

Leaching Studies on Fly Ashes by Jar Method

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Introduction

The utilization of fly ash has recently received the serious attention of researchers and practising engineers. Various applications are available for the utilization of fly ash and among those, geotechnical application is the only one that offers the scope for bulk utilization. Due to its low unit weight (because of high internal porosity and low specific gravity), good frictional properties and non-plastic nature, fly ash can be effectively used as a fill material in low lying areas, as a back fill material, as an embankment material, etc. However, the possibility of surface and/or ground water contamination due to leaching of toxic metals from fly ashes has to be carefully investigated.

The leaching characteristics of fly ash depend on its own properties such as chemical composition, specific surface area and cation exchange capacity, leachate characteristics such as pH of the leachate, valence and concentration of the metal ion and other factors such as reaction time, temperature, etc.

The chemical analysis of five fly ashes collected from Neyveli, Ramagundam, Raebarely, Vijayawada and Badarpur has been carried out and reported in Table 1. It can be seen that the fly ashes contain high percentages of silica, alumina, iron and calcium and small percentages of magnesium, sodium and potassium. The Neyveli fly ash contains the maximum percentage of free lime whereas Badarpur fly ash has the least. Due to hydration of calcium oxide, OH ions are released which eventually increases the pH of the

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TABLE 1 : Chemical Composition of Fly Ashes

Constituents	Weight (%)				
	Neyveli Fly Ash	Ramagundam Fly Ash	Raebareli Fly Ash	Vijayawada Fly Ash	Badarpur Fly Ash
SiO ₂	38.57	61	58	61	56.0
Al ₂ O ₃	42.49	24.59	30.35	30.83	32.90
TiO ₂	1.8	1.13	1.4	1.7	1.68
Fe ₂ O ₃	4.01	4.2	4.21	3.3	4.70
MnO	0.12	0.08	b.d	b.d	0.21
MgO	0.02	0.8	0.5	0.05	0.23
CaO	7.6	3.04	1.01	1.1	0.63
K ₂ O	0.05	0.9	0.7	0.6	0.6
Na ₂ O	0.43	0.4	0.11	0.13	0.23
SO ₄	0.01	b.d	b.d	b.d	b.d
L.O.I.	4.39	1.75	2.4	0.5	1.75
Free Lime (part of CaO)	(4.69)	(0.52)	(0.38)	(0.24)	(0.19)
Alkaline metals including CaO	(8.1)	(5.14)	(2.32)	(1.88)	(1.69)

b.d : below detection, L.O.I. : Loss on ignition

ambient solution. Such changes in pH affect the desorption/adsorption or dissolution/precipitation of metals (Tuncer et al., 1992). Thus, free lime affects the leaching of metal ions from the fly ash. Hence, two fly ashes (Neyveli and Badarpur) are selected as the extreme cases for the present investigation based on the free lime content.

Materials Used

The Neyveli fly ash was obtained from Neyveli thermal power plant, Tamil Nadu and will be further called as Neyveli fly ash or Fly ash (N). The other fly ash collected from Badarpur thermal power plant, Uttar Pradesh will be designated as Badarpur fly ash or Fly ash (B).

Physical and Engineering Properties of the Fly Ashes

The physical and engineering properties of the two fly ashes are studied and presented in Table 2. It shows that fly ashes are typically silt sized and non-plastic. The liquid limit exhibited is due to the flocculated structure of the fly ash and not due to their plasticity characteristics. The specific gravities

TABLE 2 : Properties of Fly Ashes Used

Property	Fly Ash (N)	Fly Ash (B)
Atterberg Limits		
Liquid Limit (%)	48	44
Plastic limit (%)	NP	NP
Shrinkage limit (%)	40	42
Specific Gravity	2.55	1.97
Particle Size Distribution		
Fine sand size fraction (%)	26.6	39
Silt size fraction (%)	63.9	60
Clay size fraction (%)	9.5	1
Standard Proctor Compaction Characteristics		
Maximum dry density (gm/cm ³)	1.22	1.03
Optimum water content (%)	40	35.3
Cation Exchange Capacity		
Total (meq/100 gm)	71.05	3.23
Ca ⁺⁺	58.94	1.07
Mg ⁺⁺	4.52	0.95
K ⁺	0.2	0.09
Na ⁺	7.39	1.12
Surface Area (m ² /gm) (Desiccator method)	9.72	0.67

NP: Non-plastic

recorded (1.97 and 2.55) are less than that for normal soil (about 2.67). The reason for low specific gravities could be due to the presence of hollow cenospheres from which the entrapped air/gases cannot be removed, or the variation in the chemical composition (in particular, iron content), or both these factors (Pandian et al., 1998). Because of low specific gravities, they have low unit weights. Fly ash (N) is having higher cation exchange capacity than that of fly ash (B). The specific surface area on weight basis for Neyveli fly ash is more than that for Badarpur fly ash.

Chemical Properties of the Fly Ashes Used

The chemical composition of both fly ashes is reported in Table 1 which shows that the total percentage of the silica, alumina and iron oxide is more than 70%, typical of ASTM class F fly ash (ASTM, 1989). Silica, alumina and iron have the capacity to adsorb metal ions and, the elements Ca, Mg, Na and K impart alkalinity to the fly ash (Weng and Huang, 1994).

