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Characterization of Unburnt Carbon Recovered from Fly Ash by Froth Flotation

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Abstract

Coal based thermal power plants are the main source of power generation in India. Since Indian coals contain high percentage of ash, as much as 40% and above, these power plants produce about 150 million tons of fly ash per annum. Presence of significant amount of unburned carbon in these fly ashes can be attributed to inefficient combustion of fuel coal in the boilers or the use of low-NO_x burners to reduce power plant emission. The carbon amount in fly ash needs to be reduced, so that these fly ashes meet the requirements for maximum loss of ignition (LOI) for various uses. On the other hand disposal of fly ash containing appreciable amount of unburnt carbon is posing serious problems causing environmental damages. It is in this context an attempt has been made to recover the unburnt carbon from fly ash by froth flotation and then characterize it further to effectively utilize it. Such an effort will find market for both the materials such as fly ash and the recovered unburnt carbon. In the present study the quality of recoverable carbon has been determined for two fly ashes collected from two thermal power plants. The raw ash and the concentrate generated out of process have been characterized by SEM and XRF techniques besides determining their proximate analysis, particle size distribution and surface area to estimate their adsorption capabilities.

INTRODUCTION

Fly ash is a byproduct of coal in coal combustion power plants through condensation and agglomeration of coal mineral matter. The mineral matter in coal is mainly composed of clay minerals, quartz, calcite and pyrite. Millions of tons of coal fly ash is produced in India every year. Disposal of this fly ash at present is environmentally unacceptable. Coal fly ash mainly consists of inorganic compounds such as silica, alumina and small proportions of iron oxide, calcium oxide, magnesium oxide, phosphorous oxide, titanium dioxide etc besides unburnt carbon. These are valuable materials and can be recycled and recovered if properly processed. Most fly ashes are either pozzolanic or cementitious and they can be exploited to produce concretes with improved workability and durability. In Europe the standards for concrete manufacturers require fly ash loss-on-ignition (LOI) to be less than 5% (BS EN 450), in the US, ASTM standards specify LOI less than 6%, whereas industry generally accepts only less than 3% LOI.

Power generation industry has been active in addressing issues related to higher LOI, including:

- Improvements in the ability for accurate measurement of LOI.
- Providing high quality ash materials by beneficiating ash to reduce carbon levels.

Due to limited application of high carbon fly ashes they are mostly being placed in landfills, which is very detrimental to environment. It is critical that new technologies be developed that will allow this high carbon fly ashes to be utilized more efficiently. There is a clear need to establish environmental friendly and cost effective strategies for the use of these carbonaceous waste products. The overall

objective of this work is to develop adsorbent material from coal combustion byproducts, mainly unburnt carbon in fly ash. In this context efforts have been made to recover unburned carbon from fly ashes of two thermal power plants, viz. BokaroThermal Power Station (BTPS) and Dishergarh Thermal Power Station (DTPS), and characterize the recovered carbon in order to increase the utility of unburned carbon and fly ash separately. The recovered carbon can be used as a sorbent in some of the applications that utilize activated carbon and at the same time, the reduction of carbon from fly ash increases the pozzolanic quality of the ash and generates high quality feed material for the production of cement. A process for the separation of unburnt carbon from fly ash has been reported in one of our earlier publications (Surabhi et al, 2005). Flotation was carried out using Denver flotation cell with constant water level arrangement and froth scrapping facility. Characterization of the recovered unburnt carbon from fly ash is essential for identifying its potential uses. This paper deals with the characterization of whole fly ash and carbonaceous material recovered from fly ash by using different methods.

EXPERIMENTAL

Fly Ash

Fly ash samples collected from Bokaro Thermal Power Station (BTPS) situated in Jharkhand state and Dishergarh Thermal Power station (DTPS) situated in the state West Bengal have been used for present study.

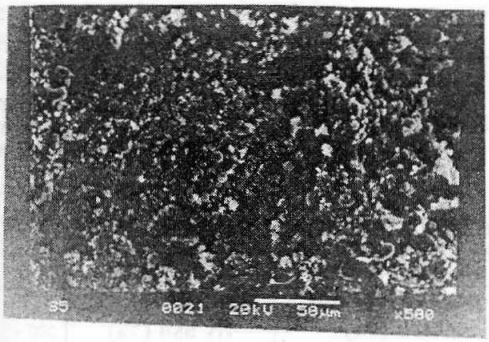

Fig. 1 (A): SEM of BTPS Fly Ash

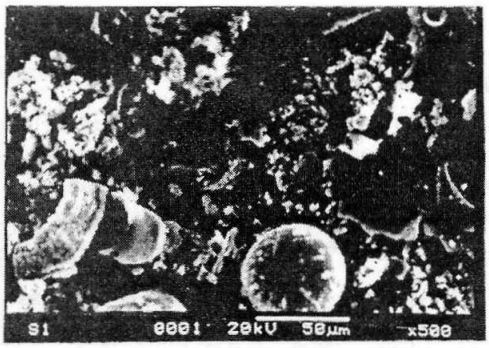

Fig. 1 (B): SEM of DTPS Fly Ash

Characterization

Fly ash samples have been characterized by different methods; viz. proximate analysis, XRF analysis, CHNS analysis, SEM analysis, Particle size analysis and Surface area measurement.

