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Heavy metals in fly ash and carbon dioxide sequestration by plants of ash ponds

Biswajit Mukhopadhyay and Tushar Kanti Mukherjee

Abstract
Fly ash is a by-product of coal dependent power generation plants which produces 71% of total electricity in India. It is estimated that 300 MT of fly ash will be generated by the end of 2017 (Maiti *et al.* 2016). The ash is disposed as ash ponds, landfills and slag heaps and is a serious environmental concern. The colour of fly ash depends upon the chemical and mineral constituents and may be dark gray to black due to high amount of unburned carbon.
Fly ash contains the more of the oxides of Si, Al, Fe, and Ca; it also contains lesser amount of of Mg, Na, K, Zn, and S, and several trace elements. The latter constitute the toxic metals with have hazardous impact on terrestrial and aquatic life including man from surface to ground level. The leachability of toxic elements depends upon several factors. The various leaching experiments and their analyses with results are discussed.
It is studied how the vast ash-sites could be rejuvenated for greenery; reduce environmental hazards and reclamation of the land for various agro-based farming. Comparative growth prolificacy of plants and reduction in time for reuse of lands are discussed.

Keywords: Fly ash, leaching experiments, toxic metals, reduction of environmental hazards by eco-conversion of ash ponds and landfills.

Introduction

India has 73 billion tons of coal reserve. A major chunk of this is burnt to generate electricity which account for more than 71% of total electricity of our country. Fly ash is a by-product of coal dependent power generation plants and many other factories which require coal fired boilers. Chatterjee (2010) [5] estimated the generation of fly ash may be 170 million tonnes in 2011-12. Maiti *et al.* (2016) [6] projected this value to be 300 MT by the end of 2017. The huge amount of the unused fly ash is disposed into holding ash ponds, landfills and slag heaps. Complete disposal and the recycling of fly ash are serious environments concern.
Fly ash is an alumino-silicate glass and constitutes 80-85% of the total ash produced. Its colour depends upon the chemical and mineral constituents. For example, high lime content makes it tan or light coloured while brownish color is due to the iron content. The ash becomes dark gray to black due to high percentage of unburned carbon.
The major amount of fly ash today is utilized in cement production. However, entire usage may account to 50% of the quantity generated. Modern researchers are developing technologies to enhance the quality and reactivity of fly ashes through mechano-chemical activation (Chatterjee, 2010) [5].
Fly ash consists of the oxides of Si, Al, Fe, and Ca, with minor amounts of Mg, Na, K, Zn, and S, plus various trace elements. The trace amounts of toxic metals in ash have negative effects on human health and on terrestrial, aquatic and even aerial life on earth. The toxic elements leached from fly ash can contaminate soil, ground water and surface water.
According to Mathur *et al.* (2003) [9], ash content of Indian coal ranges up to 45%. These are mostly dumped open as wet slurry causing leaching of heavy metals and contamination of soil, surface and underground water. There are a lot of references in this context (Sperenke *et al.*, 2000; Shi and Sengupta, 1995) [16, 14].

The leachability of metals depends upon age of fly ash, type of coal and design of thermal plants. In general, 8% of Ni and 17% of Cr leach out of ash (Singh *et al*., 2012) [15]. Depending on the type of coal, the major components of the different types of fly ashes are: the anthracite fly ash (very limited use in boilers), bituminous ash (silica, alumina, iron oxide, calcium, variable percentage of carbon), sub-bituminous ash and lignite ash (less silica and iron oxide, high amount of calcium and magnesium oxide). Class C fly ash has 30-40% calcium oxide and has higher amount of alkalis (sodium and potassium) and sulphates (SO_4); both the parameters are lower in Class F fly ash (1 – 12% of oxides and lesser amount of alkalis).

There were several attempts to use of ash ponds for agriculture, social forestry, natural vegetation thereby reuse of huge surface land area. Maiti *et al*. (2006) [7] observed that *Cynodon dactylon* is a prolific plant which covered the entire area within one year of dumping and also there is a natural succession of three more natural species within that period.

Land Requirement

(i) Ash Disposal Site

The ash content in Indian coals used in thermal power stations is 40% on average and this is 34% for washed coal. Fly ash constitutes about 80% of the total ash generated in a power plant. Thus about 2 million tonnes of ash is generated per annum for 1000 MW plant

In an ash handling plant, there are both bottom ash & fly ash collection and disposal systems. There are both dry and wet systems for the evacuation of fly ash. The bottom ash is disposed by wet method. Several systems work together during disposal of dry fly ash and they are: vacuum collection system, pressure conveying system, intermediate silo, main silo and compressor house. Therefore, there is need to construct dry ash pipelines or ash slurry pipe lines, compressor rooms, ash slurry pump house and silos. The systems that are required for the disposal of wet fly ash are: vacuum collection and subsequent wetting unit to convert ash into slurry to be discharged via the common ash slurry pit.

