An Appraisal of Coal Fly Ash Soil Amendment Technology (FASAT) of Central Institute of Mining and Fuel Research (CIMFR)

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Abstract**—**Coal will continue to be the predominant source of global energy for coming several decades. The huge generation of fly ash (FA) from combustion of coal in thermal power plants (TPPs) is apprehended to pose the concerns of its disposal and utilization. FA application based on its typical characteristics as soil ameliorant for agriculture and forestry is the potential area, and hence the global attempt. The inferences drawn suffer from the variations of ash characteristics, soil types, and agro-climatic conditions; thereby correlating the effects of ash between various plant species and soil types is difficult. Indian FAs have low bulk density, high water holding capacity and porosity, rich silt-sized particles, alkaline nature, negligible solubility, and reasonable plant nutrients. Findings of the demonstrations trials for more than two decades from lab/pot to field scale long-term experiments are developed as FA soil amendment technology (FASAT) by Central Institute of Mining and Fuel Research (CIMFR), Dhanbad. Performance of different crops and plant species in cultivable and problematic soils, are encouraging, eco-friendly, and being adopted by the farmers. FA application includes ash alone and in combination with inorganic/organic amendments; combination treatments including bio-solids perform better than FA alone. Optimum dose being up to 100 t/ha for cultivable land and up to/ or above 200 t/ha of FA for waste/degraded land/mine refuse, depending on the characteristics of ash and soil. The elemental toxicity in Indian FA is usually not of much concern owing to alkaline ashes, oxide forms of elements, and elemental concentration within the threshold limits for soil application. Combating toxicity, if any, is possible through combination treatments with organic materials and phyto-remediation. Government initiatives through extension programme involving farmers and ash generating organizations need to be accelerated

Keywords**—**Fly ash, soil quality, CIMFR, FASAT, agriculture, forestry, toxicity, remediation

I. INTRODUCTION

COAL is the predominant source of global energy; it contributes to about 38% of the total energy production. In India about 70% of the total energy requirement is met from the combustion of pulverized coal in thermal power plants (TPPs). This practice will continue for a long time into the future in view of the enormous coal reserves in the India, estimated to be 287.0 × 10^9t [1]. The combustion of coal to generate electricity in TPPs produces solid wastes like fly ash (FA) and bottom ash (BA). China, India, United States, South Africa, Australia, Greece, and Japan are the countries having higher rate of FA production [2]. Present generation of FA from coal combustion in TPPs in India is 160 MT/year and it is expected to increase to 300 MT/year by 2016-17. The use of high-ash coal with a low calorific value after the fast depletion of better quality coal, is another concern; the content of mineral elements in the ash become manifold than present in coal. Several anthropogenic activities, including coal mining have turned millions of hectares of land to wasteland. Opencast coal mining produces undesirable dumps and tailing dams, besides damaging microbial communities and nutritional status of the mined area. Thousands of hectares of land in India have been converted to ash ponds; many of them have become abandoned. Per capita availability of the forest land is 0.08ha against the world average 0.64 ha [3]. Of the total land area (328 Mha) in India, ca. 143 Mha are cultivable and about 130 Mha are unproductive including 33 Mha with potential for reclamation (http://www.bangalorebio.com), which is imperative for fast growing population (1.17 billion) [4]. Thus the reclamation of waste/degraded and non-fertile lands to make them fertile and agriculture-forest worthy is the other current point of focus.

Numerous studies point to the wider potential of coal combustion residues to increase productivity and amend problematic soils (wastelands, low-lying areas, dumping sites, surface mine soils) [5,6,7,8]. FA contains almost all the plant nutrients except N and humus, which can be supplemented by organic matter. Although management of coal ash through vegetation is one of the best alternatives for its bulk use for reclamation of problematic soils and mine spoils, it is not free from certain limitations of soluble salts, trace elements, and radionuclides for soil and plant growth [9, 6, 2].

In India for about one and half decades, much work has been undertaken on the utilization of FA in different areas including agriculture and forestry. At present FA utilization has reached to the level of 46%, but still far below the utilization level achieved by some countries abroad. The policy guidelines in India restrict the use of topsoil for building materials and encourage the use of at least 25% ash in clay bricks manufactured within a radius of 100 km from coal and lignite based TPPs [2]. There is a directive to use 100% FA in the near future. The application of FA in agriculture and forestry as soil ameliorant is significant from

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the point of view of its disposal and gainful utilization. The Central Institute of Mining and Fuel Research (CIMFR), Dhanbad (erstwhile Central Fuel Research Institute), being associated with the research and development work on coal conversion processes and associated environmental concerns, has carried out demonstration trials from laboratory/pot scale to field scale for more than past two decades. Present paper is an appraisal of such studies.

II. FA GENERATION, CLASSIFICATION, AND CHARACTERISTICS

Fly ash, a residue of combustion of coal, consists of a wide range of inorganic matter. FA and BA are the two types of the ashes generated in TPPs. The FA (contributes to 80% of total ash in a TPP), being the lighter fraction, is carried away by flue gases up into the chimney and collected by electrostatic precipitators. Emission of the remaining FA into the atmosphere is controlled by scrubbers and mechanical precipitators. Although these devices have high efficiency rates (near 99.95%), considerable amounts of FA can be emitted into the environment because the TPPs consume vast quantities of coal. The emissions are even greater if the ash content of the coal is high. The FA fraction is chemically reactive and finer in texture (0.01–100 μm) than the BA fraction. BA (constituting 20% of the total ash produced in a station) is the heavy, coarse fraction (>100 μ m) that falls through the air flow to the bottom of the furnace. It consists of coarse-grained clinkers that are spherical and cenospherical. A mixture of both FA and BA, commonly referred to as PA, is disposed of as slurry through a pipeline to ash ponds. It is also collected dry. In India many of the TPPs do not have automated dry ash collection. FAs are classified as class C (high CaO content, as found in sub-bituminous coal or lignite) or class F (low CaO content, as found in bituminous coal), however, exceptionally some low-rank coal FAs can also meet the class F requirements [10]. According to ASTM standards [11], bituminous and sub-bituminous coal in India produces class F ash, and lignite produces class C ash with a high degree of self-hardening capacity (www.flyashindia.com). Utilization oriented classifications based on Si, Fe, Ca, and Mg oxides content, and reactive water-soluble and amorphous phases in FA has also been made [12]. A new approach (based on the origin, phase-mineral and chemical composition, and properties and behavior of FA) has been presented [13]. The characteristics of FA have been comprehensively reviewed earlier [14, 15].The physico-chemical properties of FA, including the mineralogical, morphological and radioactive, in general vary with coal source and quality, combustion process, extent of weathering, particle size, and age of the ash [2]. Coal FA is a heterogeneous material between and within the particles; it has varying particle size, moisture retention, and electrical conductivity (EC); low to intermediate bulk density (BD), nonmagnetic and magnetic components, high water-holding capacity (WHC) and low cation exchange capacity (CEC) than normal soil [16, 17, 18]. The pH of FA varies from 4.5 to 12.0, but the majority of the worldwide FAs, including India, are alkaline [2]. The phase and mineral composition of FA includes inorganic, organic, and fluid constituents with non-crystalline, crystalline, liquid, gas, and gas-liquid inclusions [13]. Chemically, 90–99% of the FAs consist of Si, Al, Fe, Ca, Mg, Na, and K, with predominance of Si, Al, Fe, Ca, and minor content of Mg, Ti, and K compounds [19]. Besides, major/micro- nutrients (like P, B, Cu, Zn, and Mn), trace elements (like Cd, As, Se, Pb, Ni, Cu, Cr, Co, Mo, Be, etc.), and radionuclides (from U and Th series, as well as 40K), have been reported [20, 21]. The concerns of trace elements and radionuclides present in FA are crucial during agriculture and forestry application. The application of FA in agriculture and forestry because of its favorable physico-chemical properties, including appreciable content of essential plant nutrients, has been advocated for three decades [14]. FA with predominantly amorphous aluminosilicate glassy spheres is comparable to soil particles [22]; it is non-expanding and works well as an amendment for clay soil [23] The Ca-rich, alkaline type of FA has proven to be useful in agriculture for neutralizing acidic soils [24, 25, 26], and for facilitating re-vegetation of soils polluted with heavy metals [27]. A recent review on FA application to soil system has been made [28].

