Effectiveness of Some Simple Techniques for Fly Ash Beneficiation

A Thesis Report Submitted
in partial fulfilment of
the requirement for the award of degree of

Masters of Technology
In
Chemical Engineering

Submitted By

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July 2012

DECLARATION

I hereby declare that thesis entitled **"Effectiveness of Some Simple Techniques for Fly Ash Beneficiation",** is an authentic record of my own work carried out as per the requirements for the award of the degree of M.Tech.(Chemical Engineering) at Thapar University, Patiala, under the guidance of Dr.R.K.Gupta (Associate Professor,ChED) during July 2011 to June 2012.

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Acknowledgment

I wish to express my deep gratitude to **Dr. R.K. Gupta** , Associate Professor, Department of Chemical Engineering, Thapar University, Patiala, for providing his uncanny guidance and support throughout the thesis work.

I am thankful to **Dr. Rajeev Mehta**, Head, Chemical Engineering Department, **Dr. P.K. Bajpai,** Distinguished Professor & Dean (Research & Sponsored Projects), and all the faculty and staff members who were always there at the need of the hour and provided with the help and facilities, which I required for the completion of this thesis.

I am also very grateful to Kushal and Jasdeep for helping me in the lab. I am thankful to all my friends for accompanying me during the most outstanding year of my life and standing by me in every situation.

My special thanks to authors whose works have been consulted and quoted in this work.

Last but not least, I would like to thank God for all good deeds.

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Abstract

Fly ash, generated during the combustion of coal for energy production, is an industrial by-product which is recognized as an environmental pollutant. Because of the environmental problems created by the fly ash, considerable research has been undertaken on the subject worldwide. The utilization of fly ash in construction, as a low-cost adsorbent for the removal of organic compounds, flue gas and metals, light weight aggregate, mine back fill, road sub-base, and zeolite.

Fly ash beneficiation is the separation of carbon particles. High unburned carbon content in the fly ash makes it unsuitable for use as cement admixture. High carbon results in discoloration, poor air entrainment and segregation of mix components. Beneficiation is required to enhance the ability to extract high purity carbon and ash for the production of value-added products. Beneficiation techniques are based on the differences in size, density, electrostatic and physical properties of the particles.

Fly ash beneficiation techniques are: triboelectrostatic separation, ultrasonic column agglomeration, and column flotation, froth flotation, air classifier, magnetic separation and gravity separation, fluidized bed separation etc.

In the present study, fly ash from NFL Nangal, India, having LOI ~ 15%, is subjected to the simple beneficiation techniques namely froth flotation and fluidization. The equipment for conducting the experiments were self fabricated/designed. Using froth floatation the LOI of fly ash could be reduced to ~10%. The effectiveness of screening followed by froth floatation showed promising results, and LOI of fly ash could be reduced to ~ 8%. Fluidized bed separation, being a dry separation process, is an attractive alternative. The results for fluidized bed separator showed LOI reduction to ~ 11%. The experimental observations indicated that a shallow fluidized bed shall give better separation than a deep fluidized bed.

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Abbreviations

ASTM	American Society of Testing and Materials
CLSM	Controlled Low Strength Materials
CCR	Coal Combustion Research
OSHA	Occupational Safety and Health Act
NTPC	National Thermal Power Corporation
NIOSH	National Institute of Occupational Safety and Health
SEM	Scaning Electron Microscope
PPE	Personal Protective Equipment
LOI	Loss On Ignition
PFA	Pulverized Fuel Ash
FBA	Furnace Bottom Ash

Chapter 1
Introduction

The combustion of pulverized coal at high temperatures and pressures in power stations produces different types of ash. The 'fine' ash fraction is carried upwards with the flue gases and captured before reaching the atmosphere by highly efficient electro static precipitators. This material is known as Pulverized Fuel Ash (PFA) or 'fly ash'. It is composed mainly of extremely fine, glassy spheres and looks similar to cement. The 'coarse' ash fraction falls into the grates below the boilers, where it is mixed with water and pumped to lagoons. This material, known as Furnace Bottom Ash (FBA) has a gritty, sand-like texture.

Fly ash closely resembles volcanic ashes used in production of the earliest known hydraulic cements about 2,300 years ago. Those cements were made near the small Italian town of Pozzuoli - which later gave its name to the term "pozzolan." A pozzolan is a siliceous or siliceous / aluminous material that, when mixed with lime and water, forms a cementitious compound. Fly ash is the best known, and one of the most commonly used, pozzolans in the world. Instead of volcanoes, today's fly ash comes primarily from coal-fired electricity generating power plants. These power plants grind coal to powder fineness before it is burned. Fly ash - the mineral residue produced by burning coal - is captured from the power plant's exhaust gases and collected for use. Fly ash is a fine, glass powder recovered from the gases of burning coal during the production of electricity. These micron-sized earth elements consist primarily of silica, alumina and iron. Fly ash particles are almost totally spherical in shape, allowing them to flow and blend freely in mixtures. That capability is one of the properties making fly ash a desirable admixture for concrete.

In the past, fly ash was generally released into the atmosphere, but pollution control equipment mandated in recent decades now requires that it be captured prior to release. Depending upon the source and makeup of the coal being burned, the components of the fly ash produced vary considerably, but all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline) and calcium oxide (CaO). Fly ash is commonly used to supplement Portland cement in concrete production, where it can bring both technological and economic benefits, fly ash is increasingly finding use in the synthesis of geopolymers and zeolites.

