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Physiochemical and engineering characteristics of fly ash and its application in various field - a review

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Abstract

Fly ash is generated during the combustion of coal in thermal power plant, large amount. This large amount fly ash creates many problems like huge amount of land required for disposal and toxicity associated with heavy metal leached to groundwater. This paper focussed the physiochemical and engineering characteristics of fly ash for their valuable application. Fly ash is the inorganic part of coal containing glassy, amorphous structure and spherical shape. This is containing SiO_2, Al_2O_3, and Fe_2O_3 in higher amount. Major crystalline phases present in fly ash are quartz (SiO_2) and mullite. According to them fly ash is an excellent potential raw material for the manufacture of construction material like cement, light weight building block, and concrete. With the help of pH, electrical conductivity and presence of various trace elements, fly ash is also suitable for agriculture.

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Introduction

The main problem with the fly ash is its generation in huge quantity. In India problem is deeper due to reliance on coal–fired power plants for electricity generation. During 2011-2012, 220 million tonne fly-ash were generated as per Fly-ash utilization programme (FAUP), Department of Science and Technology, New Delhi, India. As per the estimates, its generation is expected to increase to about 1000 million tonne by 2032 (Annual Report 2012-2013, DST). Numbers of utilisation techniques are available for utilisation of this fly ash but effectiveness of such uses are property dependent. Properties of fly ash are varying from plant to plant. Therefore present study try to review the status of fly ash generation and properties with its utilisation in various fields to solve the problem of handling and storage of fly ash.

The Coal-based thermal power plants in world face serious problems for handling and disposal of the fly ash (Pandian, 2004). Be deficient in of alternative application of this ravage, the bulk of fly ash is stockpiled or slurries to ash dam (Abbott *et al.,* 2001; Mattigod *et al.,* 1990). This massive quantity of fly ash is dumped in the vast areas of ash pond and is leading to grave environmental degradation because of leaching of toxic elements. In dry season it is carried out by the current of air from ash pond areas and causes severe respiratory diseases to surrounding population. At present the bulk utilization of unused ash is a serious issue for power plant authorities due to requirement of large land area for the disposal of fly ash (Das *et al.,* 2012) and its continue to increase various environmental, economic and social problems (Basu *et al.,* 2009).

In India its utilization is very less amount for different purposes (Bhattacharjee and Kandpal, 2002). Use of fly ash in forming more productive things would have considerable environmental benefits, reducing environmental pollution. The beneficiation techniques are used to influence the characteristic of fly ash in order to optimize its utilization, increase its value and minimize disposal cost (Hwang, 1997). About the information on the degree of the unburned carbon, mineralogy, and the quality of fly ash needed in the market place are supreme in creating an opportunity for research into the modification and exploitation of the unique chemistry of fly ash (Wang *et al.,* 2004). The concentration of different heavy metals, radio nuclides and toxic elements in fly ash is very low which make its suitability for various safe utilization and other factor for its best utilization is its physical and chemical property which is very close to the range of common soils (Excise Duty on Fly Ash - c-farm.org).

Fly Ash

By product after the combustion of coal in thermal power plants is known as fly ash (Eskom, 2002). Fly ash emission from the stacks into the environment is controlled by particulate devices such as scrubbers, mechanical and electrostatic precipitators (Kumari, 2009). In other words, the most voluminous fraction of Coal combustion products is fly ash, which is a fine particulate inorganic matter collected through mechanical processes, electrostatic precipitators, and fabric filters from flue gas produced by the combustion of pulverized coal in boiler assembly (ACAA, 2011).