III. CIMFR STUDY

The application of fly ash in reclamation of cultivable and wasteland including mine spoil has been recently reviewed [2]. The distribution profile of coal ash based on particle size and magnetic/nonmagnetic components together with wide variation in the particle size distribution and BD, higher WHC, low CEC, and alkaline pH of Indian FAs from different TPPs have been discussed. Fresh and weathered lignite FAs have the predominance of <0.002 mm size particles and rich presence of available major/secondary nutrients, whereas weathered FA has more OC content than fresh FA. Indian ashes have major content of SiO_2, considerable amounts of oxides of Ca, Mg, K, P, and S; micronutrients (Cu, Zn, Mn, Fe, etc.), a low content of N (especially in PA), and absence of humus. These characteristics of Indian FAs suggest the potential of FA as soil ameliorant and in improving the fertility status and growth of various crops and plant species.

A. Soil characteristics

The influence of FA on physical characteristics of soil is primarily attributable to the changes in the texture of soil. The hollow spheres of FA replace bigger soil particles and make it possible for small silt sized particles to accumulate in voids, which modifies the texture and pore structure of the soil [29]. The application of FA comprising mostly silt-sized particles with low BD to sandy soils would permanently change the soil texture, enhance micro-porosity, and improve the water-retention capacity. The vast majority of FAs in Australia and India belong to class F and are produced from burning anthracite, bituminous coal or sub-bituminous coal and have less than 10% CaO, whereas FAs from lignite belong to class C and have up to 15% CaO [6, 30]. Indian FAs may contain sizeable amounts of silicate minerals such as mullite [31, 32, 33], which in principle can take up H+, leading to neutralization through formation of silicic acid. FA addition generally improves soil porosity, workability, and WHC due to decrease in soil BD. Liming during the application of coal and lignite FAs, in combination with other amendments like farm yard manure (FYM), etc. at different doses has enhanced the pH of a variety of acidic soils [34, 35, 36, 37, 38, 29]. Indian FAs are mostly alakaline owing to the low sulphur (except North Eastern and tertiary coals) and appreciable contents of oxides of Ca, Mg, etc in Indian coals. An increase in the pH of mine spoil after lignite FA amendments during field study has been reported [6].

Improvement in the physico-chemical properties of agricultural and problematic soils after amendment with FA alone and in combination with inorganic and organic amendments (like gypsum, FYM, bio-fertilizer, press mud, and humic acid) has been observed [39, 40, 41, 42, 34, 35, 36, 37, 38, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 6, 30, 29, 7, 53, 54, 55, 56, 57, 58, 2, 59] . The demonstration trials including the field scale for 4-5 years have shown better residual effect with negligible adverse effect on the quality of soil. While studying P adsorption, fixation and fractions in fluidized bed combustion (FBC)-FA and FBC-FA-amended acidic soil, FA and acidic soils were found to have high P-fixation capacities and mixing of the two was suggested to resolve the P-fixation problem to a great extent [60]. The physico-chemical properties (range values) of Indian FAs and soils, including the contents of minerals, major secondary and micronutrients, trace and heavy metals, and radionuclides, are shown in Table-1. The study on the effect of FA on soil microbiology is not as extensive as on soil physicochemical characteristics. The microorganisms influence soil fertility and primary production by depositing organic matter and cycling the nutrients. Enzyme activity, respiration, and microbial biomass are the indicators of overall microbial activity in soil. FA improves the biological activity of soil via improvement in the physico-chemical properties of soils, where textural improvement of the soil is crucial [42, 47, 6, 30, 7, 2]. In a number of field investigations, enhancement in the biological

TABLE I

THE PHYSICO-CHEMICAL PROPERTIES (RANGE VALUES) OF INDIAN FAS AND SOILS, INCLUDING THE CONTENTS OF MINERALS, MAJOR SECONDARY AND MICRONUTRIENTS, TRACE AND HEAVY METALS, AND RADIONUCLIDES[34, 35, 36, 37, 38, 44, 79, 80, 81]

Physical characteristics		Chemical characteristics	
pH	6.0– 11.0 (5.4-10)	SiO_2	38 – 63 (63.80-91.72)
Specific gravity (g/cc)	1.66–2.55 (2.65)	Al_2O_3	27 – 44 (2.92-13.76)
Bulk density(g/cc)	0.85–1.2 (1.3-1.6)	TiO_2	0.4 – 1.8
Grain size distribution	Sandy silt to Silt loam	Fe_2O_3	3.3 – 6.4 (2.36-1089)
Porosity (%)	45–55 (35-60)	MnO	0.1 – 0.5 (0.52-2.12)
WHC(%)	45–60 (24-59)	MgO	0.01 – 0.5 (0.52-2.47)
EC(dS/m)	0.15–0.45 (0.05-0.96)	CaO	0.2-8.0 (0.35-2.18)
CEC (mol(P^+)/Kg	- (2.3-57.2)	K_2O	0.04 – 0.9 (0.16-1.60)
		Na_2O	0.07–0.43 (0.01-0.86)
		LOI	0.2 – 3.4 (-)

Parameter	Total and available micronutrients		Total and available trace and heavy metals		
	Total (mg/kg)	Av. (mg/kg)	Parameter	Total (mg/kg)	Av. (mg/kg)
Cu	40–80 (2-100)	0.5–1.6	Se	0.6-2.6 (0.1-2.0)	0.1–0.4
Zn	50–150 (10-300)	0.4–1.8	Cr	50-225 (5-1000)	0.3 – 0.6
Mn	500–750 (200-3000)	0.9–1.5	Pb	10-70 (2-200)	BDL
Fe	3.3-6.4 (-)	10–15	Co	10-50 (1-40)	0.05 – 0.15
B	17–38 (2-100)	0.5–0.8	Ni	50-145 (5-5000)	0.15 – 0.25
Mo	2.2–6.7 (0.2-5.0)	0.1–0.6	Cd	5-10 (up to 0.5)	0.03 – 0.07
			As	1.0–4.0 (1.1)	BDL
			Hg	BDL (up to 1)	BDL

Radioactivity level (Bq/kg)	
226Ra	30 – 110 (20-40)
228Ac	30 – 110 (37-57)
40K	180 – 500 (160-270)

Figures in parenthesis for soil and not in parenthesis for FA

TABLE II

PHYSICO-CHEMICAL CHARACTERISTICS (RANGE VALUES) OF INDIAN SOILS AFTER APPLICATION OF FA (CONTROL AND AMENDED) [34, 35, 36, 37, 38, 44]

Parameters	Coal/lignite ash	Soil	
		Control	Amended
Sand (%)	35.00 – 60.00	49.60 – 92.86	46.80 - 85.80
Silt (%)	31.00 – 50.00	06.35 – 33.90	11.40 – 39.10
Clay (%)	6.100 – 9.200	0.790 – 17.50	02.23 – 16.30
BD (Mg m^{-3})	0.930 – 1.050	01.33 – 01.72	01.27 – 01.68
WHC (%)	43.90 – 57.00	19.80 – 39.70	22.90 – 45.50
Porosity (%)	52.50 – 56.30	29.20 – 47.20	33.10 – 52.90
EC (dS m^{-1})	0.042 – 04.29	0.173 – 0.436	0.195 – 0.817
pH	07.10 – 10.46	06.50 – 09.69	06.66 – 08.35
Dehydrogenase activity (mgkg^{-1} h^{-1})	-	0.29-0.31	0.34-0.40
Major and secondary nutrients (available) mg/kg			
N	BDL – 21.0	0.0009 – 0.058	22.50 – 200.0
P	01.65 – 8.25	01.97 – 9.70	03.00 – 10.56
K	38.08 – 180.0	20.60 – 190.1	24.20 – 195.0
Ca	44.00 – 100.0	13.00 – 37.80	39.80 – 55.10
S	31.00 – 190.0	16.50 – 40.20	26.00 – 68.90
Mg	17.70 – 35.10	09.80 – 22.50	13.60 – 25.30
Micronutrients and trace and heavy metals content (mg/kg)			
Cu	0.92-2.17	1.14-2.30	1.26-2.75
Zn	0.77-2.09	0.65-1.56	0.46-1.93
Mn	0.68-19.3	6.49-10.9	6.56-10.65
Fe	5.90-62.7	19.3-39.61	20.92-45.50
Pb	0.06-3.10	BDL-2.1	1.94-2.39
Ni	0.43-4.90	0.31-2.10	0.34-2.48
Co	0.03-0.46	BDL-0.02	0.03-0.05
Cr	BDL-0.54	BDL	BDL
Cd	BDL-0.28	<0.05	<0.05
As	<0.05	BDL	<0.05
Hg	BDL	BDL	BDL

Detection limit for Cu, Co, Mn, Zn, As, Hg = 5 µg/kg and for Cd, Cr, Fe, Ni, and Pb= 15 µg/kg

TABLE III

BIOLOGICAL CHARACTERISTICS (RANGE VALUES) OF INDIAN SOIL AFTER AFTER HARVEST OF CROPS GROWN WITH LIGNITE FA (CONTROL AND AMENDED)[37, 7]

