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Environmental Aspects of Coal Combustion Residues from Thermal Power Plants

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/56038>

1. Introduction

Electricity is an essential need of any industrial society and no nation can progress without adequate supply of power. Growth in its demand during the past decades has been phenomenal and has outstripped all projections. In India also, there has been impressive increase in the power generation from a low capacity of 1330 MW in 1947 at Independence to about 81,000 MW at end of March 1995[1] and at about 2,05,340 MW at the end of June 2012 [2]. However, despite this substantial growth there still remains a wide gap between demand and supply of power which is expected to worsen in the years and decades to come. We already are experiencing shortage of nearly 8% of the average demand and 16.5% of peak demand. Moreover, with the quantum jump expected in demand for power in the future due to rapid industrialization and changing life styles of populace as a result of economic liberation, shortages shall further increase unless immediate steps are taken to increase power production.

1.1. The energy scene

Per capita consumption of energy in India is one of the lowest in the world. India consumed 570 kg of oil equivalent (kgoe) per person of primary energy in 2009-10 compared to 1090 kgoe in China and the world average of 1,688 kgoe [3]. India has declared to be moving towards energy security and independence in a few decades with ambitious energy generation targets. Total installed capacity source wise for June 2012, is give below in Table 1 and Figure 1 [2].

Source	Total Capacity (MW)	Percentage
Coal	116,333.38	56.65
Hydroelectricity	39,291.40	19.13
Renewable Energy Source	24,832.68	12.09
Gas	18,903.05	9.20
Nuclear	4780	2.32
Oil	1,199.75	0.58
Total	2,05,340.26	100

(Source: Central Electricity Authority, New Delhi, June, 2012)

Table 1. Total Installed Capacity of Electricity Generation from Various Sources

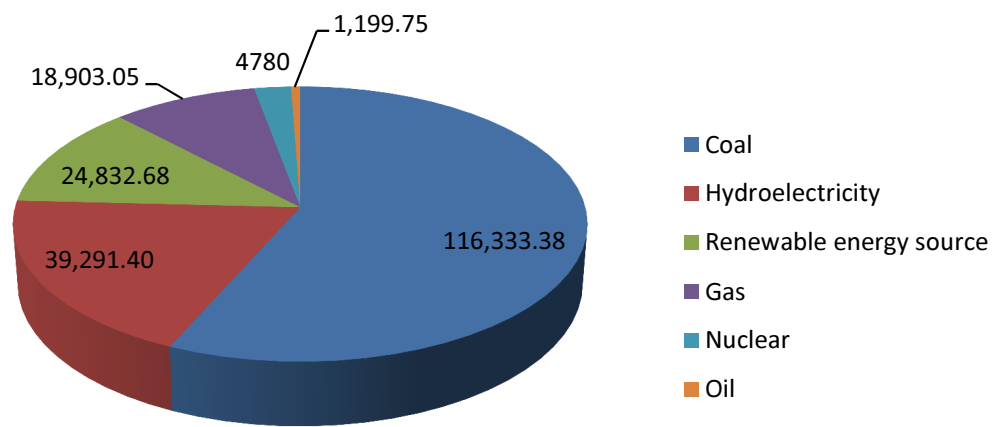


Figure 1. Total Installed Capacity of Electricity Generation from Various Sources (Source: Central Electricity Authority, New Delhi, June, 2012)

The total installed electric power generation capacity, public and private sector combined, is 2,05,340.26 MW only. Of the total installed capacity, thermal power is highest at 116.333.38MW representing almost 57%, the remaining being either gas based, oil based, hydro or nuclear [4]. Coal has been identified the mainstay fuel for thermal power generation in India and will remain so for another two decades at least.

1.2. Coal reserves and demand scenario

The Integrated Energy Policy Committee set up by GOI in 2004 emphasized the continuing dominance of coal in Indian Energy Security over the next 25 years [5]. India has vast reserves of coal and it is expected that coal remains a prime source of energy through the early part of 21st century The coal reserves in India up to the depth of 1200 meters have been estimated by the Geological Survey of India at 285.86 billion tonnes as on 1.4.2011 [6].. Only 12.5% of the resource is coking type and remaining 87.5% is non-coking or thermal coal. Coal deposits are

mainly located in Jharkhand, West Bengal, Orissa, Chhattisgarh, Maharashtra, Madhya Pradesh and Andhra Pradesh [6]. About 75% of the coal produced in the country is used for thermal power generation [7]. The coal demand is expected to rise to 2600 million tonnes at present level of consumption trend. The country's estimated demand of coal assessed by Planning Commission is 772.84 million tonnes for 2012-13 [6]. Majority of this demand will be met by our own resource of which more than 85% are high ash non-coking variety. Rapid increase in India's future power generation to meet the growing demand for domestic and industrial uses will be based on coal.

1.3. Coal combustion residues and their types

The process of coal combustion results in the generation of coal combustion residues (CCRs). India has diverse quality of coal reserves, which contain 30-55% ash. Annual production of CCRs has already crossed 120 MT and with the present rate of growth (8-10%) of power generation it is expected that this figure would be 175 MT by 2012 [8].

The quantum of CCRs generated in India is a matter of utmost concern. Out of the total CCRs generated, only 41% is being utilized [9]. Utilization that was around 1% in 1994 has shown a sharp increase in ten years period. However, the 41% utilization is still low as compared to more than 50% utilization in some other countries. One of the main reasons for the improper utilization of CCRs in India is its poor availability in usable forms and lack of characterization.

Coal combustion residues (CCRs) include materials that are left over after the burning of coal. They are fly ash, bottom ash, boiler slag and flue gas desulfurization (FGD) materials (wet or dry). The process of ash formation is influenced by the chemical composition of mineral matter in coal and its thermal properties. Other important factors include interaction between the inorganic and organic constituents of the particles and the physical and chemical environment through which these particles pass in the furnace. The distribution between the bottom ash and fly ash fraction is a function of the coal type, the boiler type and the type of boiler bottom.

1.3.1. Fly ash

Fly ash is one of the incombustible mineral residues produced from the combustion of pulverized coal in the boilers. The particle size of the fly ash is varied between less than 1 to 100 μm . The fly ash particles are removed with the help of flue gases from the stack and generally captured by electrostatic precipitators and any other air pollution control equipments such as bag houses or wet scrubbers [10].

Classification of Fly Ash: According to ASTM C 618 (American Society for Testing and Materials), fly ash is classified into two categories such as Class C and Class F fly ash. Both the type of ash contains SiO_2 , Al_2O_3 and Fe_2O_3 . Class C fly ash contains greater than 50% and Class F fly ash contains approximately 70% of these oxides. The average composition of Class C and Class F fly ash is shown in Table 2.5 [11].

Class C Fly Ash: Class C fly ash is produced from the burning of sub bituminous coal or lignite. It has pozzolanic properties and self-cementing properties. Class C fly ash will harden and

gain strength over time in the presence of water. Alkali and sulfate (SO₄) contents are generally higher in Class C fly ashes. It has higher lime (CaO) content (>10%) than Class F fly ash (<10%).

Class F Fly Ash: Class F fly ash is mainly produced by the anthracite and bituminous coal. It has pozzolanic properties and less than 10% lime content. Class F fly ash requires a cementing agent, such as hydrated lime or quicklime with the presence of water in order to produce cementitious materials.

Oxide	Class C (Wt%/std)	Class F (Wt%/std)
SiO ₂	17.6 ± 2.7	52.5 ± 9.6
Al ₂ O ₃	6.2 ± 1.1	22.8 ± 5.4
Fe ₂ O ₃	25.2 ± 2.8	7.5 ± 4.3
CaO	>10	<10
MgO	1.7 ± 1.2	1.3 ± 0.7
Na ₂ O	0.6 ± 0.6	1.0 ± 1.0
K ₂ O	2.9 ± 1.8	1.3 ± 0.8
SO ₃	2.9 ± 1.8	0.6 ± 0.5
LOI	0.06 ± 0.06	0.11 ± 0.14
Moisture	0.33 ± 0.35	2.6 ± 2.4

(Source: Scheetz et al., 1997)

Table 2. Composition of Class C and Class F Fly Ash

1.3.2. Bottom ash

Bottom ash is generally gray to blackish in colour. It is angular shaped and has a porous surface structure. Approximately 15-20% of total ash is bottom ash. It does not have any cementitious properties due to its larger size. Bottom ash consists of aggregated ash particles formed in pulverized coal boilers that are too large to be carried in the flue gases and fall through open grates to an ash hopper at the bottom of the boiler or impinge on the boiler walls [12]. Bottom ash is removed from the bottom of the boiler either in dry or wet state and is transported by the pipeline to handling system.

