Micro-analytical studies on sugar cane bagasse ash

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MS received 21 July 2014; revised 11 January 2015; accepted 22 January 2015

Abstract. The worldwide production of sugar generates large volumes of bagasse wastes, which are burnt in uncontrolled manner for heating boiler, which are deposited in landfills, which create negative effects in the environment. The ash obtained by burning bagasse is generally used as Supplementary Cementing Material (SCM) in concrete production without proper knowledge of pozzolanic material characterization. This paper summarizes the results obtained from the various techniques to determine pozzolanic mineral profiles in sugarcane bagasse ash (SCBA). Techniques employed in the present study include X-Ray Diffraction (XRD), Energy-Dispersive X-ray Analysis (EDAX) spectrometer, Fourier Transform Infra-Red Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Thermal Analysis [Thermo-Gravimetric Analysis (TGA) and Derivative Thermo-Gravimetric (DTG)] in order to understand the type, form, nature, morphology, concentration, etc. of pozzolanic minerals.

Keywords. Sugar; blended cements; supplementary cementing material; pozzolanic mineral.

1. Introduction

Cement is the third most energy intensive material to produce on a per ton basis. This makes research towards possible modifications of Ordinary Portland Cement (OPC) to better meet the increasing demands for sustainability in the construction sector. It is difficult to alter OPC but its consumption can be reduced by using SCM. In recent years, there has been a clear trend towards investigating the high strength and high performance concrete by using various SCMs obtained from both industrial and agricultural waste products. Last decade only, there is so much focus

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on wastes generated in different agro-industrial sectors (Singh *et al* 2000; Rainho *et al* 2008; Chusilp *et al* 2009; Frias *et al* 2007, 2011; Villar-Cocina *et al* 2008; Savastano *et al* 2005), which are generating serious social and environmental problems, by their accumulation in landfills and burning in uncontrolled manner. Earlier, SCBA has pozzolanic minerals is observed so that the increase in compressive strength of SCBA blended concrete (Martirena *et al* 1998; Singh *et al* 2000).

The objective of this micro-analytical study is to observe the presence of pozzolanic minerals state and their forms in SCBA by using various scientific techniques. In the present work, SCBA is subjected to mineralogical identification with help of XRD and elemental analysis is done by EDAX. Confirmation of mineralogical aspects by FTIR and morphological aspects are studied with help of SEM. Mass changes of minerals with respect to temperature are observed by Thermal analysis. SCBA is obtained from sugarcane industries which are located in Erode district, Tamil Nadu state, India. Generally, a huge amount of bagasse as by-product fibrous waste is obtained after extraction of juice from sugarcane which will yield sugar. This bagasse is used as fuel in cogen boiler for power generation purpose which yields SCBA. Considerable amount of power is generated by burning bagasse in controlled manner, which is available during crane crushing process.

2. Materials and methods

Qualitative analysis involves the identification of the peaks in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Phase identification was carried with a Bruker D2-Phaser XRD-diffractometer, Germany that used monochromatic Cu-K α 1 radiation at 30 kV and 10 mA over the specimens. The samples were scanned in the range of 10–80° 2 θ at the rate of 1.5°/min. Crystalline phases were identified by comprising the intensities and positions of Bragg peak with those listed in the JCPDS-ICDD data files.

Quantitative analyses of minerals are obtained by measuring line intensities for each element in the sample and for the same elements in calibration standards of known composition. EDAX is an analytical technique used for elemental analysis or determination of concentrations of the chemical elements present and the principal in which EDAX spectrometer working is that each voltage pulse is proportional to the energy of the incoming X-ray photon. To know the element composition EDS, ZEISS EVO18 is used in this investigation. The samples were dried and were coated with gold using a sputter coater for 30 seconds and were placed on the carbon tape held in the sample loading assembly. The micrographs were obtained from the SEM, ZEISS EVO18 to know the surface structure, morphology and size of the elements present.

The FTIR is to measure how well, the molecules or groups of atoms on large molecules absorbs or transmits light at each different wavelength on which atoms that constitute the molecule or group, its geometry and its immediate surroundings. The surface chemical bonding and the functional groups were determined by the spectra obtained from FTIR (Nicolet 6700, Thermo Scientifics, USA). The spectral resolution was 4 cm⁻¹ and 256 scans were coded into the mid infrared region (4000 cm⁻¹– 400 cm⁻¹).

