Using SEM/EDS for characterization of clay ceramic bearing sugarcane bagasse ash waste

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The sugarcane industry is based mainly on the production of sugar and ethanol, which generates huge amounts of sugarcane bagasse. In general, the sugarcane bagasse is used by the plants for energy co-generation. As a result, this industry produces huge amounts of waste named sugarcane bagasse ash. The volume of such waste is expected to continuously increase. The sugarcane bagasse ash is considered a non-biodegradable solid waste material, which is rich in crystalline silica (SiO₂). Thus, the management of this waste in an environmentally safe way is a challenge that must be met. One of the ways for solving this problem is the reuse of sugarcane bagasse ash waste for the purpose of partial replacement of natural raw material in the production of clay ceramics. This chapter focuses on the microstructural characterization of clay ceramic bearing sugarcane bagasse ash waste fired at different temperatures by scanning electron microscopy (SEM/EDS). The effect of the incorporation of sugarcane bagasse ash waste on the microstructure and technological properties of clay ceramic was investigated.

Keywords sugarcane bagasse ash; waste; clay ceramic; scanning electron microscopy

1. Introduction

In the XXI century, special attention has been devoted to the waste minimization practices, pollution prevention, and sustainable development as applied to the material field. The development of environment-friendly production processes is imperative. Despite this, large volumes of industrial solid wastes are generated worldwide every day.

A particular case is the sugarcane industry. Brazil is currently the worldwide largest producer of sugarcane. The sugarcane industry is based mainly on the production of sugar and ethanol, which generates huge volumes of sugarcane bagasse. In general, the sugarcane bagasse is used by the plants for energy co-generation [1]. As a result, this industry generates large volumes of sugarcane bagasse ash waste worldwide. The volume of such solid waste is expected to continuously increase.

The sugarcane bagasse ash (SCBA) is considered a non-biodegradable solid material. The SCBA waste is a major concern of the sugarcane industry, with disposal to soil fertilizer currently the most common practice. This option, however, has become less attractive because influence the physical and chemical characteristics of the soils. Thus, the management of this abundant waste in an environmentally safe way is a challenge that must be met.

The SCBA waste can be characterized as solid waste material rich in crystalline silica (SiO₂) [2]. Thus, it has some potential to be used as alternative ceramic raw material. In fact, the clay ceramic area has become in the recent years an alternative way highly promising for reuse of solid waste materials [3-7]. This is due to mainly the heterogeneity of the clayey formulations used in the production of clay ceramics for civil construction. In addition, mixtures of plastic and non-plastic components usually constitute these formulations, with wide variability of the chemical and mineralogical compositions.

The reuse of SCBA waste as a possible new additive to ceramic materials is an option. Borlini et al [8] reported on the use of SCBA waste in replacement for fluxes in vitrified ceramic tile formulation. It was found that the SCBA waste did not act as a fluxing agent in the ceramic tile compositions. Borlini et al [9] also investigated the influence of the firing temperature on the technological properties and microstructure of SCBA waste containing red ceramic. They concluded that no major changes in the technological properties of red ceramic fired from 900 °C to 1200 °C were found. However, they observed that the red ceramic pieces incorporated with 20 wt.% of SCBA waste fired at 1200 °C presented a large microstructural variation in relation to the other studied compositions. Ganesan et al [10] reported on the use of SCBA waste as supplementary cementitious material. It was found that the SCBA waste is an effective mineral admixture, with 20 % as optimal replacement ratio of cement. The specific advantages of such replacement are: i) the development of high early strength; ii) a reduction in water permeability; and iii) appreciable resistance to chloride permeation and diffusion. Teixeira et al [11] reported on the use of SCBA waste as a potential quartz replacement in red ceramic. It was found that the SCBA waste has a very high quartz concentration and low concentrations of fluxing oxides. The incorporation of SCBA waste had a detrimental effect on the mechanical strength of the fired pieces. They also concluded that the clay used can incorporate up to 10 wt.% of SCBA waste to produce clay bricks. Cordeiro et al [12] reported that SCBA waste has adequate properties to be used as pozzolan in building materials. Lima et al [13] reported on the use of SCBA waste in replacement of fine aggregate in the manufacture of concrete. Aigbodion et al [14] reported on the potential utilization of SCBA waste for ceramic materials production. They concluded that the SCBA waste characteristics are adequate for ceramic products such as insulation, membrane...
filters and structural ceramics. They also found that the SCBA waste can be used as facing sand moulding during casting operations. As can be observed, in spite of the fact that SCBA waste was produced in large amounts every year, insufficient attention has been devoted to microstructural characterization of clay ceramics bearing SCBA waste.