1.3.3. Pond ash

After the generation of fly ash it is transported to the specific area termed as ash pond. Generally pond ash contains fly ash and bottom ash mixture in the ratio of 80:20. About 20-40 cubic meters water is require for the transportation of 1 tonne of ash. The coarser particles are generally settled down due to the action of gravity. Pond ash creates respiratory diseases and reduction of visibility during the time of summer. That’s why water is spraying over the ash pond surface to control the air pollution.

1.3.4. Boiler slag

Boiler slag is made up of black, hard and angular particles that have a smooth and glass like appearance. It is the molten ash collected at the bottom of the cyclone and slag tap that is mixed with water. When the molten slag comes in contact with the water, it fractures, crystallizes, and forms pellets. Boiler slag is mainly used for various applications such as fill material for structural applications, component of blasting grit and raw material in concrete products etc.

1.3.5. FBC (Fluidized Bed Combustion) ash

The FBC is a technology employed to reduce the amount of sulphur released into the atmosphere while burning sulphur-rich coal. FBC ash is formed when coal is burnt in the presence of crushed limestone as a bedding material in fluidized form. It consists of unburned coal, ash, and spent bed material. SO_2 is converted to CaSO_4 through its reaction with the limestone during the time of combustion. Approximately lower temperature (815 - 870°C) is required for fluidized bed furnace than the conventional coal fired furnaces (1400 - 1600°C). FBC technology has become extensively used for reducing SO_2 emissions from power plants due to its low cost [13].

1.3.6. FGD (Flue Gas Desulfurization) ash

FGD ash is the solid residue that results from a variety of processes used to control SO_2 emissions from boiler stacks. Apart from over 95% SO_2 removal capacity, this technology can also reduce the emission of other gases like hydrogen chloride and sulphur trioxide [14]. FGD ash is generally produced in the scrubber by the reaction of limestone with SO_2 to form calcium sulfite. This calcium sulfite further oxidizes to form calcium sulfate (95% pure). Both of the compounds are produced in the scrubbers in wet form and then dried and processed for handling.

1.4. Implications of coal ash generation

Generally high ash coals are available for thermal power generation. Solid waste from combustion, mainly fly ash removed with electrostatic precipitators or bag houses and bottom ash collected in the boiler, have become an important environmental problem because of their high volume and physical and chemical characteristics. As per the available estimates the production of coal ash in India including both fly ash and bottom ash is about 120 million tonnes per annum which is likely to touch 200 million tons per annum by 2015 A.D [15]. Due to high ash content in Indian coal, emphasis is being laid now on setting up coal fired Super, Ultra and Mega Power Projects on pithead itself in order to minimize cost associated with bulk transport of ash laden coal [16]. The installed capacity is expected to increase to about 300,000 MW by 2017. Majority of these additions would be coal based which will further add to the burgeoning problems of ash disposal. A thermal power plant generating 1000 MW of electricity produces about 1.6 million tonnes of coal ash annually of which 80% is fly ash. The management of large volume of coal ash produced in power plants is a real challenge for the nation [17].

The power plants must either find purposeful utilization of these ashes or alternatively dispose them off site. Although coal ash possesses beneficial properties, both physical and chemical. Still serious concerns related to health, safety and environmental risks involving air and water quality prevail in the mind of mine planners, operators, regulators and environment groups [18]. Thus the utilization of coal ash has drawn considerable concern and attention of scientists, technologists, environmental groups, government, regulators etc. Till the early 1990's only a very small percentage (3%) of the fly ash was used productively in India and the balance material was being dumped in slurry form in vast ash ponds close to power plants. The numbers of governmental and institutional actions taken since then have increased the ash utilization to 50% during 2010-2011 [19].

2. Environmental regulations for the fly ash utilization

To address the problem of pollution, caused by fly ash and to reduce the requirement of land for disposal of fly ash in slurry form in ash ponds, Ministry of Environment & Forests (MoEF) Government of India (GOI), has issued following notifications stipulating targets for utilization of the fly ash to achieve 100% utilization in phased manner [20].

2.1. Ministry of environment and forests — Notification

Published in the Gazette of India, Extraordinary, Part II, Section 3, Subsection (ii), New Delhi, the 6th November, 2008.

S.O. 2623 (E)._Whereas by notification of the Government of India in the Ministry of Environment and Forests number S.O. 763(E), dated the 14th September, 1999 (hereinafter referred to as the said notification) issued under sub-section (1) and clause (v) of sub-section (2) of section 3 and section 5 of the Environment (Protection) Act, 1986 (29 of 1986), the Central Government, issued directions for restricting the excavation of top soil for manufacture of bricks and promoting the utilisation of fly ash in the manufacture of building materials and in construction activity within a specified radius of one hundred kilometres from coal or lignite based thermal power plants [21]; (2) All coal and, or lignite based thermal power stations and, or expansion units in operation before the date of this notification are to achieve the target of fly ash utilization as per the given below:

S. No.	Percentage Utilization of Fly Ash	Target Date
1.	At least 50% of fly ash generation	One year from the date of issue of this notification
2.	At least 65% of fly ash generation	Two years from the date of issue of this notification.
3.	At least 85% of fly ash generation	Three years from the date of issue of this notification.
4.	100% fly ash generation	Four years from the date of issue of this notification.

(Source: Fly Ash utilization Amended Notification, MoEF, New Delhi, November 2009)

Table 3. Target of Fly Ash Utilization

The unutilized fly ash in relation to the target during a year, if any, shall be utilized within next two years in addition to the targets stipulated for those years. The balance unutilized fly ash accumulated during first four years (the difference between the generation and the utilization target) shall be utilized progressively over next five years in addition to 100% utilization of current generation of fly ash.

(3) New coal and, or lignite based thermal power stations and, or expansion units commissioned after this notification to achieve the target of fly ash utilization as per given below:

S. No.	Fly ash utilization level	Target Date
1.	At least 50% of fly ash generation	One year from the date of commissioning.
2.	At least 75% of fly ash generation	Two years from the date of commissioning
3.	100% of fly ash generation	Three years from the date of commissioning.

(Source: Fly Ash utilization Amended Notification, MoEF, New Delhi, November 2009)

Table 4. Target of Fly Ash Utilization

The unutilized fly ash in relation to the target during a year, if any, shall be utilized within next two years in addition to the targets stipulated for these years. The unutilized fly ash accumulated during first three years (the difference between the generation and utilization target) shall be utilized progressively over next five years in addition to 100% utilization of current generation of fly ash.

MoEF's Notification of 3rd November, 2009 i.e. [22]

- i. All thermal power stations in operation on the date of notification should have achieved the target of 60% fly ash utilization within two years from the date of notification i.e. by 3rd November, 2011; and
- ii. All new thermal power stations which have come into operation after the date of notification should have achieved the target of 50% of fly ash utilization within one year of their commissioning.

No person or agency shall within 50 kilometers (by road) from coal or lignite based thermal power plants, undertake or approve showing of mine without using at least 25% of fly ash on weight to weight basis, of the total stowing materials used and this shall be done under the guidance of the Director General of Mines Safety (DGMS) or Central Mine Planning and Design Institute Limited (CMPDIL).

Provided that such thermal power stations shall facilitate the availability of required quality and quantity of fly ash as may be decided by the expert committee referred in subparagraph (10) for this purpose.

8(ii) No person or agency shall within fifty kilometers (by road) from coal or lignite based thermal power plants, undertake or approve without using at least 20% of fly ash on volume

to volume basis of the total materials used for external dump of overburden and same percentage in upper benches of back filling of opencast mines and this shall be done under the guidance of the Director General of Mines Safety (DGMS) or Central Mine Planning and Design Institute Limited (CMPDIL).

2.2. Strategies for coal ash utilization

Central Electricity Authority (CEA) has been working out the straggles on behalf of Government of India for effective utilization of the coal ash [15]. A large number of technologies have been developed for gainful utilization and safe management of fly ash under the concerted efforts of Fly Ash Mission of the GOI since 1994. As a result, the utilization of fly ash has increased to over 73 million tonne in 2010-11. Fly ash was moved from “hazardous industrial waste” to “waste material” category during the year 2000 and during November 2009, it became a saleable commodity. Fly ash utilization has started gaining acceptance, it being 55.79% during 2010-11.

