



HEAVY METALS LEACHING CHARACTERISTICS FROM COAL FLY ASH OF THREE THERMAL POWER PLANTS AND ITS ADVERSE EFFECTS ON ENVIRONMENT

Shyoraj Singh^[a], Netra Pal Singh^{*[b]}, and Rekha Rani^[c]

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Huge amount of coal fly ash, generated from power plants which contain trace toxic metals also like Pb, As, Hg, Ni, Cd and Ba etc., is considered as an environmental hazard worldwide. These toxic elements are leached into water, soil and ground water from coal fly ash and contaminate them. The leaching behaviour of trace toxic elements as a function of liquid/solid (L/S) ratio present in coal fly ash from three coal-fired power plants were studied by conducting US EPA leaching test methods (LEAF). The test has been conducted under a different range liquid to solid ratios. Most of trace elements show similar nature of liquid/solid partitioning (LSP) curve in the different coal fly ash samples in the leaching tests despite of elemental and mineralogical compositions and different ranks of coals fly ash. LSP curves of trace elements from fly ash samples in the L/S ratios tests (LEAF) shows some variations also. The present study is an assessment the leachability of trace elements in three coal fly ash samples collected from three power plants by LEAF at different L/S ratios.

* Corresponding Authors

E-Mail: npsmcm.in@gmail.com

- [a] Department of Chemistry, Meerut College Meerut, Ch. Charan Singh University Meerut- 250003, India
 [b] Department of Chemistry, Deen Dayal Upadhyaya Gorakhpur University, Gorakhpur- 273009, India
 [c] Department of Zoology, Nayug Kanya Mahavidyalaya, Lucknow -226004, India

(67.13 %) coal fly ash utilized against 196.44 MT generation of coal fly ash in 2017-18. Globally approximately annual generation of coal fly ash has reached 600–800 MT in 2014.⁷ India is mainly dependent on imports of fossil fuel to meet its energy requirement and by 2030, dependence on energy imports is expected to exceed 53 % of India's total energy consumption. In 2018, geological resources of coal in India have so far been estimated as 326.05 Billion tones.

INTRODUCTION

Coal and oil are two main resources of energy worldwide; coal is the most abundant and used extensively as fuel to produce electricity in different countries¹ and has been used in worldwide for decades. Coal is known as one of the most vital natural resources of energy and supported the high-speed economic development.² It was responsible for industrial revolution and in developing countries energy requirements met by mainly coal-based thermal power plants. Coal fly ash residue in powdered form is produced after combustion of coal in power plants.³ Coal-based power generation produces huge amounts of fly ash as coal residue, about 110 MT of coal fly ash was generated on average in India through power plants till 2008 increasing to about 230 MT in 2011,⁴ which may increase to about 442 MT annually by the end of 2035. India together China and US accounted for more than two thirds of global increase in energy demand. It is anticipated to manifold shortly as per report of US Energy Information Administration. Despite of increase of renewable energy resources, about 29 % of the total energy consumption production of world was from coal thermal power plants in year 2015 and it is expected that this share will remain 24 % in 2035 and energy consumption is also will be increased about 30 % by 2035. The amount of coal consumed per year is expected to increase from 3840 MT oil equivalent (mtoe) in 2015 to 4032 mtoe in 2035.⁵ In 2014, about 500 MT coal fly ash produced in U. S. A. and it has reached up to approximately 750 MT by 2015.⁶ Indian coal has high ash content, about 30-45 %. Total 131.87 MT

Worldwide, coal fly ash is the typical solid waste produced in power industry, its physical and chemical properties are mostly responsible for serious environmental pollution. Over sized ash ponds are unable to control huge amount of ash and breach, causing numerous ecological problems and severe below distress to the ground and above the ground environment and local communities.⁸ The most well-known incident caused by coal fly ash happened on 22nd December 2008, when in the Kingston Fossil Plant of USA, coal fly ash slurry spilled due to dike rupture, releasing more than 4 million cubic meter coal fly ash slurry. Most coal fly ash spill was deposited in the Emory River.⁹ Unlike other industrial by-products, it is difficult to handle fly ash due to its toxicity that needs to proper disposal. Usually, large amounts of fly ash are disposed of in ash landfills lagoons. Hence Coal fly ash management is a challenging task in achieving 100 % utilization. Some researchers trying to find out the reuse of coal fly ash from several view points, such as zeolite, adsorbent, the recovery of precious metals and utilization in commercial applications.¹⁰ Although coal fly ash utilization is increasing, mainly in applications such as concrete production, cement, grout, ash brick, road/dam construction and soil amendment,¹¹ only about 12 % of coal fly ash in these impoundments is being recycled into useful products.