This chapter focuses on the microstructural characterization of clay ceramic bearing SCBA waste fired at different temperatures via scanning electron microscopy (SEM/EDS). Emphasis is given to the SCBA waste characteristics and technological properties and microstructural variation of the pressed specimens taking place during the firing step.

2. Experimental details

A representative sample of SCBA ash waste was collected in a sugarcane plant located in south-eastern Brazil. Common red clay used by a local brick maker was selected for mixing with the SCBA waste. The chemical composition of the clay powder is given in Table 1. The clay is predominantly kaolinitic, with gibbsite, goethite, quartz, potash feldspar, and illite/mica as accessory minerals.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>wt.%</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>43.22</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>32.84</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.83</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.51</td>
</tr>
<tr>
<td>CaO</td>
<td>0.44</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.56</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.06</td>
</tr>
<tr>
<td>Loss on ignition at 1000 ºC</td>
<td>9.44</td>
</tr>
</tbody>
</table>

A series of clay and SCBA waste mixtures, were prepared, containing SCBA waste additions up to 10 wt. %. Each mixture is labelled as follows: KC-M0 contains 0 wt.% SCBA; KC-M5 contains 5 wt.% SCBA; and KC-M10 contains 10 wt.% SCBA.

X-ray diffraction analysis was done using monochromatic Cu-Kα radiation and 1.5 ° (2θ)/min scanning speed in a conventional diffractometer over non-oriented specimen. Crystalline phases were identified by comparing the intensities and positions of Bragg peaks with those listed in the JCPDS-ICCD data files. The chemical composition of the SCBA waste powder was determined by energy-dispersive X-ray spectrometer. The loss on ignition (LOI) was determined according to LOI = (Wd – Wc)/Wd x100, where Wd is the weight of the dry sample at 110 ºC, and Wc is the weight of the calcined sample at 1000 ºC during 1h. The particle size distribution of the SCBA waste powder was determined by a combination of sieving and sedimentation procedures according to the NBR 7181 standard.

The morphology of the SCBA waste powder particles was observed by secondary electrons (SE) under a scanning electron microscopy (SEM) with a coupled energy dispersive spectroscopy (EDS), at 10 kV, after gold coating.

The clay and SCBA waste powders in their respective proportions were dry mixed and homogenised in a cylindrical mixer, then humidified with 7 wt.% water (moisture mass/dry mass).

The clay ceramic pieces were prepared by single action pressing the mixed powders at 21 MP into cylindrical disks (diameter 25 mm). The pieces were then dried at 110 ºC for 24 h, and finally slowly fired in a laboratory kiln (24 h cold to cold; maximum temperatures between 700 and 1100 ºC).

The following technological properties have been determined in the fired pieces according with standardized procedures: linear shrinkage, water absorption, apparent density, and tensile strength.

The microstructure of the fractured surfaces of the fired pieces was observed by means of scanning electron microscopy / secondary electrons images, SEM/SEI, after gold coating.

