

Heavy Metal Toxicity of Fly Ash Exposed to Acidic Environments

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ABSTRACT

Fly ash is an industrial solid waste product, produced in huge quantity from industries comprising coal combustion units, especially thermal power plants. Improper Fly ash disposal practices result in severe-long-term environmental problems. The conveying disposal practice of Fly ash involves carrying with water from point of generation to holding ponds or lagoons, heaping and trucking, utilization in cement or concrete making and rest (about 40 percent) fraction is openly dumped into environment as landfill or else. During these practices, Fly ash disperses through all environmental segments and exposed to varying environmental conditions causing prolonged exposure, leaching and accumulation of many toxic metals in biosphere food chain. Comparatively, acidic environment favors more metal leaching, enhance the associated risks and become a great concern. The present study proceeded to evaluate the probable heavy metal toxicity caused by exposing Fly ash to various acids of different concentration and contact time. Metals showed varying degree of leachability from Fly ash exposed to different acids. However, the prominent order of leaching was found as in sequence of Cr > Cu > Pb > Co > Cd. The paper also describes possible toxic effects of involved metals leached from Fly ash exposed to acidic environments.

Keywords: Fly ash, Heavy metals, Leaching, Toxicity, Acidic environment

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1. INTRODUCTION

In the developing countries like India several industrial process residues like Fly-ash, Red-mud, Phosphogypsum, Lime-stone waste, Steel and blast furnace, Coal dust and Textile sludge are being produced at an appalling rate^[3]. Prime industrial solid waste i.e. Fly ash, constitutes about 13% of total solid waste (960 million tons) generated in India around 130 Mt annually that continually increasing by 2.2% annually^[1]. Though Fly ash is recycled in applications like cement, bricks etc., a large portion still remain unutilized^{[2] [3]}. The ill-chosen manners of disposal finally result in leaching into the groundwater originating serious health problems^{[2] [4] [12]}. Fly ashes contain large amount of metals and metalloids like B, Pb, Zn, Cu, Co, Cr, Cd, Mn, K, Fe, Na, Si, P, Ti, Ba, Al, As and total nitrogen and total phosphorus and even the organic compounds like polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Mostly these metals are present in the organic form in industrial wastes which become persistent in nature due to their long half-life and finally become available to all living forms like humans, plants and animals. As, these solid wastes are widely used in the construction of raw materials, so there is a need for their characterization and empathizing leaching behavior to know the possible environmental impacts^[11].

Various attempts have been done by the investigators to study the dissolution characteristics of coal Fly ash through leachate analysis. Several leaching tests such as Cascade-leaching test, strong acid digest test, strong acid digest test, ASTM shake test, 30-day shake test, TCLP, SLP, ASTM column, open percolation column test were carried on on-site piles and ash ponds in order to assess their potential in back-filling of abandoned coal mines. It was felt that long term open percolation column tests were best to simulate the open environmental conditions^[19]. Various extractants like Sulfuric Acid, Hydrochloric Acid, Nitric Acid, Glacial Acetic Acid, Distilled Water, and Sea Water were used to study the leaching behavior of heavy metals in natural environmental conditions. It was found that increase in the acidity of the extracting solution by adding sulfuric acid cause hindrance in the dissolution of Ca while the same enhanced the dissolution of Al. It was also observed that addition of HCl at pH 4 removed 65% of Ca content^[18]. Leaching studies of molybdate reactive-assimilable Si species with sea water, synthetic sea water and distilled water showed poor results with sea water because of its buffering capacity and salting –out effect^[15]. Increased demands for the raw materials have abandoned the natural reservoirs. In order to remunerate, Fly ash should be utilized for some beneficial purpose. However, various advanced technologies have been practiced in industries but large scale utilization is yet to materialize, which calls for a need to characterize and investigate the leaching behavior of different elements present in the coal Fly ash and its stabilized products under natural environmental conditions.

2. MATERIALS AND METHOD

2.1 Material Preparation

Fine particulate form of Coal Fly Ash (CFA) sample collected from the northern part of India was used in the as received form.

2.2 Instrumentation

X-ray Fluorescence (XRF) / Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used for the basic compositional analysis.

