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VALUABLE PRODUCTS FROM FLY ASH - A REVIEW

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ABSTRACT

Coal is the major source of energy in India and because of its poor quality, nearly hundred million metric tons of fly ash is generated annually from thermal power plants. Hence, the disposal of such a huge quantity of fly ash is the major environmental concern. Though the fly ashes are generated in large quantities, only a very minimum of it is utilised and the rest is being dumped in ash ponds. Fly ash mainly consists of silica, alumina, oxides of iron, calcium, magnesium and heavy metals in traces. The disposal of fly ash in ash ponds and landfills may cause soil and ground water pollution. This paper deals with a detailed review on utilisation of fly ashes in various fields and extraction of valuable products from it. Previous researchers have carried out studies on fly ash and its potential applications in different areas such as production of cement, manufacturing of bricks for construction purposes, road embankments and component in geopolymers. The fly ashes are also being utilised in the synthesis of zeolites, a low cost adsorbent in treatment of industrial wastewater. Also, the valuable products such as silica and alumina are recovered from fly ashes. However, the extent of extraction has not been investigated in detail. This review highlights the likelihood of recovery of the valuable products (silica and alumina) from Indian fly ashes.

INTRODUCTION

General

Coal is the major source of energy in India and it accounts about 70% of the power production (Kolay *et al*. 2001; Mishra *et al*. 2004). Combustion of coal in thermal power plants produces fly ash. There are different types of coal namely anthracite, bituminous, sub bituminous and lignite. Classification of coal is based on the content of volatile matter and carbon. Coal which has less volatiles and high carbon is of superior quality. High rank coals are harder, stronger with high carbon content and produce more energy. Anthracite is considered as the high grade coal with high carbon content and energy. Lignite is the low grade coal as it has high volatiles and less carbon (WCI, 2010). Though the need of alternative fuels is increasing these days, but the major source of power in India is coal. Indian coal constitutes 35% to 45% of the ash because of its poor quality (Mathur *et al*. 2003). Hence this is regarded as a prime factor for the increased ash production

Composition and Classification

Fly ash is the finely divided residue that is obtained during the combustion of coal. Classification of fly ash is based on its chemical composition. Two classes

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of fly ash are defined by ASTM C618: Class F fly ash and Class C fly ash. The major difference between these classes is the amount of calcium, silica, alumina, and iron content in the ash. Class F fly ash is produced by burning anthracite and bituminous coal and it comprises silicon dioxide, aluminium oxide and iron oxide to 70 % and has pozzolanic properties. Class C fly ash is produced by burning lignite and sub bituminous coal and comprises silicon dioxide, aluminium oxide and iron oxide to 50 %. In addition to pozzolanic properties it also has cementitious properties. (ASTM C618-08a).

Disposal

Ash produced from the thermal power plants is dumped in landfills and ash ponds. Nowadays disposal of fly ash is a major problem, because of the shortage of the landfill sites, increasing costs of the land and strict environmental regulations. In India landfill covers a vast area thus depleting the land for agricultural use (Ahmaruzzaman, 2010). This also creates many environmental hazards if not managed well and causes soil pollution and ground water pollution. Because of the wet disposal system of the fly ash the metals in it leach and slowly reach acquifer and contaminate water. In India nearly 130 MT of fly ash is spewed out annually (Burke, 2007). Hence disposal of fly ash is the major environmental concern. Research has been done on fly ash and it is mainly used for various commercial applications.

Fly Ash Characterization

Characterization of fly ash is important because it improves understanding the prediction of the consequences of the utilization and disposal problems and also the associated problems related to atmospheric dispersal of the particulate matter (Ramsden and Shibaoka., 1982). Chemical composition of the fly ash depends on the types of coal used in combustion, combustion conditions and the removal efficiency of the air pollution control device (Sarkar *et al*. 2006).

Mineralogy

X-ray diffraction (XRD) analysis of the fly ash samples gives the mineral phases found in the ash, it determines crystalline phases (Sarkar *et al*. 2006; Armesto, 1999). Quartz (SiO_2), mullite ($3Al_2O_3 . 2SiO_2$), haematite (Fe_2O_3), magnetite (Fe_3O_4), lime (CaO) and gypsum ($CaSO_4 . 2H_2O$) are the major constituents of fly ash (White and Case, 1990). A typical X-ray diffractogram of the fly ash is presented in Fig. 1. (Gutierrez *et al.* 1993).