The areas of concern include:

- Improving the collection efficiency of the ESP & of quality of fly ash generated.
- Need for development and implementation of systems for collection of classified fly ash, Certification of its quality for value addition and bulk environment friendly transportation options.
- Need for development of schemes for collection of dry bottom ash and its effective utilization.
- Need to develop energy efficient ash slurry pumps capable of handling dense ash slurry.
- Open trucks are used to transport fly ash for manufacture of building products. There is a need to develop efficient bulk transportation options for supply of fly ash from power plant to the end user. For 100% fly ash utilization at the generating stations
- Technologies are to be developed for demonstration of bulk utilization options of fly ash in roads and embankments, mine fills, sea erosion tetrapods, roller compacted concrete.
- Guideline standards to be developed to ensure quality assurance in value added products from fly ash, viz., bricks, blocks, pavers, kerbstones, tiles, etc.
- Development and application of high value added utilization of fly ash such as:
 - Extraction of cenospheres (A cenosphere is a lightweight, inert, hollow sphere filled with inert air or gas, typically produced as a by-product of coal combustion at thermal power plants.)
 - Extraction of titanium oxide, Alumina
 - Development of composite materials, acid/fire resistant bricks /tiles
 - Development of abrasion resistant materials
 - Value added building materials

- Agriculture amendments, etc.

–“**Incubation centers**” should be set up for technology validation.

–“**Self sustaining technology demonstration centers**” to be established for technology propagation schemes.

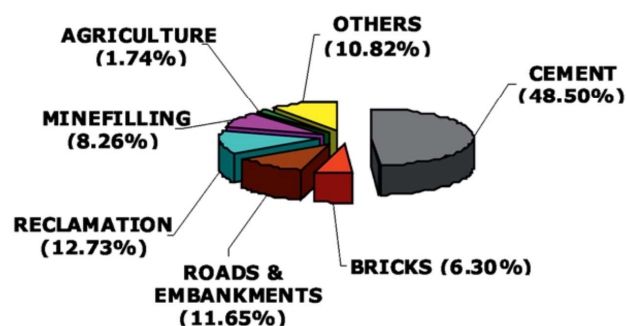
–Encourage “**Industry–Institute interactions**” for entrepreneur development, awareness, training programmes and workshops.

–Induction of “**fly ash subject in academic curriculum**” of Engineering, Architecture, and Post Graduate Science Courses.

2.3. Modes of ash utilization during 2010–11

The major modes in which ash was utilized during the year 2010-11 along with utilization in each mode is presented in the pie diagram is given in Figure-2 below [15]:

MODE OF FLY ASH UTILIZATION DURING 2010-11



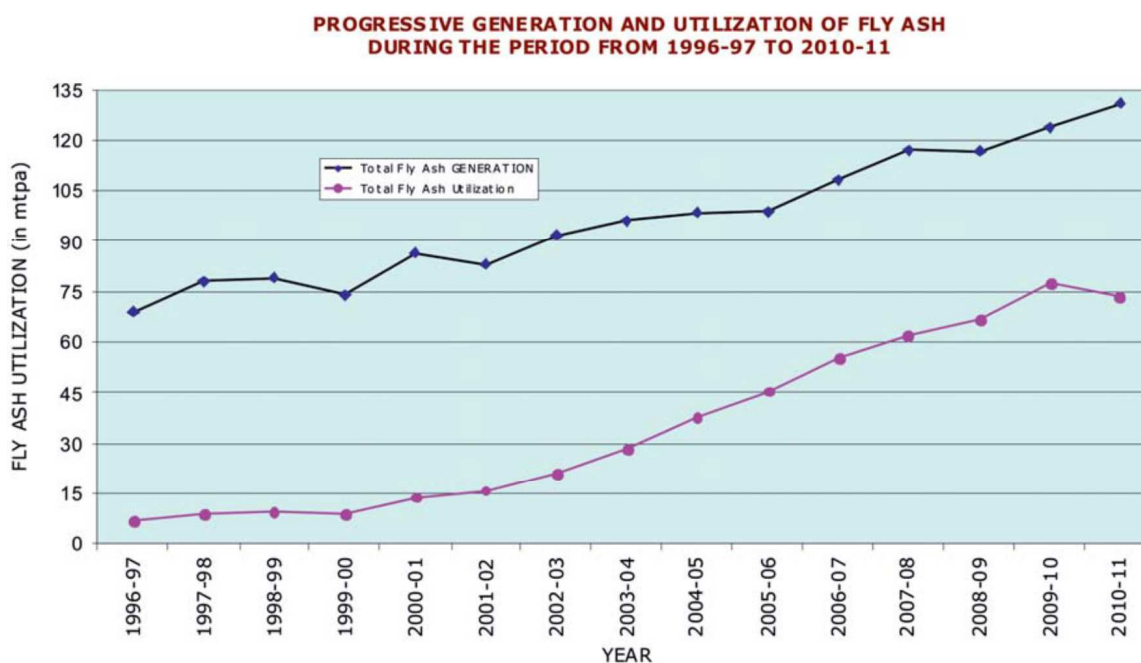
(Source: Central Electricity Authority, New Delhi, December, 2011)

Figure 2. Mode of Fly Ash Utilization during 2010-11.

It may be seen from above table that the maximum utilization of fly ash to the extent of 48.50% has been in Cement sector, followed by 12.73% in reclamation of low lying area, 11.65% in roads & embankments etc. The utilization of fly ash in mine filling was 8.26% and in making fly ash based building products like bricks, tiles etc was only 6.3%. These two areas have large potential of ash utilization which needs to be explored for increasing overall ash utilization in the country.

2.4. Progressive Fly Ash Generation and utilization during the period from 1996-97 to 2010-11

The progressive ash generation at coal/lignite based thermal power stations and its utilization for the period from 1996-97 to 2010-11 as per data received in CEA from power utilities is given in Figure 3 below [15]:



(Source: Central Electricity Authority, New Delhi, December, 2011)

Figure 3. Progressive Generation and Utilization of Fly Ash during the Period from 1996 – 97 to 2010 – 11.

3. Environmental aspects of trace elements leaching

There has been widespread concern of ground and surface water contamination due to trace elements leaching in and around the ash ponds. Leaching aspects of trace elements are presented here which are required to screen the coal combustion residues (Fly as-, bottom- & pond – ash) on environmental angle for its utilization.

3.1. Trace elements in fly ash

Studies of trace elements and the elements present in fly ash are distributed into the fractions of the fly ashes based on volatilization temperature [23]. It is found that elements appear to partition into three main classes.

Elements that are not volatilized and reported equally in both fly ash and bottom ash. These elements include Al, Ba, Ca, Ce, Co, Cu, Fe, Hf, K, La, Mg, Mn, Rb, Se, Si, Sm, Sr, Th, Ta, and Ti.

Elements that are volatilized on combustion and preferentially get adsorbed on the fly ash as flue gas cools down. These include As, Cd, Ga, Mo, Pb, Sb, Se and Zn.

Elements that remain almost entirely in the volatilised state tend to escape to the atmosphere as vapours. These are Hg, Cl and Br.

Fly ash is an alumino silicate glass consisting of the oxides of Si, Al, Fe and Ca with minor amounts of Mg, Na, K, Zn and S and various trace elements. The concentration associated with the ash may be either adsorbed on the surface of particle or incorporated into matrix [24]. A mechanism that appears to be common for all ashes during their formation is the condensation of metal and metalloid vapours on refractory core materials. As the ash particles and gas stream exist from the combustion chamber and proceed upto the flue gas, this results in locally higher concentrations of many trace elements at the surface of ash particles and accounts for the generally higher concentration of these elements as particle size decreases [25]. The association between trace elements and major elements/minerals may be an important factor in determining the leachate composition of water in contact with ashes [26].

It is recognised that the health hazards and environmental impacts from coal fired thermal power stations result from the mobilization of toxic elements from ash [18, 24]. The large amount of ash that accumulates at thermal power plants, its possible reuse and the dispersion and mobilization of toxic elements from it, requires greater attention. Mobilization of various elements from the ash into the environment depends on climate, soils, indigenous vegetation and agricultural practices [27].

