In this paper two types of class F fly ashes have been analysed to study the retention capacities of lead. Various parameters like contact time, initial concentration and pH have been varied and their effect on retention mechanism is studied. The dominant mechanisms responsible for retention are found to be precipitation, due to presence of calcium hydroxide, and adsorption due to silica and alumina oxide surfaces present in fly ash. First order kinetic plots have revealed that the rate constant increases with increase in initial concentration and pH. Langmuir adsorption isotherms have been plotted to study the maximum adsorption capacities for lead metal ion considered under different conditions. X-ray diffraction studies carried out revealed the formation of new peaks corresponding to respective metal ions precipitates under alkaline conditions.

1. INTRODUCTION

Heavy metal and metalloid removal from aqueous solutions have been commonly carried out by processes like chemical precipitation, solvent extraction, ion-exchange, reverse osmosis or adsorption. Among these processes, the adsorption with the selection of a suitable adsorbent is a simple yet effective technique for the removal of heavy metals ions from wastewater. Disposal of large quantities of fly ash generated in thermal power plants by burning coal in generating electricity on the other hand, is also assuming serious concern. Fly ash creates environmental problems like dusting and leaching of toxic metals present in it. It is estimated that 349 Mt of fly ash was produced worldwide in 2000.

In India, most of the power plants produce fly ash which contains very low amounts of lime, and this is about 40 to 50% of the coal burned whereas in USA, UK, Canada and Hong Kong, it is hardly around 10%. To minimize the disposal problem, fly ash is being used in bulk quantities for various civil engineering applications. From a power generation perspective, fly ash is a waste, while from a coal utilisation perspective, fly ash is a resource yet to be fully utilized and exploited.

Lead is a non-essential element and it is not as bioavailable as other metals. The application of lead in civil construction activities, in the manufacture of lead-acid batteries, bullets and shots, weights, solder, pewter, fusible alloys and radiation shields results in environmental pollution both directly and indirectly. It is a poisonous metal and its intake can damage nervous connections (especially in young children) causing blood and brain disorders. Long-term exposure to lead or its salts can cause nephropathy, and colic-like abdominal pains.

In this paper an attempt has been made to study the mechanism of retention in a low lime Indian fly ash by carrying out batch adsorption tests on Pb$^{+2}$. The adsorption capacities are determined from the parameters of adsorption isotherms. The efficiency of retention is found to vary considerably with the type of fly ash, nature and oxidation state of metal ions and their concentration, pH of the solution and other environmental factors. However, the mechanisms and variations in the retention of different metal ions by different fly ashes are not well documented. Factors affecting retention, such as pH, initial concentration and contact time are also investigated.

2. MATERIALS AND METHODS

Fly Ashes

Two types of fly ashes have been used in the present investigation. Neyvelli fly ash is directly collected from the electrostatic precipitators of thermal power plant located in Neyvelli town of Tamil. The chemical properties are...
presented in Table 1. This fly ash is classified as F type as per ASTM classification (ASTM C618).

**Solutions Used**

Analytical grade Lead Nitrate Trihydrate, supplied by Merck India Limited, has been used to prepare standard solutions of known concentrations.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>NFA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (SiO$_2$)</td>
<td>50.97</td>
</tr>
<tr>
<td>Alumina (Al$_2$O$_3$)</td>
<td>18.81</td>
</tr>
<tr>
<td>Ferric (Fe$_2$O$_3$)</td>
<td>16.61</td>
</tr>
<tr>
<td>Calcium (CaO)</td>
<td>9.00</td>
</tr>
<tr>
<td>Magnesium (MgO)</td>
<td>1.41</td>
</tr>
<tr>
<td>Titanium (TiO$_2$)</td>
<td>0.28</td>
</tr>
<tr>
<td>Potassium (K$_2$O)</td>
<td>0.23</td>
</tr>
<tr>
<td>Sodium (Na$_2$O)</td>
<td>0.18</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>2.60</td>
</tr>
</tbody>
</table>

**Batch Equilibrium Tests**

Batch adsorption experiments were carried out by mechanically shaking series of bottles containing fly ash sample and heavy metal ions using distilled water and at different pH values. 5g of fly ash sample was mixed with 100 ml of distilled water in polyethylene bottles to obtain fly ash slurry. The pH of the slurry was adjusted to the desired value in the range of pH 2 to 8 with 0.1M HNO$_3$ and NaOH. The slurry was agitated with a mechanical shaker at room temperature (25±2°C) for 1 h until the pH was stabilized. Then the metal ion in the form of nitrate salt was added to the bottles to various concentrations (10, 15, 20, 25 and 30 mg/l) and the bottles were further agitated until equilibrium was attained. The slurry was filtered using Whatman 42 ash less filter paper and the residual concentration of the metal ion in the filtered solution was determined using atomic absorption spectrophotometry (AAS). The amount of metal ion adsorbed by fly ash was taken as the difference between the initial and residual concentration of the metal ion. The reported values of lead metal ion adsorbed by fly ash in each test were the average of at least three measurements.

For the kinetic studies, the fly ash along with the metal ion solution was shaken for predetermined time intervals. At the end of the equilibrium time, the solution along with fly ash was filtered and the concentration of lead metal ion was determined as above.