Coal combustion residuals have attracted more attention of as a potential alternative source for rare earth elements. Combustion residues of certain types of coal can be 1.5 to 20 times rich than average crustal abundance, depending on

origin of the coal.^{12,13} Coal fly ash also contains heavy metals, it is one of the major concerns for the scientific community due its huge amount of production worldwide and its toxicity, it is the foremost waste material produced by combustion of coal in a thermal power plant.¹⁴ Coal combustion for power generation is considered as one of the major emission sources of hazardous trace elements.¹⁵ Groundwater is the most abundant available source of water for living organism and other applications.¹⁶ Quality of groundwater deteriorates due to pollutants. Naturally occurring ground water quality is generally good despite of some regional variation, however, numerous anthropogenic activities and leaching of various pollutants degrade the groundwater quality.¹⁷ The groundwater and surface water are contaminated in dumping area adverse effects were also observed on bird's population nesting around coal fly ash basin and accumulation of Sr, Cd, As and Se in their offsprings.¹⁸ People, living in villages nearby of thermal power plants, are also known to suffer more from cancer and respiratory disorders. The U. S. Clean Air Act Amendments, European Union and the Canadian Environmental Protection Agency have listed some hazardous trace elements such as Hg, As, Pb, etc., as the main environmental concerns. After combustion, trace elements, such as Hg, As, Cr, Cd and Pb in the coal are adsorbed and condensed on coal fly ash.¹⁹ In the presence of toxic metals, plants growing nearby the ash dumping area are found to have disparity in plant enzymatic activities. The I fly ash contains Si, Al, and Fe along with substantial amounts of other elements like Ca, Na, K and Ti. Aluminum in coal fly ash is typically bound as insoluble aluminosilicate structures, which control substantially the biological toxicity of coal fly ash. Trace elements in coal can be much concentrated in coal fly ash. Substantial amounts of trace metals like Mo, Mn, Zn and Cu along with significant amount of other toxic constituents (i.e. As, Cr, Co, Pb, Ni, Se), in coal combustion products, pose potential risks to the water, environment and human health. Several studies in various locations on the leaking of coal fly ash disposal ponds to adjacent surface water and shallow ground water aquifers have been reported.²⁰

Coal fly ash has special physico-chemical properties. It contains a high concentration and wide variation of valuable elements such as Si, Al, Fe, Mn, Zn, and Cu,²¹ a diverse appearance smooth, porous, and uneven surfaces and spherical and irregularly shaped particles and the presence of cenospheres.²² Researchers have attempted to develop methods for reuse of coal fly ash in construction industry with possibility of reuse in many other applications also, including the extraction of metal, synthesizing zeolites, amending soil, and treating wastewater.^{6,23} Some other elements always extracted as co-extraction, which influence the purity of the element targeted. Purity of synthesized zeolites from coal fly ash is relatively lower than that produced by traditional methods.²⁴ If coal fly ash not properly disposed, the hazardous trace elements can be leached out from the fly ash and may contaminate soil, groundwater, and surface water. The addition of coal fly ash can change the alkalinity of soil or treated wastewater if CaO is present. Further, simultaneous leaching behavior of metal/metalloid/toxic elements from the coal fly ash may contaminate water and soil that is undergoing treatment.²⁵ The adverse impacts of coal fly ash on human health and the ecosystem is to diminish beneficial use of land at disposal. Extensive studies have been conducted on the leachability of

elements from fly ash or other coal combustion products using various leaching test procedures.²⁶

Coal fly ash contain toxic metals, these metal-rich materials come into contact with water and environment that may result in further sequestration of the metals or to their release to the environment.⁴ Heavy metal pollution of ground water from geogenic sources in wide areas is not very common, except for Arsenic pollution and a few studies in Ganga-Brahmaputra basin.²⁷ Arsenic contamination has turned into a major global concern to researchers dealing with constantly growing pollution of soil, water, and crops arsenic is one of the most hazardous elements for the terrestrial and aquatic life that consequently causes ecological problems. Moreover, some studies have been done on ground water and soil quality assessment in the vicinity of a coal fly ash disposal and landfill site.^{20,28} Element present in coal fly ash are likely to be released into water from the disposal/storage/application area on contact with water. However, environment is borderless which may facilitate transfer of pollutants into soil, groundwater and river systems also either in dissolved or particulate form. This may pose serious threats for aquatic organisms, while metal inputs in groundwater resources may entail a significant health hazard. However, mobilizations of heavy metal from anthropogenic sources are widely reported throughout the world in the vicinity of industries.²⁹