3. Results and discussion

3.1 SCBA waste characterization

The chemical and mineralogical compositions of the SCBA waste powder are given in Table 2. It can be seen that the SCBA waste powder contains a large amount of silicon oxide (SiO₂), and to a lesser extent aluminium oxide (Al₂O₃), iron oxide (Fe₂O₃), calcium oxide (CaO), and potassium oxide (K₂O). Loss on ignition gave high weight loss around 9.78 %, and is believed to be due mainly to organic matter present in the SCBA waste.
The mineral phases present in the SCBA waste powder are: quartz (SiO$_2$), cristobalite (SiO$_2$), hydrated calcium phosphate (Ca$_3$(PO$_4$)$_2$.H$_2$O), potassium carbonate (K$_2$CO$_3$), mullite (3Al$_2$O$_3$.2SiO$_2$), and hematite (Fe$_2$O$_3$). However, the quartz is predominant in the SCBA waste sample. These results are in agreement with the chemical data.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>wt. %</th>
</tr>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>61.59</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.92</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>7.36</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.46</td>
</tr>
<tr>
<td>CaO</td>
<td>5.00</td>
</tr>
<tr>
<td>MgO</td>
<td>1.17</td>
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<tr>
<td>MnO</td>
<td>0.10</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>6.22</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.98</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.42</td>
</tr>
<tr>
<td>Loss on ignition at 1000 ºC</td>
<td>9.78</td>
</tr>
</tbody>
</table>

The SCBA waste sample was a dark-coulored powder. The SCBA powder also presented a wide particle size range (1 to 400 μm), where the major size ranges are clay (< 2 μm) with ~ 0.7 %, silt (2 ≤ x < 63 μm) with ~ 11.5 %, and sand (> 63 μm) with ~ 87.8 %. Morphological aspects of the SCBA waste powder particles are outlined in Fig. 1. The scanning electron micrographs of Figures 1(a) and 1(b) show the typical irregular shapes of the SCBA particles. The SCBA waste powder is rich in porous particles with fibrous morphology (Fig. 1c) of unburned bagasse, and also of angular-shaped particles (Fig. 1d) of quartz and/or cristobalite. In addition, a wide particle size range is also observed in the micrographs, corroborating the particle size data.

![Fig. 1 SEM micrographs of the SCBA waste powder particles.](image-url)
The line spectrum for SCBA waste sample determined by using EDS (Fig. 2) indicated the presence of C, O, Fe, Al, Si, and Nb. These results are consistent with the chemical composition data (Table 2), except Nb.

3.2 Technical properties

The quality of the clay ceramic pieces after firing between 700 and 1100 ºC was determined on the basis of linear shrinkage, water absorption, apparent density, and tensile strength (Figs. 3-6).

The linear shrinkage indicates the degree of densification during firing, and is very important for the dimensional control of the clay ceramic products. The measured values of linear shrinkage were in the 0.63 – 8.33 % range. These values are within the safe limits for industrial production of clay ceramics. The linear shrinkage for all the clay ceramic pieces, as shown in Fig. 3, increases with increasing firing temperature mainly above 900 ºC. This fact is related to major sinterability of the clay pieces at higher firing temperature. It may also be observed that the addition of SCBA waste tends to decrease the linear shrinkage. This behaviour can be attributed to the higher amount of quartz particles, which is a non-plastic component of the SCBA waste. Thus, the incorporation of SCBA waste into the clayey paste improves the dimensional control of clay ceramic pieces.

Fig. 4 shows the water absorption of the clay ceramic pieces. This property is related to the microstructure of the sintered ceramic matrix, and determines the open pores amount of the fired pieces. As expected, the water absorption decreases with the increase of the firing temperature mainly above 1000 ºC. At higher firing temperatures the glassy phase by the capillary action and surface tension infiltrates the open pores of the fired structure and causes densification
of the clay ceramic pieces. The results of Fig. 4 also show that, in general, the incorporation of higher SCBA waste amounts tends to lightly increase the water absorption for the studied conditions.

![Fig. 4 Water absorption of the clay ceramic pieces.](image)

The apparent density of the fired pieces is shown in Fig. 5. The density increases with the increase of the firing temperature, being more significant above 900 ºC. This is related to the vitrification that contributes to reduce the open pore amount, resulting in more dense clay ceramic pieces. In addition, the apparent density was observed to decrease with increasing SCBA waste amounts. These results are in accordance with the linear shrinkage (Fig. 3) and water absorption (Fig. 4) values.

![Fig. 5 Apparent density of the clay ceramic pieces.](image)

The mechanical strength of the clay ceramic pieces was determined in terms of tensile strength obtained by the diametral compressive method as function of the SCBA waste amount and firing temperature (Fig. 6). As can be observed, the effect of the firing temperature was to increase the tensile strength following the densification behaviour.