There are specified schedules determined by the Government of India for land requirement for ash handling and green belt development with regard to the capacity of power generation, boiler specification, nature of coat and its ash content.

According to the report by the Government of India (Ministry of Power, 2007) [12], a thermal plant of 3 x 660 MW requires 16 acres of land for disposal and handling of ash (average 40% ash content in Indian coals). The area will increase proportionately with the ash content in the coal and boiler technology but inversely proportional with the capacity of the plant. The bottom ash is discharged out in wet mode while fly ash requires both dry and wet systems. MOEF & CC in their notification dated 19th July, 1999 had specified that the fly ash utilization has to be 100% from 10th year of commissioning of the plant. As per the existing Fly ash notification, 2011, the fly ash has to be reused from the day of generation of power in maximum extent for construction purpose as an alternate material of earth and cement.

From the table-1, it is seen that the area requirement for ash handling system proportionately increases with the capacity of the plant and also with the ash content in the coal. Thus for a 2x500 MW station the area required is 6 acres whereas for the 6x660 MW station the same is 22 acres. However, while using coal with lesser ash content the land requirement gets reduced and is calculated as 14 and 21 acres for the 4x800 MW and 5x800 MW stations respectively using coal with 34% ash.

Table 1: Comparative land requirement for ash handling

Description	2 X 500 MW (40% ash)	3 X 660 MW (40% ash)	6 X 660 MW (40% ash)
Areas in acres required for ash handling	6	16	22

(ii) Landscaping & Green Belt

As per direction of Government of India, the landscaping and ground cover should be maintained to reduce the noise level, enhance soil nature, reduction in dust and air pollution and to produce an environment-friendly soothing nature of the plant. The plant cover, as stipulated by MOEF&CC, should stretch from the main gate to the service/administrative building and the total green area including landscaping area will be 1/3rd of the plant area. The area requires for installation of 3 X 660 MW TPP is 660 acres. Thus the green belt and landscaping area for 3X660 MW power plant should be 210 acres.

Selection of tree species and Carbon Sequestration

Central Pollution Control Board (CPCB) suggested Multi-Purpose Trees (MPTs) suitable for Re-vegetation of mine spoils and degraded habitats. These are mentioned in Table- 2.

Table 2: Selected species of trees suitable for fly ash ponds

Tree species suitable for Fly-Ash Area	
Acacia catechu	Khair
Acacia nilotica	Babul
Acacia tortilis	Israeli babul
Albizia lebbeck	Lebbeck
Albizia procera	Safedsiris
Azadirachta indica	Neem
Casuarinae quisetifolia	Horsetail
Dalbergia sissoo	Seesam
Dendrocalamus strictus	Baans
Dichrostachys cinerea	Sickle bush
Gmelina arborea	Gamhar
Holarrhena antidysenterica	Dysentery Rose Bay
Leucaena leucocephala	Subabul
Madhuca indica	Mahua
Prosopis cineraria	Khejri
Shorea robusta	Sal
Syzygium cumini	Jamun
Tamarindus indica	Imli
Tectona grandis	Teak
Terminalia arjuna	Arjun
Terminalia bellerica	Baheda
Zizyphus mauritiana	Jujube

For green belt development, in 2000 the CPCB, MOEF & CC advised the four species of plants most suitable in almost all the agro-climatic zones of India. The species are *Acacia Catechu* (Kher), *Acacia albida* (Winterthorn tree), *Azadirachta indica* (Neem) and *Dalbergia sissoo* (Sheesham).

Methodology

The modalities undertaken can broadly be divided into four sections, such as Acid digestion of ash, Leaching Experiments, Concentration of heavy metals in water samples and Pot Experiments (plant samples).

The Leaching Experiments includes the laboratory analysis of the concentration of heavy metals leached out from ash such as Batch Leaching Test, Toxicity Characteristics Leaching Procedure (TCLP) and Extraction Fluid for TCLP

For Landscaping & Green Belt, the plants species were selected based on the recommendations of MOEF & CC and

CPCB. Pot experiments of selected plants were performed to determine the germination and growth efficiency; finally the concentration of heavy metals absorbed by the plants was determined.

Experiments

A. Acid digestion of Ash (HNO_3 and HF)

Air dry sample 0.75 gm of ash was weighed into Teflon vessel, 5 ml of 70% conc. HNO_3 and 2 ml of HF were added to it. Teflon vessel were kept in an auto digester called Multi wave Microwave Digestion System (MDS) for 20 minutes attaining a temperature of 280 ^{0}C and pressure 35 bars for digestion. After digestion the sample was filtered and transferred to a 50 ml volumetric flask and the volume was made up to the mark by distilled water. Heavy metal analysis was carried out by following the standard methodology of AAS. The results were expressed as averages of triplicate analyses.

