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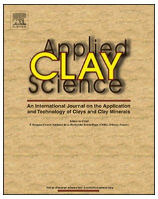

Review article

Incorporation of waste from ferromanganese alloy manufacture and soapstone powder in red ceramic production

T.G. Cota, E.L. Reis*, R.M.F. Lima, R.A.S. Cipriano

Mining Engineering and Geology Departments, Federal University of Ouro Preto, Ouro Preto, MG, Brazil

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ABSTRACT

The production of waste from the mining-metallurgical sector is one of the factors of environmental contamination and exploring ways to reuse this waste have attracted considerable research attention. This study proposes the use of residues generated from the manufacturing processes of ferromanganese alloy and soapstone powder for the production of red ceramic. Ceramic bricks were prepared with clay and sludge to investigate the effect of a number of variables, including the replacement of clay with sludge (5% and 10%), compaction pressure (14 and 28 MPa), and firing temperature (850 °C and 1000 °C) on the linear shrinkage, water absorption, firing specific weight, and compressive strength of the bricks. Also tests were carried out with replacement of part of the clay mass by sludge and steatite in the same brick. The best condition for ceramic production was found to be a firing temperature of 1000 °C and compaction pressure of 28 MPa with 5% of clay replaced by sludge. The best results were obtained for bricks with clay replaced by both sludge and steatite, which prompted the formation of the new crystalline phases, spinel and enstatite. After analysis, the brick residue was classified as Non Hazardous and Not Inert. The analyzed parameters were within the established limits for technological applications.

1. Introduction

Many manufacturing sectors aim to reduce industrial wastes due to a number of reasons, including the lack of waste disposal area, the environmental contamination, and the need to preserve non-renewable natural resources. Re-using waste products would be an effective alternative.

The production units of ferromanganese alloys generates a large amount of waste, such as the sludge formed in the settling tanks that store wastewater, arising predominantly from drainage water gutters from warehouses of raw material (e.g., manganese ore and reducing agents), product, and slag. According to Brasil (2016), in 2014, the production of ferromanganese alloys in Brazil was 303, 000 tons, and around 50 kg of sludge was generated for each ton of alloy (Castro, 2006).

Steatite is commonly exploited to produce handicrafts. The southeastern region of Minas Gerais, Brazil, particularly the Barroque cities, is well-known for its soapstone art works, including traditional handcrafted objects and soapstone cookware. In environmental terms, the production system is extremely primitive because of the large amount of waste (i.e., soapstone powder) that is generated and discarded without proper measure. According to Rodrigues and Lima (2012) soapstone artisan workshops produce a large quantity of powder; approximately 60 wt% of the rock is discharged as residue, which is discarded carelessly, often causing environmental problems. Talc is the main constituent in the steatite deposit. Brazil is the third largest producer of talc in the world, with an approximate production of 850, 000 tons in 2016 (U.S. Geological Survey, 2017).

The sludge generated during the manufacture of ferromanganese alloys is commonly composed of silicates such as quartz, muscovite, kaolinite, and albite (Silva et al., 2014). These minerals are usually found in clays and are used to produce ceramics; therefore, it is possible that this sludge can be used as a substitute for this raw materials used in clay production. Note that clays have the potential to isolate contaminants, reducing the toxicity of various types of materials.

The steatite used in this study has been previously characterized by Rodrigues and Lima (2012), Ferreira et al. (2015) and Souza et al. (2016), showing that talc is its main mineralogical phase. The characteristics of talc are advantageous for ceramic manufacturing such as low thermal and electrical conductivity, capacity to improve mechanical characteristics of the ceramics, and dimensional stability. These characteristics lead to a decrease in the firing shrinkage, the mass

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* Corresponding author at: Departamento de Engenharia de Minas, Universidade Federal de Ouro Preto, Campus Universitário, Morro do Cruzeiro, S/No, Ouro Preto 35400-000, MG, Brasil.

E-mail address: erica@demin.ufop.br (E.L. Reis).

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maturation temperature, and the expansion during water absorption (Hlavac, 1983; Carter and Norton, 2007; Torres et al., 2015; Van Vlack, 1964).

The use of residues as substitutes for clay in the production of red ceramics has been extensively studied (Souza et al., 2016; Torres et al., 2015; Mymrin et al., 2017a; Mymrin et al., 2017b). Steatite waste has been added to clay composites previously (Souza et al., 2016; Torres et al., 2015), which indicated that mixtures containing 85% steatite display properties that are suitable for possible technological applications. The partial fusion of talc promoted an increase in the liquid phase, diminishing porosity and, consequently, water absorption. In addition, an increase in sintering, density, and compressive strength was observed (Torres et al., 2015). The use of sludge, generated via the cleaning of water tanks, as a substitute for clay has been studied, and it was observed that the high values of the properties can be mainly attributed to the formation of glass and new minerals (Mymrin et al., 2017a). The industrial wastes printed circuit board, red mud from bauxite processing, and steel slag have completely replaced the raw clay and sand in the development of new ceramic composites. It has been reported that an amorphous vitreous phase is responsible for enhancing the mechanical properties of ceramics. Leaching and solubility methods showed that during sintering, the metals bind in an insoluble condition, to a level far above those required by Brazil sanitary standards; therefore, these ceramics can be used as an environmentally clean raw material (Mymrin et al., 2017b).