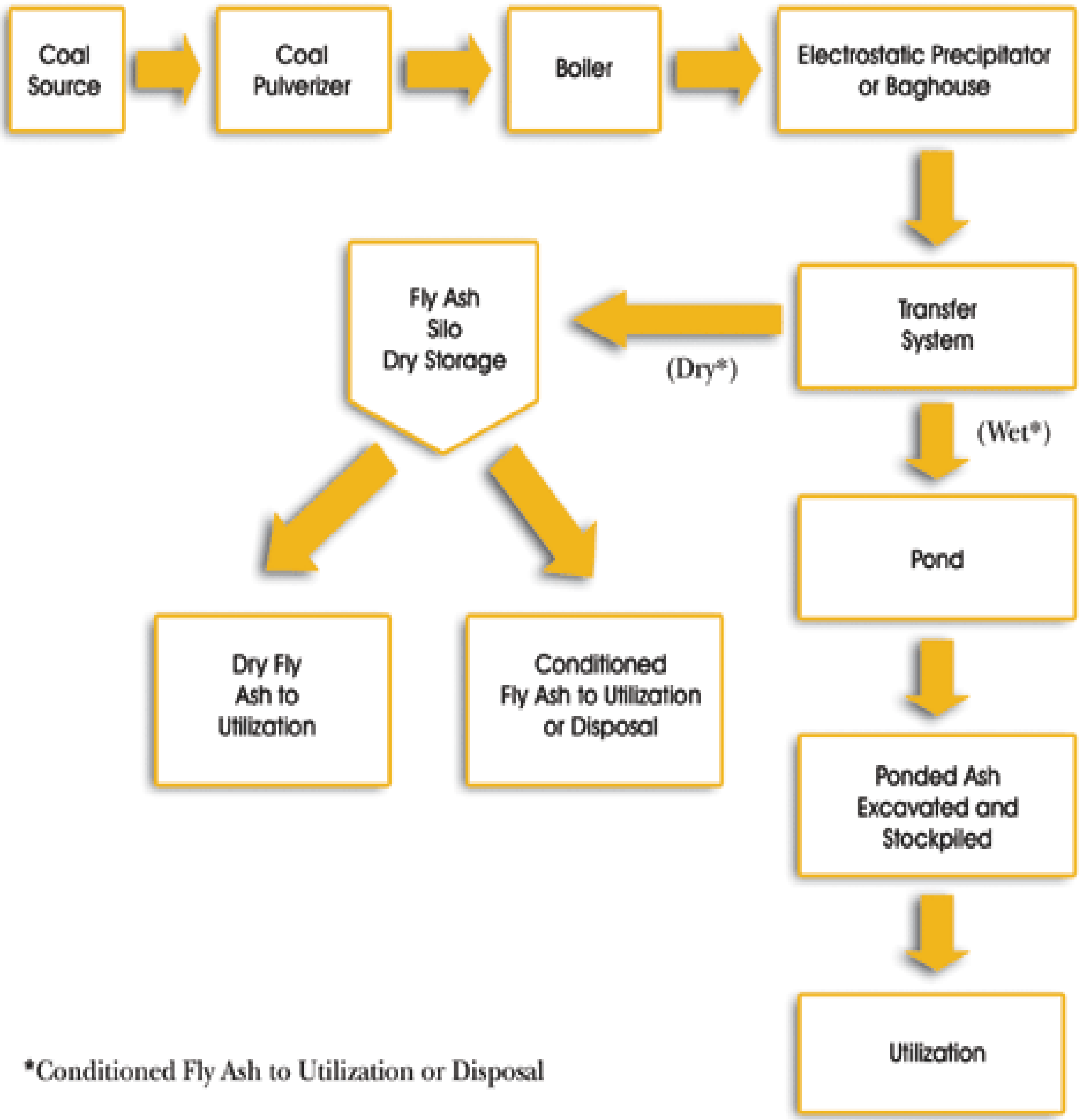


Figure 1 Methods of fly ash transfer can be dry, wet or both

Ash can be collected in the following two categories:

Dry Fly Ash

Dry ash is collected from different rows of electrostatic precipitators. It is available in two different grades of fineness in silos for use as resource material by different users.

Conditioned Fly Ash

Conditioned fly ash is also available in ash mound for use in landfills and ash building products.

1.1 Physical Properties

Fly ash particles are very fine, light weight (density 1.97-2.89 g/cc) and spherical (specific surface area 4000-10,000 cm2/g; diameter, 1-150µ), refractory and have pozzolanic ability. Fly ash grey to blackish grey and is dependent on coal type and combustion process. Fly ash has dielectric property (dielectric constant, 104) and can be used in electronic application.

1.2 Chemical Properties

Oxides of silicon, aluminum, calcium and iron in fly ash are responsible for pozzolanic activity, which decreases by loss of ignition. Fly ash contain following toxic metals Hg, 1; Cd, Ga, Sb, Se, Ti and V, 1-10; As, Cr, La, Mo, Ni, Pb, Th, U and Zn, 10-100; and B, Ba, Cu, Mn and Sr, 100-1000 mg/kg. Heavy metals (As, Mo, Mn and Fe) show leaching with concentration above permissible limits. The table 1.1 shows the typical chemistry of coal fly ash in India.

Table 1 Typical Chemistry of Coal Fly Ash (Source: Fly ash summary report in India, 2010)

	Class F	Class F	Class C	Class C
	Low- Fe	High –Fe	High –Ca	Low –Ca
SiO_2 (wt%)	46-57	42-54	25-42	46-59
Al_2O_3 (wt%)	18-29	16.5-24	15-21	14-22
Fe_2O_3 (wt%)	6-16	16-24	5-10	5-13
CaO (wt%)	1.8-5.5	1.3-3.8	17-32	8-16
MgO (wt%)	0.7-2.1	0.3-1.2	4-12.5	3.2-4.9
K_2O (wt%)	1.9-2.8	2.1-2.7	0.3-1.6	0.6-1.1
Na_2O (wt%)	0.2-1.1	0.2-0.9	0.8-6.0	1.3-4.2
SO_3 (wt%)	0.4-2.9	0.5-1.8	0.4-5.0	0.4-2.5
LOI (wt%)	0.6-4.8	1.2-5.0	0.1-1.0	0.1-2.3
TiO_2 (wt%)	1-2	1-1.5	<1	<1

Class C fly ash

Fly ash produced from the burning of younger lignite or sub bituminous coal, in addition to having pozzolanic properties, also has some self-cementing properties. In the presence of 10 water, Class C fly ash will harden and gain strength over time. Class C fly ash generally contains more than 20% lime (CaO). Unlike Class F, self-cementing Class C fly ash does not require an activator. Alkali and sulfate (SO_4) contents are generally higher in Class C fly ashes.

Figure 2 Class C fly ash

Class F fly ash

The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash is pozzolanic in nature, and contains less than 10% lime (CaO). Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime, with the presence of water in order to react and produce cementitious compounds. Alternatively, the addition of a chemical activator such as sodium silicate (water glass) to a Class F ash can lead to the formation of a geopolymer.

Figure 3 Class F fly ash

1.3 Features desirable for cement admixture

- **Spherical shape**: Fly ash particles are almost totally spherical in shape, allowing them to flow and blend freely in mixtures.
- **Ball bearing effect**: The "ball-bearing" effect of fly ash particles creates a lubricating action when concrete is in its plastic state.

- **Higher Strength**: Fly ash continues to combine with free lime, increasing structural strength over time.
- **Decreased Permeability** : Increased density and long term pozzolanic action of fly ash, which ties up free lime, results in fewer bleed channels and decreases permeability Increased Durability. Dense fly ash concrete helps keep aggressive compounds on the surface, where destructive action is lessened. Fly ash concrete is also more resistant to attack by sulfate, mild acid, soft (lime hungry) water, and seawater.
- **Reduced Sulfate Attack**: Fly ash ties up free lime that can combine with sulfate to create destructive expansion.
- **Reduced Efflorescence**: Fly ash chemically binds free lime and salts that can create efflorescence and dense concrete holds efflorescence producing compounds on the inside.
- **Reduced Shrinkage**: The largest contributor to drying shrinkage is water content. The lubricating action of fly ash reduces water content and drying shrinkage.
- **Reduced Heat of Hydration**: The pozzolanic reaction between fly ash and lime generates less heat, resulting in reduced thermal cracking when fly ash is used to replace portland cement.
- **Reduced Alkali Silica Reactivity**: Fly ash combines with alkalis from cement that might otherwise combine with silica from aggregates, causing destructive expansion.
- **Workability**: Concrete is easier to place with less effort, responding better to vibration to fill forms more completely. Ease of Pumping. Pumping requires less energy and longer pumping distances are possible.
- **Improved Finishing**: Sharp, clear architectural definition is easier to achieve, with less worry about in-place integrity.
- **Reduced Bleeding**: Fewer bleed channels decreases porosity and chemical attack. Bleed streaking is reduced for architectural finishes. Improved paste to aggregate contact results in enhanced bond strengths.
- **Reduced Segregation**: Improved cohesiveness of fly ash concrete reduces segregation that can lead to rock pockets and blemishes.
- **Reduced Slump Loss**: More dependable concrete allows for greater working time, especially in hot weather.

1.4 Fly ash utilization

The reuse of fly ash as an engineering material primarily stems from its pozzolanic nature, spherical shape, and relative uniformity. Fly ash recycling, in descending frequency, includes usage in: Portland cement and grout, embankments and structural fill, waste stabilization and solidification, raw feed for cement clinkers, mine reclamation, stabilization of soft soils, road sub base, aggregate, flow able fill, mineral filler in asphaltic concrete. Other applications include cellular concrete, geopolymers, roofing tiles, paints, metal castings, and filler in wood and plastic products.

Ash used as a cement replacement must meet strict construction standards, 75% of the ash must have a fineness of 45 μm or less, and have carbon content, measured by the loss on ignition (LOI), needs to be under 6%.

1.5 Beneficiation of Fly Ash

The utilization of fly ash in concrete has been reported to affect the required dosage of AEAs to entrain the proper amount of air in the concrete mixture. Instead of stabilizing the air–water/cement interface, the AEAs are strongly adsorbed by the carbon present in fly ash. Due to this reason the high unburned carbon content in the fly ash makes it unsuitable for use as cement admixture. When fly ash is used as part of a concrete mix, the maximum concentration of unburned carbon in the mix should be limited to 6.0.

