



## Assessment of heavy metals in fly ash of coal fired thermal power stations in Nellore, Andhra Pradesh, India

Vardi Venkateswarlu\* and Chenji Venkatrayulu

Department of Marine Biology, Vikrama Simhapuri University, Nellore-524320, Andhra Pradesh, India  
venkat9160@gmail.com

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### Abstract

Continuous production of laid-off ash from the coal-fired thermal power stations and its commercialism in Asian nation has triggered a relentless invasion of the useful territory. Because of its sensible texture and also the existence of damaging metals, the harmful effects of ash on the close surroundings area unit inevitable. Agriculture is one amongst many selections for the discarding of ash, a dangerous particulate contents made from thermal power plants based by coal fired sources. Ash includes crop development useful micro-and macronutrients. It conjointly includes virulent significant metals, however, which might migrate to crops and accumulate toxicity to crops and farm animal. Accumulation of metals in secondary substance crop parts chargeable for a selected pharmacologic activity. Advantage to their absence of biodegradability, the matter of significant metal emissions is incredibly disquieted due to their toxicity to plants, animals, and humans. Abundance focuses of significant metals have unfavorable impacts of metabolic activities hence have an effect on food production, quantitatively and qualitatively. Significant heavy metal could have a serious impact on their health if it enters human tissues through distinct mechanisms of absorption. Continuing exposure to heavy metals such as Arsenic (As), Lead (Pb), Cadmium (Cd), Mercury (Hg), Iron (Fe), Manganese (Mn), Copper (Cu), and Zinc (Zn) may trigger harmful impacts on human health. This paper tries to focus the use and their issues of fly debris bearing overwhelming heavy metals.

**Keywords:** Fly ash, heavy metals, pollution, nellore.

### Introduction

Coal is the main fossil fuel source for producing 30 percent of the global primary electricity. Coal occupied a major position in the Indian energy-producing sector since India has vast reserves of thermal grade coal. Coal is the most abundant and widely spread fossil energy resource in the world<sup>1</sup> among the total power production yearly in India, about 70% is produced by thermal power plants. The majority of thermal power plants (about 85%) are running on coal with 70 billion tons of coal reserve, while the remaining 13% run on gas and 3% on oil. About 112 million tons of fly ash is being generated annually in India by thermal power plants as a byproduct of coal combustion<sup>2</sup> Fly ash quality mainly depends on coal type used in the thermal power plants, Coal particle fineness and proportion of ash in coal, combustion methods, air / fuel ratio, and type<sup>3</sup> boiler. Fly ash disposal is regarded to be a potential cause of contamination owing to the enrichment and surface combination of trace elements in ash particles<sup>4</sup>. In the combustion process, the components in coal are significantly unstable. The components, however, appear to have lower fractions volatilized during combustion, while some components are either not evaporated or demonstrate only very rare methods linked to mineral material related to geological chemistry<sup>5</sup>.

These solid waste material of particulate fly ash can be released in more concentrations than safe standards of drinking water

and may lead to aquatic resources pollution. Fly ash contains smaller ranges of harmful toxic heavy metals that may have adverse effects on human health and on plants<sup>6</sup> Solid waste covers more land room and creates pollution of the environment. The use of dust base ash from thermal power stations currently involves preparation of brick, construction of roads, construction based concrete and cement manufacturing. Fly ash recognized as a valuable mineral source and the advancement techniques for high value-added use of coal fired fly ash is important<sup>7,8</sup>. Environmental contamination owing to harmful heavy metals was risen more potentially in nowadays and attained warning rates as far as its impact on life. Therefore, toxic metal will never change as favorable final output products<sup>9</sup> they are hard to biologically degrade. In an environment, heavy metal contamination is mainly caused by emend ores, quarrying, waste dumping, metal coating and fly ash burning furnace, preparation of nuclear stuff, dye products, blends, batteries, insecticides and preservatives<sup>10</sup> as original components of the earth's layers, heavy metals happen as their components in various non-biological structures, from which they are recovered as minerals and are consistent ecological contaminants. Through biological and food cycles they enter the metabolic system and disposition over a period of time process in the human, plant, and animal health system.