Jar Method

The leaching studies on the two fly ashes have been conducted using the Jar Method. The relevance of the Jar method is that it simulates the natural conditions of surface ponding in the ash ponds. Surface ponding is due to the nature of ash disposal itself (i.e., ash slurry being pumped into ponds) or, rainwater accumulation with or without surface run off. In this method, a sample of ten grams of each fly ash was taken into four 100 ml measuring jars. Each jar was filled with solution of known pH's 3.0, 5.0, 7.0 and 9.0 and having no toxic metals. These samples were allowed to remain, without any subsequent disturbance, for the reactions to take place. Representative fraction of supernatant solutions were sampled periodically at standard times such as 5 hrs, 1 day, 3 days, 1 week, 1 month and 2 months and the pH of each sampled leachate was measured. The samples were filtered through No.41 Whatman filter paper. The filtrate was analysed for various metal ions using Atomic Absorption Spectrophotometer. The leachate pH and the amounts of metal ion leached were considered and analysed as functions of initial pH and of reaction time.

Results and Discussions

Variation of pH

Figures 1a and 1b present the variation of final pH (pH measured at different time intervals) of the leaching solution as affected by the initial pH and the duration of reaction time respectively for fly ash (N). It can be observed that the final pH values are high for any given initial pH and increase with increasing initial pH of the solution. They also increase with increasing reaction time upto 10 days and then remain practically constant. The chemical composition (Table 1) indicates that Neyveli fly ash contains high percentages of silica, alumina, iron and calcium oxides and small percentages of magnesium, sodium and potassium oxides. Among these alkaline oxides which impart alkalinity to the fly ash, calcium oxide is very highly reactive. Due to hydration of calcium oxide, $(OH)^-$ ions are getting released. Since Neyveli fly ash is having higher percentage of free lime (4.69%), the pH value of the ambient solution is higher.

Figure 2a presents the variation of final pH with different initial pH of the solution for fly ash (B). The final pH with the duration of reaction time for fly ash (B) is shown in Fig. 2b. It can be observed that compared to the initial pH values of leaching solution, the final pH values with fly ash (B) have increased only marginally contrary to fly ash (N). This is because fly ash (B) has very less free lime content (i.e., 0.19%) compared to fly ash (N) (4.69%).

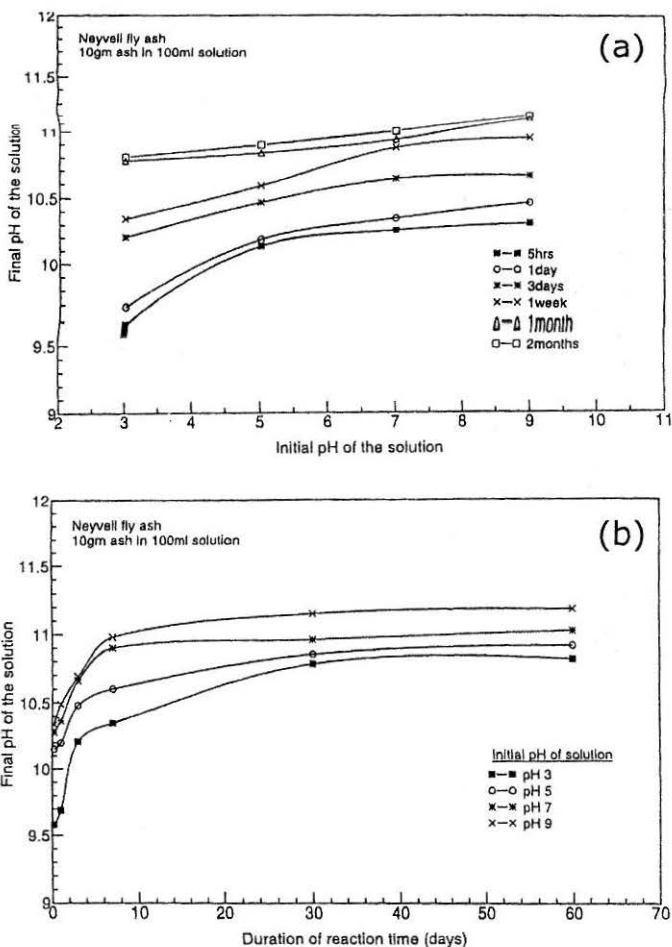
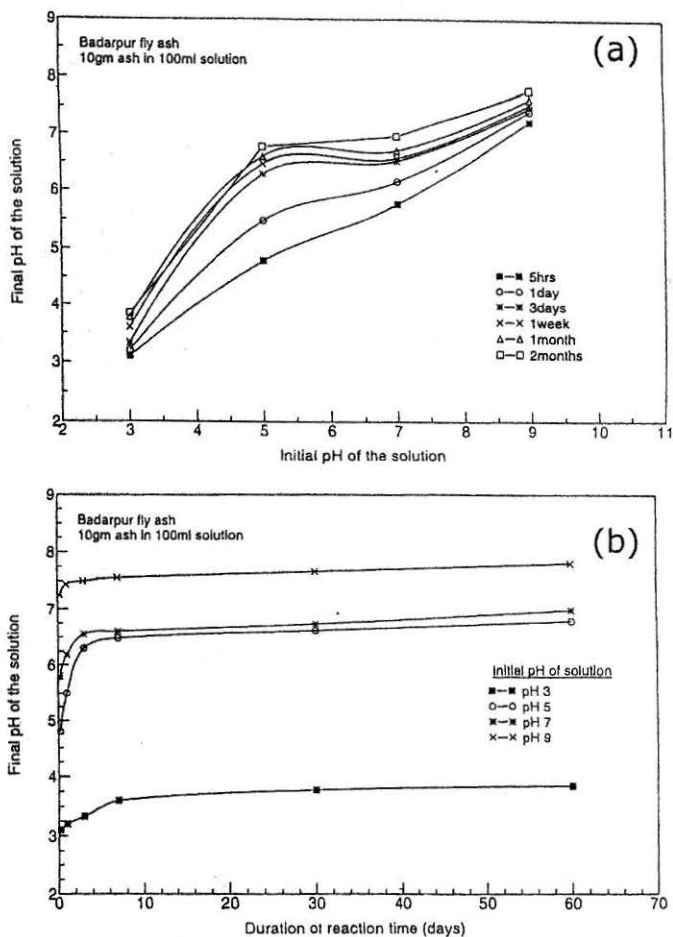


