

Sequential Extraction Procedure and TCLP for Evaluating Environmental Impacts of Wet Dumping of Pond Ash from Thermal Power Plants

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ABSTRACT: Thermal Power Plants (TPPs) which generate more than 60% of the electricity in India are responsible for generation of huge quantity of CCRs. Fly ash and bottom ash the two main by-products of TPPs are mixed along with water and the resulting slurry is carried to ash ponds through drains which contains trace metals like As, Cr, Zn, Cd and sometimes radioactive elements like U, Th etc. Three pond ash samples were collected from three different ash ponds situated around Kolaghat Thermal Plant in West Bengal, India. The leaching potentials of different elements and total leachable concentration of those elements present in the three pond ash samples were assessed by Sequential Extraction procedure. TCLP was carried out on the same pond ash samples to assess the hazardous nature of the samples to the environment. According to the results obtained from Sequential Extraction, toxic elements showed potential of getting leached varying from moderate to high ranges of concentrations. Radioactive elements like U and Th could also be detected. Results of Sequential Extraction indicate high possibility of contamination of the surrounding soil and groundwater around the ash ponds. TCLP results indicate that the pond ash samples are hazardous in nature.

Keywords – CCRs, SEP, TCLP, TPPs, USEPA, WHO, RCRA

1. INTRODUCTION

Coal is one of the major sources of energy and is mostly used for power generation in India. Coal Combustion Residues (CCRs) form one of the largest fractions of solid wastes generated throughout the world. CCR characteristics depend on coal type, coal particle fineness, % of ash in coal, combustion technique applied, air/fuel ratio, number of burners used and type of burner. Its generation is estimated to be 25% of the total solid waste generation in India [1]. Thermal Power Plants (TPPs) which generate more than 60% of the electricity in India are responsible for generation of huge quantity of CCRs. CCRs include fly ash, bottom ash, pond ash and mound ash. Fly ash and bottom ash are mixed along with water in the TPPs and the resulting slurry is carried to ash ponds through drains [2]. This slurry contains trace metals like As, Cr, Zn, Cd which are toxic in nature and sometimes radioactive elements like U, Th etc., (leached from the ashes) which has high potential of getting leached into surrounding soil and groundwater [3]. So, wet disposal of CCRs has serious environmental concerns.

Due to presence of toxic elements, it is important to determine their leaching potential in various environmental conditions. Extraction methods are generally applied for that purpose. Various extraction procedures are followed under different controlled conditions [4, 5]. Sequential Extraction procedures have been recently applied to bottom and fly ash to determine distribution of different elements in them [6, 7].

The leaching potentials of different elements and total leachable concentration of those elements present in the three pond ash samples were assessed by Sequential Extraction procedure. In this study, a four-step extraction procedure was applied which was modified from that of Tessier et al., 1979 [8]. Four different leaching solutions were used for extracting Water Soluble, Ion Exchangeable and Acid Soluble at pH ~ 3 and at pH ~ 1 fractions of different elements present in the pond ash samples collected from three different ash ponds situated around Kolaghat Thermal Plant in West Bengal, India.

Toxicity Characteristic Leaching Procedure (TCLP) was done according to EPA SW-846 Method 1311 [9] to compare toxicity data with regulatory level (RCRA requirement) and find out whether the pond ash samples were hazardous or not. Acetic acid buffer solution of pH controlled to 2.88 ± 0.1 was used as the leaching solution. The supernatant solutions were filtered, diluted and then acidified to measure different elements present in those solutions.

The objective of this study was to understand leaching behaviour of different elements present in pond ash under different pH conditions thus assessing the impacts of wet dumping of pond ash on the environment (soil and

groundwater) by performing Sequential Extraction on the same. TCLP was carried out to assess the hazardous nature of the pond ash samples to the environment by comparing the concentrations of various elements leached in the leaching solution applied with that prescribed in RCRA lists of Hazardous Wastes with ‘D’ code.

2. Materials and Methods

Three pond ash samples were collected from three different ash ponds situated around Kolaghat Thermal Plant in West Bengal, India. They were collected in three plastic buckets and were immediately sealed with plastic covers to prevent exposure to sunlight. At first Sequential Extraction of the pond ash samples was done to determine the distribution of different elements present in them. For this, different leaching solutions were applied on the pond ash samples sequentially in order of increasing aggressive nature and the concentrations of different elements in each step (some selected Alkali metals, Alkaline earth metals, Post transition metals, Metalloids, Transition elements, Lanthanides and Actinides) were measured by Inductively Coupled Plasma Mass Spectrometry and Fast Sequential Atomic Absorption Spectrometry. Then TCLP was done according to EPA SW-846 Method 1311 to compare toxicity data with regulatory level (RCRA requirement) and find out whether the pond ash samples were hazardous or not.