	Crop	T1	T2	T9	T10	T11	T12	T13	T14	LSD ($P = 0.05$)
Ectomycorrhiza (spores/g)	Groundnut (crop I)	34	46	65	70	86	90	95	98	3.26
	Maize (crop III)	65	70	90	98	97	103	106	117	3.47
	Groundnut (crop V)	70	78	110	120	126	130	136	140	4.04
	Maize (crop VI)	59	67	85	93	95	101	105	112	3.47
P-solubilizing bacteria (× 10^4 CFU/g)	Groundnut (crop I)	1.2	2.4	3.2	3.8	4.2	4.7	5.2	5.8	0.28
	Maize (crop III)	1.8	3.4	6.9	7.0	7.9	8.5	9.2	9.4	0.44
	Groundnut (crop V)	2.3	4.4	6.8	7.5	8.2	9.1	10.5	12.0	0.40
	Maize (crop VI)	2.2	2.4	2.9	3.6	4.6	6.2	7.0	8.0	0.45
Total bacterial count (× 10^4 CFU/g)	Groundnut (crop I)	2.0	4.0	5.2	5.7	7.1	7.9	8.5	9.2	0.41
	Maize (crop III)	2.5	4.1	8.0	9.2	9.7	10.5	12.0	13.4	0.54
	Groundnut (crop V)	3.0	4.6	8.6	9.5	16.0	19.0	22.0	26.0	0.53
	Maize (crop VI)	2.6	4.0	5.9	6.2	7.5	8.2	9.2	9.7	0.46
Dehydrogenase activity (mg kg^{-1} h^{-1})	Groundnut (crop I)	0.30	0.34	0.34	0.36	0.35	0.38	0.37	0.39	0.03
	Maize (crop III)	0.32	0.36	0.33	0.38	0.35	0.40	0.38	0.41	0.03
	Groundnut (crop V)	0.34	0.41	0.38	0.42	0.39	0.41	0.38	0.44	0.04
	Maize (crop VI)	0.31	0.43	0.36	0.44	0.38	0.42	0.39	0.46	0.03

CFU: colony-forming unit; LFA: lignite fly ash; LSD: least significant difference.

T_1 Control; T_2 Pressmud (10 t/ha); T_9 LFA(50 t/ha); T_{10} LFA(50 t/ha)+(PM 10 t/ha); T_{11} LFA(100 t/ha); T_{12} LFA(100 t/ha)+(PM 10 t/ha); T_{13} LFA(200 t/ha); T_{14} LFA(200 t/ha)+(PM 10 t/ha)

activities of agricultural soils(alluvial, red, black, and lateritic) on amendment with FA and PA alone and in combination with inorganic and organic amendments was observed [6, 30, 7]. Typical examples of changes in the physico-chemical and biological characteristics of Indian soils after application of FA are presented in Table -II and Table -3, respectively..

B. *Crop growth and yield*

Long-term (1996–2000) detailed field trials using lignite fly ash (LFA) were carried on lateritic soil and mine spoil at Neyveli Lignite Corporation, Tamil Nadu to grow rice, maize, and groundnut crops [6, 7]. LFA was applied at various dosages (0- 200 t/ha), with and without press mud (10 t/ha), before cultivation of the first crop. Also gypsum, humic acid, and bio-fertilizer as supplementing agents, were applied in all the treatments, including control. LFA improved the crop yield (up to 88.5%) over the control, together with better residual effects, maximum yield optimum dose being 20 t/ha for mine spoil and 200 t/ha for lateritic soil. No adverse effect on the quality of crop produce was observed up to the optimum doses of LFA applications. In general, FA is effective in enhancing growth performance and yield of the crops in majority of FA applications alone at lower doses and combination treatments at a wider range of FA levels. The effect is rather relatively better in case of weathered FA applications. Yield of crops grown in waste and alkaline lands of farmers is presented in Table 4. Economics of one time application of pond ash (@ 100 t/ha) in farmer's field at Birbhum (WB) is shown in Table 5.

TABLE IV

YIELD OF CROPS GROWN IN WASTE AND ALKALINE LANDS OF FARMERS [44, 52]

Crops produce	Ram Sakal Jaiswal, Anpara TPP (Waste land)		Khawani Singh, Harduaganj TPP (Alkaline land)	
	Control	Treated	Control	Treated
1st crop(2000-01)				
	Wheat		Wheat	
Grain(Q/ha)	31.31	40.52	25.0	28.0
Straw(Q/ha)	34.52	43.69	29.25	31.15
% Increase over control(grain)	--	29.4	--	12.0
% Increase over control(Straw)	--	26.6	--	6.5
2nd crop 2001				
	Maize		Paddy	
Grain(Q/ha)	30.76	40.95	35.0	45.0
Straw(Q/ha)	34.38	43.09	43.3	48.2
% Increase over control(grain)	--	33.12	--	28.57
% Increase over control(Straw)	--	23.33	--	11.32
3rd crop (2001-02)				
	Brinjal		Wheat	
Grain(Q/ha)	12.81	15.17	26.06	30.01
Straw(Q/ha)	--	--	28.31	34.45
% Increase over control(grain)	--	18.42	--	15.15
% Increase over control(Straw)	--	--	--	21.68

TABLE V

ECONOMICS OF ONE TIME APPLICATION OF POND ASH (@ 100 T/HA) IN FARMER'S FIELD AT BIRBHUM (WB)[40, 81]

Crops grown year	Yield of control plots(q/ha)	Yield of FA treated plots (q/ha)	Difference (q/ha)	% increase over control	Profit Rs/ha
Kharif Paddy-96	43.07	49.90	6.83	15.86	4098.00
Potato 96-97	250.00	300.00	50.00	20.00	10000.00
Boro Paddy-97	69.78	78.44	8.66	12.45	5196.00
Kharif Paddy-97	50.57	53.38	2.81	5.50	1686.00
Potato 97-98	256.70	283.70	27.00	10.52	5400.00
Boro Paddy-98	67.50	72.30	4.80	7.11	2880.00
Kharif Paddy-98	48.50	52.40	3.90	8.04	2340.00
Potato 98-99	260.00	290.00	30.00	11.00	6000.00
Boro Paddy-99	43.60	51.20	7.60	17.43	4560.00
Potato 99-00	275.00	304.00	29.00	10.54	5800.00
Boro Paddy-00	49.00	51.40	2.40	4.90	1440.00
Gross Profit		49400.00			
Cost of Transportation and Application of 100 t PA @ Rs.1/Kg		4000.00			
Net Profit/ha		45400.00			

The selling prices of Paddy and Potato Rs.600.00 and Rs.200.00 per quintal,

C. *Trace and heavy metal contents of plants*

FA containing parts per million (ppm) level concentrations of heavy metals and even some content of radionuclides, when applied to soil, these may get absorbed by plants grown on it, and finally enter into the food chain. Normal and critical levels of trace elements and radionucides in the plants species/tissues, soil, and edible crop produce are summarized in Table 6. The organic and inorganic amendments made with FA help in controlling the availability of metals by chelation, adsorption, precipitation, etc. [6, 30, 7]. Several long-term (4-5 years) residual field studies on different types of soils including waste/alkaline land and mine soil using FA /PA (alone and in combination with organic amendments) from different TPPs [37, 44, 45, 6, 30] have evinced that the uptake of most of trace/heavy metals content of the crop produce and plant species was within permissible limits. The presence of trace amounts of elements of environmental concerns and radionuclides in the FAs was not of much concern [42, 7, 54, 55, 57, 58]. This was attributable to the alkaline nature of the ash and associated impact of its application with organic

TABLE VI

NORMAL AND CRITICAL LEVELS OF TRACE ELEMENTS AND RADIONUCIDES IN THE PLANTS SPECIES/ TISSUES, SOIL, AND EDIBLE CROPS

Normal and Toxic* limits for elements in matured leaf tissues for various plant species (mg/kg) [438]

Elements	Normal	Toxic *	Elements	Normal	Toxic *
Mn	30-300	400-1000	Pb	5-10	30-300
Cu	5-30	20-100	Co	0.02-1	15-50
Zn	25-150	100-400	Cd	0.01-0.2	5-30
Ni	0.1-5	10-100	Cr	0.1-0.5	5-30
As	1-1.5	5-20	Se	0.01-2	5-30
B	10-100	50-200)	Hg	-	1-3
Mo	0.2-5	10-50	Be	<1-7	10-50

Maximum Allowable Concentration (MAC) [82, 83] and Trigger Action Value (TAV) [84] for trace metals in agricultural soil (mg/kg)