Fly ash beneficiation is the recovery of carbon particles. High unburned carbon content in the fly ash makes it unsuitable for use as cement admixture. Higher LOI levels result in discoloration, poor air entrainment and segregation of mix components. Beneficiation is required to enhance the ability to extract high purity carbon and ash for the production of value- added products. Beneficiation techniques based on the differences in size, density, electrostatic and physical properties .Unburned organic fractions can be recycled back to the burner as fuel or used as a catalyst, activated carbon, or catalyst support. The purified inorganic fraction can be utilized as a cement additive.

Chapter 2
Literature review

The main purpose of separating unburned carbon from fly ash is to obtain high quality fly ash for concrete applications. Another incentive for a well-established separation technology is that, to efficiently utilize fly ash, high value products must be generated from raw ashes to counter balance the transportation cost of the material. According to the characterization study on different fly ash samples, it has been found that the major mineral components in fly ash are silicates, iron oxides, low-density silicates (cenospheres) and unburned carbons. These particulate mineral materials, after various treatments, can be used as fillers in plastics, reinforcement material in metal matrix composites, as well as refractory materials. The unburned carbon can be used as an adsorbent in removing hazardous substances such as mercury in flue gas. By separation of individually functional components, fly ash is converted from a completely waste material into various high value-added products.

Different Techniques of Separation

- Grinding
- Sieving
- Gravity separation
- Magnetic separation
- Triboelectrostatic separation
- Oil agglomeration
- Froth flotation
- Fluidized bed separation
- Air classifier

The pozzolanic properties of pulverized coal fly ash makes it useful in the concrete industry, where several benefits arise from this such as improved workability of the freshly mixed concrete and lower heat evolution during hydration. The hardened fly ash concrete shows increased strength together with a lower permeability, where the latter leads to a higher resistance toward aggressive admixtures [1-4]. In addition, partial replacement of cement with fly ash reduces the production costs of concrete due to the lower price of fly ash compared to cement [4]. In general, the amount of fly ash for typical durable concrete ranges from 15 to 35 wt% of total mass of fly ash and cement, but the amount can be up to 70 wt% for concrete in constructions like pavement, walls and parking lots [4] and 80 wt% in autoclaved aerated concrete.

Several properties of concrete are improved when air is entrained. Air entrainment occurs during agitation of the concrete paste, and the amount, which is approximately 5–6 vol%, is controlled by air entraining admixtures (AEAs). The utilization of fly ash in concrete has been reported to affect the required dosage of AEAs to entrain the proper amount of air in the concrete mixture. Instead of stabilizing the air–water/cement interface, the AEAs are strongly adsorbed by the carbon present in fly ash. Due to this reason the high unburned carbon content in the fly ash makes it unsuitable for use as cement admixture. When fly ash is used as part of a concrete mix, the maximum concentration of unburned carbon in the mix should be limited to 6.0.

Approximately one fourth of the electricity produced worldwide is generated in coal fired power plants. The coal demand for power generation is increasing in the absence of alternative power generation methodologies. The coal fired power plants produce fly ash in large volumes. The increase in coal demand for power generation poses a substantial challenge to power plant industries for fly ash disposal. Industrial utilization of fly ash from coal combustion is an important environmental and economic issue. Disposal of fly ash, e.g. in a landfill, enhances the risk of contaminating the ground water by leaching of heavy metals contained in the fly ash. Today, the primary market for fly ash utilization is as pozzolanic additive in the production of concrete. However, the residual carbon in fly ash may interfere with air entraining admixtures (AEAs) added to enhance air entrainment in concrete in order to increase its workability and resistance toward freezing and thawing conditions. The problem has increased with implementation of low-NOx combustion technologies [5]. A lot of research activity is going on in this area. Many methods have been attempted to classify the unburned carbon content of ash,including,sieve classification, electrostatic classification [6] (two installations based on electrostatic separation for fly ash beneficiation is working at Carolina Power & Light Company, North Carolina, USA) , density gradient centrifugation [7], oil agglomeration [8], wet classification [9] , vibration classification, jet mill classification. Each has an advantage and a disadvantage but none has been used in common practice or with great success. Usually, there are four major processing techniques for the physical separation of various components from fly ash, i.e. gravity separation, electrostatic separation, magnetic separation, and froth flotation. The gravity separation process can be used to separate dense particles with light particles, here in this special case, to extract unburned carbon from the coarse fraction of fly ash. This coarse fraction of fly ash has a high LOI value and is difficult to process with other techniques such as froth flotation [10].

In a study [11], a set of nine coal fly ashes, obtained from various US utilities, were fractionated by standard dry-sieving techniques. The carbon contents of the different size fractions were measured, and the nature of the carbon particles was microscopically examined. Significant differences were found in the distribution of carbon in class F and class C ashes. In another study [12], two types of air classifiers, namely a closed-type pneumatic separator and a micron separator, have been investigated. In terms of separation efficiency, it was found that the micron separator has the potential to be applied in cenospheres recovery from coal fly ash. An industrial fly ash sample was cleaned by three different processes [13], which were triboelectrostatic separation, ultrasonic column agglomeration, and column flotation. The unburned carbon concentrates were collected at purities ranging up to 62% at recoveries of 62%. Column flotation was determined to be the most effective process for the collection of carbon concentrates at a LOI value of 61% and a carbon recovery of 62% with 90% of the ash reporting to the tails with LOI values <8% for the Shawville fly ash. Authors concluded that, in all cases, there is room for significant improvement in the cleaning performance of these separation processes.

The thermal power plants are still the main source of power generation in India. These thermal power plants have been generating about two thirds of the power demands of the country. There are about forty major thermal power plants in India. The economy of India is developing at a high rate. Fly ash, a coal combustion residue (CCR) is a complex heterogeneous material. Although, in the strictest sense, fly ash is the finest CCR (0.2–90 Ǻm) formed due to the transformation of mineral matter present in coal particles during combustion [14], it has become a misnomer, particularly in respect of fly ash generated at

Thermal Power Plants in India. Because of the poor combustion efficiency of the combustors, lack of proper quality control in maintaining the particle size of the pulverised coal feed etc, the fly ash has a wide distribution of char, semi-coke or coked carbon matters of large dimension (90–300 Ǻm). It is irregularly shaped, containing lacy, vesicular, alumino-siliceous matter of complex composition and fine solid/hollow alumino-siliceous spheres.
There are very few publications in this research area from India. The characterization of fly ash helps in understanding the utilization potential of the fly ash. Sarkar et al. [15, 16] from Indian School of Mines, Dhanbad have characterized the fly ash from Bokaro Thermal Power Plant Jharkhand. The results of their study reveal that there is a striking difference in the features and properties of the coarser and finer particles. The coarser fractions of the non-magnetic component seem to contain high percentage of char and semicoked/coked carbonaceous particles. Nayak [4] studied the agglomeration of fly ash for refractory applications.

Power demand in the country is on the rise and most of the new proposed power plants will be using coal as fuel. This will lead to increase in the generation of fly ash. In a densely populated country like India the fly ash disposal in landfills is not a viable option. Industrial utilization of fly ash from coal combustion is an important environmental and economic issue.

In the study [18], the specific gravity and the fineness of the fly ashes increased with an increase in the grinding time. Themorphology of the fly ashes was changed by grinding. Most of the plerospheres and large, irregular-shaped particles were crushed. However, the number of the spherical particles reduced with increased grinding.

M.L. Gray et al.[13], described the operating conditions of triboelectrostatic separator :-
The tribo parallel plate separator used for this study consists of a venturi feed system driven by nitrogen pressure, an injection nozzle, and a high voltage separation section. The fly ash particles pass through the venturi feeder and become charged in this turbulent flow zone by contact with the copper tubing and with one another. The contact of the particles with copper surfaces, especially in the turbulent zone of the in line static mixer, results in effective charging of both unburned carbon and mineral. These charged particles then are forced out the nozzle in a ribbon of entrained particles approximately7.62* 0.3175 cm. This plume of particles is directed between two parallel charged plates15.24 cm long 7.62 cm apart. For fly ash separations, this unit is operated 25,000 V on the separator plates. The positively charge

unburned carbon particles are attracted to the negative electrode and the negatively charged mineral particles are moved to the positive electrode. A splitter is placed 15.24 cm downstream from the nozzle to separate the unburned carbon-rich and ash-rich fractions and directs them to two collection cyclones. The entire separator is swept with laboratory air by applying vacuum to the outlets of the collection cyclones.

