HYDRATION STUDY OF SUGAR CANE BAGASSE ASH AND CALCIUM HYDROXIDE PASTES OF VARIOUS INITIAL C/S RATIOS

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Abstract

The present paper exhibits an investigation on the reactions between calcium hydroxide (CH) and sugar cane bagasse ash (SCBA). For this purpose, pastes of various initial CaO/SiO₂ (C/S) molar ratios were produced. The formed products were analyzed by thermal analyses, X-ray diffraction, scanning electron microscopy and energy dispersive spectrometer. The results show that the main product was found to be C-S-H of not specific morphology and that could not be related to the known products C-S-H (I)/C-S-H (II). Calcium alumino silicate hydrates and calcium aluminate hydrate, in the form of fine plates or needles, were also produced.

1. INTRODUCTION

The sugar cane bagasse ash (SCBA) is a by-product of the sugar and alcohol industry and its incorporation as pozzolanic admixture in cement-based materials has shown to be of great value. Indeed, the current literature has shown that this addition can bring both environmental and technological benefits. The use of SCBA as cement replacement assumes sustainable aspect once it provides a final destination for a residue of difficult degradation and it reduces CO₂ emissions generated by cement production. In fact, Fairbairn et al. [1] have shown the great potential for the generation of carbon credit if the addition of SCBA is applied in industrial scale. On the other hand, several studies [2-4] have demonstrated that this addition results in the enhancement of mechanical and chemo-physical properties, such as compressive strength and durability, and also of rheological characteristics of concretes, mortars and pastes.

The effect of the addition in the performance of cement-based materials can be explained by both physical and pozzolanic effect. While the first is related to the influence of the ash in...
the packing characteristics of the granular mixture, the second is associated with the ash’s potential in providing siliceous/aluminous amorphous compounds to react with calcium hydroxide (CH) in the presence of water. The study of the pozzolanic reaction is commonly performed in systems formed by CH, water and pozzolan due to their simplicity, when compared to cement-pozzolan-water systems [5].

Few authors have investigated the products formed in the system SCBA-CH-water [6-9]. The main product of this reaction is known to be calcium silicate hydrate (C-S-H). However, besides its usually high silica content (60%-70%), this ash normally presents significant amounts of alumina [e.g. 4, 7, 9]. Therefore, the production of calcium alumino silicate hydrates (C-A-S-H) and calcium aluminate hydrate (C-A-H) is also expected [8]. Also, not much about the C-S-H formed has been said. Frias and Villar-Cociña [9] stated that it is mainly amorphous and of low CaO/SiO₂ (C/S) ratio. Because of these characteristics, it would be reasonable to correlate this product with the C-S-H (I) formed in the reaction between hydrous silica and CH, as described by Taylor [10]. Nevertheless, no attempt in that direction has been made.

In the present paper, the reaction between SCBA and CH, in the presence of water, and its products were studied. The evolution of the reaction and the nature of the products were investigated by thermal analyses and X-ray diffraction. Scanning electron microscopy (SEM) images and energy dispersive spectrometer were used in the study of the composition and morphology of the products.

2. EXPERIMENTAL METHODS

2.1 Materials and Mixtures

The sugar cane bagasse ash was obtained from the controlled burning and grinding of a residual ash. The raw ash was collected during the cleaning procedure of the main boiler in a sugar/alcohol plant located in the state of Rio de Janeiro, Brazil. In order to decrease the high carbon content of that ash (indicated by the value of loss on ignition presented in Table 1), the residual ash was burnt in a muffle furnace at 350 ºC for 3 hours, and then at 600 ºC for another 3 hours [11]. Finally, the ash was dry ground during 8 hours in a rotational ball mill at 30 rpm.

