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Review

Potential fly-ash utilization in agriculture: A global review

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Abstract

Though in last four decades various alternate energy sources have come into the limelight, the hyperbolic use of coal as a prime energy source cannot be counterbalanced. Disposal of high amount of fly-ash from thermal power plants absorbs huge amount of water, energy and land area by ash ponds. In order to meet the growing energy demand, various environmental, economic and social problems associated with the disposal of fly-ash would continue to increase. Therefore, fly-ash management would remain a great concern of the century. Fly-ash has great potentiality in agriculture due to its efficacy in modification of soil health and crop performance. The high concentration of elements (K, Na, Zn, Ca, Mg and Fe) in fly-ash increases the yield of many agricultural crops. But compared to other sectors, the use of fly-ash in agriculture is limited. An exhaustive review of numerous studies of last four decades took place in this paper, which systematically covers the importance, scope and apprehension regarding utilization of fly-ash in agriculture. The authors concluded that though studies have established some solutions to handle the problems of radioactivity and heavy metal content in fly-ash, long-term confirmatory research and demonstration are necessary. This paper also identified some areas, like proper handling of dry ash in plants as well as in fields, ash pond management (i.e., faster decantation, recycling of water, vertical expansion rather than horizontal), monitoring of soil health, crop quality, and fate of fly-ash in time domain, where research thrust is required. Agricultural lime application contributes to global warming as Intergovernmental Panel on Climate Change (IPCC) assumes that all the carbon in agricultural lime is finally released as CO_2 to the atmosphere. It is expected that use of fly-ash instead of lime in agriculture can reduce net CO_2 emission, thus reduce global warming also.

Keywords: Coal fly-ash; Agriculture; Soil health; Crop yield; Radioactivity; Global warming

1. Introduction

Fly-ash is the end residue from combustion of pulverized bituminous or sub-bituminus coal (lignite) in the furnace of thermal power plants and consists of mineral constituents of coal which is not fully burnt. Fine minute particles of ash are carried away with flue gases in electrostatic precipitators or cyclone separators and are collected by wet (slurry form) or dry scrubbing method, which requires large volumes of land, water and energy. Use of high ash containing (30–50%) bituminous or sub-bituminus coal in thermal power stations, in addition to several captive power plants, contributes to indiscriminate disposal of this industrial waste every year [1,2]. The coal ash by-product has been classified as a Green List waste under the Organization for Economic Cooperation and Development (OECD). It is not considered as a waste under Basel Convention. However, in many countries this industrial by-product has not been properly utilized rather it has been neglected like a waste substance.

In China, about 100 MT (million tons) of coal combustion products are produced each year [3]. In India,

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presently, the figure is around 112 MT and is likely to exceed 170 MT by 2012 [4]. During 2005, the utilization of fly-ash was 100% in Italy, Denmark and Netherlands with an annual production of 2 MT, 50–85% in USA and Germany and 45% in China (Table 1) [3]. In India, fly-ash utilization has increased from 3% in the 1990s [5] to 38% in 2005 [3]. The reason of low fly-ash utilization in India is the unavailability of appropriate cost-effective technologies [6]. According to the report of American Coal Ash Association [7], in agriculture, wasteland reclamation and civil engineering purposes use 32% of the fly-ash, 30% of the bottom ash, 94% of the boiler slag and 9% of flue gas desulfurization sludge.

Many experiments and studies on the effect and potentiality of fly-ash as an amendment in agricultural applications have been conducted by various agencies, research institutes at dispersed locations all over the world. In this paper, utilization of fly-ash as a value-added product of agriculture is reviewed with the aim of helping opening up the usage of fly-ash and reducing the environmental and economic impacts of disposal.

2. Physical properties of fly-ash

The physical properties of fly-ash vary widely depending on the coal type, boiler type, ash content in coal, combustion method and collector setup. Fly-ash generally has a silt loam texture with 65–90% of the particles having a diameter of less than 0.010 mm [8,9]. Ash from bituminous coal is usually finer as compared with that of lignite one [10]. Fly-ash particles are empty spheres (cenospheres) filled with smaller amorphous particles and crystals (plerospheres). The cenosphere fraction constitutes as much as 1% of the total mass and gets easily airborne [11]. In general, fly-ash has low bulk density (1.01–1.43 g cm^{-3}), hydraulic conductivity and specific gravity (1.6–3.1 g cm^{-3}) [9,10,12]. Mean particle densities for non-magnetic and magnetic particles are 2.7 and 3.4 g cm^{-3}, respectively, while the moisture retention ranges from 6.1% at 15 bar to 13.4% at 1/3 bar [13].

Table 1
Generation and utilization of fly-ash in different countries.

Country	Fly-ash production (million tons per year)	Fly-ash utilization (%)
India	112	38
China	100	45
USA	75	65
Germany	40	85
UK	15	50
Australia	10	85
Canada	6	75
France	3	85
Denmark	2	100
Italy	2	100
Netherlands	2	100

Source: [3].

By virtue of its physical characteristics and sheer volumes generated, fly-ash is a serious problem. Some of the aspects of the problem are [14]:

(1) Due to heavy disposal, fly-ash particles both as dry ash and pond ash occupy many hectares of land in the vicinity of power station.
(2) Because of its fineness, it is very difficult to handle fly-ash in dry state. Flying fine particles of ash corrode structural surfaces and affect horticulture.
(3) It disturbs the ecology through soil, air and water pollution.
(4) Long inhalation of fly-ash causes various serious diseases like silicosis, fibrosis of lungs, bronchitis, and pneumonitis.

Moreover, the oxides of iron and aluminium present on the surface of the fly-ash particles attract toxic trace elements, such as Sb, As, Be, Cd, Pb, Hg, Se, and V, and they are found to be concentrated largely on the surface of fly-ash [15]. A study was conducted by Hicks and Yager [16] with six bituminus, sub-bituminus and lignite coal-fired thermal power plants to measure the amount of airborne respirable crystalline silica in the breathing zone of workers engaged in fly-ash-related operations. It was found that in the bituminus, sub-bituminus and lignite coal-fired plants, the air samples (60%) collected during maintenance-related work exceeded the threshold limit. Similarly, in the case of normal production-related activities, the samples from bituminus (54%) and sub-bituminus (65%) coal-fired plants surpassed the limit. In the bituminus/sub-bituminus and lignite coal, the minimum crystalline silica contents were observed to be 7.5% and 1.7%, respectively [16].

