



## Research paper

## Untreated coffee husk ashes used as flux in ceramic tiles

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## ABSTRACT

The agro-industrial activities are responsible for the production of large amounts of solid wastes, which, so far, have found scarce reuse alternatives. Among the former, coffee bean beneficiation generates an equal amount of coffee husks whose highest reuse potential is as fuel. The resulting ashes are frequently an object of illegal covert disposal and a serious source of environmental impact. However, coffee husk ashes (CHA) are particularly rich in alkaline and alkaline-earth metals, and might be adequate to replace the traditional feldspars, which are used in high content as fluxes in clay-based ceramic formulations but are becoming scarce and costly. In this work, the fluxing effect of CHA additions to an industrial clay-based mixture was evaluated. Based on the characterization results and the mullite–silica–leucite phase diagram, additions of 5 to 20 wt.% CHA were made to the clay-based mixture and the resulting compositions were evaluated after sintering at temperatures between 1100 and 1200 °C (60 min soaking time). The results obtained show that firing temperatures near 1180 °C and ~10 wt.% CHA addition lead to linear shrinkage, water absorption and flexural strength values that fall within the range specified by floor tile standards (NBR 13817, EN 176 and ISO 13006), requiring no significant changes in processing parameters. Coffee husk ashes can thus advantageously replace feldspars in the role of fluxing material, with the potential to reduce not only natural ceramic raw material consumption, but also production and landfill costs as well as waste disposal area requirements.

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## 1. Introduction

Recent decades have witnessed a growing concern with the environment's degradation, with key environmental policies becoming focused on waste prevention and landfill reduction, waste inertization, natural resource preservation, energy recovery from waste and waste material reuse and recycling. As a consequence, industrial waste disposal became both stricter and costlier.

Industrial processes were optimized in order to reduce the amount of waste produced and sintering and vitrification stood up among the most promising techniques to accomplish waste inertization, mostly due to the comparatively high processing temperatures, which lead to chemical stability of potentially hazardous components and significant waste volume reduction, with obvious benefits in storage and dumping requirements (Bingham and Hand, 2006; Lee et al., 2007; Rawlings et al., 2006).

The ceramic industries, particularly those dealing with the fabrication of building materials, became the target for the incorporation of other industries' rejects (Rawlings et al., 2006; Segadães, 2006; Vieira and Monteiro, 2009) and waste materials such as coal ashes,

process sludges and slags, mineral rejects, and construction and demolition rubble, have been incorporated in various ceramic products with little effect on the final products properties (Acchar et al., 2006, 2008; Bernardo et al., 2007; Corinaldesi and Moriconi, 2009; Jordán et al., 2005; Oliveira et al., 2008a; Pontikes et al., 2009; Tam and Tam, 2006). The results of such studies led to the recognition that many wastes often contain substances that are beneficial for the process (Acchar et al., 2005; Bernardo et al., 2009; Jonker and Potgieter, 2005; Leite et al., 2009; Segadães et al., 2005; Sobolev et al., 2007) and that using abundant and cheap industrial wastes as alternative ceramic raw materials might be both technically and economically attractive, as long as the technical standards for the envisaged application can be met and the new total cost is comparable to that of the traditional solution.

Thus, particularly in those countries where raw materials are strategic, industries started looking for alternative, less expensive raw materials, frequently among proposed recycling or reuse alternatives of a variety of industrial wastes.

Agro-industrial activities are among those responsible for the production of large amounts of solid wastes. Given the peculiarities of the sector, waste covert disposal in landfill areas or lagoons is rather common, which causes a serious environmental impact, and the most frequent waste management option is the use of such rejects in other agricultural activities. Efforts keep being made to find higher added-value reuse alternatives (Singh et al., 2009; Ulloa et al., 2004).

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Brazil is, today, the world's major coffee producer, accounting for 30% of the international market and surpassing the joint production of the next six major producers. Brazil is also the second consumer market, following the United States of America (ABIC, 2011). The production of coffee, from planting to final product, generates large amounts of rejects, namely during the first stage of beneficiation, when coffee beans are transformed into dry coffee and husks are separated. Untreated coffee husks represent near 50% of coffee beans (Vale et al., 2007) and have found applications in biotechnology, mostly as animal feeds (Bayne et al., 1976; Christensen, 1981; Ulloa et al., 2004) and as efficient biosorbents for metal ion removal from aqueous solutions (Oliveira et al., 2008b). But the highest reuse potential of dried coffee husks still is as fuel. Various studies showed that the calorific value of coffee husks is near 4000 kcal·kg<sup>-1</sup>, higher than that of various other agricultural rejects, namely cotton seed husks, rice husks and corncobs (Saenger et al., 2001; Vale et al., 2007). When the comparison is made in terms of generated heat per volume unit of reject, coffee husk is around 18% better than wood sawdust. Thus, coffee husks are commonly used in the producing facility itself, as fuel for the bean driers, ensuring the facility's self sustainability in terms of energy requirements.

According to data from the Brazilian Ministry of Agriculture (SPA), around 46 millions of 60 kg bags of beneficiated coffee were produced in 2008, which entail roughly 2.7 million tonnes of husks (Vale et al., 2007). Husk burning generates ashes (~14%), so far without any commercial value, which are simply disposed of in the vicinity of the producing facilities. Given that such ashes are particularly rich in alkaline and alkaline-earth metals (Saenger et al., 2001), an investigation of their fluxing potential in clay-based ceramic formulations is amply justified: ashes might be a strong candidate to replace traditional feldspars, which are used in contents that might reach up to 40 wt.%, are becoming scarce and frequently are not readily available in areas where ceramic industries concentrate (Lee et al., 2007).

