CHAPTER 2
Review of Literature

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REVIEW OF LITERATURE

2.1 General features of fly ash

Fly ash is a by-product of combustion of pulverized coal in thermal power plants that is collected by the electrostatic precipitators or cyclones. It is generated as the residue in the combustion process and comprises of fine particles that rise with the flue gases (Cho et al., 2005, Kurniawan et al., 2006, Krishnani et al., 2008). Fly ash is a very fine material, non-volatile, incombustible, thermally altered mineral matter comprising of the inorganic constituents that were initially contained in coal (Scheetz and Earl, 1998). Fly ash is the most abundant residue among other residues such as flue gas desulphurization sludge, fluidized bed boiler waste, slag and bottom ash (Adriano et al., 1980) that are generated from the combustion of coal for power generation (Sharama et al., 1989, Fulekar and Dave, 1989). It was observed that approximately about 80 percent of the solid residue released from the combustion of coal is released as fly ash, while the rest 20 percent consist of larger particles that are retained within the furnace as bottom ash (Jankowski et al., 2006).

Power generation in India is mostly by thermal power plant that depends on bituminous and sub- bituminous coal that produce huge amounts of fly ash. The Central Electricity Authority of India has reported that there are about 155 large coal-fired thermal power plants in India. Indian coal is predominantly sub-bituminous, followed by bituminous and lignite (brown coal). The ash content in the Indian coal ranges from 30 to 40%. The calorific value of Indian coal (~ 15 MJ/kg) is less than normal range from 21 to 33 MJ/kg (gross). Fly ash is generated in large quantity in most countries of the world as a result of increase in the demand of electricity. Studies on coal consumption indicate that the combustion of coal to generate electricity will continue for the next several decades, which will eventually result in the generation of more fly ash. Several countries including India generate huge amounts of fly ash annually. Large quantities of fly ash produced

annually by thermal power stations in most countries including India due to the increase in demand for electricity are disposed of in landfills, slurry pond or ash dumps, with only small amounts been productively used (Iyer, 2002). Currently, 150 million tons of fly ash being generated annually in India, with 65000 acres of land being occupied by ash ponds. Such a huge quantity does pose challenging problems, in the form of land usage, health hazards and environmental dangers. Both in disposal, as well as in utilization, utmost care has to be taken, to safeguard the interest of human life, wild life and environment.

The components of fly ash vary considerably depending upon the source and make up of coal being burned. But all fly ash includes substantial quantities of silicon dioxide (both amorphous and crystalline) and calcium oxide, both being ingredients in many coal-bearing rock strata. Toxic constituents include the elements in quantities from trace amounts like: beryllium, arsenic, boron, chromium, cadmium, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, vanadium, and thallium etc. These trace elements in various quantities and during combustion process of coal they all get enriched as a result of carbon loss as carbon dioxide and trace elements get associated on the surface of ash particles due to evaporation and condensation. The characteristics of the coal used and the type of installations used for the generation of a fly ash have a direct influence on chemical and mineralogical composition of fly ash (Benito et al., 2001).

2.2 Properties of fly ash

The physical, chemical and mineralogical properties of fly ash depend on the nature of coal, conditions of combustion, type of emission control devices and storage and handling methods (Jala and Goyal, 2006). Characterization of fly ash in terms of composition, mineralogy, surface chemistry and reactivity are of fundamental importance in the development of various fly ash applications.

2.2.1 Physical properties

The fly ash is made up of very fine and glass-like powdery particles, mainly spherical in shape, either solid or hollow and mostly glassy (amorphous) in nature. The carbonaceous

material in fly ash is composed of angular particles. The particle size range of fly ash is generally although the sub-bituminous fly ash is also the size of the silt, it is generally from 0.01 to 100 mm (average diameter of <10 mm) (Wigley and Williamson, 1998) and it has a low bulk density, high surface area and light texture (Jala and Goyal, 2006). The specific gravity of fly ash varies usually between 2.1 and 3.0, while its specific surface area can vary from 170 to 1000m^2/kg (Ahmaruzzaman, 2010). The colour of fly ash may vary from tan to gray to black, depending on the amount of unburned carbon in the ash. The lighter colour shows the lower carbon content. The fly ash of lignite or sub-bituminous is usually from light brown to buff, which indicates relatively low amounts of carbon, as well as the presence of some calcium or lime. Bituminous fly ash generally has some shades of gray, usually indicating a high quality of ash with lighter colours of gray. The physical properties of fly ash are shown in Table 2.1 (Yadla 2012).

Table 2.1: Physical characteristics of fly ash

Sl. No.	Parameter	Range
1.	pH	6.0 – 11.0
2.	Specific gravity	1.66 – 2.55
3.	Bulk density (mg/m^3)	0.85-1.2
4.	Electrical conductivity (dS/m)	0.15-0.45
5.	Water holding capacity (%)	45-60
6.	Grain size distribution	Sand silt to silt loam

2.2.2 Chemical properties

The chemical properties of fly ash are influenced to a large extent by the properties of combustion coal and the techniques used for handling and storage. Basically, there are four types of coal, each variable in heating value, chemical composition, ash content and geological origin. The four types of coal are anthracite, bituminous, sub-bituminous and lignite. In addition to handling in dry, conditioned or wet form, fly ash is sometimes classified according to the type of coal from which the ash is derived.

The main components of the fly ash of bituminous coal are silica, alumina, iron oxide and calcium, with varying amounts of carbon, measured by ignition loss (LOI). Lignite and

sub-bituminous coal fly ash are characterized by higher concentrations of calcium and magnesium oxide and reduced silica percentages of silica and iron oxide, as well as lower carbon content, compared to fly ash from bituminous coal. The anthracite coal burns very little boiler service, so there are only small quantities of anthracite coal fly ash. The chemical characteristics of fly ash are shown in Table 2.2 (Ahmaruzzaman, 2010). Table 2.2 compares the normal range of chemical components of bituminous coal fly ash with lignite and sub bituminous coal fly ash. From the table, it is clear that lignite and sub bituminous coal fly ash have high calcium oxide content and low loss on ignition compared to fly ash from bituminous coils. Lignite and sub bituminous coal fly ash may have the maximum concentration of sulfate compounds compared to bituminous coal fly ash.

Table 2.2: Chemical composition of fly ash generated from different types of coal

S. No.	Component (wt. %)	Bituminous	Sub Bituminous	Lignite
1	SiO_2	20-60	40-60	15-45
2	Al_2O_3	5-35	20-30	10-25
3	Fe_2O_3	10-40	4-10	4-15
4	CaO	1-12	5-30	15-40
5	MgO	0-5	1-6	3-10
6	SO_3	0-4	0-2	0-10
7	Na_2O	0-4	0-2	0-6
8	K_2O	0-3	0-4	0-4
9	LOI	0-15	0-3	0-5

2.3 Classification of fly ash

Generally, fly ash is classified according to the type of coal used. The basic difference between these classes is the amount of calcium, silica, alumina and iron contained in the ash. The chemical properties of fly ash are strongly affected by chemical content of the coal burned (i.e., anthracite, bituminous and lignite). There are two types of fly ashes produced by combustion of coal as classified by American Society for Testing and Materials (ASTM) into class F or C by their aggregate alumina, silica, and ferric oxide contents. The distinction between Class F and Class C fly ash is based on the sum of the total silica, aluminium and iron oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) in the fly ash.

2.3.1 Class 'F' fly ash

Class F type fly ash is produced from burning of anthracite, bituminous or sub-bituminous coal. It has low lime content (<7%) and more silica, alumina, and iron oxide (Iyer, 2002). When the sum of the total silica, aluminium and iron oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) in the fly ash is greater than 70% an ash is classified as Class F (ASTM C 618, 1993). Class F coal fly ashes are generated from the combustion of higher rank coals (coal which have lower calcium content). Class F fly ash possesses little or no cementitious value but in finely divided form and in the presence of moisture, will chemically react with calcium hydroxide at ordinary temperature to form cementitious compounds.