Table 1: Chemical composition of the residual SCBA and SCBA (% by mass)

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>K₂O</th>
<th>MnO</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual SCBA</td>
<td>53.17</td>
<td>13.92</td>
<td>4.44</td>
<td>1.48</td>
<td>2.35</td>
<td>0.06</td>
<td>0.76</td>
<td>1.25</td>
<td>1.63</td>
<td>20.92</td>
</tr>
<tr>
<td>SCBA</td>
<td>69.58</td>
<td>15.72</td>
<td>5.68</td>
<td>1.33</td>
<td>2.15</td>
<td>0.08</td>
<td>0.88</td>
<td>0.93</td>
<td>1.56</td>
<td>2.09</td>
</tr>
</tbody>
</table>

*LOI – loss on ignition

The obtained SCBA had BET specific surface area of 25.00 m²/g. From the particle size distribution (Figure 1), it is possible to observe that the SCBA presents D₅₀ of 7.37 μm and, therefore, can be classified as ultrafine (D₅₀ < 10 μm). Table 1 exhibits the chemical composition of the SCBA, obtained by X-ray fluorescence method (EDX 800-Shimadzu with
Rh tube target), and its loss on ignition. It is noteworthy the final SCBA presented high silica content (almost 70%) and low loss on ignition. The X-ray diffraction pattern, shown in Figure 3, indicates the presence of quartz. In addition, the detail in Figure 3b reveals a slight background hump between the Bragg’s angles of 15º and 30º, indicating that there is amorphous silica in the ash. Similar findings have been observed in several works on residual bagasse ash [4,7,9].

![Figure 1: Particle size distribution of the SCBA](image1)

![Figure 2: X-ray diffraction pattern of SCBA. In (b), the detail of the background hump between the Bragg’s angles of 15º and 30º, an indicative of the presence of amorphous silica in the ash.](image2)

Besides the produced SCBA, chemically pure calcium hydroxide and deionized water were used, in the preparation of the pastes. They were manually prepared, with initial molar C/S ratios of 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 and 1.4. The water/solid ratio, in mass, was 1.3 for all mixtures. This ratio was selected in order to allow the homogeneous mixing of the
components. The pastes were cured in sealed plastic films in a temperature controlled room at 40 °C until the tests. In the present work, the samples were named as SCBA-\(x\), where \(x\) stands for the C/S ratio of the mixture.

### 2.2 Testing

The thermal analyses (TG, DTG and DTA) were performed in a TA Instruments SDT Q 600 thermoanalyser under the following experimental conditions: inert atmosphere (N\(_2\)), maximum flow of 100 ml/min, heating rate of 10 °C/min, from 25 °C to 1000 °C and sample of approximately 10 mg in a platinum crucible. The samples were analysed after 28 and 50 days of curing, without previous drying. Their high water content explains the large step found at the beginning of the TG curve (Figure 3). The unreacted CH and CaCO\(_3\) present in the mixtures were quantified based on the mass losses (\(\Delta m\)) that occurred during the decomposition of each compound, according to:

\[
CH(\%) = 4.11 \times \Delta m_{CH} \\
CaCO_3(\%) = 2.27 \times \Delta m_{CaCO_3}
\]

![Figure 3: Typical TG curve for the SCBA-CH pastes.](image)

The characterization by X-ray diffraction (XRD) was carried out in a Bruker D8 Focus diffractometer with Cu\(_{\alpha}\) tube, 40 kV and 40 mA. Only three pastes were selected to be tested: SCBA-0.5, SCBA-0.7 and SBCA-1.4 and the tests were performed at 50 days of curing. Scanning electron microscope (SEM) images were obtained in a JEOL JSM 6460 LV microscope, operating in 20 kV and with working distance of about 10 mm. An energy dispersive x-ray spectrometer (EDS) Thermo C 1015 was also used. The samples were gold-coated under vacuum.

### 3. RESULTS AND DISCUSSION

The thermal analyses results at the ages of 28 and 50 days of curing are shown in Figures 4 and 5, respectively. The DTG and DTA curves exhibit endothermic peaks at approximately 90 °C, 400 °C and 600-650 °C, which are related to the decomposition of C-S-H, CH and CaCO\(_3\), respectively. Other endothermic peaks can be noticed in the DTG curves - they
correspond to the decomposition of gehlenite hydrate (C$_2$ASH$_8$), tetracalcium aluminate hydrate (C$_4$AH$_{13}$) and hydrogarnet (C$_3$ASH$_6$), at about 120 ºC, 195 ºC and 240ºC, respectively [12]. It is worthy of note that, while the gehlenite hydrate can be found in all pastes, tetracalcium aluminate hydrate is not detected in the mixtures with C/S ratios from 0.9 to 1.4. Besides that, SCBA-1.4 is the only mixture that exhibited the peak related to the dehydration of hydrogarnet.

