Glass-Ceramic Material from the SiO$_2$-Al$_2$O$_3$-CaO System Using Sugar-Cane Bagasse Ash (SCBA)

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Glass-Ceramic Material from the SiO$_2$-Al$_2$O$_3$-CaO System Using Sugar-Cane Bagasse Ash (SCBA)

S R Teixeira$^1$, M Romero$^2$, J Ma Rincón$^1$, R S Magalhães$^1$, A E Souza$^1$, G T A Santos$^2$, R A Silva$^1$

$^1$Universidade Estadual Paulista – Unesp/FCT – Presidente Prudente, SP, Brazil
$^2$Instituto Eduardo Torroja de Ciencias de la Construcción – IETCC/CSIC, Madrid, Spain

E-mail: rainho@fct.unesp.br

Abstract. Brazil is the world's largest producer of alcohol and sugar from sugarcane. Currently, sugarcane bagasse is burned in boilers to produce steam and electrical energy, producing a huge volume of ash. The major component of the ash is SiO$_2$ and among the minor components there are some mineralizing agents or fluxing. Published works have shown the potential of transforming silicate-based residues into glass-ceramic products of great utility. This work reports the research results of SCBA use to produce glass-ceramics with wollastonite, rankinite and gehlenite as the major phases. These silicates have important applications as building industry materials, principally wollastonite, due to their special properties: high resistance to weathering, zero water absorption, and hardness among others. The glasses (frits) were prepared mixing ash, calcium carbonate and sodium or potassium carbonates as fluxing agents, in different concentrations. 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 crystallization kinetics was evaluated using the Kissinger method, giving activation energies ranging from 200 to 600 kJ/mol.

1. Introduction

Currently, many researchers have been concerned with studying waste to recycle them or reuse them in new products. From the sustainable perspective development, it is necessary to implement new technologies to help reduce waste and thus minimize the environmental problems associated with disposal. Among the many types of waste studied, the ash generated from burning bagasse from sugar cane, has received special attention due to their characteristics and because it is abundant in countries producing sugar and alcohol. Brazil is the world's largest producer of sugar and ethanol (45% of world production) using sugar cane [1]. For the functioning of the sugar/alcohol industry, sugarcane is ground and the resulting soup is used to extract sugar or used in a fermentation process to produce alcohol. Currently, sugarcane bagasse is burned in a boiler to produce steam which is utilized in the factory’s processes and also to power turbines for the production of electrical energy. As a result of this process obtains two ash (bottom and fly ashes) rich in silicates (> 70 wt %) useless, and therefore it is discarded in the sugarcane plantations [2]. However, the composition of this ash lets use it to obtain stable glass and then turning it into a useful glass-ceramic material [3]. Some silicates with wollastonite as major phase (Neoparies™ and Cryston®) are widely used by the construction industry [4]. This work shows the direct application of sugar cane bagasse ash in the glass-ceramic materials development and evaluates the influence of different ash compositions and fluxing agents in the final crystalline phases obtained.

1 Silvio Rainho Teixeira
Rua Roberto Simonsen, 305, Presidente Prudente, SP, Brazil, 19060-080
Phone number: +55 18 3229 5355

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2. Materials and Method
We used two sugarcane bagasse ash collected at Usina Alto Alegre (denominated SI) and Usina Aralco (denominated MAR), both in Brazil. The ashes were used as a source of silica to obtain the glass (frit). The ashes (AS) were mixed with carbonates of calcium (CC) and sodium (SC) or potassium (PC) in three different concentrations (wt%) which were named: (G2) Glass2 (49.1 AS, 45.9 CC, 5.0 SC), (G3) Glass3 (59.5 AS, 33.4 CC, 7.1 PC) and (G4) Glass4 (50.3 AS, 42.6 CC, 7.1 SC). The initial glass compositions were chosen based on the desired melting temperature calculated for each one (Tf <1450°C) [5]. The glasses were prepared in two steps: (1) the mixtures were kept for two hours at 950°C in a muffle furnace for evaporation of volatile materials and (2) they were melted (750°C/hour) using an oven melting of glass (in LaMaV at UFSCar, Brazil), at 1500°C for one hour. The liquid was poured into a container with water at room temperature for production of frit. They were powdered and analyzed using the techniques of X-ray diffraction and fluorescence (XRD and XRF) to determine whether there was crystallization during cooling and determine the chemical composition of the glass.