2.3 Leaching Test

Modified ASTM batch extraction method (ASTM D 5233-92) was conducted in which different extracting solutions were employed. Extracting solution prepared with glacial acetic acid and sodium hydroxide with a pH of 4.93 +/- 0.05 was used for the acidic sample. Sample kept in a shaker at 50 rpm for 18 hours was maintained at L/S ratio of 20 using the extracting solutions. Leachate filtered with filter paper of size 8 microns was examined for the

concentration of Mg, Mn, Ni, K, Fe, Ca, P, Si, Pb, Cd, Cr, Co, Cu through spectrophotometer and Atomic Absorption Spectrometry (AAS).

2.4 Pretreatment of Fly ash

In this study three methods have been adopted for pretreatment of Fly ash samples.

- a) Fly ash samples were dried at 105°C for 24 h. After this, they were treated with 2 M solution of NaOH or 1 M solution of HCl (solution: fly ash 10:1 by weight). The mixture was dried at 100°C for 24h and filtered, washed, & dried at 105°C for 24h (C1)^[14].
- b) Fly ash samples were treated with 2M HCl solution for 24h at room temperature and then washed, & dried at 110°C overnight (C2)^[10].
- c) Fly ash samples were treated with concentrated nitric acid (acid/ash = 5 ml/g) at 700°C for 1h. Sample were then washed & dried at 300°C for 3h (N3)^[21].

3. Results and Discussion

Metals like Si, Al, Fe, P, Ca, Mg, K, Cr, Cu, Ni, Pb, which are usually present in the coal Fly ash, were selected for their mobility studies in both ASTM D 5233-92. XRF/ICP-OES were used to determine the chemical composition. It was observed that SiO₂ constitutes the highest amount of the total percentage. CFA also contains high volatile content but the presence of high SiO₂ percentage lowered its LOI factor. Silica cause silicate formation with Na₂O and K₂O which bind the metals and precludes them from contributing to LOI. Oxides of Cr were also present significantly.

Table 3.1: Chemical composition of CFA

ELEMENTS	CFA (%)	ELEMENTS	CFA (%)
SiO ₂	57.36	CaO	7.62
Al ₂ O ₃	31.78	MgO	0.23
Fe ₂ O ₃	4.62	Na ₂ O	0.23
TiO ₂	1.65	K ₂ O	0.59
P ₂ O ₅	-	Cl	-
LOI	2.66	Cr ₂ O ₃	2.28

It was observed that CFA is nearly neutral (i.e. 7.5) after mixing with the distilled water. Addition of 1N HCl reduced (i.e. 0.51) pH due to the internalization of hydrogen ions. Acid digestion test has shown very high ion exchanging capability. Extracting solution of higher alkalinity (i.e. 4.37) was used for better extracting potential.

3.1 AAS results from leaching test:

Metal concentration of the leachates is the most important indicator to access the environmental impacts which provide path for the safe disposal practices. The concentration results of various elements analyzed through AAS (Atomic Absorption Spectroscopy) and UV-visible spectrophotometer showed that leaching potential increased with the decrease in pH because of the dissolution of heavy metal ions in exchange of H⁺ ions of leaching solution. As the leaching increases with the increased radius, so the leaching order is observed in the order of: Cr (128 pm) > Mn (127 pm) > Ni (124 pm) > Fe (126 pm) [Figure 01]. Here Fe (126 pm) is showing irregular behavior because of the presence of Fe mainly in oxide form i.e. Fe₂O₃ which is more stable. Ca, Mg, P, Mn, and Ni are responsible for high leaching potential as property of forming salts, acids and hydroxides. Heavy metals like Cr was observed in significant amount while Cu, Cd and Co was below detection limit. SiO₂ content was also not observed in noteworthy amount.