Elements	MAC	TAV	Elements	MAC	TAV
Mn	-	-	Pb	20-300	50-3000
Cu	60—150	60-500	Co	25-50	30-100
Zn	100-3000	200-1500	Cd	1-5	2-10
Ni	20-60	75-150	Cr	50-200	50-450
As	15-20	10-65	Se	-	3-10
B	-	-	Hg	0.5-5	1.5-10
Mo	4-10	5-20	Be	10	10-300

Radio nuclides	Permissible limits	
	Soil (Bq/kg)[348]	Edible crop produce [85, 86] Permissible daily intake limit (at 600 g/day) (Bq)
^{226}Ra	370	0.61
^{228}Ac	259	2.2
^{40}K	925	104

*: Not applicable for very sensitive plants

TABLE VII

CHARACTERISTICS (RANGE VALUES) OF THE CROP PRODUCE (PADDY AND WHEAT) GROWN IN FLY ASH AMENDED SOILS [34, 35, 36, 37, 38, 44]

	Grain		Straw	
	Control	Amended	Control	Amended
Major and Secondary Nutrients, Available (mg/kg)				
N	1.28-1.39	1.18-1.51	0.509-0.563	0.523-0.604
P	0.058-0.061	0.057-0.074	0.033-0.037	0.035-0.057
K	0.65-0.68	0.58-0.87	0.34-0.39	0.37-0.53
S	0.068-0.071	0.056-0.085	0.055-0.059	0.058-0.073
Ca	0.0350-0.039	0.032-0.051	0.026-0.030	0.021-0.041
Mg	0.019-0.025	0.015-0.038	0.010-0.014	0.010-0.024
Micro-nutrients and trace/heavy metals, Total (mg/kg)				
Cu	3.38-4.19	3.50-4.58	3.18-3.28	3.40-3.88
Zn	17.96-18.63	17.96-19.05	13.95-14.11	14.15-15.36
Mn	31.68-33.21	30.90-34.51	29.74-30.65	29.96-34.10
Fe	79.35-82.67	78.55-84.55	59.78-62.85	61.56-72.53
Pb	1.16-1.22	1.18-1.51	0.66-0.70	0.75-0.95
Ni	4.79-5.21	5.11-6.45	1.67-1.73	1.82-2.22

Data not included in respect of some trace elements are below detection limit (BDL)

Detection limit for Cu, Co, Mn, Zn, As, Hg = 5 µg/kg and for Cd, Cr, Fe, Ni, and Pb= 15 µg/kg;

TABLE VIII

EFFECT OF APPLICATION OF LFA ON γ-RADIOACTIVITY OF SOIL AFTER THE HARVEST OF CROP VI (FINAL) MAIZE CROP AND ON PRODUCE (MEAN ± SE) [37, 7]

	Treatment (t LFA/ha)	Radioactivity (Bq/kg)				
		Soil	Groundnut (crop I)	Maize (crop III)	Groundnut (crop V)	Maize (crop VI)
^{226}Ra	Control	18.1 ± 0.47	0.65 ± 0.02	0.57 ± 0.012	0.67 ± 0.02	0.61 ± 0.014
	100	27.3 ± 0.72	0.71 ± 0.05	0.63 ± 0.03	0.80 ± 0.05	0.66 ± 0.04
	200	32.5 ± 0.93	0.82 ± 0.07	0.69 ± 0.04	0.86 ± 0.05	0.72 ± 0.02
^{228}Ac	Control	35.8 ± 0.98	0.72 ± 0.04	0.76 ±0.03	0.77 ± 0.03	0.79 ± 0.02
	100	41.9 ± 1.62	0.81 ± 0.07	0.81 ± 0.06	0.84 ±0.05	0.84 ± 0.05
	200	47.2 ± 1.69	0.99 ± 0.08	0.84 ± 0.05	0.97 ± 0.07	0.87 ± 0.05
^{40}K	Control	208.7 ± 9.2	97.8 ± 3.2	57.5 ± 2.9	98.2 ± 3.8	58.2 ± 3.1
	100	219.4 ± 11.7	106.9 ± 4.3	61.7 ± 3.6	107.6 ± 4.7	62.2 ± 4.1
	200	224.1 ± 13.6	120.3 ± 4.8	62.1 ± 3.4	122.5 ± 6.1	63.5 ± 4.7

Detection Limits of ^{226}Ra, ^{238}Ac, and ^{40}K for soil samples was 5Bq/kg and for crop produce 0.05Bq/kg;

TABLE IX

THE DIETARY INTAKE OF METALS THROUGH THE CONSUMPTION OF THE EDIBLE CROP PRODUCE (WHEAT, MAIZE, AND EGGPLANTS [57]

Element	Calculated maximum daily intake		RDA (mg/day)	TUIL (mg/day)
	Wheat or maize (mg/day)	Eggplant (mg/day)		
Cu	0.774	0.92	1.50–3.00	10.00
Zn	3.9	2.46	15.00	40.00
Mn	4.29	3.3	2.00–5.00	11.00
Fe	11.4	2.42	10.00	45.00
Pb	0.165	0.082	-	0.21
Ni	0.219	0.062	-	1.00
Cr	0.183	0.06	0.035	0.20
Se	0.075	0.04	0.07	0.40
Mo	0.15	0.082	0.045	2.00

RDA, recommended dietary allowances; TUIL, tolerable upper intake levels

substrate (FYM/cow dung manure), which help in the controlled carryover of these elements, besides the accompanying dilution of these elements due to enhancement in the yield of crop produce. Table 7 shows the characteristics (range values) of the crop produce (paddy and wheat) grown in fly ash amended soils. Table 8 shows the effect of application of lignite FA on gamma-radioactivity of soil and crop produce after the harvest .No adverse effects due to consumption of the wheat grown on FA amended soil particularly in respect of haematological, chemical and histopathological parameters support the fact that crop produce grown in fly ash treated soils may be safe for human consumption [61]. Further the dietary intake of metals through the consumption of the edible crop produce like wheat, maize, and egg plants, based on the metal content and the Indian average dietary intake of cereals (300 g) and vegetables (200 g) [62], was below the tolerable limits (Table-9) [57].

D. Fly Ash as Fertilizer Additive and Insecticide

In field demonstration trials on the amendments of Ultisol with LFA (@50t/ha) and 50% of the recommended dose of N-fertilizer (without P and K) showed almost the same yield as that of the *Zea mays* and *Arachis hypogea* crops grown with 100% recommended dose of fertilizer, thereby evincing a substantial saving **[7]**. When FA was treated with cow dung manure at different concentrations, the P-soluble bacteria populations were active and solubilized P from FA to a major extent [63]. A synergistic FA based soil conditioner cum fertilizer composition has been formulated [64]. The loss of nitrogen from the soil by volatilization, leaching and de-nitrification is significantly inhibited, increasing the efficiency of nitrogenous fertilizers and reducing nitrate pollution of soil, surface, and water. FA can also help soil retain inorganic fertilizers for longer periods [36, 37], leading to residual, beneficial effects from FA application. The insecticidal property of ash from solid fuel (wood, biomass, and cow dung cakes) in India is well known since a long time; there is tradition of using ashes from cooking biomass/wood fuel as insecticide. Fewer incidences of the pests, particularly *Helicoverpa armigera* and *Spodoptera litura*, were concluded in LFA treated plots as compared to control [7].

E. FA for Reclamation of Mine Spoil/Waste Land/landfills/Ash Ponds

The fast growth of world population and the increasing energy demand have accelerated the degradation of the natural environment, thereby making the land suitable for cultivation/plantations imperative. Establishing vegetative cover on coal-mine spoil is a big challenge for the reasons of compaction, poor WHC and fertility, high acidity or salinity, nutrient deficiency, phytotoxic heavy metals, extreme temperatures, water logging, accelerated runoff erosion, and pyritic oxidation to form sulphuric acid. The addition of energy-related by-products, such as FA/PA to degraded mine soil and wasteland, can address their adverse characteristics through a variety of mechanisms. For example, FA comprising Ca and other basic cations causes improvement in the soil structure and increase in the pH. FA also directly or indirectly contributes to the release of nutrients in the soil and stabilizes the toxic metals. Recently the application of FA in reclamation of mine spoil has been reviewed [2]. In a number of field investigations, enhancement in the biological activities of waste/degraded land, alkaline soil, and mine spoil on amendment with FA and PA alone and in combination with inorganic and organic amendments was observed [6, 30, 7]

TABLE X

PHYSICO-CHEMICAL AND BIOLOGICAL CHARACTERISTICS OF MINE REFUSE BEFORE AND AFTER PLANTATION [30, 45]

