Studies on SCLA composite Portland cement

N B Singh*, S S Das†, N P Singh‡ & V N Dwivedi‡
*Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273 009, India
†Department of Chemistry, U P Autonomous College, Varanasi 221 005, India

Received 28 January 2009; accepted 16 October 2009

Ecofriendly composite cements may be obtained by partial replacement of Portland cement with certain low cost materials. Sugarcane leaf ash (SCLA) is one such material which is obtained by firing sugar cane leaf in an open atmosphere and then calcined at 600°C for 2 h in a muffle furnace under oxygen atmosphere. Hydration of 10 wt% SCLA composite Portland cement was studied by using powder X-ray diffraction, FTIR spectroscopy, differential scanning calorimetric and other techniques. The results have shown that the pozzolanic reaction of sugarcane leaf ash increases with time. The compressive strength of 10 wt% SCLA composite Portland cement at 28 days of hydration is comparable to that of OPC alone.

The critical housing situation in many developing countries necessitates finding appropriate low-cost building materials. Building materials such as lime and Portland cement are energy based and therefore expensive. However, pozzolanic waste-materials can be used as partial substitutes for Portland cement. It is well known that generation of solid waste materials poses large number of disposal problems and pollute the atmosphere. For this reason it is important to develop some technology which can use these waste materials for useful purposes. In recent years numbers of industrial and agricultural byproducts and wastes have been used to prepare composite cements. The behaviour of composite cement is quite similar to that of Portland cement. The most common replacement materials are latent hydraulic component slag or a pozzolanic component such as pozzolana, fly ash, rice husk ash, condensed silica fume, burnt clay or filler components such as limestone and other waste materials.

The reuse of waste materials for concrete production is a worldwide practice. It is known that the incessant generation of solid waste materials present serious problem. The recycling of industrial wastes from the agricultural sector is increasingly encouraged, particularly in developing countries. In recent years, the use of solid waste derived from agriculture as pozzolanas in the manufacture of blended mortars and concrete has been the focus of research. The utilization of waste materials in concrete manufacture provides a satisfactory solution to some of the environmental concerns and problems associated with waste management. Agro wastes such as rice husk ash, wheat straw ash, hazel nutshell and sugarcane bagasse ash are used as pozzolanic materials for the development of blended cements. At the same time the addition of these waste materials reduce CO₂ gas emission responsible for global warming. Most of these ashes have pozzolanic properties. These materials increase the durability of concrete and the rate of gain in the strength of the cement. They may also reduce the rate of heat librations which is beneficial in mass concrete.

Sugarcane bagasse ashes (SCBA) have been used for making blended cements. The ashes from bagasse of the sugarcane have been shown to have pozzolanic properties and when added to cement, improve its strength and durability. The ash produced by controlled burning of agro waste materials below 700°C for one hour transforms silica content of the ash into amorphous silica and can be used as a pozzolanic material. SCBA calcined at 800-1000°C were found to have high pozzolanic activity. However it is also reported that pozzolanic activities decreased with increasing calcining temperatures. This fact could be related to the recrystallization of amorphous silica. Further, it is not clear whether the improvement in properties in the presence of SCBA is due to physical or chemical effects.

*For correspondence (E-mail: dr_n_b_singh@rediffmail.com)
Ashes obtained from other parts of the sugarcane also possess pozzolanic properties and can be used for making composite cements. A limited study on the use of sugarcane straw ash (SCSA) as a blending component has also been made. It is reported that calcining temperature has no effect on pozzolanic activity of SCSA. Practically no literature is available on exclusive use of sugarcane leaf ash as a blending component. It is experienced that it is easy to make ash from sugarcane leaf comparatively at lower temperature. Therefore, the objective of the present investigation is to prepare sugarcane leaf ash composite Portland cement and study its hydration characteristics to understand physico-chemical properties.

Experimental Procedure

Materials

Preparation of sugarcane leaf ash

Dry sugarcane leaves were burned in an open air and the black coloured ash was collected and crushed into fine powder. The ash was then calcined in a muffle furnace under the supply of oxygen at 500, 600, 700 and 800°C for 1, 2, 3 and 4 h. Heating even for 4 h at 500°C did not remove the unburned carbon from the ash. When the ash was calcined at 600°C for 2 h, all the carbon particles burned. Heating at higher temperatures reduced the time of burning of carbon particles. Thus, sugarcane leaf ash was prepared by calcining the ash at 600°C for 2 h. The ash was ground into fine powder and allowed to pass through a sieve of 300 mesh. This fine powder of sugarcane leaf ash (SCLA) was used as a blending component. The SCLA was characterized by SEM and powder X-ray diffraction techniques (Figs 1 and 2).

