Fly Ash Utilisation for Value Added Products
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Characterization and utilisation of fly ash

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ABSTRACT

This paper briefly outlines the characterization of fly ash which is a prerequisite for its ulilization on various purposes. The characterisation which includes determination of size, morphology, crystallinity, mineralogy and chemical composition (both major and minor elements) has been briefly taken care of. Fly ash utilization in various fields i.e. construction of building, highway etc., wall tiles, insulator, mineral wools useful by product in the electrical utility industry and for the recovery of value added products has also been touched upon in this paper.

Key words : *Flyash utilisation, Flyash characterisation, Building materials*

1.0 INTRODUCTION

About 65 percent of the coal produced in India goes for power generation in some 75 thermal power plants located in various parts of the country. Indian coals, though low in sulphur, are rich in ash, as high as 40% indeed, and consequently, the power plants generate a staggering amount of combustion residues (Flyash and Bottom ash) which continue to accumulate at their back-yards, occupy precious lands and pose several environmental problems. Presently about 60 to 70 million tonnes of ash is produced annually and this is likely to reach 100 million tonnes by early next century. Only 5 to 10 percent of the production goes for utilization as low value products.

The magnitude of the generated amounts and the negative impacts of the accumulations either in "Ponds" or "Dumps" have given clear warning that the limits of generation of electricity in Indian thermal power plants will be soon decided by our limits of ash utilization.

2.0 ASH CHARACTERISATION

2.1 Need of Ash Characterization

Any use of a primary material pre-supposes establishment of its properties (characters) and behaviour (interactions) with other substances, with which it may have to be mixed.

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Although coal combustion products (Ash) are generally accepted as fine to medium grained, grannular, silicious residue, which, like river sand or soil, can straight be used for various civil engineering practices like manufacture of bricks etc., detailed observation opens up wealth of informations of its variability in forms, composition and content and consequent possibilities of multiple utilization of the ash. Flyash is no more looked upon as a solid waste product to be disposed off but as a useful by-product of electrical utility and stands to take off for large scale utilization.

The characteristics (properties) of the ash depend on :

(a) The nature of inorganic constituents in the coal, which again is dependent on provenance and depositional process in coal basin etc.

(b) The mechanism of burning of coal and the temperature attained in the furnace, i.e., the type of furnace, rate of supply of air (oxidation), extent of melting and rate of removal from the furnace.

(c) The point at which the ash residue is collected; for example, below the boiler (Bottom Ash) or along the line of collectors such as, Economiser, Mechanical precipitator, Electrostatic precipitators and even atmospheric fallouts.

Along the ash generation line, normally two distinct types of ash are recognised :

1. *The Bottom Ash* -Solidified from molten slags with semimolten particles, obviously solid, saccharoidal, glassy to crystalline or cryptocrystalline in nature and makes up 25% of the total ash generated in the plant.
2. *Flyash* - Materials blown out from the furnace, spherical in shape and makes up 75% of the ash generated. The spherules when empty are called Cenosphere and when filled up with smaller spheres are called Plerospheres.

The Pond ash is a mixture of fly ash and bottom ash, hydraulically transported and stored in an ash pond, the disposal process is called wet-ponding. In dry disposal the ash forms a mound with provision for segregation of bottom ash and fly ash so that either of them may be utilised separately when required. Wet disposal destroys the pozzolanic properties to a considerable extent.

Although, there are only fine differences in the chemistry of the two types of ashes, the morphological characters and particle size varies widely. It must also be noted that the overall composition of the ash varies from one thermal plant to another depending on the sources of coal fields from which the feed coal is derived. Even, coal derived from the same mine but from different seams, produces considerable difference in ash composition. In India the lignitic ash (ash from lignite based thermal power plants) has more calcium than those derived from Gondowano coal. It is therefore not intended to produce a large volume of analytical data on fly ash, except that a synoptic table on flyash properties is presented below (Table 1).