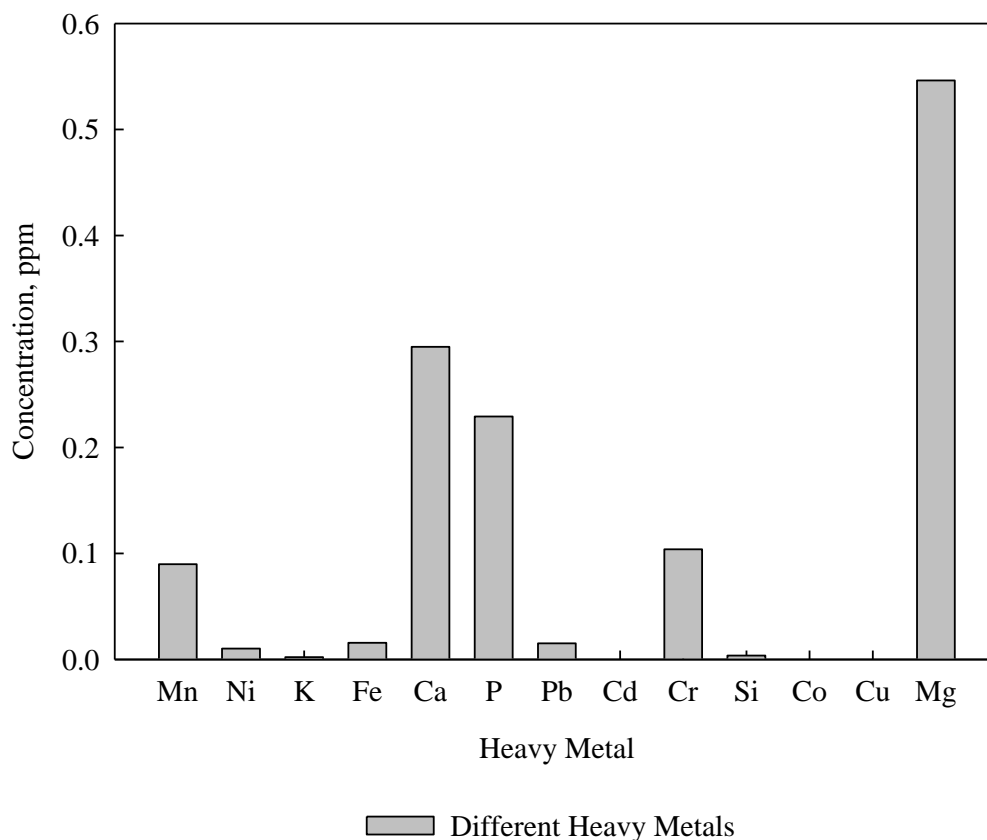


Figure 1: AAS analysis of leachate from Fly ash during ASTM batch extraction method

3.2 A Comparison Assessment of Leaching of Heavy Metals:

A comparative study has been done here of present study with the work done by Prasad *et., al* (2008). The results in table 3.2 showed similar type of composition of the samples from North India, Jharkhand and Andhra Pradesh fly ash except the presence of TiO₂, MgO and Cr₂O₃ in the North India fly ash.

Table 3.2: Comparison of Chemical composition of CFA

ELEMENTS	CFA (%)		
	North India Fly Ash (This Study)	Jharkhand Fly Ash (Prasad <i>et., al</i>)	Andhra Pradesh Fly Ash (Prasad <i>et., al</i>)
SiO ₂	57.36	60.11	56.70
Al ₂ O ₃	31.78	26.53	23.80
Fe ₂ O ₃	4.62	4.25	4.70
TiO ₂	1.65	-	-
P ₂ O ₅	-	-	-
Loss of Ignition	2.66	0.88	10.35
CaO	7.62	4.00	2.10
MgO	0.23	-	-
Na ₂ O	0.23	0.22	0.25
K ₂ O	0.59	0.75	0.50
Cl	-	-	-
Cr ₂ O ₃	2.28	-	-

4. Environmental Impact Assessment of Pretreatment Process

Impact assessment of pretreatment process of F1, F2, and F3 had been done by AAS. Analysis of residual had been done, in which the concentration of specific heavy metals examined. Because heavy metals present in the Fly ash are the main problem during disposal and land filling.

4.1 Pretreatment of F1, F2 and F3

Pretreatment of F1, F2 and F3 describes the pretreatment of all raw Fly ash samples, which are shown by Figure 2, Figure 3 and Figure 4 respectively. It requires for enhancing the surface area which is important for the good catalytic activity but due to these pretreatments, the effluent comes out that going to be discarded. The used Fly ash samples have some heavy metals which come out through the pretreatment methods, so there is need to determine the concentration of heavy metals that are going into effluent. AAS has been used for getting the concentrations of Co, Pb, Cd, Cr, and Cu.

In all these pretreatments, the Cr is in very high concentration among all these heavy metals. The concentration of Co and Cd is very less using 2M and 16 M HNO₃. The results obtained by AAS are shown in tabular form for F1, F2 and F3 pretreatment in Table 4.1, Table 4.2 and Table 4.3 respectively.