Particle Size Distribution

Particle size distribution is an important parameter for many applications like replacement of aggregates in cement and concrete, it also has marked influence on the geotechnical properties for disposal (Armesto *et al.* 1999). Fly ashes are collected from the hoppers of the electrostatic precipitators. Hoppers are installed in the collection fields of ESP (Fig. 2). The properties of the fly ashes collected from each hopper in an ESP system varies with the distance of the collection field from the boiler. As the distance from the boiler increases, the maximum particle size of the fly ashes becomes smaller and the range of the particle size distribution becomes narrower (Lee *et al*. 1999).

Morphology

Microscopic observations are made to study the morphology of the fly ash (Sarbak *et a*l. 2004). The fly ash consists of mixed aluminosilicates occurring in the

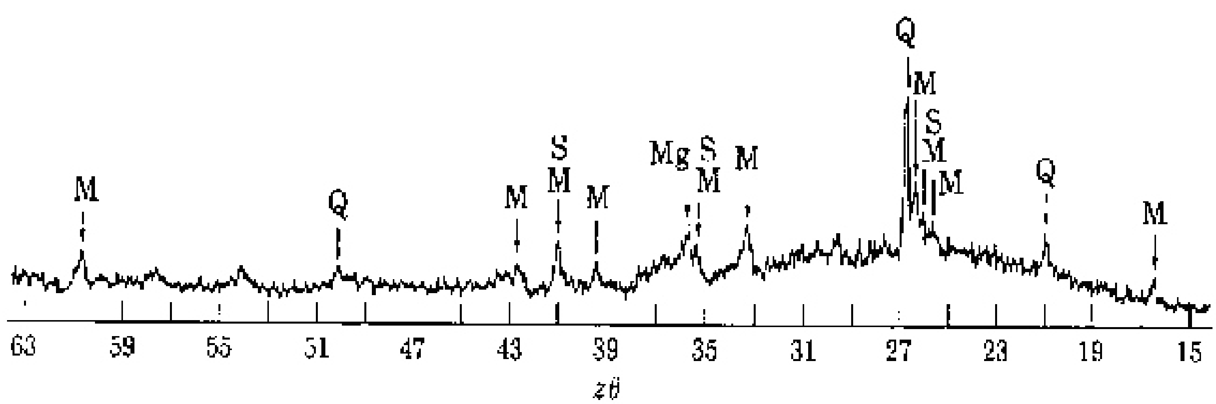

Fig. 1 X-Ray Diffractogram of Fly Ash

Table 1. Chemical Composition of fly ash

Chemical Compound	Content (% wt)
SiO_2	63.73
Al_2O_3	26.33
Fe_2O_3	5.21
CaO	0.98
MgO	0.38
Na_2O	0.01
K_2O	1.01
MnO	0.04
P_2O_5	0.32
SO_3	0.02
TiO_2	1.82

form of small spherical grains and unburnt carbon particles are present in the form of large irregular grains (Grochowiaka *et al*., 2004). The morphology of the coal combustion residues observed by scanning electron microscopy is shown in Fig. 3 (Asokan *et al*., 2005).

Chemical Composition

The elemental composition of fly ashes is studied by using Inductively Coupled Plasma - Mass spectroscopy (ICP-MS) (Wang and Vipulanandan, 1996; Georgakopolous *et al.,* 2002) & X-Ray Fluorescence (XRF) analysis (Goodarzi *et al.,* 2006; Hjelmar *et al.* 1990). Chemical analysis of the raw fly ash and the other products obtained from it is done by XRF (Kolay and Singh, 2002). The chemical composition of a typical fly ash sample from coal based thermal power station in India is presented in the Table 1 (Shanthakumar *et al*., 2008).

APPLICATIONS

Zeolites

Zeolites are crystalline aluminium silicates with high cation exchange capacity with group I or II elements as counter ions. They have microporous structure with a frame work of $[SiO_2]^{4-}$ & $[AlO_4]^{5-}$ tetrahedral linked to one another at the corners sharing oxygen atoms (Querol *et al*. 2002). The structure of the zeolite is shown in the Fig. 4. Zeolites are obtained naturally and can also be synthesized artificially in the laboratory. Commonly adopted ash disposal technique is the wet (or) slurry disposal technique. In the wet disposal of ash from the thermal power plants, the ash and the alkalies present in the ash interacts with water leading to the formation of ash zeolites. This process is termed as zeolitization of the ash which is a natural process (Querol *et al*., 2002).