To develop value-added ash usage techniques, understanding the features of ash particles and transforming carbon minerals

during combustion are crucial. There are two forms of minerals in coal, i.e. innate inorganic mineral substances that distribute within coal particles and cannot be removed away by cleaning procedures; and remaining discrete minerals are divided from coal particles and can be removed by washing. It is very complex to transform solid fuel fossil minerals into ash during burning in boilers. Approximately 80 percent of coal minerals are changed during pf combustion into light weight ash. The composition of coal ash is intricate, containing shapeless particulate materials and crystals like sand silicate, porcelonite, ferric oxide, quick lime, etc. Some of the particulate ash material possess an elevated concentration of iron and are called magnetic microspheres. There may also be some permeable carbon compound particles in the<sup>11,12</sup> coal fired fly ash. Some vacant weightless ash particles are created during pf carbon combustion at elevated temperatures, known as light weight hallow materials, and their formation was reported in some studies<sup>13,14</sup>. Light weight hallow materials and filling materials or coating due to their properties such as less bulk density, less thermal conductivity, less electric conductivity, excellent chemical stability, etc. Cenospheres with their size <10 µm are called superfine cenospheres and can be used as amalgam mixture materials for making latex elastic materials and polymers, as well as sophisticated composites. Analysis of ash features is helpful for understanding and promoting the development of various ash particles. Studies have clarified that heavy metals such as Fe, Cu, Zn, Ca, and Mg are healthfully fundamental to a working life, yet gigantic measures of any of these can trigger negative hurting, while others, for instance, As,

Cd, Pb, and Hg are of no known bio-essentialness in human natural science and physiology and can be dangerous even at uncommonly little levels. Relentless significant metal intoxications hurt the central tangible framework, lungs, kidneys, liver, the cardiovascular and gastrointestinal (GI) structures, endocrine organs and bones and may fabricate the threat of certain dangerous developments. Generous metals can be transmitted into the earth by trademark and anthropogenic poisons like mechanical wastewaters from mining, metal getting ready, pharmaceuticals, tanneries, pesticides, flexible and plastics, natural synthetic concoctions, timber and wood items. In this way to maintain a strategic distance from wellbeing perils it is fundamental to expel these dangerous substantial metals from wastewaters before their transfer<sup>15,16</sup>.

**Fly ash generation:** Fly ash is produced in the thermal power plant at the point when coal is nourished into a sequence of mills pulverizingat the point when coal is nourished. In the boiler that burns the coal to generate heat, this powder is subsequently supplied. In particular, the thermal power plant uses three kinds of coal-fired boiler furnaces. They can be called dry-base boilers, wet-base boilers, and heaters of the typhoon. The dry- base bottom furnace is frequently used<sup>18</sup>.

Fly fiery remains is created by consuming pummeled coal in the evaporator heater and shipped by pipe gas, passing one by one to the re-heater, economizer and air preheater in the superheater from there. At last, entered into the precipitator electrostatic. The route of flue gas is indicated in Figure-1.