Proximate Analysis

The proximate analysis represents the determination of moisture, ash, volatile materials and fixed carbon in the sample. The first three are determined experimentally and the results are expressed in percentage and the fixed carbon is determined by subtracting the total percentage of moisture, ash and volatile materials from hundred.

Proximate analysis of the samples was carried out as per IS.1350 (part-1)(1969).

The result of this analysis is given in Table 1.

Table 1: Results of Proximate Analysis of Ash Samples

Sample	Moisture (%)	Volatile matter (%)	Ash (%)	Fixed Carbon (%)	LOI (%)
BTPS Fly Ash	1.43	2.44	86.5	9.63	13.5
DTPS Fly Ash	0.71	4.9	70.68	23.21	28.82

XRF Analysis

Pellets were made by mixing 1 gram of sample with 1-2 drops of paraffin oil and a load of 10-12 tons/cm^2 with boric acid support. The pellets were analysed with a wavelength dispersive X-ray fluorescence spectrophotometer model SRS 3400 S/N 418 of Bruker AXS, Germany with its software for standardless analysis. Chemical compositions of the ashes as determined by XRF analysis are presented in Table 2.

Table 2: Results of Analysis of Fly Ash Samples Chemical Analysis by XRF

Chemical Constituent	BTPS Fly ash (%) conc.	DTPS Fly ash (%) conc.
SiO_2	51.41	50.4
Al_2O_3	25.62	19.1
Fe_2O_3	3.89	13.1
MnO	-	0.121
MgO	-	0.803
CaO	-	5.6
Na_2O	-	0.17
K_2O	-	3.58
TiO_2	1.74	3.8
P_2O_5	0.61	2.11

CHNS Analysis

CHNS analyses were carried out on the BTPS and DTPS whole fly ash fraction and carbonaceous part recovered from this fly ash separately using CHNS Analyzer Elementar model ELVARIO 3. The results of these analyses are given in Table 3.

Table 3: Results of CHNS Analysis of Ash Samples

	BTPS fly ash (%)	DTPS Fly ash (%)	Carbonaceous part of BTPS fly ash (%)	Carbonaceous part of DTPS fly ash (%)
Nitrogen	1.755	3.035	3.653	2.214
Carbon	23.58	40.17	32.48	44.35
Sulphur	0.139	0.372	0.358	0.281
Hydrogen	0.209	0.310	0.268	0.555