FIGURE 1 : Variation of Final pH of the Leaching Solution
(a) with Initial pH for Fly Ash (N);
(b) as Affected by Duration of Reaction Time for Fly Ash (N)

Leaching of Ions

Figures 3a and 3b present the variation of zinc ions leached for different initial pH of the leaching solution as well as with duration of reaction time for fly ash (N). It can be noted that the amount of zinc ions leached increases with an increase in the duration of reaction time upto 3 days and slightly decreases with increase in the initial pH conditions. The leaching of zinc ions increasing up to 3 days is due to the dissolution of zinc hydroxide precipitates. The pH required to begin the dissolution of zinc hydroxide precipitate is 8.5 (Table 3). The total concentration of different metal ions present in the Neyveli and



**FIGURE 2 : Variation of Final pH of the Leaching Solution
(a) with Initial pH for Fly Ash (B);
(b) as Affected by Duration of Reaction Time for Fly Ash (B)**

Badarpur Fly Ashes is given in Table 4. It has been reported that the solubility of metals in the solution is often regulated by their hydroxide and carbonate precipitates (Pagenkopf, 1978). After 3 days, zinc concentration decreased due to the formation of zinc carbonate precipitates.

However, the ambient pH was higher than the pH required to form the hydroxide precipitation of zinc and lesser than the pH required to complete the zinc carbonate precipitation. Even then, the concentration of zinc increased in the leachate because of the rate of dissolution of zinc hydroxide precipitate is more than the rate of formation of zinc carbonate precipitate.

TABLE 3 : pH Required to Form and Complete the Hydroxide Precipitation of some Metal Ions and also the Completion of Carbonate Precipitation (Rajasekhar, 1996)

Metal Ions	Hydroxide Precipitation Begins at pH	Completion of Hydroxide Precipitation at pH	Completion of Carbonate Precipitation at pH
Ca ⁺⁺	11	13.5	12.85
Fe ⁺⁺	5.5	9.34	11.25
Zn ⁺⁺	7.9	8.50	11.60
Mg ⁺⁺	10	11.3	14.0
Mn ⁺⁺	8.5	10.3	11.13
Ni ⁺⁺	6.7	9.4	11.19
Cu ⁺⁺	5.3	7.37	11.69
Pb ⁺⁺	6.5	9.04	10.59
Cd ⁺⁺	6.7	10.04	10.12
Ag ⁺⁺	9.0	12.71	11.40
Co ⁺⁺	6.9	9.15	10.07

TABLE 4 : Total Concentration of Different Metal Ions Present in the Neyveli and Badarpur Fly Ashes in ppm

Metal Ions	Neyveli Fly Ash	Badarpur Fly Ash
Ca	335.08	13.47
Fe	230.37	308.20
Zn	2.98	1.33
Mg	113.09	46.65
Mn	4.66	2.66
Ni	1.34	0.88
Cu	1.57	1.55
Li	0.37	0.79
Na	42.09	13.13
K	5.91	96.58
Pb	5.91	10.97
Cd	0.35	0.48
Cr	4.19	3.51
Ag	0.23	0.20
Co	1.43	1.55