Ordinary Portland cement

Vikram premium OPC 53 cement was used for hydration studies. The chemical compositions of SCLA and ordinary Portland cement (OPC) are given in Table 1. The mineralogical composition of OPC is given in Table 2. The particle size distributions of SCLA and OPC determined by laser granulometer are shown in Fig. 3.

Methods

Preparation of composite cement

Composite cement was prepared by mixing 10 wt% SCLA with ordinary Portland cement thoroughly in a ball mill.

Determination of standard water consistency

The water consistencies of OPC and the composite cement were determined by Vicat apparatus (I S: 4031 part 4, 1988).

Determination of setting times

The Initial and final setting time of the cement in the absence and presence of 10 wt% SCLA was

---

### Table 1 – Oxide compositions

<table>
<thead>
<tr>
<th>System</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>SO₃</th>
<th>IR</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>21.40</td>
<td>5.03</td>
<td>4.40</td>
<td>61.14</td>
<td>1.35</td>
<td>0.48</td>
<td>0.24</td>
<td>-</td>
<td>2.53</td>
<td>1.65</td>
<td>1.29</td>
</tr>
<tr>
<td>SCLA</td>
<td>74.79</td>
<td>1.87</td>
<td>0.48</td>
<td>6.39</td>
<td>2.42</td>
<td>2.37</td>
<td>0.15</td>
<td>0.10</td>
<td>1.36</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

---

### Table 2 – Mineralogical composition of OPC-53

<table>
<thead>
<tr>
<th>Mineral phase</th>
<th>Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_S</td>
<td>38.89</td>
</tr>
<tr>
<td>C₂S</td>
<td>31.83</td>
</tr>
<tr>
<td>C₃A</td>
<td>6.06</td>
</tr>
<tr>
<td>C₆AF</td>
<td>13.37</td>
</tr>
</tbody>
</table>

---

Fig. 1—SEM picture of sugarcane leaf ash heated at 600°C for 2 h

Fig. 2—Powder X-ray diffraction pattern of Sugarcane leaf ash

---
determined with the help of Vicat apparatus (I S: 4031 part 5, 1988).

**Determination of compressive strength**

OPC and OPC–10 wt% SCLA composite cement were mixed separately with sand (in 1:3 ratios) and water (I S: 4031 part 4, 1988). The mortars were placed in steal moulds of 70.6 mm\(^3\) dimension. The cubes were demoulded after one day and stored in water at 27ºC for different days (1, 3, 7 and 28). These cubes were taken out from water prior to testing. The compressive strengths were determined after 1, 3, 7 and 28 days of hydration as per I S: 4031 part 6, 1988 method.

**Preparation of hydrated Samples**

10 g of OPC and OPC-10 wt% SCLA composite cement were weighed separately in different polythene bags and mixed with 3 mL water so that w/s ratio was 0.3. The air inside the bags was removed to avoid carbonation. The hydration reaction was allowed to occur at room temperature (≈28 ºC). The hydrations of OPC and OPC-10 wt% SCLA composite cement were stopped after 1, 3, 7, 14, 28 and 90 days by adding isopropyl alcohol and diethyl ether. The hydrated samples were heated at 105ºC for 1 h, stored in polythene bags and kept in a desiccator.

**X-Ray diffraction studies**

Powder X-ray diffraction studies of OPC-10 wt% SCLA composite cement hydrated for 1, 7 and 28 days were made by using CuK\(_{α1}\) radiation.

**DSC studies of hydrated samples**

DSC studies of the hydrated cement samples were made on NETZSCH STA 409 PC instrument in the temperature range of 30-1000ºC in nitrogen atmosphere at a heating rate of 10ºC/min.

**FTIR Spectral studies**

FTIR spectra of the hydrated samples were recorded in the range 400-4000 cm\(^{-1}\) with the help of a Bruker Vertex 70 spectrometer using KBr pellets.