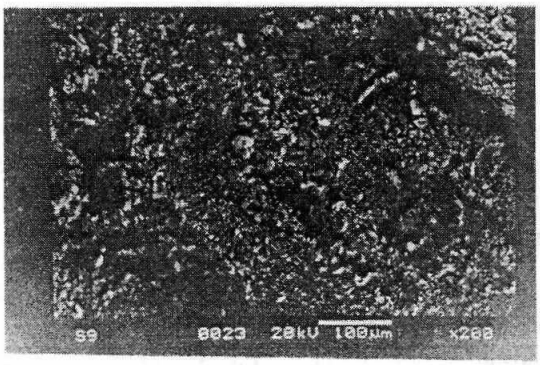

Fig. 2 (A): SEM of Carbonaceous Part of BTPS Fly Ash at * 200 Magnification

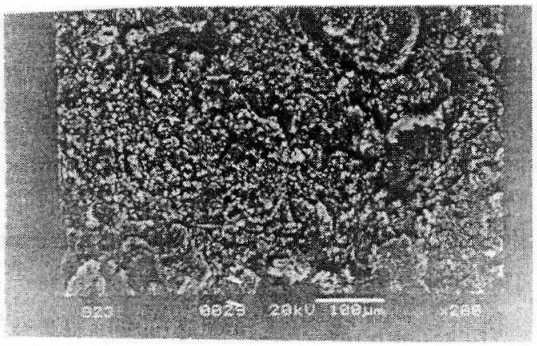

Fig. 2 (B): SEM of Carbonaceous Part of DTPS Fly Ash at * 200 Magnification

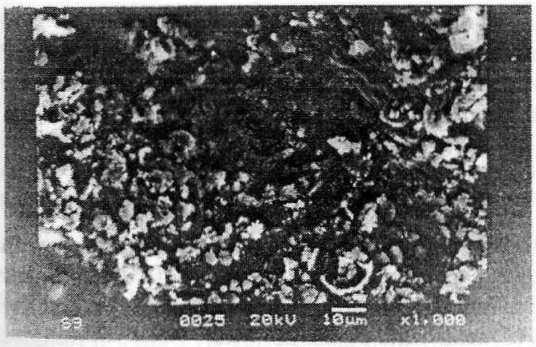

Fig. 2 (C): SEM of Carbonaceous Part of BTPS Fly Ash at * 1000 Magnification

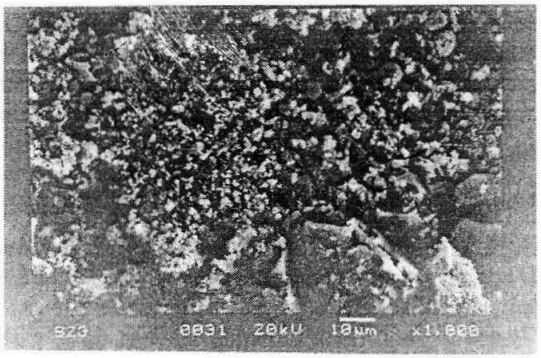

Fig. 2 (D): SEM of Carbonaceous Part of DTPS Fly Ash at * 1000 Magnification

SEM Analysis

Scanning electron microscopy was used to obtain particle morphology and size data. This required obtaining specimens with sufficient density to produce a reasonable number of particles in an image at the desired magnifications while minimizing overlap. To record SEM of fly ash, a thin layer of the sample was sprinkled on a SEM high-resolution stub. Then, samples were coated by carbon layer with E5200 autosputter coater of BIO-RAD. The SEM images were obtained using a JEOL JSM-5800 scanning electron microscope.

Particle Size Analysis

Particle size analysis of the samples was carried out using CILAS 1064 liquid model particle size analyzer. BTPS fly ash, DTPS fly ash, carbonaceous parts and non-carbonaceous parts of BTPS and DTPS fly ashes after flotation were analyzed and results are shown in Fig.3 (a) (b) and (c).

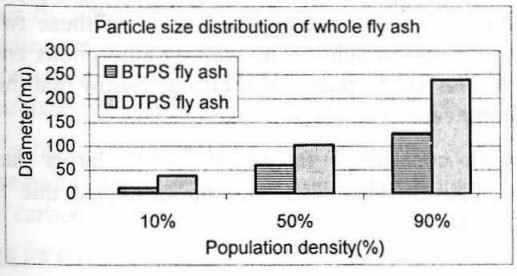

Fig. 3(A): Particle Size Distribution of Whole Fly Ash Samples

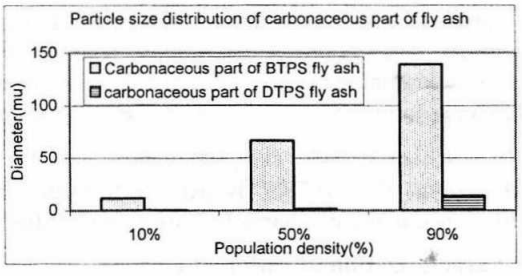

Fig. 3(B): Particle Size Distribution of Carbonaceous Part of Fly Ash

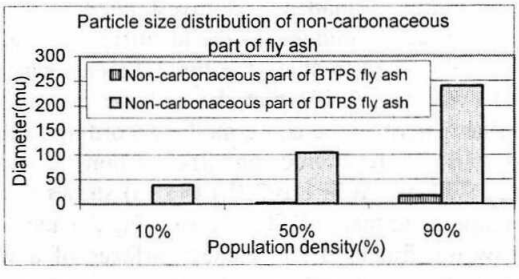

Fig. 3(C): Particle Size Distribution of Non-Carbonaceous Part of Fly Ash

Total Surface Area

Surface area of samples was measured by BET method. The weight of the sample taken was 0.522 gram. The BET surface area was measured with a volumetric apparatus (Micrometrics model) by absorbing and desorbing nitrogen on previously dried samples.

RESULTS AND DISCUSSION

Characterization of Fly Ash

Results of proximate analysis prescuted in Table.1 show that the percentage of unburnt carbon in DTPS fly ash is much higher than that of BTPS fly ash. From the power plant point of view a higher ash content for fly ash represents lost carbon as well as an unsaleable byproducts since the use of the fly ash in the cement industry depends on its carbon content, which must be lower. Both ash samples contain appreciably higher amounts of unburnt carbon than permissible for its use as cement additive.