In Sequential Extraction, initially 1 g of pond ash was taken from any one of the collected ash samples and it was distributed in 10 centrifuge tubes each of 12 ml capacity. Then 100 ml of the first leaching solution i.e., reagent grade water was poured into all of the centrifuge tubes (10 ml in each of the tubes). Then the tubes were kept inside an Incubator and agitated @30 rpm for specified time period (mentioned in Table 1). After agitation, the samples were centrifuged @10,000 rpm for 10 minutes. The supernatant was decanted, filtered through 0.45 μ filter paper and was diluted by 1000 times. The diluted solutions were acidified to 2% by 69% concentrated nitric acid and stored for elemental analyses using 820 ICP-MS and VARIAN AAS240FS. Remaining leaching solutions were applied in succession to the residual solids obtained from the previous step and the same procedure mentioned above was applied for preserving the supernatant solutions. FSAAS was performed to measure Fe and Cu and other elements were detected by ICP-MS. The different leaching solutions used and the durations of agitation for different fractions are compiled in the following table:

Table 1 Details of Sequential Extraction Procedure (SEP)

Steps	Different Fractions of Leaching	Leaching Solutions	Duration of Agitation for Sequential Extraction	Description of Leaching Solution Preparation
1	Water Soluble (WS)	Reagent Grade Water	4 hrs at ambient temperature	100ml of reagent grade water
2	Ion Exchangeable (IE)	0.1M MgCl ₂	4 hrs at ambient temperature	2.033 g of MgCl ₂ in 100ml of reagent grade water
3	Acid Soluble at pH~3 (AS3)	0.11M Acetic Acid	24 hrs at ambient temperature	0.630ml of acetic acid in 100ml reagent grade water
4	Acid Soluble at pH~1 (AS1)	Few drops of concentrated HCl	6 hrs at ambient temperature	Few drops of concentrated HCl addition

The USEPA SW 864 method 1311 depicts the procedure for performing Toxicity Characteristic Leaching Procedure. Glacial Acetic Acid and reagent grade water mixture was used as the extraction fluid (Shivpuri et al., 2011). For preparing extraction solution, Glacial acetic acid was added drop by drop in 200 ml reagent grade

water and pH of the mixture was brought down to 2.88 ± 0.1 . For analysis, 1g of a dried pond ash sample was mixed with 20ml of the extraction solution in 100ml Tarsons PMP (Polymethylpentene) beakers. Same procedure was followed for all the samples. Then the solutions were agitated in a Shaking Incubator for 18 hours at 30 rpm and at 30°C. After that, the supernatant solutions were collected in 12ml centrifuge tubes and the same were centrifuged at 10,000 rpm for 10 minutes. The supernatant solutions were filtered through 0.2µ Whatman Nucleopore Track-Etch Membrane Filter Papers using syringe filtration apparatus. The filtrates were then diluted by 1000 dilution factor using reagent grade water and the diluted solutions were acidified to 2% by 69% concentrated nitric acid and stored for elemental analyses using 820 ICP-MS and VARIAN AAS240FS.