Zeolites can be synthesized in the laboratory by the hydrothermal activation methods (Singer & Berkgaut, 1995; Amrhein *et al*., 1996). In this method fly ashes containing Al-Si phases are dissolved in alkaline solutions like (NaOH & KOH solutions) and then followed by the precipiatation of zeolitic material. Because of their high cation exchange capacity and microporous structure they are used for various industrial applications (Querol *et al*., 2002). Zeolites are used as ion exchangers in the industrial waste water treatment (Patane *et al*., 1996; Lin *et al.,* 1998; Querol *et al*., 1997), use of zeolites as molecular sieves in the treatment of flue gas treatment and recovery of gases (Srinivasan and Grutzek 1999; Querol *et al*., 1999), replacement of phosphate in detergent (Udhoji

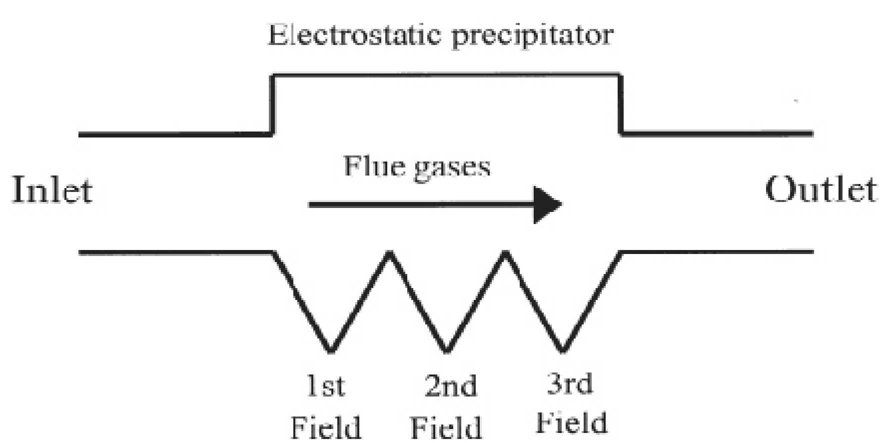

Fig. 2 Schematic of an Electrostatic Precipitator

et al., 2005), removal of radioactive wastes (Kolay & Singh, 2002). Zeolites synthesized from Spanish fly ashes using NaOH and KOH as activating agents are divided into high and low industrial application groups based on their cationic exchange capacity. Zeolites like NaP1, phillipsite/KM-Zeolite, K-chabazite, F linde zeolite, herschelite, faujite, zeolite A have high industrial application potential due to high cationic exchange capacity. And other zeolites like perlialite, analcime, hydroxyl-sodalite, hydroxyl cancrinite, kalsilite, tobermorite have low industrial application. (Querol *et al.*, 1999).

Geopolymers

Concrete, an essential building material is widely used in the construction of infrastructures such as buildings, bridges, highways, dams, and many other facilities. Ordinary Portland Cement (OPC) is commonly used as a binder in the manufacture of concrete. However, it is well known that the production of OPC not only consumes significant amount of natural resources and energy but also releases substantial quantity of carbon dioxide (CO_2) to the atmosphere (Davidovits, 2005). Geopolymers are a class of versatile materials that have the potential for utilisation as a cement replacement, fireproof barriers, materials for high temperatures and biological implant applications (Williams & Riessen, 2010). Displaying excellent mechanical strength and resistance to attack by aggressive environments, these materials signify an opportunity to simultaneously improve both environmental and engineering performance compared to traditional technologies (Duxson *et al.* 2007; Duxson *et al.* 2007).

Geopolymers were introduced by Davidovits in the early 1970s to describe inorganic materials obtained from the chemical reaction of alumino-silicate oxides with alkali silicates, yielding polymeric Si-O-Al bonds (Davidovits, 1991). According to author, geopolymerization is a geosynthesis that chemically integrates materials containing silicon and aluminium. During the process, silicon and aluminium atoms are combined to form the building blocks that are chemically and structurally comparable to those binding the natural rocks. The empirical formula of geopolymers is as follows Eq. (1) (Davidovits, 1991):

$$Mn\{-(SiO_2)_{z-}AlO_2\}_n \cdot wH_2O \quad \text{---------} (1)$$

Where M is a cation such as K^+, Na^+ or Ca^{2+}; *n*, the degree of polycondensation and z is 1, 2 or 3. Other cations such as Li^+, Ba^{2+}, NH^{4+} and H_30^+ may also be present. Generally, alkali metal (Na or K) silicate or hydroxide is often used as an activator for synthesis of the metakaolin-based or fly ash-based geopolymers (Van Jaarsveld & van Deventer, 2002; Van Jaarsveld & van Deventer, 2003). Geopolymer binder is synthesized in a temperature range of 20ºC to 90ºC (Khale & Chaudhary, 2007).

Geopolymerization has become a promising technology as it offers attractive possibilities for commercial applications such as fast hardening, high and early compressive strength, optimal acid resistance , long term durability, high fire and erosion resistances (Davidovits, 1988; Davidovits, 1991). Geopolymer matrices can also stabilize metallic and radioactive wastes or industrial wastewater (Herman *et al.*, 1999; Hanzlicek *et al.*, 2006; Tavor *et al.*, 2007).