The XRF analysis of BTPS and DTPS whole fly ash presented in Table 2 show that the percentage of CaO is not detectable in BTPS fly ash while in case of DTPS fly ash, it is 5.6 %. This indicates that BTPS fly ash will not have any cementitious property on its own, while DTPS fly ash may exhibit this property to some extent. However the presence of appreciable amount of unburnt carbon in these samples make the ashes unsuitable as pozzolanic material. The appreciable difference in the composition of the two ashes revealed by the ash analysis is a pointer to the nature of the two ash samples. While BTPS ash is pure fly ash, the DTPS ash is in fact Coal Combustion Byproduct (CCB). This fact and the difference in the coals used for burning as well as the difference in the technology adopted for the combustors may be responsible for the significant difference in the chemical composition of the two ashes.

CHNS analysis of the two samples (Table 3) also exhibits significant differences. Nitrogen, Carbon, Sulphur and Hydrogen contents of DTPS ash are higher than that of BTPS ash. This is expected, as the organic matter content in DTPS ash is more than twice that in BTPS ash.

SEM images of the two samples under same magnification are presented in Fig.1 (a) and Fig 1 (b). It is obvious from these images that there is significant difference in the morphology of these two samples. The BTPS fly ash sample contains well-rounded solid spheres as well as amorphous and glassy material in addition to unburnt carbon particles. The SEM images of DTPS ash show that this has a predominantly amorphous nature with lot of unburnt carbon or char.

Particle size analysis (Fig 4a) shows that DTPS sample contains larger particles (50% larger than 102.76μm) than BTPS fly ash (50% larger than 60.25μm). This also may be explained due to difference in the mechanism of formation of the two ashes.

Characterization of Unburnt Carbon

This study has coupled the analysis of fly ash samples with characterization of unburnt carbon to gain insights into potential for its utilization as adsorbent. The morphology of unburnt carbon and the nature of its association with inorganic matter were investigated by scanning electron microscopy. SEM is one of the most widely used techniques for the identification and characterization of unburnt carbon and fly ash. SEM is well suited to study the three-dimensional nature of unburnt carbon in ashes. It has been reported (Vassilev, 2005) that the carbons present can be classified into four categories termed flat, lamellar, intermediate and granular according to their appearance. Fig 2 show scanning electron micrographs of recovered unburnt carbon at same magnification. Carbon concentrate recovered from DTPS given in Fig 2 (b) and (d) shows that the carbonaceous material appears as fused material compared to that in BTPS fly ash (Fig 2 a and c) at the magnification of 200 and 1000. SEM image show the fractured and etched surfaces of a wide range of carbonaceous material. The examination of fractured and etched surfaces using scanning electron microscope

provides a useful method of characterizing cokes and carbons in terms of their texture. Unburnt carbon in the fly ash has been reported (Stutzman, 1995) to be a mixture of porous char particles and aggregate of sub microns particles. It is suggested that the highly porous, fragmented particle structures and visible, fused surface ash was due to presence of the residual carbon particles. Comparison of the Figure 2 (a), (b), (c) and (d) show that the carbonaceous material recovered in DTPS ash is predominantly char and is of smaller size whereas that of BTPS ash is predominantly aggregates of smaller particles and is relatively of larger size.

As shown in Table 4, the value of surface area of carbonaceous part of BTPS ash is about 2.5 times more than the carbonaceous part of DTPS fly ash, which illustrates the possibility of former having a better adsorption capacity than the latter. Surface area of unburnt carbon varies depending upon the parent coal and combustion residence time. While the surface area of activated carbons typically ranges from 500-3000m^2/gm primarily as a micropore structures, fly ash carbon rarely exceed 10 m^2/gm with the large majority of surface area associated with macropores and mesopores. The surface area values reported here are therefore primarily useful for identifying trends and revealing gross differences between samples for adsorption study.

Table 4: Results of Surface Area Measurement of Ash Fractions

Name of sample	Total surface area (m^2/gm)
Carbonaceous part of BTPS fly ash	6.8836
Carbonaceous part of DTPS fly ash	2.8052

CONCLUSION

Concentrates of unburnt carbon have been generated from two high carbon content fly ash samples using froth flotation. The unburnt carbon has highly porous fragmented particle structure and visible as fused surface ash. This work has shown that these two carbon types from two different power plants viz BTPS and DTPS are not only visually different, but also present distinctive characteristics like nitrogen, carbon, sulphur and hydrogen contents as well as surface area. Proximate analysis of this fly ash shows different carbon contents and need to recover this unburnt carbon for its effective utilization. These distinctive properties of the two samples will be reflected in difference in adsorption properties. From the results of characterization of the concentrates, it may be concluded that the carbonaceous material obtained from BTPS ash may be more effective as adsorbent.

Finally, the unburnt carbon can also be considered as a valuable precursor for the production of premium carbon products. Ongoing work is focused on the development of routes for the generation of carbon adsorbent from the unburnt carbon present in fly ash.

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