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Simulation of Leaching Characteristics of a Fly Ash in an Ash Pond

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Introduction

The conventional practices adopted for disposing off the fly ash are either its 'wet disposal' wherein the fly ash is mixed with water and is disposed off into the ash ponds (commonly termed as the lagoons) or its 'dry disposal'. From the point of view of the ash utilisation, dry disposal method is considered better but the same is difficult to adopt. Also, fly ash being light in weight, gets airborne easily and forms aerosol which is responsible for various pulmonary diseases viz. silicosis and fibrosis. Further, fly ash being a combustion residue of the coal, contains a number of toxic heavy metals and trace elements. Infiltration of water through the ash ponds leaches out these metals and contaminates the subsoil and the ground water.

This calls for studying the leaching characteristics of the fly ash, by simulating various toxic metals leached out and their environmental impact, which would help in adopting an efficient disposal strategy. The data obtained from the leaching tests may also be useful for designing proper containment facilities for minimising the environmental impact of the leached out toxic constituents. The use of clay liners and other barrier materials along with leachate collection systems can be considered at sites with proven ground water contamination potential. However, complete characterisation of ash (i.e. knowledge about its physical, chemical and mineralogical properties)

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along with an understanding of its leaching behaviour is a must in order to design such containment and barrier systems.

In this context, several researchers have studied the leaching mechanisms and the various characteristics of the fly ash, which influence its leachability (Treybal, 1956; Theis and Wirth, 1977; Tessier et al., 1979; Hansen and Fisher, 1980; Dudas, 1981; Roy et al., 1984; Sloot, 1984, 1991; Palit et al., 1991; La Grega and Evan, 1994; Bucholz and Landberger, 1995; Sloot et al., 1996; Shivakumar and Dutta, 1996). These researchers have used column tests, sequential batch or cascade tests, US-EPTOX and TCLP, multiple extraction procedure, Swiss leach test (TVA), NNI, etc. Although, these procedures have some basic differences, the results obtained can be correlated when the leaching characteristics of the fly ash are interpreted against the background of Liquid to Solid ratio (L/S) chosen.

The relation between L/S ratio and the actual time may also be presented by the time required for a certain L/S ratio to be attained under different field conditions. Sloot (1984) has demonstrated one of the most effective means of assessing leaching characteristics by combining the tests related to time and release behaviour under different pH conditions.

When water percolates through the ash pond, cumulative leaching occurs in a cascade manner. As such, the leachates get concentrated when they finally reach to the bottom of the ash pond. While simulating this condition, a close approximation will result if a counter-current scheme is used wherein the final withdrawn solution is taken from fresh ash and fresh leachant added to the already leached ash. The leaching experiments presented in this paper are a combination of column tests and a more refined batch extraction technique. This method addresses both short-term leaching of readily exchanged toxic heavy metals, in a neutral or alkaline environment, likely to be encountered in the ash pond and the long-term slow release of metals in the geo-environment.

In order to study this, complete characterization (physical, chemical and mineralogical) of the fly ash has been done and leaching tests have been conducted to ascertain the possibility of migration of heavy metals, or trace elements, into the ground water and to estimate the maximum concentration of each element actually available for leaching.

Experimental Investigations

Fly ash from Ukai Thermal Power Plant, Surat, Gujarat, India, has been taken for the present study. Various tests were conducted on the ash sample (collected from electro-static precipitator, ESP) for its characterization.

Physical Properties

Specific gravity

Specific gravity of the fly ash sample has been determined as per ASTM D-854-92. The average specific gravity of the fly ash sample is found to be 2.03.

Specific surface area

The specific surface area of the fly ash sample has been determined as per ASTM C-204, using a Blaine's apparatus and Portland cement has been taken as the benchmark. The average specific surface area of the fly ash sample has been found to be 1856 cm^2/g.

Gradational characteristics

The gradational characteristics of the fly ash sample have been obtained by sieving and hydrometer analysis (ASTM D-422-63). The particle size distribution curve for the ash sample is presented in Fig.1. From the figure, it can be noticed that the fly ash sample consists of 6.5% clay (< 0.002 mm),