Parameter		Bare	Year 1	Year 2	Year 3
Particle size (%)	>2.0 mm	73.65 ± 6.4	70.86 ± 5.8	68.96±4.7	64.46 ± 5.4
	<2.0 mm	26.35 ± 2.1	29.14 ± 2.3	30.11 ± 2.6	33.54 ± 2.2
BD (Mg m^{-3})		1.53 ± 0.06	1.49 ± 0.07	1.31 ± 0.04	1.23 ± 0.03
WHC (%)		15.70 ± 0.09	17.46 ± 0.08	22.58 ± 1.15	26.32 ± 1.35
Porosity (%)		53.69 ± 2.85	54.86 ± 2.65	58.12 ± 2.56	59.26 ± 2.62
EC (dS m^{-1})		0.256 ± 0.005	0.245 ± 0.004	0.162 ± 0.002	0.157 ± 0.003
pH		7.79 ± 0.21	7.43 ± 0.23	6.87 ± 0.24	6.83 ± 0.28
Organic carbon (%)		0.32 ± 0.002	0.41 ± 0.003	0.51 ± 0.002	0.53 ± 0.003
Available Major and Secondary Nutrients					
N (%)		0.012 ± 0.001	0.017 ± 0.001	0.022 ± 0.002	0.034 ± 0.002
P (mg kg^{-1})		3.02 ± 0.02	4.27 ± 0.03	5.02 ± 0.03	5.23 ± 0.03
K (mg kg^{-1})		62.94 ± 4.2	68.39 ± 4.8	71.13 ± 5.2	73.05 ± 5.8
S (mg kg^{-1})		21.50 ± 1.7	26.20 ± 1.9	32.48 ± 2.1	33.84 ± 1.8
Ca (mg kg^{-1})		15.46 ± 1.2	16.12 ± 1.3	18.62 ± 1.5	20.48 ± 1.4
Mg (mg kg^{-1})		10.80 ± 0.76	13.72 ± 0.92	15.59 ± 0.75	16.95 ± 1.2
Micronutrients and Trace and Heavy Metals					
Cu (mg kg^{-1})		1.90 ± 0.010	1.97 ± 0.014	2.08 ± 0.06	2.15 ± 0.015
Zn (mg kg^{-1})		1.36 ± 0.007	1.45 ± 0.009	1.58 ± 0.008	1.60 ± 0.01
Mn (mg kg^{-1})		5.45 ± 0.32	8.92 ± 0.48	10.25 ± 0.65	10.75 ± 0.72
Fe (mg kg^{-1})		17.36 ± 1.1	19.86 ± 1.3	21.95 ± 1.5	22.50 ± 1.5
Ni (mg kg^{-1})		1.93 ± 0.01	2.26 ± 0.01	2.41 ± 0.02	2.52 ± 0.02
Co (mg kg^{-1})		BDL	0.10 ± 0.006	0.15 ± 0.008	0.15 ± 0.001

Biological Characteristics

Parameters	Before plantation	1st yr	2nd yr	3rd yr
Ectomycorrhiza (Spore/g)	-	7	14	35
N-fixing bacteria (CFU× 10^4/g)	-	4	9	16
P-solubilizing bacteria (CFU× 10^4/g)	-	3	7	14
Total bacterial count (CFU× 10^4/g)	-	6	***13***	26
Dehydrogenase activity (mg kg^{-1} h^{-1})	0.01	0.09	0.16	0.30

In the field demonstration trials on bulk use of PA in association with FYM for reclamation of waste/alkaline land for agriculture purposes [51, 27], the productivity of various crops such as wheat (Triticum aestivum), maize (Zea mays), paddy (Oryza sativa), and brinjal (Solanum melongena) substantially increased (20 – 45% yield) over control along with noticeable enhancement in the nutrient content of crop produce, early maturity of crops grown, and improvement in the fertility status of the soil on sustainable basis. Applying FA to acidic mine soils increased the yields of different crops in several places, which were credited to increased plant nutrient availability and no toxicity effects due to trace and heavy metals and radionuclides [37, 6, 30]. Re-vegetation of FA land-fills and ash dumps with different species has been attempted. This includes yellow sweet clover (Melilotus officinalis), white sweet clover (Melilotus alba), and other tree species [34, 38, 2]. The plant species contribute to improving the nutrient status of the reclamation site (mine spoil/ash-filled area) through littering and subsequent bio-decomposition proliferation in microbial activity [65]. The planted species like sissoo (Dalbergia sissoo), siris (Albizzia lebbek) and acacia (Acacia auriculaeformis) played an important role in restoring the ecology on a sustainable basis [45, 49, 50, 30, 53, 54, 2, 59, 55, 56]. An example of Physico-chemical and biological characteristics of mine refuse before and after plantation is presented inTable 10. Forestry species grown on degraded soil amended with FA (up to 20%) showed beneficial use of FA in forestry sector involving nursery development and corresponding plantation [34].

F. Concerns and Remediation

High soluble salt concentrations in un-weathered FA may limit the use of fresh FA; the principal cations in water extracts are Ca and Na, and dominant anions are F, Cl, SO4, OH and CO3 [66]. The application of un-weathered FA to soil may cause an increase in soil and groundwater salinity. The higher concentration of total dissolved solids, total hardness, cations and anions in FA leachates may lead to an increase in soil salinity [29, 7]. Fluoride, though relatively insoluble, but more soluble under strongly acidic conditions (pH 2.5); chloride is readily soluble and forms complex with some heavy metals and may enhance the metal mobility. FA salinity from highly soluble salts and B is the major problems in successful re-vegetation; the effect is more in case of FA application to acidic soil; long-term phytotoxicity may result from slow release of B from aluminosilicate matrices of FA [2].

Trace elements may cause contamination risk to soil, plants and groundwater; other risk may be due to soluble salts, acidity/alkalinity, and radionuclides present in FA. However, trace elements in Indian FAs are measurable but with lower concentration than in FAs from Europe, North America and other parts of the world [67, 34, 38, 44, 68, 69]. The salinity may also affect physiology of the plants; alter the osmotic potential, soil structure, permeability, hydraulic conductivity, and infiltration due to sealing and dispersion of clays and slaking of aggregates. The enhanced dispersion promotes surface crusts or seals, which may lead in to water logging, surface runoff and erosion, and high mobilization of inorganic/organic colloids. Two - three years of weathering in an ash pond can drop soluble salt concentrations substantially and may no longer represent a limitation to using ash for soil treatment [66].

The leaching of fresh and un-weathered FA could be the significant limiting factors. Trace element concentrations in the FA leachates from simulated condition at various solvent pHs were within permissible limits [70, 71]. TDS, total hardness, anions and cations in the leachates from shake and column tests of lignite/coal FAs in water and buffer solutions were above and trace metals were within the prescribed limits for drinking water, industrial effluents, and landfill drainage [29]. The leaching of potential toxicants was lower and within acceptable limits from alkaline ash, but higher from acidic FA [72, 73] observed extraction equilibrium for Ca, Fe, Na and Zn during a 180 day study, however, a single release pattern sustained over for Mn, K, Cu, Pb, Cr, and As. Most of the Indian FAs being alkaline, leaching of toxic constituents is less of a concern during agriculture and silviculture applications [29, 74, 75]. With some cases of salinity and carryover/uptake of trace and heavy metals, enormous potential exists for the application of ash alone and in combination with inorganic and organic amendments to improve cultivable and problematic soils [2].

The observations on the gamma emitters (226Ra, 228Ac, and 40K) in the soils/mine soil and crop produce samples from FA/PA treated plots (@ 200t/ha) did not show no much concern [6, 30, 7], rather the values were well within the normal range prescribed [2]. The increase in 40K level was possibly due to the higher radioactivity values for 40K in LFA than soils. The radioactivity of muriate of potash, a component of the basal dose of chemical fertilizer (NPK) during cultivation with relatively higher level (460Bq/kg) than LFAs (350-415Bq/kg) [6, 7], was also considered to contribute to raise 40K level in the produce [76]. Nonetheless, the low energy of 40K is not of much concern. In a separate study, concern was expressed about radioactivity in the produce from crops where chemical fertilizers including KCl were applied [77]. In so far as the remedial measures is concerned, some metals can be immobilized and rendered non-bioavailable by a range of inorganic compounds, such as lime, phosphate and organic materials, including crop residues and manure.Various fast-growing, high-biomass plants, including agronomic crops, have been evaluated for their ability to tolerate and accumulate metals and radionuclides have been discussed [78, 59].