3. Chemical properties of fly-ash

The factors influencing the physical properties are also responsible for wide variation of chemical properties of fly-ash. In a study of 11 fly-ashes from various U.S. power plants, Theis and Wirth [17] found that the major components were Al, Fe and Si, with smaller concentrations of Ca, K, Na, Ti, and S. Fly-ash contains varying amounts of numerous trace elements, some of which are required by plant and animals in varying amounts, whereas some may have toxic effect. Fly-ash contains essential macronutrients including P, K, Ca, Mg and S and micronutrients like Fe, Mn, Zn, Cu, Co, B and Mo. Some are rich in heavy metals such as Cd and Ni [18]. According to Kumar et al. [19], on an average 95–99% of fly-ash consists of oxides of Si, Al, Fe and Ca and about 0.5–3.5% consists of Na, P, K and S and the remainder of the ash is composed of trace elements. It is considerably rich in trace elements like lanthanum, terbium, mercury, cobalt and chromium [18,20]. According to Page et al. [21], many trace elements including As, B, Ca, Mo, S, Se and Sr in fly-ash are concentrated in the smaller ash particles [18]. In fact, fly-ash consists of practically all the elements present in soil except organic carbon and nitrogen [19]. On the basis of silica, alumina and iron oxide content, fly-ash has been classified into two types: Class F (low lime) and Class C (high lime) (ASTM C618). The chemical properties of the fly-ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite). Anthracite is a hard, compact variety of mineral coals that has a high lustre. It has the highest carbon count and contains the fewest impurities of all coals, despite its lower calorific content. Lignite, also referred to as brown coal, is the lowest rank of coal and used almost exclusively as fuel for steam-electric power generation. The burning of harder, older anthracite and bituminous coal typically produces Class F fly-ash. Fly-ash produced from the burning of younger lignite or sub-bituminus coal is of Class C. Alkali and sulfate (SO_4) contents are generally higher in Class C than Class F fly-ash [21]. Lignite or brown coal is used almost exclusively as fuel for steam-electric power generation, resulting in the production of huge amount of fly-ash. Therefore, use of brown fly-ash in agriculture deserves special attention.

Al in fly-ash is mostly bound in insoluble aluminosilicate structures, which greatly confines its biological toxicity [21]. Fly-ash also contains minerals such as quartz, mullite, hematite, magnetite, calcite and borax, and oxidation of C and N during combustion drastically reduces their quantity in ash [11]. Depending on the sulfur content of the parent coal, the pH of fly-ash varies from 4.5 to 12.0 [22] and the type of coal used for combustion affects the S content of fly-ash [21]. Eastern US anthracite contains generally high S and produces acidic ash, while western US lignite coals are lower in S and higher in Ca and thereby produce alkaline ash [21,23–25]. The coal in India contains low S but high ash (40%) [26].

A large portion of inorganic compounds vaporizes in the cooler parts of the installation during the combustion of ground coal at a high temperature of 400–1500 °C and condenses on fly-ash particles [12]. Three groups of elements were recognized on the basis of this volatilization–condensation hypothesis which established correlation between mineral concentrations with the particle size [27]. These groups are: group I with pronounced concentration of As, Cd, Ni, Pb, S, Sb, Se, Ti and Zn; group II with limited concentration of Be, C, Fe, Mg, Mn, Si and V and group III with no concentration of Ca, Co, Bi, Cu, Sn and Ti. Group I elements are classified as 'litho files' (Al, Ca, Fe, K, Mg, Na, Ti) with little or no enrichment in smaller fly-ash particles, group II elements as 'Chalco files' (As, Cd, Mu, Pb, Sb, Se) with increased concentration with decreasing particle size and group III elements (Be, Cu, Ni, V, Co) have intermediate behavior and are enriched in smaller particles but to a lesser extent than those of group II. The properties and contents of major and trace elements of soil and fly-ash that are available in the literature are presented in Table 2.

Table 2
Physical characteristics and the major and trace elements in electrostatic precipitator (ESP) fly-ash and soil.

Properties	Fly-ash[a]	Soil[b]
Bulk density ($g\,cc^{-1}$)	<1.0	1.33
Water-holding capacity (%)	35–40	<20
Porosity (%)	50–60	<25
Major elements in percentages		
N	–	0.01–1.0
P	0.004–0.8	0.005–0.2
K	0.15–3.5	0.04–3.0
Ca	0.11–22.2	0.7–50
Mg	0.04–7.6	0.06–0.6
S	0.1–1.5	0.01–2.0
Al	0.1–17.3	4–30
Na	0.01–2.03	0.04–3.0
Fe	36–1333	0.7–55
Trace elements in mg kg^{-1}		
Mn	58–3000	100–4000
Zn	10–3500	10–300
Cu	14–2800	2–100
B	10–618	2–100
As	2.3–6300	0.1–40
Cd	0.7–130	0.01–7.0
Co	7–520	1–40
Cr	10–1000	5–3000
Hg	0.02–1.0	–
Mo	7–160	0.2–5.0
Ni	6.3–4300	10–1000
Pb	3.1–5000	2–100
Se	0.2–134	0.1–2.0

–: Data not available.
[a] Unweathered ESP fly-ash generated from F-grade coal with 40% coal ash: [26].
[b] Red lateritic soil of order Ultisols. Source: [21,28].

4. Fly-ash for improving soil properties

Soil properties as influenced by fly-ash application have been studied by several workers [29–35] for utilizing this industrial waste as an agronomic amendment. Physical and chemical properties of soil due to fly-ash amendment vary according to the original properties of soil and fly-ash but certain generalization could be made in most cases.

4.1. Soil texture

Alteration of the soil texture is possible through the addition of appropriate quantities of fly-ash (Several experiments have been performed to measure the physical properties for a variety of soils mixed with up to 50% fly-ash [8], which revealed that soil fly-ash mixture tend to have lower bulk density, higher water-holding capacity and lower hydraulic conductivity than soil alone) due to its textural manipulation through fly-ash mixing. Application of high rates of fly-ash can change the surface texture of soils, usually by increasing the silt content [36,37]. Fly-ash addition at 70 t ha^{-1} has been reported to alter the texture of sandy and clayey soil to loamy [38,39]. Addition of fly-ash at 200 t acre^{-1} improved the physical and chemical properties of soil and shifted the USDA textural class of the refuge from sandy loam to silt loam [40].

