LEACHING BEHAVIOUR OF ELEMENTS FROM SUB-BITUMINOUS COAL FLY ASH

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY IN MINING ENGINEERING

BY SANTOSH KUMAR 10605002



DEPARTMENT OF MINING ENGINEERING NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA - 769008 2009-10

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CERTIFICATE

This is to certify that the thesis entitled "LEACHING BEHAVIOUR OF ELEMNETS FROM SUB-BITUMINOUS COAL FLY ASH" submitted by Sri SANTOSH KUMAR in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ABSTRACT

The disposal or use of coal fly ash in ponds, landfills or in construction of roads is a great concern, because of its leaching behavior. It has problem especially when elements from fly ash get leached and contaminate or degrade the quality of drinking water. The aim of this study is to investigate leaching behavior of metals from northeastern coal fly ash. Serial batch leaching test for elements namely Fe, Mn, Zn, Cu and Pb has been carried out with liquid to solid (L/S) ratio at 4 and 12. The pH of the leachate was weekly alkaline in nature, ranging from 7.39 to 7.90. Concentration of Fe and Mn in the leachate is higher than the maximum contaminant level of drinking water. However, concentration of elements in the leachate from the northeastern fly ash is less than that of the Gondwana fly ash. This is possibly due to the different physico-chemical properties of the fly ash.

CHAPTER 1

INTRODUCTION OBJECTIVES

INTRODUCTION

What is fly ash?

Fly ash is generally the by-product produced due to the combustion process. It is actually captured from the chimneys of coal fired power plants. The bottom ash and fly ash jointly is known as coal ash, the bottom ash is generally removed from the bottom of coal furnaces.

The component of fly ash varies significantly, which depends on the makeup of coal being burned. But all the fly ash includes some amount of silicon dioxide (SiO_2) both amorphous and crystalline and calcium oxide (CaO). Coal contains various trace elements in various quantities and during combustion process of coal they all get enriched as a result of carbon loss as carbon dioxide and trace elements get associated on the surface of ash particles due to evaporation and condensation. The characteristics of the coal used and the type of installations used for the generation of a fly ash have a direct influence on chemical and mineralogical composition of fly ash (Benito et al., 2001).

Origin of fly ash

The fly ash produced from burning pulverized coal in a coal-fired boiler is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected by means of electrostatic precipitators, bag houses, or mechanical collection devices such as cyclones.

In general, there are three types of coal-fired boiler furnaces used in the electric utility industry. They are referred to as dry-bottom boilers, wet-bottom boilers, and cyclone furnaces. The most common type of coal burning furnace is the dry-bottom furnace.

When pulverized coal is combusted in a dry-ash, dry-bottom boiler, about 80 percent of all the ash leaves the furnace as fly ash entrained in the flue gas. When pulverized coal is combusted in a wet-bottom (or slag-tap) furnace, as much as 50 percent of the ash is retained in the furnace, with the other 50 percent being entrained in the flue gas. In a cyclone furnace, where crushed coal is used as a fuel, 70 to 80 percent of the ash is retained as boiler slag and only 20 to 30

percent leaves the furnace as dry ash in the flue gas. A general flow diagram of fly ash production in a dry-bottom coal-fired utility boiler operation is presented in Figure 1.1.



Figure 1.1: Generation of fly ash (www.tfhrc.gov/hnr20/recycle/waste/cfa51.htm)

OBJECTIVE

The specific objective of this study is

- Characterization of Northeastern fly ash
- > Study the behavior of metals during leaching of fly ash.
- To compare the leaching behavior of metals from Northeast fly ash with its Gondwana counter part.

CHAPTER 2

LITERATURE REVIEW

LITERATURE REVIEW

Increase in demand of coal supply by energy sector leads to increase in coal production, which in turn increases the amount of fly ash produced. Around 112 million tonnes of fly ash was generated in 2007 (Dhadse et al., 2008). The problem with fly ash lies in the fact that not only does its disposal require large quantities of land, water, and energy, its fine particles, if not managed well, by virtue of their weightlessness, can become airborne .Fly ash has occupied 65 acres of land (Chakravarthi et al., 2007). Leaching studies are important in predicting the environmental impact associated with ash pond disposal techniques (Prahraj et al., 2002).Utilization of fly ash in India is very low as compared to other coal producing countries (Table 2.1) as majority of fly ash is lying in the ash pond.