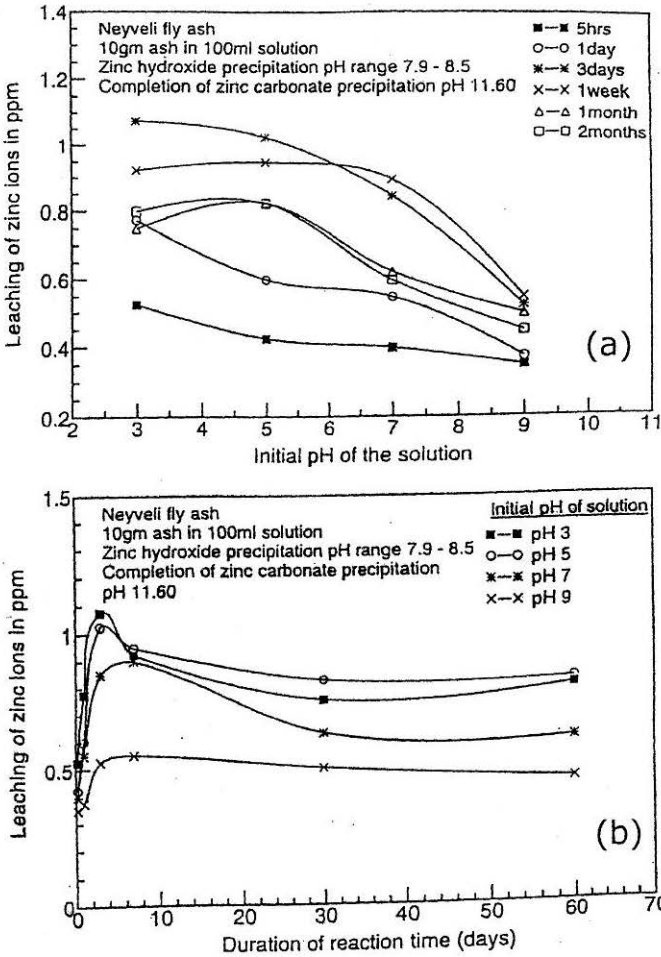


FIGURE 3 : Variation of Amount of Zinc Ions Leached
 (a) with Initial pH of the Leaching Solution for Fly Ash (N);
 (b) by Fly Ash (N) as Affected by Duration of Reaction Time

Figures 4a and 4b present the variation of amount of zinc ions leached as affected by initial pH of the solution and duration of reaction time by fly ash (B). It can be observed that the zinc ion leached was more at initial pH 3.0 and is due to the higher solubility of zinc ions at acidic pH values and also competition from H^+ ions at adsorption sites. It has been reported that at acidic pH regions, the solubility of metals like zinc is more (Stumm and Morgan, 1970). For pH values greater than 3.0, the amount of zinc ions leached has decreased abruptly. This is due to cation exchange capacity and/or adsorption of zinc ions onto the surface of fly ash (B) particles. It has been reported (Reed, 1990) that precipitation onto the surface of the materials

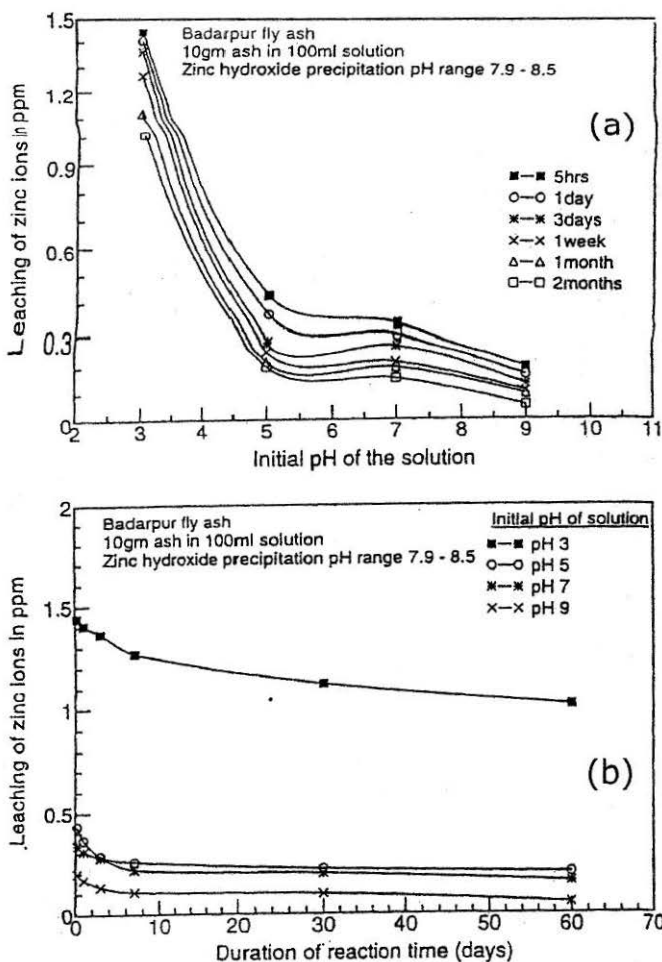


FIGURE 4 : Variation of Amount of Zinc Ions Leached
 (a) with Initial pH of the Leaching Solution for Fly Ash (B);
 (b) by Fly Ash (B) as Affected by Duration of Reaction Time

occurs at pH values of 0.5 to 1.0 unit lower than the pH at which solution precipitation occurs. This is because of the fact that the surface pH is found to be 0.5 to 1.0 unit more than the solution pH and the surface also acts as a nucleus for the precipitation. Hence, the surface precipitation onto the surface of fly ash (B) is possible only after the ambient pH value of 6.9. The pH range over which the zinc hydroxide precipitation occurs is 7.9 to 8.5 (Table 3). The final pH values of Badarpur fly ash never increased beyond 7.80. Therefore, the formation of zinc hydroxide precipitates is not possible and hence, zinc concentration can not decrease due to precipitation. It can be also observed that for a given initial pH value, the zinc concentration

decreases with increasing duration. The mechanisms such as ion exchange and/or adsorption and surface precipitation are responsible for this.