Geopolymerization of fly ash has many environmental benefits; it reduces the utilization of natural resources and decreases the net production of CO_2. This results in low cost and environmentally friendly materials with cementing properties resembling those of OPC. It is estimated that the geopolymer cement synthesis emits 5-6 times less CO_2 when compared with Portland cement (Davidovits, 2005).

Use of fly ash in cement, bricks & road embankments

Earlier fly ash and other coal combustion residues (CCRs) were mainly regarded as waste products. Now a days, it is used as a substitute for cement production. Fly ash is used in the production of Portland Pozzolana Cement (PPC) in three different ways (1) as a raw material along with limestone in the cement kiln, (2) grinding of fly ash and cement in the mill and (3) blending of Ordinary Portland Cement (OPC) with fine fly ash (Bhattacharjee & Kandpal, 2002). About 12 lakh tonnes of ash is being used every year in India for the production of cement (Roongta, 2000). Production of coal combustion residues based cement increases the overall availability of cement production and is cost effective.

The demand for road construction is increasing with increasing population and lack of mineral resources. Hence road construction is becoming very hard and expensive. Use of low cost materials helps to utilize the available natural resources more efficiently. Mineral wastes or by products such as fly ash produced from thermal power plants provide a great potential as a low cost mineral resource for construction materials (Baykal *et al.*, 2004). Fly ash has been used as a structural fill material for constructing high-

