



Valorization of sugarcane bagasse ash: Producing glass-ceramic materials



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ABSTRACT

Some aluminosilicates, for example mullite and wollastonite, are very important in the ceramic and construction industries. The most significant glass-ceramic for building applications has wollastonite as the main crystal phase. In this work we report on the use of sugarcane bagasse ash (SCBA) to produce glass-ceramics with silicates as the major crystalline phases. The glasses (frits) were prepared by mixing ash, limestone (calcium and magnesium carbonates) and potassium carbonate as the fluxing agent. X-ray fluorescence was used to determine the chemical composition of the glasses and their crystallization was assessed by using thermal analysis (DTA/DSC/TGA) and X-ray diffraction. The results showed that glass-ceramic material can be produced with wollastonite as the major phase, at a temperature lower than 900 °C.

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1. Introduction

In the last years, the sugar/alcohol industry has produced the largest amount of agricultural waste in Brazil, called bagasse. This fibrous matter (lignocelluloses) is left over after sugarcane has been crushed to extract the juice. Currently, sugarcane bagasse (SCB) is burned in boilers to produce electrical energy, resulting in a huge volume of ash (fly and bottom ashes). This ash (SCBA) contains high amounts of organic material (~35% charcoal and bagasse debris by weight). We have shown (Teixeira et al., 2008, 2010a,b, 2011a) that it is possible to concentrate both fractions (inorganic and organic) and to use the first one to produce materials for the construction industry (glass-ceramic, ceramic plates and frits). The major inorganic component of the ash is SiO₂, and among the minor components there are some mineralizing or fluxing agents. Therefore, SCBA can be used in building materials (Frías et al., 2011; Faria et al., 2012) and for several other applications (Teixeira et al., 2011b). The most important glass-forming systems are based on silicate compositions, and therefore, silicates are the major crystalline components of glass-ceramics. Published works have shown the potential of transforming silicate-based residues into ceramic and glass-ceramic products of great utility (Cheng et al., 2011; Höland and Beall, 2002; Karamanov et al., 2009; López et al., 2012; Pérez-

Villarejo et al., 2012; Rawlings et al., 2006; Schabbach et al., 2012; Souza et al., 2011; Vu et al., 2012).

Glass-ceramic materials (Höland and Beall, 2002) are obtained through the controlled crystallization of glass and are characterized by one or more crystalline phases dispersed within the glassy phase. The amounts of glassy and crystalline phases in the mixture may vary, and can also be established by controlling the temperature and the crystallization time. The addition of fluxing and modifying agents and nucleating agents (transition metal oxides, alkali and alkaline earth metals) contribute to reducing the melting temperature of the precursors to obtain the glasses and their viscosity, as well as the process of nucleation and formation of crystalline phases. The precursors and fluxing agents are critical factors in defining the desired glass-ceramic composition (crystalline and amorphous phases). In recent years, industrial and agricultural residues have been studied and used as raw materials or some components in ceramics and glass-ceramic materials (Rawlings et al., 2006). In addition to recycling these wastes and preventing them from being discharged into the environment, natural resources used by industries are saved. In this case, the glass-ceramics are complex due to the numerous secondary components and impurities that induce the crystallization of several secondary phases (Chen, 2007; Goel et al., 2007; Höland and Beall, 2002; Montero et al., 2009; Navarro, 2003; Pinckney and Beall, 2008; Rawlings et al., 2006; Romero et al., 2006; Teixeira et al., 2010b).

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In previous work (Teixeira et al., 2010b), we have shown that it is possible to produce glass-ceramic materials useful in the construction industry, using sugarcane bagasse ashes (SCBA) with wollastonite being the major phase. Glass-ceramic materials with wollastonite as the main crystalline phase are produced from glasses of the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$ system by controlled surface crystallization using in the process conventional nucleating agents such as TiO_2 and ZrO_2 . Such glassy materials show special visual effects and other important properties (harder than natural stones, zero water absorption, lower density, etc.). They are produced on a large scale and used as coatings (floor and internal and external walls) in the construction industry. One of the most important wollastonite glass-ceramic for applications in the construction industry is produced by the Japanese company “Nippon Electric Glass” with the name NEOPARIES™. A major advantage of this material, in relation to natural stones, is that it allows the production of large flat and curved panels (Höland and Beall, 2002).

In this work, we sought a material widely available and affordable (such as limestone) to make the process viable on an industrial scale. Therefore, SCBA was mixed with limestone and a fluxing agent to obtain glass-ceramic material with properties comparable to those of natural stones, which would be useful to the construction industry.

2. Materials and methods

SCBA (in fact a soot) has about 30 wt% charcoal and organic materials mixed with the ash (Teixeira et al., 2011a, 2011b). Soot (called SCBA here) samples were collected at the solid/water exit of the gas washer in the Santo Inácio (SI) mill, near Presidente Prudente city in São Paulo State, Brazil. The ash was characterized using X-ray fluorescence (XRF – 1800, Shimadzu) and X-ray diffraction (XRD – 6000, Shimadzu), to determine its chemical composition and the main crystalline phases, respectively.