**XRD Studies**

The samples at the end of batch equilibrium test were transferred into Petri dishes by washing the contents using distilled water from the filter paper. The contents were air dried for 48 hours and the residue was powdered and sieved through 75i. The powder was then used for XRD studies. XRD has been carried out using Bruker D8 Advance system. Samples were scanned from 5° (2θ) to 80° (2θ) using copper K alpha radiation at a scanning rate of 1 degree per minute, in slow scan mode. XRD patterns of samples were compared with standard pattern of possible types of compounds to identify the new compounds (JCPDS, Powder Diffraction File, 1990).

**3. RESULTS AND DISCUSSIONS**

**Effect of Contact Period**

With increase in initial concentration, the adsorption was found to increase with time. The equilibrium concentration times increased with increase in initial concentration (Fig. 1).

![Fig. 1: Amount Adsorbed with Time at 30 mg/l](image)

**Effect of pH**

The pH of the solution is known as the one of the most important variable that can be effect the protonation of the function group on the adsorbent surface as well as the metal chemistry. The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate. The oxides of SiO$_2$, Fe$_2$O$_3$, and Al$_2$O$_3$ are found on the surface of the fly ash particles in significant quantities. The silica (SiO$_2$) in fly ash could adsorb either positive or negative contaminants depending on the pH of the solution. The central ion of silicates has an electron affinity, giving the oxygen atoms bound to it low basicity. This allows the silica surface to act as a weak acid, which can react with water, forming surface silanol.
(SiOH) groups. As a result, at low pH the silica surface is positively charged and at high pH values it is negatively charged. Other solid materials such as iron and alumina also show this same phenomenon of developing positive or negative charges depending on pH. Metal cations in aqueous solutions hydrolyze according to the generalized expression for divalent metals, as shown in equation 1.

\[
M^{2+} (aq) + nH_2O \rightarrow M(OH)_{2-n} + nH^+ \quad (1)
\]

The distribution of various hydroxyl complexes depends on pH of the solution and the respective stability constants. Hydroxyl–metal complexes are known to adsorb with a higher affinity than the completely hydrated metals because the formation of an OH group on the metal reduces the free energy requirement for adsorption (Alinnor, 2007). Therefore the adsorption of metal ions can be related to the change in availability of MOH\(^+\). The increase in the adsorption of Pb (II) is due to cation hydrolysis such as Pb (OH)\(^+\). With increase in pH both amount adsorbed per gram increased for both the fly ashes, Fig. 1, which can be mainly attributed to precipitation of respective metal as metal oxide on to the surface of fly ash particles.

**Percent Removal**

The percent removal of metal ion from solution increased gradually with increase in initial concentration. With increase in pH the percent removal further increased in case of both the fly ashes for the metal ions considered in the study (Fig. 2). The maximum percent removal of 71% was achieved at an initial concentration of 15 mg/l at a pH 8 for Pb.

\[
\ln \left( \frac{C_0}{C_t} \right) = k t \quad (2)
\]

Where, ‘\(C_0\)’, is the initial metal ion solution concentration, ‘\(C_t\)’, concentration at time \(t\), and ‘\(k\)’ is the rate constant.

A plot of \(\ln \left( \frac{C_0}{C_t} \right)\) versus time yields a straight line from the slope of which the rate constant \(k\) is calculated. In general, the \(k\) value increases with increase in pH, as more amount of solute gets precipitated onto the fly ash surface particles. For Pb, the maximum \(k\) value of \(1.64 \times 10^{-3} /s\) was obtained at pH of 8 at an initial concentration of 10 mg/l (Fig. 3).

**Adsorption Isotherm**

Equilibrium sorption is described by a sorption isotherm. A sorption isotherm is the relationship between the amount of metal sorbed and the equilibrium concentration of the metal or more correctly the activity of the free metal in the fly ash solution. Equation most frequently used, because of its relative simplicity to describe the curvilinear sorption behaviour of metal in fly ash is the Langmuir equation.

The equation was developed to model liquid adsorption on solid surface. The derivation of the equation was based on the assumption that adsorption is independent of surface coverage, that there is no interaction between adsorption ions and that only a mono layer of adsorption occurs on the surface. The mineralised form of the Langmuir equation is:

\[
\frac{C_t}{q} = \frac{C_t}{q_m} + \frac{1}{q_m K_{ads}} \quad (3)
\]

Where, ‘\(C_t\)’, concentration or activity of the free metal in solution; ‘\(q\)’, quantity of the metal ion sorbed by the fly ash; ‘\(q_m\)’, maximum sorption capacity of the MFA and ‘\(K_{ads}\)’ is the coefficient related to bonding energy.

The maximum adsorbent capacities corresponding to Pb were found out to be 0.4801 mg/g at pH 8 (Fig. 4).
The XRD pattern of NFA after Pb retention showed the formation of new peaks. Figure 5 shows new peaks corresponding to the respective stable hydroxide precipitates i.e., lead nitrate (JCPDF 78-1526), having a d spacing of 4.54 °A, 3.93 °A, 2.78 °A were observed other than quartz and mullite.

5. CONCLUSIONS
The study revealed the application of low lime fly ash as an alternative adsorbent for the removal of lead metal ions from wastewater. The equilibrium concentration values decreased steadily with increase in pH In general, the time required to arrive at equilibrium concentration, reduced considerably with increase in pH. The rate constant values also steadily increased with increase in the pH of the system. The hydration of fly ash increases in the pH range of 8, where higher degree of precipitation of metal ions can be expected, thereby enhancing the removal of lead metal ions from the solution. The hydroxide precipitation of the respective metal ions can be observed from the XRD analyses of the fly ash samples.

REFERENCES