**Free lime determination**

Free limes in all the hydrated samples were determined by a method described elsewhere\(^{33}\). About one gram of the hydrated cement was refluxed with 40 mL of isopropyl alcohol and acetoacetic ester mixture (20:3) for one hour. The solution was filtered and titrated against 0.1N HCl using bromophenol blue as an indicator. The percent free lime was determined by using the following equation;

\[
\% \text{ free lime} = 0.2804 \times \frac{V}{W}
\]

where \(V\) is the volume of 0.1N HCl used in the titration and \(W\) is the weight of the hydrated cement.

**Determination of non-evaporable water contents**

Approximately one gram of the cement samples hydrated for different time intervals (1, 3, 7, 14, 28 and 90 days) were weighed separately in ceramic crucibles and heated at 105ºC for 1 h and weighed. The crucibles were heated at 1000ºC for 1 h and from the weight losses the non-evaporable water contents (\(W_n\)) were calculated.

**Determination of Ca\(^{++}\) ion concentration in solution**

10 g of OPC and OPC-10 wt% SCLA composite cement were taken separately in different polythene bags. 20 mL water was added in each bag (w/s = 2.0). At different intervals of time, viz., 5, 10, 20, 30, 60, 120, 180, 240 and 300 min, the solutions were filtered and titrated against standard EDTA solution to determine Ca\(^{++}\) ion concentration. Due care was taken to avoid carbonation.

**Results and Discussion**

The standard water consistency and setting times of OPC and OPC-10 wt% SCLA composite cement are given in Table 3. The values of non-evaporable water contents (\(W_n\)) of both hydrated OPC and OPC-10 wt% SCLA composite cement were found to increase with time indicating an increase in hydration (Fig. 4). However, the values of \(W_n\) up to 28 days of hydration for OPC–10 wt% SCLA composite cement were found to be lower than those of ordinary Portland cement but at 90 days, they are quite comparable. This shows that the pozzolanic activity of SCLA is increased between 28-90 days of hydration.
In order to know the pozzolanic activity of SCLA, free lime contents during hydration were determined. The variation of percent free lime values with hydration time is shown in Fig. 5. The free lime values in both the cases were found to increase with time showing increased hydration. The free lime values in the case of composite cement are found to be lower than those of OPC and this lowering was enhanced between 28-90 days. This is due to acceleration of pozzolanic reaction between the amorphous silica present in SCLA and Ca (OH)$_2$ formed during the hydration of Portland cement.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water consistency (SC %)</th>
<th>Setting times (min)</th>
<th>Initial setting time</th>
<th>Final setting time</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>25.75</td>
<td>150</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>OPC-10 wt% SCLA</td>
<td>28.5</td>
<td>145</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

Powder X-ray diffraction patterns of OPC-10 wt% SCLA composite cement hydrated for 1, 7 and 28 days give information regarding the hydration products (Fig. 6). The diffraction patterns show that the intensity of the calcium hydroxide peak decreased with the increasing hydration time. This indicates that the pozzolanic reaction between Ca (OH)$_2$ and amorphous silica present in SCLA has increased. Low intensity peaks for ettringite formation are observed in the diffraction pattern of the composite cement hydrated for 1 day. However these peaks disappeared in the composite cement hydrated for 7 and 28 days. This may be due to conversion of ettringite into monosulphate phase after 1 day of hydration.

Solution concentrations control the hydration process, so the Ca$^{++}$ ion concentrations in the liquid phase were determined. The variation of concentrations of Ca$^{++}$ ions for OPC and OPC-10 wt% SCLA composite cement in the liquid phase for different hydration times are given in Fig. 7. The figures show that Ca$^{++}$ ion concentrations decreased with time in both the cases. When cement comes in
contact with water, Ca\(^{++}\) ions go into the solution. The concentration of Ca\(^{++}\) ions, in the liquid phase, increases and reaches to a maximum value making the solution saturated or supersaturated with respect to Ca\(^{++}\) ion concentration. Once the concentration of Ca\(^{++}\) ions become maximum, its value starts decreasing with time due to precipitation of different hydration products of calcium. In the case of OPC-10 wt% SCLA composite cement, the trend is similar but the values of Ca\(^{++}\) ions are lower. This is due to pozzolanic reaction. Thus in general OPC–10 wt% SCLA composite cement behaves in a similar way as OPC.