2.3.2 Class 'C' fly ash

Class C type fly ash is produced by burning of lignite coal and it has more lime content (18%) (Iyer, 2002). Type C ashes are generally produced from the combustion of lower rank coals and contain more calcium in their bulk chemical compositions. When the sum of the total silica, aluminium and iron oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) in the fly ash is between 50% and 70% the ash is classified as Class C (ASTM C 618, 1993). Class C fly ash having pozzolanic properties, also has some cementitious properties (ASTM C 618-1993). Table 2.3 shows the ASTM standard classification of fly ash.

Table 2.3: Classification of fly ash based on ASTM C 618 (ASTM, 2012)

Chemical requirements	Class F	Class C
$SiO_2 + Al_2O_3 + Fe_2O_3$, min %	70	50
SO_3, max %	5	5
Moisture content, max %	3	3
LOI, max %	6	6
Available alkalis, as Na_2O, max %	1.5	1.5

2.4 Mineralogical composition of fly ash

The mineralogical composition of the fly ash, which depends on geological factors, related to coal formation and deposition and varies according to the quality and fineness of the pulverised coal, type and quantity of mineralogical matters associated with it,

method of combustion and combusting temperature, can be established by X-ray diffraction (XRD) analysis (Jala and Goyal, 2006).

The fly ash includes forming (>10%), major (1-10%), minor (0.1-1%) and accessory (<0.1%) minerals and phases. Several groups of minerals generally associated with Indian coals are hydrated silicates such as kaolinite, mullite, muscovite, montmorillonite, silicates such as feldspar minerals, quartz, phosphates such as apatite, sulfates such as pyrite, carbonate like siderite, calcite, aragonite; hydroxides such as limonite, goethite, etc. The dominant mineral phases are quartz, kaolinite, ilite and sideraete. The less predominant minerals in unreacted coal include calcite, pyrite and hematite. Quartz and mullite are the main crystalline components of ash with low calcium content, while the high calcium content fly ash is consist of quartz, C_3A, CS and C_4AS. During the coal combustion process, these mineral materials have undergone structural changes due to the effect of temperature and results in the ash components.

2.5 Major and trace elements in fly ash

Chemically, 90–99% of fly ash is composed of Si, Al, Fe, Ca, Mg, Na and K with Si and Al forming the major matrix (Adriano et al., 1980). Typical concentrations of major and trace elements in fly ash are presented in Table 2.4. C and N are oxidized into gaseous constituents during combustion so they are present in fly ash in negligible quantities. The pH of fly ash varies from 4.5 to 12 depending largely on the S content of the parent coal, type of coal used for combustion and S content of the fly ash (Carlson and Adriano, 1993).

Table 2.4: Typical concentrations of major and trace elements in fly ash

Major elements (%)		Trace elements (mg kg^{-1})	
Al	5.0-25	As	2.0-70
Ca	0.8-30	B	2.0-5000
Fe	1.0–35	Sb	0.8–25
Si	2.0–3.0	Cd	0.1–100
Mg	0.04–5.0	Co	1.0–100
Na	0.04–7.9	Cr	3.0–900
K	0.15–6.0	Cu	10.0–2000

S	0.03–5.0	Hg	0.01–12
P	0.01–3.0	Mn	30.0–3000
N	0.01–1.0	Mo	1.0–250
		Ni	10.0–3000
		Pb	3.0–500
		Se	0.2–50
		Zn	10.0–1000
		Ba	0.01–1.0
		La	17–100
		Rb	30–200
		Cs	1.5–20

Source: Page et al., 1979, Bilski et al., 1995, Asokan et al., 2005.

Fly ash contains essential macronutrients such as P, K, Ca, Mg and S and micronutrients such as Fe, Mn, Zn, Cu, Co, B and Mo. Some are rich in heavy metals like as Cd and Ni (Adriano et al., 1980). On average, 95-99% of fly ash is consist of oxides of Si, Al, Fe and Ca, about 0.5-3.5% consists of Na, P, K and S and the rest is composed of trace elements (Adriano et al., 1980, Haynes, 2009). It is considerably rich in trace elements such as La, Tb, Hg, Co and Cr (Van hook 1979, Adriano et al., 1980). According to Page et al. (1979), many trace elements including As, B, Ca, Mo, S, Se and Sr in fly ash are concentrated in the smaller ash particles. In fact, fly ash consists of practically all the elements present in the soil, with the exception of organic carbon and nitrogen (Kumar et al., 2000).

Fly ash contains environmental toxic elements like Ba, As, Be, Cd, B, Cr, Cu, Co, F, Pb, Mn, Ni, Se, Sr, V, Th and Zn. The above quantities of trace elements change according to the type of coal burnt to form fly ash. In fact, for bituminous coal, with the exception of boron, trace element quantities are similar to trace element quantities in uncontaminated soils. This large quantity of this material will be increasingly brought into contact with the water and soil environment (Fulekar and Dave, 1991).

2.6 Characterization of fly ash leachates

The fly ash leachate is generated through the contact of water with the ash (Brannon and Myers, 1994). The water soluble salts on the surface of the ash particles are mobilized

into solution, creating a potentially high salinity leachate (Summers et al., 1983). The chemistry of the leachate varies quite considerably, with pH ranging from low (acidic) to high (alkaline), and medium to high total dissolved solids (Roy and Griffin, 1984). The majority of fly ash leachates tend to be alkaline due to the presents of lime (Mattigod et al., 1990), although present of high Fe in fly ash can lead to an acidic ash through oxidation and the release of hydrogen ions. Indeed, the alkaline nature of many ashes has seen an increasing number of applications with examples including the neutralization and or prevention of acid mine drainage (Misra et al., 1996), soil cover material for tailings or landfills (Mamane and Gottlieb, 1992), structural fill for road bases or underground mine backfill and substitute fertilizer or soil amendment (Balsamo, 1998). The chemistry of leachate, controlled by the varying proportions of soluble minerals within the ash, is often dominated by high concentrations of Na, SO_4 and Ca, and to a lesser extent Cl. The solubility and extent of leaching of a particular trace element will depend on the pH and redox conditions of the leachate over time, sorption characteristics of the ash and major element chemistry (Eighmy et al., 1995). The solubility of trace elements, therefore, needs to be determined on a site specific basis due to the significant variability between ash mineralogy, geochemical conditions and disposal environments. On the basis of difficulties highlighted earlier in characterizing trace element speciation in coal ash, it is similarly difficult to quantify trace element behaviour in leachate.

2.7 Size dependent leaching properties of fly ash

Coal fly ash is a heterogeneous material, both within the particle and between particles (Smith, 1980). A detailed study on the elements versus particle size distribution shows that there is an inverse dependence on concentration with respect to particle size for some elements. Elements were divided into two groups on the basis of their concentration dependence upon particle size, those with no enrichment in the smallest particle size and those which are enriched. Results of the analysis by particle size indicates that the elements Mn, Ba, V, Co, Cr, Ni, Ln, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg and S are usually volatile to a significant extent in the combustion process. The volatility for these elements is inversely proportional to the particle size. Elements Mg, Na, K, Mo, Ce, Rb, Cs and Nb appear to have a smaller fraction volatilized during coal combustion or have

significant variations in behavior between plants. Here the volatility is directly proportional to particle size. The measured elements Si, As, Fe, Ca, Sr, La, Sm, Eu, Tb, Py, Yb, Y, Se, Zr, Ta, Na, Th, Ag and Zn are either not volatilized or may show minor trends which is related to geochemistry of the mineral matter In some cases, the concentration dependence on particle size has yielded surprising results. In one example the concentration of Ca and Sr reach a maximum concentration in a particle size of 5µm and then decreases with increase in particle size. The volatility of trace elements increased from a larger particle size to a smaller particle size which establishes an inverse relationship of volatility and particle size (Fischer, 1976). It was found that the surface layer of fly ash particles probably only microns in thickness contains a significant amount of readily leachable material which is deposited during cooling after combustion (Wilberley, 1982).