Country	Ash production	Ash Utilization
	(Million tones)	%
India	112	38
China	100	45
USA	75	65
Germany	410	85
UK	15	50
Australia	10	85
Canada	6	75
France	3	85
Denmark	2	100
Italy	2	100
Netherlands	2	100

Table 2.1: Production of fly ash worldwide (Dhadse et al., 2008)

Composition of fly ash

The chemical properties of fly ash are generally influenced to a great extent by the chemical content of the coal burned, the air pollution control strategy at the power plant, and the techniques used for handling and storage.

Table 2.2 summarizes the normal range of chemical constituents of fly ashes from bituminous coal, lignite coal, and sub bituminous coal. Lignite and sub bituminous coal fly ashes have higher calcium oxide content than fly ashes from bituminous coals. Lignite and sub bituminous coal fly ashes may have a higher amount of sulfate compounds than bituminous coal fly ashes.

Component	Bituminous	Sub-bituminous	Lignite
SiO ₂	20-60	40-60	15-45
Al ₂ O ₃	5-35	20-30	10-25
Fe ₂ O ₃	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO_3	0-4	0-2	0-10
Na ₂ O	0-4	0-2	0-6
K ₂ O	0-3	0-4	0-4
LOI	0-15	0-3	0-5

Table 2.2: Normal range of chemical composition for fly ash produced from different coal types (expressed as percent by weight). (www.tfhrc.gov/hnr20/recycle/waste/cfa51.htm)

Two classes of fly ash are defined by ASTM C618: Class F fly ash and Class C fly ash. The chief difference between these classes is the amount of calcium, silica, alumina, and iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite).

Ash contain various elements like As ,B, Be, Ca, Cd, Cr, Fe, Hg, Mg, Mo, Na, Ni, Pb, Ra, Se, Th, U,V, Zn, etc either on the surface of the ash particles or on the aluminosilicates or in both as a result of condensation during combustion (Ram et al., 2007). Concentration of various metals in Indian fly as is given in Table 2.3.

Trace element	West Bengal ¹	Delhi ²	Orissa ³
As	490	-	-
Pb	9.5	56	83.63
Cr	20	103	145.75
Zn	290	124	69
Cu	20	18	83.36
V	30	-	-
Zr	30	-	-
Ba	550	-	-
Sc	10	-	-
Y	10	-	-
Со	_	18	16. 88
Ni	_	63	56.50
Mn	—	62	338.91

Table 2.3: Trace elements in fly ash from different states in India (Unit: mg/kg)

¹Dutta et al. (2009); ² Sushil et al. (2006); ³ Sushil et al. (2006); – data not available

Utilization

The reuse of fly ash as an engineering material primarily stems from its pozzolanic nature, spherical shape, and relative uniformity. Dhadse et al. (2008) has reviewed various utilization of fly ash in India as follows:

- Portland cement and grout
- Embankments and structural fill
- Waste stabilization and solidification
- Raw feed for cement clinkers
- Mine reclamation
- Stabilization of soft soils
- Road sub base
- Aggregate
- Flow able fill
- Mineral filler in asphaltic concrete
- Other applications include cellular concrete, geopolymers, roofing tiles, paints, metal castings, and filler in wood and plastic products
- For agriculture purpose

Hazard from Fly Ash

Ash pond is a common available disposal facility for thermal power plants. The pond ash is subjected to weathering and the metals present in ash migrate to the soil and subsequently to the ground water over a period of time. At Vijayawada thermal power station, Andhra Pradesh, ground water quality monitored has been deteriorated due to the presence of fly ash ions (macro and micro such as Fe, Ca, Mg etc.) which were leached out from the ash up to some extent. The contamination is likely to increase in the case of toxic and other ions with the passage of time (Suresh et al., 1998). Recently, Praharaj et al. (2002) has reported that groundwater close to the ash pond in Angul, Orissa is highly contaminated with Fe, Ba, Cu, Mn, S, Pb, V, and Zn. This is due to very high leachability of many trace elements from fly ash by the infiltrating rainwater.

NEED OF LEACHING STUDY

- ✓ While transporting, disposal and storage of fly ash, the residues from coal combustion undergo a process called leaching due to rainfall or by weathering, by which an undesirable components get leached of into ground water, surface water, in soil, creating pollution. These leached out components in higher concentration than drinking water can cause contamination in drinking standards (Ugurlu 2004).
- ✓ It is important to predict the leaching behavior of the fly ash for the prevention of its effects to the environment, especially for the aquatic environment, when ash is majorly disposed off in water (Ram et al., 2007).