4.2. Bulk density

The particle size range of fly-ash is similar to silt and changes the bulk density of soil. (Several experiments have been performed to measure the physical properties for a variety of soils mixed with up to 50% fly-ash [8,36], which reveals that soil fly-ash mixture tend to have lower bulk density, higher water-holding capacity and lower hydraulic conductivity than soil alone.) Chang et al. [8] observed that among five soil types, Reyes silty clay showed an increase in bulk density from 0.89 to 1.01 $g\,cc^{-1}$ and a marked decrease in soils having bulk density varying between 1.25 and 1.60 $g\,cc^{-1}$ when the corresponding rates of fly-ash amendment increased from 0% to 100%. Application of fly-ash at 0%, 5%, 10% and 15% by weight in clay soil significantly reduced the bulk density and improved the soil structure, which in turn improves porosity, workability, root penetration and moisture-retention capacity of the soil [2,41]. According to Prabakar et al. [42], addition of fly-ash up to 46% reduced the dry density of the soil in the order of 15–20% due to the low specific gravity and unit weight of soil.

4.3. Water-holding capacity

Fly-ash application to sandy soil could permanently alter soil texture, increase microporosity and improve the water-holding capacity [43] as it is mainly comprised of silt-sized particles. Fly-ash generally decreased the bulk density of soils leading to improved soil porosity, workability and enhanced water-retention capacity [21]. A gradual increase in fly-ash concentration in the normal field soil (0, 10, 20 up to 100% v/v) was reported to increase the porosity, water-holding capacity, conductivity and cation-exchange capacity [44]. This improvement in water-holding capacity is beneficial for the growth of plants especially under rainfed agriculture. Amendment with fly-ash up to 40% also increased soil porosity from 43% to 53% and water-holding capacity from 39% to 55% [45]. Fly-ash had been shown to increase the amount of plant available water in sandy soils [46]. Chang et al. [8] found that fly-ash amendment increased the water-holding capacity of sandy/loamy soils by 8%, which in turn caused improvement in hydraulic conductivity and thereby helped in reducing surface encrustation. Water-holding capacities of fly-ashes from different thermal power plants in Eastern India were compared, and the effect of size fractionation on the water-holding capacity was determined in an investigation by Sarkar and Rano [47]. Results revealed that the fly-ash obtained from a thermal power plant working on stoker-fired combustor produced the highest water-holding capacity, followed by the one working on pulverized fuel combustor. Fly-ash collected from super thermal power plant had the least water-holding capacity (40.7%). The coarser size fractions of fly-ashes in general comprised higher water-holding capacity than the finer ones. According to Jala and Goyal [26], the Ca in fly-ash readily replaces Na at clay exchange sites and thereby enhances flocculation of soil clay particles, keeps the soils friable, enhances water penetration and allows roots to penetrate compact soil layers.

4.4. Soil pH

Depending on the source, fly-ash can be acidic or alkaline, which could be useful to buffer the soil pH [48–50]. The hydroxide and carbonate salts give fly-ash one of its principal beneficial chemical characteristics, the ability to neutralize acidity in soils [51–53]. Fly-ash has been shown to act as a liming material to neutralize soil acidity and provide plant-available nutrients [46]. Most of the fly-ash produced in India is alkaline in nature; hence, its application to agricultural soils could increase the soil pH and thereby neutralize acidic soils [50]. Researches have shown that the use of fly-ash as liming agent in acid soils may improve soil properties and increase crop yield [51]. According to Poykio et al. [54], the concentration of easily soluble Ca (24.5 $g\,kg^{-1}$ (dry weight)) in the fly-ash from a fluidized bed boiler at the industrial power plant of Laanilan Voima Oy in Oulu, Northern Finland was 15 times higher than the typical value of 1.6 $g\,kg^{-1}$ (dry weight) in arable land in Central Finland. It is indicative of the fact that fly-ash is a potential agent for soil remediation and soil fertility improvement. The use of excessive quantity of fly-ash to alter pH can increase the soil salinity especially with unweathered fly-ash [55]. An appreciable change in the soil physicochemical properties, an increase in pH and increased rice crop yield were obtained by mixed application of fly-ash, paper factory sludge and farmyard manure [56,57].

4.5. Biological properties

Information regarding the effect of fly-ash amendment on soil biological properties is very scanty [58]. The results of several laboratory experiments revealed that application of unweathered fly-ash particularly to sandy soil greatly inhibited the microbial respiration, enzymatic activity and soil N cycling processes like nitrification and N mineralization [59–63]. These adverse effects were partly due to the presence of excessive levels of soluble salts and trace elements in unweathered fly-ash. However, the concentration of soluble salts and other trace elements was found to decrease due to weathering of fly-ash during natural leaching, thereby reducing the detrimental effects over time [64]. Moreover, the use of extremely alkaline (pH 11–12) fly-ash could also be the reason for those adverse effects. The application of lignite fly-ash reduced the growth of seven soilborne pathogenic microorganisms as reported by Karpagavalli and Ramabadran [65], whereas the population of *Rhizobium* sp. and P-solubilizing bacteria were increased under the soil amended with either farmyard manure or fly-ash individually or in combination [66]. Gaind and Gaur [67] found that the application of fly-ash at 40 t ha^{-1} in conjunction with *Pseudomonas striata* inoculation improved the bean yield, nutrient uptake by grain and highest population of the bacteria in the inoculated series, though both 40 and 60 t ha^{-1} of fly-ash along with *P. striata* resulted in the same amount of available P_2O_5 in the soil (Table 3). The soil fly-ash environment was the most suitable for the proliferation of these bacteria, thereby contributing towards enhanced availability of soil phosphorus [68]. Amendment of Class F, bituminous fly-ash to soil at a rate of 505 Mg ha^{-1} did not cause any negative effect on soil microbial communities and improved the populations of fungi, including arbuscular mycorrhizal fungi and gram-negative bacteria as revealed from analysis of community fatty acids [58].