Fly ash is spherical particles makes up 10 to 85% part of the total coal ash residue, usually ranging in diameter from 0.5 to 100 microns (Jafri and Kumar, 2013). It is a heterogeneous material primarily consisting of amorphous aluminosilicate spheres with minor amounts of iron-rich spheres, some crystalline phases, and a small amount of unburned carbon (Tishmack and Burns, 2004; Kiilaots *et al.,* 2004; Kutchko and Kim, 2006; Jegadeesan *et al.,* 2008). The Heavy metal content of Indian fly ash is reported to be lower than the fly ash of other countries like from Greece, Spain, China and UK (Sushil and Batra, 2006). Indian fly ashes are generally found to be safe from the point of view of radioactivity (Singh and Singh, 2005). The most common elements in Indian fly ash is Si, Al, Fe, Ca, Mg, K and Na (Styszko-Grochowiak *et al.,* 2004; Akinyemi *et al.,* 2012) and trace elements such as As, Zn, Pb and Se, base metals are Ga and Ge and rare earth elements occur in fly ash (Hower, 2012).

Classification of fly ash

Coal combustion based power plants generated fly ash typically fall within the American Society for Testing and Materials (ASTM) fly ash classes C and F. The difference between Class F and Class C fly ash is given in Table 1.

Table 1. Differences between class F and class C fly ash.

Class F	Class C	References
Class F fly ash produces by burning of harder anthracite and bituminous coal.	Class C fly ash produces by burning of younger lignite or sub bituminous coal.	Page *et al.,* 1979
This class of fly ash contains less than 20 % of lime.	This class of fly ash contains more than 20 % of lime.	Obla, 2008
Alkali and sulfate contents are generally lower in class F.	Alkali and sulfate contents are generally higher in class C.	Page *et al.,* 1979
The quantities of Si, Fe & K oxides are higher in Class F.	The quantities of Si, Fe & K oxides are lower in Class C.	Murty and Narasimha, 1999
The CaO, MgO, SO_3 & Na_2O quantities are lower in Class F.	While CaO, MgO, SO_3 & Na_2O quantities are higher in Class C	Murty and Narasimha, 1999
Class F fly ash has been rarely cemetitious when mixed with water.	Class C fly ash usually has cementitious properties in addition to pozzolanic properties.	Shetty, 2005

Generation of fly ash

In thermal power plant, Fly ash is generated when coal is fed to a series of mills that pulverize the coal to a very fine powder. This powder is then fed into a boiler which combusts the coal to produce heat (flyash Australia). In general, three types of coal-fired boiler furnaces used in the thermal power plant. They are referred to as dry-bottom boilers, wet-bottom boilers, and cyclone furnaces. In them dry-bottom furnace is most commonly used (Oram, 2009).

Fly ash is generated by burning of pulverized coal in the boiler furnace and carried by flue gas, passed in superheater from there it goes to the reheater, economizer and air pre-heater one by one. Finally reached in to electrostatic precipitator. The path followed by flue gas is given in Fig. 1.

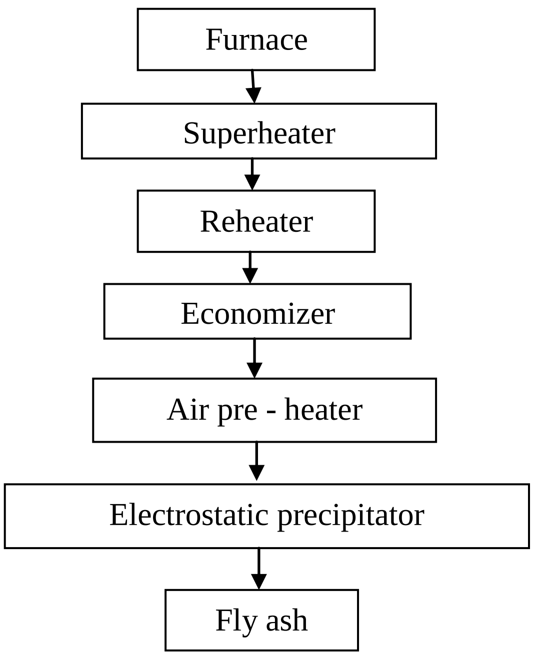


Fig. 1. Pathway of fly ash generation.