3.2. Leaching aspects of fly ash

The leaching characteristics of fly ash are mainly controlled by factors such as its chemical composition, mineralogy and morphology. Fly ash from thermal power plants vary in chemical composition not only from plant to plant but also within the same plant [26, 28]. Chemically fly ash consists of Si, Al, Mg, Ca, K, Ti and Fe in greater proportion with many trace elements as V, Mn, Cr, Cu, Ni, As, Pb, Cd and smaller quantity of various potential toxic elements. Chemical composition study shows mostly the presence of four major elements viz. aluminium, silicon, iron and calcium in the fly ash. Others such as potassium, magnesium, barium, cobalt, cadmium, zinc, molybdenum, lead etc. are present in traces [29]. Though in the traces, compared to the original coal, most of the elements are enriched in the fly ash, giving birth to the growing environmental concerns in the disposal and utilization environment due to release of trace/heavy elements metals [30].

Crystalline phases in fly ash as major constituent is quartz and others such as mullite, magnetite, hematite etc. are also present as minor constituents. The mineralogy of fly ash refers to both amorphous and crystalline phases and other mineral fractions [29]. The leaching behavior of fly ash can be related to their mineralogical characteristics. Most of the toxic elements reside on major phases and are easily available during leaching [26].

Morphologically, particles of fly ash may be irregularly shaped particles, solid spheres and cenospheres. Morphology of fly ash similarly, controls the leaching of toxic elements/heavy metals. Morphology of fly ash is related to the conditions of combustion and composition of inorganic materials in coal. Particle morphology is one of the most important morphological aspects of fly ash. In this particle size particle distribution also holds its importance. Finer particles mean more surface area and so more concentration of condensing elements. In fact, specific surface area of fly ash is determined by both particle size and particle morphology.

The leaching of fly ash is a time dependent phenomenon. The initial leaching of the fly ash can be characterized by the surface hydrolysis and the dissolution of reactive phases formed under high temperature combustion. A close examination of the leaching studies show a rapid early dissolution followed by a later, slower release of the elements. The water-soluble fraction of a combustion residue may reflect the early dissolution process in the natural environment. In fact, the early dissolution mainly involves the soluble salts or the oxides on the particle surface of the fly ash. So, the dominant features of the initial dissolution stage are a high dissolution rate and the solution chemistry being controlled by buffering components of the fly ash. At this stage of high dissolution rate, release of salts or heavy metals associated with surface phases occur. The long term leaching of the fly ash occurs primarily in the aluminosilicate glass and some acid-soluble magnetic spinel phases. These phases usually constitute the matrix of the fly ash. The dominant leaching features of the matrix phases are a low dissolution rate and phase alteration over a long period of time [26].

Present study on environmental characterization is in continuation with earlier studies, to evaluate leaching of trace elements from coal ashes from a few Thermal Power Stations situated in eastern India are presented in this study [26, 28, 31]. The possible water contamination is also envisaged through the leachate analysis from ash pond disposal sites in real life situation.

3.3. Leaching chemistry

Short-term leaching (shake) tests and open column percolation leaching experiments were carried out on the fly ash samples to ascertain its leachate chemistry as briefly described below.

3.3.1. Strong acid digest test

This is short term leaching study and is carried out in the presence of strong acids to provide the available concentration levels of trace/heavy elements in the samples.

For the purpose of the experiment 0.5gm fly ash sample is taken in a conical flask and to it is added 10ml nitric acid and 2ml perchloric acid. Mixture is then heated till dryness on hot plate. The conical flask is covered during the process of heating by funnel. The dried residue in the conical flask is then boiled with 2ml HNO_3 and then filtered. This is repeated with distilled water, warmed up and filtered till no residue is left in the conical flask. The filter paper in the silica dish is kept in the muffle furnace and heated to 850°C . Silica dish is then allowed to cool with residue in it and residue is collected for further analysis. The filtered solution is stored in polypropylene beaker for further analysis (elemental).

3.3.2. ASTM shake test

This is the rigorous and short term leaching study. This test is run for twenty four hours and deionised water is used as the leaching medium. Shake tests can only be useful to a limited extent, and with variability in results in identifying the elements most likely to leach out of a material and to estimate the equilibrium constants for some of the reactions that takes place during the test. However, shake tests are poor indicators of the conditions that might be expected in the field [32].

In this test 80gm fly ash sample is taken and put in the measuring bottle and to it is added two litre of distilled water. The bottle with the sample is then taken in the rotary agitator and rotated for twenty-four hours and this way sample with water is agitated for thorough mixing to result leaching. The extraction is performed in triplicate on each fly ash sample and the three replicates are then mixed to get the composite leachate sample. The leachate so obtained is filtered using Whatmann No. 42 filter paper. The filtrate so collected is then stored in the polypropylene bottle for further analysis. Once the potentiometric analysis is over, few drops of 6N nitric acid are added to the leachate collected in polypropylene bottle to avoid contamination and the bottle stored to be used for further elemental analysis of the leachate by AAS.

3.3.3. 30-Day shake test

This test is similar to 24-hr shake test and is carried over a period of 30 days and is intended to indicate the solubility of elements that may reach equilibrium with the surrounding water more easily. This test is required by some regulatory agencies of some of the States in the USA.

3.3.4. Toxicity characteristics leachate procedure

The toxicity characteristic leachate procedure (TCLP) requires the use of an extraction fluid made of buffered acidic medium to run the test. For this the selection of the extraction fluid is made prior to conducting the test. Once the extraction fluid to be used in the test is determined, 40g fly ash sample is taken and then extraction fluid equal to twenty times the amount of sample taken is added in the zero head extractor under pressure. The system is tightly closed and then placed in an end-over-end rotary shaker for 18 hours, rotating at 30 ± 2 rpm at a room temperature of about 25°C. Leachate after the said period of shaking is pressure filtered using 0.7 micron pore size filter paper.

3.3.5. Modified Synthetic Leachate Procedure (SLP)

This test is a modified SLP rather than a standard SLP. Here, unlike the standard SLP test which make use of a mineralized synthetic leaching medium prepared from deionized water, water from an actual field site (containing ions and impurities similar to those found in groundwater in an area of interest) is used. This test aims to detect the ion exchange reactions that can only be observed in the field like ion bearing water. This test is run for 24 hours.

3.3.6. ASTM column

In the ASTM column procedure, one pore volume of distilled water is forced through a packed column of fly ash each day in a saturated upflow mode. Leaching in this column is conducted under a nitrogen atmosphere and thus present leaching in an oxygen poor environment. In the field, this type of leaching would occur below the water table where there is low concentration of oxygen. One pore volume corresponds to the void space between the material grains in the test column. The rate of percolation of the leaching medium regardless of the hydraulic conductivity of the material is controlled by applying variable nitrogen pressure. The test is run for 16 days and leachate collected after 1, 2, 4, 8, 16 days of leaching [33].

3.3.7. Open percolation column experiments

In these experiments, deionized water is percolated through a packed column of fly ash in the presence of oxygen at a rate which depends on the natural permeability of the material. The open columns for leaching experiments are made of PVC pipe four inches in diameter and two feet in length. The column setup involved packing the coal ash material at optimum moisture and density conditions as determined by the Proctor test. The fly ash material is packed into the column in two inch lifts with a 2" x 2" wooden rod, about 4 feet long. Each packed layer is scarified, by lightly scraping the top of the packed layer with a long thin rod to ensure proper interlocking of the material. The top six inches of the column was left unpacked to allow for the addition and maintenance of the leaching medium. About 200 ml of leaching medium (de-ionized water) is added at the top of the column once every alternate day to maintain sufficient supply of water to the packed coal ash material. The top end of the column is exposed to the atmosphere and the bottom end is connected to quarter inch tubing. The columns discharged the leachates through this tubing into the 250 ml polypropylene beakers. The leachates are collected in these beakers and analyzed.

3.4. Elemental analysis of leachates

The leachate samples are filtered and acidified with 2 ml of nitric acid and then preserved in polypropylene sampling bottles. The samples are kept in a refrigerator until further analysis. Sodium and potassium were determined using flame photometer. Concentration levels of trace elements were evaluated using Atomic Absorption Spectrophotometer (AAS). Working/standards solutions were prepared according to instructions given in the operation manual of the GBC-902 AAS [34]. Optimized operating conditions such as lamp current, wave length, slit width, sensitivity, flame type etc. as specified in the manual, are used for analysis of a particular element. -AAS standards are used for standardization and calibration of AAS. Three standards and a blank of the concerned element are used to cover the range 0.1-0.8 Abs. The calibration is performed by using the blank solution to zero the instrument. The standards are then analyzed with the lowest concentrations first and the blank is run between standards to ensure that baseline (zero point) has not changed. Samples are then analyzed and their absorbance recorded. The calibration is performed in the concentration mode in which the concentration of sample is recorded. ICP-MS can be used to arrive at the precise and quick results wherever affordable.