2.8 Heavy metal

The rapid growth of industrialization alters the natural flow of materials and introduces novel chemicals into the environment (Faisal and Hasnain, 2004). The rate at which effluents are discharged into the environment especially water bodies have been on the increase as a result of urbanization. Most of these effluents contain toxic substances especially heavy metals. The presence of heavy metals in the environment is a major concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment (Jadia and Fulekar, 2008, Jnr and Spiff, 2005). Another point of concern is the effect of leaching on these contaminated sites which in turn contaminate water tables (Gratao et al., 2005). The most common heavy metals at hazardous waste sites are cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni) and zinc (Zn) (EPA, U., 1997).

Heavy metals are among the conservative pollutants that are not subject to bacterial attack or degradation process as a result of this their concentrations often exceed the permissible levels normally found in soil, water ways and sediments. Hence, they find their way up the food pyramid. When they accumulate in the environment and in food chains, they can profoundly disrupt biological processes. The primary sources of heavy

metals pollution in coastal lagoons are input from rivers, sediments and atmosphere, which can affect aquaculture profitability in certain areas (Krishnan et al., 2004). The anthropogenic sources of heavy metals include wastes from the electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, leather tanning industries, fertilizer industries, and pigment manufacturing industries, leachates from landfills and contaminated ground water from hazardous waste sites (Faisal and Hasnain, 2004). Heavy metals are also emitted from resource recovery plants in relatively high levels on fly ash particles.

Heavy metals, industrial pollutants, in contrast with organic materials can not be degraded and therefore accumulate in water, soil, bottom sediments and living organisms. Water contamination with heavy metals is a very important problem in the current world. Occurrence of toxic metals in pond, ditch and river water affect the lives of local people that depend upon these water sources for their daily requirements. Consumption of such aquatic food stuff enriched with toxic metals may cause serious health hazards through food-chain magnification (Miretzky et al., 2004).

Heavy metals are defined as those elements with a specific density at least five times the specific gravity of water. Heavy metals include cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), iron (Fe), and the platinum group elements. The important heavy metals from water pollution view include mercury, cadmium, lead, zinc, copper, nickel and chromium. Copper and zinc are essential trace elements for living organism at low concentration (< 10 mg/L), however it become toxic at high concentration (>10 mg/L). Most of these metal ions (Cd, Cu, Zn, Hg, As, Ag, Cr, and Fe etc.) release from the industries are in simple cationic (+) forms. Heavy metals are the most dangerous substances in the environment due to their high level of durability and toxicity to the biota (Alkorta, 2004). The mobilization of heavy metals by man (through mining from ores and processing for different applications) has led to the contamination of different environmental segments by these elements. By contaminating food chain, these elements pose a risk to environmental and human health. As a result of their release and presence in the ecosystem, these pollutants are accumulated by living organisms in their bodies and subsequently biomagnified as

they pass from one trophic level to the next. Since man also is at the top of food chain, he is vulnerable to heavy metal pollution.

Regarding the role of heavy metals in living systems, they are divided into two classes: essential and non-essential. Essential heavy metals are those, which are needed by living organisms for their growth, development and physiological functions like Mn, Fe, Ni, Cu and Zn (Gohre and Paszkowski, 2006) while non-essential heavy metals are those, which are not needed by living organisms for any physiological functions like Cd, Pb, Hg and As (Peng et al., 2009). Higher levels of heavy metals disturb the normal physiology and biochemistry of living systems. The most dangerous heavy metals are Pb, Hg, As, Cd, Sn, Cr, Zn and Cu (Dutta and Gosh, 2013). Among these, Cd and Pb are the most dangerous metals for human health (Sekara et al., 2005). Cd is considered as the most serious pollutant of the modern age (Fulekar and Dave, 1991). Cd concentrations above the threshold limit values have been found to be carcinogenic, mutagenic and teratogenic for a large number of animal species (Degraeve, 1981). Cd has also been implicated as an endocrine disruptor (Awofolu, 2005). Pb has been found to be responsible for quite a number of ailments in humans such as chronic neurological disorders especially in fetus and children. This eventually results in behavioral and attitude changes with progressive retardation (Awofolu, 2005). Pb-poisoning in children causes neurological damage leading to reduced intelligence, loss of short-term memory, learning disabilities and coordination problems (Padmavathiamma and Li, 2007).

Toxic heavy metal pollution of water and soil is a major environmental problem, and most established remediation approaches do not provide acceptable solutions (Lu, et al., 2004). Waters and soils in many parts of the world are polluted by all kinds of chemicals and toxic heavy metals like cadmium, lead, zinc, chromium and mercury. In several countries effluents are often disposed directly into the surface waters. The heavy metals have an adverse effect on living things and ultimately have an impact on human health. There is an urgent need to develop technologies to control pollution from industrial effluents and remove or detoxify these materials from the environment. The maximum permissible concentration for metal ions according to the standards of the environmental

regulations guidelines is about 1mg/L each. The total limit should not be more than 5mg/L. Heavy metals can cause health problems to living things. Some species of nickel can cause skin rashes, asthma and cancer. Copper, nickel, selenium and zinc are essential micronutrients but can become toxic at high concentrations. Vanadium may cause dehydration, weight loss, breathing difficulties, irregular cardiac and renal functions and depressed growth. Cadmium can damage to cell membranes. Millions of children have suffered the ill-effects of lead. Chromium (VI) can cause nasal problems and ulcers as well as kidney and liver damage and Chromium (VI) is a known carcinogen. Mercury is problematic in cryogenic petrochemical facilities, and is toxic to humans. The concentrations of heavy metals increase in the environment from year to year (Govindasamy, 2011).

2.8.1 Heavy metal pollution in water

Heavy metals are frequent waste products of anthropogenic activities and their emission often results in the contamination of the surrounding environment (Eeva and Lehikoinen, 2000). Industrial waste, geo–chemical structure of the catchment and mining create potential sources of heavy metal pollution in the aquatic environment. Under certain environmental conditions, metals may accumulate to toxic proportions and can cause ecological damage. Heavy metal pollution of freshwater environments is a serious global environmental concern in the industrial areas. Water pollution by heavy metals (elements with an atomic density greater than $6g/cm^3$) has become therefore a global issue that needs considerable attention towards combating. The common heavy metals that have been identified in polluted water include As, Cu, Cd, Pb, Cr, Ni, Hg and Zn. The release of these metals without proper treatment poses a significant threat to public health because of their persistence, bio-magnification and accumulation in food chain. Their presence in water is due to discharges from residential dwellings, groundwater infiltration and industrial discharges. Their occurrence and accumulation in the environment is a result of direct or indirect human activities, such as modern growth of industrialization, urbanization and anthropogenic sources. Severe toxic effects of heavy metal intake include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. The danger of heavy metal pollutants in water lies

in two aspects of their impact. Firstly, heavy metals have the ability to persist in natural ecosystems for an extended period. Secondly, they have the ability to accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. The presence of heavy metals in aquatic environments can cause severe damage to aquatic life, and can also kill microorganisms during biological water purification process.