The glasses powdered were passed through a 170 mesh (<88 μm) sieve and analyzed using a thermal analysis (DTA/DSC) equipment (TA Instruments, model SDT Q600) to determine the crystallization temperatures. A fraction of each sample was crystallized (1 hour) using a laboratory furnace, at temperatures just above the crystallization temperatures, determined by DTA/DSC. Some samples also were heated at temperatures around the crystallization peaks and quenched. All treated samples were analyzed using XRD equipment (Shimadzu XRD-6000) to identify the formed phases and XRF equipment (Shimadzu EDX 700) to determine the samples chemical compositions. To study the kinetics, the crystallization of each glass sample was monitored using the thermal analysis equipment at heating rates of 10, 15, 20, 25 and 30°C/min and the Kissinger method [6].

3. Results and Discussion
The chemical analyses (XRF) of the ashes (Table 1) show that the ash chemical composition varies according to the region where sugar cane is produced.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Ash</th>
<th>SI</th>
<th>MAR</th>
<th>Glass</th>
<th>SI</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
<th>Glass</th>
<th>SI</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>96.43</td>
<td>90.57</td>
<td>42.58</td>
<td>56.97</td>
<td>45.44</td>
<td>38.26</td>
<td>51.50</td>
<td>36.87</td>
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<tr>
<td>Al₂O₃</td>
<td>0.55</td>
<td>1.05</td>
<td>9.81</td>
<td>1.92</td>
<td>9.66</td>
<td>15.02</td>
<td>5.95</td>
<td>17.55</td>
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<tr>
<td>Fe₂O₃</td>
<td>1.47</td>
<td>2.46</td>
<td>0.37</td>
<td>0.48</td>
<td>0.37</td>
<td>0.92</td>
<td>1.26</td>
<td>0.89</td>
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<tr>
<td>Na₂O</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>6.24</td>
<td>&lt; 0.001</td>
<td>9.55</td>
<td>5.75</td>
<td>&lt; 0.001</td>
<td>9.42</td>
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<td>K₂O</td>
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<td>3.03</td>
<td>0.45</td>
<td>6.34</td>
<td>0.49</td>
<td>1.29</td>
<td>7.61</td>
<td>1.33</td>
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<td>CaO</td>
<td>0.10</td>
<td>0.56</td>
<td>38.12</td>
<td>32.5</td>
<td>32.99</td>
<td>36.94</td>
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<td>32.15</td>
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<tr>
<td>MgO</td>
<td>0.17</td>
<td>0.62</td>
<td>0.70</td>
<td>0.54</td>
<td>0.75</td>
<td>0.91</td>
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<td>TiO₂</td>
<td>0.19</td>
<td>0.4</td>
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<td>0.07</td>
<td>0.15</td>
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<td>P₂O₅</td>
<td>0.18</td>
<td>0.55</td>
<td>0.23</td>
<td>0.25</td>
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<td>0.37</td>
<td>0.41</td>
<td>0.28</td>
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<tr>
<td>L.O.I.</td>
<td>0.10</td>
<td>0.73</td>
<td>0.61</td>
<td>0.22</td>
<td>0.38</td>
<td>0.30</td>
<td>0.26</td>
<td>0.39</td>
<td></td>
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</tr>
</tbody>
</table>

Table 1: Chemical composition (XRF) of the ashes and glasses.

Ash SI has a higher concentration of silica because it was collected in the water channel that came from the gas washer and pass underneath the boilers carrying both ashes (fly and bottom). Therefore, this is a washed ash with higher silica and lesser salts concentrations. The main difference in the chemical compositions of glasses is due to differences in the ashes composition (ash MAR has
more flux, iron oxide and nucleating agents, than the ash SI). The highest concentration of flux results in a higher corrosion of alumina crucible, increasing the concentration of aluminum and sodium in the glass. Therefore, glass obtained with the ash MAR have higher concentrations of these two oxides.