4. Leachate analysis results

Comparative evaluation of short-term leaching (shake) tests is presented in Table 2. Acid digest data provides the available concentration levels of Trace elements in fly ash whereas in comparison to this shake tests resulted significantly lower concentration levels particularly in 24 hr. ASTM, 30 Day and SLP shake tests. TCLP leachate data however, gives rise to significantly higher levels as this involved leaching in slightly acidic buffered conditions and as such does not reflect the actual behavior. It may be emphasized that these shake test presented the accelerated leaching because of 1:20 solid to liquid (leachant) ratio. Nevertheless these short

term (shake) leaching tests provide an immediate and rapid indication of leachable concentration levels of trace elements from fly ash.

Analysis of twenty two elements were carried out from each of the leachate samples collected from open column experiments and the observations are summarized in Tables 3 & 4 for fly ash, pond ash and actual ash pond leachates, respectively. It is noticed from the observations that the concentration of thirteen elements, namely, chromium, nickel, cobalt, cadmium, selenium, aluminum, silver, arsenic, boron, barium, vanadium, antimony and molybdenum were below the detection limit (.001 mg/l) in the entire study period. Among the other nine elements only calcium and magnesium were observed in the leachates throughout the study period while the concentration of other elements showed a decreasing trend to below detection limit (.001 mg/l). In the leachates from actual ash ponds, lead and manganese were found absent but iron, calcium, magnesium, sodium, potassium, copper and zinc were present throughout the study period.

A comparison of the concentration levels observed in the leachates of fly ash, pond ash and also leachates from actual ash pond disposal site with the permissible limits as per IS:2490, is presented in Tables 3 & 4 which indicates that the concentration levels of all the elements during the entire study period were either below detection limits (BDL) or below the permissible limits.

It can be inferred that no significant leaching occurs and toxicity is manageable with respect to trace elements both in the ash pond disposal site as well as in the open column leaching experiments. Further, analysis results of leachates from open column percolation experiments resemble closely with those of actual ash pond leachates. The physical set up of the open columns more closely resembles with because the flow of the leaching medium is influenced by gravity alone and the solid to liquid ratio is more close to the field situation. Hence, open column leaching experiments may be used in predicting the long term leaching behaviour that can be observed in the field. Fly ash leachates as generated from open percolation column leaching experiments and those from ash pond disposal site closely resemble and as such do not pose any significant environmental impacts in the disposal system. Overall, fly ash would not seem to pose any environmental problem during its utilization and/or disposal. Leaching pattern trace elements over three years open percolation column experiments is depicted in Figures 2-13 – which clearly reflect that trace elements leaching is not a significant concern and coal combustion residues can be appropriately utilized as these are established generally as environmentally benign material.

5. Concluding remarks

On the basis of the study of the leaching of trace elements from coal ashes, following conclusions can be drawn:

1. In the study period of about three (3) years there was practically no leaching of thirteen elements namely, chromium, nickel, cobalt, cadmium, selenium, aluminum, silver, arsenic, boron, barium, vanadium, antimony and molybdenum from all the ash samples.

2. Out of the nine elements found in the leachates only calcium and magnesium were found to be leaching in the entire period. The leaching of other seven elements namely, iron, lead, copper, zinc, manganese, sodium and potassium was intermittent. The leaching of sodium and potassium practically stopped due to first flash phenomenon after 35 and 40 days, respectively. It is emphasised long-term leaching results should be considered to arrive at the environmental screening of such materials.
3. The concentration of the elements in the leachates was invariably well below the permissible limits for discharge of effluents as per IS: 2490 and also for drinking water as per IS: 10500.

Parameter	Acid digest	TCLP	24-hr	30-D	SLP	SLP Blank
pH	--	4.29	6.22	6.26	7.08	7.06
Conductivity	--	3.56	0.096	0.099	0.075	0.085
TDS	--	1.78	48	63	51	58
Iron	82.41	0.089	0.045	0.05	0.029	0.038
Lead	BDL	BDL	BDL	BDL	BDL	BDL
Magnesium	7.579	7.512	3.15	4.50	2.4	2.8
Calcium	304.00	304.13	3.37	5.12	63	70
Copper	0.094	0.215	BDL	BDL	BDL	BDL
Zinc	0.276	2.140	0.020	0.025	0.180	0.185
Manganese	0.638	0.314	0.031	0.030	0.021	0.028
Sodium	54.60	1452	39.80	41.10	6	10
Potassium	7.60	8.10	2.80	5.36	3	4
Chromium	0.860	0.803	BDL	BDL	BDL	BDL
Nickel	0.118	0.112	BDL	BDL	BDL	BDL
Cobalt	BDL	BDL	BDL	BDL	BDL	BDL
Cadmium	BDL	BDL	BDL	BDL	BDL	BDL
Selenium	BDL	BDL	BDL	BDL	BDL	BDL
Aluminium	BDL	BDL	BDL	BDL	BDL	BDL
Silver	BDL	BDL	BDL	BDL	BDL	BDL
Arsenic	BDL	BDL	BDL	BDL	BDL	BDL
Boron	BDL	BDL	BDL	BDL	BDL	BDL
Barium	BDL	BDL	BDL	BDL	BDL	BDL
Vanadium	BDL	BDL	BDL	BDL	BDL	BDL
Antimony	BDL	BDL	BDL	BDL	BDL	BDL
Molybdenum	BDL	BDL	BDL	BDL	BDL	BDL
Mercury	BDL	BDL	BDL	BDL	BDL	BDL

BDL- Below Detectable Limit; Concentration of Elements in ppm; TDS in ppm; Conductivity in mmhos/cm

Table 5. Comparative Leachate Analysis Results of Shake Tests for Fly Ash

Parameter	Open Percolation Column Experiments Leachates			Ash Pond Leachate	(IS: 2490, 1981)
	Samples				Inland Surface Water
	FA#A	FA#B	PA		
pH	5.97-10.51	5.82-9.10	5.86-9.03	6.95-8.26	5.5-9.0
Conductivity	0.042-0.750	0.037-0.820	0.052-0.920	543-796	-
TDS	21-375	19-410	30-460	272-400	2100
Iron	BDL-0.740	BDL-1.220	BDL-1.369	0.89-1.983	-
Lead	BDL-0.420	BDL-0.396	BDL-0.490	0.121-0.462	0.1
Magnesium	BDL-15.53	0.039-38.00	0.065-44.00	17-29	-
Calcium	1.00-103.92	0.265-189.20	0.798-102-20	21-58	-
Copper	BDL-0.190	BDL-0.068	BDL-0.090	0.023-0.055	3
Zinc	BDL-0.380	BDL-0.372	BDL-1.529	0.295-1.763	5
Manganese	0.009-0.057	0.010-0.105	0.007-0.076	0.027-0.089	-
Sodium	3-56	3-49	3-47	19-43	-
Potassium	2-42	2-36	2-33	7-51	-
Chromium	BDL	BDL	BDL	BDL	2
Nickel	BDL	BDL	BDL	BDL	3
Cobalt	BDL	BDL	BDL	BDL	-
Cadmium	BDL	BDL	BDL	BDL	2
Selenium	BDL	BDL	BDL	BDL	0.05
Aluminium	BDL	BDL	BDL	BDL	-
Silver	BDL	BDL	BDL	BDL	-
Arsenic	BDL	BDL	BDL	BDL	0.2
Boron	BDL	BDL	BDL	BDL	2
Barium	BDL	BDL	BDL	BDL	-
Vanadium	BDL	BDL	BDL	BDL	-
Antimony	BDL	BDL	BDL	BDL	-
Molybdenum	BDL	BDL	BDL	BDL	-
Mercury	BDL	BDL	BDL	BDL	0.01

BDL- Below Detectable Limit; Concentration of Elements in ppm; TDS in ppm; Conductivity in mmhos/cm

Table 6. Summary of the Leachate Analysis of Fly Ash from Thermal Power Stations# 1

