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Original Research

Extraction and Leaching of Heavy Metals from Thermal Power Plant Fly Ash and Its Admixtures

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Abstract

The leachability of heavy metals from fly ash, bottom ash, dumping site ash, cement, and brick samples admixtured with fly ash in the area of a thermal power plant were compared. During these studies, extraction and leaching of various heavy metals like Zn, Ni, Cu, Fe, Pb, Mn, Mg, and Cd was carried out by applying batch leach test and toxicity characteristic leaching procedure (TCLP) to check the possibility of ground water contamination. The ground water samples in the vicinity of ash dumping sites were also analyzed for heavy metal concentrations and results obtained were compared with Indian and WHO permissible limits.

Mg, Mn, and Fe were leached to a larger Zn, Cu, and Pb to moderate, and Ni to a smaller extent, from the ash and admixtured samples. Cd was not leached at all from any sample in batch leach as well as TCLP tests. The concentrations of Zn, Fe, Mn, Mg, and Cd in groundwater samples were below the permissible limits of WHO and Indian standards. The concentrations of Ni and Pb were slightly higher than WHO permissible limits but below the Indian standards. The concentration of Cu was within the WHO permissible limits but slightly higher than Indian Standards. The admixturing of thermal power plant fly ash in cement and bricks seems to be an eco-friendly practice as far as leaching of heavy metals in groundwater is concerned.

Keywords: heavy metals, fly ash, extraction, leaching and water contamination

Introduction

Coal occupies an important position in the Indian energy sector since India has vast reserves of thermal grade coal. Coal is the most abundant and widely spread fossil energy resource in the world [1]. Among the total power generated annually in India, about 70% is produced by thermal power plants. The majority of thermal power plants (about 84%) are running on coal with 70 billion tons of coal reserve, while the remaining 13% run on gas and 3% on oil [2]. About 112 million tons of fly ash is being generated annually in India by thermal power plants as a byproduct of coal combustion. Fly ash quality depends on coal type, coal particle fineness, percentage of ash in coal, combustion technique, air/fuel ratio, and boiler type [3].

In India, studies have been carried out toward management of fly ash disposal and utilization [4, 5]. Fly ash is utilized in cement and construction. However, the rate of production is greater than consumption. The unused fly ash is disposed into holding ponds, lagoons, landfills and slag heaps. Disposal of huge amounts of fly ash in landfills, and surface impoundments or its reuse in construction materials is of environmental concern [6].

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Coal contains significant quantities of various trace elements, and during combustion of coal, trace elements are enriched as a result of carbon loss as carbon dioxide and the trace elements are associated with the surface of the ash particles due to evaporation and condensation. The characteristics of the coal used and the type of the installation employed in generating the solid combustion wastes have a direct influence on chemical and mineralogical composition of fly ash [1].

The disposal of fly ash is considered a potential source of contamination due to the enrichment and surface association of trace elements in the ash particles [7]. The elements Mn, Ba, V, Co, Cr, Ni, Ln, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg, and S in coal are volatile to a significant extent in the combustion process. However, the elements Mg, Na, K, Mo, Ce, Rb, Cs, and Nb appear to have smaller fractions volatilized during combustion, whereas Si, Fe, Ca, Sr, La, Sm, Eu, Tb, Py, Yb, Y, Se, Zr, Ta, Na, Ag, and Zn are either not volatilized or show only minor trends related to the geochemistry of mineral matter [8]. During transport, disposal, and storage phases, the residues from coal combustion are subjected to leaching effects of rain and part of the undesirable components in the ashes may pollute both ground and surface waters [1]. These solid residues (fly ash) can be leached in higher concentrations than drinking water standards and can cause contamination in drinking water sources. Fly ash contains trace amounts of toxic metals that may have negative effects on human health and on plants [9].

Disposal of fly ash in surface water sources disrupts aquatic life, whereas toxic metals leached contaminate underground water resources. Therefore, it is important to predict the leaching behavior of residues to prevent the environmental effects, especially for the aquatic environment when ash is in contact with water. The toxic elements leached from fly ash can contaminate soil, ground water and surface water. Therefore, effective water management plans are required for fly ash disposal [10, 11]. Although chemical composition of coal waste can give us an idea about the pollutants passing through water, in order to quantify these phenomena it is necessary to carry out leaching tests. Lau and Wong (2001) found that different elements have different leaching behaviors because of differences in elemental properties and pH of the solution and leaching time, which strongly influence leaching behavior [12]. Seferinoglu et al. (2003) reported that trace-element leaching from bottom ash is slower and often requires that the entire bulk matrix be dissolved [13].