It is necessary to further investigate the use of residues such as sludge from the settling tanks of ferromanganese alloys and soapstone powder from the manufacture of soapstone handicrafts. This study aims to analyze the use of these wastes in the manufacture of ceramics. The proposed alternative is a practical and low cost way to reuse waste.

2. Materials and methods

2.1. Characterization of raw material

The clay used for the preparation of the test specimens and the steatite residue, both from Ouro Preto region, Minas Gerais, Brazil, was previously characterized by Rodrigues and Lima (2012), Ferreira et al. (2015) and Souza et al. (2016). The results concerning the physical and mineralogical characterization are presented in Table 1. Table 2 shows the chemical composition of the clay and steatite residue.

The sludge was obtained from a settling tank of a ferromanganese alloy manufacturing plant, located in the Ouro Preto region, Brazil, and the physical, chemical, and mineralogical characteristics were determined.

Particle-size distribution was performed by wet sieving (Tyler series 300–37 µm), particle under 37 µm were then measured with laser granulometer (Cilas 1064) using sodium hexametaphosphate 0.1% (w/v) dispersant solution. The humidity was measured in an electrical resistance ID200-Marte scale with 3 g of material for 3 min. The specific surface area was determined by the nitrogen absorption using the BET, 1200e model. The specific density was measured by the helium pycnometer model Ultrapyc 1200e.

The chemical composition was determined by inductively coupled plasma/optical emission spectrometry (ICP/OES) with radion vision, Agilent 725 model. The crystalline phases, before and after firing, were determined by X-ray diffraction (XRD) using PanAnalytical diffractometer, X'Pert^3 Powder model, with CuKα radiation. The mineralogical quantification was performed by the Rietveld method of refinement, software HighScorePlus. Morphological features were observed by scanning electron microscopy with X-ray microanalysis (SEM/EDS), Jeol JSN6010la model.

Table 1
Physical properties of the raw ceramic materials.

Property	Clay	Soapstone powder
Specific surface area (m^2/g)	32.414	3.430
Density (g/cm^3)	2.593	2.960
Humidity (%)	7	0.340
Porosity (%)	1.6	0.2
D_{80} (µm)	90	48
Mineralogical composition	Quartz, kaolinite, muscovite	Talc, chlorite

Table 2
Chemical composition of the clay and the soapstone.

Grade/compound		Clay	Soapstone powder
Wt (%)	SiO_2	62.62	58.91
	MnO	–	0.04
	Al_2O_3	28.91	2.30
	Fe_2O_3	5.96	4.99
	TiO_2	1.48	–
	K_2O	0.64	–
	MgO	0.143	27.80
	CaO	–	0.07
	SO_3	–	0.96
	LOI	12.05	5.05
ppm	Zn	36.70	–
	As	5.38	2.32
	Cu	–	16.30

2.2. Preparation and characterization of ceramic brick samples

Ceramic bricks constituted only from clay and bricks constituted from clay and steatite residue was previously described (Souza et al., 2016). For ceramics bricks prepared from clay and sludge was design the factorial experiment to investigate whether variables (replacement of clay for sludge, compaction pressure, and firing temperature) has some influence in the variable responses. The physical and mechanical properties of the bricks were characterized to comply with the standards NBR 15270–2 (ABNT, 2005) that govern the testing methodology of ceramic blocks. The analyzed properties were linear shrinkage, water absorption, firing specific weight, and compressive strength. Each test was repeated, and the levels and factors studied was replacement of clay for sludge (5–10%), compaction pressure (14–28 MPa) and firing temperature (850–1000 °C).

The natural humidity of the compounds was used in the conformation process under pressure provided that it was within the 8–10% range. The mass was distributed in a prismatic mold of dimensions 70 mm × 20 mm × 10 mm. The bricks were dried at 65 °C for 72 h. The bricks were then fired, with temperature set in each test, for a period of 2 h, at a heating rate of 5 °C/min.

By analyzing the results of the technological tests with clay replaced by sludge, it was possible to determine which composition generated the best response. Tests were performed with the clay mass being replaced by sludge and steatite in the same specimen. Additional tests were performed to determine the three-point flexural strength and chemical-structural characterization. Besides the classification of the ceramic brick for disposal as solid waste according to NBR 10004 (ABNT, 2004).

3. Experimental results

3.1. Raw material characterization

Diffractogram patterns of sludge (Fig. 1) demonstrate that quartz, calcite, muscovite, and kaolinite are the main crystalline phases. The diffractogram exhibits a high background level, a common indication of low crystallinity phase or amorphous material.

For the identification of manganese alloy residues and slag with amorphous phases, images were taken using scanning electron