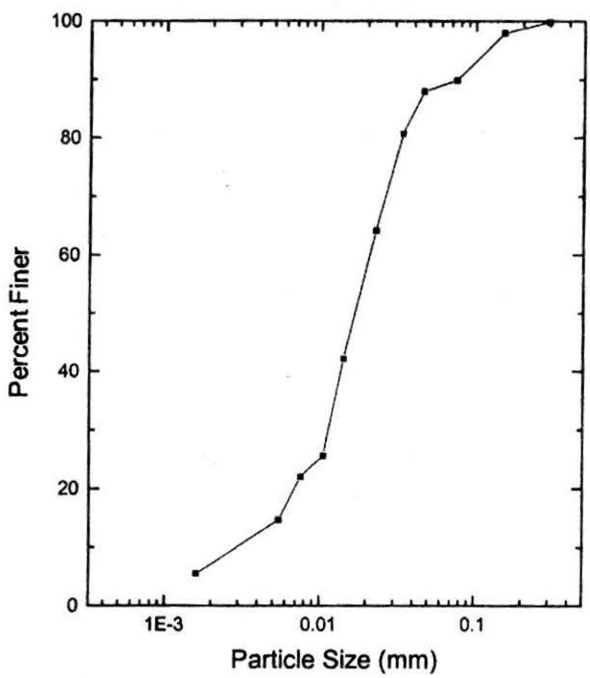

FIGURE 1 : Particle Size Distribution of the Fly Ash

Table 1 : Chemical Composition of the Fly Ash Sample

Oxide	% by weight
SiO_2	61.59
Al_2O_3	30.15
Fe_2O_3	3.40
TiO_2	2.29
K_2O	1.15
CaO	0.72
MgO	0.38
P_2O_5	0.17
MnO_2	0.07
Na_2O	0.05
SO_3	0.03

84.5% silt (0.002 to 0.075 mm) and 9.0% sand (0.075 to 4.75 mm) fractions, respectively.

Chemical Composition

The chemical composition of the fly ash sample, for major oxides, has been obtained with the help of X-ray fluorescence (XRF) technique (Phillips 1410, Holland). The results obtained are presented in Table 1.

From the table, it can be noticed that the Ukai fly ash is ASTM Class 'F' fly ash (ASTM, C-618). The major constituents of the fly ash sample are silica (SiO_2), alumina (Al_2O_3) and ferric oxide (Fe_2O_3). However, traces of calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O), potassium oxide (K_2O), titanium oxide (TiO_2), phosphorus (P_2O_5), manganese oxide (MnO_2) and sulphur tri-oxide (SO_3) are also present in the ash sample.

pH Characteristics

The pH of the ash sample has been determined by mixing it with deionised water (with L/S = 100). As suggested by Sloot (1984), the fly ashes can be classified as acidic (pH < 7, after 10min), alkaline (pH > 10, after 1min) and neutral ($7 < pH < 10$). As per this classification system, the ash sample can be classified as neutral.

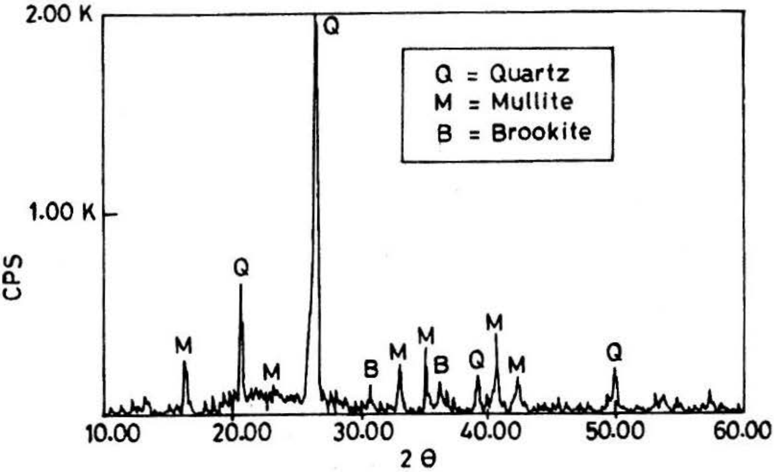

FIGURE 2 : X-Ray Diffraction Pattern of the Fly Ash

Mineralogical Composition

The fly ash sample has been tested for its mineralogical composition by conducting X-ray diffraction (XRD) studies (Rigaku, Japan), using a graphite monochromator and Cu-Ka radiation (scanned from 2θ varying from 10° to 60°), as shown in Fig.2. With the help of JCPDS search match data files, the minerals present in the fly ash sample have been identified. It can be noticed that the ash sample consists of quartz (most predominant), mullite (predominant) and brookite (present).

Trace Elements

The fly ash has been dissolved in hydrofluoric acid, perchloric acid and nitric acid for the measurement of elemental concentration. One gram of the dry fly ash is moistened with perchloric acid and then treated with 20 ml of hydrofluoric acid in a teflon beaker for approximately eight hours, till it stops fuming. Then 10 ml concentrated nitric acid is added to dissolve the contents. The contents are boiled to dryness. Five ml of concentrated HNO_3 is added to dissolve the dried up contents and the final volume is made up to 100 ml by using demineralised water. The concentration of trace elements in this solution is determined using ICP (Inductively Coupled Plasma) technique. The concentration of various trace elements present in the fly ash sample is presented in Table 2.