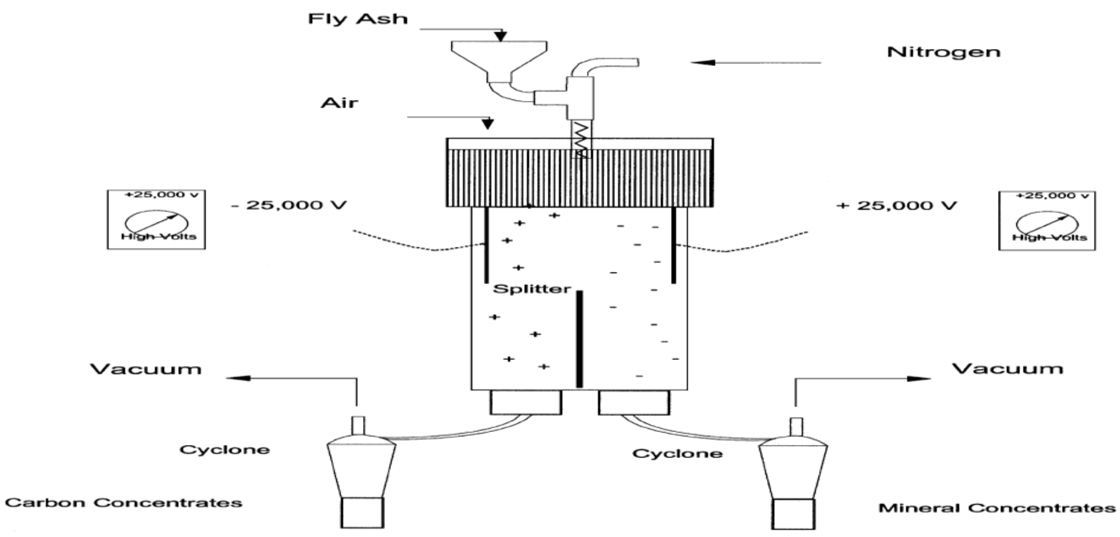


Figure 4 Triboelectrostatic separator (source :-Gray M. L. et al.(2002). Physical cleaning of high carbon fly ash. Fuel Processing Technology 76, 11-12)

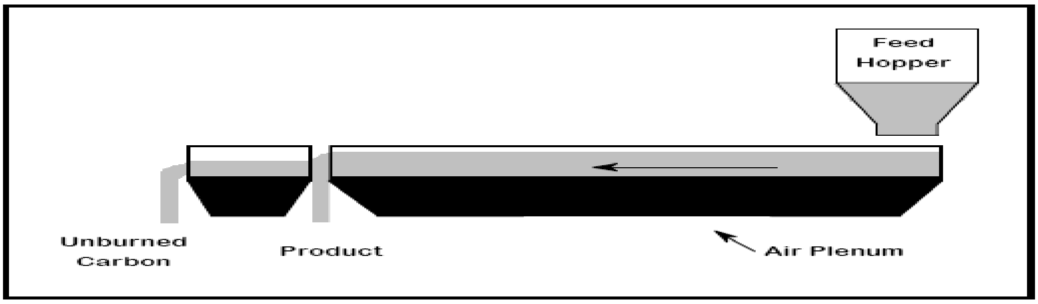
TAO Daniel et al.[19],studied important parameters of triboelectrostactic separator :-

1) The separation performance of the rotary triboelectrostatic separator with fly ash is dependent on the operating parameters such as roller rotation speed, roller charging voltage, injection flow, and coflow rate, etc. Compared to other electrostatic processes, the performance of the rotary triboelectrostaticseparatoris significantly less sensitive to feed rate change. Air humidity has marginal effect on the separation in the range of 20%–50%.
2) Faster roller rotation speed tends to generate better separation as a result of enhanced particle surface charging density. A rotation speed of around 5000 r/min appears to be the best for all fly ash samples tested.
3) Compared to other operating parameters, the roller charging voltage had the least significant impact on the separation performance. However, it has been observed that separation performance of many fly ash samples were strongly dependent on the roller charging voltage.

4) Coflow and injection flow rates had very strong effects on the fly ash separation efficiency. The optimum conditions were 2.3 m/s for the coflow velocity and 2.5–3.1 m/s for injection flow velocity.

Heng Ban et al.[20],studied that dry triboelectrostatic separation of fly ash has the potential to be an effective method of separating unburned carbon from fly ash. Laboratory tests on a simple parallel flow separator showed that 60-80% of ash could be recovered at carbon contents below 5%, and 50%of carbon could be recovered at carbon concentrations over 50%. Additional studies should be initiated to evaluate the effects of ash properties on separation with the goal of optimizing the beneficiation process.

In the study [21], when a gas, such as air, flows upward through a container filled with particles, some of the gas flows through the bed in the form of voids of gas or bubbles if the gas flow rate is high enough. As the bubbles move upward through the bed, they cause agitation and motion of the solid particles and circulation of bed material in the vertical direction. This leads to transport of low density particles to the top of the bed and high density particles to the region of the distributor at the bottom of the bed. In the case of fly ash, the relatively low density carbon particles segregate towards the top of the bed, permitting a separation between the unburned carbon and the inert portion of the fly ash.



Unburned carbon is removed from the fly ash in a long horizontal fluidized bed. The material is separated into carbon-rich and carbon-lean streams at the discharge end.

Figure 5 Horizontal fluidized bed separator (source : Lehigh energy update, april 1996, vol. 14(2))

J.Y. Hwang et al.[10], studied this process, froth flotation is a widely used separation technique. In the slurry of solid and water, physico-chemical processes take place at the interface of solid, liquid and gas phases, during the process of froth flotation. A collector selectively coats the surfaces of certain mineral particles causing the surface of one or more of the components in the slurry to become hydrophobic and responsive to the attachment of air bubbles introduced into the slurry. Separation is accomplished as the mineral- laden air bubbles rise to the surface in a froth (or a concentrate) which flows over a weir, leaving in the slurry particles that are not coated with the collector. These pass out the bottom of the cell. Under proper conditions, almost all materials can be made to float. Success depends on the capability to control the surface chemistry to yield selective adsorption of collectors. A second reagent, known as a frother, is used to stabilize the air bubbles upon which the floatable minerals become attached.

M.L.Gray et al.[22], described the oil agglomeration process and gave the optimum operating conditions for the recovery of unburned carbon. The experimental setup in figure 6 consisted of a 6 ft by 4 in. Plexiglas column equipped with a variable speed electrical motor, a slurry tank equipped with a variable air motor, a solvent recovery tank and 60-mesh stainless steel screen. Initially, the solvent and fly ash slurry was prepared at about a 5:1 weight ratio and conditioned for two minutes before it was pumped into the column at the feed rate of 930 ml/min. During the course of these tests the agitation speed was maintained at 400 rpm with airflow of 189 ml/min. The overflow unburned carbon product was collected on a 60-mesh screen, air-dried and analyzed to determine its purity. All of the carbon recoveries were calculated on a total weight carbon basis present in the feed fly ash. These conditions were predetermined during the initial developmental stages of this process.