The leaching behavior appears relatively common patterns, do not differ significantly regardless of the composition and characteristics of the ash. The advantages and disadvantages of these studies are fly ash utilization, future research considerations and understanding of current hazardous nature of coal fly ash if it is not properly disposed of, it can cause water and soil pollution, disrupt ecological cycles and pose environmental hazards.³⁰ Most of the concern about coal fly ash in the environment stems from reports of its toxicological effects on vital life, including mutagenicity,³¹ cytotoxicity and oxidative DNA damage or genotoxicity of its components.³² Coal fly ash has many heavy metals including As, Cu, Ni, Zn, Pb, Cd, Cr, Hg, that are usually implicated in causing adverse effects on living systems attributed to various oxidative stress reactions.³³ The concentration of different elements in coal depends on source, the total concentration of Hg, As, Cr, Cd, Ba, Mn and Pb was found in range of 0.06-0.22, 0.63-4.01, 8.91-13.09, 0.06-0.15, 108.67-229.21, 49.94-100.24 and 6.74-26.38 mg Kg⁻¹ respectively in four coal samples and 0.17-1.26, 5.15-25.74, 43.25-64.61, 0.56-0.70, 777.05-970.70, 163.83-831.47 and 28.94-119.57 mg Kg⁻¹ in fly ash collected from four power plants in Japan.³⁴ Lots of researchers have investigated the leaching behavior of hazardous elements in fly ash using column leaching test, Zn leached out significantly in short time as compare to Cd,³⁵ while concentration of Cd remains stable after 16 days.³⁶ Synthetic groundwater leaching procedure (SGLP) and long-term leaching (LTL) procedure have been used to explore to compare leaching characteristics of trace elements (Al, As, Ba, Cr, Mn, Pb, etc.) between coal fly ash, mill rejects and bottom ash. In addition, most of the hazardous trace elements concentration in leachates increased with increasing SGLP and LTL leaching time. Leachability is higher at lower pH, leachability of Cr decreased with increasing solid-liquid ratio from 1/20 to 1/5.³⁷

Toxicity Characteristic Leaching Procedure (TCLP, 1311) and Synthetic Precipitation Leaching Procedure (SPLP, 1312) of the U.S. Environmental Protection Agency (USEPA) have been widely applied to understand the leachability of elements from coal combustion products. However, the TCLP, SPLP as well as other single-point extraction tests supply limited information on the elemental leaching characteristics under various environmental conditions that are expected in specific management condition. TCLP especially over estimates metal release under conditions that are not likely occur as in actual disposal or reuse scenarios.³⁸ TCLP was basically formulated for assessing the leachability of municipal waste but is not really appropriate for characterization of leaching behaviour of coal fly ash. Many researchers focussed on coal fly ash leaching using SPLP and TCLP.³⁹ These tests, however, are not able to simulate all the conditions encountered during coal fly ash reuse and disposal conditions, including differences in pH, liquid to solid ratio (L/S), organic matter growth, redox state, and the presence of common/competing ions, all those factors which are known to affect mobility of elements.⁴⁰ The standard leaching tests are found in various studies.^{35,37} Due to limitations TCLP and SPLP methods, the USEPA has developed an integrated approach for assessing leaching behaviour of materials called the Leaching Environmental Assessment Framework (LEAF). LEAF is a leaching evaluation assessment system consisting of four leaching tests i.e., USEPA Methods 1313, 1314, 1315 and 1316; USEPA, 2012f, 2013a, 2013b, 2013c. These methods provide guidance for beneficial use of disposal, treatment and remediation applications to leaching potential of COPCs. These methods are designed to provide liquid-solid partitioning (LSP) curve as a function of extract pH using parallel batch extraction (LEAF method 1313), on different solid liquid ratios as a function of the liquid to solid ratio (L/S) under percolation column (LEAF Method 1314), on different solid liquid ratios as a function of L/S under conditions that liquid solid chemical equilibrium may be approached (LEAF Method 1316). Hazardous Waste Test Methods (SW-846) include these LEAF methods under the USEPA compendium of leaching tests.³⁸ LEAF test has been applied on coal fly ash with bottom ash from power plant of China Hebei Province, but this was limited to only the one power plant.⁴¹