A pot-culture experiment was conducted by Garampalli et al. [69] using sterile, phosphorus-deficient soil to study the effect of fly-ash at three different concentrations viz., 10 g, 20 g and 30 g fly-ash kg^{-1} soil on the infectivity and effectiveness of Vescicular-arbusculer mycorrhiza (VAM) *Glomus aggregatum* in pigeonpea (*Cajanus cajan* (L.) Millsp.) cv. Maruti. All the three different concentrations of fly-ash amendment in soil were found to significantly affect the intensity of VAM colonization inside the plant roots and at higher concentration (30 g fly-ash kg^{-1} soil); the formation of VAM fungal structure was suppressed completely. The dry weight of the pigeonpea plants under the influence of fly-ash amendment in VAM fungus-infested soils was found to be considerably less (though not significant enough) when compared to the plants grown without fly-ash that otherwise resulted in significant increase in growth over the plants without *G. aggregatum* inoculation. However, fly-ash amendment without VAM inoculation was also found to enhance the growth of plants as compared to control plants (without fly-ash and VAM inoculum). Tiwari et al. [70] isolated 11 bacterial strains from the rhizospheric zone of *Typha latifolia* and inoculated separately in the fly-ash with additional source of carbon to investigate their ability to increase the bioavailability or immobilization of toxic metals like Cu, Zn, Pb, Cd and Mn. It was found that most of the bacterial strains either enhanced the mobility of Zn, Fe and Mn or immobilized Cu and Cd with the exceptions that NBRFT6 enhanced immobility of Zn and Fe and NBRFT2 of Mn. The study also revealed that NBRFT8 and NBRFT9 enhanced bioavailability of Cu and all the strains immobilized Cd. They explained that it was the specific function of bacterial strains, which caused the mobility/immobility of trace metals from the exchangeable fractions depending upon the several edaphic and environmental factors. Therefore, based on the extractability of metals from fly-ash, bacterial strains can be utilized to enhance the phytoextraction of metals from fly-ash by metal-accumulating plants or for arresting their leaching to water bodies.

5. Fly-ash as a source of plant nutrients

To solve the soil-shortage problem in subsided land of coal mines, the principal chemical properties of artificial soil comprising organic furfural residue and inorganic fly-ash were examined by Feng et al. [71]. The results indicated that the artificial soil was suitable for agricultural use after irrigation and desalination. The available nutrients in the artificial soil could satisfy the growth demand of plants, and the pH tended to neutrality. Chemically, fly-ash contains elements like Ca, Fe, Mg, and K, essential to plant growth, but also other elements such as B, Se, and Mo, and metals that can be toxic to the plants [34,35,72–74]. Lime in fly-ash readily reacts with acidic components in soil leading to release of nutrients such as S, B and Mo in the form and amount favourable to crop plants [26]. Fly-ash contains negligible amount of soluble salt and organic carbon and adequate quantity of K, CaO, MgO, Zn and Mo. However, it is potentially toxic to plants due to high B content (345 mg kg^{-1}) [75]. After application of fly-ash, the downward move of nutrients through soil col-

Table 3
Effect of fly-ash on the rhizosphere population of PSB and available P_2O_5 content of soil under soybean crop.

Treatments	Available P_2O_5 in soil (mg kg^{-1})		Population ($\times 10^4$ g^{-1} soil)		Grain yield (g $plant^{-1}$)
	30[a]	90[a]	30[a]	90[a]	
F_0 (control)	14.3	10.2	–	–	4.23
F_0 + *P. striata*	19.3	17.7	14	16	7.0
F_{20}	24.3	19.8	02	02	6.07
F_{20} + *P. striata*	26.8	20.2	21	18	10.13
F_{40}	26.8	20.4	02	02	6.93
F_{40} + *P. striata*	34.7	27.0	28	15	11.67
F_{60}	26.8	18.6	04	04	27.0
F_{60} + *P. striata*	34.7	24.8	29	31	8.90
F_{80}	19.2	15.6	02	02	6.50
F_{80} + *P. striata*	29.4	25.4	16	12	6.07
S. Em±	2.4	3.1	0.81	0.82	1.8
CD ($P = 0.05$)	7.2	9.2	2.44	2.46	5.4

F_0, F_{20}, F_{40}, F_{60} and F_{80}, rates of fly-ash application to soil (t ha^{-1}); PSB, phosphate-solubilizing bacteria.
[a] These are sampling interval in days. Source: [67].

umn and the availability of nutrients for plant growth became limited to a depth of 80 cm from the soil surface [76]. According to Khan and Khan [44], a gradual increase in fly-ash concentration in the normal field soil from 0, 10, 20 up to 100% v/v increased the pH, thereby improving the availability of sulfate, carbonate, bicarbonate, chloride, P, K, Ca, Mg, Mn, Cu, Zn and B. They also found that addition of fly-ash to acidic and alkaline soil decreased the amounts of Fe, Mn, Ni, Co and Pb released from acid soil. However, the release of these metals from alkaline soil remained unchanged. The changes in the selected properties and heavy metal contents of three soil types in India were studied by Veeresh et al. [77]. The mixtures of soil with different proportion of fly-ash and sludge, either alone or in combination, at a maximum application rate of 52 t ha^{-1} were incubated for 90 day at near field capacity moisture level. Sewage sludge, due to its acidic and saline nature, high organic matter and heavy metal contents, had more impact on soil properties than the fly-ash. Electrostatic precipitator (ESP) ash collected directly from thermal power station in Bathinda, India, was more fine-textured, lower in pH and richer in nutrients than the ash of dumping sites [30]. The ashes had both higher saturation moisture percentage and lower bulk density as compared to the normal cultivated soils. The dominant cation on the exchange complex was found to be Ca^{2+} followed by Mg^{2+}, Na^{+} and K^{+} in addition to high S content. In a study with methi (*Trigonella foenum–graecum*), Inam [35] applied different basal doses of fly-ash at 0, 5, 10 and 15 t ha^{-1} along with two doses of nitrogen (40 and 20 kg ha^{-1}). Uniform basal dose of 30 kg P and 40 kg K ha^{-1} was also applied. In general, fly-ash at 10 t ha^{-1} with 20 kg N ha^{-1} proved better, while higher dose of fly-ash proved deleterious. Fly-ash is not recognized as an optimal source of phosphorus as it was found inferior to monocalcium phosphate [78]. However, it hastened Ca^{2+} and Mg^{2+} uptake by legumes [21].