G. Highlights of Soil Amendment Technology of CIMFR

The findings of numerous demonstration trials in different soil types and agro-climatic conditions for longer durations establish the versatility and vast scope of the applicability of fly ash soil amendment technology (FASAT) developed at CIMFR. The novelty lies in judicious selection of the dose of ash and other amendments, depending on the soil types and characteristics, to obtain soils of desired characteristics for cultivation of various agricultural crops. This technology is also applicable to reclaim the otherwise unproductive problematic soils for social forestry, bio-fuel, agro-horticulture, floriculture and for growing aromatic/medicinal plants. Based on the findings on the field scale demonstration trials in different parts of the country, the farmers are presently using FA/PA in their fields for raising various crops. However, the study on the aspect of toxicity for longer and longer duration needs to be continued in parallel for infallible dispelling of apprehensions, if any. The main findings arising out of these studies are: improvement in physico-chemical properties of the soils; substantial increase in the crop yield (20-60%); early maturity of the crops; higher nutritional value of the crops; less incidence of pests; no carryover of the trace heavy metals/radioactivity beyond permissible limits and without any other adverse effect; encouraging growth performance of various plant species including the timber, oil yielding, fruit bearing and ornamental and medicinal plants.

H.Limitations and Future Directions

The limitations of FA application in agriculture and forestry include heterogeneity of FA; cost involvement, material loss, and contamination during FA transport; apprehension of environmental concerns of FA; lack of awareness of advantages of FA uses among producers /end-users; priority for enhancing coal/power production than ash use for soil reclamations by coal/power producers, and lack of specific directives and polices. Future directives comprise long-term continuous field studies on the effect of FA on different soils properties; development of mathematical models for soil characteristics, suitability and application dose of FA/other amendments, and plant species; continuous monitoring of potential contaminants (on and off site); lab-scale leaching studies on ash-soil mixtures, identifying thresholds for toxic elements in FA; development of FA-based slow release silicate/zeolite fertilizers, commercial synthetic soil media, etc. Efforts of Government of India needs to be accelerated involving farmers and ash/coal generating organizations and other potential users to attain major utilization of FA in agriculture and forestry together with specific directives and policies.

IV. CONCLUSIONS

Globally lot of efforts has been made on the utilization of FA in agriculture and forestry, the findings suffere from variations owing the variation in soil types and FA characteristics. The development of suitable mathematical models is needed for judicious combination of FA dose, soil conditions, and selectivity of plant species along with co-application of inorganic and readily oxidizable organic substrate. The studies from pot to field scale at CIMFR cover a wide range of food crops, plant species, soil types, and agro climatic conditions. Indian FA/PA acts as an excellent soil modifier, a source of plant nutrients, and a good liming agent for improving the fertility status of the cultivable and problematic soils; as much as 100 t /ha of ash could be used for cultivable land and 200t/ha for problematic soils. The crop yield/growth performance of plant species show significant increase, better residual effect, and infrequent carry over/uptake of toxic trace elements to an alarming level. Toxic elements in Indian FAs are with relatively less concentration and concerns than the ash from other parts of the world; also they are within the limits prescribed for soil application of waste materials. Long-term field trials with FA (alone and with inorganic/organic substrates) in agricultural and problematic soils reveal no adverse rather beneficial effect on soil quality, crop produce/plant species, and field water. Apart from restoring the ecosystem, the disposal problem of ash could be solved in an eco-friendly manner. The evaluation of impact of FA use for much longer period on the characteristics of the soil, crop produce, and field water in respect of trace elements/radionuclides is imperative. The concerted effort of Government of India in collaboration with various producers and users of ash under well defined regulatory measures is desirable.

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REFERENCES

[1] CIL (Coal India Ltd. Coal Reserves in India), 2007. (http//www.coalindia.nic.in/coalreserve.htm).

[2] L.C. Ram, R.E. Masto, "Review: An appraisal of the potential use of fly ash for reclaiming coal mine spoil," J. of Environmental Management, vol. 91, pp. 603–617, 2010.

[3] D.N.Tewari, "Review of forest management and policies," in Advances in Land Resource Management for 21st Century: Soil Conservation Society of India, 2000, pp. 415- 422.

[4] J. Veron, K. Horko, R. Kneipp, G. Rogers, "The Demography of South Asia from the 1950s to the 2000s," 2008.

[5] D.K. Bhumbla, R.N. Singh, R.F. Keeker, Water quality from surface mined land reclaimed with fly ash, in Proceedings of the Nineth Ash Use Symposium American Coal Ash Association," vol. 57, pp. 1–22, Academic Press, Orlando, FL., 1991.

[6] L.C. Ram, N.K. Srivastava, R.C. Tripathi, , S.K. Jha, A.K. Sinha, G.Singh, V. Manoharan, "Management of mine spoil for crop productivity with lignite fly ash and biological amendments,"J. Environ Management, vol. 79, pp. 173–187, 2006a.

[7] L.C. Ram, N.K. Srivastava, S.K. Jha, A.K. Sinha, R.E. Masto, V.A. Selvi, "Management of lignite fly ash through its bulk use via biological amendments for improving the fertility and crop productivity of soil," Environmental Management, vol. 40, pp. 438–452, 2007b.

[8] S. Karmakar, B.N. Mittra, B.C. Ghosh, "Enriched coal ash utilization for augmenting production of rice under acid lateritic soil," Coal Combustion and Gasification Products, vol. 2, pp. 45-50, 2010,

[9] V. Vijayan, S.N. Behera, "Studies on heavy elements and radioactivity of crops grown in soils treated with fly ash, in L.C. Ram et al., editor.," Proc. National Seminar 'Utilization of Fly Ash in Agriculture and for Value Added Products' (ISBN 81–7525-184-0), Technical Session II, CFRI, Dhanbad, India, 1999, pp. 61.

[10] O.E. Manz, "Coal fly ash: a retrospective and future look," Fuel, vol. 78, pp. 133–136, 1999.

[11] ASTM C618-99, "Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as Mineral Admixture in Concrete," ASTM International/10-Jun-1999/3 pages.

[12] G.R. Dewey, L.L. Sutter, J.F. Sandell, "Reactivity based approach for classifying fly ash," in American Power Conference. Chicago: IL, 1996 6, pp.1–4.

[13] S.V. Vassilev, C.G. Vassileva, "Anewapproach for the classification of coalflyashes based on their origin, composition, properties, and behavior," Fuel, vol. 86, pp. 1490–1512, 2006.

[14] A.L. Page, A.A. Elseevi, I.R. Straughan, "Physical and chemical properties of fly ash from coal fired power plants with reference to environmental impact," Residue Review, vol. 71, pp. 83–120, 1979 .

[15] U. Bhattacharjee, T.C. Kandpal, "Potential of fly ash utilisation in India," Energy, vol. 27, pp. 151–166, 2002.

[16] U.R. Khandkar, M.S. Gangwar, P.C. Srivastava, M. Singh, "Edaphological characteristics of unweathered and weathered fly ashes from Gondwana and lignite coal," Environmental Pollution, vol.79, pp. 297–302,1993.

[17] A. Sarkar, R. Rano, K.K. Mishra, I.N. Sinha, "Particle size distribution profile of some Indian fly ash: a comparative study to assess their possible uses," Fuel Processing Technology, vol. 86, pp. 1221–1238, 2005.

[18] A. Sarkar, R. Rano, "Water holding capacities of fly ashes: effect of size fractionation," Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, vol. 29, pp. 471–482, 2007.

[19] A.W. Schumann, M.E. Sumner, “Chemical evaluation of nutrient supply from fly ash-biosolids mixtures,” Soil Science Society of America J. vol. 64, pp. 419–426, 2000.

[20] R.L. Aitken, L.C. Bell, “Plant uptake and phytotoxicity of boron in Australian fly ashes,” Plant and Soil, vol. 84, pp. 245–257, 1985.

[21] J. Jankowski, C.R. Ward, D. French, S. Groves, “Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems,” , vol. 85, pp. 243–256, 2006.

[22] D. El-Mogazi, D.J. Lisk, L.H. Weinstein, “A review of physical, chemical, and biological properties of fly ash and effects on agricultural ecosystems,” Sci Total Environ, vol. 74, pp. 1–37, 1988.

[23] D.C. Adriano, A.L. Page, A.A. Elseewi, A.Chang, I.A. Straughan, “Utilization and disposal of fly ash and other coal residues in terrestrial ecosystem: a review,” J. of Environmental Quality, vol. 9, pp. 333–344, 1980.

[24] L.C. Mishra, K.N. Shukla, “Effect of fly ash deposition on growth, metabolism and dry matter production of maize and soybean,” Environmental Pollution, vol. 42, pp. 1–13, 1986a.

[25] L.C. Mishra, K.N. Shukla, “Elemental concentration of corn and soybean grown on fly ash amended soil,” Environmental Pollution Series B: Chemical and Physical, vol. 12, pp. 313–321, 1986b.

[26] Jr.E.M. Taylor, G.E. Schuman, “Fly ash and lime amendment of acidic coal spoil to aid revegetation,” J. of Environmental Quality, vol. 17, pp. 120–124, 1988.