Ash is collected in two forms - wet ash and dry ash. Wet ash collected in bottom hopper and fly ash is collected in economizer hopper, air-preheater and in electrostatic precipitator hopper during follows the flue gas path and finally all fly ash is collected into the silo by vacuumed pump. Bottom ash is disposed in the form of ash slurry into the ash pond by the help of pump.

Distribution of elements in fly ash

At the time of the coal combustion only the organic part of coal burns and producing carbon dioxide and water, i.e. its vapour. While the ash is part of inorganic portion of coal, which do not burn, and by-product of combustion. Since coal, contains more than 50% organic substances which are found in the very low concentrations or negligible in the fly ash, it is clear that the inorganic part of coal is fly ash which including trace elements. During combustion different processes occur, which influence the non-uniform distribution of the elements. (Xu *et al.,* 2004; Goodarzi, 2006; Ward and French, 2006). Highest trace element concentrations were observed in the fly ash collected from the mechanical hoppers and from the cyclone, and contain various trace elements such as As, B, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Ti and Zn, suggesting the volatile nature of these elements. (Levandowski and Kalkreuth, 2009). The concentration of many trace elements higher at the surface of fly ash particles (Markowski and Fibly, 1985).

In coal, sulfur content higher, and tends to produce fly ash with greater levels of the elements (As, Cd, Hg, Mo, Ni and Pb), which are connected mainly with sulfide minerals (Goodarzi, 2006). The trace element analyzed in fly ash and coal by following method which reported by Chen *et al.,* 2011 and Li *et al.,* 2013. Trace element's content (Be, Co, Cr, Cu, Ga, Ni, Pb, V, Zn, Mo and Cd) were determined by inductively coupled-plasma mass spectrometry (ICPMS) after digestion by an acid mixture of HNO3: HCl: HF (3:1:1) in a microwave oven.

Many of the trace elements in fly ash shows a definite concentration trend with decreasing particle size that's shown by a number of investigations (Davison *et al.,* 1974; Kaakinen *et al.,* 1975 and Klein *et al.,* 1975). Extra than 70% of the As, Se, Mo, Zn, Cd, W, V, U, and Sb are associated with surface material on the ash particles (Hansen and Fisher, 1980). The element of Indian, fly ash was occur to be in the order of Fe > Mn > Zn > Cu > Cr > Ni > Mg > Pb > Li > Co > Hg > Cd > As (Bhangare *et al.,* 2011).

Physical characteristics of fly ash

The physical and chemical characteristics of fly ash depend on a number of factors. Chemical composition and pH values of fly ash possess a wide range of depending on the nature of coal and process of coal burnt (Rollings and Rollings, 1996). Due to low sulfur content of coal and presence of hydroxides and carbonates of calcium and magnesium the pH of fly ash 6.52 which generally highly alkaline (Tripathi *et al.,* 2004). In physical properties of fly ash, Colour is one of the important in terms of estimating the lime content qualitatively. It gives us a suggestion that darker colour suggest high organic content while lighter colour indicate the presence of high calcium oxide (Cockrell and Leonard, 1970). Specific gravity another important physical property needed for the geotechnical use of fly ash. In general, the specific gravity of coal ashes lies around 2.0 but can vary to a large extent (1.6 to 3.1) (McLaren and Digioia, 1987). Fly ash containing a relatively slighter specific gravity than the normal soils (Gyanen *et al.,* 2013). Specific gravity of fly ash depends considerably upon its carbon and iron content. More carbon content decreases its specific gravity, whereas presence of iron content increases the specific gravity (Sahu and Gayathri, 2014).

Mishra, 2008 found that the bulk density and porosity of the ash samples varied from 0.828 to 1.256 gm/cm^3 and 50.25 to 70.25 %, respectively. According to Mishra and Das (2010) the bulk density of the fly ash samples ranges between 1.00 and 1.06 gm/cm^3. The porosity and Water holding capacity of fly ash samples varies from the range of 51.15 to 53.27% and 50.70-55.11% (Mishra and Das 2010). The specific surface area of fly ash ranges between 1 to 9.44 m^2/g (Jena, 1993). Mishra and Das (2010) observed that fly ash specific surface area varies in the range of 0.5747-0.5845 m^2/cm^3.

