

# An Effect Of Cation On Leaching Of Fluoride From Saline Soils: A Kinetic Approach

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**Abstract:** Leaching kinetics of fluoride by loading  $\text{AlF}_3$  on undisturbed vertical saline soil columns has been investigated and compared using various kinetic models. Saline soils from Sambhar region of Rajasthan was selected to study leaching mechanism and effects of various parameters on leaching mechanism under atmospheric pressure. Linear relationship is established between the concentrations of leachable fluoride  $[\text{F}]_i$  and rate of leaching ( $\text{LR}_{\text{obs}}$ ).  $[\text{F}]_i$  and  $\text{LR}_{\text{obs}}$  are found to decrease with increase in  $\text{Na}^+$  and  $\text{Ca}^{+2}$  levels of extractant, while an increase has been observed with increase in temperature and  $\text{OH}^-$  ions. Maximum  $[\text{F}]_i$  are resulted with addition of  $\text{NH}_4\text{OH}$  in percolating water and minimum with addition of  $\text{KOH}$ . Total leachable F was found to be unaffected by incubation time. First Order model are found to be best fit for representing fluoride leaching in the present experimental conditions.

**Keywords:** Leaching Kinetics, First Order Kinetic Model, Fluoride, Pore Volume, Saturated Flow, Saline Soil, Ion Exchange.

## I. INTRODUCTION

Fluoride is regarded as one of the most important environmental micro pollutant responsible for soil and groundwater pollution causing dental and skeletal fluorosis [1,2,3]. The risk for human health and the environment can largely be determined by the concentration of fluoride that occurs in groundwater and the rate by which fluoride migrates to groundwater as both these processes can strongly be influenced by the interaction of dissolved fluoride with the soil solid phase via adsorption and desorption [4] and cation-anion exchange. Thus it is important to study its migration and leaching. The study become more important in saline soils, as above pH 7.0, most of the inorganic fluoride salts are either complexed with Fe and Al show maximum solubility or remain in soluble ionic form in soil water [5].

Aluminium a dominant metal in earths' atmosphere 7.5% when present naturally in large water bodies does not affect the water quality much but it reaches in drinking water predominantly through aluminium sulphate which is used in the coagulation process during water treatment. F<sup>-</sup> present in soil is bound in complexes and is usually transported through the water cycle dominantly complexed with aluminium.

The maximum adsorption of fluoride is reported to occur at pH 5.5 [6]. In soils, with pH below 6, most of the fluoride remains complexed with either Al or Fe (e.g.  $\text{AlF}_2^{2+}$ ,  $\text{AlF}_2^+$ ,  $\text{AlF}_3^0$ ,  $\text{AlF}_4^-$ ,  $\text{FeF}_2^{2+}$ ,  $\text{FeF}_2^+$ ,  $\text{FeF}_3^0$ ). At pH 6, dissolved fluoride species in presence of Al are mainly  $\text{AlF}_2^{2+}$  (60.40%) whereas  $\text{AlF}_2^+$ ,  $\text{AlF}_3^0$ ,  $\text{AlF}_4^-$  remain dissolved upto 12.8–0.08 % only. The free F<sup>-</sup> ion dissolution is approximately only 20% at pH 6. The dissolution of different aluminium fluoride decreases with increase in pH and at pH 8 and above, only free ionic fluoride, F<sup>-</sup>, remains 100 % dissolved [7]. Increasing amount of F<sup>-</sup> and  $\text{Al}^{+3}$  in medicine, industry and agriculture, drinks and other food products have made us concerned about its ill effect.

$\text{AlF}_x$  influences the proper function of entire human body by affecting pituitary-thyroid gland system which has major role in regulating growth development and metabolism of many tissues etc [8]. Chronic exposure of humans to  $\text{AlF}_3$

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begins in the foetus only. It may affect all pathological hallmark of the diseases by playing the role of a devil in various vital processes like neurotransmission, amyloid generation, transport of ions, energy metabolism, calcium homeostasis etc [9,10].