CHAPTER 3

MATERIAL AND METHODS

MATERIALS AND METHODS

Ash samples were collected from Naogaon paper mill, Assam, India. The ash samples were dried and sieved (63 μ m) before laboratory analysis and serial batch leaching. To understand the short term leaching effects, serial batch leaching test was carried out. The leaching test was carried out for different L/S ratios, 4 and 12 at pH 5.6 following the method of Praharaj et al. (2002). Both the solutions were then stirred constantly and kept for 24 hrs. After 24 hrs the lechate were immediately filtered, and it was added with HNO₃ to pH less than 2 for the analysis of metals. The filtrate was stored in tightly capped acid washed bottles. For each next step, additional 60 ml of buffer solution was added along with the filter paper from the last step. Each leaching stage was carried out for 24 hrs .Similarlily the above mentioned procedure was followed for 4 days .Then the filtrate samples of all days were analyzed using Atomic Absorption Spectrophotometer (PerkinElmer).

Mineralogy of the fly and was studied using a Phillips PW-1710 X-ray diffractometer (XRD) employing Cu $K\alpha$ radiation at 1.2°/minute scanning rate. Morphology of fresh and leached fly ash samples was studied using scanning electron microscopy (SEM), JEOL JSM-6480LV, attached with energy dispersive X-ray (EDX).

Total concentration of elements in the fly ash was determined using Philips PW 2400 X-ray fluorescence (XRF) from the press pellets.

LOI (loss on ignition) for ash samples were also calculated. First, the weight of crucible was measured and then a known weight of fly ash was taken in crucible. Then the crucible was covered with lid, and it was inserted in Muffle furnace for half an hour at 550° C. After ignition, the weight of crucible was measured along with sample. From the difference between weight of crucible with fly ash before ignition and after ignition, LOI was calculated, dividing by actual ash sample taken in crucible.

CHAPTER 4

RESULTS AND DISCUSSION

MINERALOGY OF FLY ASH

From the XRD study of fly ash samples, it was confirmed that quartz, anhydrite, and hematite are the dominant phases while calcite present in trace. The presence of large humps and irregular background in diffractograms indicated the presence of glassy or amorphous constituents in the ash. The principal component of fly ash comprising of quartz, anhydrite and hametite along with minor phases of aluminosilcate in weathering environment may form clay minerals (Bradely et.al 1999) and elements may be released into solution and can contaminate groundwater (Fulekar, 1993).



Figure 4.1: XRD pattern of fly ash

COMPOSITION OF SUB-BITUMINOUS COAL FLY ASH

It was observed that the major and minor elements concentration of Northeast fly ash was much higher than that of Gondwana fly ash (Table 4.1), but the leached out elements concentration was higher in Gondwana fly ash than Northeast fly ash. The LOI of present study was also much higher than the Gondwana because of presence of high unburned carbon in fly ash. The sulphur content is also high in present study, since the fly ash is from North East Indian coal (Chandra et al., 1980). All the minor elements concentration in Northeast fly ash is higher than Gondwana leaving Mn, which is higher than Gondwana.

Elements	Gondwana fly ash*	Northeast fly ash
	(%)	(%)
Fe	0.8	6.23
S	0.03	0.244
	Ppm	ppm
Cu	15.96	94
Mn	109.63	105
Zn	10.56	156
Pb	6.64	213
LOI	0.1%	18.5%

Table 4.1: Comparison of Composition of fly ash

*Prahraj et.al. (2002)

MORPHOLOGY

The scanning electron micrograph of fly ash shows the presence of solid spherical cenospheres. In all the micrographs, the preleached fly ash spherical cenospheres were observed to be possessing relatively smooth surfaces compared to the postleached ash spherical cenospheres (Figure 4.2). The occurrence of rod shaped anhydrite crystal is also confirmed under SEM with the help of EDX. The unburnt carbon is clearly distinguishable under SEM due to very high porous structure (Figure 4.3). The EDX spectra (Figure 4.4) also indicate the presence of high carbon and oxygen content and are due to the presence of high concentration of unburnt carbon.



Figure 4.2: SEM photomicrographs of cenospheres of fly ash before leaching (A) and after leaching (B).