Fly ash is an alumino-silicate glass consisting of the oxides of Si, Al, Fe, and Ca, with minor amounts of Mg, Na, K, Zn, and S, plus various trace elements. The concentration associated with the ash may be either adsorbed on the surface of a particle or incorporated into its matrix [14]. A mechanism that appears to be common for all ashes during their formation is the condensation of metal and metalloid vapours on refractory core materials. As the ash particles and gas stream exit from the combustion chamber and proceed up to the flue gas, this results in locally higher concentrations of many trace elements at the surface of ash particles and accounts for the generally higher concentration of these elements as particle size decreases [15]. The association between trace elements and major elements/minerals may be an important factor in determining the leachate composition of water in contact with ashes. It is recognized that the health hazards and environmental impacts from coal-fired thermal power stations result from the mobilization of toxic elements from ash. The large amount of ash that accumulates in thermal power plants, its possible reuse and the dispersion and mobilization of toxic elements from it requires greater attention [16]. Mobilization of various elements from the ash into the environment depends on climate, soils, indigenous vegetation and agricultural practices [17].

The aim of this study was to investigate the leaching behavior of fly ash disposed in the ash pond at Bhusawal Thermal Power Plant (M.S.) in India, and to investigate the potential influence from the ash disposal on ground water quality. In these studies, the leaching of heavy metals like Zn, Ni, Cu, Fe, Pb, Mn, Mg, and Cd from fly ash and its admixtures were investigated in order to predict potential environmental pollution [18].

Experimental Procedures

The main method of disposal of fly ash from the power plant throughout the world is mixing with water. The resultant slurry is transferred to an ash disposal pond. Samples of freshly generated fly ash have been collected from the electrostatic precipitators in the Bhusawal Thermal Power Plant. The other samples were collected from the surrounding area of the Thermal Power Plant. Five different types of samples were selected, like fine fly ash (FA-1), bottom ash (FA-2), cement sample (FA-3), brick sample (FA-4) and dumping site ash (FA-5). After sampling, the samples were stored in a polyethylene bottle and kept in a refrigerator (4ºC) until the leaching tests were performed and heavy metal analysis was carried out [19].

Sample Storage and Pretreatment for Leaching

Extraction was carried out by shaking the samples of ash with the extractant in polypropylene bottles. The extraction was carried out using ash samples in as-it-is form instead of dried samples, since according to Kosson et al. (2002) it is preferable to avoid sample drying before extraction in order to minimize possible chemical and/or microbiological changes in the ash during the extraction procedure [20]. After the extraction, the extracts were separated from the solid residue by filtration through a Whatmann No. 42 filter paper. Few drops of 1 N nitric acid were added to it, and extracts were stored in a refrigerator (4ºC) until the element determination. The element concentrations in the acid digested extracts, batch leach, and TCLP were determined using an atomic absorption spectrophotometer, AAS (Thermo Scientific, U.K. make, Solaar S series model).

Batch Leaching Tests

A series of batch leaching tests were conducted in the laboratory. In order to better simulate the natural conditions and susceptibility to release, a lower liquid-to-solid (L/S) ratio was used. Therefore, 5 g fly ash samples were mixed with 25 ml of deionized water, giving a liquid:solid ratio of 5. Triplicate extractions with the same weight of sample and same volume of extracting reagent were applied for one type of sample. A gentle stirring was continued during extraction (24 h) on a rotary shaker (Steelmate Novatech India, Tabletop model). Heavy metal analysis was carried out on AAS. The results were expressed as averages of triplicate analyses.

Toxicity Characteristic Leaching Procedure (TCLP)

The toxicity characteristic leaching procedure (TCLP) requires the use of an extraction fluid made of buffered acidic medium to run the test. For this the selection of the extraction fluid was made prior to conducting the test [21]. 1M sodium acetate buffer was used as an extraction liquid; pH was maintained at 4.99 as per United States Environmental Protection Agency (USEPA) procedure [22]. A 4 g fly ash sample was taken and then extraction fluid equal to 20 times the amount of sample taken was added to it. The system was tightly closed and then placed on the rotary shaker for 18 hours, rotating at 30±2 rpm at a room temperature of about 25ºC. Triplicate extractions were performed using the same weight of the sample and the same volume of the extracting reagent. Heavy metal analysis was carried out on AAS and the results are expressed as averages of results of triplicate estimations.