6. Use of fly-ash in composting

In sewage sludge composting, lime is used to raise the pH and thereby to kill pathogens and to reduce the availability of heavy metals enriched in sludge [79]. Since alkaline coal fly-ash contain a large amount of CaO, it can serve the purpose of lime [80], as it reduced the availability of heavy metals by physical adsorption and precipitation at high pH [81]. Moreover, it is also cheaper than lime. Co-composting of fly-ash at 20% level with wheat straw and 2% rock phosphate (w/w) for 90 day recorded lowest C:N of 16.4:1 and highest available and total phosphorus [82]. Mixing alkaline fly-ash with highly carbonaceous acidic material to make compost for soil treatment had also been suggested [18]. The low nitrogen content of fly-ash is an important constraint for its agricultural application. In a study, Bhattacharya and Chattapadhyaya [83] investigated the possibility of improving the N status in mixtures of fly-ash and organic matter by implementing vermicomposting technology. Different combinations of fly-ash and cow dung viz., fly-ash alone, cow dung alone and fly-ash + cow dung at 1:1, 1:3 and 3:1 ratios were incubated with and without epigeic earthworms (*Eisenia foetida*) for 50 day. Results revealed that different bio-available forms of N, such as easily mineralizable NH_4^{+} and NO_3^{-}, considerably increased in the series treated with earthworms. It could be largely attributed to augmented microbiological activity in the vermicomposted samples and also to considerable rise in the concentration of N-fixing bacteria in this series. Among the three combinations, the highest availability of N was recorded in 1:1 mixture of vermicomposted fly-ash and cow dung. For proper fly-ash/sludge ratios, the fly-ash could also act as an outstanding neutralizer in the acidic waste. Leaching of heavy metals from the aggregate samples was below the environmental limits within a pH range between 3 and 9 [84,85].

7. Fly-ash for improving crop growth and yield

Several reports are available related to the use of fly-ash as a soil amendment for the benefit of a large number of field crops. The safe and sustainable use of sewage sludge/fly-ash combination on agricultural soils is suggested to be a highly promising endeavor from environmental point of view [86]. Fly-ash, having both the soil amending and nutrient-enriching properties, is helpful in improving crop growth and yield in low fertility acid lateritic soils [87]. Many researchers [2,21,32,56,78,88–93] have demonstrated that fly-ash increased the crop yield of wheat (*Tritiucm aestivum*), alfalfa (*Medicago sativa*), barley (*Hordeum vulgare*), bermuda grass (*Cynodon dactylon*), Sabai grass (*Eulaiopsis binata*), mung (*Vigna unguiculata*) and white clover (*Trifolium repens*) and improved the physical and chemical characteristics of the soil. Furr et al. [94] demonstrated that alfalfa, sorghum (*Sorghum bicolor*), field corn (*Zea mays*), millet (*Echinochloa crusgalli*), carrots (*Daucas carota*), onion (*Allium cepa*), beans (*Phaseolus vulgaris*), cabbage (*Brassica oleracea*), potatoes (*Solanum tuberosum*) and tomatoes (*Lycopersicon esculentum*) grew on a slightly acidic soil (pH 6.0) treated with 125 MT ha^{-1} of unweathered fly-ash and that these crops showed higher contents of As, B, Mg and Se. Application of weathered coal fly-ash at 5% resulted in higher seed germination rate and root length of lettuce (*Lactuca sativa*) [95]. The crop response to fly-ash application may vary widely from beneficial to toxic depending on the concentration of various elements present in it [32,96]. Application of fly-ash extract in the lower concentration range of 0.5–1.0% (w/w) had no significant effect on germination and seedling growth of corn and soybean, whereas higher concentration of fly-ash extract had deleterious effect on germination, viability, number of roots, shoot and root length, fresh weight and dry matter of seedling of both the crops [97]. Use of swine manure with fly-ash balanced the ratio between monovalent and bivalent cations ($Na^{+} + K^{+}/Ca^{2+} + Mg^{2+}$), which are detrimental to the soil and thereby increased the availability of Ca and Mg [98]. Application of fly-ash at 10 and 20 t ha^{-1} improved rice yield from 1.02 to 3.83 t ha^{-1} in 1979 and 4.65 t ha^{-1} in 1980. Similarly, wheat yield was improved from 0.57 t ha^{-1} (control) to 2.53 t ha^{-1} in 1979 and 2.85 t ha^{-1} during 1980s [99]. Amendment of fly-ash up to 40% improved the growth and yield of rice crop, whereas the gradual decline in plant growth and yield parameters was found from 60% to 100% fly-ash-amended soil. This adverse effect was attributed to salinity caused by higher levels of sulfate, chloride, carbonate and bicarbonate in fly-ash-amended soil [45]. Possessing alkalinity and containing some essential mineral elements, coal fly-ash could be an alternative to lime amendment and a nutrient source of container substrates for ornamental plant growth [100]. Fly-ash amendment also improved the performance of oilseed crops such as sunflower (*Helianthus* sp.), sesame (*Sesamum indicum*), turnip (*Brassica rapa*) and groundnut (*Arachis hypogaea*) [26,34,87,101,102]. According to Kuchanwar et al. [5], application of 10 t fly-ash ha^{-1} and 25:50:0 kg NPK ha^{-1} resulted in better growth and yield attributes which led to the highest pod yield of groundnut. Medicinal plants such as cornmint (*Mentha arvensis*) and vetiver (*Vetiver zizanoides*) were successfully planted in fly-ash mixed with 20% farmyard manure and mycorrhiza [103–105]. Amendment of different fly-ash–soil combinations resulted in high yield of aromatic grasses, particularly palmarosa (*Cymbopogon martini*) and citronella (*Cymbopogon nardus*), which was due to increased availability of major plant nutrients [106,107]. Lee et al. [108] applied fly-ash at 0, 40, 80, and 120 Mg ha^{-1} in paddy soil to determine boron (B) uptake by rice and characteristics of B accumulation in the soil. Results indicated that in all fly-ash treatments, B content in rice leaves and available B in soil at all growing stages were higher than those of control but all were below toxicity levels. Boron occluded in amorphous iron and aluminium oxides was 20–39% of total B and was not influenced by fly-ash application. Most of the B accumulated by fly-ash application was residual B which is of plant-unavailable form and comprised >60% of the total B in soil. Therefore, it could reasonably be stated that fly-ash could be a good soil amendment for rice production without B toxicity.

8. Saving of chemical fertilizers

Use of fly-ash along with chemical fertilizers and organic materials in an integrated way can save chemical fertilizer as well as increase the fertilizer use efficiency (FUE). According to Mittra et al. [109], integrated use of fly-ash, organic and inorganic fertilizers saved N, P and K fertilizers to the range of 45.8%, 33.5% and 69.6%, respectively, and gave higher FUE than chemical fertilizers alone or combined use of organic and chemical fertilizers in a rice–groundnut cropping system (Table 4).