Particle size mostly depends on the fly ash source. Fly ash particles are spherical shape, various sizes and highly porous in nature. The finest ones are micro porous and coarser fractions are macro porous (White and Case, 1990; Sarkar *et al.,* 2006; Das and Yudhbir, 2006). The particles of fly ash usually range from less than 1 µm to 150 µm in size and are commonly finer than Portland cement (Siddique, 2007). Table 2 shows the typical physical characteristics of fly ash.

Table 2. Physical characteristics of fly ash.

Parameters	Range	
	Ahmad and Mahanwar, 2010	**Mishra and Das, 2010**
Colour	Gray	Gray
Electrical conductivity (dS/m)	0.15 - 0.45	-
pH	6.00 – 10.0	-
Moisture content, %	2	-
Bulk density, g/cm3	1.26	1.00 – 1.06
Porosity, %	45 - 55	51.15 - 53.27
Specific gravity	1.66 – 2.55	2.14 – 2.17
Water holding capacity, %	45- 60	50.70 – 55.11
Specific surface area, m2/cm3	-	0.5747 – 0.5845
Particle shape	Spherical/Irregular	-

Geotechnical characteristics of fly ash

The values of Liquid limit for Badarpur fly ash and Dadri fly ash were observed to be 39% and 30.5%, respectively by Sahu and Gayathri, 2014. The uniform silt size, spherical nature and tiny surface area of individual particles shows fly ash has no plasticity (Jafri and Kumar, 2013) so the plasticity index and plastic limit values do not arise for fly ash (Sahu and Gayathri, 2014).

Maximum dry density and optimum moisture content for all fly ash samples have been determine by the Standard Proctor test (ASTM D 698- 07) (Deb and Pal, 2014). Tanjung Bin ash samples compaction behavior was investigated by Muhardi *et al*., 2010. According to them maximum dry density ($\gamma d_{(max)}$) of 1.53 Mg/m^3 (15.01 kN/m^3) with optimum moisture content ($w_{(opt)}$) of fly ash is 9.75%. It is evident that compaction characteristics vary from source to source due to different low specific gravity and a high air void content. Generally ash contains 5-15% air voids at maximum dry density (Kim, 2003).

Permeability is determined the rate at which a fluid passes through a material (Recycle Materials Resource Centre, 2010). The permeability of fly ash depends grain size, degree of compaction and pozzolanic activity (Pandian, 2004). The permeability of fly ashes is in the range of 8 x 10^{-6} cm/s to 1.87 x 10^{-4} cm/s (Sahu, 2009). Geotechnical characteristics of fly ash reported by different researchers shows in Table 3.

chemical composition and mineralogy of fly ash

In fly ash Chemical composition is depending upon which type of coal used in combustion, combustion conditions and removal efficiency of controlling instrument (Torrey, 1978; Fernandez-Jimenez and Palomo, 2003). Indian coal contains low Sulfur and high ash content (40%) (Jala and Goyal, 2006).

The X-ray Fluorescence test given the idea about the chemical compositions of fly ash. The investigation for an Indian fly ash demonstrates that all the fly ash contains silica, alumina, iron and calcium oxide (Pandian and Balasubramonian, 2000). In fly ash silica content is between 38 and 63%, alumina content ranges between 27 and 44%, calcium oxide is in the range of 0 to 8% (Pandian, 2004). The fly ash mainly consists of SiO_2 (71%), Al_2O_3 (32%) and Fe_2O_3 (6%) (Salunkhe and Mandal, 2014). In the fly ash, the elements present in declining order of their plenty are O, Si, Al, Fe, Ti, K, Ca, P and Mg. Moreover, trace quantity of Mn, Cr, Ni and Cu are identified in some of the fly ash (Mishra and Das, 2010). A number of studies have been done by various researchers to study on chemical composition of fly ash in Table 4.

Table 3. Geotechnical Characteristics of fly ash.