STUDY AREA IN GEOLOGICAL CONTEXT

Sonebhadra district southern region of Eastern Uttar Pradesh, is called Energy Capital of India due to large numbers of power plants of UPRVUNL and NTPC and has large reserves of coal and water resources. This Energy Capital region produces more than 10,000 MW of electricity from various power plants. This area is used for coal mines, coal-fired power plants, coal fly ash and coal slurry disposal areas. The Sardar Gobind Ballabh Pant Sagar (Rihand Dam) situated in Sonebhadra district, has area of spread in Madhya Pradesh, Uttar Pradesh and Jharkhand. It plays an important role to supply irrigation water to Bihar state of India. It is located on a tributary of the Son River called Rihand River. The Dam present between latitude 24° 00' 00" & 24° 12' 43" N and longitudes 82° 38' 00" & 83° 00' 00" N. To stop and let down the floods of the Rihand, the dam is provided a spill-way of 190 meters. Downstream of the dam has 300 MW capacity hydro power plant (6 X 50 MW).

Many thermal power stations are installed in area of the dam. These are Anpara, Rihand, Singrauli, Vindychal and Sasan super thermal power stations. The high contaminated water from the ash dumping area of these coal-fired power stations ultimately collects in this reservoir enhancing its water contamination.

EXPERIMENTAL

Sample Collection & Preparation

Three samples of fly ash samples were collected from the three coal power plants of UP India (NTPC Shaktinagar UP (SSTPS), NTPC Rihand UP (RhSTPS) and NTPC Vindhyanager MP (VSTPS)). The samples were of high-sulfur sub-bituminous coal combustion. The electrostatic precipitators (ESP) collected fly ash in power plants, to stop to spread fly ash in environment. A single composite sample made by mixing of periodically collected coal fly ash from each power plant. The detail information of the three studied coal-fired power plants from which samples has collected in India is shown in Table 1. The fly ash is transported into the ESP of unit by air and collected in ash hopper, in this area fly ash is mixed uniformly. The fly ash was collected from the ESP ash hopper of each unit directly. Coal fly ash collected from electrostatic precipitators has temperature about 60-70 °C, fly ash allowed to cool down at ambient temperature before mixing. Total 104 samples collected from all 26 units of different capacities of all three plants. A composite sample has prepared by mixing of all collected samples from each power station in equal proportion and all composite samples from three power plants had taken for further processing of elemental analysis. All three composite ashes were air-dried before subjected to further analysis, as well as the leaching tests.

Table 1. List of locations of sample collection.

Power plant	Location	Capacity	Total units
No. 1	NTPC, Shaktinagar, (U. P.)	2000 MW	7 5 x 200 2 x 500
No. 2	NTPC, Rihandnagar (U. P.)	3000 MW	6 6 x 500
No. 3	NTPC, Vindhyanager, (M. P.)	4760 MW	13 6 x 210 7 x 500

Coal fly ash is hygroscopic in nature, each composite sample air dried as per IS 1350-1:1984 (R2007). Composite samples put in muffle furnace make M/s Usha Instrument Pvt Ltd. at 108 ± 2 °C for one hour to one and half hour to determine of moisture contain on air dried basis. Coal fly ash samples put in air tight packing for analysis.

Techniques used and elemental analysis

Nature (acidic or basic) of coal fly ash depends on numbers of factors in which concentration of Ca and S plays major role. Coal fly ash composite samples collected from all three power plants conducted test to analyzed nature of coal fly ash.

Leaching of elements from coal fly ash depends on numbers of factors such as concentration of elements present in coal fly ash, oxidation states and matrix present in coal fly ash, pH, liquid/ solid ratio, leaching time etc. The USEPA published TCLP (1311) and SPLP (1312) procedure outlined by US EPA July 1992 and September 1994 respectively. USEPA LEAF methods 1316 (USEPA, 2017c) were conducted on the three composite fly ash samples. Ultra-pure Milli-Q water has been used in this study. All the vessels which are used in all experiment were soaked in 2–5 % nitric acid for 24 h and thoroughly washed with ultra-pure Milli-Q water before using for experiment. For US LEAF method USEPA 1316, total six bottles have been used (one for method blank and five for test sample) for different liquid to solid ratio (L/S) of 2:1, 4:1, 6:1, 8:1 and 10:1 (mL dry-g⁻¹) at pH 4 and other six bottles have been used at pH 10 for same liquid to solid ratios (L/S). They were tumbled end-over-end at a speed of 28±2 rpm for a contact time of 24 h at room temp 25±2 °C. In coal fly ash moisture contains calculated by separate experiment, In L/S ratio the total liquid volume contains in coal fly ash excluded from L/S ratio of solid sample equivalent to the dry mass of the solid material. After leaching, the leachates from each experiment were filtered by using vacuum filtration system through 0.2 µm pore size filters, one part of leachate samples used to test pH, electrical conductivity immediately and other part of each leachate was acidified with analytical grade nitric acid and stored in a refrigerator at 4 °C for farther elemental analysis.