Extraction of Heavy Metals from Fly Ash

This short-term leaching study was carried out in the presence of strong acids to provide the available concentration levels of trace/heavy elements in the fly ash samples [21]. A direct acid digestion method was carried out for the determination of heavy metals. About 0.5 g of dry fly ash was roundly selected from composite samples and weighed. They were digested with 10 ml nitric acid and 5 ml perchloric acid. The digested material was filtered through Whatmann No. 42 filter paper and diluted to 100 ml with distilled water. Aliquots were taken for heavy metal determination [19]. Metals like Zn, Ni, Cu, Fe, Pb, Mn, Mg, and Cd were analyzed by AAS.

Heavy Metal Analysis in Water Samples

The water samples were collected from the surface as well as ground water sources in the vicinity of ash disposal sites and analyzed for heavy metal concentrations on AAS.

The results obtained were compared for the maximum permissible limit of various heavy metals in drinking water (IS: 10,500 and WHO limits).

Table 1. Heavy metal concentrations leached as a result of batch leach test (n=3).

Metal	FA-1	FA-2	FA-3	FA-4	FA-5
Zn	ND	ND	0.14	0.02	ND
Ni	ND	ND	ND	ND	ND
Cu	0.18	0.13	0.04	0.20	0.21
Fe	ND	ND	ND	0.02	0.13
Pb	0.18	ND	ND	0.30	ND
Mn	0.04	0.02	ND	ND	0.01
Mg	11.30	8.95	3.00	2.90	6.60
Cd	ND	ND	ND	ND	ND

Concentrations in mg/kg ash, ND – Not Detected, FA-1– fly ash, FA-2 – bottom ash, FA-3 – cement sample, FA-4 – brick sample, and FA-5 – dumping site ash.

Results

Leaching studies of heavy metals from fly ash are important in predicting the environmental impacts associated with the disposal of fly ash into ponds. In these studies, the leachability of heavy metals from fine fly ash, bottom ash, dumping site ash taken from the ash pond, cement sample and brick samples in the area of Bhusawal Power Plant were compared. During these studies, leaching behaviors of various heavy metals like Zn, Ni, Cu, Fe, Pb, Mn, Mg, and Cd from fly ash and its admixtures was studied.

Discussion of Results

Batch Leach Test

The concentrations of the heavy metals that were leached out with deionized water as a result of the batch leaching test are shown in Table 1. Ni and Cd did not leach from the fly ash samples. Mg and Cu show solubility with deionized water and leached in higher concentration in all samples of fly ash and its admixtures. The leached Cu con-

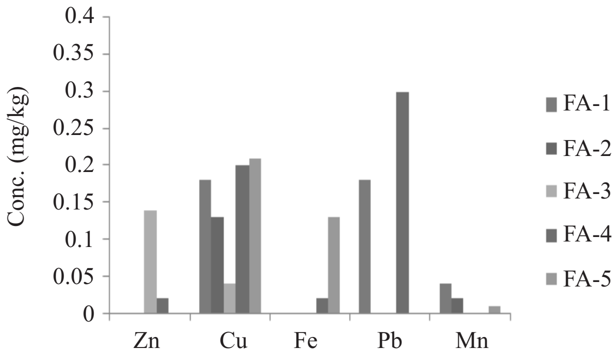

Fig. 1. Comparison of heavy metal concentrations leached as a result of batch leach test.

Table 2. Heavy metal concentrations leached as a result of TCLP test (n=3).

Metal	FA-1	FA-2	FA-3	FA-4	FA-5
Zn	1.45	1.93	2.43	1.28	0.58
Ni	0.33	0.53	2.18	1.05	0.43
Cu	7.75	5.25	11.75	23.25	8.75
Fe	1.95	2.23	2.33	2.03	1.15
Pb	0.88	ND	ND	1.48	ND
Mn	58.25	154.75	180.25	86.25	28.25
Mg	239.25	184.75	396.50	320.25	164.48
Cd	ND	ND	ND	ND	ND

Concentrations in mg/kg ash, ND – Not Detected, FA-1– fly ash, FA-2 – bottom ash, FA-3 – cement sample, FA-4 – brick sample, and FA-5 – dumping site ash.