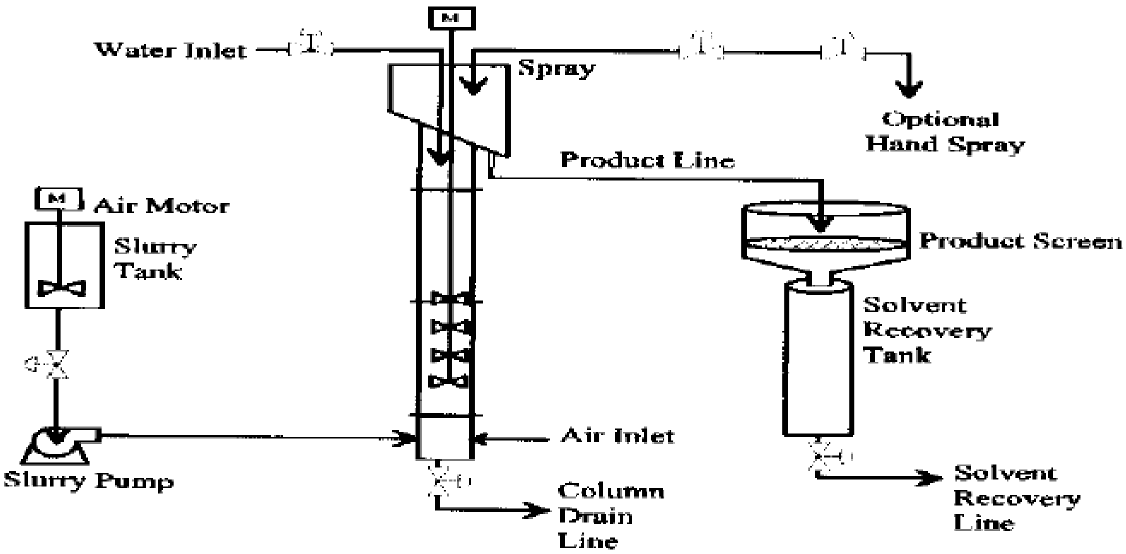


Figure 6 Agglomeration column (Gray M. L. et al.,2001)

Chapter 3
Objectives

The objective of this study was to study the effectiveness of some simple techniques for fly ash beneficiation. The high LOI of fly ash used in this work was taken from NFL Nangal, India. The following processes were selected for effectiveness study:

1. Froth flotation
2. Screening followed by froth flotation
3. Fluidized bed separation

Chapter 4
Materials and Methods

4.1 Loss on Ignition

Loss on Ignition is a test used in inorganic analytical chemistry, particularly in the analysis of minerals. It consists of strongly heating ("igniting") a sample of the material at a specified temperature, allowing volatile substances to escape, until its mass ceases to change. This may be done in air, or in some other reactive or inert atmosphere. The simple test typically consists of placing a few grams of the material in a tarred, pre-ignited crucible and determining its mass, placing it in a temperature-controlled furnace for a set time, cooling it in a controlled (e.g. water-free, CO_2-free) atmosphere, and redetermining the mass. The process may be repeated to show that mass-change is complete

The loss on ignition is reported as part of an elemental or oxide analysis of a mineral. The volatile materials lost usually consist of "combined water" (hydrates and labile hydroxy-compounds) and carbon dioxide from carbonates. It may be used as a quality test, commonly carried out for minerals such as iron ore. The loss on ignition of a fly ash consists of contaminant unburnt fuel.

In pyroprocessing industries such as lime, calcined bauxite, refractories or cement manufacture, the loss on ignition of the raw material is roughly equivalent to the loss in mass that it will undergo in a kiln. Similarly for minerals the loss on ignition represents the actual material lost during smelting or refining in a furnace or smelter. The loss on ignition of the product indicates the extent to which the pyroprocessing was incomplete. ASTM tests are defined for limestone and lime and cement among others.

Method for calculating LOI

1. Dry crucibles at 105 ^oC for at least 1hour.
2. Cool in dessicator for 30 minutes.
3. Taken the weight of dried crucible (W_C).
4. Add sample, say about half full.
5. Dry crucible + sample in oven (at about 105 ^oC overnight).
6. Cool crucible in dessicator and reweigh (W_S).
7. Place crucible in the muffle furnace at 750 ^oC and leave for 2 hours.
8. Place crucibles in a dessicator to fully cool.

9. Reweigh crucible + ash (W_A).

Calculation:

$$\text{LOI (\%)} = \frac{(W_s) - (W_A)}{(W_S) - (W_C)} \times 100$$

4.2 Froth flotation cell

Fabrication

A low cost floatation cell design was conceived and the floatation cell was self fabricated as described below.

A plastic container was taken.

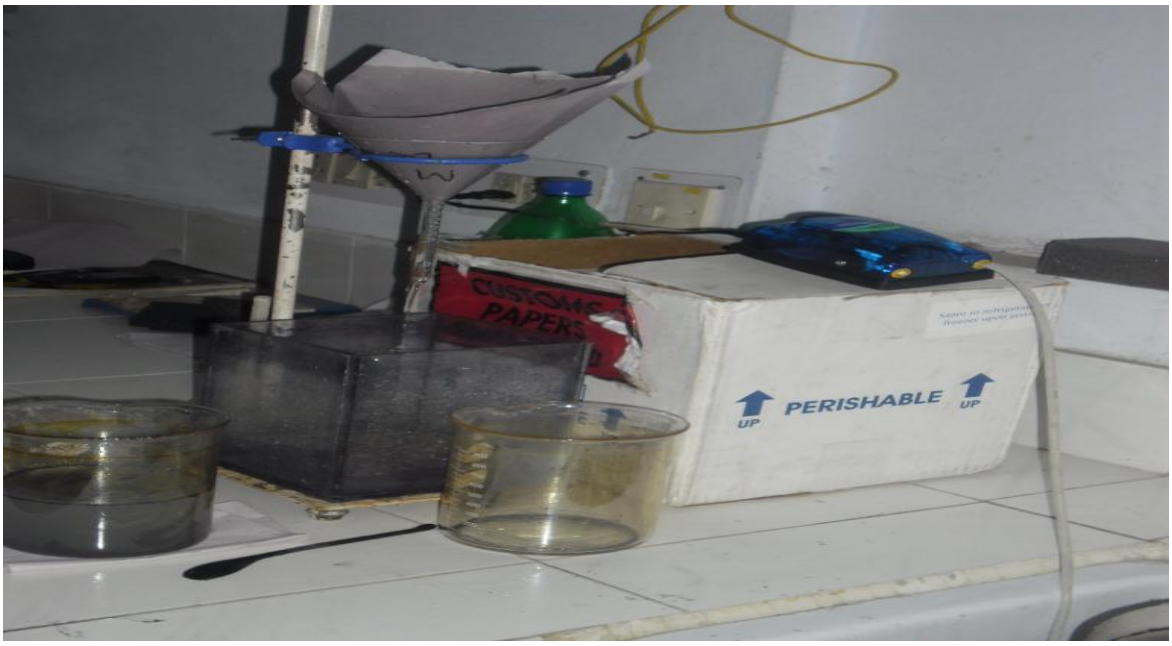
A rubber pipe was coiled at the base of the container and an arrangement for the outflow collection was provided

Air pump was connected at other end of the coiled pipe for air bubbling

Figure 7 Fabrication of froth flotation cell

Experimental procedure:

A mixture of fly ash and collector is prepared in a beaker, mixture was agitated to ensure uniformity. Carbon rich fraction is collected from the top and ash settled at the bottom.



The top and bottom particles were filtered for analysis.

Figure 8 Working of froth flotation cell

The following standard procedure was used for the flotation experiments:

1. Collector (kerosene oil) was added at the desired dosage in 30 g fly ash. The sample was then agitated in 1L beaker filled with water for some time to thoroughly mix the collector with the suspended fly ash.
2. The air pump was switched on, and the slurry was added into the cell .
3. The products from flotation were filtered, dried, weighed, and analyzed. Percentage of loss-on-ignition (% LOI) was determined.

4.3. Fluidized bed separator

Fabrication

A cylindrical glass tube (height = 2' and diameter = 1.5") was used for fluidizing the fly ash particles. A sintered disk is provided at the bottom of the column for proper air distribution and to avoid choking of the air inlet connection. The regulated air supply was provided from another already existing setup. The particle collection arrangement was designed so as to recover all the particles from the exhaust air.