Table 1 : Physical and Chemical Properties of Ash

Particle Size	Bottom Ash	More than 100 microns.
	Fly Ash	100 to 0.5 microns.
	Fallouts	Less than 0.5 microns.
Specific Gravity	1.3 to 3.0 (Higher value is for Bottom ash).	
Specific Surface	Calculated	150 to 1100 cm^2/gm.
	Measured	1 to 2 m^2/gm
Morphology	Crystallinity	20% crystalline, 80% glass.
	Bottom Ash	Saccharoidal,
	Fly Ash	Spherical (Cenosphere, Plerosphere)
Mineralogy	Quartz (B-Tridymite), Mullite, Feldspar, Magnetite, Hematite, Corrundum, Hercynite.	
Chemical Composition		
Matrix (in %)	SiO_2	40 to 80
	Al_2O_3	10 to 20
	Fe_2O_3	2 to 5
	MgO_2	1 to 2
	CaO	2 to 10
	Na_2O	1 to 3
	K_2O	1 to 2
	TiO_2	1
Non matrix (ppm or ppb)	Pb, Zn, Cu, Cd, As, Hg, Se, Ge etc.	

2.2 Methods of Characterisation

2.2.1 Size : Size analysis is carried out by mechanical sieving with or without water or hot air. The finer fraction may be size analysed either by sedimentation technique or by various sophisticated Size Analysers available in the market. Results of sedimentation technique are considerably effected by the presence of hollow spheres which tend to float in the suspending medium, Size vector has also been brought out for ash particles of micron and submicron levels using optical and scanning electron microscopes.

2.2.2 Shape & Morphology : The morphological features of ash are best brought out under optical/electron microscopes. The majority of the fly ash particles are spherical (solid, empty, gas filled or filled with smaller and spheres). The hollow cenospheres have a thin wall of 2 to 5 microns thickness and often carry surface depositions of gypsum, anhydrite or zeolites. The spheres are glass-clear or coloured depending on trace elemental composition (Fe, Ti, Cr etc) or opaque (wustite, hematite, magnetite or their exsolution). Devitrification of internal contents or crystallization of sillimanite needles and a variety of inclusions may be found inside. Broken shells of the spheres are recognised by abundance of curved fragments. Formation of cenosphere and plerosphere are best explained by melting of silica and silicates on carbon surface in the furnace followed by bubble formation with the blast of air and blowing out of the site of formation. Formation of plerosphere is explained by mechanism of bubble bursting.

The spherical morphology of the ash particles develops a large magnitude of internal surface such that the measured surface area far exceeds the surface area calculated from the particle dia. The surface area of the ash is usually measured by BET method by a monolayer adsorption of Nitrogen. With decreasing particle size and increasing internal surface the fly ash poses an extremely large specific surface, in the order of 1000 cm^2 per gram. The reactivity arising out of large specific surface is well-known in all industrial processes. As a matter of fact, the pozzolanic properties of the ash is consequent to high surface area which is normally charged by broken bonds.

The spherical morphology, low bulk density (0.34 gm/ml.) and low Sp. Gr. (0.05) bring great limitation in stacking height of fly ash and restricts the height of ash dykes created for increasing the storage capacity of ash ponds.

2.2.3 Crystallinity : Fly ash is in general 80% glassy and 20% crystalline. It is the glassy nature that makes the ash highly reactive. While the crystallinity or amorphous characters are easily recognised in an XRD pattern of the ash showing a broad hump in the diffractogram, crystallinity can be actually estimated under a polarising microscope by grain count of crystalline and noncrystalline particles in crossed nicols.

Since crystallinity depends on rate of cooling, the near surface region of a spherical grain cools faster, therefore less crystalline than the inner surface of a cenosphere, thereby making the particle surface more reactive or subject to easy alteration when in contact with water in the ash pond.In other words, absence of a proper lattice site with normal chemical bonds, cations of heavy metals, so common in the ash tend to leach out quickly from ash particles and this makes the fly ash a "hazardous waste".