3. Results and Discussions

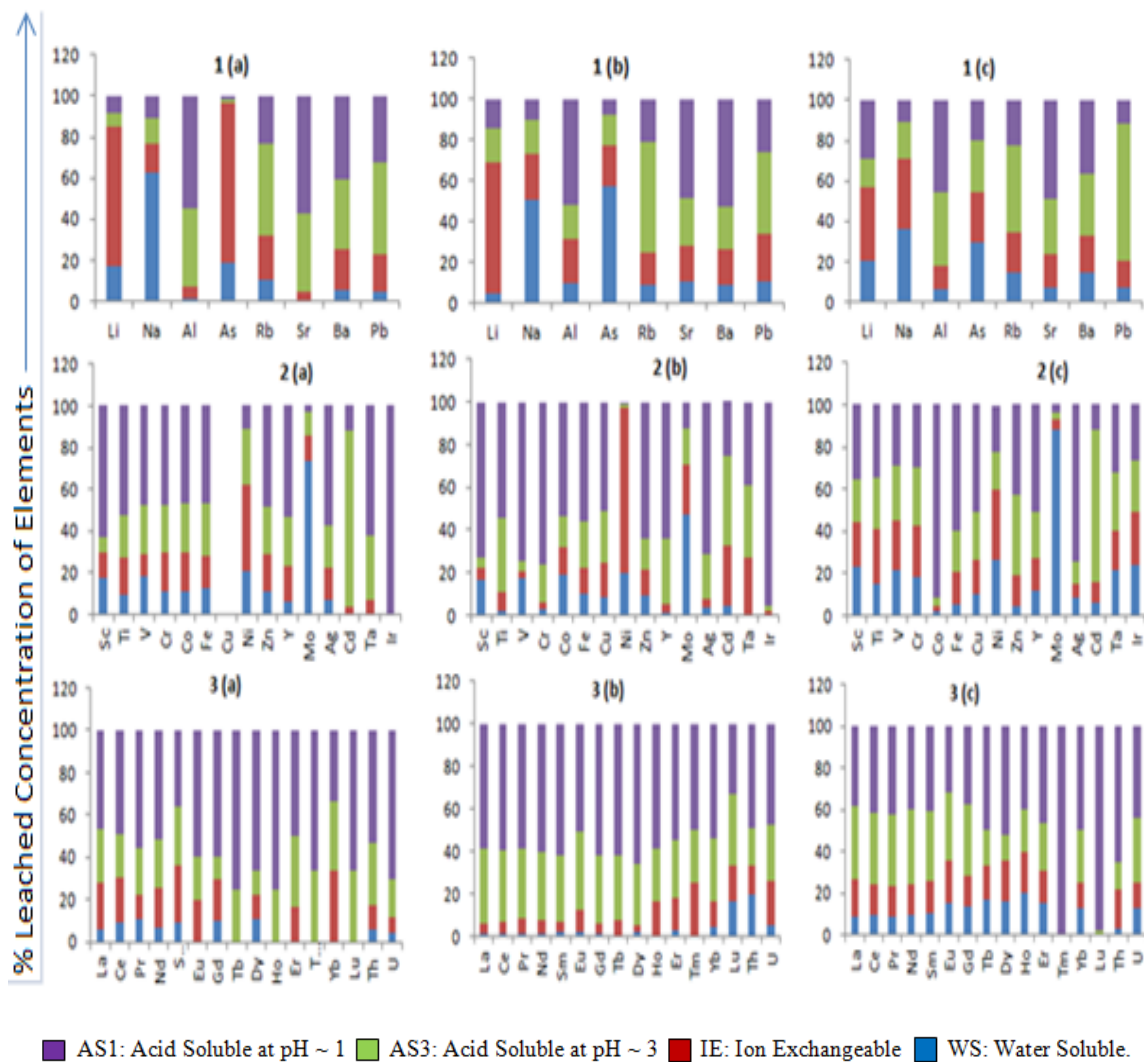


Figure 1 % Leached concentrations of different elements (out of total leached concentration) in contact with different leaching solutions during Sequential Extraction of pond ash (a, b and c represent three pond ash samples).

Table 2 Total Measured Concentrations of Different Elements after SEP

Elements	Total Elements Leached (mg/kg)			Elements	Total Elements Leached (mg/kg)			Elements	Total Elements Leached (mg/kg)		
	Sample-I	Sample -II	Sample-III		Sample-I	Sample -II	Sample-III		Sample-I	Sample -II	Sample-III
Li	5.88	2.82	3.46	Sr	14.84	7.75	19.15	Dy	6.09	2.59	1.25
Na	12.42	13.89	9.57	Y	9.17	3.14	11.51	Ho	1.04	3.12	1.05
Al	313.55	579.28	533.6	Mo	19022	22064	26024	Er	3.06	8.33	5.13
Sc	33.3	38.2	45.87	Ag	58.9	29.23	37.84	Tm	0.43	0.74	0.71
Ti	22717.12	24294.95	26293.59	Cd	2.25	3.48	2.95	Yb	2.03	6.24	4.08
V	74.07	197.11	57.99	Ba	276.89	123.5	111.02	Lu	0.36	0.46	0.33
Cr	59.92	61.94	49.16	La	34.032	95	82.51	Ta	8.82	5.39	17.37
Co	12.72	24.47	18.7	Ce	5.73	18.25	25.34	Ir	2.68	2.7	2.684
*Fe	18	15	17	Pr	7.09	21.21	21.68	Pb	393.67	191.25	182.09
*Cu	0.85	0.87	0.845	Nd	2.31	8.42	9.53	Th	0.38	0.391	0.37
Ni	106.73	147.03	185.91	Sm	7.11	21.87	16.47	U	0.44	0.53	0.36
Zn	137.22	150.25	197.06	Eu	3.1	2.49	5.73				
As	4.84	5.4	7.08	Gd	7.1	20.04	1.53				
Rb	56.15	40.6	74.37	Tb	1.04	4.13	2.06				

* Measured by FSAAS.