Each composite samples of coal fly ash generated after burning of fine coal powder of size 212 micron (~ 200 mesh). Samples were split into equal representative portions for different analyses. Carbon and sulfur contents in coal fly ash samples were determined by Sytab sulfur analyzer Model TSH 15/50/180. Moisture content of the fly ashes were determined by drying the samples in muffle furnace at 108±2 °C until reaching a constant mass as per IS 1350-1 :1984 (R2007) and ASTM Standard D2216-10 (2010). All samples of coal fly ash were heated up to at 815±2 °C for 1 h; then resultant coal fly ash samples subjected to elemental analysis to determine the contents of major element oxides by inductively coupled plasma - optical emission spectrometry (ICP-OES). The fine powdered coal fly ash samples were subjected to microwave digestion in a mixed-acids reagent. For this, 100 mg of each coal fly ash sample was digested in aqua regia at 220 °C for 30 min and diluted with ultra pure distilled water prior to analysis in ICP-OES. Total 21 element concentrations in the fly ash and the leachate samples were determined by ICP-OES.

Analysis of coal fly ash done by using instrument ICP-OES model Optima™ 3300 RL ICP-OES make PerkinElmer® equipped with WinLab32™ for ICP Version 4.0 software for simultaneous measurement of all wavelengths. The Optima 3300 RL has been optimized to provide high speed analysis by combining an SCD detector and an echelle optical system, the Optima 3300 RL can measure many elements simultaneously. The parameters that applied for this analysis to the ICP-OES 3300 RL has shown in Table 2. Standard solution prepared by Perkin Elmer and VHG NIST® traceable quality control standards for ICP-OES (N9302946, 987841-2), standard used as the stock standards for preparing different working standards. Millipore water acidified with 5% nitric acid was used as blank. All standards were prepared in ultrapure distilled

water acidified with nitric acid of required range; the standard solution was prepared from 1000 ppm stock solution. If sample is clear then run in the instrument directly with Millipore water acidified with 5% nitric acid, if sample is not clear then digestion step carried out before analysis. pH meter model SensION+ PH3 make HACH, Thermo Scientific Orion 3-Star Benchtop conductivity meter and portable turbidity meter model 2100P make HACH were used.

Table 2. Summary of parameters for coal fly ash elemental analysis as applied to the ICP-OES 3300 RL.

Plasma gas flow (argon)	16 L min ⁻¹
Auxillary gas flow (argon)	1 L min ⁻¹
Nebulizer gas flow (argon)	0.95 L min ⁻¹
RF power	1100 watt
Operating temp	7000-9000 °C

Unburned carbon content in coal fly ash sample was determined by weight loss as per ASTM D 7348. The sample were placed in muffle furnace make M/s Usha Instrument Pvt. Ltd. at 815 ± 10 °C for 1 h after being dried at 108 ± 2 °C.

RESULTS AND DISCUSSION

Coal fly ash samples were pulverized before elemental analysis. Carbon, sulphur and moisture contents in the composite coal fly ash samples are given in Table 3 and the major elements in coal fly ash are given in Table 4. All the composite coal fly ash meets the specific requirements of class F fly ash as ASTM Standard C618-19, 2019 and they may be used as pozzolana in cement, cement mortar and concrete. As per Indian standard (IS:3812, 1981) total percentage sum of oxides of three elements (Fe₂O₃, SiO₂ and Al₂O₃) content in coal fly ash should not be lower than 70 % and CaO content should be less than 10 %. Similar results were revealed in study of coal fly ash collected from Badarpur Thermal Power Plants and fly ash bricks.⁴² The ratio of Ca/S are indicative of the acidity / alkalinity of coal fly ash, Low Ca (low Ca/S ratios) and high Ca concentrations (high Ca/S ratios) shows of low pH-acidic to alkaline- high pH values respectively. In present study Ca/S ratios in all the coal fly ashes is low from 1.17 to 1.32 (Table 3), that indicate all coal fly ashes are acidic. In LEAF methods the final pH, when the ash is extracted with deionized water, of the fly ashes ranges from 4.00 to 4.11, that indicate sulphur rich chemical composition of the coal fly ashes. In coal fly ash samples Ca as CaO, silicon as SiO₂, Al as Al₂O₃ and iron as Fe₂O₃ are present from 0.813- 0.877 %, (62.02 – 62.53 %, (27.93-28.71 % a and 5.43 -6.02 % respectively (Table No.4). Three oxides of elements Si, Al and Fe contribute major parts (96.29 to 96.65 %) of the coal fly ash. Sulphur as SO₃ is in 1.1-1.4 % amount.