DSC studies give information about the nature of hydration products. The DSC curves of OPC hydrated for 1 day and 28 days in the absence and presence of 10 wt% SCLA are shown in Fig. 8. In the case of OPC, hydrated for one day, number of endothermic peaks is obtained which indicate decomposition of different hydration products. A broad endothermic peak at about 120°C is due to the decomposition of ettringite/gypsum/aluminohydrate and calcium silicate hydrate (C-S-H) phases\(^{23,24}\). A very strong endothermic peak at 486.3°C is due to dehydroxylation of the portlandite (calcium hydroxide). An endothermic peak at 701.9°C may be due to decomposition of monocarbonate phase, whereas a peak at 746.4°C is due to the decomposition of calcium carbonate formed as a result of carbonation during hydration. The DSC thermogram of OPC hydrated for 28 days shows almost same number of endothermic peaks as shown by OPC hydrated for one day. The only difference is that the peaks are shifted towards higher temperatures with an increase in the peak areas. This indicates that large amounts of hydration products are formed when the time of hydration is increased. The onset and peak temperatures (443.7°C, 486.3°C) for the decomposition of portlandite at one day of hydration are lower than those of the cements hydrated for 28 days (454.6°C, 499.8°C). These results show that the portlandite is converted to a more crystalline form when subjected to hydration for a longer time. The two endothermic peaks appearing at 691.3°C and 750.7°C may be due to the decomposition of monocarbonate phase and crystalline calcium carbonate.

In the DSC curve of OPC-10wt% SCLA composite cement hydrated for one day, a broad endothermic peak at 120.4°C is obtained. This is again due to the decomposition of the ettringite / gypsum / aluminohydrate and C-S-H phases. The intensity of the peak due to decomposition of calcium hydroxide at 469.8°C is much lower as compared to that of OPC hydrated for 1 day. This indicates that in the presence of 10 wt% SCLA, the pozzolanic reactions occur at an early time of hydration. Two endothermic peaks at 768.2 and 780.7°C are due to decomposition of monocarbonate and crystalline calcium carbonate respectively. The cement hydrated for 28 days in the presence of 10 wt% SCLA, shows a broad endothermic peak at 127.4°C again due to the decomposition of ettringite/gypsum/aluminohydrate and C-S-H phases. An endothermic peak at 493.8°C is due to dehydroxylation of the portlandite. The intensity

![DSC curves of OPC and OPC-10 wt% SCLA composite cement hydrated for 1 and 28 days](image-url)
of this peak is lower than that of OPC hydrated for 28 days. The endothermic peaks at 721.4°C and 761.3°C may be due to the decompositions of monocarbonate and calcium carbonate respectively.

The heat of dehydroxylation of calcium hydroxide increases with the hydration time in the absence and presence of 10 wt% SCLA (Fig. 9). This in turn indicates that the formation of portlandite has increased with the hydration time. However, the values are lower in the presence of 10 wt% SCLA. The lowering in the amount of calcium hydroxide indicates the pozzolanic reaction of SCLA.

To identify the hydration products, FTIR spectra were recorded. The FTIR spectra of anhydrous ordinary Portland cement is shown in Fig.10a. The bands appearing at 465.0, 521.7 and 930.4 cm\(^{-1}\) are due to Si–O in plane bending (\(\nu_2\)), Si–O out-of-plane bending (\(\nu_4\)) and Si–O asymmetric stretching (\(\nu_3\)) vibrations respectively. These vibrations occur due to the silicate phase of the cement. The \(\text{SO}_4^{2-}\) group of gypsum shows a sharp band at 1108.3 and a shoulder at 1186.4 cm\(^{-1}\) respectively which are due to S–O stretching vibrations (\(\nu_3\)). The two bands appearing at 619.6 and 638.32 cm\(^{-1}\) are due to the bending vibrations of S–O linkage in the \(\text{SO}_4^{2-}\) group respectively. These vibrations occur due to the carbonate group present in the cement. The bands at 3425.8 (stretching) and 1596.7 cm\(^{-1}\) (bending) are due to adsorbed water molecules.