Thus by looking deep into the toxic effects of  $AlF_x$  in plants and humans, the leaching of fluoride in fluoride endemic soil with pH 8.2 has been investigated by further adding  $AlF_3$  on to it in soluble form. In the present study, leaching kinetics of  $F^-$  has been investigated in detail on  $AlF_3$  added columns. The effects of change in physico-chemical characteristics of percolating water such as  $Ca^{+2}$  hardness, Na levels,  $OH^-$  ions and its associated cations, temperature etc have been studied on leaching rates. All the kinetic data are fitted on various kinetic models and a linear power form equation has been derived to show the relationship between added concentrations and initial leaching rates.

## II. MATERIAL & METHOD

Saline soil (pH= 8.2) has been collected from Sambhar region of Rajasthan, India and was dried in open air in sunlight. Dried soil was sieved for uniform particle size. The physico chemical properties of the soil used in columns are given in Table 1.

The leaching kinetics of  $AlF_3$  has been studied by determining the fluoride concentrations in the leachate with time. Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB [11].

Columns of soil were prepared surrounded by glass jacket of continuously flowing thermostated water. 60 g soil of pH 8.2 and of particle size ( $53 > r$ ) was gently packed at water filled porosity  $0.315 \text{ cm}^3 \text{ cm}^{-3}$ . The leachate's pore volume was determined using equation (1)

$$Pv = q' t / \theta V \quad (1)$$

where

$q'$  =Volume of effluent collected per unit time i.e. flow rate  $\text{cm}^3 \text{ h}^{-1}$

$t$  =Time that has elapsed since the slug was introduced

$\theta$  =water filled porosity  $\text{cm}^3 \text{ cm}^{-3}$

$V$  =Total volume of soil column

Table I  
SOME PHYSICO-CHEMICAL CHARACTERISTICS OF THE COLUMN SOIL

| Soil Parameters | Value                  |
|-----------------|------------------------|
| pH              | 8.2                    |
| ECe             | 4 $\text{dsm}^{-1}$    |
| OC              | 1.17 %                 |
| $Na^+$          | 3840 meq/l             |
| $Ca^{+2}$       | 5 meq/l                |
| $Mg^{+2}$       | 5 meq/l                |
| Colour          | Light Grey             |
| Bulk Density    | 1.48 $\text{gcm}^{-3}$ |
| Type            | Loamy sand             |
| Sand %          | 21.9%                  |
| Silt %          | 10.7%                  |
| Clay %          | 6.8%                   |

The flow rate of extractant was found constant ( $2 \pm 0.5 \text{ ml}/10 \text{ min}$ ). A fixed volume of aqueous salt solution (slug) with desired anion concentration was added at the top of the soil column in each experiment. Salt solution was allowed to get adsorbed uniformly in the column for 24 hrs, after which the columns was continuously leached with de-ionized water or with other extractant as per requirement of the study. The leaching was carried out till the soluble anions were completely removed. The total leachable concentration was taken equal to the total leachable concentration present initially during leaching (i.e. concentration  $t=0$ ). During each kinetic run the concentration of ions were determined in leachate collected periodically at an interval of 2 min. The treatment of result obtained in leaching studies is based on calculations of initial leaching rates as well as on applications of various kinetic models for establishing the nature of leaching kinetics of water soluble fluoride salt.

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The treatment of data is based on the calculation of the following parameters as defined below:

- $[F^-]_s$  = Leachable fluoride present naturally in column soil, 210 mg/kg.
- $[AlF_3]_{add}$  =  $[F^-]_{ad}$  =  $F^-$  concentration introduced in the soil column as soluble  $AlF_3$ .
- $[F^-]_i$  = Total leachable content present initially.
- $[F^-]_{complex}$  = Complexed fluoride i.e.  $F^-$  concentration retained in column.
- i.e.  $[F^-]_{complex}$  =  $\{ [F^-]_s + [F^-]_{ad} \} - [F^-]_i$  (2)
- $[F^-]_t$  = leached concentration at time 't'.
- $[F^-]_l$  =  $[F^-]_i - [F^-]_t$
- = Leachable concentration remaining at time 't'.