From Fig. 4b, it is seen that at acidic pH values, the zinc ion leached into the solution is more due to the solubility of zinc ions (Stumm and Morgan, 1970) and competition from H^+ ions at the exchange sites (Yong and Phadungchewit, 1993). As the pH increases, the leaching of zinc ions decreases due to cation exchange and/or adsorption onto the surface of fly ash (B) particles. At higher pH values, the amount of zinc ions leached into the solution is very less and is due to precipitation onto the surface of fly ash (B). The zinc hydroxide precipitation is not possible, because the ambient pH value for even higher initial pH was 7.8. This is less than the pH value (7.9) required for the formation of zinc hydroxide precipitate. Similar plots were obtained with respect to lead, nickel, cadmium, copper, cobalt, iron and lithium ions.

Figure 5a shows the variation of amount of silver ions leached by fly ash (N) with different initial pH values and that with duration of reaction time is shown in Fig. 5b. It can be observed that for a given initial pH value, the amount of silver ion leached decreases with increase in duration of reaction time. It can be also noted that the quantity of silver ions leached decreases with increasing initial pH values. This is due to the formation of hydroxide and carbonate precipitates of silver ion in the leaching solution. Since the final pH values lie within the range of hydroxide precipitation and carbonate precipitation of silver ions, the formation of hydroxide and carbonate precipitates of silver ion is possible in the leaching solution. It can be observed from Fig. 5b that for a given duration, the leached silver ions decreased with increasing initial pH. This is due to hydroxide and carbonate precipitation of silver ions. Similar behaviour was exhibited by fly ash (B) also.

Figures 6a and 6b present, respectively, the variation of amount of chromium ions leached for different initial pH and duration of reaction time by fly ash (N). It has been reported that chromium is retained only by soils, which have high concentration of free Fe oxides (Korte et al., 1976). Since, the Neyveli fly ash is having more iron content, the leaching of chromium ion is not likely. But, in the present case, at lower initial pH values (3.0 and 4.0), chromium has leached out from fly ash (N) because of the solubility of iron oxides. Similar trends were exhibited by fly ash (B) also.

Manganese ions were not at all leached from fly ash (N). This is mainly because of the formation of manganese hydroxide and carbonate precipitates. The pH range, over which manganese hydroxide precipitation can occur is 8.5–10.3 and the pH, required to complete the manganese carbonate precipitation is 11.13. The final pH values shown in Fig. 1a are conducive for the formation of both hydroxide and carbonate precipitates of manganese ions in the solution and hence the absence of leaching.

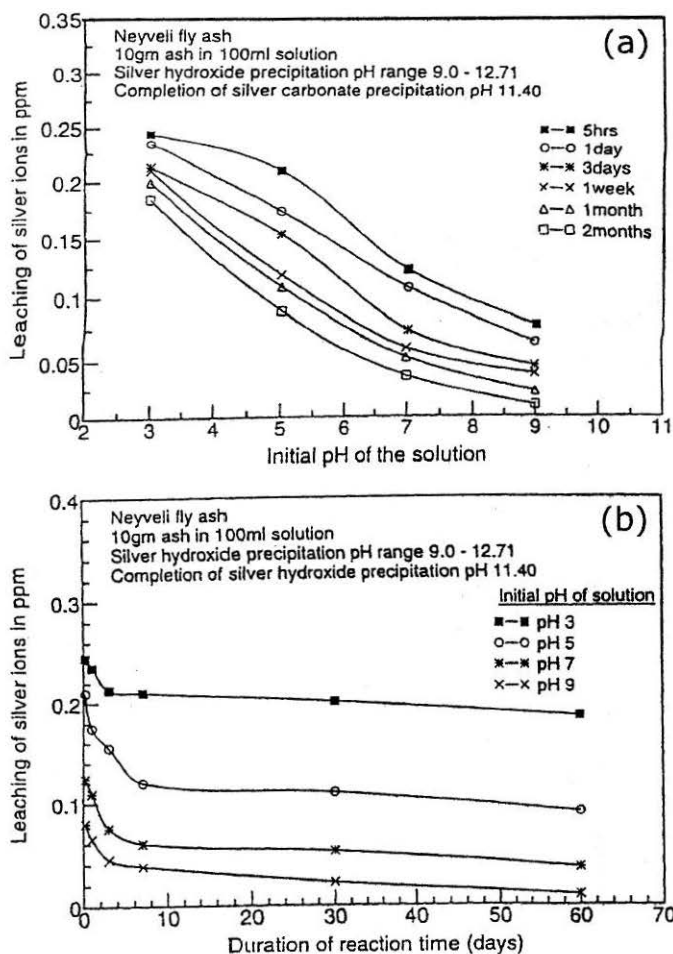


FIGURE 5 : Variation of Amount of Silver Ions Leached
 (a) with Initial pH of the Leaching Solution for Fly Ash (N);
 (b) by Fly Ash (N) as Affected by Duration of Reaction Time

The variation of amount of manganese ions leached for different initial pH values by fly ash (B) is shown in Fig. 7a and that with reaction time is shown in Fig. 7b. From Fig. 7b, it can be observed that with the exception of lower initial pH value of 3.0, all the manganese ions were adsorbed onto the surface of the fly ash (B) particles. It can be noted from Figs. 2a and 2b that the maximum pH values of the solution is 7.80. The pH value required for the formation of manganese hydroxide precipitate is 8.5 and hence hydroxide precipitation is not possible. The decrease of leaching of manganese is therefore, not through its hydroxide formation. However, surface precipitation is possible for the ambient pH value upto 7.5 leading to decrease