9. Fly-ash as pesticide

According to Narayanasamy [110], more than 50 species of insect pests of various major crops were susceptible to fly-ash treatment. He also stated that fly-ash dusting at 40 kg ha^{-1} on rice could control both chewing and sucking pests such as leaf folder, yellow caterpillar, spiny beetle, ear head bug, brown bug, black bug, grasshoppers, brown plant hopper and green leafhopper. Serious polyphagous pests of cotton such as *Helicoverpa armigera* and *Spodoptera litura* also could be controlled effectively. Scientists from other research centres have also proved that the fly-ash could be effectively used to keep away pests from many vegetables such as brinjal, ladies finger, tomato and cauliflower. According to Narayanasamy [111], fly-ash controlled the larvae of crop pests by affecting their mouthparts and digestive system, and it could also induce plant resistance against diseases such as the blast fungus of rice. The addition of 5% fly-ash to soil was also found to significantly increase the growth of tomato plants and reduce the amount of galling on the roots caused by root-knot nematode [112]. The application of 30% fly-ash reduced the penetration and reproductive potential of root-knot nematode on tomatoes [113]. Alkaline fly-ash was added to swine manure at 10% and 20% (w/v), and production of CO_2 was studied over 12-day period [114]. They observed reduction in CO_2 production and concluded this as the effect of high pH value, caused by fly-ash addition, rather than inhibition of microbial activity and noticeable mobilization of inorganic phosphorus in the fly-ash-amended manure, probably as a result of microbial activity. Prospect of use of fly-ash as a dust insecticide, adjuvant in insecticide formulations and a carrier in pesticide formulation were also reported [115,116]. Bio-efficacy of fly-ash-based herbal pesticides on certain insect groups was tested by Arputha Sankari and Narayanasamy [117]. Among the eight fly-ash-based herbal pesticides applied to rice and vegetables, fly-ash + turmeric 10% dust and fly-ash + neem seed kernel 10% dust were found to be the

Table 4
Saving of chemical fertilizers and nutrient use efficiency under different modes of fertilization sources in rice–peanut cropping system.

Fertilization sources	Saving of chemical fertilizer (%)			Nutrient use efficiency (kg grain or kg pod kg^{-1} nutrient)		
	N	P	K	N	P	K
Chemical fertilizer (CF)	–	–	–	34.4	34.4	45.9
Organic[a] + CF	37.5	22.0	32.0	37.2	86.5	59.8
Organic + Fly-ash + CF	45.8	33.5	69.6	45.4	105.5	72.9

[a] Mean of farmyard manure and paper factory sludge at 30 kg N ha^{-1} for rice and half of these dose for peanut. Source: [109].

most effective against all the test insects, including *Epilachna* on brinjal and *Spodoptera* on okra, followed by fly-ash + vitex 10% dust and fly-ash + *Eucalyptus* 10% dust and fly-ash + *Ocimum* 10% dust. Thiyagarajan and Narayanasamy [118] reported successful use of fly-ash as an insecticide in horticultural crops. Development and use of four modes of fly-ash as termiticide was tried, and the results revealed that topical application of the fly-ash on termites was superior followed by fly-ash paste treatment, fly-ash-dusted wood and fly-ash + moist soil mixture against worker termites. Mandibulate type soldiers went through highest mortality with the topical application of fly-ash followed by fly-ash-pasted wood. However, no variation in the impact of the fly-ash application at different times of treatment was noticed [117]. Bio-efficacy of fly-ash-based herbal pesticides against pests rice and vegetable has been reported [119]. Pesticide dusting formulation with fly-ash up to 40% was a suitable dispersant to solve the problem of agglomeration in the case of pulverized white clay, and moreover, it also saved the time, electricity, manpower, natural resource with no adverse effect on paddy (*Oryza sativa*), tomato (*Solanum lycopersicum*), brinjal (*Solanum melongena*) and jatropha (*Jatropha curcas*) in the trials with regard to yield and quality [120].

10. Effect of fly-ash on uptake of nutrients and toxic elements and quality of crop yield

The high concentration of elements like K, Na, Zn, Ca, Mg and Fe in fly-ash increases the yield of agricultural crops. However, application of unweathered fly-ash may have a tendency of accumulating elements such as B, Mo, Se and Al, which at toxic levels are responsible for reductions in the crop yields and consequently influence animal and human health [121]. Fly-ash application might also decrease the uptake of heavy metals including Cd, Cu, Cr, Fe, Mn and Zn in plant tissues [122,123], which could be probably due to the increased pH of fly-ash-amended soil. According to El-Mogazi et al. [124], the supply of As from fly-ash to plants might be short-term. Integrated nutrient treatments involving fly-ash at $10\ \mathrm{t\ ha^{-1}}$, organic wastes and chemical fertilizers resulted in higher uptake of N, P, K, Ca, Mg, Fe, Mn, Zn and Cu in rice grain than application of only chemical fertilizers, which in turn was responsible for higher rice yield [125–127]. They also observed lower concentration of Cd and Ni in both grain and straw of rice and the reason might be the increase in soil pH due to the application of fly-ash to the rice crop which precipitated the native Cd and Ni. In rice-based cropping system, uptake of N, P, K, Ca, Mg, S, Fe, Mn, Zn and Cu by subsequent mustard crop was higher under the residual fertility of fly-ash at $10\ \mathrm{t\ ha^{-1}}$ + paddy straw at $5\ \mathrm{t\ ha^{-1}}$ + chemical fertilizers or fly-ash at $10\ \mathrm{t\ ha^{-1}}$ + farmyard manure at $5\ \mathrm{t\ ha^{-1}}$ + chemical fertilizers or fly-ash at $10\ \mathrm{t\ ha^{-1}}$ + green manure at $2.5\ \mathrm{t\ ha^{-1}}$ + chemical fertilizers as compared to chemical fertilizers or fly-ash alone [127]. According to Mittra et al. [109], the uptake of Zn, Cu, Cd and As by rice and peanut from fly-ash-amended soil were within the safe limits as given by Prevention of Food Adulteration Act (1997). Application of fly-ash-stabilized sludge to an acid loamy soil significantly increased the corn yield as well as reduced the uptake of heavy metals including Cu, Zn, Ni and Cd present in sludge [128]. Topac et al. [129] used lignite fly-ash as an additive in three different alkaline stabilization processes and tested the effects on some chemical properties of wastewater sludge. The results revealed that sludges added with 40% fly-ash (dry weight) caused no significant differences in the sludge properties; however, application of 80% and 120% fly-ash reduced the concentrations of NH_4–N, No_3–N, available P and soluble B in sludges. A significant decrease in available forms of N and P and a significant increase in pH were found in the processes of alkaline stabilization (10–15% quicklime + 40–120% fly-ash) and alkaline pasteurisation (10–15% quicklime + 40–120% fly-ash + heating at 70 °C for 30 min).