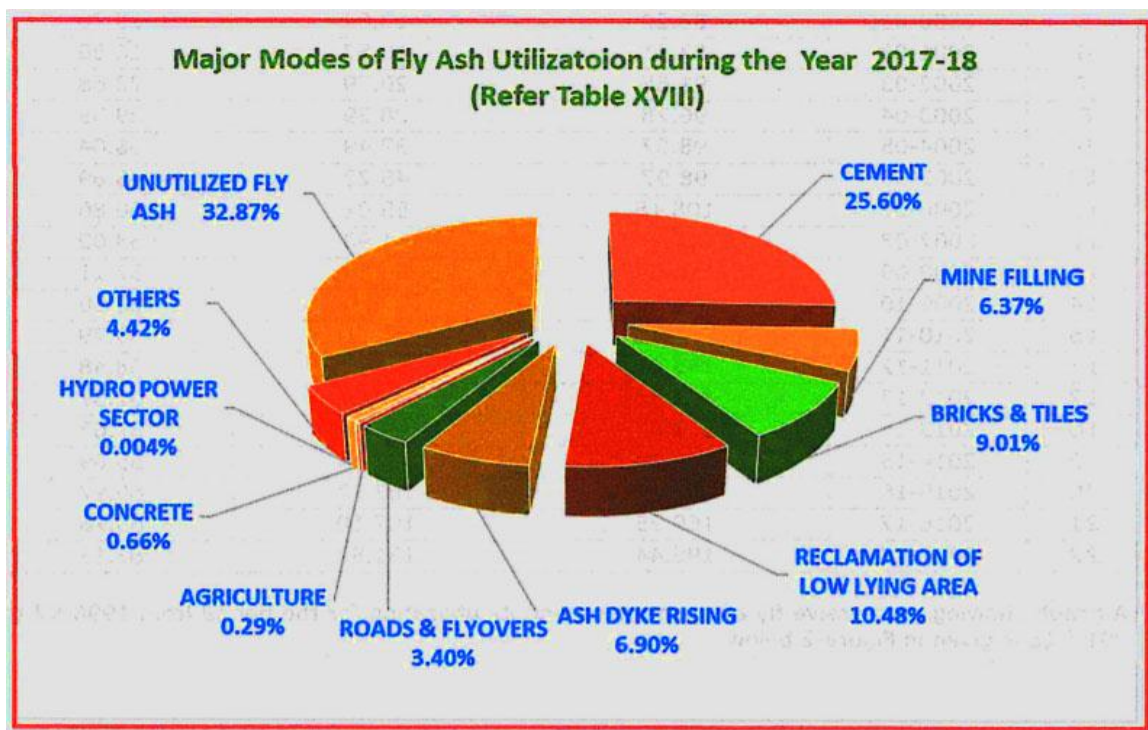


Figure-1: Fly debris usage in Indian situation, in various parts/businesses in the year 2017-18.<sup>17</sup>

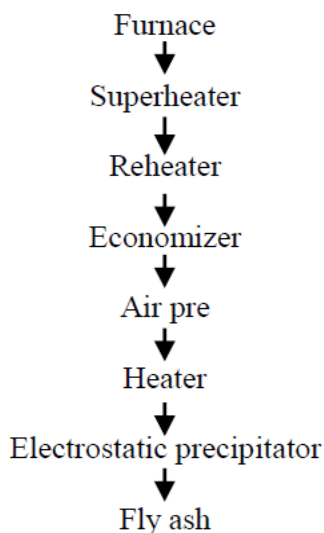


Figure-2: Pathway of fly ash generation<sup>19</sup>.

**Fly ash properties:** Szponder and Trybalski 2009<sup>20</sup> indicated in energy boilers that fly slag is inorganic buildup from coal ignition. FA has a wide variety in morphology, stage and concoction structure dependent on the utilization of unmistakable ignition strategies (standard and fluidized bed boilers), fuel arrangement (bituminous coal, lignite, and biomass), raised mineral scattering in energizes, and warmth process elements. There are three central FA bunches silicate fly fiery debris (sFA), aluminum fly slag (aFA) and calcium fly powder (cFA).

**Physical properties:** Fly ash is generally colored light dim to dark (contingent upon the amount of buildup of unburned carbon and natural issue). Some of the time the shading might be light darker to dull dark colored (for the most part from the burning of darker coal and biomass). FA (fly slag) comprises of fine, shiny particles, which range in molecule size from 0.01 to 100  $\mu\text{m}$ . Their structure is overwhelmed by circular grains (mineral or undefined), either strong (Pirospheres), honor (cenospheres) or loaded up with littler indistinct particles (Plerospheres). These grains show up independently, or as totals. Likewise, there is an enormous gathering of sporadic, exceptionally permeable, adjusted or sharp-edged paticles in solfa syllable (carbon development and dregs). solfa syllable incorporates a Low Mass thickness, high surface scene, and light-weight surface<sup>21</sup>.

## Materials and methods

**Study area:** The present examination stations led at Nelaturu, Muthukuru encompassing regions of the Nellore, this region is secured with about four warm power stations and these encompassing force plants are utilizing bituminous and sub-bituminous coals mined from Indian coalfields while some of utilizing imported coal. The nearby fly fiery remains block creators are buying the fly powder from the warm power plants

and utilizing that fly slag for causing concrete and fly to approach blocks for utilizing the development reason.

**Sample collection:** Two coal fly ashes named as Fly Ash #1(FA1), Fly Ash #2 (FA2) were collected from Fly Ash brick makers, the source of the fly ask from three full-scale thermal power plants in and around Nelaturu, Muthukuru areas of Nellore. The fly ash samples collected by following the quality sample assortment protocol and tips given in Indian Standards strategies IS 3025 part-1 and American Public Health Association (APHA) twenty-second edition<sup>21</sup>. The ash content of FA2 is about 10-15% while that of FA1 and FA is 35%, also these are rich in sand respectively. The special precautions were taken throughout the sampling of water within the elite places of study areas. Before the gathering of the samples, the sample containers square measure soaked night long in a pair of aqua fortis and washed with double  $\text{H}_2\text{O}$  and dried during a clean space. At every sampling location, water samples were collected in 2 pre-cleaned containers for duplicate mensuration. The bottles were rinsed thrice with the coastal saltwater sample of the actual location. Total 0.5 mL of above pure grade aqua fortis was added into the collected samples to avoid the contamination and also to stop the loss of metals from the sample. All the collected samples were preserved at 4°C by employing a thermo-coal box with ice packs at the sample assortment site.