Figure 9 Fabrication of fluidized bed separator

Experimental procedure:

Fly ash (20 g/10 g) sample was charged into the column. Air flow was increased steadily using a pressure regulator till the bed was uniformly fluidized. The fine particles escaping from the bed were collected in a flask. The particles that were escaping with the air were collected by contacting the air with water. LOI values of the fraction elutriated and the fraction retained in the bed were determined.

4.4 Sieve analysis

A **sieve analysis** is a procedure used to assess the particle size distribution (also called *gradation*) of a granular material.

The size distribution is often of critical importance to the way the material performs in use. A sieve analysis can be performed on any type of non-organic or organic granular materials including sands, crushed rock, clays, granite, feldspars, coal, soil, a wide range of manufactured powders, grain and seeds, down to a minimum size depending on the exact method. Being such a simple technique of particle sizing, it is probably the most common.

4.4.1 Procedure

Sieve analysis involves a nested column of sieves with wire mesh cloth (screen). A stack of four sieves having sizes 90µ, 75µ, 45µ and 25µ and a pan were used for sieve analysis. A 100 g sample was put into the top sieve which has the largest openings. Each lower sieve in the column has smaller openings than the one above. At the base was a round pan, called the receiver. The column was placed in a mechanical shaker. The sieving was done for 10 min. After the shaking was complete the material on each sieve is weighed. The weight of the sample of each sieve was then divided by the total weight to give a percentage retained on each sieve.

Figure 10 Sieve shaker used for sieve analysis

Chapter 5

Results and Discussion

The fly ash sample, obtained from NFL Nangal, Punjab, was taken for LOI determination. All the fly ash was well mixed before subjecting to LOI determination and beneficiation. The well mixed sample of fly ash showed good reproducibility for LOI determination as shown in Table 2. These results show that the LOI of the fly ash is 14.9± 0.2 (wt%).

Table 2 LOI of fly ash sample obtained from NFL, Nangal

Trail no.	LOI (wt%)
1	15.08
2	14.79
3	14.72

5.1 Froth flotation process

The froth flotation process is shown to be very promising for fly ash LOI reduction [10]. However, the success of the process depends on the doses of collector/frother. In the present study, few initial experiments were done without the use of collector. In these experiments 15 g fly ash sample was taken in beaker and slurry was prepared. This slurry was slowly added into the floatation cell and the overflow was collected in a beaker. No separation was obtained as the carbon particles did not attach with the rising air bubbles. Figure 11 shows the top surface of the floatation cell.

Figure 11 Froth flotation separation without collector dose

A second set of experiments were conducted by using a collector (kerosene) dose of 5 ml in 15 g fly ash sample. In this case the carbon particles got coated with the collector and rose to the surface after attaching with the air bubbles. The Figure below shows the top surface of the flotation cell and the collecting beaker when the collector was added to the fly ash sample.

Figure 12 Froth flotation separation with collector dose

The LOI results of top and bottom fractions for these experiments showed good reproducibility and are reported in Table 3. The results show that with the froth flotation process when collector dose is 5ml/15 g of fly ash sample, the LOI of bottom fraction was reduced to 10±0.5 (wt%) and the carbon concentrate in the top fraction had had LOI 48±1 (wt%).

Table 3 LOI of top and bottom fraction of froth flotation cell

Trail no.	LOI of top fraction(%)	LOI of bottom fraction(%)
1.	48.30	10.42
2.	48.87	10.37
3.	46.91	9.64

Figure 13 and 14 shows the fractions obtained from froth flotation. The difference in the colour of top and bottom fractions is because of difference in carbon content.

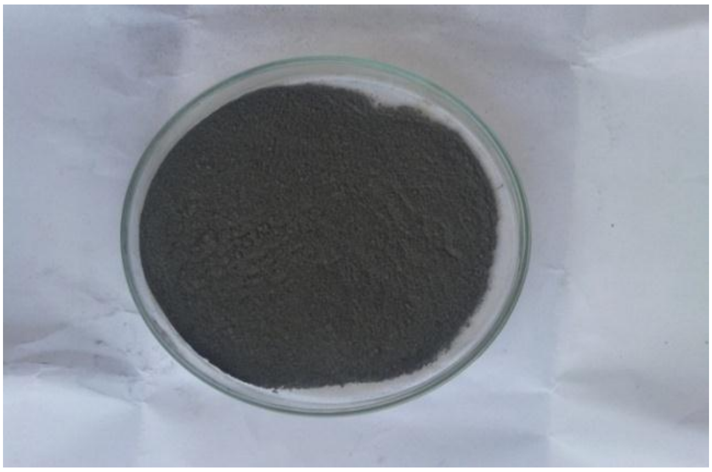


Figure 13 Bottom fraction from froth flotation

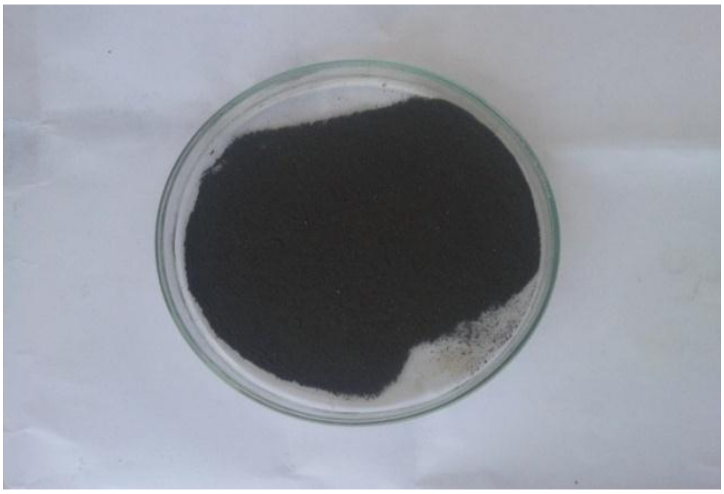


Figure 14 Top fraction from froth flotation process

Collector dose:

In the following set of experiments, the collector dose was optimized. For these experiments 30 g sample of fly ash with varying dose of collector was subjected to separation by froth flotation. The LOI of top and bottom fractions were determined and are given in table 4. The results show that a collector dose of 0.5 ml/30 g fly ash was sufficient for the separation. Therefore, for the further experimentation the optimum collector dose of 0.5 ml/30g of fly ash sample was taken.

Table 4 LOI of froth flotation fractions with and varying collector dose

Collector dose (ml)	Fly ash sample (g)	LOI of top fraction (wt%)	LOI of bottom fraction (wt%)
4	30	46.04	10.42
3	30	42.35	10.77
2	30	47.73	9.91
1	30	46.21	10.09
0.5	30	51.62	10.13
0.25	30	48.72	13.71

5.2 Screening followed by froth flotation

In these experiments, the fly ash samples were first sieved and the various fractions obtained were then subjected to separation by froth flotation. Four sieves having sizes 90µ, 75µ, 45µ and 25µ were used for sieve analysis. Table 5 shows the LOI obtained for different sieve sizes. As expected, the sieve size < 25µ gave least LOI value.

Table 5 Sieve analysis results

Particle size	Weight obtained (g)	Mass fraction (%)	LOI (%)
>90 µ	74.89	27.33	15.74
<90 µ & > 75 µ	21.72	7.93	22.13
<75 µ & > 45 µ	81.95	29.91	11
<45 µ & > 25 µ	67.28	24.55	10.02
< 25 µ	28.12	10.28	8.07

Table 6 shows the results obtained for different size fractions (having LOI less than the feed fly ash sample) subjected to separation by froth flotation. For all these fractions the LOI value in bottom fraction of the froth flotation was about 8%.