2.9 Role of heavy metals in the environment

The presence of heavy metals in the environment is a cause of great concern due to its toxicity and threat to human life and the environment. Contamination of heavy metals occurs in areas that have a concentration of industries, particularly those that belong to the metal prospecting, extraction and processing. Some other sectors, like the battery production, production of colours and pigments, ammunition, ceramics and glass industries, etc., also contribute to the loading of metals into the environment. The presence of heavy metals in streams and lakes lead to bioaccumulation in living organisms, causing health problems in animals, plants and human beings. Exposure to heavy metals has been linked to developmental delay, renal damage, severe gastrointestinal irritation, muscle pain, anemia, discoloration of the teeth, loss of smell and possible necrosis changes in the liver and kidneys, rheumatoid arthritis, diseases of the circulatory system or central nervous system, different types of cancer, including death in some cases of exposure to very high concentrations (Randall et al., 1974, Friberg and Elinder, 1985, Garg et al., 2007). The metals of major concern are aluminum, arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel and zinc (Friedman and Waiss, 1972, Kjellstrom et al., 1977, Pastircakova, 2004, Celik and Demirbas, 2005).

Trace metals contamination of the soil is of great concern all over the world. The trace metals are known for their environmental persistence and toxicity to living organisms (Clemens et al., 2006, Thompson, 2008, Zhuang et al., 2016). There are metal tolerant plants that reduce the mobility, phyto-availability and toxicity of metals (Kidd et al., 2009). Plant cover in contaminated soils is crucial for phyto-stabilisation of metals stability (Pulford and Watson, 2003, Fitzgerald et al., 2006).

2.10 Pollution due to disposal and current uses of fly ash

The application of fly ash to soil or water can generate unacceptable levels of contamination. The wet disposal of fly ash has been associated with developmental abnormalities in animals (Minnesota Office of Environmental Services, 1997) and the negative impacts on aquatic-biota (Walia, 1995). When fly ash is applied to the soil or water, As, B, Be, Cr, Mn, Mo, Pb, S, Sb, Se, V and Zn can become a significant environmental problem (Adriano et al., 2002, Nugteren et al., 2001, Praharaj et al., 2002, Vageesh and Siddaramapappa, 2002). When applied to grasslands, the ash can increase the rumen pH of grazing animals to the extent that fermentation can be markedly reduced (Dewes et al., 1995). There is a case to claim that some ashes can be used in limited quantities without treatment. Such ashes have use value because they can supply minerals to the soil to improve it or maintain it fertility. In view of sustainability, ash additions must be such that all relevant information inputs pollutants considered, the practice can be maintained indefinitely without exceeding levels (Reijnders, 2000). In practice, this requirement leads to severe restrictions also in the use of ash from the combustion of "clean" fuels based on biomass (Hansen et al., 2001, Pedersen, 2003). For other applications, such as in building and geotechnical materials, leachablity tends to be a disadvantage when the substances involved they are hazardous.

Viewed from the point of industrial ecology (Ayres, 1992), one should first consider the option of reducing the source to limit the presence of dangerous substances that can be leached from ashes. This option clearly has the potential to limit the amount of such items in the ashes associated with combustion of coal in thermal power plants. In the same way, levels of hazardous organic compounds present in the ashes can be reduced by source reduction.

However, regarding the presence of dangerous elements in the fly ash deriving from combustion of fossil fuels, the source reduction has only limited value because the composition of fossil fuels was so geologically determined a long time ago. There is still potential for reducing the source because, for example, fossil fuels can be purchased with

low levels of elements that can make the ashes dangerous. The quantities of Ni and V in heavy fuel can be reduced in the refinery phase. Looking beyond the reduction of sources at the ashes that originate in the combustion of fuels, while focusing on industrial ecology, two main roads are open: permanent safe disposal and use (Mroueh et al., 2001). The fly ash utilization has raised the problem of the mobilization of hazardous components. The ashes show a great variety in this sense. In part, this variety originates in different amounts of elements in the fuels used. For example, for elements such as Cd, As and F concentrations in coal, they can vary by a factor between 103 and 104 (Minnesota Office of Environmental Services, 1997, Jandova and Vu, 1998, Piekos and Paslawska, 1998). Using the same combustion process, the trace element partition can also be different in a fuel-dependent manner. When combustion is simulated in a fluid bed of coal and biomass, the partition of Be, Pb, Mo, V and Zn is dependent on the fuel sample (Ishak et al., 2002).

2.11 Mechanism of leaching: Leaching test methods applied to the fly ash

There are several leaching methods available to predict the potential for leaching of contaminants through porous media. Some of these are carried out under natural climatic conditions and the others are carried out under controlled laboratory conditions. Although different organisations have their own specifications to perform leaching tests, the basic principles of the tests are the same. Tests conducted under natural conditions can provide a better representation of the field conditions, but they are less reproducible because climatic conditions can not be controlled. Various procedures have been used to perform the analysis of fly ash from thermal power plants and to evaluate their effectiveness. Each method has a specific advantages and are applicable for a given data collection system. So to evaluate such methods, the knowledge of the leaching behaviour of the studied material is very important. One of the factors influencing the leaching behaviour is the composition and mineralogy of solids.

Leaching is the most probable way in which the constituents of fly ash would become mobile and contaminate the environment. The amount of elements that will be available for the leaching in an aqueous medium will depend on the fixation of these elements in

the ash particles and pH of the aqueous medium (Sivakumar and Dutta, 1996). Besides this, the other factors that influence leaching include the ash source and the leaching time. Generally under acidic conditions, the rate and amount of leaching is higher.

There is a wide range of standardized leaching tests with variables reagents, complexity, temperature, stirring method, solid-liquid ratio (S:L), contact time (among other parameters) along with some others not standardized but appropriate for specific purposes. Some of them are designed to reproduce specific scenarios, some others are aim to obtain predictions on the available concentrations and used as a substitute for long-term extractions. There are numerous test methods that have been used to determine the release of contaminants from fly ash. These methods have indicated a variety of results related to the composition of coal, type of combustion and adopted extraction process. Leaching procedures are generally classified into different types of leaching tests. These types of tests are briefly described following.

2.11.1 Lysimeter tests

Generally, Lysimeter tests are performed in the field with large samples of fly ash as leaching experiments. In this process, the sample is subject to natural weather conditions for a couple of years and the percolates are collected and analyzed. The lysimeter tests are performed in a number of different lysimeter cells. Each lysimeter cell has a fairly large surface and contains a substantial amount of the sample. The base of each lysimeter cell is aligned to prevent infiltration of leachate into the soil. A drainage system is used to collect the leachate produced in the lysimeter cells. The percolate accumulates in the wells of the pumps that contain buffer tanks from where it is pumped into the storage tanks. Percolate samples can be analyzed periodically. The amount of leachate produced and the precipitation received during the trial period are also calculated from the available data.

2.11.2 Column tests

Column leaching tests are laboratory tests. In this type of test, the fly ash samples are packed in to transparent plastic cylinders. The influent and effluent tanks are used for the

generation of influx and the effluent collection process respectively. To avoid clogging of the piping system from material that is washed away, the filters are used on the inlet and outlet sides of the fly ash column. The flow direction through the column can be up or downward depending on the specific research objectives. To minimize the channelling effect, the upward flow mode is recommended. The constant flow through the material can be achieved by using constant flow rate pumps between the influx tank and the column inlet. To simulate one-dimensional flow situations, the column leaching test is preferred.

2.11.3 Batch leaching tests

Batch leaching tests are also laboratory tests performed to determine the leachability of materials. These tests consist of a series of extraction performed sequentially. In this test, known amount of material and volumes of influx fluid, which should be infiltrated by a given period of time, they are placed in polyethylene bottles. The bottles are then rotated at the end for the same period of leaching time taken at a specified RPM. Once this process is completed, the leachate is removed from the bottle and filtered for further analysis. A new part of the inlet fluid is added to the waste for a second extraction. The number of the extraction made depends on the needs of the researcher. The amount of the material to be taken for the test and the number of revolutions to rotate may vary according to the specifications established by different organisations. The American Society for Testing and Materials (ASTM) procedure uses reagent water as a leaching fluid and the method does not require the reduction of particle size.