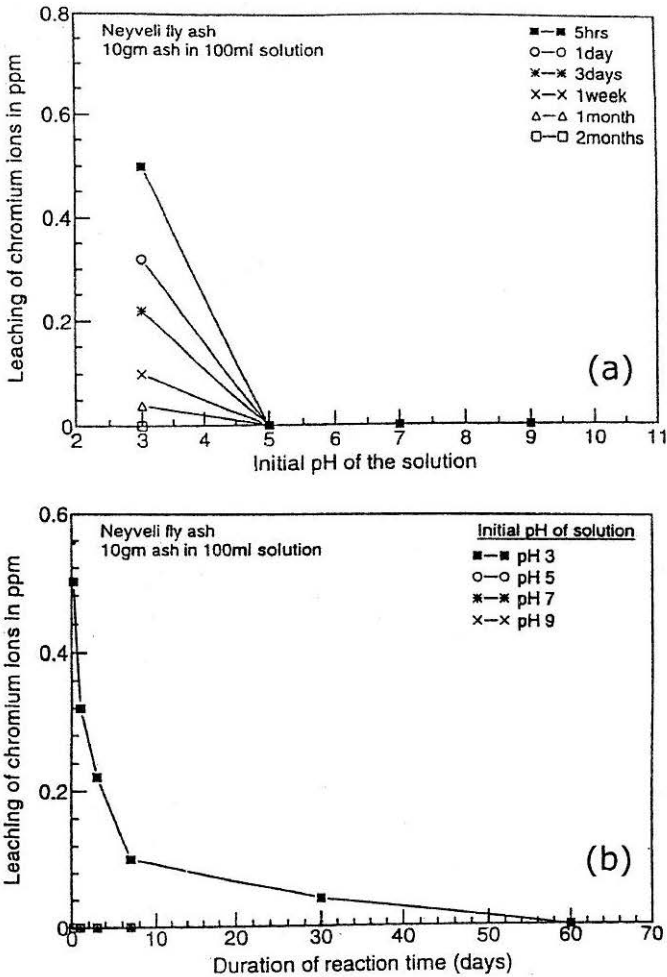


FIGURE 6 : Variation of Amount of Chromium Ions Leached
(a) with Initial pH of the Leaching Solution for Fly Ash (N);
(b) by Fly Ash (N) as Affected by Duration of Reaction Time

in leaching. This is because, the surface pH value is 0.5 to 1.0 unit more than the solution pH (Reed, 1990). The complete adsorption of manganese ions onto the surface of fly ash (B) for initial pH more than 5 is due to some other mechanism most likely through cation exchange capacity and/or adsorption onto the surface of the fly ash (B) particles. Since, the solubility of metal ion is more at acidic pH regions (Stumm and Morgan, 1970), the available manganese ions at lower initial pH values of 3.0 and 4.0 is due to solubility of manganese ions as well as due to the competition from H^+ ion at the exchangeable sites (Yong and Phadungchewit, 1993).

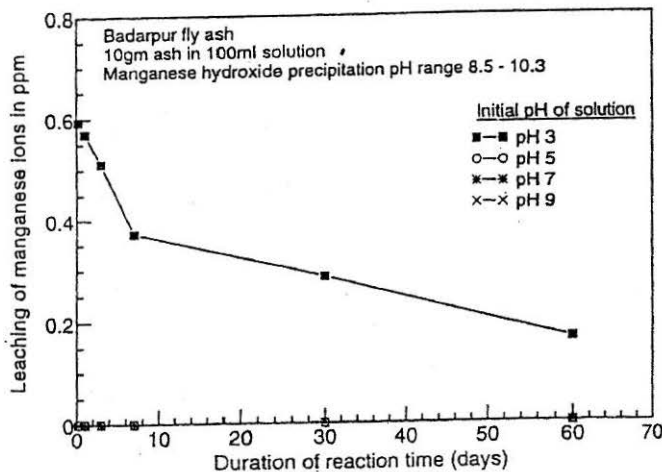
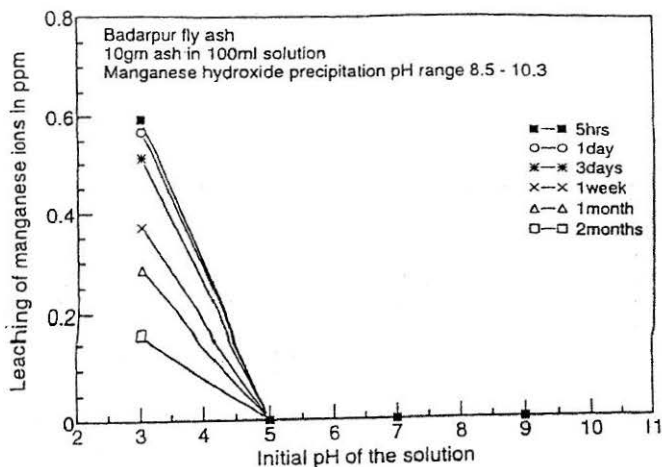


FIGURE 7 : Variation of Amount of Manganese Ions Leached (a) with Initial pH of the Leaching Solution for Fly Ash (B); (b) by Fly Ash (B) as Affected by Duration of Reaction Time