Parameters	Range				
	Maher, and Balaguru, 1993	**Mishra and Karanam, 2006**	**Mitash, 2007**	**Muhardi *et al.*, 2010**	**Jafri and Kumar, 2013**
Grain Size Distribution					
% of Gravel	-	-	-	-	0
% of Sand	-	-	-	-	42.01 - 46.61
% of silt + Clay	-	-	-	-	53.41 - 58.03
Coefficient of Uniformity Cu	2.5	-	3.1-10.7	-	1.35 – 1.50
Coefficient of Curvature Cc	-	-	-	-	1.04 – 1.18
Direct shear Test					
Cohesion	-	-	Negligible	3.34Kpa	0.34 Kg/cm^2–0.3 Kg/cm^2
Angle of shear Resistance	-	-	-	-	
Proctor's Density					
Optimum Moisture Content	-	38.7%	-	-	33% - 34 %
Maximum Dry Density	1.65 g/cm^3	-	0.9-1.6 g/cm^3	1.53 g/cm^3cc	1.10 (gm/cc) – 1.14 (gm/cc)
Permeability Tests					
Coefficient of Permeability	0.9×10^{-5} cm/s	(3.5-3.7) 10^{-6} m/sec	10^{-5} – 10^{-3} cm/s	4.87×10^{-7} cm/s	2.981×10^{-2} cm/min - 3.183×10^{-2} cm/min
Liquid Limit	16.8	40.89 %	-	-	-
Plastic Limit		Non plastic	-	-	-

Table 4. Chemical composition of fly ash as determined by XRF-analysis.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LIO	TiO_2	K_2O	Na_2O	P_2O_5	References
51.49	29.03	7.67	5.51	2.35	-	-	-	2.83	0.66	-	Puertas *et al.,* 2000
46.28	21.27	4.29	9.82	2.62	-	-	1.20	0.95	-	0.67	Swanepoel, and Strydom, 2002
55.3	25.70	5.3	5.6	2.1	1.4	1.9	1.3	0.6	0.4	-	Siddique, 2003
47.42	30.90	5.38	1.88	1.93	0.78	7.8	1.50	1.36	0.59	-	Xu *et al.,* 2006
58.9	27.73	8.83	1.11	0.84	0.24	-	2.09	0.79	0.14	0.17	Mishra and karana, 2006
38.7	20.8	15.3	16.6	1.5	2.6	0.1	0.4	2.7	1.2	-	Chindaprasirt *et al.,* 2007
53.09	24.80	8.01	2.44	1.94	0.23	3.59	1.07	3.78	0.73	-	Criado *et al.,* 2007
48.8	27.00	10.2	6.2	1.4	0.22	1.7	1.3	0.85	0.37	1.2	Kong *et al.,* 2007
45.98	23.55	4.91	18.67	1.54	1.47	2.13	-	1.80	0.24	-	Yazici and Arel, 2012
62.22	7.63	0.13	5.30	6.09	3.00	9.98	-	1.80	0.24	-	Belani and Pitroda, 2013
71.046	32.077	5.908	0.626	0.819	0.039	-	1.776	0.962	0.136	0.349	Salunkhe and Mandal, 2014

Mineralogical composition depends on combustion temperature, parent coals petrography, rate of cooling and boiler type etc. More than 55 minerals have been identified in fly ash (Hansen *et al.,* 1981; Hower *et al.,* 1999; Vassilev, 1992; Vassilev and Vassileva, 1996). Indian fly ashes mostly consist of quartz, mullite, magnetite, hematite, faylite and glass (Tripathy and Mukherjee, 1997). The different phases in fly ash are investigated thorough X-ray diagnosis. The X-ray diffraction is a powerful tool for known that different phases of fly ash yield different diffraction patterns (Sahu and Gayathri, 2014). From the X-ray diffraction patterns, it was found by many researchers that the major crystalline phases present in fly ash are quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$) and minor phases are iron oxides such as hematite (Fe_2O_3) and magnetite (Fe_3O_4) (Moreno *et al.,* 2005; Bada and Potgieter -Vermaak, 2008). Fly ash used was sourced from Gladstone in Queensland, Australia has some crystalline inclusions of mullite, hematite and quartz (Fig. 2) (Bakharev, 2005).