B. Leaching Experiments

(i) Batch Leaching Test

In order to better simulate the natural conditions and susceptibility to release, a lower liquid-to-solid (L/S) ratio was used in batch leaching tests. Therefore, 20 gm fly ash samples were mixed with 100 ml of deionised water, giving a liquid: solid ratio of 5:1. Triplicate extractions with the same weight of sample and same volume of extracting reagent were applied for one type of sample. A gentle stirring was continued during extraction (24 h) on a rotary shaker. Heavy metal analysis was carried out by following the standard methodology of AAS. The results were expressed as averages of triplicate analyses.

(ii) Toxicity Characteristics Leaching Procedure (TCLP)

TCLP requires the extraction fluid made of buffered acidic medium to perform the taste. It is 1 (M) Sodium acetate buffer which is pH is 4.99 as per United States Environmental Protection Agency (USEPA). 5 gm sample of ash was taken in extraction fluid of 20-times of 250 ml container i.e. 5 gm in 100 ml of liquid (1: 20). The extraction bottle was tightly closed and placed in rotary shakers for 18 hours, rotating at 30+/-2 rpm at ambient temperature of 25^{0}C. The triplicate extraction was performed using the same ratio of solid and extraction fluid. The heavy metals like Fe, Mn, Cu, Ni, Zn, Cd and Pb, were analysed by following the standard methodology of Atomic Absorption Spectrophotometry (AAS).

(iii) Extraction Fluid for TCLP

5.7 ml glacial CH_3CH_2OOH was added to 500 ml of distilled water and 64.3 ml of 1N NaOH. The volume was made up to the mark of 1 litre of the volumetric flask. The pH of the extraction fluid was 4.93 + 0.05.

C. Determination of heavy metals in water samples

In this part, the surface and ground water samples were tested for the heavy metals. Present investigation is based on observation on the revegetation of ash ponds in several sites. For the study of surface and ground water samples, 1 lit of sample was collected in 1 lit Teflon air tight bottle and 2 ml of 1:1 conc. $HNO_3$was added to it as preservative. Samples were analysed at the earliest and transport/stored in 4 ^{0}C. The sample is filtered by using Whatman – 42 filter paper. Heavy metals in filtrate (water sample) were analysed by following the standard methodology of AAS. The results were expressed as averages of triplicate analyses. The ash was subjected to following tests.

D. Determination of heavy metals in plant samples

0.50 gm of plant (leaf, stem, branches and roots) air oven dry at 90 ^{0}C was weighed into Teflon vessel, 5 ml of 70% conc. HNO_3 and 1.66 ml of $HClO_4$ were added to it. Teflon vessel were kept in an auto digester called Multi wave Microwave Digestion System (MDS) for 20 minutes attaining a temperature of 280 ^{0}C and pressure 35 bars for digestion. After digestion the sample was filtered and transferred to a 50 ml volumetric flask and the volume was made up to the mark by distilled water.

E. Carbon Sequestration

Average tree volume is based on median diameter class of respective species. For the purpose of calculation median diameter class or the girth size is taken 40-50 cm.

BEF (Biomass Expansion Factor) is the ratio of above ground oven dried biomass of a tree to oven dried biomass of its inventoried volume. Based on the default values mentioned in the report of Inter-governmental panel for Climate Change, 2006, BEF= (Crown Weight + Bole Weight) / Bole Weight

Wood density is taken from Global Wood Density database, (Zanne, *et al,* 2009) [19]. The standard average density of 0.6 gm per cubic cm is applied wherever the density value is not available for tree species (Pandya, *et al,* 2013) [11].

Carbon Factor is arrived at by dividing molecular weight of CO_2 (44 gm/mol) by atomic weight of carbon (12 gm/mol)

Carbon Sequestration Formula = Volume X Wood Density X BEF x CF x 1.45

GHG Emission factor of wood

During burning a tree will produce the amount of carbon it sequestered during its life. The formulae used to calculate this carbon is based on following parameters.

For trees with D < 11:

$W = 0.25*D^2 * H$…………………… (2)

For trees with D >= 11:

$W = 0.15* D^2 * H$ …………………. (3)

Where,

W = Above-ground weight of the tree in pounds

D = Diameter of the trunk in inches

H = Height of the tree in feet

Based on tree species, equations (2) and (3) can be used to calculate the weight of a tree. These two equations could be seen as an “average” of all the species’ equations. The root system weighs about 20% as much as the above-ground weight of the tree. Therefore, to determine the total green weight of the tree, multiply the above-ground weight of the tree by 120%.

An average tree is 72.5% dry matter and 27.5% moisture. Therefore, to determine the dry weight of the tree, multiply the weight of the tree by 72.5%. The average carbon content is generally 50% of the tree’s total volume. Therefore, to determine the weight of carbon in the tree, multiply the dry weight of the tree by 50%.