2.11.4 Serial batch leaching procedure (SBLP)

The series leaching procedure (SBLP), intends to quickly provide information with regard to the total leachable material in fly ash and to estimate the rate at which an element can be extracted under normal environmental conditions (Hesbach PA, et. al., 2005). The SBLP method includes a serial batch leaching procedure at four pH's to estimate the cumulative elemental availability and a serial batch procedure at increasing liquid to solid ratios to estimate long-term elemental extraction.

2.11.5 Synthetic groundwater leaching procedure and long term leaching (SGLP)

The synthetic groundwater leaching procedure and long term leaching (SGLP) is intended to simulate field leaching conditions (Hasset D J., 2005). Deionized water is used as leachant under the assumption that most fly ash would be exposed to rainwater and that the acidity of rainwater would be effectively neutralized by the alkalinity of fly ash. The purpose of the long-term leaching process is to identify the effects associated with mineralogy changes that occur during long-term contact with water.

2.11.6 Mine water leaching procedure (MWLP)

The goal of this procedure is to provide the leachability of heavy metals and trace elements from fly ash when in contact with acidic, metal bearing groundwater, such as acid mine drainage (AMD). This method involves the serial addition of acid mine water to an ash sample until complete alkalinity has finished the ash and the filtrate has a pH close to unreacted acid water (Ziemkiewicz P F., et. al., 2003).

2.11.7 Toxicity characteristic leaching procedure (TCLP)

The toxicity characteristic leaching procedure (TCLP) (US EPA, 1997), as indicated in the EPA SW846, is designed to determine the mobility of both organic and inorganic analytes present in solid, liquid and multiphase waste. For this study, the method for a solid waste was used. The extraction fluid was glacial acetic acid diluted with DI water at a pH of 2.88 ± 0.05. If the addition of HCl lowers the pH to <5.0, or if the original pH was <5.0, the previous reagent was changed to includes NaOH. If properly prepared, the pH of this second fluid will be 4.93 ± 0.05.Fly ash is a heterogeneous material and therefore the concentration of pollutants produced by different leaching test methods varies significantly from one test procedure to another. However, among the most commonly used methods, the batch leaching test (laboratory test) was selected for research. Since the goal of this study is to use a laboratory method to study the leaching behaviour of metals from fly ash, the batch leaching test was selected on other test methods such as the test procedure that will best meet the objectives of this investigation.

2.12 Utilization of fly ash

In recent years, fly ash utilization has increased in different sectors due to many economic, technological and environmental reasons. In general, programs for using fly ash can be viewed by different angles, that is, Firstly, lower disposal costs and less area requirements for disposal are provided. Secondly, there is less environmental pollution with the use of fly ash in many sectors. Thirdly, fly ash can be used as a partial substitute for some important natural resources. Another important advantage is that fly ash is also used as an essential additive in some sectors to improve the properties of final products, such as the special pozzolan additive in the cement and concrete industry (Ahmaruzzaman, 2010).

According to the Central Electricity Authority (CEA), in 2016-17, 63.28% of total produced fly ash was used in various applications in India (CEA, 2018). In addition to the cement and concrete industry, fly ash has different uses and utilization areas that include cover materials and structural fill, use of roads and sidewalks, construction materials such as light weight aggregates, solidification and stabilization of waste, ceramics industry, metallurgy and valuable metal extraction, agriculture and water and environmental improvement (Ahmaruzzaman, 2010, Tuzcu, 2005).

Fly ash is used in the cement and construction industry. However, the production rate is higher than consumption. Unused fly ash is deposited in ponds, lagoons, landfills and slag heaps. The disposal of huge amounts of fly ash in landfills and surface impoundments or their reuse in construction materials is of environmental concern (Piekos and Paslawska, 1998). Fly ash is classified as a hazardous waste. Coal contains significant amounts of various trace elements and during the combustion of coal the trace elements are enriched as a result of the loss of carbon as carbon dioxide and trace elements are associated with the surface of the ash particle because evaporation and condensation. The characteristics of the coal used and the type of equipment used in the production of solid combustion waste (fly ash) have a direct influence on the chemical and mineralogical composition of fly ash (Benito et al., 2001).

The use of fly ash in plastic compounds has shown promising results (Jarvela and Jarvela, 1996, Verghese and Chaturvedi 1996, Yildirim et al, 1996), as the application of metallic compounds, in particular aluminum (Rohatgi et al., 1995, Guo et al., 1996, 1997). Aluminum alloy fly ash compounds produced by stirring have hardness and similar elastic modulus or higher and greater wear resistance and materials have been considered potential for components such as pulleys, oil pots, intake manifolds and valve covers (Rohatgi et al., 1997). It has been found that coatings made of nickel fly ash compounds have better wear resistance than the "smooth" nickel coating. The wear resistance of the excellent bond composites was attributed between the ultrafine ash and nickel particles (Ramesh Iyer and 1991). Fly ash can be used to reduce the density of metal compounds, with cenospheres (hollow spherical particles) inside the ash provides greater buoyancy, better insulation properties, reduced shrinkage and curvature age values (Wandell, 1996).

Fig. 2.1 Utilization of fly ash in various applications

2.12.1 Fly ash utilization in cement and concrete industry

Fly ash has been widely used in the cement and concrete industry as an additional cementitious material. There are three main purposes of using fly ash in cement. Firstly, fly ash can be used as a partial substitute for cement in concrete. Secondly, it can also be used as a pozzolanic material in the production of pozzolanic cements. Thirdly, fly ash slows down the setting of cement as a substitute for gypsum (Ahmaruzzaman, 2010).

There are many beneficial effects of utilization of fly ash in the cement and concrete industries. Fly ash improves the properties of concrete products, such as the workability

of fresh concrete and the formation of microstructures, and offer better mechanical properties and durability. In addition, fly ash reduces the cost of concrete materials and saves energy and natural resources due to the reduced need for raw material in the process. Furthermore, it is possible to achieve a significant reduction in CO_2 emissions in cement production with the utilization of fly ash. Furthermore, less environmental pollution occurs in the area of fly ash removal with the use of this waste in the construction industry (Zeng et al., 2011, Langan et al., 2002).

The utilization of class C fly ash seems to be quite adequate in Portland cement due to its high content of calcium and reactive glass contents. High strength concrete can be manufactured using class C fly ash and plasticizers. Class F fly ash can also be used as raw material for the production of high strength and high performance concrete. The spherical shape of the fly ash particles improves the pumpability of the concrete and also causes a reduction in permeability and better packaging. In addition, the fly ash provides a dense paste and a pozzolanic reaction. A lower heat of hydration compared to the Portland cement control is obtained in the production of bulk concrete through the use of particularly of class F fly ash with high replacement of cement. Cement replacement rates are generally 15-25% and 25-40% for fly ash of class F and C, respectively. This replacement ratio can be increased to 75% for class C fly ash in the construction of car parks, driveways and streets. Nowadays chemical mixtures are essential components in the production of concrete, since they substantially reduce the demand for water without loss of workability. The hardening rates of fly ash can be accelerated by using these chemicals to achieve good yield (Ahmaruzzaman, 2010).

2.12.2 Utilization of fly ash as a lightweight aggregate (bricks and tiles)

The use of fly ash as a lightweight aggregate provides important advantages to the manufacturer. The main advantage is the reduction in shipping costs of the shipment of the finished product compared to natural raw materials. The weight becomes more important if use of fly ash in the production of bricks, as the fly ash bricks are about two-third lighter than traditional clay-fired bricks. Secondly, with the use of low-cost fly ash in the process, environmental pollution can be reduced due to the reduction of solid waste

and dust in nature. Fly ash bricks can be produced with better physical and mechanical properties such as porosity, water absorption and compressive strength compared to those of clay bricks (Ahmaruzzaman, 2010).