Table 3. Moisture, carbon and sulfur, calcium contents (%) in the fly ashes and Ca/S ratio.

Samples	Moisture	C	Ca	S	Ca/S
SSTPS	0.14	1.0	0.612	0.52	1.17
RhSTPS	0.21	0.7	0.627	0.56	1.12
VSTPS	0.16	0.9	0.581	0.44	1.32

SSTPS: NTPC, Shaktinagar Sonebhadra (U. P), RhSTPS - NTPC, Rihandnagar Sonebhadra,(U. P), VSTPS: NTPC, Vindhyanagar, Singarauli (M. P.)

Table 4. Loss on ignition (LOI, %) and concentration given as oxides (%).

Sample	LOI	SiO ₂	Al ₂ O ₃	MgO	SO ₃	CaO	TiO ₂	Fe ₂ O ₃	Total Oxides
SSTPS	0.223	62.34	27.93	0.656	1.3	0.855	1.29	6.02	99.44
RhSTPS	0.284	62.02	28.71	0.632	1.4	0.877	1.36	5.66	99.68
VSTPS	0.261	62.53	28.69	0.548	1.1	0.813	1.33	5.43	99.71

Table 5. Trace Elements concentration ($\mu\text{g g}^{-1}$) in coal fly ash samples before leachate.

Sample	P	Mn	Ni	Cu	Cr	V	Zn	Pb	Hg	Ba	As	Se	Cd	Sb
SSTPS	296	497	81	84	67	312	206	41	23	25	26	42	11	9
RhSTPS	323	538	59	115	88	356	180	29	14	21	24	23	8	7
VSTPS	281	501	92	132	107	289	173	34	13	33	18	28	9	10

Table 6. Coal fly ash leaching behaviour at different L/S ratio (LEAF method 1316).

Week	SSTPS			RhSTPS			VSTPS		
	pH	Cond	TDS	pH	Cond	TDS	pH	Cond	TDS
1st	3.89	1916	1244	3.84	1667	1017	3.98	1854	915
2nd	3.91	2073	1389	3.86	1789	1084	3.98	1974	950
3rd	3.88	2113	1403	3.85	1879	1125	3.99	2023	1010
4th	3.90	2169	1453	3.88	1888	1265	3.97	2177	1056
5th	3.92	2228	1493	3.92	2093	1402	3.98	2324	1118
6th	3.94	2316	1530	3.94	2140	1434	4.00	2485	1288
7th	3.95	2218	1486	3.95	2316	1552	4.01	2637	1368
8th	3.93	2325	1558	3.94	2412	1616	3.99	2633	1316
9th	3.95	2369	1587	3.96	2606	1746	3.98	2694	1460
10th	3.98	2424	1624	3.96	2924	1959	3.99	2758	1570
11th	3.99	2467	1653	3.98	3054	2046	4.00	2845	1625
12th	3.98	2518	1687	3.98	3315	2221	4.01	2922	1666
13th	3.97	2487	1751	3.99	3437	2303	4.03	3003	1732
14th	3.98	2655	1779	3.99	3560	2385	4.05	3042	1855
15th	3.99	2775	1859	4.01	3709	2485	4.07	3111	1962
16th	4.00	2903	1945	4.01	3901	2614	4.07	3165	2020
17th	3.99	3094	2073	4.00	4131	2768	4.06	3258	2116
18th	4.01	3261	2185	4.03	4196	2811	4.08	3388	2306
19th	4.01	3504	2348	4.02	4312	2889	4.10	3559	2458
20th	4.00	3484	2484	4.05	4483	3086	4.11	3884	2670

