amount of quartz, some smectite and minor amounts of kaolinite (Fig. 1a).

The XRD patterns of the clay dried at 110 °C, and fired at 800, 950, and 1100 °C (Fig. 1b) and the XRD patterns of the clay fired at 1100 °C with varying amounts of EAFD (Fig. 1c) indicate that EAFD addition increased the peak intensity of the reflections of hematite and magnetite, and the formation of diopside (CaMgSi<sub>2</sub>O<sub>6</sub>), especially at large EAFD contents, due to the presence of calcium and magnesium in EAFD.

## 3.2. Water absorption and apparent porosity

The amount of water absorbed decreased with increasing firing temperatures but was not strongly affected by the EAFD content (Table 1). In addition, the porosity of the fired material decreased with increasing firing temperature and EAFD content (Table 1) in agreement with other studies (Melo et al., 2002; Moravia et al., 2006).

The SEM image of the samples with 90% EADF fired at 800 °C (Fig. 2a) shows that the EAFD and clay particles ware separated demonstrating incomplete sinterization. The SEM image of the sample with 90% EADF fired at 1100 °C (Fig. 2b) indicating the higher degree of sintering and the reduced porosity. The EAFD changed the shape during sintering making the ceramics less porous (Table 1) (Mikhail et al., 1996; Pelino et al., 2002). Some elements such as Fe in EAFD retarded sintering blends with an EAFD content >50% fired at >950 °C revealed increased apparent porosity and water absorption with increasing EAFD content (Table 1) (Machado, 2005).

Water absorption can restrict the use of ceramics as building material (Machado, 2005). Ceramics used as flooring should have a water absorption <1%, as roofing tiles <20%, and as hollow bricks about 25%. The materials described in this study can be used as roofing tiles, except for the samples with 20% EAFD and hollow bricks fired at 800 °C did not show an adequate water absorption for the use as road surface. Moreover, the samples fired at 800 and 950 °C presented apparent porosity values within the range expected for Brazilian clays (5–45%) (Machado, 2005; Melo et al., 2002; Moravia et al., 2006).

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