Determine the weight of carbon dioxide sequestered in the tree

CO_2 is composed of one molecule of Carbon and 2 molecules of Oxygen.

The atomic weight of Carbon is 12.001115.

The atomic weight of Oxygen is 15.9994.

The weight of CO_2 is C+2*O=43.999915.

The ratio of CO_2 to C is 43.999915/12.001115=3.6663.

Therefore, to determine the weight of carbon dioxide sequestered in the tree, multiply the weight of carbon in the tree by 3.6663.

F. Phytoremediation
A cover by plantation is a remedial technique utilized on FA landfills for soil stabilization and for the physical and chemical immobilization of contaminants (Bilski *et al*. 1995) [2]. Many herbaceous plants, primarily grasses, which exhibit rapid growth, are moderately resistant to environmental stress, and are therefore often used as cover crops in environmental restoration and remediation projects. It include at least some of bioethanol producing plants, such as corn, reed canary grass, cord grass, sorghum, switchgrass into FA phytoremediation project. Studies on the effects of coal fly ash on growth and mineral nutrition of various plants have shown the potential benefit of different soil-FA mixtures on plant germination rates and productivity (Kraft 2012).

G. Pot experiments
Selected plants were cultured on ash soil-mixture. The growth efficiency and the concentration of heavy metals absorbed by the plants were analyzed. The three types of plants used are very common and naturally growing in any hard environment, particularly in soils with less water. They are found to the founder plant species in an un-utilized field. Given some years to develop, they modify the soil that would facilitate other plant species to grown in those barren lands. The experiments were done on the two aspects such as,
(i) Germination and growth efficiency
(ii) Extraction of heavy metals from plants

Analysis & Findings

Table 3: Heavy metal concentrations in ash by acid digestion (n=3).

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Fe	6525	6750	6875	8540	7260	7315
Mn	210	235	265	425	260	275
Ni	52	58	62	68	48	52
Cu	38	41	42	50	38	40
Zn	110	140	135	185	95	130
Cd	BDL	4.5	BDL	5	BDL	5.2
Pb	17	BDL	12.5	13.5	6.4	5.5

FA-Fly Ash; BA-Bottom Ash and PA- Pond Ash; Concentration of metal in Ash mg/kg (BDL: Below Detection Limit, BDL-Pb: 2.8 mg/kg and BDL-Cd: 0.75 mg/kg)

Table 4: Heavy metal concentrations in leachate of batch leach test (n=3).

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Fe	4.8	5.6	6.2	7.25	4.9	4.95
Mn	1.62	1.45	1.69	1.78	1.10	1.24
Ni	0.08	0.06	0.02	0.05	0.04	0.09
Cu	BDL	0.15	BDL	0.28	0.12	0.15
Zn	1.23	0.95	1.28	1.10	1.35	1.48
Cd	BDL	BDL	BDL	BDL	BDL	BDL
Pb	BDL	BDL	BDL	BDL	BDL	BDL

FA-Fly Ash; BA-Bottom Ash and PA- Pond Ash; Concentration of metal in leachate mg/lit. (BDL: Below Detection Limit, BDL-Cu: 0.005 mg/lit; BDL-Pb: 0.045 mg/lit and BDL-Cd: 0.007mg/lit).

Table 5: Heavy metal concentrations in the extract of TCLP test (n=3).

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Fe	5.3	6.1	6.8	8.8	6.9	5.95
Mn	1.82	1.95	1.52	2.01	1.45	1.54
Ni	0.10	0.08	0.04	0.07	0.06	0.08
Cu	0.01	0.15	0.08	0.38	0.17	0.15
Zn	2.33	1.05	1.62	1.98	1.50	1.69
Cd	BDL	BDL	BDL	BDL	BDL	BDL
Pb	BDL	BDL	BDL	0.06	BDL	BDL

FA-Fly Ash; BA-Bottom Ash and PA- Pond Ash; Concentration of metal in extract of TCLPis mg/lit. (BDL: Below Detection Limit, BDL-Cu: 0.005 mg/lit; BDL-Pb: 0.045 mg/lit and BDL-Cd: 0.007mg/lit).

Table 6: Heavy metal concentrations in water samples (n=3).

Element	SW-1	SW-2	SW-3	GW-1	GW-2	GW-3
Fe	0.075	3.55	2.28	1.62	0.95	0.98
Mn	0.01	1.10	0.75	0.02	BDL	0.015
Ni	BDL	0.09	0.06	BDL	BDL	BDL
Cu	0.025	0.45	0.08	BDL	0.008	0.007
Zn	0.06	0.98	1.26	0.32	0.09	0.10
Cd	BDL	BDL	BDL	BDL	BDL	BDL
Pb	BDL	0.06	BDL	BDL	BDL	BDL

SW – Surface Water, GW – Ground Water; Concentration of metal in water samples is mg/lit. (BDL: Below Detection Limit, BDL-Mn: 0.008 mg/lit; BDL-Ni: 0.01; BDL-Cu: 0.005 mg/lit; BDL-Pb: 0.045 mg/lit and BDL-Cd: 0.007mg/lit).