### A. Total Leachable Fluoride $[F^-]_i$ and $[F^-]_{complex}$

Changes in total leachable fluoride  $[F^-]_i$  can be seen clearly from the Figure 1 which shows that  $[F^-]_i$  increases linearly on increasing  $[F^-]_{ad}$ . Soil itself has high leachable fluoride present in it, which is shown by the intercept of Figure 1.

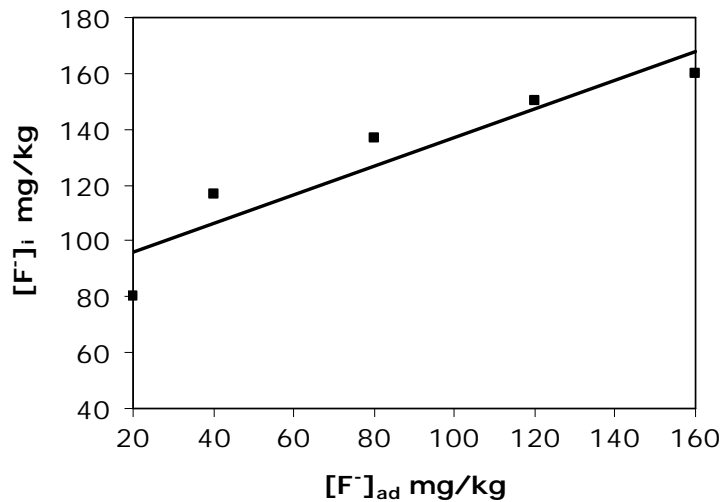


Fig. 1: Variation of  $[F^-]_i$  with  $[F^-]_{ad}$  for  $AlF_3$  addition at 30° C. Soil= 30 g and  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$

Leaching of fluoride during saturated flow has given very interesting results confirming role of co-cation in the  $F^-$  mobility in experimental soil conditions.

Added fluoride  $[F^-]_{ad}$  is complexed with the cations such as  $Al^{3+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  and is converted into immobilized form  $[F^-]_{complex}$ .  $Al^{3+}$  ions are added during experiment while Ca and Mg are present naturally in the column soil.

Concentration of available co-cation is controlled to some extent by (i) cation-exchange occurring in the soil solution and sites soil matrix (ii) competitive adsorption of the cation on the soil matrix.

For  $AlF_3$ ,  $[F^-]_{complex}$  can also be represented as equation 2:

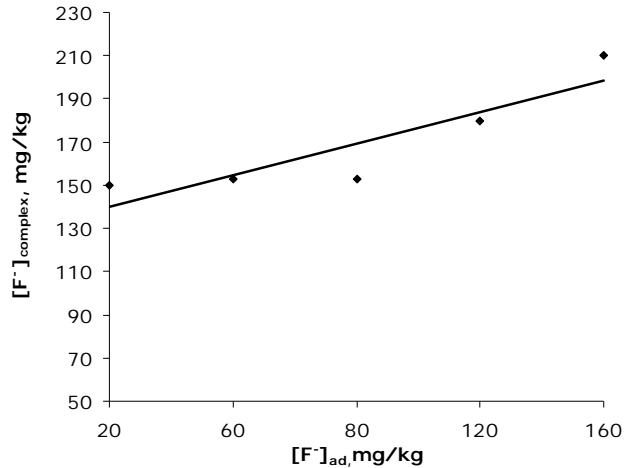
$$[F^-]_{complex} = a \times [\text{cation added}] + b \quad (3)$$

$$\text{For } AlF_3 \text{ added } [Al^{3+}] = \frac{1}{3} [F^-]_{ad}$$

Thus equation 3 converts as equation 4

$$[F^-]_{complex} = \frac{a}{3} [F^-]_{ad} + b \quad (4)$$

A plot of  $[F^-]_{complex}$  vs  $[F^-]_{ad}$  is given in Figure 2. The values of 'a' and 'b' are calculated as 0.46 and 127.5 respectively for  $AlF_3$  leaching.