Heavy trace elements present in coal fly ash

The elemental analysis of coal fly ash samples revealed that many heavy metals are also present such as Cr, Ni, Cd, Pb, Hg, As, Cu etc. (Table 5). Heavy metals are toxic in nature and pose serious hazards for health and environment. These seven hazardous trace elements were found in coal and corresponding fly ash in four China power plants also.³⁴ It was found that elements concentration in coal fly ash is greater than that in coal. The concentration of Hg, As, Cr, Cd, Ba, Mn and Pb in the four samples of coal fly ash were in the range of 0.17–1.26, 5.15–25.74, 43.25–64.61, 0.56–0.56, 777.05–970.70, 163.83–831.47 and 28.94–119.57 mg kg⁻¹, respectively.³⁴

In present study the concentration of Hg, As, Cr, Cd, Ba, Mn and Pb in the three samples of coal fly ash are in the range of 13–23, 18–26, 67–107, 8–11, 21–33, 497–538 and 29–41 $\mu\text{g g}^{-1}$ respectively.

Coal fly ash leaching behavior at different L/S ratio (LEAF method 1316)

Conductivity, pH and TDS of all composite coal fly ash samples are shown in table 6. Although pH generally has not much difference as L/S increases, in despite of some variations in LSP curves of elements in leachate such as Zn, Cd, Cr, Cu, Sb, Ba and Se (over L/S 2–10). pH of all coal fly ash samples collected from SSTPS, RhSTPS and VSTPS is 3.89, 3.84 and 3.98 respectively which shows all coal fly ashes are acidic in nature, broadly pH increases with time. The conductivity and TDS of three coal fly ash samples also increases with time with, it is due to dissolution of other basic oxides of elements presents in coal fly ash samples. pH of all coal fly ash samples suddenly drops as water is added to coal fly ash due to presence of sulphur in notable quantity in samples, coal fly ash makes sulfuric acids due to presence of oxides of sulphur as it comes into contact with water.

Table 7. Concentration of elements in leachate water from coal fly ash samples as function of L/S ratio.

Sample	L/S	P	Mn	Ni	Cu	Cr	V	Zn	Pb	Hg	Ba	As	Se	Cd	Sb
SSTPS	2	399	482	456	962	397	687	733	47	15	788	219	476	23	35
	4	275	333	276	758	326	446	567	29	11	457	246	367	17	39
	6	134	201	227	438	283	278	494	15	9	246	173	353	13	64
	8	103	180	137	374	193	253	331	9	7	164	103	291	8	45
	10	77	118	136	268	79	123	232	7	10	141	106	201	9	38
RhSTPS	2	410	366	401	684	336	708	880	36	11	729	286	598	26	53
	4	238	299	252	523	247	534	502	31	12	553	193	406	19	36
	6	219	256	248	322	205	385	312	21	13	331	229	233	11	32
	8	162	143	188	276	102	293	234	13	8	283	139	328	13	24
	10	58	132	99	112	58	198	185	10	7	117	153	266	11	23
VSTPS	2	373	375	374	821	444	620	984	44	16	635	342	517	21	43
	4	199	238	322	579	221	582	691	23	13	387	266	322	13	46
	6	168	153	188	538	156	324	417	12	8	376	261	281	10	51
	8	123	126	213	213	89	216	176	6	10	226	231	199	9	59
	10	102	85	103	171	112	168	287	9	12	203	197	234	7	63

TDS, pH and conductivity of leachate increases with time due to dissolution of other basic oxides with time, broadly have highest value at the end of 20th week of the experiment time frame. Trace elements concentrations in leachates of all coal fly ash samples as a function of L/S ratios are given in Table No. 7. The mobility of elements from coal fly ash towards leachate is remarkably reportable, most of elements concentrations is varying in magnitude in the leachate with varying L/S ratios, it may depend upon many factors e. g. inherent nature of elements, matrix of element etc. The present study is mainly controlled by dilution effects L/S ratio, broadly overall leachate concentrations of all elements steadily decreasing with increasing L/S. The maximum leachable amount limitation has been reached at lower L/S ratio, the leaching solution is under-saturated at high L/S ratio.⁴³ These leaching elements probably have reached up to capability of upper limits of their respective soluble nature at lower L/S values, given that pH value does not change significantly over the higher L/S range, which means that pH does not play an important role in the change of element leachability over this higher L/S range. In coal fly ash barium is sparingly soluble as carbonates and sulphates. The presence of Ca in large amounts in solution would promote the co-precipitation of more insoluble sulphate, more likely as BaSO₄ or SrSO₄.⁴⁴

A number of studies have been conducted for Cr leachate from coal fly ash, its hexavalent Cr (VI) oxidation state is widely recognized as potentially carcinogenic and highly soluble in aqueous media,⁴⁵ whereas Cr (III) oxidation state is less soluble and of much less risk to human health, however literature reflects Cr (III) as predominant speciation as compared to Cr (VI), certain fly ash samples exhibit up to 20% Cr as Cr (VI).⁴⁶