Thermal analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere and it can use to quantify the loss of water, loss of solvent, oxidation, decomposition and weight % of ash. The thermal degradation reaction, phase transitions and phase diagrams were obtained from TGA/DTG, NETZCH STA 449F3. The samples were

loaded carefully in to the alumina crucibles and were assessed for thermal degradation from 100°C to 1400°C. The peaks corresponding to the thermal degradation was obtained from the graph.

3. Results and discussion

In XRD, there are continuous intensity changes and the gradual two theta changes which confirmed the continuous gradual change in the internal atomic arrangement of the materials. The continual change in intensity through the diffraction angle shows that there is an abrupt energy reaction occurs and where characteristics of material change is in accordance with structural consideration of minerals.

Most of researchers (Ramirez *et al* 2012; Martirena *et al* 1998; Castaldelli *et al* 2013) worldwide found that the common diffraction angle for SCBA is between 15° and 35° (2 θ), a similar observation is seen in figure 1 having quartz (Q) and cristobalite (C). But most common minerals found are silica in form of quartz and cristobalite form. The presence of silica in the form of cristobalite indicates that part of silica present in SCBA which is in the form of elongated spheres. The material essentially consists of silica structure with small quantities of crystal-phases form as quartz is identified (Abbasi & Zargar 2013; Martirena *et al* 1998). Several other peaks of intensity curve even after 35° (2 θ) also indicates that the presence of quartz. Large amount of quartz is available due to the presence of sand adhering to the sugarcane (Cordeiro *et al* 2008, 2009a, b) or the presence of quartz in fibrous waste itself.

Each element within the sample will have its own critical ionization energy and its own excitation depth. The most of elemental observed in SCBA are observed well below 3 keV and some others up to 7 keV. The presence of Al and Si with oxygen elements shows broadest and tallest peak when compared to all other elemental composition. The most of minerals are observed within 3keV ranges which indicate that the minerals present are lower energy range. For lower energy range, the peaks correspond to the k-shell X rays. The presence of low energy range minerals like Al, K, Mn, P, and Fe having low atomic numbers in the SCBA was observed with EDAX. The higher a peak in the spectrum, the more concentrated is the element in the specimen. EDAX analysis has also confirmed the presence of 11.29% of total silica in the SCBA sample

Figure 1. XRD analysis of SCBA.

Figure 2. EDAX analysis of SCBA.

as shown in figure 2. Apart from the silica other minerals composition observed are Al, Fe, Mn, and K with O elements as higher which indicates that the SCBA has enough pozzolanic mineral. From figure 2, it can be seen that the concentrations of these pozzolanic minerals are high when compared to other lower atomic number minerals.

The FTIR spectrum for SCBA sample is shown in figure 3. The X-ray diffraction is only applicable to materials with a long-range order; it is unable to determine non-crystalline materials. In contrast, FTIR depends on the response of short range molecular scale energetic vibrations such as O–H stretching and bending (Langer & Florke 1974; Kronenberg 1994). As a result FTIR can be applied equally well to crystalline and non-crystalline silica like amorphous, making it as ideal for observing phase transition of cristobalite minerals forms. During this phase of change or transition, the behaviour of oxygen bond to silica present as quartz form can change considerably.

Two different stretching groups are identified in SCBA sample, one is strong band between 500 cm^{-1} and 1100 cm^{-1} and other one is broad band at 3400 cm^{-1} . The strong band clearly indicates that the presence of symmetric stretching vibration of silicon bonds. Sharp absorption peaks below 1400 cm^{-1} are recognised as relating to stretching and bending of Si–O bonds (Langer & Florke 1974). The SiO_4 symmetric stretching vibration is at 820 cm^{-1} and 620 cm^{-1} were observed clearly. The lowest bending mode of Si–O is noted at a band of 500 cm^{-1} . The wavelength band of 1100 cm^{-1} shows that quartz in form of SiO_4 in asymmetric vibration which

Figure 3. FTIR analysis of SCBA.

is tetrahedral shape. Silica in form of cristobalite is present in agreement to the results obtained in XRD analysis.