Figures 8a and 8b show the variation of amount of magnesium ions leached with different initial pH of the solution and that with duration of reaction time respectively from fly ash (N). It can be observed that for a given initial pH, the leached magnesium ions decrease with increasing duration (Fig. 8a). From Fig. 8b, it can be noted that for a given reaction time, the concentration of magnesium ions in the solution decreases with increasing initial pH levels. These are due to the formation of magnesium hydroxide and carbonate precipitates. The pH value required for magnesium hydroxide precipitation and completion of magnesium carbonate precipitation are 10.0 and 14.00 respectively (Table 3). The final pH values from Figs. 1a and 1b

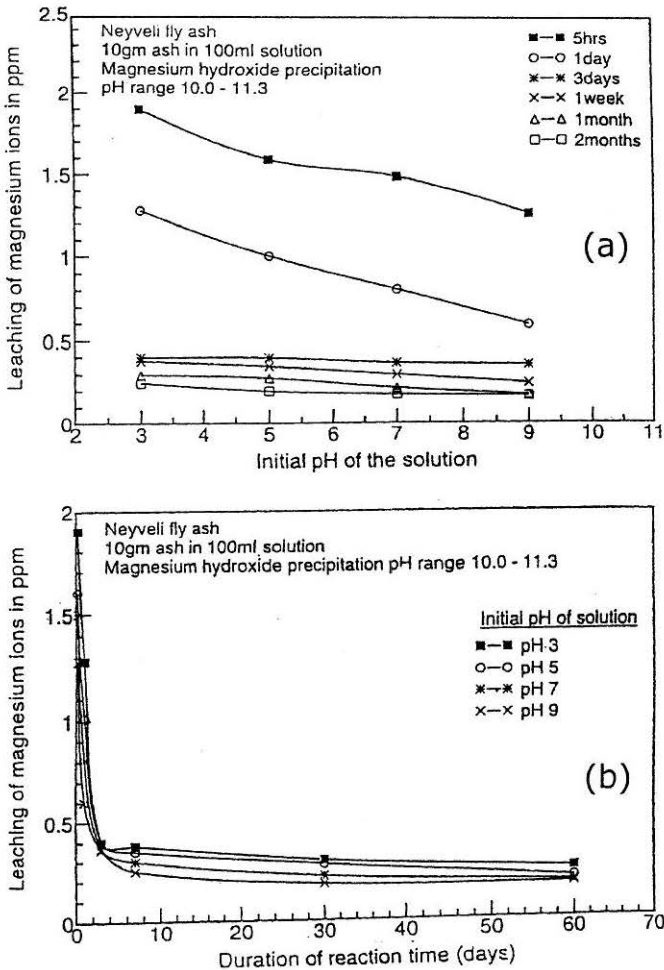


FIGURE 8 : Variation of Amount of Magnesium Ions Leached
(a) with Initial pH of the Leaching Solution for Fly Ash (N);
(b) by Fly Ash (N) as Affected by Duration of Reaction Time

of Neyveli fly ash lie within this range. Hence, leaching of magnesium ion decreases due to the formation of both hydroxide and carbonate precipitates.

Figure 9a shows the variation of amount of magnesium ions leached as affected by the initial pH of the solution and, that with duration of reaction time is shown in Fig. 9b, for fly ash (B). It can be observed that for a given initial pH condition, the amount of magnesium ions leached decreases with increasing time of reaction. It can be also seen that for a given reaction time, the amount of magnesium leached decreases with increase in the initial pH of the solution from fly ash (B). As discussed earlier, the leaching of metals

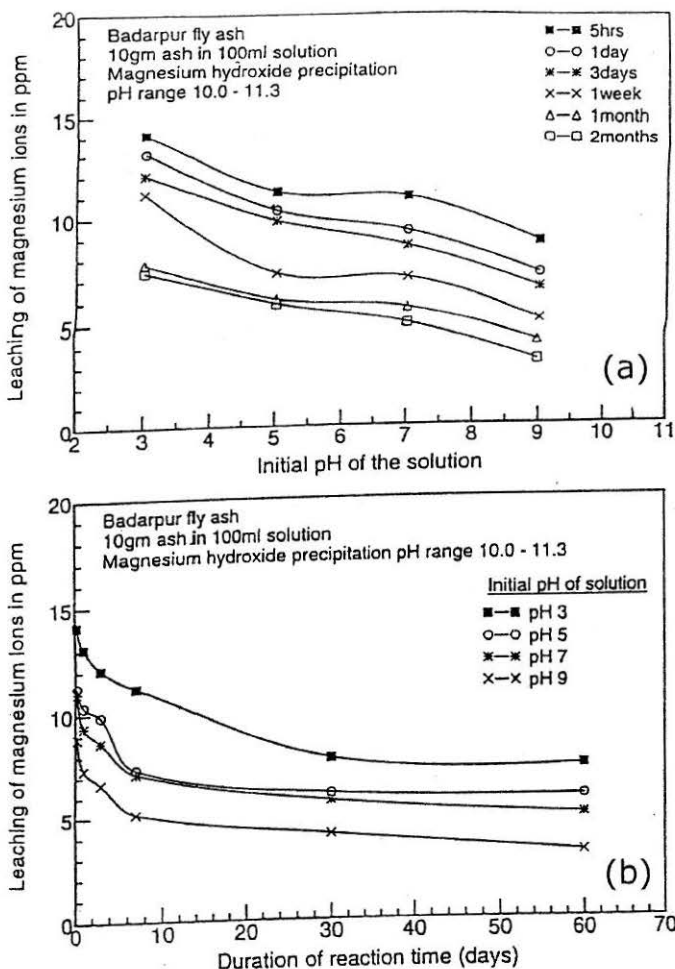


FIGURE 9 : Variation of Amount of Magnesium Ions Leached (a) with Initial pH of the Leaching Solution for Fly Ash (B); (b) by Fly Ash (B) as Affected by Duration of Reaction Time