Parameter	Open Percolation Column Experiments Leachates			Ash Pond Leachates	(IS: 2490, 1981)
	Samples				Inland Surface Water
	FA#1	FA#2	PA		
pH	4.98-9.92	4.38-8.90	4.71-8.92	7.2-8.58	5.5-9.0
Conductivity	0.060-0.962	0.070-0.848	0.036-0.973	645-892	-
TDS	30-481	35-424	30-487	320-445	2100
Iron	BDL-3.850	BDL-3.120	BDL-3.120	1.02-2.941	-
Lead	BDL-0.098	BDL-0.080	BDL-0.249	-	0.1
Magnesium	BDL-37.9	BDL-36.4	BDL-21.0	10-19	-
Calcium	1-87.6	2-72.2	2.12-48.0	18-46	-
Copper	BDL-0.094	BDL-0.088	BDL-0.052	0.011-0.047	3
Zinc	BDL-1.082	BDL-1.100	BDL-1.290	0.93-1.015	5
Manganese	BDL-0.099	BDL-0.092	BDL-0.069	-	-
Sodium	BDL-48	BDL-23	BDL-82	5-10	-
Potassium	BDL28	BDL-36	BDL-18	8-18	-
Chromium	BDL	BDL	BDL	BDL	2
Nickel	BDL	BDL	BDL	BDL	3
Cobalt	BDL	BDL	BDL	BDL	-
Cadmium	BDL	BDL	BDL	BDL	2
Selenium	BDL	BDL	BDL	BDL	0.05
Aluminium	BDL	BDL	BDL	BDL	-
Silver	BDL	BDL	BDL	BDL	-
Arsenic	BDL	BDL	BDL	BDL	0.2
Boron	BDL	BDL	BDL	BDL	2
Barium	BDL	BDL	BDL	BDL	-
Vanadium	BDL	BDL	BDL	BDL	-
Antimony	BDL	BDL	BDL	BDL	-
Molybdenum	BDL	BDL	BDL	BDL	-
Mercury	BDL	BDL	BDL	BDL	0.01

BDL- Below Detectable Limit;

Concentration of Elements in ppm;

TDS in ppm;

Conductivity in mmhos/cm

Table 7. Summary of the Leachate Analysis of Fly Ash from Thermal Power Stations# 2

Overall, the fly ash samples from various Thermal Power Stations evaluated in this study were found to be environmentally benign and can be engineered for their bulk utilization particularly for mined out areas reclamation and for soil amendment for good vegetation.

The Centre of Mining Environment at ISM Dhanbad is currently engaged in evolving low technology high volume field demonstration to show that fly ash particularly fly ash can be disposed and utilized as fill material in an environmentally acceptable way in reclamation of abandoned mines [35, 36]. Fly ash has been successfully used as backfill in material in reclamation of mined out (goaf) area and at the top of the surface Helipad is set up, at Jamadoba Tata Steel Mining Area [37]. This has attracted a lots of public attention as a result of aesthetic and scenic value provided in the Eco-Park thus resulted. Similarly a considerable quantity of fly ash has also been utilised at Ghantotand OB Dumps and Damoda worked out opencast mine sites. At these sites trace elements leaching even after three years of monitoring does not seem to pose any environmental problem. With these encouraging results cooperative arrangements are being made by power utilities and mining authorities for utilisation of fly ash in reclamation of various mined out areas in SECL, MCL, NCL, BCCL, SCCL etc. [38].

Use of fly ash as backfill material for reclamation of mined out sites provide benefits such as easy availability, cheaper to transport because empty coal carriers returning from the power plant can "back haul" it to the mine site. From the standpoint of the power plant, this is essentially a waste material which requires large costs of handling and a disposal to comply with environmental regulations. From the environmental point, this waste material will go back to the same place where it was mined and use of this material serves as extra benefit to power plants. Studies are also in progress to use fly ash for agriculture development.