2.2.4 Mineralogy : The mineral composition of fly ash is represented by (a) original mineral particles which have not undergone melting or partly yielded to the temperature in the furnace, (b) minerals that have formed by crystallization of the melt produced in the furnace and (c) minerals formed by subsequent reaction of the second types with flue gas and moisture. The last variety of minerals are found as surface incrustation of ash particle. However, a major portion of the ash being glassy and cryptocrystalline, identification of mineral constituents is a difficult task.

The common mineral contents of the fly ash, determined by X-Ray analysis and partly by optical microscopy (Table 2) :

Table. 2 : Minerals in Fly Ash*

Quartz : β-quartz, Tridymite (x^+)
Feldspars : Orthoclase, Sanidine, Alk. Felspar, Plagioclase (x)
Feldspathoids : Nephelene, Carnegeite (xxx)
Garnet : Gehlinite (xx)
Olivine : Fayalite (xx)
Pyroxenes : Augite, Diopside, Acmite (xx)
Spinel : Magnesian, Aluminian, Chromian spinels (xx)
Sillimanite : Andalucite (xx)
Kaolinite (x)
Magnetite (x)
Ilmenite, Rutile (xx)
Hematite (x)
Corrundum (x)
Apatite (xx)
Zircon (xxx)
Carbon-Graphite (x)
Pyrites (xx)
Arsenides (xxx)

*Sulphates, Carbonates and Zeolites as secondary minerals. x^+ : Order of Abundance

An indirect method of arriving at theoritical mineral contents in ash is by normative calculation of stoichiometric possible mineral phases from the chemical analysis data.This of course, presupposes gradual and sequential formation of mineral phases from a melt equivalent to the chemistry of the bulk ash composition, as the silicate melt cools. The surface depositions are however the reaction products of the particle surface and flue gas including moisture.

2.2.5 Chemical Characters : Chemical characterization of fly ash is made by several methods and for various purposes :

Determination of major chemical constituents like Si, Al, Fe, Mg, Na, K, Ti etc. is carried out by standard dissolution and fusion techniques and the elements determined colorimetrically, spectrophotometrically, by titration or by sophisticated equipments like aas and icps. aas and icps are particularly useful for trace metal analysis in ppm/ppb levels. For analysis of Hg and As, a Hydride generator is used and the elements are analysed by cold vapour extraction.

Bulk analysis can also be carried out by modern techniques like X-Ray Fluorescence analysis and individual grain of ash or part of it can be analysed for specific element (s) under an SEM, coupled with an EDAX.

Leachability of toxic heavy metals from fly ash, a dreaded feature associated with most ash ponds, is estimated by stirring a measured weight of ash in known amount of water at desired pH for a fixed or variable time period followed by analysis of the leachate for the metals. The ash can also be packed in a leaching column and scavenging solution passed through it to leach away the metals. Such process decreases asymtotally with time.

The occurrences of heavy metals at or near the particle surface is observed and actually estimated by surface analytical techniques like Secondary Ions Mass Spectrometry (sims) which strips layers of materials by sputter as the analysis of successive layers are being carried out. The surface analysis has shown that most heavy metals in fly ash are available within few hundred angstrom depth from the particle surface and therefore vulnerable to easy leaching.

2.3 Importance of Ash Characterization

Physical and chemical characters of ash have great significance in functioning of power plants, in corrosion, erosion, wears & tears of internal surfaces, in slag formation, in the efficiency of precipitators, in stack emissions and fallouts, in environmental and health problems as well as in technological usage of the material.

In classifying fly ash for major civil engineering uses, the calcium content of the ash is taken into consideration. For example, ash with more than 10% Ca is known as C type and the lower calcium variety is called F type. Other major analytical components such as SiO_2 + Al_2O_3 + Fe_2O_3 are also considered in classifying ash but have little technological implications. The K/Al ratio indicating the fluxing activity of the ash, has also been suggested to classify the ash types. The important contribution of some of the minor elements in ash is their surface location, which makes the ash particles charged for easy arrest on electrostatic precipitators.