Graphical representation of various metals in water samples
[Acid digestion (A), Leachate Extract in water (L), TCLP Extract (T), Concentration in Water Sample (W)]

(a) Available iron content by acid digestion, Leachate Extract in water, TCLP Extract, Concentration in Water Sample (Fig. 1)

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Fe(A)-gm/Kg	6.525	6.75	6.875	8.54	7.26	7.315
Fe (L)-mg/Kg	24	28	31	36.25	24.5	24.75
Fe (T)-mg/Kg	26.5	30.5	34	44	34.5	29.75
Fe (W)-mg/L	0.075	3.55	2.28	1.62	0.95	0.98

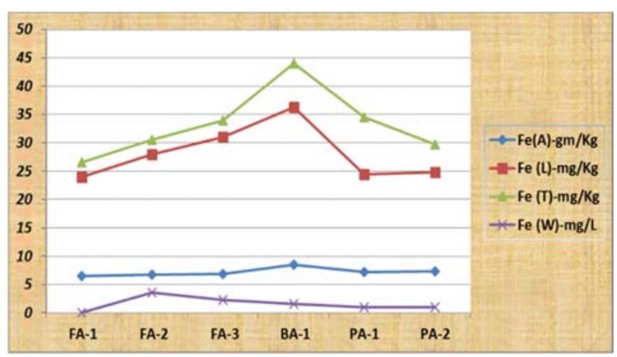

Fig 1

(b) Available nickel content by acid digestion, Leachate Extract in water, TCLP Extract, Concentration in Water Sample

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Ni (A)-gm/Kg	0.052	0.058	0.062	0.068	0.048	0.052
Ni (L)-mg/Kg	0.4	0.3	0.1	0.25	0.2	0.45
Ni (T)-mg/Kg	0.5	0.4	0.2	0.35	0.3	0.4
Ni(W)-mg/L	BDL	0.09	0.06	BDL	BDL	BDL

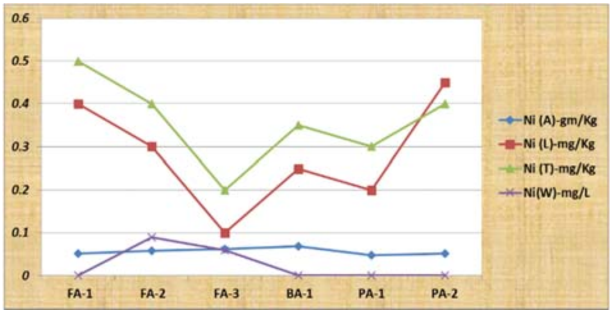

Fig2

(c) Available manganese content by acid digestion, Leachate Extract in water, TCLP Extract, Concentration in Water Sample

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Mn (A)-gm/Kg	0.21	0.235	0.265	0.425	0.26	0.275
Mn (L)-mg/Kg	8.1	7.25	8.45	8.9	5.5	6.2
Mn (T)-mg/Kg	9.1	9.75	7.6	10.05	7.25	7.7
Mn (W)-mg/L	0.01	1.1	0.75	0.02	BDL	0.015

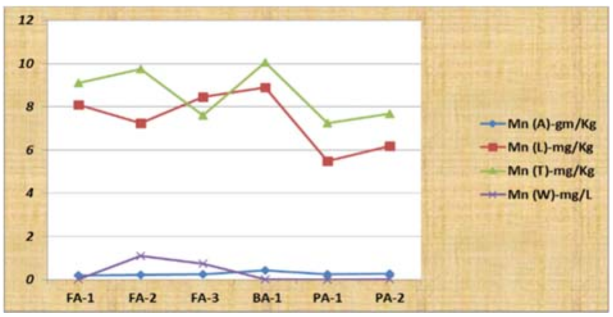

Fig 3

(d) Available copper content by acid digestion, Leachate Extract in water, TCLP Extract, Concentration in Water Sample

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Cu (A)-gm/Kg	0.038	0.041	0.042	0.05	0.038	0.04
Cu (L)-mg/Kg	BDL	0.75	BDL	1.4	0.6	0.75
Cu (T)-mg/Kg	0.05	0.75	0.4	1.9	0.85	0.75
Cu (W)-mg/L	0.025	0.45	0.08	BDL	0.008	0.007