Lingling et al., 2005 studied the effect of fly ash with high clay substitution on brick's properties. Based on the test results, fired bricks with high compressive strength, low water absorption, no breakage due to lime, without frost and high resistance to frost melting occurred with the utilization of the high volume ratio of fly ash . Cicek and Tanriverdi, 2007, reported the utilization possibility of mixtures of fly ash with sand and hydrated lime in the production of light weights bricks. The results obtained indicated that good quality light bricks can be produced using mixtures of fly ash, sand and hydrated lime. In addition to brick products, fly ash can also be used in the production of light weight roofing materials such as hard roofing tiles. The fly ash roofing tiles are lighter than conventional ones and have excellent fire-proof   properties (class A fire-rating). This Class A fire-rating property makes the fly ash roofing tiles a good candidate for the utilization in high fire danger areas (Ahmaruzzaman, 2010).

2.12.3 Fly ash use in road sub-base

The roadway embankment is another important area for the utilizaion of fly ash. The fly ash has been widely used as raw material for soil stabilization, aggregate filler, paving additive and mineral filler. The fly ash has several advantages as a stabilizer of the soil along the roadway embankments. Firstly, fly ash can be used as abundant stocks if the fill and cover material is scarce in the area. However, thermal power stations should be close. Otherwise, this process would be uneconomical due to the high transport costs. The availability and positive physical properties of fly ash are the other important advantages for soil stabilization. In addition, fly ash generally has a higher shear strength, which is one of the most important properties for the utilization of fly ash in soil stabilization, compared to the resistance of soils generally used for embankments. The utilization of fly ash in road works provides approximately an increase of 10-20% in the construction cost (Ahmaruzzaman, 2010).

2.12.4 Fly ash utilization in mine back fills

The utilization of fly ash in the mine backfilling appears to be a good option for power plants located near the coal mine. The filling of the underground mine with fly ash is technically feasible and has great potential for areas where the cover material is poor. Fly ash can also be used as reclaimed material for open pit mines. At present, fly ash is generally used in underground mining sites closed with the grout injection method. The main goal of the injection process is to reduce the acid mine drainage (AMD). Fly ash reduces AMD through two mechanisms, i.e. neutralization of existing AMD due to its alkaline nature and inhibition of AMD appearance avoiding contact between water and pyritic materials (Ahmaruzzaman, 2010).

2.12.5 Utilization of fly ash in agriculture

The effects of the utilization of fly ash on soil properties have been studied by many researchers. The acidic or alkaline nature of fly ash depending on the type of coal can be used to buffer pH of the soil. The fly ash also increases the electrical conductivity of the soil. The high content of lime in some fly ash, in particular the fly ash of lignite, provides the release of nutrients in the soil such as S, B and Mo in the form and amounts beneficial for the cultivated plants. The use of fly ash has been studied to increase the pH of acidic soils and improve the soil texture to obtain agronomic benefits and improve the nutritional status of the soil. Boron toxicity is one of the main limiting factors for the use of fly ash in agriculture. The adverse effects of boron on soil microbes can be prevented by using an easily oxidizable organic substrate such as a carbonaceous acidic material. Promising changes in soil properties, increased pH and improved crop yields can be achieved by using the mixed application of fly ash, paper mill sludge and farmyard dung (Jala and Goyal, 2006).

2.12.6 Uses of fly ash as adsorbents for waste management

There are considerable body of literature exists on the use of fly ash as adsorbents for the cleaning of exhaust gases and the removal of organic and inorganic components, toxic metals and dyes for waste water. Activated carbon has been widely used to oxidise reduced sulfur compounds due to its superior adsorption properties. On the other hand,

for the utilization of large scale applications, it is too costly. Fly ash can be used as a cheap adsorbent for dry type flue gas desulfurization (FGD). Some promising results have been obtained for recycling of fly ash in the desulfurization process (Ahmaruzzaman, 2010). Adsorption properties of fly ash for NOx removal from flue gases were investigated by Lu and Do, 1991. According to the test results, adsorption capacity of fly ash particles can be improved by using controlled gasification of the unburned carbon.

The fly ash has a wide range of applications in the treatment of waste water due to its appropriate physical properties and chemical composition. Furthermore, the alkaline nature provides neutralizing properties for the fly ash. In this process, it is essential to adjust the pH of the wastewater by using lime and sodium hydroxide to maximize adsorption efficiency (Ahmaruzzaman, 2010).

2.12.7 Utilization of fly ash in composite materials

The use of fly ash in plastic and metal composites, especially aluminium, has been increased in recent years. Competitive products with a elastic module and similar or higher hardness and better wear resistance can be obtained by using aluminium ash fly composites which are considered potential materials for components such as pulleys, oil pans, intake manifolds and valve covers. Better wear resistance of nickel fly ash composite coatings compared to smooth nickel coatings has been achieved. It was considered that improved wear-resistance properties probably derived from the excellent combination of fly ash particles and nickel (Iyer and Scott, 2001). Because of its hollow spherical particles, cenosphere, some fly ash can also be used to reduce the density of metal compounds with better insulation properties, reduction of shrinkage and deformation values (Wandell, 1996).

2.12.8 Production of ceramics and glass like materials

Fly ash consists of mainly SiO_2, Al_2O_3, CaO and Fe_2O_3 depending on the types of coal. These oxide resources have generally been accepted as low-cost raw materials for glass and glass ceramic production. In addition to its appropriate chemical composition, as fly

ash physically occurs as fine particles, high-cost grinding operation is eliminated in most cases. The use of fly ash in glass and ceramic glass production includes three main advantages. Firstly, a zero cost raw material is used in the process, if the plant is close to the production unit. Secondly, natural resources can be preserved through the use of fly ash as raw material. Third, environmental pollution can be reduced by eliminating this waste product (Erol et al., 2008). The glass obtained can be assessed as a secondary raw material in the construction sector. The glass ceramic materials can be produced by the heat treatment process of the fly ash of vitrified coal. This process provides better micro-structural, mechanical and physical properties to waste containers, which leads them to find more areas of application (Erol et al., 2007).

2.12.9 Extraction of valuable metal from fly ash

Fly ash is mainly consists of low-value species such as silica, alumina, iron oxide and calcium oxide. This main matrix contains a very low concentration of valuable metals including boron, lithium, vanadium, gallium and germanium (Tsuboi et al., 1991). Fly ash can be considered as source of valuable metals. Therefore, the potential for recovery of valuable metals from fly ash should be investigated. This area of research has been promised with a larger ash generation worldwide (Tsuboi et al., 1990). As these high-value metals have very low concentrations in commercial minerals, the recovery and purification of numerous rare metals from fly ash has been studied.

In literature, there are several studies on the recovery of gallium, germanium, vanadium and boron from fly ash. These studies mainly include methods of leaching and extraction of gallium with commercial extractants (Gutierrez et al., 1997), ionic flotation of germanium from aqueous leachate with complexating agent and a surfactant as collector (Hernandez-Exposito et al., 2006) and leaching of the boron with dilute sulfuric acid and its further treatment with solvent extraction (Tsuboi et al., 1990).