Alkaline fly-ash was also reported to act as binding agent for fixation of heavy metals and nutrients in waste and organic matters [114,130,131]. Some scientific workers used modified fly-ash for removal of pollutants from water and wastewater [132–135] and as adsorbent for water and wastewater reclamation [131]. Boron toxicity is the major problem in agricultural use of fly-ash. Co-application of a readily oxidizable organic substrate could prohibit B-induced inhibition of microbial respiration [21]. Increased selenium accumulation in plant tissues with increased fly-ash application calls for close examination and use of appropriate quantity of weathered fly-ash depending upon the end use of the produced biomass [25,136]. Rios et al. [137] observed that coal fly-ash can be used for removal of heavy metals like Fe, As, Pb, Zn, Cu, Ni, Cr from acid mine drainage. Goodarzi and Hower [138] tested fly-ashes produced from Canadian power plants using pulverized coal and fluidized bed combustors for their carbon content to determine their ability to capture Hg and reported that the quantity of carbon in the fly-ash alone does not determine the amount of Hg captured. The types of carbon like isotropic and anisotropic vitrinitic, isotropic inertinitic and anisotropic Petcoke, the halogen content, the types of fly-ash control devices, and the temperatures of the fly-ash control devices also play major roles in the capture of Hg. Wang et al. [139] tested single and co-adsorption of heavy metals and humic acid (HA) on fly-ash and observed that for single-pollutant system, adsorption of Pb^{2+} was at $18\ \mathrm{mg\ g^{-1}}$, Cu^{2+} was at $7\ \mathrm{mg\ g^{-1}}$ and HA was at $36\ \mathrm{mg\ g^{-1}}$, while in the case of co-adsorption, the presence of HA in water would provide additional binding sites for heavy metals, resulting in increased adsorption of Pb^{2+} and Cu^{2+} to 37 and $28\ \mathrm{mg\ g^{-1}}$, respectively, for Pb–HA and Cu–HA systems, respectively, at pH 5.0 and 30 °C. They reported that the heavy metal ions present in the system competed with the adsorption of HA on fly-ash, thus resulting in a decrease in HA adsorption.

11. Radionuclides in fly-ash

Compared to common soils or rocks, majority of fly-ash are not considerably enriched in radioactive elements or in associated radioactivity [140]. While less than 10% thorium is contained in phosphate minerals such as monazite or apatite, the concentration of natural uranium may vary from 14 to 100 $mg\,kg^{-1}$, and in exceptional cases, it may be as high as 1500 $mg\,kg^{-1}$ and it is concentrated more in finer-sized particles of fly-ash. Fly-ash contains the radiochemical pollution of uranium and thorium series [141,142] along with other radioactive contaminants like ^{222}Ru and ^{220}Ru [55]. Though several reports regarding the presence of radionuclides in fly-ash are available, studies on their impact are lacking [143]. The results of radioactivity analyses revealed that the activity levels of gamma emitting radionuclides ^{40}K, ^{226}Ra, ^{228}and Ac were within the permissible limits and that mixing of fly-ash with soil at 24% (v/v) was of no consequence [144]. Mathur et al. [145] investigated the radon exhalation rates in coal and fly-ash samples from the thermal power plants at Kolaghat (WB, India) and Kasimpur (UP, India) using sealed-can technique having LR-115 type II detectors. They observed that the radon exhalation rate from fly-ash samples from Kolaghat was higher than from coal samples and that the activity concentration of radionuclides in fly-ash was enhanced after the combustion of coal, while fly-ash samples from Kasimpur showed no appreciable change in radon exhalation. Papastefanou [146] examined the radioactivity of coals and fly-ashes in Greece and found that the activity concentrations of the coals ranged from 117 to 435 $Bq\,kg^{-1}$ for ^{238}U, from 44 to 255 $Bq\,kg^{-1}$ for ^{226}Ra, from 59 to 205 $Bq\,kg^{-1}$ for ^{210}Pb, from 9 to 41 $Bq\,kg^{-1}$ for ^{228}Ra and from 59 to 227 $Bq\,kg^{-1}$ for ^{40}K. He reported that these levels are comparable to those present in coals of different countries worldwide. The activity concentrations of the fly-ashes produced in coal-fired power plants ranged from 263 to 950 $Bq\,kg^{-1}$ for ^{238}U, from 142 to 605 $Bq\,kg^{-1}$ for ^{226}Ra, from 133 to 428 $Bq\,kg^{-1}$ for ^{210}Pb, from 27 to 68 $Bq\,kg^{-1}$ for ^{228}Ra and from 204 to 382 $Bq\,kg^{-1}$ for ^{40}K. These results indicated that there is an increment of the radionuclides in fly-ash as compared to the coal during combustion and the enrichment factors ranged from 0.60 to 0.76 for ^{238}U, from 0.69 to 1.07 for ^{226}Ra, from 0.57 to 0.75 for ^{210}Pb, from 0.86 to 1.11 for ^{228}Ra and from 0.95 to 1.10 for ^{40}K. Mittra et al. [109] found that fly-ash-amended soil at 40 $t\,ha^{-1}$ showed higher radioactivity ($Bq\,kg^{-1}$) of ^{226}Ra, ^{228}Ac and ^{40}K than fly-ash and for ^{137}Cs the trend was reverse. They also reported that the radioactivity due to the addition of fly-ash was due to dilution effect of soil, though these marginal variations were within the safe limits. Kumar et al. [147] observed that the radon exhalation rate from fly-ash was less than that from soil and coal, although fly-ash contains a higher concentration of uranium than typical soil.