Table 3 Total Measured Concentrations of Different Elements after TCLP

Elements	Leached Conc. During TCLP (ppm)			Elements	Leached Conc. During TCLP (ppm)			Elements	Leached Conc. During TCLP (ppm)		
	Sample I	Sample II	Sample III		Sample I	Sample II	Sample III		Sample I	Sample II	Sample III
Li	0.606	0.594	0.207	Sr	2.991	251.671	290.351	Dy	0.0625	6.756	4.28
Na	2.219	1.644	5.519	Y	23.151	64.37	3.741	Ho	0.271	1.367	0.022
Al	94.78	125.84	184.25	Mo	4283.15	5341.4	4971.813	Er	0.673	3.413	2.589
Sc	5.445	13.404	12.478	Ag	6.096	5.939	3.846	Tm	0.0483	0.457	0.269
Ti	1525.59	1320	1533.58	Cd	1.441	1.621	1.031	Yb	0.137	1.255	1.366
V	27.279	68.409	19.915	Ba	61.911	44.13	28.491	Lu	0.0244	0.0248	0.0359
Cr	15.122	12.545	16.456	La	3.172	37.133	39.091	Ta	2.65	2.23	1.845
Co	2.01	9.874	1.848	Ce	3.634	5.477	9.6	Ir	0.785	0.665	0.5925
*Fe	10.25	8.122	4.70	Pr	0.464	8.658	8.897	Pb	217.229	96.934	117.897
*Cu	0.215	0.252	0.825	Nd	0.549	3.154	2.402	Th	0.247	0.175	0.163
Ni	28.14	43.776	56.82	Sm	0.894	7.051	5.549	U	0.133	0.137	0.172
Zn	30.713	37.708	50.626	Eu	0.44	2.68	1.431				
As	0.911	0.642	0.143	Gd	0.155	8.376	7.102				
Rb	18.065	14.394	19.035	Tb	0.381	1.452	0.973				

* Measured by FSAAS.

From the results of Sequential Extraction (Fig. 1) on pond ash samples it is observed that leaching potentials of different elements from the samples varied with change in pH. Na and Mo were mostly water soluble. Li and Ni mostly leached in Ion Exchangeable fraction. Arsenic could be traced mostly in Water Soluble and Ion Exchangeable fractions. Leaching of toxic elements like Cr, Zn, Pb, Cd and Cu increased with decrease in pH of the leaching solutions (except Arsenic) and they were mostly Acid soluble (AS3 and AS1 fractions). Leaching of Lanthanides and Actinides was the maximum in AS1 fraction. Other elements were detected in high concentrations in both Acid Soluble fractions (AS3 and AS1). Toxic elements in the Water Soluble fractions leached in higher concentrations than the WHO prescribed limits for drinking water. Sequential Extraction results also gave the total leached concentrations of those elements from the pond ash samples as shown in Table 2. Elements like Al, Ti, V, Ni, Zn, Mo, Ba, Ce and Pb could be extracted in high concentrations varying from few hundreds to tens of thousands mg/kg of the pond ash samples. Total leachable content of toxic elements were moderately high for Cr and low for Cd, Cu and As. Radioactive elements like Th and U could also be detected in all the fractions extracted from the ash samples. Other elements leached from pond ash in concentrations varying from few mg/kg to few 100 mg/kg of pond ash samples.

The purpose of performing Sequential Extraction was to measure the total amounts of elements leaching and the leaching potentials of those elements from the same sample in contact with different leaching solutions. Toxic element Arsenic has high chance of getting leached in normal pH conditions prevailing in the ash ponds. If the pH of the ash pond system changes by any natural phenomena like acid rain or any anthropogenic activity, then there is a high chance of leaching of toxic and radioactive elements in much higher concentrations. If the water present in ash ponds are not taken out periodically and if there is no protective barrier between soil and pond ash layers, then there remains high potential of contamination of the surrounding soil and the groundwater due to percolation of the water prevailing in the ash ponds through soil media.