Table 6 LOI of various sieved fractions followed by froth flotation

Sieve size	LOI(%) after sieve analysis	LOI after sieving and froth flotation	
		LOI(%) of top fraction	LOI(%) of bottom fraction
>90 μ	15.739	--	--
<90 μ &> 75 μ	22.13	--	--
<75 μ &> 45 μ	11	32.71	7.73
<45 μ &> 25 μ	10.022	40.37	7.51
< 25 μ	8.074	37.249	8

5.3 Fluidized bed separation

Initially 20 g sample of fly ash was taken for these experiments, but the results were not reproducible. Then 10 g sample of fly ash (shallow bed) was subjected to fluidized bed separation. For these experiments, the reproducible results were obtained. Table 7 shows the results obtained from the fluidized bed separation process, the LOI reduced to 10.5 ± 1% in top fraction.

Table 7 LOI of fly ash fractions obtained from fluidization bed separation

Trail no.	LOI of top fraction (%)	LOI of bottom fraction (%)
1.	11.39	20.25
2.	10.96	18.76
3.	9.52	17.91
4.	11.25	20.61
5.	11.18	20.26

Fractions obtained from fluidized bed separation

Figure 15 and 16 shows the fractions obtained from fluidized bed separation process. There is difference in the colour of the bottom (high LOI) and top (low LOI) fractions.

Figure 15 Top fraction from fuidized bed separation

Figure 16 Bottom fraction from fuidized bed separation

Chapter 6
Conclusions and recommendations

Conclusions

The effectiveness of froth flotation (wet process) and fluidized bed separation (dry process), for LOI reduction from fly ash, are studied. The fly ash sample was procured from NFL Nangal, Punjab, India. The froth flotation cell and fluidized bed experimental setup used for the study were designed and fabricated/assembled.

The froth flotation process could reduce the fly ash LOI from ~15% to ~10%. Screening of the fly ash sample before subjecting to separation by froth flotation showed promising results in LOI reduction. For all three size fractions below 75µ, the LOI could be reduced to ~8%.

Fluidized bed separation process studied for LOI reduction also showed promising results. In a shallow bed, the effectiveness of the fluidization process was close to froth flotation process. The major advantage of using fluidized bed process is its environmental friendliness as the wet process (froth flotation) causes several other environmental issues.

Recommendations:

Unburned carbon is an important component of fly ash, whose composition in fly ash varies with combustion efficiency. Low cost carbon separation processes should be investigated further. Unburned carbon is similar to the precursors for production of premium carbon materials, such as, activated carbon. Activated carbon made from unburned carbon of fly ash has a significant potential of cost advantage over other activated carbon. Therefore, separation of unburned carbon from fly ash will be beneficial to fly ash application, either for carbon recycling or mineral fly ash application in cement production and zeolite synthesis. However, few investigations have been currently conducted in the utilization of unburned carbon for production of activated carbon. More efforts should be attempted in this area.

Chapter 7
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Appendix I
Indian Scenario

Source of Fly Ash In India

According to Central Electricity authority of India, there are around 83 major coal fired thermal power plants and 305 hydro plants existing in India. As per the ministry of power statistics, the total installed generating capacity (Thermal+ wind) during 2003-2004 was about 79838 MW and hydropower generation was 29500 MW. In addition to this, there are more than 1800 selected industrial units which had captive thermal power plants of >1MW.

Present Scenario on Fly Ash in India

- Over 75% of the total installed power generation is coal-based
- 230 - 250 million MT coal is being used every year
- High ash contents varying from 30 to 50%
- More than 110 million MT of ash generated every year
- Ash generation likely to reach 170 million MT by 2010
- Presently 65,000 acres of land occupied by ash ponds
- Presently as per the Ministry of Environment & Forest Figures, 30% of Ash is being used in Fillings, embankments, construction, block & tiles, etc.

Ash Content in Indian Coal

The quality of coal depends upon its rank and grade. The coal rank arranged in an ascending order of carbon contents is:

Lignite --> sub-bituminous coal --> bituminous coal --> anthracite

Indian coal is of mostly sub-bituminous rank, followed by bituminous and lignite (brown coal). The ash content in Indian coal ranges from 35% to 50%.
According to National Thermal Power Corporation (NTPC), coal is used for approximately 62.3% of electric power generation in India, oil and gas accounts for 10.2%, hydro's share is 24.1%, nuclear, wind, and other contribute remaining 3.4%.

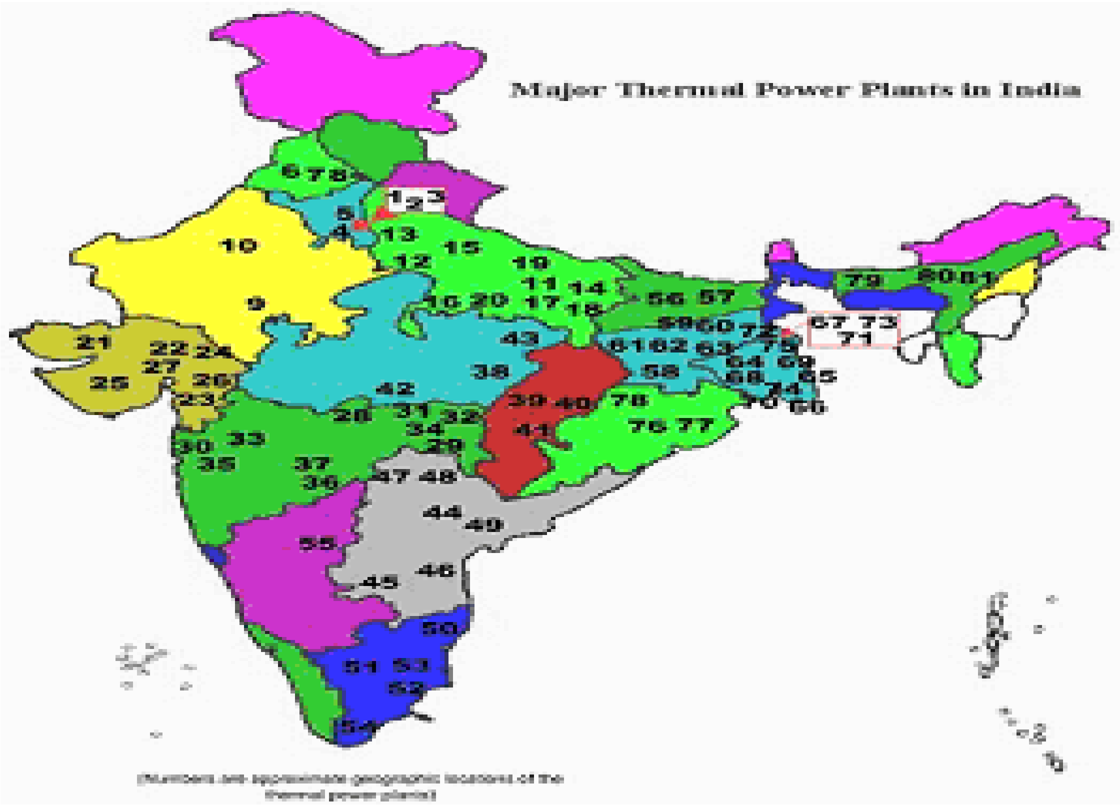

FIGURE 17 Geographical location of major thermal power plants in India (source:-Fly ash summary report in India 2010)

Current Fly Ash Generation in India

According to an estimate 100,000 MW capacity or more would be required in the next 10 years due to continually increasing demand for electricity. In India fly ash generation is around 110 million tonnes / year and is set to continue at a high rate into the foreseeable future. Presently majority of the coal ash generated is being handled in wet form and disposed off in ash ponds which is harmful for the environment and moreover ash remains unutilized for gainful applications. India has sufficient coal reserves. In India almost 65-70% of electricity production is dependent on coal which produces a huge quantity of Fly Ash as residue which is allegedly a waste product in Thermal Power Stations. Fly Ash has a vast potential for use in High Volume fly ash concrete especially due its physic-chemical properties. A good amount of research has already been done in India and abroad on its strength and other requisite parameters.