The broad band at 3400 cm^{-1} is due to symmetric and asymmetric vibration of (O–H) water bounded in ash particles due to hygroscopic nature of it. Broad absorption bands are due to O–H stretching vibrations, with the broad asymmetric band at around 3400 cm^{-1} due to hydrogen bonded molecular water molecule (Graetsch *et al* 1985; Kronenberg 1994). Table 1 confirms the minerals present in SCBA by other researchers related to wave number by using FTIR.

The SEM figure 4(a) shows that their surface contains more number of pores which is elongated oval in shape indicates that they can absorb water or oxygen which promotes the characteristics like sponge, as observed from figure 4(d). The cellulose sheet like pattern is observed in figure 4(d) shows that the crystalline formation of SCBA is not yet completed so that they are accumulated as sub-microcrystalline masses which make them spongy.

The spongy particle indicates that the temperature is not yet reached above sufficient in boiler of sugarcane industry to evolve it. The layered nature of SCBA is observed in figure 4(b) indicates that the elongated shape of SCBA looks like columnar fibrous structure. Figure 4(c) shows that the prismatic tetrahedral systems shape of crystals are present in SCBA and also show that their shape is irregular and their surfaces are smooth in nature.

The SEM has showing characteristics like tetrahedral shape (prismatic), fibrous nature, crystalline masses, and layers, which is similar to that of cristobalite mineral of silica which are crystalline nature. The metastable cristobalite mineral and porous nature of SCBA indicates that the temperature in boiler is reached below 800°C they needed further temperature to form stable reactive pozzolanic mineral. Generally, cristobalite is formed at 1470°C and melts at 1713°C (Deer *et al* 1975; Torikai *et al* 1987). However, it may be formed at lower temperatures when silica is present in high concentrations which show that conformation of results of SEM, XRD and EDAX. Similar observations are observed by other researchers as silica mineral as in large

Table 1. Possible assignment to some of the peaks observed in figure 3.

Wave number (cm^{-1})	Possible assignment	Reference
656–658	SiO_4	Mollah <i>et al</i> (2003), Pera <i>et al</i> (1999)
714	CO_3	Pera <i>et al</i> (1999), Klopogge (2002), Trezza & Lavat (2001), Yu (1999)
847–848	Al–O, Al–OH	Mollah <i>et al</i> (2003), Trezza & Lavat <i>et al</i> (2001)
877–878	CO_3	Mollah <i>et al</i> (2003), Pera <i>et al</i> (1999), Trezza & Lavat (2001), Yu (1999)
1011–1080	Polymerized silica	Mollah (2000)
1100–1200	SO_4	Mollah <i>et al</i> (2000), Pera <i>et al</i> (1999), Ghosh & Handoo (1980), Klopogge (2002)
1400–1500	CO_3	Mollah <i>et al</i> (2000, 2003), Pera <i>et al</i> (1999), Trezza & Lavat (2001), Yu (1999)
1620–1624	Water in sulphates	Pera <i>et al</i> (1999), Ghosh & Handoo (1980), Vazquez-Moreno & Blanco-Varela (1981)
1640–1650	H_2O	Mollah <i>et al</i> (2003), Trezza & Lavat (2001), Richard (2006)
3398–3408	H_2O , capillary water	Richard (2006)
3457	H_2O	Mollah <i>et al</i> (2003), Richard (2006)
3554	H_2O	Mollah <i>et al</i> (2003), Ghosh & Handoo (1980)

Figure 4. SEM analysis of SCBA.

concentrations (Ganesan *et al* 2007; Cordeiro *et al* 2009a, b; Amin *et al* 2011). So, during burning of bagasse, silica reacts to temperature and changes its properties. The dark colour of SCBA indicates that the presence of carbon in it is huge amount. The presence of carbon is high as observed from EDAX, which shows the behaviour of incomplete calcination process of SCBA.

Four decomposition characteristics of endothermic reactions are observed in TGA curve of SCBA as shown in figure 5. The first inflection point of SCBA occurs at peak of 300°C which shows a mass change around -3.44% is due to hygroscopic nature of ash particles which will evolve surface water adsorbed at low temperature of 79.8°C, the mass change per minute about -0.36% is observed in DTG curve and it is already recorded in FTIR results. The next TGA endothermic curve is after 800°C where increase in mass change up to -4.92% because structural rearrangement begins with heating of quartz mineral. However, it is not completed up to approximately 1200°C, after that there is an abrupt change in the Si–O–Si bonding arrangement which is indicated by sharp endothermic reaction on the third TGA curve having a mass change of -3.48% . With an additional increase in temperature, however, there is a continued preferential rearrangement of silica tetrahedral with in newly developed structural framework to attain a more desired arrangement which is observed by change in mass as indicated by TGA curve.