12. Effect of fly-ash on ground water

Physical and chemical characteristics of fly-ash and hydrogeologic and climatic conditions of the disposal site are the main factors, which determine the influence of ash on ground water [148]. Weathered fly-ash contains higher level of soluble salt; therefore, deposition of this ash causes more ground–water contamination. In case of unweathered ash, there is generally a higher release of soluble salts initially, but it declines rapidly with time [12,149,150]. When water saturated, weathered ash from a settling pond is deposited in a landfill, there is a rapid release of leachate containing much lower concentration of soluble salts, while it may take a year or longer for dry unweathered ash to absorb sufficient moisture to release leachates [150].

Fly-ash contains trace and heavy metals, which readily percolate down from conventionally used earth-lined lagoons. The solubility of trace and heavy metals present in fly-ash is <10% [151]. Laboratory experiments by Natusch [152] revealed that 5–30% of toxic elements especially Cd, Cu and Pb are leachable. Moreover, the concentration of these elements in fly-ash is very low; hence, the chance for leaching of these elements to ground water is negligible. However, close monitoring of this aspect may be advisable. Experiments conducted at Central Fuel Research Institute (CFRI), Dhanbad, India showed that there was no negative influence of fly-ash application on the quality of ground water and that the trace and toxic metal contents were within the permissible limits. The potential use of fly-ash from coal-fired power plant for the removal of Zn(II) and Ni(II) from aqueous solutions has been reported by Cetin and Pehlivan [53]. A study conducted on soils from Italian mine site contaminated severely with heavy metals showed decreased levels of heavy metal content in percolating water when mixed with fly-ash, which was indicative of the fact that fly-ash in such soils can lead to immobilization of heavy metal ions [153].

13. Fly-ash utilization and global warming

Agriculture plays a major role in the global fluxes of the greenhouse gases like carbon dioxide, nitrous oxide, and methane. Many studies suggested that additional opportunities have arisen for lessening the GWP (global warming potential) by altering the agronomic practices [154]. With the assumption by the Intergovernmental Panel on Climate Change (IPCC) that all the carbon in agricultural lime (aglime) is eventually released as CO_2 to the atmosphere, the US EPA estimated that 9 Tg (Teragram $= 10^{12}$ g $= 10^6$ metric tonne) CO_2 was emitted from an approximate 20 Tg of applied aglime in 2001 [155]. As per another estimate, in US agriculture only, aglime is applied to the tune of 20–30 $Tg\,year^{-1}$ and the same study estimated that 4.4–6.6 Tg CO_2 was emitted in 2001 from that lime [156]. Bernoux [157] estimated the net CO_2 fluxes from liming of agricultural soils in Brazil for the period 1990–2000.

The calculation was based on the methodology proposed by the IPCC, but separately conducted for the five administrative Brazilian regions. The summarized annual CO_2 emission for Brazil varied from 4.9 to 9.4 Tg CO_2 $year^{-1}$ with a mean CO_2 emission of about 7.2 Tg CO_2 $year^{-1}$. But agricultural lime can be a source or a sink for CO_2, depending on whether reaction occurs with strong acids or carbonic acids. A study showed that infiltrating waters tended to indicate net CO_2 uptake, as did tile drainage waters and streams draining agricultural watersheds. As nitrate concentrations increased in infiltrating waters, lime switched from a net CO_2 sink to a source, implying nitrification as a major acidifying process [158]. One experimental study demonstrated that 1 ton of fly-ash could sequester up to 26 kg of CO_2, i.e., 38.18 ton of fly-ash per ton of CO_2 sequestered. This confirmed the possibility to use this alkaline residue for CO_2 mitigation [159]. Use of fly-ash as soil ameliorant in place of lime could lead to reduction in CO_2 emissions, thus contributing to minimize global warming [160].

14. Summary

To meet the growing energy demand and thereby increase power generating capacity, the dependency on coal for power generation and disposal of fly-ash will continue to increase along with various unavoidable problems. Moreover, keeping in view of developmental problems like burgeoning population, growing food demand, shrinking natural resources, it is necessary to sustain the production of crop yield as well as soil health in an eco-friendly way. Hence, it is required to involve fly-ash more effectively in agriculture sector to exploit its various physical and chemical properties fully, which are beneficial for soil and crop health.

In view of the above discussions, the salient points from this extensive review could be summarized in the following sections:

(1) Advantages of fly-ash use in agriculture:

(i) It could be stated that the potentiality of fly-ash for its use in agriculture is popularizing day by day due to the fact that it contains almost all the essential plant nutrients i.e., macronutrients including P, K, Ca, Mg and S and micronutrients like Fe, Mn, Zn, Cu, Co, B and Mo, except organic carbon and nitrogen.

(ii) It is now well proved that though it can substitute lime, a costly amendment for acid soils, it cannot be a substitute for chemical fertilizers or organic manures. However, integrated application of all these can foreshorten the plant uptake of different heavy metals from fly-ash-amended soils as well as can reduce the use of chemical fertilizers and thereby reduces environment pollution.

(iii) Fly-ash is also useful for stabilizing erosion-prone soils. Phytoremediation can prevent cycling of toxicants from fly-ash and growing of multipurpose tree species on problem soils.

(iv) According to IPCC, agricultural lime application contributes to global warming through emission of CO_2 to the atmosphere. Use of fly-ash instead of lime as soil ameliorant can reduce net CO_2 emission and thereby lessen global warming.

(2) Disadvantages/apprehensions that need further research:

(i) In spite of several advantages of using fly-ash in agricultural field, many are afraid of its natural radioactivity and heavy metal content. Researches have proved that the effect of this radioactivity and heavy metal content is in the safe limit if fly-ash is being applied in optimum quantity. However, long-term confirmatory research and demonstration are necessary for convincement at the grass root level, as is the case for any new agricultural input materials like fertilizers, amendments or pesticides.

(ii) As in the case with fertilizers and any other agricultural inputs, the amount, time and method of fly-ash application would vary with the type of soil, the crop to be grown, the prevailing agro-climatic condition and also the type of fly-ash available. Research on these aspects needs attention for utilization of fly-ash in a better way.

(iii) Simultaneously, in future, attention should be given on some important areas related to fly-ash utilization, like proper handling of dry ash in plants as well as in fields, ash pond management (i.e., faster decantation, recycling of water, vertical expansion rather than horizontal, etc.), long-term studies of impact of fly-ash on soil health, crop quality, and continuous monitoring on the characteristics of soil as well as fly-ash.

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