Current Ash Utilization

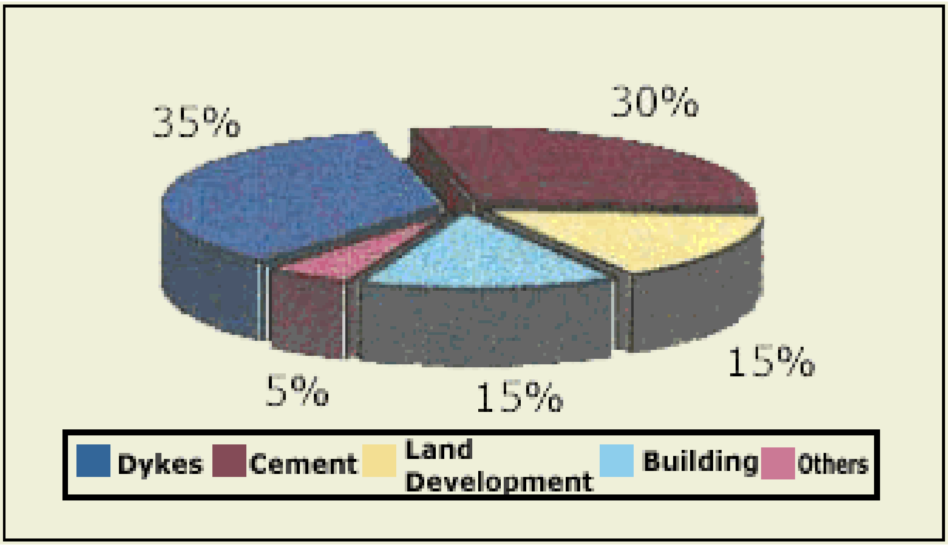

Figure 18 Ash utilization areas (source:-Fly ash summary report in India 2010)

Appendix II
Morphological Analysis of fly ash

The Scanning electron microscopic study (SEM) of the fly ash fractions reveal some interesting features related to the morphology of fly ash samples. A distinct difference is observed between the magnetic and non-magnetic components. The non-magnetic components are usually irregular in shape and size. The magnetic components have a general tendency to be spheroidal. Figure 19 shows that our sample is non-magnetic as the particles observed are irregular in shape.

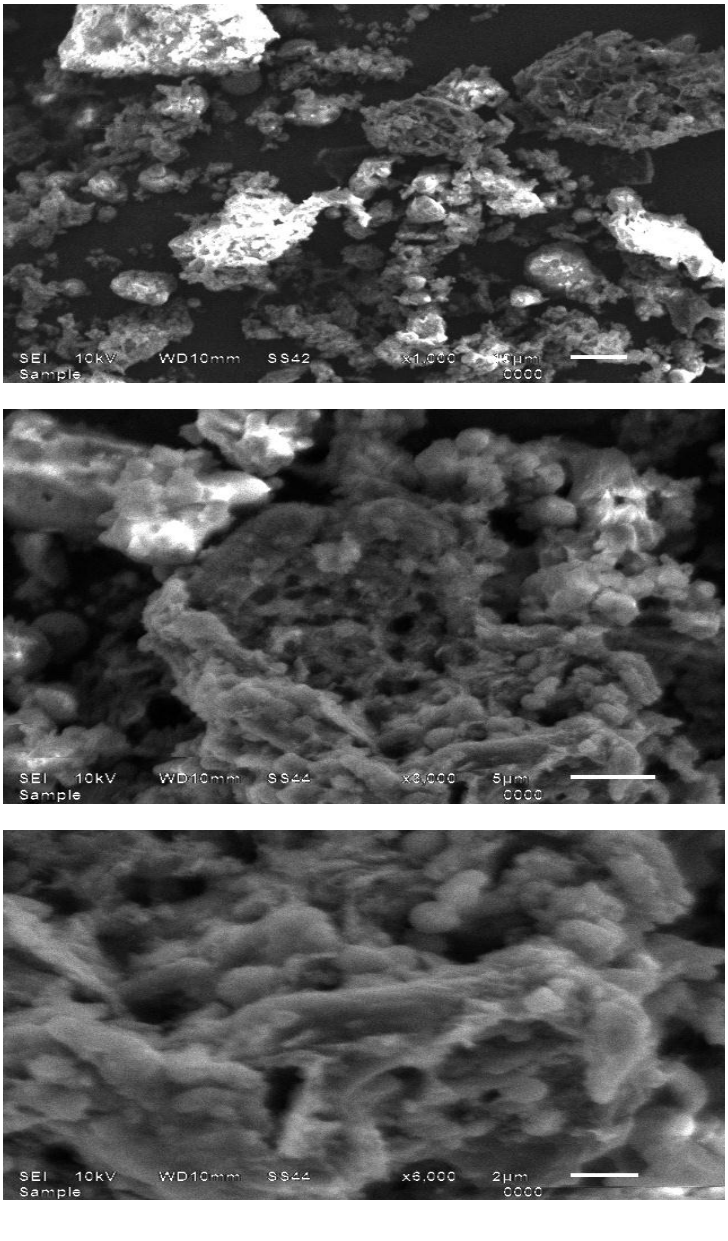

Figure 19 SEM images of fly ash sample

In the present study, it has been observed that in one of the particles, partial surface deposition of iron oxides/elemental iron has taken place. EDX –analysis reveals (Fig. 20) that there is high enrichment of Al, Si, O with trace s of K, S and Ti.

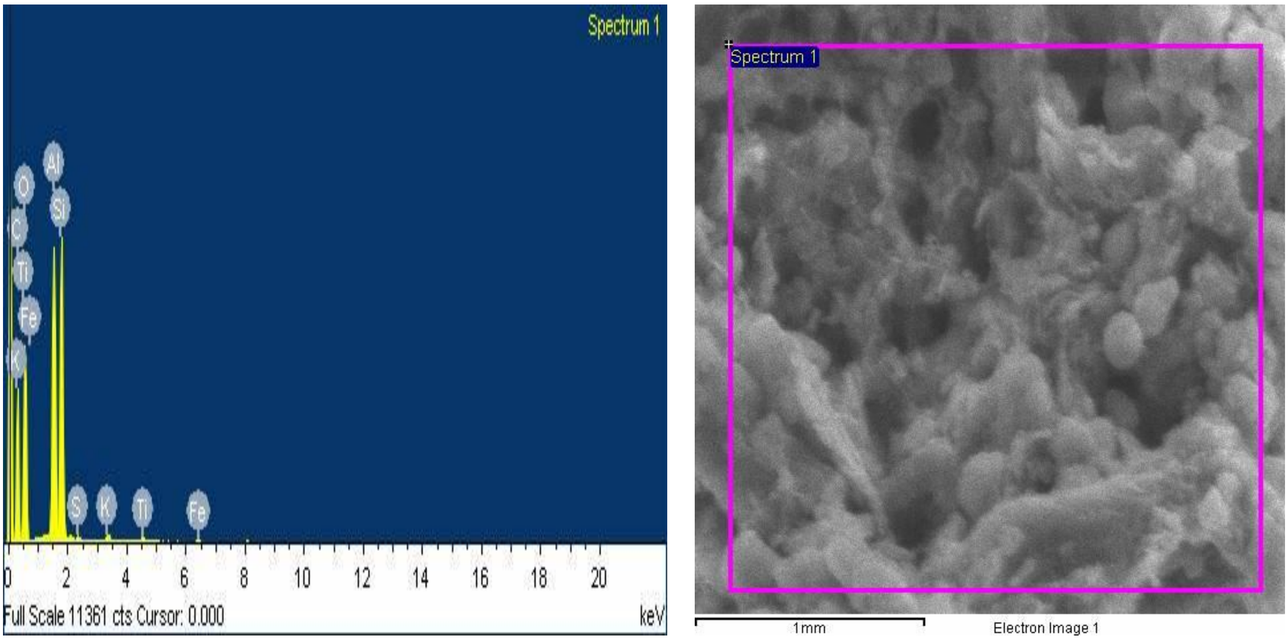

Figure 20 EDX of SEM image.