Limestone is a commercial product used by industries and for agricultural applications. Its chemical composition was given by the supplier.

Sieves, an electrical oven and a balance were used to determine the amount of organic matter and carbonates in SCBA. SCBA was fractionated by passing it through an 18-mesh sieve (1 mm) and 30-mesh sieve (0.59 mm). The three fractions were fired (900 °C for 30 min) in an electrical laboratory furnace and weighed before and after firing. The values obtained were the averages of three samples (triplicates). Since the organic matter (charcoal and debris) was concentrated in the coarser ash fraction, only the fraction smaller than 0.59 mm, which had about 16 wt% organic matter, was used to produce the glasses.

All raw materials, limestone-100 (passed through a 100-mesh sieve), SI – SCBA and ash–limestone–potassium combinations, were analyzed using a thermal analysis apparatus, model SDT Q-600 (TA Instruments). Platinum crucibles, air flow (100 mL/min) and heating ramp of 20 °C/min, from room temperature up to 1400 °C, were used.

The glass was prepared mixing SCBA (<0.59 mm) with limestone and K_2CO_3 (fluxing agent) using the melt-quenching method. The glass composition was prepared using ternary phase diagrams and considering the composition of the ash, the desired final crystalline phase and the calculated melting temperature. The theoretical melting temperature of the composition for silicate glass production was calculated using the method proposed by Chengyu and Ying (1983).

The mixtures were melted at 1400 °C using a lift oven (INTI – FE 1700) from Laboratório de Reciclagem, Tratamento de Resíduos e Metalurgia Extrativa – LAREX (Recycling, Waste Treatment and Extractive Metallurgy Laboratory) at the São Paulo University (USP).

The melted mixtures were poured into containers with water at room temperature to produce frits, which were dried, manually milled and passed through a sieve (30 mesh; <0.59 mm). Part of the powder was submitted to XRD and thermal analysis (DTA/DSC/TGA), and another part was moistened with ethylene glycol and pressed (2 tons) in the form of pellets ($\phi = 12$ mm, $h = 3$ mm) using a manual hydraulic press. These pellets were treated at three different temperatures (770, 880 and 1010 °C, for 30 min) in the region of glass transition and crystallization, determined by DSC. One surface of each pellet was polished using sandpaper (P# 800, 1200 and 2400), and analyzed by XRD to identify the phases formed during heat treatment. The flowchart in Fig. 1 summarizes the main steps described above.

3. Results and discussion

The chemical compositions of the limestone and ash-SI are shown in Table 1. These compositions were obtained from the limestone manufacturer and previous studies of the ash (Teixeira et al., 2010b, 2011a,b). The ash consisted mainly of quartz and the limestone contained mainly calcium and magnesium carbonates. Based on these compositions, more soot (16 wt%) was added to compensate for the volume of organic material in the fraction <0.59 mm used in the mixture, so as to increase the percentage of inorganic materials considered in the calculation of the melting temperatures for various compositions (ash/lime/fluxing agent). It was observed that the mixture with the lowest melting point used to obtain the glass had approximately the following composition: 44% ash, 49% limestone and 7% potassium oxide. This combination resulted in the following oxide percentages: 50.5% SiO_2 , 33% CaO, 7% K_2O and 5.5% MgO. This composition gave a melting temperature (calculated) of around 1300 °C, which was confirmed by thermal analysis (DSC) (Fig. 2).

Fig. 2 shows two endothermic peaks, close to 100 °C, associated with loss of water, a broad exothermic peak around 442 °C due to burning of organic material from ash and an endothermic peak at 766 °C due to release of CO_2 from carbonates. Close to 1280 °C, the fusion of the material occurs, characterized by the small endothermic peak near this temperature. During the cooling of the samples, there was no reaction, and the total loss of mass, due to carbonates and organic material, was 30 wt% (67 wt% residual mass). The glass drop formed in the platinum crucible was again

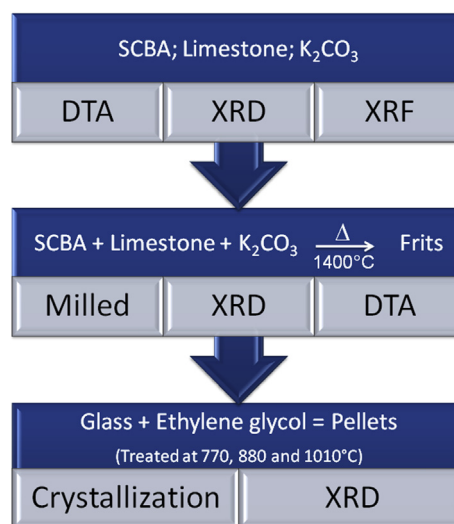


Fig. 1. Flowchart of materials and characterization methods.

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