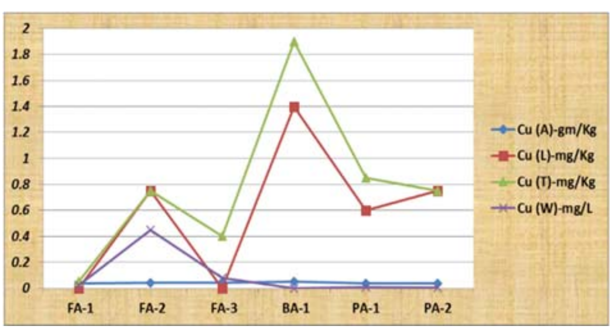

Fig4

(e) Available zinc content by acid digestion, Leachate Extract in water, TCLP Extract, Concentration in Water Sample

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Zn (A)-gm/Kg	0.11	0.14	0.135	0.185	0.095	0.13
Zn (L)-mg/Kg	6.15	4.75	6.4	5.5	6.75	7.4
Zn (T)-mg/Kg	11.65	5.25	8.1	9.9	7.5	8.45
Zn (W)-mg/L	0.06	0.98	1.26	0.32	0.09	0.1

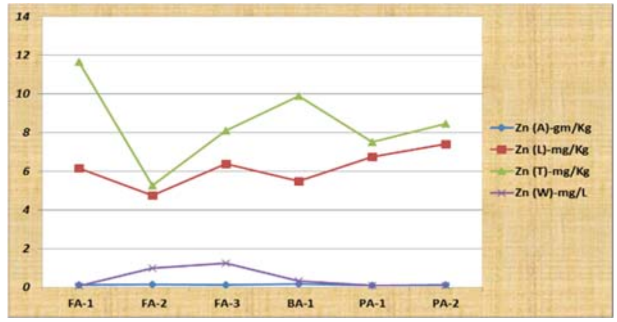

Fig 5

(f) Cadmium content

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Cd(A)-gm/Kg	BDL	0.0045	BDL	0.005	BDL	0.0052
Cd (L)-mg/Kg	BDL	BDL	BDL	BDL	BDL	BDL
Cd (T)-mg/Kg	BDL	BDL	BDL	BDL	BDL	BDL
Cd(W)-mg/L	BDL	BDL	BDL	BDL	BDL	BDL

(g) Lead content

Element	FA-1	FA-2	FA-3	BA-1	PA-1	PA-2
Pb (A)-gm/Kg	0.017	BDL	0.0125	0.0135	0.0064	0.0055
Pb (L)-mg/Kg	BDL	BDL	BDL	BDL	BDL	BDL
Pb (T)-mg/Kg	BDL	BDL	BDL	0.3	BDL	BDL
Pb(W)-mg/L	BDL	0.06	BDL	BDL	BDL	BDL

Pot Experiments
Three species of plants were used and their characteristics are stated.

Leucaena leucocephala: it is a very useful tree or shrub, commonly called Kubabul (or subabul) is long-lived, devoid of thorns, with a maximum height of 10 meters and variously used for nutritious forage tree, firewood, timber, green manure, shade and erosion control.

Cymbopogon flexuosus: (Citronella): it is also known as lemon grass, Cochin grass or Malabar grass and may grow up to 2 meters. Lemongrass is also used in Asian cuisine. The oil is used in perfumery, cosmetic, incense, and insect repellent. It has anti-fungal property.

Cynodon dactylon: (durba grass): it is also known as devil's grass, *Vilfa stellata, Dhoob* and others. It is usually 4 inches in height, green, narrow and long leaves. Most important is that the root penetrates up to 2 meters below soil, can withstand dryness of soil, fast growing, quick recovery and desired turf grass and highly aggressive (hence called devil's grass).

Preparation of pots
Fresh fly ash normally does support natural vegetation (Bisht, *et al*. 2011) [4]. It requires several months to years of processing through natural factors such as sunlight, rain and natural addition of soil particles and dust. Each plastic pot of about 2 liter volume was used and set in open air of the garden for experiments. The pots were divided into two groups to study the germination efficiency. Batch -O (only fly ash) and Batch- S (fly ash with 1 inch top layer of garden soil).

The plants were uprooted after 30 days, washed by clean water and entire portion (root, leaves and shoot) was taken for total metal content. The samples were oven-dried at 90^o C for 10 hours, grinded to powder. Acid digestion was done in Microwave. 0.5 gm powdered plant sample (leaf, stem, branches and roots) was weighed into Teflon vessel, 5 ml of 70% conc. HNO_3 and 1.66 ml of $HClO_4$.AAS was used to find out the concentration of Fe, Mn, Ni, Cu, Zn, Cd, Pb accumulated by plants. Heavy metal analysis was carried out by following the standard methodology of AAS. The results were expressed as averages of triplicate analyses.

Germination and growth efficiency

On an average, the germination and growth rate of plants was half of that taken to grown in Batch –O.