Figure 5. Thermal analysis of SCBA.

The degree of tetrahedral organization is a direct function of temperature and as temperature is increased, and the rearrangement accomplished as observed in DTG curve at 1327.7°C, where mass change per minute is -1% as recorded in DTG curve, indicates that there is a progressive change in dimension of material up to 1449.1°C and it is recorded as drastic change in mass about -15.19% in TGA curve. The total residue finally obtained is 72.84%. Tetrahedral characterization of silica mineral is with cristobalite mineral and mass change after 1200°C indicates that presence of α -cristobalite mineral. This additional change in dimension is slow between 300°C and 800°C due to the metastable nature of quartz minerals, but becomes more stable when the crystallization temperature increases.

The tetrahedral reorganization which occurs above 800°C takes place, which indicates pozzolanic activity of SCBA is only function of temperature. Cristobalite is a high temperature phase of silica, undergoes phase transformation from cubic to tetrahedral structure around 220°C. The high temperature phase of silica, SiO_2 , is stable when temperature is in the range of 1470°C and the melting point at 1728°C is known as β -cristobalite which persists in metastable form up to 275°C and inverts low temperature phase α -cristobalite (Wahal *et al* 1961). The α - β phase transition is rapid and reversible. While heating of SCBA to 1400°C will yield β -cristobalite so that there is a tremendous loss in its mass and while it is again cooled down, it gets converted to α -cristobalite mineral so that it is stable at normal temperatures. Cristobalite is stable at temperatures below 268°C. At higher temperatures it is β -Cristobalite, which is stable in form, with a different crystal structure. This confirms the presence of silicone in the form of crystalline cristobalite mineral from figure 5 by showing a mass loss of 6.62% to 15.19% between temperatures 800°C and 1400°C.

4. Conclusion

An in-depth micro-analytical study of SCBA shows either mechanical method or physical method or chemical method or combination of these methods to form appropriate shape, size, particle surface area, nature of particle surface, etc. of pozzolanic mineral which is directly helpful for improving the pozzolanic activity of SCBA, so that it can be used as supplementary cementitious material in concrete. The cristobalite form of silica which is reactive and easily

combine with calcium and water to form calcium silicate hydrate which will directly contribute to the strength aspects of concrete (Chuanlin Hu *et al* 2014). The present scientific and technical studies on the SCBA by using XRD, EDAX, FTIR, SEM and thermal analysis enabled the following conclusions:

- Silica in form of quartz is present even after 30° (2-theta) by XRD
- In XRD, quartz is observed in the form of cristobalite
- Most of minerals are observed in EDAX are in lower energy range
- K-shell X-rays indicates that the elements present are having mostly lower atomic number
- Other pozzolanic minerals similar to silica like Fe and Al are observed along with oxides in EDAX
- The strong band observation in FTIR shows that the presence of silicon bonds
- The weak band shows the presence of water molecules bonds
- Incomplete calcination of SCBA is observed in XRD, SEM and EDAX
- Crystalline cristobalite mineral of silica is observed in SEM
- Endothermic reaction of SCBA is noted in TGA indicating that the sufficient reactive minerals are formed above calcination temperature
- The silica in SCBA is present in α -cristobalite mineral form
- The tetrahedral shape of cristobalite mineral is observed
- The pozzolanic activity of SCBA is function of temperature

The technical and economic advantages of incorporating SCBA in concrete should be exploited by the construction and sugarcane industries.

Acknowledgements

The authors wish to thank the CSIR-Structural Engineering Research Centre, Council for Scientific and Industrial Research, Taramani, Chennai, Tamil Nadu, India for their knowledgeable, experimental supports and also thank the Sugar Cane Industry in Erode for providing the sugar cane bagasse ash used in this investigation.

List of symbols

Q	Quartz
C	Cristobalite
O	Oxygen
Al	Aluminium
K	Potassium
Si	Silica
Mn	Manganese
Fe	Iron
P	Phosphorus
Ti	Titanium
Ca	Calcium
Mg	Magnesium
Na	Sodium
S	Sulphur

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