decreases in the solution due to liquid precipitation and surface precipitation as magnesium hydroxide and ion exchange and/or adsorption onto the surface of the materials. Liquid precipitation and precipitation onto the surface (surface precipitation) depend on the pH value of the solution. The pH value required for the formation of magnesium hydroxide precipitation is 10.0. Since the pH value of the leaching solution never increased beyond a value of 7.8, hydroxide precipitation is not possible. Surface precipitation on the surfaces of fly ash (B) particles is also not possible as the pH value required to form the surface precipitation is 0.5 to 1.0 unit lower than the pH required to form the surface precipitation (Reed, 1990). Therefore, a decrease in leaching of

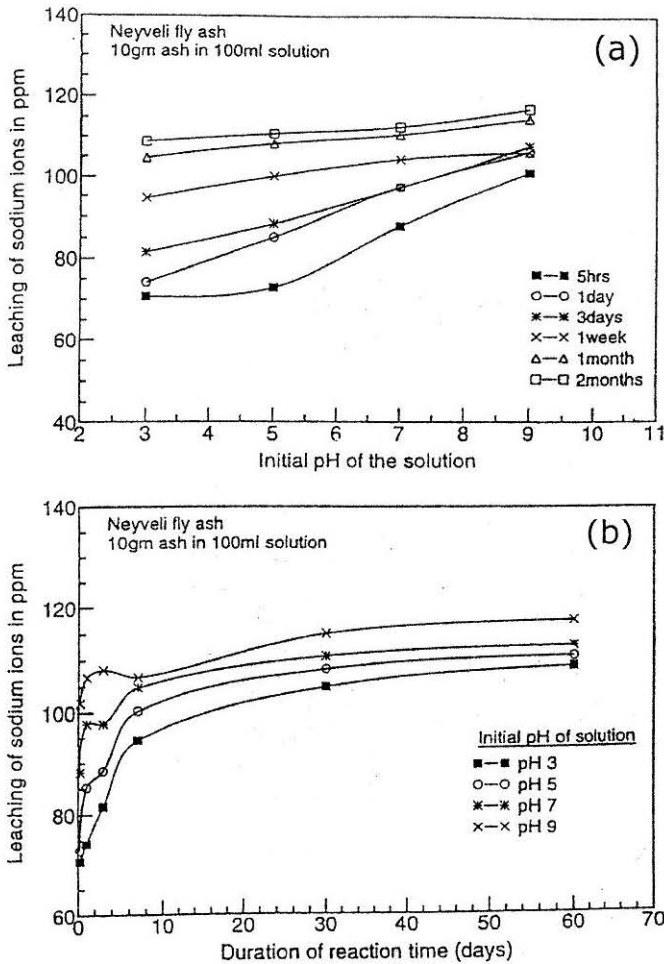


FIGURE 10 : Variation of Amount of Sodium Ions Leached
 (a) with Initial pH of the Leaching Solution for Fly Ash (N);
 (b) by Fly Ash (N) as Affected by Duration of Reaction Time

magnesium ions is most likely through other mechanisms such as cation exchange capacity and/or adsorption onto the surface of the fly ash (B) particles. Similar plots were obtained for calcium and potassium ions also.

Figures 10a and 10b show the variation of amount of sodium ions leached as a function of initial pH of the solution and as a function of duration of reaction time respectively by fly ash (N). It can be observed that the sodium ions leached increase with increasing duration for a given initial pH (Fig. 10a). This is because the dissolution of sodium ions increases with increasing time. This behaviour of sodium ion is responsible for the marginal

increase in the final pH values at higher initial pH values and later part of the reaction time. It can be also observed from Fig. 10b that the amount of sodium ions leached increases with increasing initial pH at a given time. This is due to the dissolution of more sodium ions with increase in pH value. Similar behaviour was exhibited by fly ash (B) also.

Summary and Concluding Remarks

From the above results, it can be observed that compared to fly ash (B), most of the trace elements get leached out from fly ash (N) since the later has a higher percentage of free lime (4.69%). This leads to higher final pH values for leachates and this higher pH is responsible for the leaching of more metal ions for fly ash (N) samples.

However, for silver and magnesium, the concentration in the leachate decreases with increase in pH for fly ash (N) and is due to the formation of hydroxide and carbonate precipitates. Chromium could not be leached out at higher pH than the initial pH 5.0 from both the fly ashes. Lithium has leached out from both fly ash (N) and fly ash (B). From the above available results, it can be observed that the leaching of trace elements from fly ash mainly depends on the pH of the leaching solution and duration of reaction time. Hence the possibility of reducing the leaching of toxic metals from ash ponds etc. by pH control (with the addition of materials like lime) needs to be investigated in depth.

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