2.13 Leaching of fly ash into the aquatic system

The utilization of fly ash in water leads to the potential leaching of some elements into the water. This creates a problem of secondary environmental pollution. The surface layer

of fly ash particles, probably of micron in thickness, contains a significant amount of easily entrained material deposited during cooling after combustion. Therefore, the charge on the surface of the fly ash particles and the widespread double layer formation plays an important role in leaching. The elements present were divided into two groups based on their dependence on the concentration of the particle size. The elements Mn, Ba, V, Co, Cr, Ni, Ln, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg and S are usually volatile to a large extent in the combustion process. Volatility for these elements it is inversely proportional to the particle size. They possess elements such as Mg, Na, K, Mo, Ce, Rb, Cs and Nb a smaller volatized fraction during coal combustion (Iyer R, 2002).

There were many important aspects of the leaching behaviour of fly ash reported by a number of reseacrhers (Iyer R, 2002, Hansen L D., et al., 1984, Prasad B, et al., 1996). Leachability of heavy metals from fly ash are relatively low and leaching extent is depends on the conditions of the water system. Trace metal concentration in the leachate depends on the weight/solution of fly ash, pH, concentration of elements, temperature, pressure and time. In water, rapid leaching of most trace metals (except Cu), takes place from the surface of the ash particles in a lower pH range, all trace elements are within acceptable limits (Prasad B, et al., 1996).

Several authors have been studied the ability of fly ash to improve the quality of leachate generated by coal waste (Stewart B R, et al., 1997), by oxidation of a mineral residue rich in sulfur (Perez Lopez, et al., 2007) and passive treatment of acid mines drainage (Gitari M W, et al., 2008). These authors have observed that generation of acidic leachate was prevented and inorganic contaminant significantly reduces. Several authors (Doye I. and Duchesne J., 2003, Reardon E J, et al., 1995) established that performed leaching tests on a particular waste material at least at two different solid/liquid (S/L) ratios can distinguish between these two types of species. They found out that if a species concentration does not double when the S/L ratio is reduced by half, there must be a solid phase control on its concentration in solution.

Determination of the concentration of an element in the fly ash leachates is controlled by the solubility of the minerals is a challenge. In reactions involving acid mine drainage

with fly ash, precipitates formed are largely amorphous (Gitari M W, et al., 2008, Warren C J and Dudas M J, 1985).

2.14 Leaching behaviour of elements from coal combustion fly ash

Fly ash is a heterogeneous material as the elements are not evenly distributed throughout. The mineral fraction in coal undergoes different transformations during and after combustion, namely decomposition, volatilization, fusion, agglomeration or condensation (Jones, 1995). As the flue gas cools down after combustion, volatile elements such as As, B, Hg, Cl, Cr, Se and most prominently S, condense on the surface of the fly ash particles, forming compounds with a variable solubility (commonly on the high side) and essentially combined with Ca. This results not only in a strong gradient of element concentrations within fly ash particles (Kukier et al., 2003) but also in a gradient of leachability. The surface layer of fly ash particles, only microns in thickness, contains a significant amount of readily leachable elements (Iyer, 2002) that, with the exception of S, stand out for being inherently more toxic at low levels than major elements. Alongside the above listed elements, Cd, Cu, Mo, Sb, V and Zn are also preferentially enriched on the surface, whereas Ba, Co, Cr, Mn, Ni and Pb tend to be more evenly distributed between the surface and the matrix (Jones, 1995). The elements enriched in the cores of fly ash particles are not directly exposed to leaching and therefore their releases are diffusion controlled and also dependent on the dissolution rates of the surface layers (Kukier et al., 2003). Surface-associated elements are therefore more susceptible to leaching in an aqueous environment.

There is a wide range of standardized leaching tests with variable complexity, reagents, temperature, agitation method, liquid to solid ratio (L/S), contact time (among other parameters) along with some others non-standardized but appropriated for specific purposes. Some of them are devised to mimic specific scenarios, some others are aimed at obtaining predictions on available concentrations and used as a surrogate for long-term releases. A detailed discussion on the worldwide standard leaching tests is out of the scope of this study and can be found elsewhere.

Among the variety of available leaching procedures, four types are commonly used in the leaching behaviour of coal ash: (i) batch leaching tests using demonized water or similar as leachant (no pH buffering) are often conducted to obtain information on the leachability of elements when the pH is governed by the ash itself, (ii) column/flow-through tests provide valuable data on the release pattern of elements under uncontrolled pH conditions, (iii) Toxicity Characteristic Leaching Procedure (TCLP), designed by US EPA and mandated for use in determining the hazardousness of materials to be disposed of (Hassett et al., 2005). The US EPA does not specifically recommend this test for coal combustion products, as it does not provide an accurate assessment of this material (USEPA, 2010, Hassett et al., 2005). However, the TCLP appears to be the worst-case test most often used throughout the literature. The test is conducted using buffered acetic acid solutions with pH=2.88 or pH=4.93 depending on the pH of the material, (iv) acid extractions, performed under aggressive conditions (pH=2) that are difficult to relate to field conditions, but are aimed at gaining an in-depth knowledge of the ash chemistry. Leaching behaviour of some selected elements from fly ashes is described following.

Major elements

2.14.1 Iron

The iron becomes soluble at pH $\leq$ 1.5 (Seidel and Zimmels, 1998), but the releases are of little significance in relation to the concentration in the fly ash. The leaching levels decrease drastically towards slightly acidic values (pH 3-5) and remain very low in the rest of the pH range. Any solution of Fe in precipitates such as amorphous hydroxide in response to an increase in pH values (Warren and Dudas, 1988). The insignificant proportions of Fe were leached from the fly ash (Ward et al., 2004). Less than 10 mg/kg of Fe are leachable in almost neutral and alkaline solutions and the concentrations in most cases are below the detection limit (Kim et al., 2003, Moreno et al., 2005). The iron present in fly ash is mainly present as magnetite mixed in various proportions with hematite, although a small proportion may be assimilated into the vitreous matrix (Kukier et al., 2003). The spinel structures are highly stable and resistant to atmospheric agents such as weathering and therefore Fe and any isomorphously substituted element are not

easily released into the environment. Iron oxides are also present in fly ash (Dudas, 1981). It is known that these species play a key role in the absorption of a series of elements of environmental concern, attenuating the concentrations in the leachates (Turner, 1981).

Trace elements

2.14.2. Cadmium

Environmental concerns related to cadmium derive from its potential solubility and toxicity in aquatic systems. Fly ash is, however, exhausted in Cd in comparison with other trace elements (except Hg) and environmental level sensitive element is constantly immobile in almost neutral and alkaline conditions. Despite its association with the surface of the fly ash particles, water leaching concentrations rarely exceed 0.01 mg/kg in alkaline nature fly ash (Fruchter et al., 1990, Moreno et al., 2005, Nathan et al., 1999, Medina et al., 2010) while the values of Australian fly ash equivalent to 0.1 mg/kg at pH≈4 (Ward, 2004, Ward et al., 2009). Cadmium is something leached in acidic conditions but still poorly extracted. Less than 10% Cd was removed from US alkaline fly ash at a pH of 1 (Kim et al., 2003), while 3-9% was extracted at a pH of 4 from Australian acidic nature fly ash (Ward, 2004). The solubility of Cd decreases towards almost neutral conditions (which result in detectable concentrations under TCLP conditions), Cd remains practically immobile in the pH range above 7, although some authors have noticed a soft amphoteric behaviour. Of particular interest is the effect of Cl on the leaching model of Cd, high chloride content can shift the solubility curve of the Cd to a higher pH values as a result of complexation processes that improve mobility (Jones, 1995).