In present study coal fly is ash acidic in nature due to high S and low Ca concentration in samples, and Ba is considerably soluble. Various studies conducted that shows Ba is sparingly soluble where coal fly ash has alkaline in nature and Ca present in large amount in coal fly ash, however, some studies showed that Ba is poorly leached throughout the pH range.⁴⁷ The environmental concerns arise due to toxicity of Cd and its potential solubility in

aquatic systems in acidic coal fly ash, it is environmentally sensitive element is consistently rarely mobile in near neutral to alkaline conditions.^{44,47} The quantity of elements decreases, which are available for leaching from coal fly ash sample quantity, with increasing L/S ratio, which is in support of study done by Zhao et al.⁴⁸ Concentrations in leachate of As and Sb broadly increases with increasing L/S ratio, both elements are sensitive to pH changes over alkaline conditions with minimum leachability, at higher pH (pH of ~12) the solubility of both elements increases. The leachability of As, Sb, Se varies widely depending on the nature of the fly ash. Arsenic has attracted considerable attention of research due to its mobility throughout a wide pH range and its highly toxic nature. Arsenic release from acidic fly ash increases with pH, however, not all elements that typically occur as oxyanions exhibit such LSP curve trends. Further investigations on leachable amount and its trends of the elements in coal fly ash samples are needed to better understand the LSP characteristics. Indian Standard 10500:2012 represent a risk-based water quality threshold and acceptable limit of various parameters including heavy metals in drinking water. Although concentration of leachate elements in most of the fly ash has been diluted with mixing in water bodies but still it has alarming concentrations for human beings. Most of elements present in fly ash have tendency to leached out from fly ash to water.

Mobility of trace elements from coal fly ash

The elements are released from coal fly ash after they come into contact with water when it exposed in landfill, decomposition or by other means. The main objective of this study was to determine the elemental concentration released in solution from coal fly ash on different L/S ratios. All three coal fly ash samples are acidic in nature while four fly ash samples collected from China power stations were basic in nature and observed pH was 12.27, 12.19, 11.25 and 11.21.³⁴ The elements are released into leachate solution from coal fly ash after they come into contact with water. Broadly LSP curves of individual elements in leachate as a function of L/S ratio are not always similar among different fly ash samples of different ranks of coal.

The main factor is the elemental concentration and quantity present in huge amount of coal fly ash which had been disposed of near water bodies while pH plays major role in composition of leachates, it is one of the important factors that determines the concentration of the elements in the leachate. The behaviour of leaching element does not necessarily correlate with the concentration of that element present in coal fly ash samples.⁴⁸

Implication of toxic elements for potential environment impact

As studies on coal fly ash have shown, caution should be paid to the mobility tendency of various elements which are present in coal fly ash. Most of the heavy metal including Hg, Cd, Pb, Se, As, Ni and Cr are above the acceptable limits of drinking water which is defined in Indian Standard for drinking water (IS 10500:2012 second revision). Concentration of some of the elements is above the acceptable limit over the entire pH range studied. This indicates that these elements may have more adverse impacts on the ground water and water bodies near disposal area. As and Sb, as typical oxyanionic species, have maximum leachability at neutral to slightly alkaline conditions (pH of 7–9). These elements in the studied coal fly ash samples should be of concern at pH conditions when their maximum leachability is reached are close to their natural pH values.

CONCLUSIONS

The present study is an assessment the elemental leachability present in three coal fly ash samples. The results of leaching test indicates broadly that the LSP curves of individual elements in leachate as a function of L/S ratio are not always similar among different fly ash samples of different ranks of coal. The L/S ratio is also may play important role in controlling the leaching activity, but the further impact needs to be evaluated with the change of pH, as the studies indicate that pH is the major factor that may controls the leaching tendency of elements from coal fly ash. More caution should be paid in aspects of Indian coal which has acidic nature of coal fly ash that may impact leachability. Most of the elements show more leaching at lower pH. This may deteriorate soil and ground water quality in disposal area of coal fly ash in the vicinity of the thermal power plant. Those elements that occur as cations show maximum leachability at acidic conditions and generally are of more concern. This research work provides significant evidence to the scientific community for taking adaptive measures to dispose of coal fly ash in better manner and has requirement of appropriate process for its uses or disposal to stop contamination of ground water and soil

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