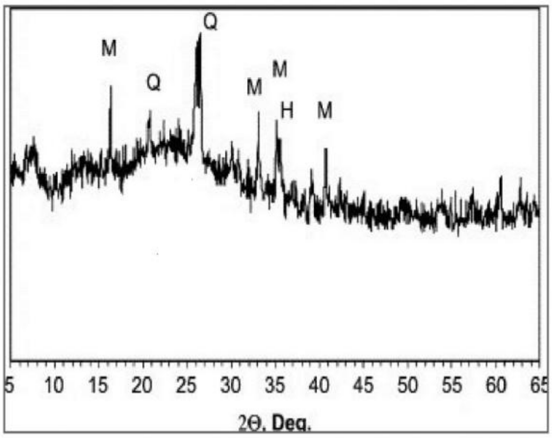


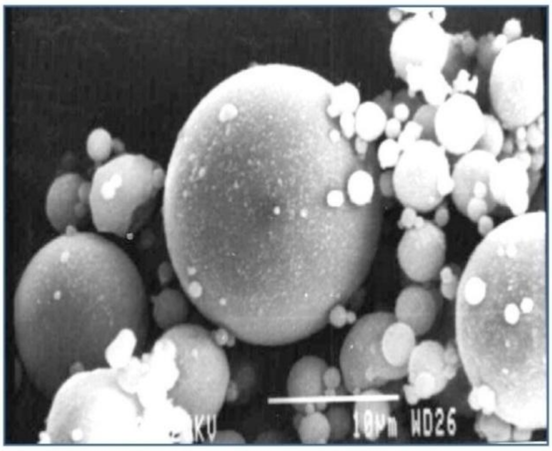
Fig. 2. XRD traces of fly ash. Q=quartz, M=mullite, H=hematite.
(Source : Bakharev, 2005).

Medina *et al.,* 2010 found that average values of quartz (9.5%), mullite (11.8%), calcite (0.5%) and the amorphous material (78.3%) in fly ash. The studies of X-ray diffraction shows that fly ash predominantly consist of quartz and feldspar minerals. Sarkar *et al.,* 2006 observed that the enhance in quartz content leads to reduce in particle size distribution of fly ash.

Morphology of fly ash particles

The submicron particles presence in fly ash in significant quantity is confirmed by SEM observations. The fact that the sample consisted mainly of respirable size particles is very important in point of view for health risk assessment (Davison *et al.,* 1974; Gieré *et al.,* 2003; Hansen and Fisher, 1980).

Fig. 3 shows spherical and sub-angular particles with relatively smooth grains consisting of quartz, while Fig. 4 shows iron clusters (Fe-oxide) particles formed due to partial decomposition of pyrite and with dark quartz inclusions. (Bada and Potgieter -Vermaak, 2008).



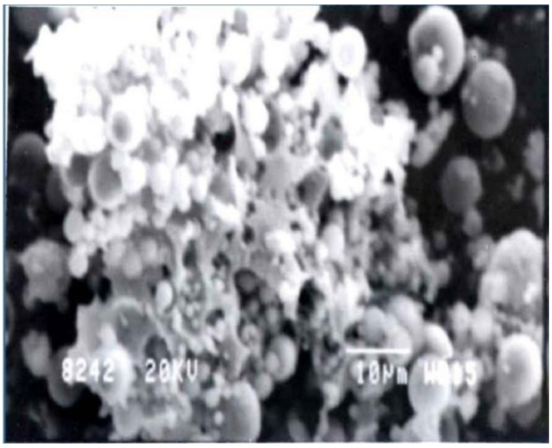


Fig. 3 & 4. SEM micrographs of fly Ash.
(source : Bada and Potgieter –Vermaak, 2008).