Table 4.1: Pretreatment of F1

Metal	1M HCl	2M HCl	16M HNO ₃
Cd	0.10 ppm	0.02 ppm	0.08 ppm
Co	2.81 ppm	0.00 ppm	0.00 ppm
Pb	5.49 ppm	1.70 ppm	1.51 ppm
Cu	10.25 ppm	2.78 ppm	1.07 ppm
Cr	17.91 ppm	5.08 ppm	5.62 ppm

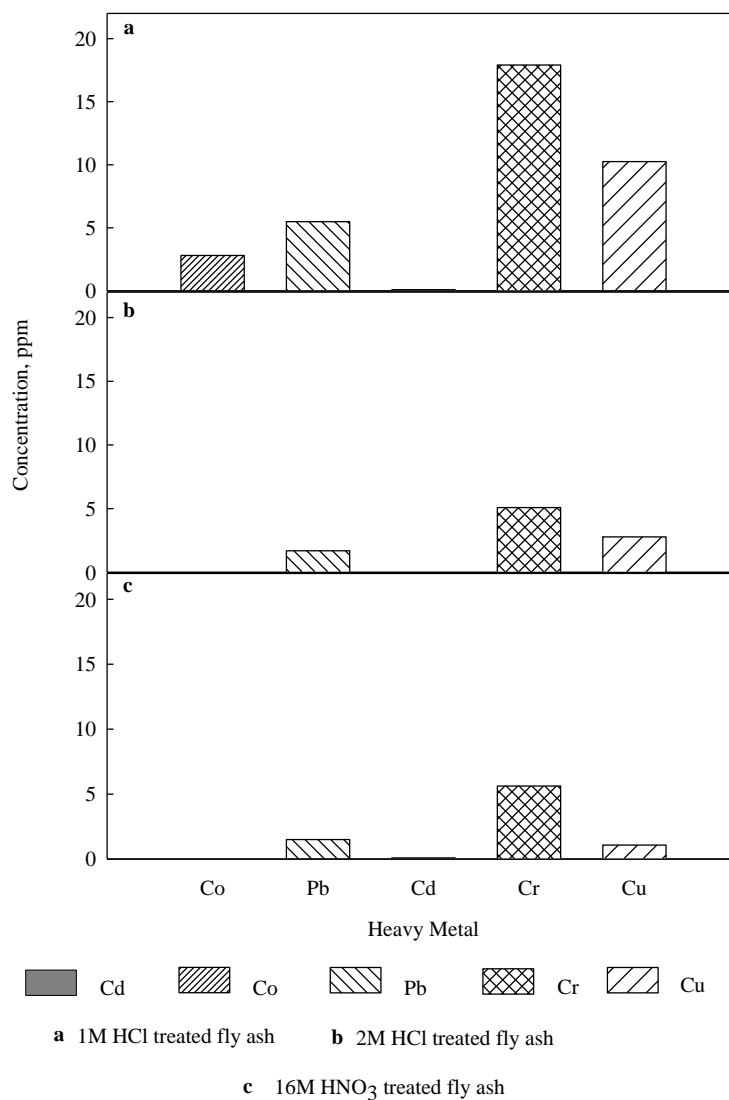


Figure 4.1: Various Toxic Metals in Residual of Pretreated F1 Fly ash

Table 4.2: Pretreatment of F2

Metal	1M HCl	2M HCl	16M HNO ₃
Cd	0.09 ppm	0.03 ppm	0.05 ppm
Co	2.87 ppm	0.00 ppm	0.00 ppm
Pb	4.11 ppm	1.43 ppm	1.28 ppm
Cu	7.96 ppm	2.17 ppm	1.00 ppm
Cr	15.49 ppm	5.03 ppm	5.46 ppm