It is not easy to obtain a sound estimate of the amount of ashes produced, mostly because the proportion of coffee husks that are actually burnt is also not known. Also, being a seasonal crop, the rate at which ashes are produced is not constant and presumably peaks with the coffee bean harvest, which occurs in Brazil in June–July every year (data from SPA). Nevertheless, in the major coffee producing states (southeast), which coincidentally also host the major ceramic centres in the country, if ashes are stored the year around, enough quantity will be available to regularly supply the local ceramic industry.

Thus, the objective of this work was to evaluate the fluxing effect of coffee husk ash additions to clay-based ceramic formulations, seeking an alternative raw material to replace feldspars in the ceramic industry. Such application would simultaneously ameliorate the environmental impact of this abundant waste covert disposal.

## 2. Experimental procedure

A typical brick-making mixture of medium plasticity, made of equal amounts of commercial kaolin and kaolinitic clay, obtained from a local industry, was wet ground to <45 µm, dried and deagglomerated, and used as clay-based raw material. Coffee husk ashes (CHA) were collected from ash dumps at a coffee producing facility (variety *robusta*, Bahia, Brazil) and dry milled to <74 µm. The characterization of raw materials included chemical composition (X-ray fluorescence, XRF), mineralogical composition (X-ray diffraction, XRD) and thermal behaviour (differential thermal analysis, DTA, and thermogravimetric analysis, TGA).

The XRF characterization was carried out in a semi-quantitative mode, using a representative sample of each powder (particle size below 74 µm) with the Shimadzu EDX-700 energy dispersive X-ray fluorescence spectrophotometer in vacuum.

The XRD characterization enabled the identification of the crystalline phases present in the powder samples and was carried out

using a Shimadzu XRD-6000 diffractometer with the Cu K $\alpha$  radiation ( $\lambda = 1,5418 \text{ \AA}$ ) at 40 kV and 30 mA, and a scanning speed of 2° 2 $\theta$  min<sup>-1</sup> between 5 and 80° 2 $\theta$ . Crystalline phases were identified against the JCPDS-ICDD diffraction files.

Thermogravimetric analysis (TGA) was carried out under flowing synthetic air on powder samples (~15 mg) up to 1200 °C, using a Shimadzu TGA-51 thermobalance and 10 °C min<sup>-1</sup> heating rate, alumina crucibles and Pt–Pt10Rh thermocouples. This analysis records mass losses occurring during heating. Similarly, differential thermal analysis (DTA) identifies thermal events, such as phase transformations, by comparison with those of a standard sample (alumina powder): in this work DTA was carried out under the same experimental conditions using Shimadzu DTA-50 instrument. Both TGA and DTA results were handled by the instruments' software (Shimadzu TA-60).

Based on the characterization results and the mullite–silica–leucite phase diagram, additions of 5 to 20 wt.% CHA were made to the clay-based mixture. The resulting compositions were homogenised (~6.5 min in porcelain jar with alumina balls, with 8 wt.% water, dry basis) and uniaxially pressed (45 MPa) into 60 mm × 20 mm rectangular tiles. The tiles were then dried (110 °C, 24 h), sintered in air (5 °C/min heating and cooling rates) at temperatures between 1100 and 1200 °C (60 min soaking time), and characterized (average of five specimens for each value). The sintering conditions were chosen based on the thermal expansion behaviour of compacted dry samples, which was recorded as relative length change with a BP Engineering dilatometer (RB-3000) up to 1200 °C and 10 °C min<sup>-1</sup> heating rate.

Linear firing shrinkage was determined from the change in length of the sintered tiles relative to that of dried tiles. Apparent density and water absorption were determined using the Archimedes water displacement method (from the relationships between dry, water-immersed and water-soaked weights of each sample, as described in EN 99 and ISO 10545-3 standards). Crystalline phases were identified by X-ray diffraction.

Mechanical strength was determined as the modulus of rupture in three-point bending geometry (50 mm between outer knives), calculated from the applied load at rupture, the dimensions of the test sample and the test geometry. Tests were carried out with a universal testing machine (Zwick-Roell, 2.5 kN load cell) at a constant cross-head speed of 0.5 mm/min, as described in the ISO 10545-4/95 standard.

The microstructure of sintered samples was observed on fracture surfaces after HF chemical etching (2 vol.%). Observations were carried out by scanning electron microscopy (SEM, Shimadzu SSX-550, 20 kV). During SEM observation, chemical composition of phases was qualitatively accessed by energy dispersive X-ray fluorescence spectrophotometry (EDX).

## 3. Results and discussion

Table 1 shows the chemical composition of the raw materials, as determined by XRF. Both clay and kaolin show the expected typical high contents of alumina and silica, with excess silica relative to kaolinite itself, and minor contents of Mg, Ti, Ca and Na oxides. The clay shows slightly higher contents of iron and potassium oxides, which will, respectively, be responsible for the reddish colour of fired bodies and enable low temperature sintering. On the contrary, ~92% of the coffee husk ashes (CHA) are K<sub>2</sub>O and CaO, accompanied by smaller amounts of MgO and P<sub>2</sub>O<sub>5</sub>. These oxides will have a joint strong fluxing effect at high temperatures over alumina and silica, particularly when compared with the average potash feldspar, whose K<sub>2</sub>O content is ~17 wt.%.

Fig. 1 shows the X-ray diffraction patterns of the clay, kaolin and CHA. As expected from the XRF results, only quartz and kaolinite were detected in both clay and kaolin. The X-ray diffraction pattern of CHA is comparatively much noisier and the major phases identified were carbonates (potassium, K<sub>2</sub>CO<sub>3</sub>, magnesium, MgCO<sub>3</sub>, and calcium, CaCO<sub>3</sub>), calcium silicates (larnite, Ca<sub>2</sub>SiO<sub>4</sub>, rankinite, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, anorthite,

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