3.0 ASH UTILIZATION

Indian Scientists and Technologists are seized with the problem of fly ash utilization as can be seen from the mission mode approach of the Fly Ash Mission (TIFAC) specially created by Deptt. Of Science & Technology.

In general, use of fly ash can be grouped into 3 categories :

1. Low value uses such as, manufacture of bricks, for mine filling, embankments, sufacings and reclamations etc., where large bulk of ash is consumed. Serious attempts have been made for brick manufacture by various agencies, using lime, cement, gypsum, clays, resins etc. at different proportion and a variety of products are in the market. Among others, Fal-G bricks seem to be most prefered. Brick

manufacture from fly ash is emphasised because it saves valuable top soil. Similarly, exhaustion of river sands for mine stowing in underground collieries would lead to use of the ash in large scale for filling up of mine excavations. But leachability studies on ash must be done for use in such purpose.

2. Medium value uses such as cement additive, light weight aggregates for prestressed structures, wall tiles, insulation blocks (made from cenospheres) and as herbicide in agriculture may be attempted.

Table 3. Strength of cenosphere and binding system

Binder	Binder:Cen.Sp.	Curing T°	Density kg/m^3	Crush. Strength lb. ft/in sq.
Portland Cemt.	1 : 1	Ambient	490	190
------------	1 : 8	--------	470	350
Polyester Resin	1: 12	395	390	330
----------	--	445	380	380
Phen. formaldehyde	1: 12	445	410	900
------------	1 : 9	---	440	1050
Cement Fondu	1 : 8	1175	440	100
----------	1 : 8	1475	440	350

(From : Rask, E. A light weight material, Br.Ch.Eng, 1970)

3. High value uses such as recovery of magnetic oxides, aluminium oxides (alumina) and trace metals, synthesis of zeolites and production of mineral wools.

Flyash carries 2 to 10 percent of magnetic cenosphere, of which about 80% are in the range of less than 40 micron size. Recovery of the magnetic material being easier, these can be economically collected for use in heavy media separation in coal washeries. An added use of magnetic cenosphere has been proposed for opening and closing of magnetic values in places of zero gravity. Such free flowing, micron size magnetic spheres may therefore find use in space flight, where channels are required to be closed or opened by movement of free flowing materials.

Fly ash carries 20 to 30% of alumina and variable traces of heavy metals. Several methods have been developed all over the world for extraction of alumina from the ash. These include reaction leach processes of lime-sinter, lime-soda sinter, pressure digestion acid leaching etc. Other metal values may be recovered from the liquor even by cation exchange process, as side product of alumina production, so that the process can be acceptable in India in spite of availability of large resources of bauxite. CPRI, Bangalore has successfully developed a technology of alumina extraction from Indian fly ash in which 99.4% pure alumina is extracted from the ash.

Flyash is an important starting material for synthesis of zeolite because of its ideal content of silica, alumina, alkalis and calcium. Zeolite is a common reaction product of ash when in contact with water and the mineral is found as incrustation on ash particles. Zeolites have also been produced by interaction of fly ash with dilute sodium hydroxides. The reaction is enhanced by increasing temperature and pressure. Zeolite has many industrial uses.

A positive implication of zeolite formation on ash particles by ash - water interaction is application of ash in soil for agricultural purpose. Suitable manipulation of this reaction can generate a polysialate (zeolite) with two different exchangeable sites in its crystal structure, one of 6-fold co-ordination to house micronutrients like Ni, Co, Mn, Zn etc. (all around 0.6 Ao size) and the other of 12-fold co-ordination to house macronutrients like K+, nitrate, phosphate etc. (all need space larger than 1 A0), so that each ash particle in the soil becomes a repository of nutrients and a potential nutrient pump. Adsorption, desorption and exchange being pH dependant, it is possible to energise the mineral pump selectively for nutrient transfer to achieve rapid agricultural production. However, a negative implication of zeolite formation on ash particle, which Civil Engineers must note, is the possibility of loss of strength of ash bricks in due course of time, since zeolite is softer than ash or binding materials used in the brick and this may threaten long term stability of structures built with ash bricks.

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