Tomeczek and Palugnoik, 2002 found that in fly ash most important carbonaceous particles char present and formed due to devolatilisation of the coal particles. The cenosphere formation process during coal combustion is already investigated by several researchers (Fisher *et al.,* 1976; Raask, 1985; Goodarzi and Sanai, 2009). During the time burning of coal the mineral matter within the coal may oxidize, fuse or decompose. Rapid cooling in the post-combustion zone results in the formation of spherical and amorphous particles. Expansion of trapped volatile matter can cause the particle to expand to form a hollow cenosphere (Kutchko and Kim, 2006). Cenosphere is based on the model of particles with a plastic or solid core covered by visco-plastic shell. The shell is formed from easy-to-melt inorganic components and the core is formed of less easy-to-melt components (Fenelonov *et al.,* 2010).

Cenospheres are having the thickness, about 2 µm. (Brouwers and Van eijk, 2002).

Analysis of fly ash particles also by high resolution transmission electron microscope (Chen *et al.,* 2005). They found that fly ash samples exhibit carbonaceous particles in the form of soot aggregates with primary particle size ranged between 20-50 nm.

Discussion

Many researchers have conducted characterization studies in order to evaluate the suitability of fly ash for several fields of applications. The Indian fly ash is alkaline in nature; hence, its application for agricultural soils could increase the soil pH and thereby neutralize acidic soils (Phung *et al.,* 1978). The electrical conductivity of fly ash shows the availability of different ions in the fly ash as well as soil and its affects the properties of salinity (Singh, 1990).

It has been observed that increase in bulk density of fly ash generally indicates a poorer environment for the plants root growth and vice versa (Phung *et al.,* 1978) and the low bulk density makes these fly ashes a good material for lightweight building blocks, but an increase in the potential for dust formation which creates problems in the transportation and storage of dry fly ash. (Bayat, 1998). Many researchers shows that higher porosity indicates a lesser density, which shows a lesser compressive strength in the landfill areas and High specific gravity is problematic for the flow pipelines because the majority of particles tend to settle down in the water (Naik, 2013) while the fly ash with low specific gravity and pozzolanic activity use for construction purposes along with cement (Upadhyay and Kamal, 2007). High values for WHC indicates that fine particles are dominating in fly ash, which have to high levels of water absorption due to greater surface area (Mishra, 2008).

Due to small particle size and lesser permeability fly ash is less suitable for stowing. (Mishra and Das, 2010). The liquid limit of fly ash is extensively related to construction purposes (Mishra, 2008). Optimum moisture content and Maximum dry density are essential to establish the density of the samples for good compaction. Compacted fly ash is very much useful in highway sub bases and load-bearing fills (Gray and Lin, 1972).

The spherical shape particles of fly ash help them to flow and blend freely in water mixtures. Therefore, it can significantly improve the rheology of the slurry over sand and result in a frictionless flow in the stowing range, causing less wear and tear of the pipelines. (Mishra and Das, 2010). Some cenosphere, which is smaller in size present on bigger size particles of fly ash. These cenosphere helps as aggregate in developing lightweight concrete and other lightweight sound absorbing structural materials (Blanco *et al.,* 2000; Tiwari *et al.,* 2004).

Conclusion

The fly ash generated from the coal based thermal power plants are one of the major sources of pollution and affecting environment in terms of land use, health hazards, air, soil and water and thus leads to environmental dangers. Various approaches are cited in literature for the effective utilisation of fly ash mainly limited to limited quantity. Due to low lime content in Indian fly ash use of fly ash as additive didn't show fruitful results in literature cited. Therefore bulk utilisation of fly ash is recommended to resolve the issue of storage and handling of fly ash in huge volume. One of the potential large volume disposal techniques for the vast quantities of the fly ash generated in the country is to utilise the material as a fill either in the abandoned or in active mines, whether surface or underground. Availability of the fly ash in the proximity of a mining site can create favourable conditions for its use as a fill medium. The environmental implications of such scheme is in most instances are favourable and the scope of water recycling enhances the acceptability of this technique of disposal.

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