[27] W.E. Sopper, “Re-vegetation of a contaminated zinc smelter site,” Landscape and Urban Planning, vol. 17, pp. 241–250, 1989.

[28] V.C. Pandey, N. Singh, “Review: Impact of fly ash incorporation in soil systems, Agriculture,” Ecosystems & Environment, vol. 136 no. 1-2, pp. 16-27, 2010.

[29] L.C. Ram, R.E. Masto, S.K. Jha, V.A. Selvi, N.K. Srivastava, A.K. Sinha, “Reclamation of coal mine spoil using fly ash: a synoptic review,” in 2007a Proc. of the 1st International Conference on Managing the Social and Environmental Consequences of Coal Mining in India (MSECCMI), pp. 771 - 801.

[30] L.C. Ram, N.K. Srivastava, S.K. Jha, A.K. Sinha, “Eco-friendly reclamation of mine spoil for agro-forestry through fly ash and biological amendments,” in 2006b Proc. of the 23rd Annual International Pittsburgh Coal Conf., Session 52, pp. 1–25.

[31] L.C. Ram, “Moessbauer Spectroscopic and Gamma Radiolytic Studies of Some Indian Coals. PhD Thesis (unpublished),” Banaras Hindu University, Varanasi, India, 1992.

[32] L.C. Ram, P.S.M. Tripathi, S.P. Mishra, “Iron-bearing minerals in bituminous and semianthracitic Indian coals: Moessbauer spectroscopic characterization and studies on their transformations during ashing and carbonization/devolatilisation in K.S. Narsimhan, S. Sen, editors.,” Proc. Golden Jubilee Int. Symposium,” Coal Science Technology Industry Business and Environment: Coal-96’, 1995a, pp. 38–57.

[33] L.C. Ram, P.S.M.Tripathi, S.P.Mishra, “Moessbauer spectroscopic studies on the transformations of Fe-bearing minerals during combustion of coal: Correlation with fouling and slagging,” Fuel Process Technology, vol. 42, pp. 47–60, 1995b.

[34] CFRI (Central Fuel Research Institute), “Bulk Scale Utilisation of Coal Ash in Agricultural Lands of Birbhum District in West Bengal,” CFRI, Dhanbad, Jharkhand. CFRI Report No. CFRI/3.03/1999–2000, 2000a.

[35] CFRI (Central Fuel Research Institute), “Bulk Scale Utilization of Coal Ash in Agriculture and for Reclamation of Waste/Degraded Lands of Murshidabad District in West Bengal,” CFRI, Dhanbad, Jharkhand. CFRI Report No. TR/CFRI/ 3.04/1999–2000, 2000b.

[36] CFRI (Central Fuel Research Institute), “Utilization of Fly Ash from Chandrapur and Bhusawal TPPs in Agriculture and for Reclamation of Degraded Land,” CFRI, Dhanbad, Jharkhand. CFRI Report No. TR/CFRI/1.01/2000–2001, 2001a.

[37] CFRI (Central Fuel Research Institute), “Utilisation of Fly Ash in Agriculture at Neyveli Lignite Corporation, Neyveli,” CFRI, Dhanbad, Jharkhand. CFRI Report No. TR/CFRI/3.01/2000–2001, 2001b.

[38] CFRI (Central Fuel Research Institute), “Role of Riparian Vegetation in Ecosystem Recovery on Fast Deteriorating Riparian Wetland Under Anthropogenic Stress,” CFRI, Dhanbad, Jharkhand. CFRI Report No. TR/CFRI/3.01/2001–2002, 2002a.

[39] CFRI (Central Fuel Research Institute). Technical Reports Nos. TR/CFRI/2.05/88; 1988.

[40] CFRI (Central Fuel Research Institute), “Utilization of Fly ash in Agriculture, at Bakreswar Thermal Power Project, Bakreswar (West Bengal),” CFRI, Dhanbad, Jharkhand. CFRI Report No. TR/C.F.R.I./1.01/96, 1996a.

[41] CFRI (Central Fuel Research Institute), “Utilization of Fly Ash in Agriculture, at Farakka Super Thermal Power Project Farakka (West Bengal)” CFRI, Dhanbad, Jharkhand. CFRI Report No. TR/C.F.R.I./1.02/96, 1996b.

[42] L.C. Ram, S.K.Jha, G.K. Jha, M.C. Das, G. Singh, “Effect of fly ash from FSTPP on the cultivation of wheat and paddy crops in alluvial soil of Murshidabad district. In: L.C. Ram, (Ed.),” Proceedings of the National Seminar on Bulk Utilization of Fly Ash in Agriculture and for Value-added Products. Technical Session V. CFRI, Dhanbad, India, 1999a, pp. 200–210.

[43] CFRI (Central Fuel Research Institute), “Bulk Utilisation of Fly Ash from Ramagundam Super Thermal Power Project in Agriculture and for Reclamation of Waste/Degraded Land,” CFRI. CFRI Report No. TR/CFRI/1.15/2001–2002, 2002b.

[44] CFRI (Central Fuel Research Institute), “Demonstration trials in Farmer’s Field for the Popularization of Bulk Use of Fly-ash from Anpara, Obra and Hardugang TPPs of UPRVUNL in Agriculture and for Reclamation of Degraded/Wasteland,” CFRI, Dhanbad, Jharkhand. CFRI TR/CFRI/1.08/2002–2003, 2003a.

[45] CFRI (Central Fuel Research Institute), “Bio-restoration of O.B. Dumps Through the Plantation of Selected Efficient Photosynthetic/Soil Conserver Species in Eastern Jharia Coalfields (Sponsored by SSRC, Dept. of Coal),” CFRI, Dhanbad, Jharkhand. CFRI Report No.TR/CFRI/1.01/2002–2003, 2003b.

[46] N.K. Srivastava, L.C. Ram, S.K. Jha, R.C. Tripathi, G. Singh, “Role of CFRI’s fly ash soil amendment technology (FASAT) in improving the socio-economic condition of farmers via improvement in soil fertility and crop productivity,” J. Ecophy Occup Hlth, vol. 3, pp. 127–142, 2003.

[47] L.C. Ram, N.K. Srivastava, S.K. Jha, M.K. Singh, N.K. Vaishya, K.C. Gupta, G. Singh, “Agro-forestry a potential area for sustainable bulk use of fly ash,” in Proc. Fly Ash India, 2005, International Congress. Fly Ash Utilization Programme. Session XII. TIFAC, Department of Science and Technology, New Delhi, 2005, pp. 1–14.

[48] L.C. Ram, N.K. Srivastava, S.K. Jha, M.K. Singh, N.K. Vaishya, K.C. Gupta, G.Singh,. “Agro-forestry a potential area for sustainable bulk use of fly ash,” in Proc. International Congress on Fly Ash India: Fly Ash Utilization Programme, Technical Session XII. TIFAC, Department of Science and Technology, New Delhi, 2005, pp. 14.1-14.15.

[49] N.K. Srivastava, L.C. Ram, S.K. Jha, R.C. Tripathi, A.K. Sinha, “Bio-restoration of wastelands/abandoned ash ponds/OB dumps in the vicinity of TPPs/coalfields on sustainable basis, in A.K. Singh, A. Sinha, S.K. Hazra, editors,” Proc. Int. Seminar Global Coal 2005 ‘Coal Science and Technology—Emerging Global Dimensions:’ (ISBN 81-7764-818-7), New Delhi, Allied Publishers, 2005a, pp. 614–626.

[50] N.K. Srivastava, L.C. Ram, A.K. Sinha, “Sustainable improvement of mining environment through selective plantation,” in Proc. International Symposium on Advances in mining Technology and Management, IIT Kharaghpur, 2005b, pp. 505–512.

[51] R.C. Tripathi, L.C. Ram, A.K. Sinha, S.K. Jha, N.K. Srivastava, P.S.M. Tripathi, G. Singh, “Popularisation of bulk use of pond ash in agriculture through demonstration trials in farmers’ fields in the vicinity of TPPs of UPRVUNL in A.K. Singh, K. Sen, A. Sinha, S.K. Hazra, (Eds.),” International Seminar on Coal Science & TechnologydEmerging Global Dimensions, Proceedings of Global Coal 2005. Allied Publishers, New Delhi, 2005a, pp. 586–590.

[52] R.C. Tripathi, L.C. Ram, A.K. Sinha, S.K. Jha, N.K. Srivastava, “Bulk use of pond ash for reclamation of waste/alkaline land for agriculture purposes,” in Proc. International Congress on Fly Ash India, Fly Ash Utilization Programme, Technical Session XII, TIFAC, DST, New Delhi, 2005b, pp. 15.1–15.18.