Table 3. Heavy metal concentrations as a result of acid digestion (n=3).

Metal	FA-1	FA-2	FA-3	FA-4	FA-5
Zn	0.039	0.052	0.056	0.038	0.011
Ni	0.011	0.014	0.032	0.018	0.003
Cu	0.014	0.009	0.018	0.072	0.008
Fe	0.500	0.552	0.570	0.530	0.462
Pb	0.004	0.002	0.042	0.007	ND
Mn	0.066	0.257	0.263	0.121	0.051
Mg	0.262	0.202	0.544	0.481	0.183
Cd	0.004	ND	0.008	0.002	ND

Concentrations in %, ND – Not Detected, FA-1– fly ash, FA-2 – bottom ash, FA-3 – cement sample, FA-4 – brick sample, and FA-5 – dumping site ash.

centrations were low in comparison with Mg, this is probably because Cu is precipitated as their insoluble hydroxides. The Pb is leached out in only fly ash and brick samples to a similar extent, but below permissible limits. Mn is leached in fly ash samples but shows very low concentration. Zn did not leach from fly ash samples, but leached in trace amounts from cement and brick samples. Iron oxides have a lower solubility in deionized water. Iron leached from pond ash is probably precipitated as hydroxides due to the alkaline nature of fly ash.

During the leaching studies, the resulting high pH in the leachates led to a limited removal of Pb and Fe from fly ash, which was even less than Cu and Mn. The leachability of trace elements will depend more or less on the leachability of iron [23]. Choi et al. (2002) have suggested that the elements in the ash particles were mainly associated with the surface, and these surface-associated fractions might dominate the leachate chemistry at the early stages of fly-ash disposal in contact with water [7]. However, the elements incorporated within the interior of the fly ash dissolved at a slower rate compared with the readily leachable surface-associated elements.

TCLP Test

The heavy metal concentrations as a result of TCLP are shown in Table 2. In this procedure sodium acetate buffer was used at pH 4.99. Mg, Mn, and Cu show solubility in weakly acidic medium and were leached at higher amounts in all samples. Cd was insoluble and does not leach out from these samples. Zn, Ni, Fe, and Pb also leached but at very low concentrations.

The concentration of metals in TCLP was higher than the concentration of metals found in batch leach test. This is because metal solubility generally decreases with increasing pH [24]. TCLP involved leaching in slightly acidic buffered conditions (4.99), and in batch leach test the pH was around 7.2. This is due to the precipitation of metal ions as insoluble hydroxides at high pH values.

For all metals, the lowest solubility was found in water extracts. Trace metal concentrations in fly ash and its admixture were well within the Indian standards for disposal of effluents. A similar comparison of TCLP and batch leach test indicates that all metals were well within specified limits.

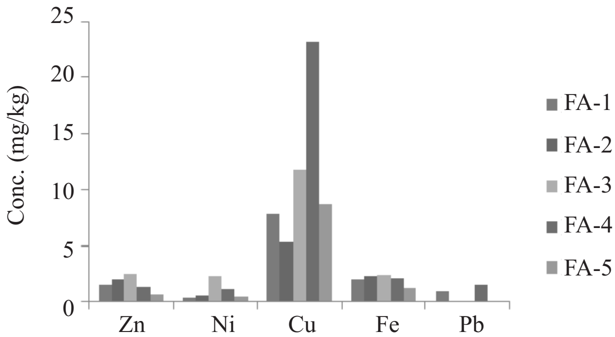

Fig. 2. Comparison of heavy metal concentrations leached as a result of TCLP test.

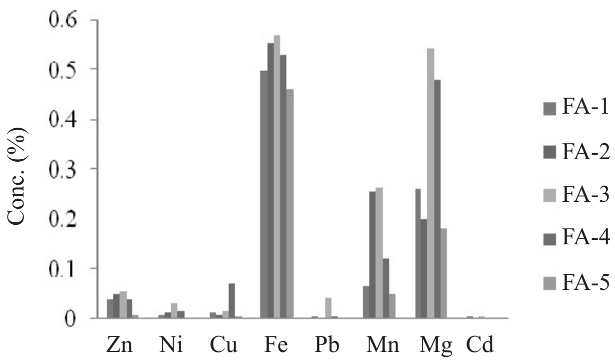

Fig. 3. Comparison of heavy metal concentrations as a result of acid digestion.