**Sample preparation for analysis:** Dry Ash test 1.8 gram was weighed into Teflon vessel so as to decide the all-out substance of overwhelming metals. Five milliliters 70 percent conc.  $\text{HNO}_3$  and 2 mL of HF was added to these vessels and put away for assimilation in an auto digester called the Multivalve Microwave Digestion System (MDS) at a temperature of 280°C and weight of up to 35 bars for 20 minutes. After the absorption procedure, the example was sifted and moved to a volumetric flagon and the volume was made up to 50 mL. Nitric corrosive ( $\text{HNO}_3$ ) for the absorption of the example was finished to be appeared in the funnel shaped carafe by a light shading clear arrangement. Washed and separated with refined water after that funnel shaped flagon. At that point the filtrate was moved to a volumetric jar of 10 mL with two 5 ml of water, adding these flushing to the volumetric carafe, cooled and weakened to the imprint and altogether blended<sup>21</sup>. A segment of the example answer for the metal judgments required moving through APHA<sup>22</sup> was taken.

**Heavy metals analysis by Atomic Absorption Spectroscopy:** AAS is most broadly utilizing a systematic procedure for the assurance of follow and overwhelming metals up to parts per billion levels. AAS is a valuable strategy to decide follow levels of multi-components in single goal. AA-6800 AAS combined with GFA-EX7 graphite heater atomizer and ASC-6100 autosampler from Shimadzu (Koyoto, Japan) was utilized for substantial metal examination. A high-thickness graphite cylinder was utilized for atomization. Ordinary single empty cathode lights were utilized for illumination pursued by APHA<sup>22</sup>.

## Results and discussion

The scope of the attributes of base cinder got from family units is outlined in Table-1 as far as the overwhelming metal substance. The information contained in this table give the groupings of components decided after APHA procedure. AAS is most broadly utilizing a systematic procedure for the assurance of follow and overwhelming metals up to parts per billion levels. AAS is a valuable strategy to decide follow levels of multi-components in single goal. AA-6800 AAS combined with GFA-EX7 graphite heater atomizer and ASC-6100 autosampler from Shimadzu (Koyoto, Japan) was utilized for substantial metal examination. A high-thickness graphite cylinder was utilized for atomization. Ordinary single empty cathode lights were utilized for illumination pursued by APHA 22.

**Table-1:** Heavy metal concentrations (Mean±SD) of fly ash.

Heavy Metal	FA1	FA2
Arsenic (As)	1.86±0.18	2.12±0.22
Lead (Pb)	21.31±2.94	19.84±2.61
Cadmium (Cd)	ND	ND
Mercury (Hg)	ND	ND
Iron (Fe)	22723.46±463.57	29286.74±526.68
Manganese (Mn)	315.88±26.74	309.69±29.67
Copper (Cu)	27.23±4.95	28.54±5.26
Zinc (Zn)	122.49±18.16	132.96±21.88

N.D-Not Detected.

Concentrations of elements (As, Pb, Cd, Hg, Fe, Mn, Cu, Zn) determined in two different types of coal fly ash samples (FA1 and FA2), and the final data arrived from the duplicate analysis presented in Table-1. The concentration of heavy metals in fly ash samples followed the order of abundance was Fe>Mn>Zn>Cu>Pb and As in the fly ash samples.

This could be due to the finer grain size of fly ash samples, which provided greater surface area for adsorption of heavy metals or alternatively leaching of heavy metals in fly ash samples could have resulted in the relative enrichment of these elements in coal fly ash samples. Toxic elements in fly ash are preferentially enriched in a thin layer at the particle surface and may be more readily leached in water than from the bulk ash constituents<sup>23</sup>.