Batch –O

Plant	Germination (average of days)	Average Length after 10 days	Average Length after 30 days
Leucaena leucocephala	21	0.02	0.2
Cymbopogon flexuosus	10	0.3	1.5
Cynodon dactylon	8	0.3	3.2

Batch –S

Plant	Germination (average of days)	Average Length (cm) after 10 days	Average Length (cm) after 30 days
Leucaena leucocephala	14	0.07	2.2
Cymbopogon flexuosus	6	0.8	5.5
Cynodon dactylon	4	0.7	6.2

Extraction of heavy metals from plants

The concentration of metals in plants served to indicate the metal content status and also the abilities of various plant species to take up and accumulate the metals from the fly ash.

Table 7: Metal concentration in plants

Element	*Leucaena leucocephala*	*Cymbopogon flexuosus*	*Cynodon dactylon*
Fe (gm/Kg)	0.715	0.814	1.203
Mn (mg/Kg)	4.85	11.6	25
Ni (mg/Kg)	5.4	22	10.5
Cu (mg/Kg)	3.4	14.5	16.5
Zn (mg/Kg)	13.2	28	36
Cd (mg/Kg)	BDL	1.8	1.56
Pb (mg/Kg)	BDL	20	9

(BDL: Below Detection Limit, BDL-Pb: 2.8 mg/kg and BDL-Cd: 0.75 mg/kg)

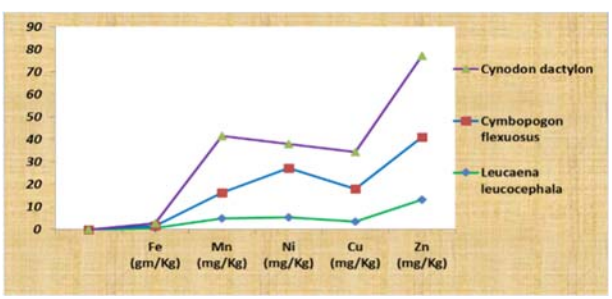

Fig 6

Phytoremediation and Block Plantation on Ash Pod

Sharma *et al*., 2014 mentioned several mechanisms by which plants can effect on the volume, mobility, or toxicity of contaminants. These are: Phytoextraction (uptake of metal contaminants in the soil by plant roots into the above ground portions of the plants, used for contaminated soils); Rhizofiltration (absorption of contaminants surrounding the root zone, mainly used for removal of metals or other inorganic compounds in ground, surface or waste water); Phytovolatilization (removal of contaminants from the soil, transforming them into volatile forms and transpiring them into the atmosphere, mainly used to remove mercury); Phytostabilization (to immobilize contaminants in the soil and ground water through absorption and accumulation by roots); Phytodegradation (degradation of complex organic contaminant molecules to simple molecules) and Rhizodegradation (breakdown of contaminants within the plant root zone, or rhizosphere by microorganisms). Miller (1996) [8] suggested only two steps for soil remediation which are phytoextraction and phytostabilization.

Maiti *et al*., 2016, observed 15 species have naturally occupied the fly ash dump sites of thermal plants in U.P. and M.P.*Ipomoea carnea*, *Lantana camara*, and *Solanum surattense* were found to grow quite naturally in the fly ash disposal site of Patratu thermal power station, Jharkhand, India (Pandey *et al*., 2016) [10] and only *Ipomoea carnea* is common in above sites. *Solanum surattense* is best among the above three plant species as phytostabilizer. Experimental evidences suggest *Ipomoea carnea* and *Lantana camara* are better as phytoextractor of metal from fly ash and thereby help in soil reclamation.

Agarwal1, *et al*., 2011 found 18 plant species are naturally grown in Feroze Gandhi Unchahar Thermal Power Plant. However, ten species were found to be best tolerant to exclusively on flyash. These were *Acacia nilotica*, *Bauhinia variegata*, *Cassia siamea*, *Dalbergia sissoo*, *Delonix regia*, *Leucaena leucocephala*, *Morus alba*, *Pithecellobium dulce*, *Prosopis juliflora* and *Terminalia arjuna*. These trees are highly important for high biomass production (and hence carbon sequestration capacity), deep root system, high growth rate in nutrient deficient soil and metal extraction.

The natural growth of some types of grasses on fly ash sites is an indication of possibilities to try plantation of cereal crops on fly ash. Bilski, 2015 found that the cereal crops grown on fly ash-soil medium can accumulate elevated amounts of Fe, Zn and Se and this has two-fold benefit of phytoremediation and biofortification of crops.

Carbon Sequestration

Pandya *et al*., 2013 estimated the carbon storage in 25 species belongs to Gujarat, India from the data of tree's girth and height. The maximum carbon storage in 55.95 tC followed by 44.81 tC in is concluded. The lowest carbon storage value estimated in 1.77tC.

Suryawanshi *et al*., 2014 worked similarly on 10 trees species of North Maharashtra University Jalgaon campus. *Moringa oleifera* species was found to be dominant sequestrated 15.775 tons of carbon and having 14 trees followed by *Azadirachta indica* 12.272 tones. The species *Eucalyptus citriodora* has lowest carbon sequestration potential i.e. 1.814 tones.