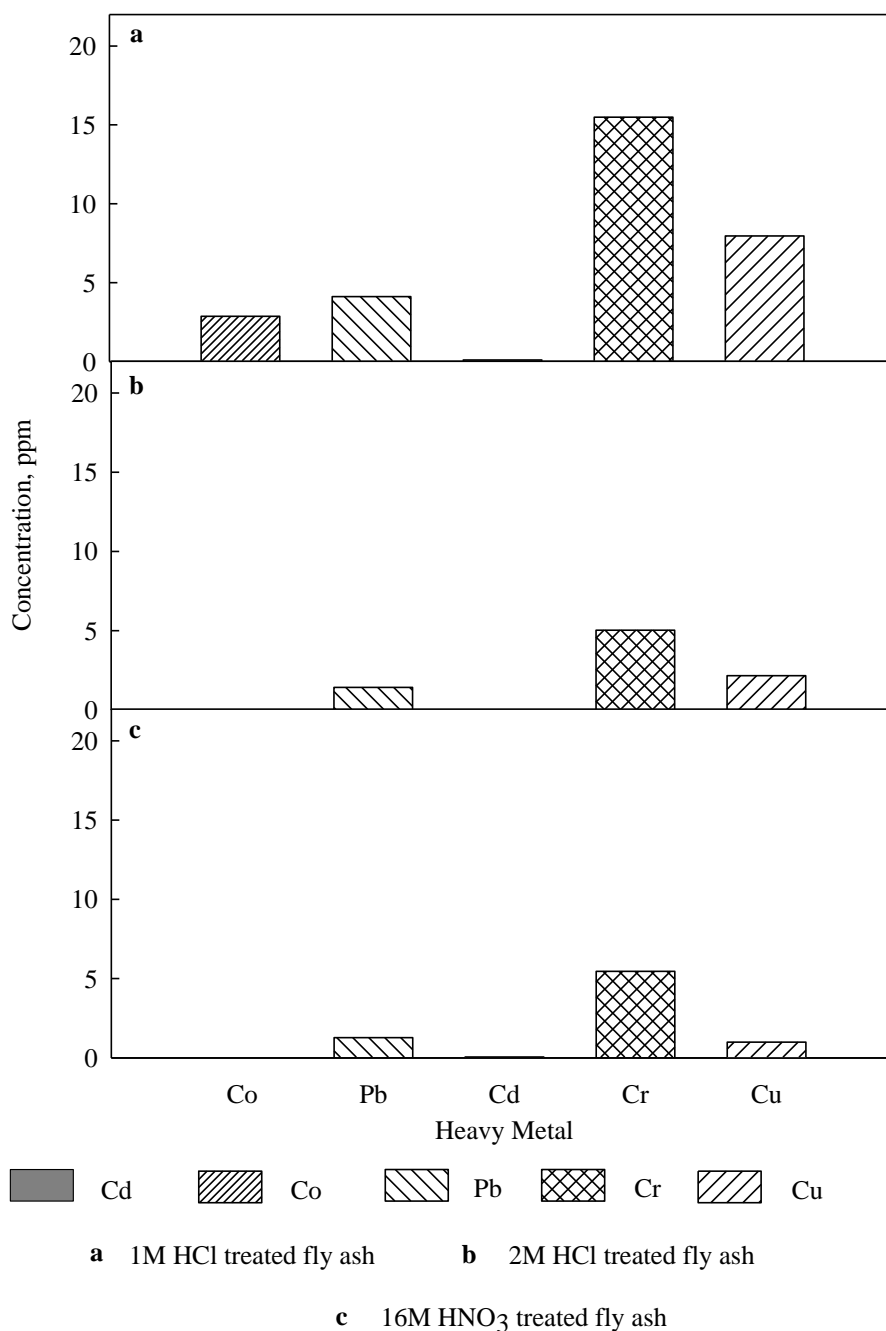


Figure 4.2: Various Toxic Metals in Residual of Pretreated F2 Fly ash

Table 4.3: Pretreatment of F3

Metal	1M HCl	2M HCl	16M HNO ₃
Cd	0.09 ppm	0.02 ppm	0.06 ppm
Co	1.89 ppm	0.00 ppm	0.00 ppm
Pb	6.57 ppm	2.28 ppm	1.52 ppm
Cu	10.13 ppm	3.91 ppm	1.77 ppm
Cr	10.64 ppm	5.33 ppm	5.22 ppm