2.14.3 Chromium

A number of studies were done to the resolution of speciation Cr in coal and fly ash because of different oxidation states cause different threats to the environment. Cr its hexavalent oxidation state, which include chromates or dichromate, is widely recognized as potentially carcinogenic and highly soluble in the aqueous media (Huggins and

Huffman, 2004), while the trivalent Cr (III) is less soluble and of much less concern to human health**.**

Most of data in the literature shows the predominant speciation of Cr^{3+}. Leaching tests on acidic fly ash from Australia have been hardly mobilized any Cr (0.03%) (Dubikova, 2006). Dubikova, 2006 also reported slightly higher mobility for alkaline ash and increasing releases with an increase in pH. The leaching pattern of Cr shows a marked dependence on the pH, reaching the lowest values at near neutral pH (0.02 mg/kg) and shows a leachability plateau between pH and 12 (typically around 5 mg/kg). In terms of mobility, these experiments indicate proportions of extractable water of 1-4%, reaching a maximum at higher pH values. The results of other researchers fall within this narrow range every time water is used (Baba and Kaya, 2004, Kim and Hesbach, 2009) and although according to Querol et al., 2001, columns test yield higher cumulative release about 8%.

Soco and Kalembkiewicz (2009) concluded that 8.2% of the total Cr can be leached from a Polish fly ash in environmental conditions. In alkaline and oxidizing conditions, it is probable that any soluble Cr is present in the form of chromate. The high sulfate concentrations together with the alkaline pH depress the adsorption processes (Fruchter et al., 1990). In contrast to As, large amounts of Ca in the solution does not prevent the dissolution of the easily soluble chromates.

Some fly ash shows the leachabilty of Cr in water reaches 20 mg/kg (Izquierdo et al., 2012). Few fly ash samples show up to 20% Cr as Cr^{6+} (Huggins et al., 1999). The presence of organic substances rich in oxygen in coal can lead to a higher percentage of chromates that form during combustion. In addition, the different leaching behavior could also due to the depositional configuration of the original peat environments. Cr^{3+} leached out from ultramafic bodies exposed to the elements could reach the lignite beds in aqueous form, as reported for Ni^{2+} (Ruppert et al., 1996), and remain organically associated. The organic bonds increase the volatilization of Cr during combustion, oxidation and precipitation of chromates soluble in fly ash.

2.14.4 Copper

Kukier et al. (2003) stated that about 2-5% of the total Cu is leached at pH≈3 from the point of the magnetic and non-magnetic fraction of the fly ash samples from U S. This observation, together with the small difference between the solubility of the two fractions suggests that Cu show some of them degree of mobility in acidic environment, regardless of the mode of occurrence.

Querol et al. (1996) noted markedly variable mobility such as a function of the occurrence mode in the parent carbon. A dominant association with clay minerals in coal results in a primary association of glass in fly ash which in the UK fly can reach up to 60% (Spears, 2004). Therefore, copper is assimilated into the glass and is not easily released. On the other hand, the oxidation of Cu-Fe- sulphides in coal leads to a higher mobility of Cu in fly ash.

The mobile fraction of Cu in environmental conditions was estimated at 2.6% (Soco and Kalembkiewicz, 2007). Results of TCLP yielded 0.5-3% Cu extractable for alkaline fly ash (Ward et al., 2004). However, Cu was leached in a much more in acidic extractants, since the release increased by a few orders of magnitude. Mobility at pH≈1 reached 8% (Dreesen et al., 1977, Kim et al., 2003). Generally 0.05- 0.1% of Cu is eliminated by leaching with water from alkaline fly ash (Ward et al., 2004, Moreno et al., 2005), which in terms of release would be about 0.05 mg/kg. These values can increase in the acid generating fly ash. The study of Ward, 2004 reported that Cu would be slightly amphoteric though data from other surveys in the literature do not follow this trend and they remain at very low levels at pH 12 (Ugurlu, 2004, Moreno et al., 2005, Izquierdo et al., 2012).

2.14.5 Lead

Being an element associated with sulfides in coal, one can expect an association of Pb to ash. It is estimated that about 50-60% of Pb is in surface association in fly ash (Spears and Martinez-Tarrazona, 2004), despite the results of Warren and Dudas (1988), i.e. suggest that most Pb is probably associated with the internal glass matrix of fly ash, and

therefore does not easily lose anything under the extinction of acidic atmospheric agents. Kim and Kazonich (2004) also reported an association of dominant silicates. Pb was found to be highly insoluble and practically immovable (<1% and often <0.1%) in samples of alkaline fly ash, independently of the pH leaching test (Praharaj et al., 2002, Kim et al., 2003, Ward et al., 2004, Moreno et al. al., 2005).

As with other cations, acidic conditions slightly improve the leaching of Pb (Jones, 1995). However, the leachable concentrations are still at very low levels. Less than 1 mg/kg of Pb was released from US fly ash using a range of tests (Kim and Hesbach, 2009, Kim et al., 2003). Of all the experiments, it is worth mentioning that only 0.4 mg/kg of Pb was leached using pH = 1.2 leachant. According to Dubikova, 2006, Pb mobility appears to be controlled by precipitation of phosphate minerals, which are highly insoluble over a wide range of pH.

As an amphoteric metal, the solubility of Pb is thought to decrease to minimum around pH 9, and after that show a marked increase at pH> 11.5 as a result of the formation of more soluble anionic hydroxo complexes (Jones, 1995). However, a number of studies are not consistent with this pattern of leaching. Ward et al., 2004, Moreno et al., 2005, Dubikova, 2006 and Izquierdo et al., 2012, reported over of 30 fly ashes with pH 11-13, no sample showed leached Pb levels above 0.06 mg/kg. Since the metals have products with low solubility, their precipitation under alkaline conditions it can attenuate the leaching of Pb (Cornelis et al., 2008) and alter their early amphoteric nature. Lead was not leached during a 2-year column test (Dudas, 1981). In another column leaching test, Querol et al. (2001) found no delayed release. These results, together with the low solubility observed of this element in the entire pH range, provide evidence that Pb leaching does not pose a risk to the environment, regardless of the total content in fly ash.

2.14.6 Nickel

There is a lot of evidence to link this element with organic constituents (Palmer et al., 1995), although a variety of patterns of occurrence in coal has been reported. Nickel was found mainly in the form of oxide in coal (Goodarzi et al., 2008) and minerals containing Ni (spinels and illites) are common in coal deposits near ultramafic bodies (Ruppert et al.,

1996), while sulfur minerals containing Ni have also been reported (Palmer et al., 1995). Whatever the association in coal, Ni seems to be distributed between the silicate fraction and the magnetic fraction of fly ash during combustion. All of these studies agreed that a much part of Ni leachable is solubilised from the non-magnetic fraction.

The solubility of Ni is markedly sensitive to pH and covers some orders of magnitude. Up to 10% of Ni was removed when using pH~1leachant (Kim et al., 2003). Mobility has decreased dramatically 1% at slightly acidic conditions, such as those of TCLP on alkaline and acidic fly ash and water-based acid leaching test on acidic fly ash (Ward et al., 2004). These authors have emphasized some exceptions to the above, which could be related to different mode of occurrence. The lowest levels of leaching are achieved in the region of pH 8-10 (<0.05 mg/kg and extractable <0.01%) and release increase up to 0.2 mg/kg with increasing pH, providing a test of the amphoteric behaviour.

Previous works relate to qualitative observation on leaching behaviour of toxic metals from fly ash. These observations help us to understand the general effects of utilization of fly ash in materials. The practical utility of these qualitative studies may not be really useful unless a framework is developed based on which the assessment can be made for use in strength and stability calculation. The aanalysis and assessment of the leaching behaviour of toxic metals from fly ash materials should lead to a sort of generalization based on which field engineers can effectively use and exploit the use of fly ash in materials. The results of characterization and leaching tests of fly ash materials (bricks, blocks and cements) with varying properties are presented together with the characteristics and leaching tests of fly ash. The results of characterizations confirm that it is possible to develop a basic frame work to understanding the fly ash utilization status and leaching of fly ash toxic metals from materials would have scope to develop strategies for pollution prevention control.