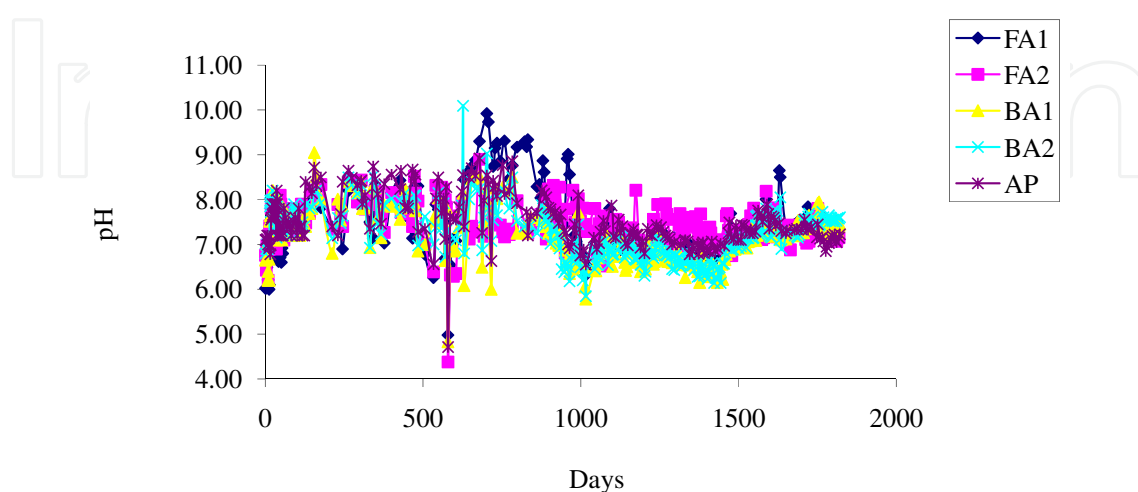


Figure 4. Open Column Leachate Analysis for pH

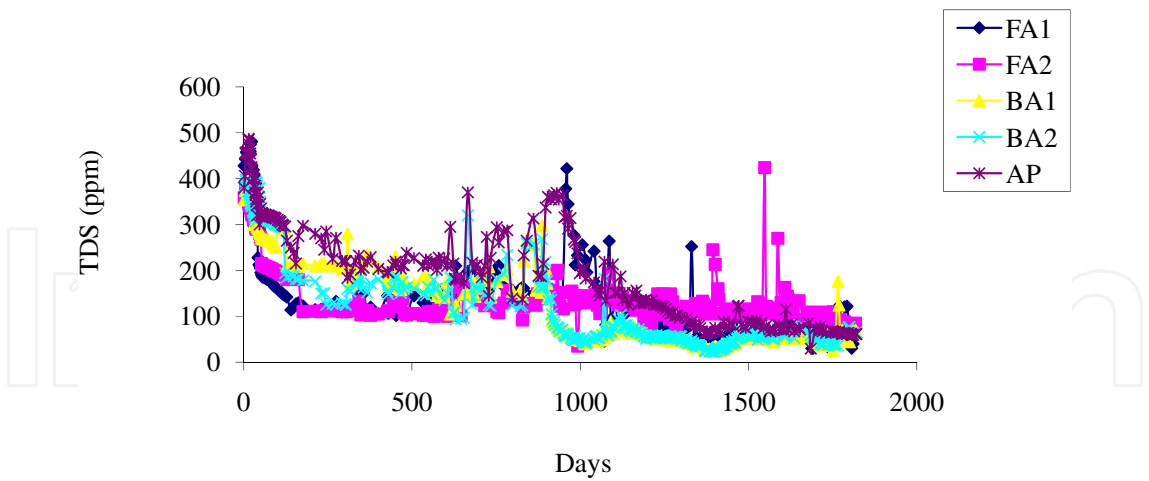


Figure 5. Open Column Leachate Analysis for Conductivity

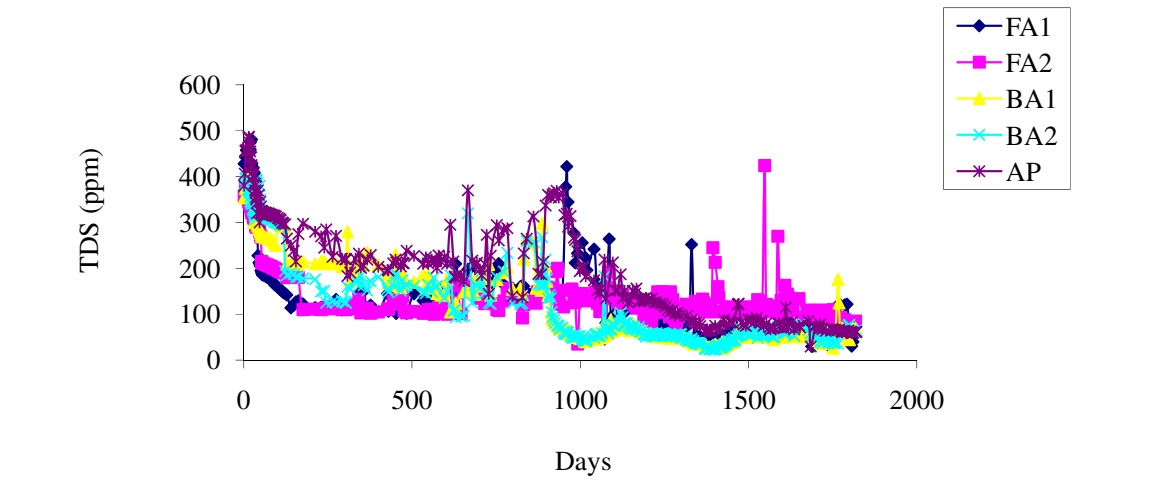


Figure 6. Open Column Leachate Analysis for TDS

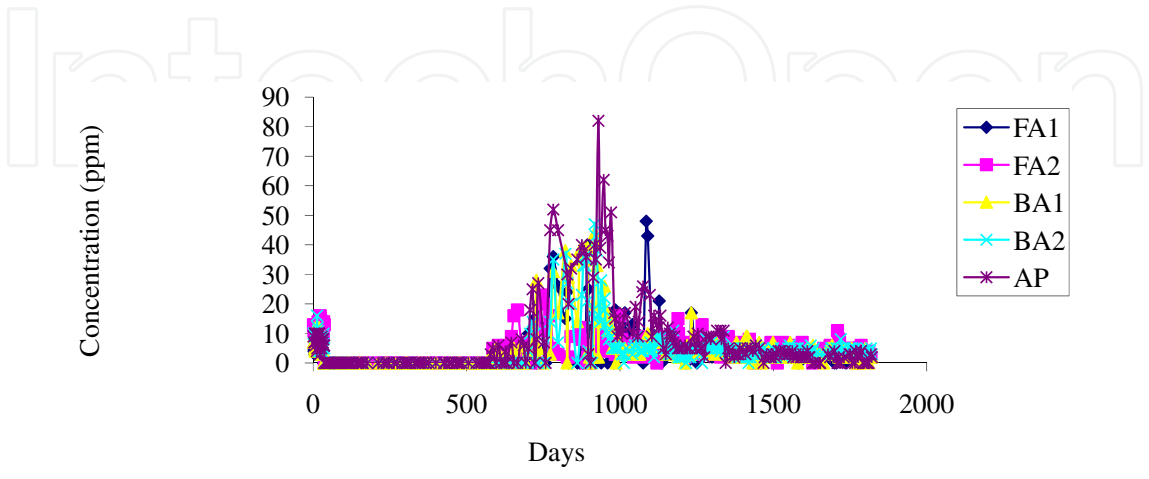


Figure 7. Open Column Leachate Analysis for Sodium

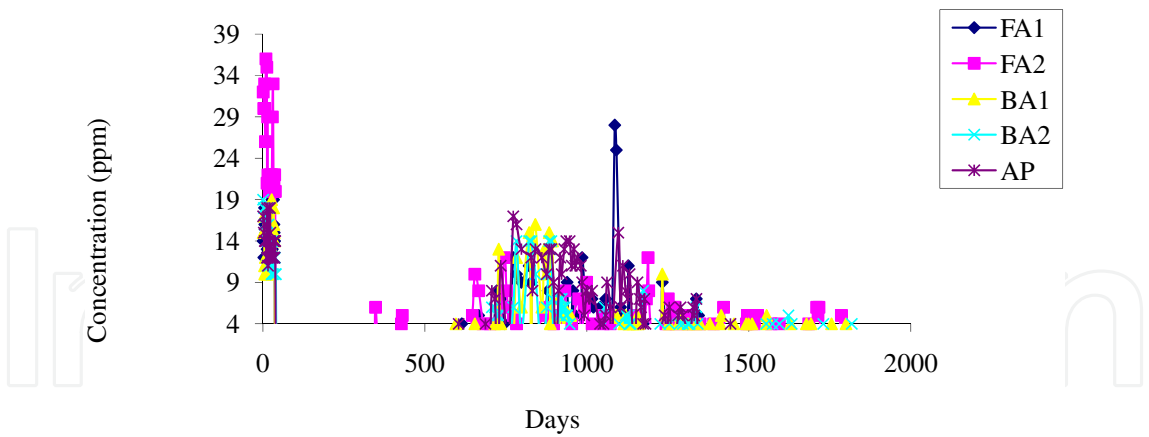


Figure 8. Open Column Leachate Analysis for Potassium

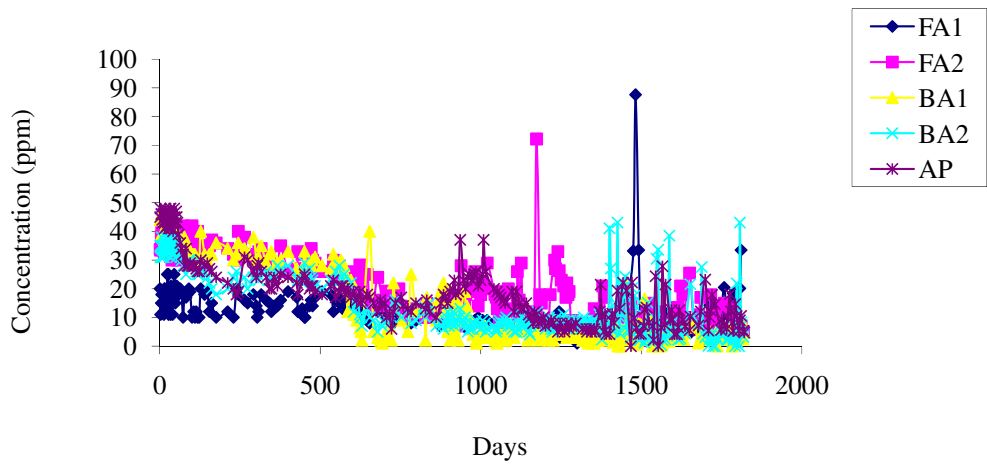


Figure 9. Open Column Leachate Analysis for Calcium

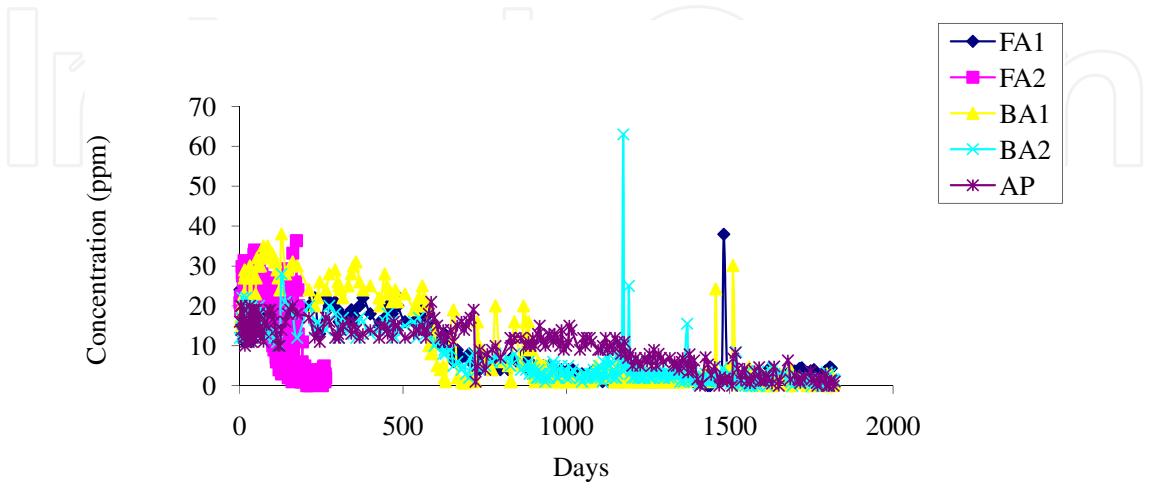