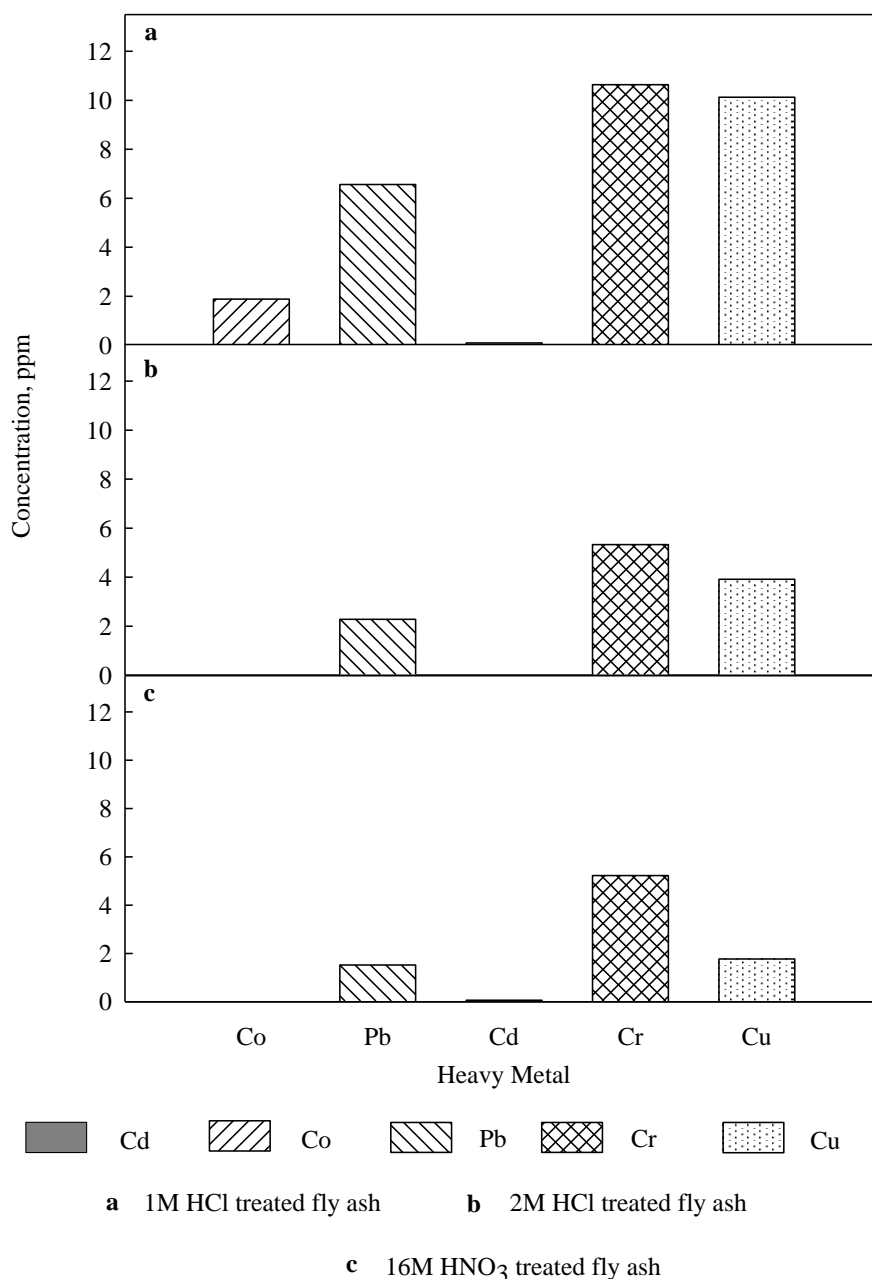


Figure 4.3: Various Toxic Metals in Residual of Pretreated F3 Fly ash

CONCLUSIONS

This is beyond question that power plants produce a significant amount of Fly ash. The limits for the heavy metal concentration in surface water, groundwater and sewage water differs from place to place. To find out the possible environmental impacts with the concentrations beyond acceptable limit, this study has been carried out. In general Fly ash contain heavy metals like As, B, Cd, Cr, Co, Hg, Mo, Mn, Ni, Pb, Se, V, Zn which are present in either free form, surface bound or in complexion with aluminosilicate matrix [5] [6] [20]. Elements present in the complex form have lower leaching potential than those associated with surface particles [17]. Leaching of metals in presence of aqueous media is affected by L/S ratio, pH [6] [7] [16], type of leachant, stirring conditions, duration of leaching, temperature and particle size distribution [6] [7] [8]. It is also believed that the major elements like Ca, K, Mg, Al have higher leaching tendency compared to Fe, Na, Mn, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Th, U, V, Zn under acidic

conditions^[13]. Release of cationic species depends on the amount of Ca concentration. Higher the calcium concentration, higher will be the amount of acid required and the time period for the release of metals^[9].

Release of cationic species depends on the amount of Ca concentration. Higher the calcium concentration, higher will be the amount of acid required and the time period for the release of metals^[9]. The major elements in the Fly ash were Si, AL, Fe, Ti, P, Ca, Mg, Na, K. Coal Fly ash (pH=7.5) was found slightly acidic in nature. Ca and P were found with higher leaching potential while K, Fe leached out less because of their ability to form insoluble stable oxides.

The findings of above explained leaching experiments provide useful information for field scenarios. Nevertheless, some additional work is required to be done to study various leaching aspects with stabilizing agents who are still under cover.

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