[53] L.C. Ram, “Fly Ash: A Resource Material for Reclamation of Coal Mine Spoil. In Sustainable Rehabilitatiohukla of Degraded Ecosystems (Eds: OP Choubey, Vijay Bahadur, PK Shukla),” Published by Avishkar Publishers, Distributors (ISBN 978-81-7910-288-6), Jaipur (Rajsthan), 2009, Ch. 4, pp.14-45.

[54] N.K. Srivastava, L.C. Ram, “Bio-restoration of coal mine spoil with fly ash and biological amendments. In Sustainable Rehabilitation of Degraded Ecosystems, Editors: O.P. Chaubey, Vijay Bahadur, P.K. Shukla,” published by Avishkar Publishers, Distributors (ISBN 978-81-7910-288-6), Jaipur (Rajsthan), 2009, Ch 7, pp 77-91.

[55] N.K. Srivastava, L.C. Ram,. "Reclamation of coal mine spoil dump through fly ash and biological amendments," International J. Ecology & Development, 2010a, vol.17 no. F10, pp. 17-33.

[56] N.K. Srivastava, L.C. Ram, 2010b. "Reclamation of mine over-burden and low-lying area with coal fly ash, a sustainable ecological approach," Proc. 4th International Conference on "Sustainable Energy & Environmental Protection (SEEP-2010) 'Environmental Protection in the New Era- Part-2 (ISBN: 978-88-905185-2-2), DIMeG, Politecnico di Bari, BARI – ITALY. Edited by: Michele Dassisti, Abdul Ghani Olabi, Michele De Nicolo, Michela Chimienti (http://seep2010.poliba.it)

[57] R.C. Tripathi, R.E. Masto, L.C. Ram, "Bulk use of pond ash for cultivation of wheat–maize–eggplant crops in sequence on a fallow land, Resources, Conservation and Recycling," vol. 54, pp. 134-139, 2009.

[58] R.C. Tripathi, S.K. Jha, L.C. Ram, "Impact of fly ash application on trace metal content in some root crops," Energy sources, Part A: Recovery, Utilization, and Environmental Effects, vol. 32, pp. 576-589, 2010.

[59] L.C. Ram, S. Singh, R.E. Masto, S.K. Jha, R.C. Tripathi, A.K. Sinha, N.K. Srivastava, V.A. Selvi, "Potential of Indian Fly ashes as Soil Ameliorant: State-of-the-Art," Twenty-Fifth International Conference on Solid Waste Technology and Management, Philadelphia USA, 2010, Session 3C, pp 710-721.

[60] M.K. Mahato, R.E. Masto, V.A. Selvi, L.C. Ram, N.K. Srivastava, R.C.Tripathi, S.K. Jha, A.K. Sinha,. "Phosphorus adsorption, fixation and fractions in fly ash and ash amended soil," in Proc. of the International Congress on fly ash India, 2005, pp. 12.1–12.8.

[61] V. Kandlakuntha, R. Punna, U. Paruchuri, B. Sangras, K. Krishnaswamy, S.Qadri, U. Putcha, S. Boindala, "Nutritional and toxicological evaluation of wheat grown on soils with or without fly ash treatment," J. of the Science of Food and Agriculture, vol. 89, pp. 384–389, 2009.

[62] V. Singh, A.N. Garg, "INAA of trace elements in Indian vegetarian diet and its adequacy vis-a-vis recommended dietary allowances," J. of Radioanalytical and Nuclear Chemistry, vol. 217, 139–45, 1997.

[63] Urvashi, R.E. Ma sto, V.A. Selvi, L.C. Ram , N.K. Srivastava,. "An international study: effect of farm yard manure on the release of P from fly ash," Remediation Autumn, pp. 70-81, 2007.

[64] G. Singh, L.C. Ram, S.K. Jha, R.C. Tripathi, N.K. Srivastava, "A synergistic fly ash based soil conditioner cum fertilizer composition," CFRI (Central Fuel Research Institute), Indian. Patent No. 031 NF 2002, 2002c.

[65] L.C. Ram, S.K. Jha, R.C. Tripathi, R.E. Masto, V.A. Selvi, "Remediation of fly ash landfills through plantation," Remediation Autumn, 2008, p. 71-90.

[66] R.J. Haynes, Reclamation and revegetation of fly ash disposal sites: challenges and research needs. J. of Environmental Management, vol. 90, pp.43–53, 2009.

[67] EIS Suppl, "Waste Management. Bundaberg 2K+ Industrial development, Sinclair Knight Merz," Report-2000, pp. 11.3.

[68] S. Sushil, V.S. Batra, "Analysis of fly ash heavy metal content and disposal in three thermal power plants in India," Fuel, vol. 85, pp. 2676–2679, 2006.

[69] W. Riley, "Benchmarking of fly ash," CCSD Research Report No. 67. CRC for Coal in sustainable Development, Pullenvale, Qld, Australia, 2007.

[70] L.C. Ram, N.K. Srivastava, M.C. Das, G. Singh, "Leaching behavior of fly ash under simulated conditions vis-a-vis quality of the leachate, in L.C. Ram (Ed.)," Proc.of the National Seminar on Bulk Utilization of Fly Ash in Agriculture and for Value-added Products. Technical Session I. CFRI, Dhanbad, India, 1999b, pp. 14–25.

[71] L.C. Ram, N.K. Srivastava, G. Singh, "Prediction of leaching behavior of TPP Ash under simulated conditions by column studies, in C.V.J.Varma, , S.V.R. Rao, V. Kumar, , R. Krishnamurthy, (Eds.)," Proc. of the Second International Conference on Fly ash Disposal and Utilization. Session IV, vol. I. Central Board of Irrigation and Power, New Delhi, 2000, pp. 16–28.

[72] T. Praharaj, M.A. Powell, B.R. Hart, S. Tripathy, "Leachability of elements from sub-bituminous coal fly ash from India," Environment International, vol. 27, pp. 609–615, 2002.

[73] B.K. Dutta, S. Khanra, D. Mallick, "Leaching of elements from coal fly ash: assessment of its potential for use in filling abandoned coal mines," Fuel, 2009.

[74] S.U. Khan, R.K. Bhardwaj, S. Jabin, J.A. Khan,. "Influence of some chemical fertilizers on the mobility of trace metals through soil amended with fly ash," Pollution Research, vol. 19, pp. 241–244, 2000.

[75] A.B. Mukherjee, R. Zevenhoven, "Mercury in coal ash and its fate in the Indian subcontinent: a synoptic review," Science of the Total Environment vol. 368, pp. 384–392, 2006.

[76] P.C. Srivastava, U.C. Gupta, "Trace Elements in Crop Production. Oxford and IBH Publishing Co. Pvt. Ltd.," New Delhi, 1996.

[77] G.C. Maxino, Environmental Potassium radioactivity and public health, 2001 (http:// physics.msuiit.edu.ph/spvm/ papers/2001/maxino.pdf).

[78] G.L. Guo, Q. Zhou, L.Q. Ma, "Availability and assessment of fixing additives for the in situ remediation of heavy metal contaminated soils: a review," EnvironmentalMonitoring and Assessment, vol. 116, pp. 513–528, 2006.

[79] ICAR (Indian Council of Agriculture Research), "Handbook of Aghriculture, ICAR," New Delhi, India, 1996.

[80] J. Sehgal, "Pedology: Concepts and Applications," Kalyani Publishers, Ludhiana, India, 1996.

[81] V. Kumar, G. Singh, R. Rai,. "A material for another green revolution, in V. Kumar, S.M. Mathur, G. Singh, (Eds.)," Proc. of the International Conference 'Fly Ash India'. Flyash Utilization Programme. Technical Session XII, vol. 5. TIFAC, Department of Science and Technology, New Delhi, 2005, pp. 2.1–12.16.

[82] Z.S. Chen, "Selecting indicators to evaluate soil quality (www.fftc.agent.org)," 1999.

[83] A. Kabata-Pendias, W.Sadurski, "Trace elements and compounds in soil, in E. Merina, M. Anke, M. Ihnat, M. Stoeppler, editors," Elements and their Compounds in the Environment. 2nd edn., Weinheim: Wiley-VCH, 2004, pp. 77-99.

[84] A. Kabata-Pendias, A.B. Mukherjeem, "Trace Elements from Soils to Human. Heidelberg: Springer-Verlag Berlin," 2007, pp. 35.

[85] H.J.W. Bowen, "Trace Elements in Biochemistry," London UK: Academic Press, 1966, pp. 748.

[86] M. Eisenbud, H.C. Petrow, "Radioactivity in the atmospheric effluents of power plants that use fossil fuel," Science, vol. 144, pp. 288, 1964.W.-K. Chen, *Linear Networks and Systems* (Book style). Belmont, CA: Wadsworth, 1993, pp. 123–135.