It is also important to notice that in the DTA curves, no exothermic peak was detected in high temperatures. This is an indicative that the C-S-H formed in the reactions between CH and SCBA cannot be related to the one from the reaction between hydrous silica and CH studied by Taylor [10].

Figure 4: DTG (a) and DTA (b) curves of the SCBA-CH pastes after 28 days of curing

Figure 5: DTG (a) and DTA (b) curves of the SCBA-CH pastes after 50 days of curing

The quantification of unreacted CH and CaCO3 present in the pastes after 28 and 50 days of curing is shown in Table 2. In the SCBA-0.5 and SCBA-0.6, all CH was consumed after 28 days, whereas in the other mixtures, not even 50 days were enough for the complete consumption of CH. It is likely that in the pastes of C/S ratio of 0.5 and 0.6, all CH reacted due to excess of ash in the system - once more CH was added to the system, there was evidence of reaction after 28 days. From the mixtures that exhibited CH consumption between 28 and 50 days of curing, SCBA-0.7 is the one with least unreacted compounds.
The thermal analyses results were corroborated by those obtained from the X-ray diffraction of the pastes SCBA-0.5, SCBA-0.7 and SCBA-1.4 (Figure 6). The X-ray patterns show peaks related to CaCO$_3$ and quartz in all three mixtures, whereas only SCBA-1.4 exhibited peaks associated with CH. It is worth noting that the X-ray analyses did not suggest the presence of any crystalline product from the reaction between SCBA and CH, an indicative they most likely have low or null crystallinity degree. Frías and Villar-Cociña [8] had similar findings in their work.

Table 2: Amount of CH and CaCO$_3$ in the SCBA pastes after 28 and 50 days of curing, from the thermogravimetric analyses

<table>
<thead>
<tr>
<th>C/S</th>
<th>CH (%)</th>
<th>CaCO$_3$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>28 days</td>
<td>50 days</td>
</tr>
<tr>
<td>0.5</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.6</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.7</td>
<td>2.01</td>
<td>1.36</td>
</tr>
<tr>
<td>0.8</td>
<td>3.74</td>
<td>2.26</td>
</tr>
<tr>
<td>0.9</td>
<td>4.32</td>
<td>2.92</td>
</tr>
<tr>
<td>1.0</td>
<td>5.39</td>
<td>3.66</td>
</tr>
<tr>
<td>1.4</td>
<td>6.13</td>
<td>6.04</td>
</tr>
</tbody>
</table>

Figure 6: X-ray diffraction patterns of SCBA-0.5, SCBA-0.7 and SCBA-1.4

SEM images of the products formed in the paste SCBA-0.7 are shown in Figure 7. The C-S-H appears as a dense net with inclusions of C-A-S-H/C-A-H in the shape or thin plates.
and needles deposited inside its pores (Figure 7a). In Figure 7b, the SEM image was made with higher magnification and it is possible to better observe that the C-S-H net is formed by amorphous agglomerations, and not by fibrillar structures, as it is the case of C-S-H (I). Although the plate like structures are very much alike the known shape for CH, the EDS analysis of the plate marked in Figure 7c indicated that it is, in fact, an aluminate product. The spectrum is presented in Figure 7d.

Figure 7: Scanning electron microscopy images of SCBA-0.7. In (b), the amorphous agglomerations that form the C-S-H net. In detail (c), a plate of C-A-S-H is marked and in (d), its EDS spectrum is presented.

4. CONCLUSIONS

- The main product formed in the pozzolanic reactions between SCBA and CH is C-S-H and it appears as a dense net of amorphous agglomerations. In addition, it cannot be correlated with the C-S-H (I) formed in the reaction of hydrous silica and CH.
- C2ASH8, C4AH13 and C3ASH6 are also formed and they appear as thin places or needles deposited inside the pores of the C-S-H net.
In SCBA-0.5 and SCBA-0.6, there was the consumption of all CH after 28 days, probably due to lack of this compound in the system. From the mixtures in which reaction took place after 28 days, SCBA-0.7 is the one that presented the least amount of unreacted compounds.

REFERENCES