The FTIR spectra of OPC and OPC-10 wt% SCLA composite cement, both hydrated for 1 day, are shown in Figs10b and 10c respectively. From their spectra it has been observed that the asymmetric Si–O vibrational frequencies in the case of OPC and OPC-10 wt% SCLA composite cement were found to shift towards higher wave numbers (985.8 cm\(^{-1}\) and 994.0 cm\(^{-1}\) respectively). This indicates the polymerization of \(\text{SiO}_4^{4-}\) units leading to the formation of calcium silicate hydrate. The other Si–O vibrational frequencies were also found to shift. The intensity of the shoulder at 1186.4 \(\text{cm}^{-1}\) due to S–O stretching vibration of \(\text{SO}_4^{2-}\) group in the spectra of anhydrous cement decreased considerably when it was hydrated for one day. However, in the spectra of hydrated OPC-10 wt% SCLA composite cement the shoulder appearing around 1118 \(\text{cm}^{-1}\) with very low intensity indicates the formation of mono calcium alumino sulphate hydrate phase after one day of hydration\(^\text{25,26}\).

The bands due to carbonate group appearing in the spectra of anhydrous OPC are converted into a single broad band in the range 1430-1500 \(\text{cm}^{-1}\) in the case of OPC hydrated for 1 day. But in the case of OPC-10 wt% SCLA composite cement hydrated for one day, this band splits into three bands appearing at 1353.2, 1406.7 and 1463.2 cm\(^{-1}\). These spectral bands are probably due to the interaction products of SCLA with OPC, or hydration products in addition to the carbonate group present in the composite cement. The bands appearing around 3434.8 \(\text{cm}^{-1}\) in the IR spectra of OPC (hydrated for one day) is due to metal bonded hydroxide which shifts to lower frequency at 3424.2 cm\(^{-1}\) in OPC-10 wt% SCLA composite cement.
hydrated for 1 day. The bending vibrational band appearing at 1600.9 cm\(^{-1}\) in the case of OPC hydrated for one day remains almost unchanged (1598.5 cm\(^{-1}\)) in the presence of 10 wt% SCLA.

The FTIR spectra of OPC and OPC-10 wt% SCLA composite cement samples hydrated for 28 days are given in Figs 10d and 10e respectively. The Si – O vibrational frequencies are shifted and the intensities changed. The Si–O asymmetric vibrational frequency is found to shift towards higher wave numbers, i.e., 976.4 cm\(^{-1}\) and 988.5 cm\(^{-1}\) in the cases of OPC and OPC-10 wt% SCLA composite cement respectively. Similar shifts in the position of other Si–O vibrational frequencies were observed. The shoulder at 1101.6 cm\(^{-1}\) observed for OPC is seen to appear at 1076.2 cm\(^{-1}\) in the case of OPC-10 wt% SCLA composite cement. The bands due to carbonate and metal bonded hydroxide groups were also found to shift in both the cement samples hydrated for 28 days and the change in the intensities of the bands also occurred. During hydration, the bands due to carbonate and metal bonded hydroxide group also shifted and their intensities were changed. The overall IR spectral studies indicate that there is some interaction (both physical and chemical) between cement/hydration products and sugarcane leaf ash during the course of hydration.

The variation of compressive strength of the cement samples with time are shown in Fig. 11. The compressive strength values show an increase with time. But the compressive strength of OPC-10 wt% SCLA composite cement is lower than OPC. However, at 28 days of hydration, the compressive strength of OPC – 10 wt% SCLA composite cement is very close to that of OPC. This may be due to increase of C-S-H phase as a result of pozzolanic reaction as well as packing effect of SCLA particles.

Conclusions
The results have shown that sugarcane leaf ash calcined at 600°C is a pozzolanic material. Up to 10 wt% ordinary Portland cement can be optimally replaced with SCLA without any adverse effect. OPC–10 wt% SCLA composite cement gives compressive strength comparable to that of OPC at 28 days of hydration. However, some additional experiments such as role of calcining temperature, heating duration and use of activators on the pozzolanic activity of SCLA be studied before it can be recommended as a blending component to OPC for low cost construction.

Acknowledgements
The authors are thankful to Prof. Hari Ji Singh, Head, Chemistry Department, DDU Gorakhpur University, Gorakhpur, India for providing laboratory facilities. Authors also thank UGC, New Delhi for financial support.

References