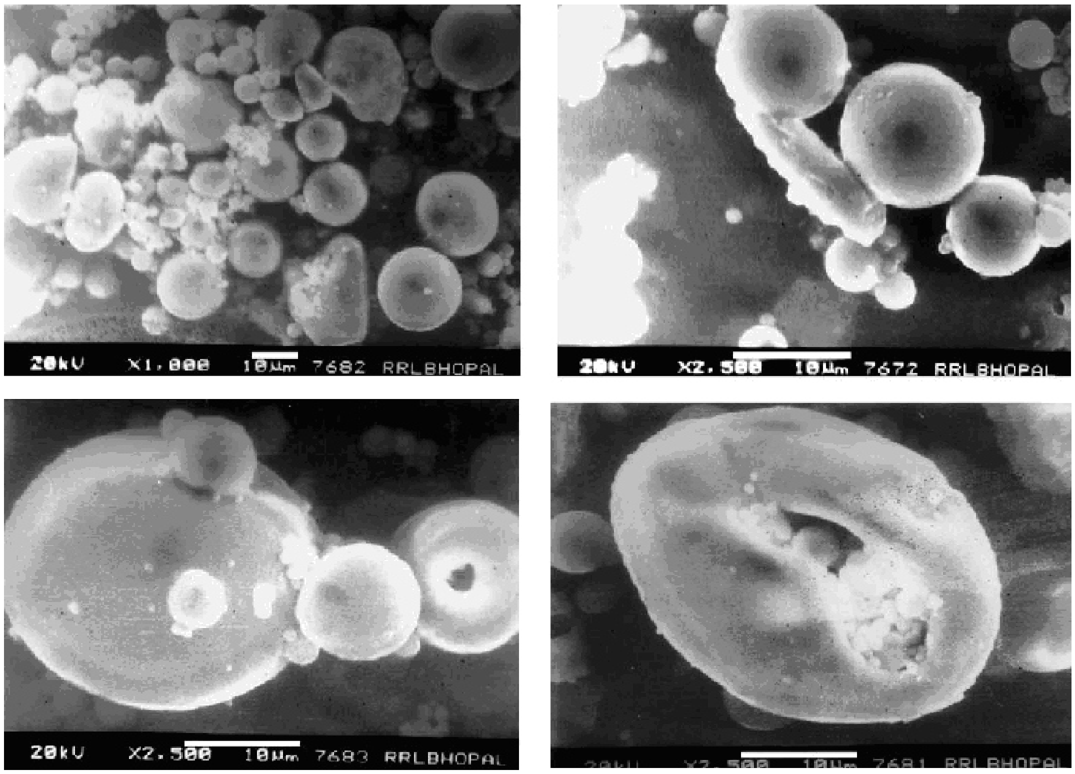

Fig. 3 Microstructure of Coal Combustion Residues

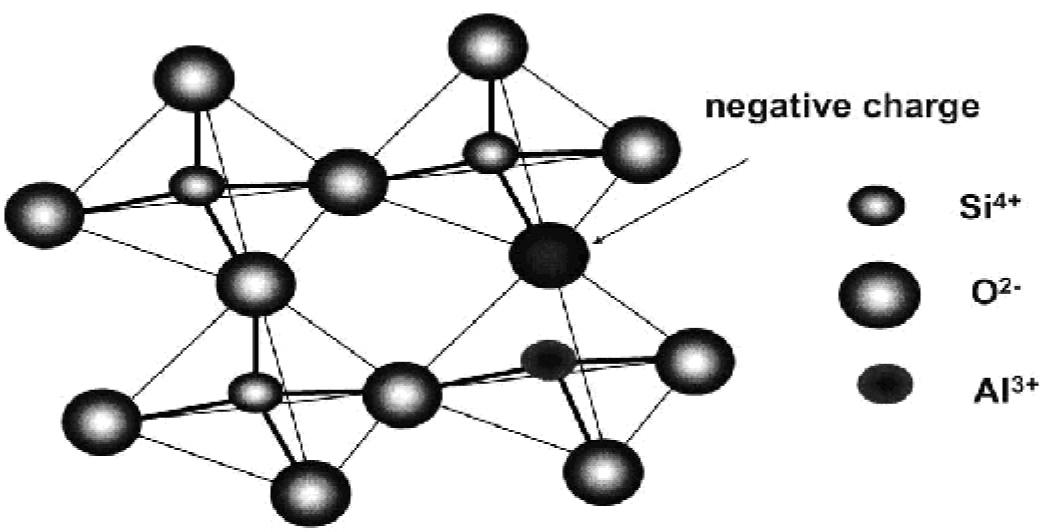

Fig. 4 Structure of zeolite (Querol *et al.* 2002).

way embankments in various locations throughout the world (Singh, 1996; Vishwanadham, 1999; Chand & Subbarao, 2007).Fly ash alone or with granite or limestone can be used as a final top surface for roads, parking lots, other industrial and commercial applications. It can also be used as a stabilized base course which satisfies compaction requirements for civil applications (Jackson *et al.*, 2009).

Different types of fly ash bricks such as clay- fly ash bricks, fly ash- sand-lime and fly ash -sandlime -gypsum bricks are used for construction purposes and other civil works (Bhattacharjee & Kandpal, 2002).

Presence of CaO, soluble silica, Al_2O_3 and higher surface area improves the quality of bricks (Kumar *et al.*, 1999). The compressive strength of clay CCRs brick is as high as 120 $kgcm^{-1}$, water absorption is less than 18% and shrinkage is less than 10% (Karade *et al.* 1995).

Recovery of Silica and Alumina

Although increasing amounts of fly ash have been used beneficially in recent civil engineering applications but the vast majority of the fly ash is held in ash ponds and landfills (Iyer & Scott, 2001). And is likely being disposed as waste as an alternative to disposal, coal ash can be used as a resource to recover valuable minerals (Murtha & Burnet, 1982). Nehari *et al*. (1999) invented a process for the simultaneous recovery of both silica and alumina from fly ash. Kamaruddin *et al*. (2009) reported the extraction of soluble silicates and aluminates from coal fly ash using microwave irradiation in a domestic microwave oven with different experimental conditions. Chemistry of three methods direct acid leach, calsinter & pressure digestion acid leach was reviewed by Kelmers *et al*. (1982). Most important parameter affecting the extraction of metals from coal fly ash is the calcium content of the ash. Other parameters such as the type of furnace and operating temperature have very less effects on metal extraction (Gabler & Stoll, 1982). Alumina recovery from fly ash can be enhanced with the addition of cement kiln dust in the place of lime stone-fly ash sinter process (Murtha & Burnet, 1982).

Pure alumina can be obtained from solvent extraction which is technologically efficient and economically favourable process. It is the best method that can be used for the separation of iron from aluminium salts (Muhl *et al*. 1980). Nayak & Panda (2010) worked on Indian fly ash generated from Talcher thermal power plants in Orissa and reported that the direct acid leaching at low concentrations and ambient temperature is not suitable for high recovery of alumina. Many other researchers worked on different types of fly ash to extract alumina (Guang-hui *et al*. 2010; Font *et al*. 2010; Matjie *et al*. 2005).

CONCLUSION

In view of the above mentioned applications, fly ash from the coal fired power plants has proved to have a significant value added potential for many commercial applications. The reasons for less utilization of fly ash in India are poor quality of ash, non availability of fly ash due to wet disposal system of ash and uncertainty of product marketing. However extensive research work should be carried in various fields to explore new ways and methods to utilize fly ash as a value added product. Effective utilization of fly ash not only reduces disposal problem but also leads to sustainable development.

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