Figure 4.3: Porous structure of the unburnt carbon in the fly ash



Figure 4.4: EDX spectra of the fly ash sample

LEACHING STUDY OF THE FLY ASH

pH of Leachate

The pH of the leachate (Table 4.2) ranged from 7.39 to 7.70 for L/S ratio 4 and 7.43 to 7.90 for L/S ratio 12. Alkaline pH is due to the utilization of coal and lime together in the boiler at the Naogaon paper mill. The pH of solution for L/S ratio 4 decreased with increase in contact time while the trend is reversed in case of L/S ratio 12. The pH of solution was weakly alkaline in nature.

L/S ratio	Day	pН
4	1	7.70
	2	7.60
	3	7.55
	4	7.39
12	1	7.43
	2	7.85
	3	7.42
	4	7.90

Table 4.2: pH of solutions in different days with L/S ratio 4 and 12

Element concentrations in leachate

The concentrations of elements such as Mn, Fe, Cu and Zn in the leachate from the ash samples are given in Table 4.3. Concentration of Fe and Mn are above maximum contaminant level of the drinking water prescribed by USEPA (Table 4.4) while concentrations of Zn and Cu are within the limits. Leaching behaviour of metals are given in Figure 4.5 to 4.8. But the leached out elements concentration was higher in Gondwana fly ash than Northeast fly ash, because of high unburnt carbon content in Northeast fly ash, which has the tendency of absorbing the elements. As unburnt carbon particles are highly porous in nature and having very high surface area therefore retained the metals (Hequet et al., 2001). All the elements except Fe (Figure 4.5), showed a decreasing trend in leaching with increase in contact time, whereas Fe showed increase in leaching trend.

Present study (Northeastern fly ash)					
L/S	Day	Fe	Zn	Cu	Mn
4	1	0.088	0.048	0.044	0.372
	2	0.064	0.024	0.024	0.196
	3	0.216	0.004	0.004	0.068
	4	1.72	0.003	0.016	0.024
12	1	0.252	0.096	0.06	0.648
	2	0.36	0.005	0.042	0.345
	3	0.264	0.004	0.004	0.12
	4	0.42	0.004	0.004	0.42
	Gondwa	ana fly ash (Sou	urce: Prahraj et al	., 2002)	I
4	1	0.04	0.01	0.07	0.28
	2	0.53	0.08	0.02	0.53
	3	0.06	0.25	0.02	0.63
	4	0.08	0.48	0.54	0.75
12	1	0.52	0.07	0.004	0.06
	2	0.69	0.06	0.004	0.07
	3	4.24	0.09	0.07	0.10
	4	1.36	0.03	0.004	0.07
Maximum pe (US	rmissible limit EPA)	0.3	5	1.3	0.03

Table 4.3: Concentration of elements in fly ash leachate at different L/S ratios (all values in ppm)

 Table 4.4: Maximum Contaminant level for different elements for drinking water prescribed by

 the USEPA (Unit: ppm).

Elements	Maximum contaminant level
Cu	1.3
Fe	0.3
Mn	0.03
Zn	5



Figure 4.5 Comparison of Fe concentration in Lechate from Gondwana and Northeast fly ash



Figure 4.6 Comparison of Zn concentration in Lechate from Gondwana and Northeast fly ash



Figure 4.7: Comparison of Cu concentration in Lechate from Gondwana and Northeast fly ash



Figure 4.8: Comparison of Mn concentration in Lechate from Gondwana and Northeast fly ash

CHAPTER 5

CONCLUSIONS

CONCLUSIONS

- ✓ Serial Batch leaching test was carried out in this study. The serial batch leaching was carried out in the Northeast fly ash.
- ✓ Concentration of elements in the Northeastern fly as is much higher than the Gondwana fly ash except Mn.
- \checkmark Fly ash has high loss on ignition due to the presence of high unburnt carbon content.
- ✓ It was observed that Fe and Mn in the Lechate exceeded the maximum permissible limit of drinking water prescribed by USEPA in some cases. Concentration of Fe and Mn increased with increase in contact time, whereas the values of Zn and Cu decreased with increase in contact time and they were under the maximum permissible limits.
- ✓ The leachates had alkaline pH throughout the experiment because of storage of fly ash along with lime in paper mill industry.
- Concentration of elements in the leachate was less in comparison to the Gondwana coal fly ash due to presence of very high unburnt carbon.

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