Figure 10. Open Column Leachate Analysis for Magnesium

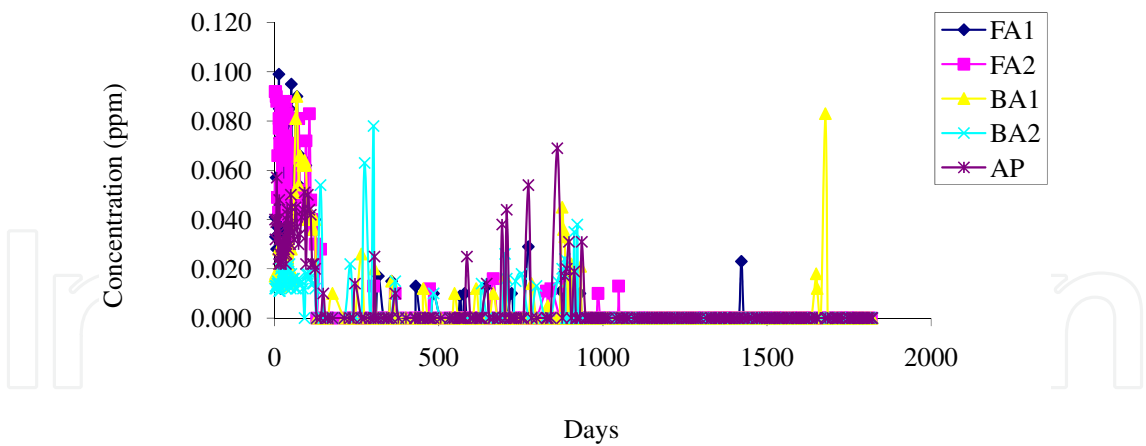


Figure 11. Open Column Leachate Analysis for Manganese

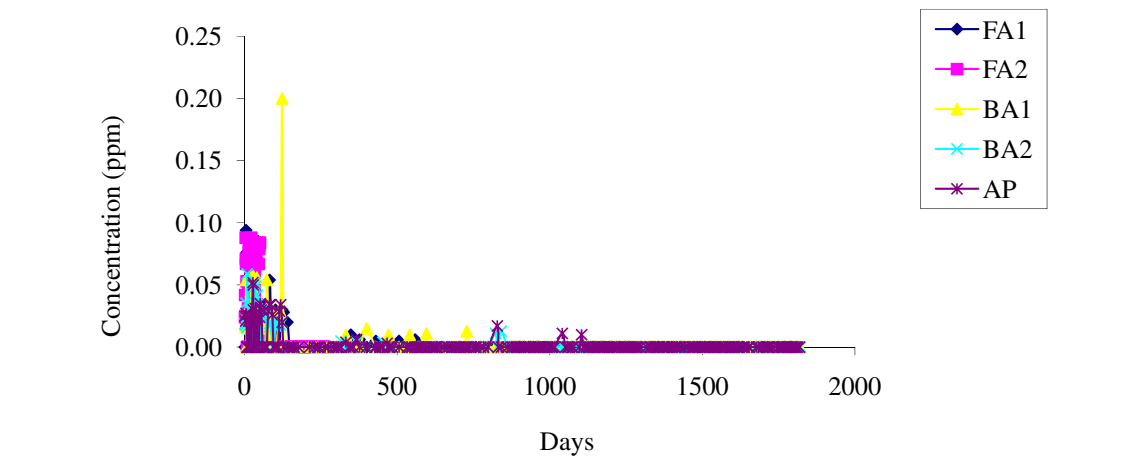


Figure 12. Open Column Leachate Analysis for Copper

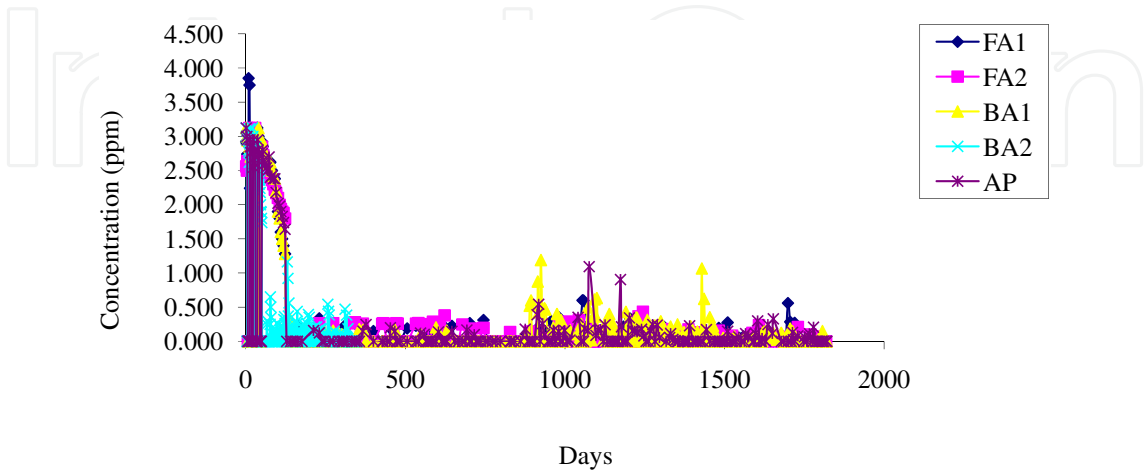


Figure 13. Open Column Leachate Analysis for Iron

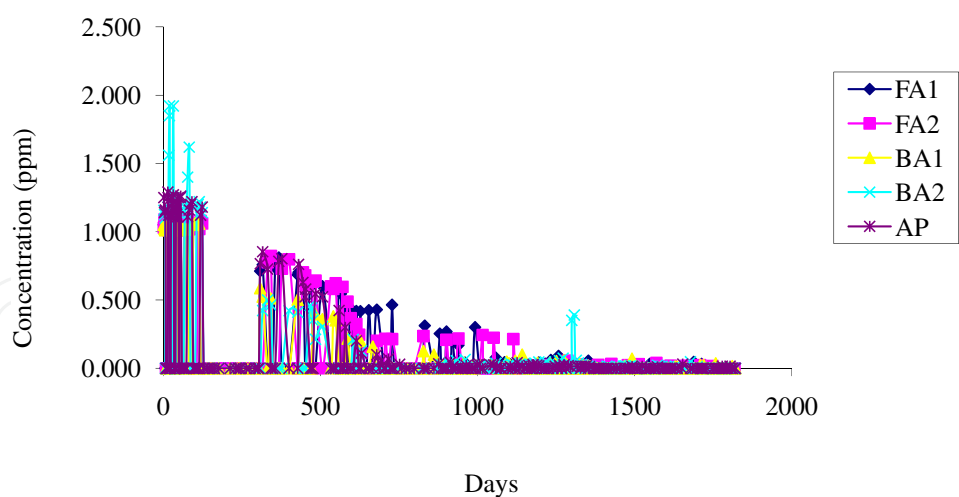


Figure 14. Open Column Leachate Analysis for Zinc

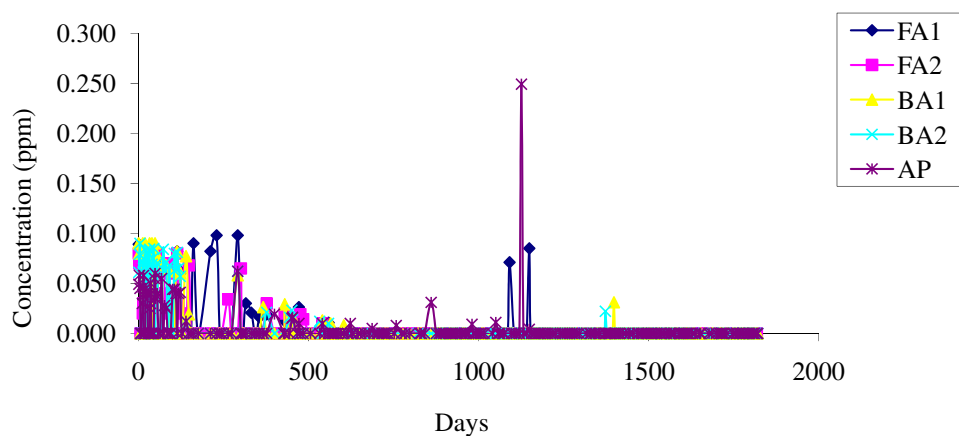


Figure 15. Open Column Leachate Analysis for Lead

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