Internal variations within different samples of either type indicate the differential extent of leaching one pondydyke than another. Among all the elements studied here, a strong

correlation was observed for the six overwhelming metals As, Pb, Fe, Mn, Cu, and Zn in two samples collected from Nelaturu, Muthukuru areas of Nellore. These are the metals, which are harmful to our environment if their concentration goes beyond certain threshold values in water, soil, and sediments through leaching or other changing local environmental conditions.

If we are looking for a way to use bottom ash from homes, the processes outlined in the Waste Act need to be followed first. The waste must be recycled to the biggest possible extent on the grounds of the rules described in this law and, lastly, must be used with due regard to ecological security criteria. One approach to reuse the base cinders from fuel burning incorporates a technique called R10 - land treatment that advantages cultivating or biological improvement<sup>24</sup>. Therefore, the results of the degrees of the particular overwhelming metals decided in this examination were appeared differently in relation to the data in the principles set out in the Minister of Agriculture and Rural Development's Regulation actualizing a part of the guidelines of the Fertilizer Act<sup>25</sup>.

**Arsenic (As)** concentrations were observed 1.86±0.18 in FA1, 2.12±0.22 in FA2. The maximum concentrations were observed in collected FA1, FA2. Long-time exposure to arsenic can cause cancer in the skin, lungs, bladder, and kidney. It can also cause other skin changes such as thickening and pigmentation<sup>25</sup>.

**Lead (Pb)** concentrations were observed 21.31±2.94 in FA1, 19.84±2.61 FA2. The maximum concentrations were observed in collected FA1, FA2. Lead is an exceptionally harmful metal substance, introduction to which can create a wide scope of unfriendly wellbeing impacts in the two grown-ups and kids. Consistently, ventures delivering about 2.5 million tons of lead all through the world that utilized for making batteries. In grown-ups, lead can build pulse and mess fruitlessness up, nerve issue, muscle, joint torment, fractiousness, and memory or fixation issues come<sup>26,27</sup>.

**Cadmium (Cd)** were not detected in both FA1 and FA2 samples. Cadmium focuses on the liver, placenta, kidneys, lungs, mind, and bones. Utilization of nourishment or drinking water with high cadmium levels seriously bothers the stomach, prompting heaving and looseness of the bowels and some of the time causes passing<sup>28</sup>.

**Mercury (Hg)** was not detected in both FA1 and FA2. There are three types of mercury and among these the most lethal one is the natural structure, viz., methyl mercury. Methyl mercury is a microbiologically changed type of inorganic mercury when it arrives at sea-going situations, water bodies or in soils. Inorganic and natural mercury is poisonous to the human body in various manners, influencing various organs in various ways it might essentially open to mercury by means of nourishment, where fish is the significant wellspring of methyl mercury presentation by bio amplification. Mercury has no important capacity in any living being and is considered as an insignificant

metal, and is among the most lethal components to man and numerous higher creatures<sup>29</sup>.

**Iron (Fe)** concentrations were observed 22723.46±463.57 in FA1, 29286.74±526.68 in watched high in FA2 than FA1. A wide extent of pernicious free radicals is formed when the ingested iron fails to bind to the protein, which along these lines truly impacts the centralization of iron in mammalian cells and natural fluids. This orbiting unbound iron results in the dangerous effect of the gastrointestinal tract and common fluids. Higher centralization of iron goes into the body crossing the rate-limiting maintenance step and winds up drenched. These free iron can clearly penetrate into cells of the heart, liver, and psyche. As a result of oxidative phosphorylation by free iron, the ferrous iron is changed over to ferric iron that releases hydrogen particles, as such extending metabolic destructiveness. The free iron can moreover provoke lipid peroxidation, which results in genuine mischief to mitochondria and other cell organelles<sup>30</sup>. The lethality of iron on cells has incited iron-interceded tissue damage including cell oxidizing and decreasing parts and their toxic quality towards intracellular organelles, for instance, mitochondria and lysosomes. A wide extent of free radicals that are acknowledged to cause potential cell damage is conveyed by bounty affirmation of iron. The iron conveyed hydrogen free radicals strike DNA, realizing cell mischief, change, and compromising changes which in this manner cause an assortment of infections<sup>31</sup>.