![Fig. 6 Tensile strength of the clay ceramic pieces.](image)
(linear shrinkage and water absorption). According to Fig. 6, the tensile strength also tends to decrease with the SCBA waste addition. This finding is substantiated by the presence of quartz particles and organic matter in the SCBA waste.

3.3 Microstructural analysis via SEM/EDS

In order to enlighten the densification behaviour on firing, the fracture surfaces of the as-fired pieces of the KC-M0 formulation were examined via SEM/EDS (Fig. 7a-f). The micrographs show the evolution of the structure of clay ceramic pieces as firing temperature increase. The correlation between sintered microstructure and technological properties is well established.

![SEM micrographs of fracture surfaces of fired clay ceramic pieces (sample KC-M0): a) 700 °C; b) 800 °C; c) 900 °C; d) 1000 °C; e) 1100 °C; and f) EDS fired at 1000 °C.](image)

Fig. 7 SEM micrographs of fracture surfaces of fired clay ceramic pieces (sample KC-M0): a) 700 °C; b) 800 °C; c) 900 °C; d) 1000 °C; e) 1100 °C; and f) EDS fired at 1000 °C.

Between 700 and 900 °C (Fig. 7a-c), the fracture surface is rough and the porosity is clearly visible. In this temperature range, the sintering process is governed via solid state mechanism, especially surface diffusion. In addition, the green pieces on heating up to 900 °C underwent a series of phase transformations such as dehydration of hydroxides
(gibbsite and goethite) and dehydroxylation of kaolinite to metakaolinite formation. Necks between contacting metakaolinite platelets grow and smoothening of the particles surfaces occurs. Thus, the clay ceramic pieces in this temperature range tend to have a more open structure and only a small variation of the technical properties. At 1000 ºC (Fig. 7d), the porosity starts to reduce. At 1100 ºC (Fig. 7e), however, the clay ceramic pieces presented advanced sintering stage. In this case, the elimination of a large amount of open porosity that exists within the structure occurred. In addition, the vitrification is in progress. In fact, the glassy phase infiltrates the pores of the structure and cause densification via liquid phase sintering. This justifies the improved technological properties (lower water absorption and higher mechanical strength) of the clay ceramic pieces. The EDS spectrum of clay ceramic fired at 1000 ºC (Fig. 7f) showed mainly the presence of Si, Al, and Fe. This is consistent with the chemical composition of the plastic clay powder used (Table 1).

![Fig. 8 SEM micrographs of fracture surfaces of fired clay ceramic pieces (sample KC-M10): a) 700 ºC; b) 800 ºC; c) 900 ºC; d) 1000 ºC; e) 1100 ºC; and f) EDS fired at 1000 ºC.](image-url)

The typical microstructure of the fracture surfaces of clay ceramic pieces containing SCBA waste fired between 700 and 1100 ºC is shown in Fig. 8a-f. As can be observed, the sintered microstructure of clay ceramic containing SCBA waste tends to be more porous than those of waste-free clay ceramics. These results are consistent with the values of the
technological properties (linear shrinkage, water absorption, apparent density, and tensile strength). Thus, the SCBA waste powder as added to a clayey body causes modification on the texture and porosity of the fired clay ceramic pieces. In particular, the additions of very high SCBA waste amounts in clay ceramics should be avoided, because it impairs the mechanical of the fired pieces.

4. Conclusions

In this chapter, the microstructural characterization of clay ceramics bearing SCBA waste was investigated. The results showed that the SEM/EDS is a powerful tool to monitor the microstructural evolution and densification behaviour of clay ceramics during firing.

SEM/SEI analysis showed that that SCBA waste powder is composed of a mixture of mineral particles of different morphologies. In addition, it was also observed the presence of unburned bagasse particles. Microstructural analysis has demonstrated that the structure of the clay ceramic pieces bearing SCBA waste experienced an increase in open porosity on firing. The main effects of the SCBA waste addition were to increase of the water absorption and the decrease of the mechanical strength. This behaviour is caused by the high amounts of quartz and unburned bagasse particles in the SCBA waste. These results suggest that only small additions of SCBA waste should be used to produce clay ceramics.

Acknowledgements

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References