During TCLP Al, Ti, Mo and Pb leached in high concentrations varying from approximately hundred to several tens of thousands of ppm in the leaching solution applied (Table 3). Toxic elements like Cr, Zn, As and Cu (except Pb) leached varying from less than 1 ppm to less than 100 ppm. Radioactive elements like Th and U could also be detected in all the fractions extracted from the ash samples. Other elements from pond ash leached in concentrations varying from few ppm to 100 ppm.

According to the RCRA list of Hazardous Wastes with ‘D’ code the following elements are considered for assessing whether a waste is hazardous after performing TCLP on the same:

Table 4 Comparison of Data Obtained from TCLP and Regulatory Level

Constituents	TCLP (S-I) mg/L	TCLP (S-II) mg/L	TCLP (S-III) mg/L	Regulatory Level (mg/L)
As	0.911	0.642	0.143	5
Ba	61.911	44.13	28.491	100
Cd	1.441	1.621	1.031	1
Cr	15.122	12.545	16.456	5
Pb	217.229	96.934	117.897	5
Se	NA	NA	NA	1
Ag	6.096	5.939	3.846	5

Note: NA - Not Analysed.

Source: <<http://www.epa.gov/region2/children/k12/english/art-3of5.pdf>>

Comparing the data listed in the above table, it can be concluded that Pb and Cr were present in the extracted solutions (from the three pond ash samples) far exceeding the regulatory levels. Ba and As leached within the regulatory standard for the same. Cd and Ag leached just crossing the regulatory standard levels. So, the ash samples can be classified as hazardous material.

4. Conclusions

Following conclusions can be made from the above discussed results:

1. Leaching of different elements from pond ash samples was pH dependent.

2. Sequential extraction results considering Fig. 1 (leaching potentials of different elements) showed:

- i. Toxic elements like Cr, Zn, Pb, Cd and Cu mostly leached in AS3 and AS1 fractions.
- ii. Arsenic leached mostly in WS and IE fractions. So, there remains high potential of contamination of soil and groundwater due to Arsenic leaching under normal pH conditions.
- iii. All Lanthanides and Actinides mostly leached in AS1 fractions.

Sequential extraction results considering Table 2 (total extractable concentrations of different elements) showed:

- i. Higher leaching of Al, Ti, V, Ni, Zn, Mo, Ba, Ce and Pb.
- ii. Moderately high leaching of Cr.
- iii. Low leaching of Cd, Cu and As.
- iv. Radioactive elements like Th and U could also be detected.

3. There are high chances of Soil and Groundwater contamination if protective barriers are not provided between soil and pond ash layers.

4. Comparing the results of TCLP with the RCRA list of Hazardous Wastes with 'D' code, it can be concluded that the samples are environmentally hazardous in nature.

5. Further study can be done on pH and time dependent leaching behaviour of the elements detected during SEP and TCLP.

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References

- [1] Pappu A., Saxena M. and Asolekar S.R. Solid wastes generation in India and their recycling potential in building materials. *Building and Environment*, 42(6), 2007, 2311-2320.
- [2] Shivpuri K.K., Lokeshappa B., Kulkarni D.A., Dikshit A.K. Metal Leaching Potential in Coal Fly Ash. *American Journal of Environmental Engineering*, 1(1), 2011, 21-27.
- [3] Mandal A. and Sengupta D. Radionuclide and trace element contamination around Kolaghat Thermal Power Station, West Bengal –Environmental implications. *Current Science*, 88(4), 2005, 617-624.
- [4] Shan X., Chen B. Evaluation of sequential extraction for speciation of trace metals in model soil containing natural minerals and humic acid, *Anal. Chem.*, 65(6), 1993, 802–807.
- [5] Chang C. F., Wang C. F., Mui D. T. and Chiang H. L. Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: A case study for BCR 176. *Journal of Hazardous Materials*, 163(2-3), 2009, 578-587.
- [6] Bruder-Hubscher V., Lagarde F., Leroy M.J.F., Coughanowr C., Enguehard F. Application of a sequential extraction procedure to study the release of elements from municipal solid waste incineration bottom ash. *Analytica Chimica Acta*, 451(2), 2002, 285–295.
- [7] Huang S. J., Chang C. Y., Mui D. T., Chang F. C., Lee M. Y. and Wang C. F. Sequential extraction for evaluating the leaching behaviour of selected elements in municipal solid waste incineration fly ash. *Journal of Hazardous Materials*, 149(1), 2007, 180-188.
- [8] Tessier A., Campbell P.G.C., Bisson M. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51(7), 1979, 844-851.
- [9] USEPA SW 864 method 1311