Leaching Studies

These tests have been conducted using acidulated water (with the help

Table 2 : Trace Elements Present in the Fly Ash Sample

Element	Concentration (ppm)
Ba	535.85
Co	35.41
Cr	167.20
Cu	65.35
Mo	80.30
Ni	52.00
V	141.00
Zn	167.30

of high purity nitric acid with pH = 4) since many of the trace elements may be extracted in much higher percentages when the fly ash sample is subjected to leaching in an acidic medium (Sloot, 1984).

Sequential batch tests

These tests employ a counter-current leaching scheme and simulate ash pond leaching condition. As such, water (leachate) percolates through the ash and gets cumulatively enriched by its leachable constituents, as it comes in contact with fresh ash continuously.

Sequential batch experiments have been conducted, in the present study, by placing known amounts of the fly ash sample in flasks and adding measured volume of acidulated water in the desired liquid solid ratio, as shown in Fig.3. In the figure, A, B and C represent an increasingly fresh state of the ash and the numerals associated with them correspond to various L/S ratios. The resulting fly ash slurries are gently agitated using a magnetic stirrer, intermittently, over a period of 24 hrs. At the end of each 24 hrs period the leachate (referred to as sample in the figure) is decanted and filtered through a 0.45 mm Whatman filter paper.

The moist solids and the appropriate volume of leachate solution from the previous test were advanced in sequence according to the matrix illustrated in Fig.3. The figure indicates advancement of liquid from left to right and ash sample from top to the bottom. Precaution has been taken to transfer all the ash including the one sticking to the filter paper.

Starting with a L/S ratio of 5, the cumulative L/S ratio was gradually increased to 100 in steps of 5, 10 and 20 respectively. Sequential batch tests

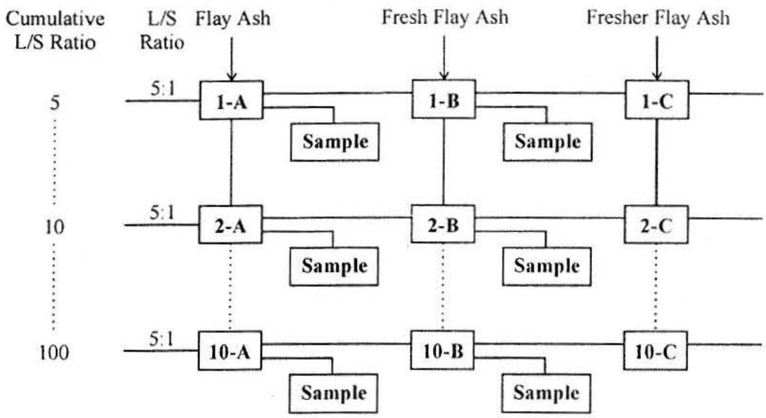

FIGURE 3 : Flow Diagram Depicting Sequential Bench Tests

were employed till L/S ratio of 100 is achieved. As such in the Fig.3, the following test programme is adopted.

Column tests

Column tests have been carried out, by allowing a continuous flow of acidulated distilled water through a fixed bed of ash, at different L/S ratios. These tests closely represent field conditions and simulate leaching of heavy metals as water percolates from ash pond under gravity. The objective of these tests is to force the leachate solutions through the columns of fly ash so as to obtain representative samples of leachate solutions containing chemical constituents at higher concentrations.

For these tests, 50 g of the fly ash sample is mixed with 50 g of acid washed quartz sand (with average particle size of 0.5 mm) and placed in columns of 30 cm length and 4.5 cm diameter. This has been done to increase the permeability of the ash so as to reduce the time of testing. However, the sand used has been repeatedly washed with acidulated water of low pH to eliminate the possibility of interference of leaching by sand. The composition of the first percolate is of prime importance since it will contain high concentrations particularly of the elements deposited on the surface of ash particles. These tests are terminated when a cumulative L/S ratio of approximately 100 is reached. This is mainly due to the fact that it takes a very long time for higher L/S ratios to be reached as in the practical situation, viz. ash ponds etc.