In the year 2000, CPCB, MoEF published the guidelines for the development of green corridor. The report suggested the following four species of plants as most suitable for Fly ash dump areas in almost all the agro climatic zones of India. However, the list of species is variable and depends upon agro climatic zones based on the parameters defined in CPCB.

1- Plant species name,
2- Avg. vol. of mature tree (m^3)
3- Avg. wood density – total Dry Matter per m^3
4- Biomass Expansion Factor (Std) - gm/ m^3
5- Carbon Factor
6- Average Carbon Sequestration per tree (Tons)
7- Carbon Sequestration For 1000 trees (Tons)
8- Carbon Sequestration Per Hectare (Kilo Tons of Carbon)

Table 8: The Carbon Sequestration per hectare in respect of other factors

1	2	3	4	5	6	7	8	
							5 X 5 spacing (m)	5 X 3 spacing (m)
Acacia Catechu (Kher)	1.414	0.88	3.4	3.6	22.08	22084	8.83	14.72
Acacia Albida (Winter thorn tree)	1.4	0.6	3.4	3.6	14.9	14908	5.96	9.93
Azadirachta Indica (Neem)	0.91	0.69	3.4	3.6	11.14	11144	4.45	7.42
Dalbergia Sissoo (Sheesham)	1.392	0.6	3.4	3.6	14.82	14823	5.92	9.88

Conclusion

There are a lot of information on the characterization of fly ash, its leaching properties, accumulation of heavy metals in soil and soil remediation. Moreover, we know a lot on the effective utilization of selected plants species for phytoremediation of contaminated soil and fly ash disposal sites.

While working on phytoremediation of ash disposal sites, following lacunae should be addressed to. These are:

(i) Crops and vegetable grown on such soil should not be consumed unless enough time has elapsed (10-15 years post phytoremediation) to get rid of hazardous elements. The soil should be tested prior to such agricultural practice. Local awareness and government regulation be strictly followed to avoid farming in such sites. The time should be given for natural breakdown of toxic metals by oxidation.

(ii) Since we have lot of information on suitable trees for fly ash disposal sites, we can plant them on such soil. However, a six inch layering of natural soil fortified by a natural rain during first year is advisable.

(iii) Wood producing trees are all time valuable. Therefore more attention to the wood producing forestry should be given. The side advantage is that the toxic metals will be transpired into wood and not contaminate the soil again. Such wood can be used for furniture, in factories and many types of constructive programmes.

(iv) The fly ash site should be properly sealed for domestic grazers (cow, goat etc.) to avoid toxic contamination.

(v) As in forestry, some years are given to wood plants for substantial growth before felling, we have to provide remedial period for the ash dump site for the proper generation of top soil and soil reclamation.

(vi) Various grass species are the forerunner of all plants to establish themselves in most harsh type of soil. Even in one year they can cover the entire fly ash site. They are grown naturally and are best friends for top soil generation. They act as metal excluder and no amendments are required. After few years, such plants which have imbibed toxic metals will be burnt on the same soil to provide further nourishment to the soil and breakdown of toxic elements.

There is lack of awareness, mismanagement and regulation regarding the proper utilization of fly ash dumping sites. We should be concerned with the generation of lost top soil, reduce environmental pollution, phytoremediation and generation of plant biomass for carbon sequestration to sustain quality life.

Fly ash is not a problem now a day. The major use of fly ash is in construction purposes (brick and cement factory). It can be used for the filling of low lying areas for the construction of roads, factories and such things. Moderate amount of fly ash mixed in clay soil gives better performance by plants. Alkaline fly ash can be mixed with acidic soils and thus degraded soil can be enriched for potential agriculture.

The dumping sites can be better used for wood and plywood producing trees, pulp producing trees, for fire wood trees and importantly for biodiesel plant species. These may contain some toxic element to some extent but will not cause any damage to life on earth.

As per Report by Nath (2007) [12] on the land requirement of thermal power stations, the area requires for installation of 3 X 660 MW TPP is 660 acres or 267 hectare. Accordingly the green belt and landscaping area for 3 X 660 MW power plant should be 210 acres or 85 hectare. The carbon sequestration per hectare (kilo tons of carbon) varies with species of plants and spacing ratio (vide Table- 8). Considering a spacing of 5*5, we find carbon sequestration per hectare (kilo tons of carbon) are 8.83, 5.96, 4.45, 5.92 for the species *Acacia catechu*, *Acacia albida*, *Azadirachta indica* and *Dalbergia sisso* respectively. The highest sequestration (8.83 kilo tons)is done by *Acacia catechu*. Therefore using this species alone our benefit for 85 hectare becomes 750.55 kilo tons of carbon.

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