Table 4. Comparison of heavy metal concentrations observed in groundwater samples with drinking water standards (n=16).

Metal	Pond water	Stream water	Wells near ash pond	Tube wells in nearby villages	WHO limits for drinking water	IS:10500-1991
Zn	0.024	ND	0.091	0.075	3.0	5.0
Ni	ND	ND	0.054	0.040	0.02	-
Cu	0.068	0.030	0.052	0.057	2.0	0.05
Fe	0.021	ND	0.037	ND	0.3	0.3
Pb	ND	0.037	ND	ND	0.01	0.1
Mn	ND	0.002	0.024	0.019	0.1	-
Mg	3.45	10.80	19.69	14.93	-	30.0
Cd	ND	ND	ND	ND	-	0.01

Concentrations in mg/l, ND – Not Detected

Acid Digestion

Acid digestion data provides the total available concentration levels of trace elements in fly ash and its admixture, which is shown in Table 3. The results obtained from acid digestion test was found to be significantly higher in composition to the above shake test, i.e. batch leaching test and TCLP. Mg and Fe were extracted to a large extent. Zn and Mn were extracted to medium level while Ni, Cu, Pb, and Cd were extracted to lower level in comparison with other heavy metals.

Heavy Metal Analysis in Water Samples

After study of the comparative evaluation of short-term leaching (shake) tests (i.e. batch leach test and TCLP in the laboratory) it is essential to evaluate the actual field condition for environmental escape of heavy metals from fly ash and its admixtures. For this reason ground water analysis was performed on the water samples collected from the wells and bore wells from different locations in the area of the fly ash dumpsite.

Details of the concentration of heavy metals in the groundwater samples near the ash ponds and at the surrounding villages are given in Table 4. pH of the water samples ranged from 7.02 to 8.70, indicating the alkaline nature of the water. The elements found in highest concentration in the tube well waters were Mg followed by Zn and Ni. Mg and Zn are present in higher amounts in the tube well waters in the villages than those near the ash pond. A comparison of data is also made between the concentrations of the trace elements in the waters of the tube wells near the ash pond and those of the tube wells in the villages. The concentration of Cu and Mn is lower and nearly similar in the water samples in all locations, while Pb and Cd are absent in all water samples.

Conclusions

On the basis of the study of the leaching of heavy metals from coal ashes, the following conclusions can be drawn:

- The concentrations of all the heavy metals under study in the leachates were invariably well below the permissible limits for discharge of effluents as per the Indian standards.
- Comparison of water samples near the ash ponds and at the surrounding villages shows that the concentration of

Table 5. Harmful effects of heavy metals on human health.

Metal	Effect on human health
Zn	Gastroenteritis and stomach cramps
Ni	Heart attack and respiratory diseases
Cu	Liver cancer, kidney, and intestinal disorders
Fe	Nausea, vomiting, and liver failure
Pb	Cardiovascular, reproductive, gastrointestinal, and renal disorders
Mn	Mental disorders
Mg	Diarrhea and abdominal cramping
Cd	Pulmonary cancer

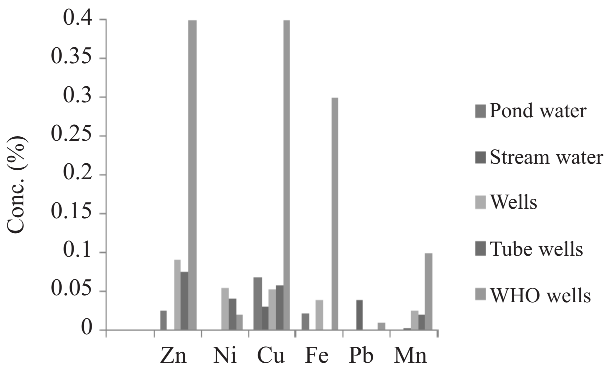

Fig. 4. Comparison of heavy metal concentrations observed in groundwater samples with WHO permissible limits for drinking water.

heavy metals is within the permissible limits of Indian standard IS: 10500 and WHO limits for drinking water quality.

- From the leaching study of heavy metals from cement and bricks it can be concluded that utilization of fly ash in cement and brick manufacturing is safe from an environmental point of view as it does not impart any hazardous effect of heavy metal leaching.
- The fly ash samples from Bhusawal Thermal Power Plant were found to be environmentally safe for disposal and can be engineered for their bulk utilization in industry and agriculture.

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