Results and Discussion

ICP analysis (for Ba, Co, Cr, Cu, Mo, Ni, V and Zn) of different

Table 3 : pH of Leachates at various Stages of Sequential Batch Tests

S.No.	L/S Ratio	Cumulative L/S Ratio	A	B	C
1	5	5	7.80	8.00	8.71
2	5	10	8.22	8.51	8.80
3	5	15	8.12	8.48	9.08
4	5	20	8.10	9.09	9.16
5	10	30	7.57	8.83	8.96
6	10	40	6.49	8.38	8.60
7	10	50	5.32	7.97	8.53
8	10	60	4.71	7.96	8.52
9	20	80	4.55	7.79	8.32
10	20	100	4.23	7.72	8.27

leachate samples, indicates that the concentration of these elements is < 1 ppm. This is mainly due to the limitations associated with the instrument available. Hence a comparative study of leaching against the parameters chosen for the test, i.e. pH and L/S ratio at various stages of sequential batch and column tests could not be done. However, the pH trends shown by the leachate samples can be taken to represent the leachability, at various stages, and an analysis of the results on the basis of pH, as governed by the L/S ratio, is attempted and presented in the following:

Sequential Batch Tests

The results of sequential batch tests are presented in Table 3. From the table, it can be noticed that with each successive wash the cumulative L/S ratio increases. The L/S ratio employed for each wash is also presented. For various initial states of the ash samples (marked as A, B and C) the resulting pH values are also obtained. However, it must be borne in mind that for all L/S ratios considered in the study the initial pH of the leachant is 4.0.

The trends indicate that for a given L/S ratio, the pH of the leachate goes on increasing as it comes in contact with more and more fresh ash. Although this indicates more cumulative leaching, the ability of leachates to extract leachable constituents, from the fresh ash, goes down appreciably as compared with the fresh solutions. This indicates saturation of leachates, as they come in contact with a relatively fresh ash.

As expected, repeated washes (increasing cumulative L/S ratios) by the

Table 4 : pH of Leachates in Column Tests

S.No.	L/S Ratio	Cumulative L/S Ratio	pH
1	0.2	0.2	8.84
2	0.2	0.4	8.92
3	0.2	0.6	8.91
4	0.4	1.0	8.67
5	0.5	1.5	8.71
6	0.5	2.0	8.76
7	1.0	3.0	8.74
8	1.0	4.0	8.61
9	1.0	5.0	8.42

fresh leaching agent on the same fly ash yield decreasing concentrations of most of the leachable elements. This can be attributed to the fact that ability of the ash to neutralize the pH, decreases with repeated washes with the same solution. This indicates that the major amount of leaching is over by the initial contact of the leachate with fly ash. Even though the rate of leaching or leachability decreases with increasing cumulative L/S ratio, successive washes are necessary to estimate the total quantity of each element that is actually available for leaching from the ash. However, it is speculated that this trend may be violated by some matrix elements, such as Si and Al, which, in the absence of the exact ICP results, could not be validated.

Thus batch tests are useful in determining the total leachable elements and provide an estimate of possible long-term leaching or maximum release, i.e. the percentage of the elemental concentration actually available for leaching.

Column Tests

Column tests have been performed as discussed earlier and the pH of the leachates is reported in Table 4.

It can be noticed from the table that the pH of the first few leachate samples is high and show no appreciable difference for smaller L/S ratios, till a L/S ratio of at least 1.0 is reached. This can be attributed to the presence of volatile heavy metals, alkaline earth metals such as Cd, Cl, Sr, Pb, Zn and S, which are deposited on the surface of the ash particles and are known to be water leachable. It is these elements, which enter the leachate at higher concentrations in the initial few washes. By the time a cumulative L/S ratio of 2 to 3 has been reached, all these elements have already been leached. The elements such as Al and Si trapped in the center of the ash matrix are stable in alkaline environment and enter the leachate slowly as the outer constituents are washed away.

In the case of batch test where the test has been started with L/S ratio of 5.0, all these water leachable elements enter the leachate in the first few washes and the same trend appears over a wide range of samples in the column test. For L/S ratios greater than 2.0 the trends obtained in the column studies are consistent with the result of the batch tests and it can be seen that the rate of leaching decreases with subsequent washes. Column tests are more close to simulating field conditions. However, it must be noticed that the column tests are more severe for mobilizing higher concentrations of most of the leachable elements present in the fly ash. Thus column tests are invaluable in studying the dynamic aspects of leaching (i.e. time dependence) and estimating the maximum concentration of elements, in the leachates, which gets reflected from their pH values.

The study suggests that to simulate higher concentrations of most of the elements leaching out, the column tests are more useful than the batch tests. However, both tests have their distinct advantages, as mentioned earlier, and for the prediction of the overall leachability of the ash, they must be carried out complementary to each other i.e. for determining the maximum quantity of each element ultimately available for leaching and maximum release concentration of a particular element.

Conclusions

An effort has been made, in this paper, to simulate leaching from the ash ponds by conducting sequential batch and column tests. The sequential batch tests, which have been proposed, are a refinement over simple batch extractions, when used in conjunction with the column tests and simulate leaching through the ash pond, very precisely.

The leaching characteristics of the individual tests have been interpreted against the background of L/S ratio and pH of the leachate solution, in the absence of exact concentration of each element in the leachate samples.

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