Ashes with sodium (G2 and G4) erode the crucibles more than those (G3) with potassium. The presence of alumina reduces the tendency to devitrification increases the viscosity and melting temperature of the glass. It also induces the crystallization of silicates of the system SiO₂-Al₂O₃-CaO.

The thermograms (DSC/DTA), Figures 1(a) and (b), of SI and MAR glasses, show the crystallization peak (T_c), the glass transition (T_g) and melting temperature (T_m). The crystallization DTA peaks shifts with the heating rate so, the peak temperatures in table 2 were obtained from thermograms using higher (dT/dt) than those shown in figure 1. The X-ray diffraction data (Figure 2) of the crystallized glasses show that there is a simultaneous crystallization of several silicates, with crystallization temperatures very close, as shown in the results of DTA/DSC. The crystallization temperatures (T_c) shift to higher values as the heating rate increases. The activation energy of crystallization (total, not separate phases) for each peak of crystallization was determined using the Kissinger method (Table 2), which takes into account the heating rate and crystallization temperature.

Table 2 shows that the formation of calcium silicates is dominant. In the other samples with high concentration of aluminum, G2 and G4, were also identified some aluminum silicates. These results are consistent with the phase diagram of the system SiO₂-Al₂O₃-CaO [4,7]. The main identified phases were wollastonite, gehlenite and rankinite, which are similar to natural stones such as marble and granite. This glass-ceramic material has properties equal or superior to those presented by natural stones used as coating in buildings.

![Figure 1: DTA/TG of glasses (a) SI, (b) Mar (heating rate, 15°C/min, except to G4 SI).](image)

![Figure 2: XRD patterns of glasses G2, G3 and G4: (a) SI 940°C; (b) Mar 940°C; (c) Mar 1050°C](image)
Table 2: Activation energy (Kissinger) and crystalline phases (XRD) glasses

<table>
<thead>
<tr>
<th>Glasses</th>
<th>Peak 1 (°C)</th>
<th>$E_a$ (kJ/mol)</th>
<th>XRD Phases</th>
<th>Peak 2 (°C)</th>
<th>$E_a$ (kJ/mol)</th>
<th>XRD Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2</td>
<td>948</td>
<td>235 ± 3.4</td>
<td>Ge; Wo 2M; Ra</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>SI G3</td>
<td>931</td>
<td>341 ± 33</td>
<td>Ca-Si; Wo 1A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G4</td>
<td>928</td>
<td>355 ± 10</td>
<td>Ca-Si; Cri; Ca-Al-Na-Si; Ne Ge; Na-Ca Si; Wo 2M</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>G2</td>
<td>910</td>
<td>223 ± 5.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mar G3</td>
<td>935</td>
<td>291 ± 22</td>
<td>Wo 2M; Ca Oxide-Si; Ge</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G4</td>
<td>879</td>
<td>572 ± 66</td>
<td>Cri; Ca-Si; Ge; Ne</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Si: Silicate; Ge: Gehelenite; Wo: Wollastonite; Ra: Rankinite; Cri: Cristoballite; Ne: Nepheline. Peak 1 and 2 were obtained with a heating rate of 20 °C/min.

The crystallized phases (Fig. 2) were defined by the chemical compositions of the glasses shown in Table 1. Therefore, the chemical composition of glass is more important than that of the initial mixture. Moreover, the chemical composition of the glass need not be exact because the ash has numerous secondary components and impurities, as usually happens with other waste used to produce glass ceramic material [4].

4. Conclusion
The ash chemical composition varies according to the soil where sugar cane is harvested. Comparing the results, we can state that potassium (G3) favors the formation of a glass-ceramic with a smaller number of phases, one of which is wollastonite. With respect to the concentration of sodium, G2 (5%) with lower concentration than G4 (7%) presents the three phases (Ge, Wo and Ra) provided in the phase diagram that are important for building applications. Therefore, a useful and interesting use for the SCBA is the production of ceramic plates for the civil construction industry.

Acknowledgments
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References