**Manganese (Mn)** concentrations were observed 315.88±26.74 in FA1 and less observed 309.69±29.67 than FA1 in FA2. Manganese brings about a decline in fetal weight and hindrance of the advancement of the skeleton and inward organs<sup>32</sup>. What's more, manganese causes DNA harm and chromosomal distortions and was poisonous to the developing life and fetus<sup>33</sup>. Epidemiological investigations of inhabitants presented to manganese uncovered a neurotoxic impact and Parkinson-like disorder<sup>34</sup>. In people presented to elevated levels of this metal, manganese can aggregate in different cerebrum areas, prompting neurotoxicity<sup>35</sup>. It has been hypothesized that manganese might be engaged with the age of responsive oxygen species and generation of oxidative pressure<sup>36,37</sup>.

**Copper (Cu)** concentrations were observed 27.23±4.95 in FA1 and FA2 28.54±5.26 was observed high than FA1. Copper is one of the essential metals to life despite being as inherently toxic as non-essential heavy metal exemplified by lead and mercury. Plants and animals rapidly accumulate it. It is toxic at minute low concentration in water and is known to cause brain damage in mammals. The natural inputs of copper to the marine aquatic environment are from erosion of mineralized rocks or maybe from the industries. Anthropogenic inputs of copper are from electrical spare parts industries, paints and lubricants. It also forms complexes with organic molecules. Mollusks have a tremendous capacity to accumulate copper from contaminated water CPCB<sup>38</sup>.

**Zinc (Zn)** concentrations were observed 122.49±18.16 in FA1 and observed high than FA1 in FA2 range 132.96±21.88. Zinc is a fundamental supplement for the human body and has significance for wellbeing additionally it goes about as a reactant or auxiliary segment in numerous compounds that are associated with vitality digestion moreover. Manifestations of zinc harmfulness are moderate reflexes, tremors, deadening of limits, weakness, metabolic issue, teratogenicity impacts and expanded mortality in people CPCB<sup>38</sup>.

This was performed to break down the potential for base powder to be applied as a mineral manure or stimulant for advancement. Just data about the reasonable measure of lead and cadmium, for example 140 mg/kg d.m. what's more, around 50 mg/kg d.m. Both in the compost. It isn't basic to test the convergences of staying substantial metals as per this regulation<sup>39</sup>. This infers the waste can be utilized for cultivating purposes. Another measure that increases critical fame and is applied to the utilization of base powder incorporates its execution for post-mechanical fields and landfill locales restoration. In view of base fiery debris mixed with balanced out sewage slime, the material utilized for such restoration is created. In this technique, wastewater muck is coupled in a mass proportion of 1:140 with fiery debris assembled specifically.

The presentation of this material into the landfill site's surface layer may bring about an ascent in soil natural issue content and an expansion in soil supplement content. The higher mass of organic material, in turn, adds to the initiation of topsoil procedures and can thus boost the concentrations of absorbable nutrient types in the soil. These procedures generate more favorable circumstances on post-industrial and degraded lands to support vegetation.

## Conclusion

Environmental pollution from fly ash and industrial effluents are of particular interest as they pose an important threat to human wellbeing and nature. Because of its extraordinary physical and synthetic properties, fly fiery remains can be utilized in farming. FA has a particular structure and incorporates almost every one of the supplements expected to develop and create crops appropriately. To begin with, fly slag is utilized as a mineral manure that upgrades soil properties. It can likewise be applied as a specialist, which expands plant development and the measure of the got yields. Albeit fly powder application in horticulture has numerous advantages, there are a few drawbacks associated with this application cause overwhelming metals and radionuclides pollution of soils and surface waters, soil saltiness. Furthermore, there is likewise hazard related with absence of data on the long stretch effects of fly soot application on soil quality and condition. The immense application bought not to be suggested for developing yields, it is attractive to screen the substantial metal substance normally in plant parts to guarantee that it doesn't surpass the edge estimation of human utilization. Accordingly, it is important to proceed with research

on this theme to explain the impacts of the fly fiery debris expansion to the dirt on farming creation and the earth.

This is indicative of the leaching of these metals from dike samples and suggests dike coal fly ash can become more harmful to the environment. This shows that after dumping of fly fiery remains, the concentration of mobile, and mobilizable metals increases, subject to changing environmental conditions. This mobilizable fraction will be easily available to the terrestrial and aquatic systems. Since various possibly unsafe substance components are discharged from fly cinder, coming about because of the ignition of coal for electric power age, the development of these synthetic concoctions into water and natural pecking order is of genuine concern before their application in landfilling and agricultural activities. We propose a long term study should be carried out on the present as well as previous disposed fly ash sites. The long term leaching effects from old fly ash deposits need to be understood.

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