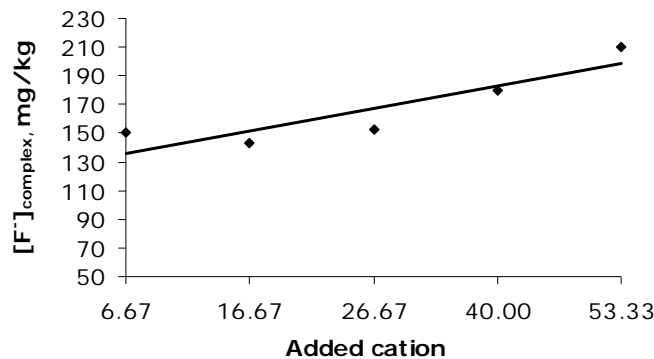


**Fig 2 :** Variation of  $[F^-]_{\text{complex}}$  with  $[F^-]_{\text{ad}}$  for leaching of  $AlF_3$  at  $30^\circ C$  in undisturbed soil column. Soil = 30 g and  $\theta=0.315 \text{ cm}^3 \text{ cm}^{-3}$ .

### III. RESULT AND DISCUSSIONS

In our soil pH (8.2), fluoride remains as  $F^-$  species. The dissolved aluminium species in presence of fluoride may be  $Al(OH)_4^-$  as reported earlier research [7]. As the  $OH^-$  ions are replaced readily with  $F^-$  formation of  $AlF_4^-$  and  $AlF_3$  is always possible in the soil system which is adsorbed very fast on soil matrix binding the free  $F^-$ . An increase in  $[F^-]_{\text{complex}}$  with increase in concentration of the added aluminium which is a co-cation of the  $[F^-]_{\text{ad}}$  confirm the complexation of free aluminium species with ionic fluoride resulting in decrease in  $[F^-]_i$  and  $LR_{\text{obs}}$  as shown in Figure 3.

The complexation of free  $F^-$  with added aluminium species is further confirmed by adding aluminium salts eg  $AlCl_3$ ,  $Al_2(SO_4)_3$  in extractant. It is clear from Table 2,  $[F^-]_s$  was decreased from 120 to 0 and 110 to 0 mg/kg for  $AlCl_3$  and  $Al_2(SO_4)_3$  respectively. It is thus proved that if aluminium ions are present in the saline soil in concentration lesser than the free  $F^-$ , fluoride leaching will not be stopped. However, if the aluminium concentration is increased upto the amount greater than the free  $F^-$ , leaching will stop completely.



**Fig. 3:** Variation of  $[F^-]_{\text{complex}}$  with added cation  $Al^{+3}$  during leaching of  $F^-$  during addition of different  $AlF_3$ . Soil = 30g,  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$ , Temp =  $30^\circ C$ .

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TABLE II  
EFFECT OF OTHER ALUMINIUM SALTS ON  $[F^-]_i$  LEACHING. SOIL= 30 G,  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$  AND TEMP =  $30^\circ \text{ C}$ .

| Aluminium Salt               | Amount added in ppm | $[F^-]_i$ , mg/kg |
|------------------------------|---------------------|-------------------|
| $\text{AlCl}_3$              | 20                  | 120               |
|                              | 50                  | 80                |
|                              | 300                 | Nil               |
| $\text{Al}_2(\text{SO}_4)_3$ | 20                  | 110               |
|                              | 50                  | 75                |
|                              | 300                 | Nil               |
| $\text{H}_2\text{O}$         | -                   | 210               |

### A. Leaching Rate Profile

The change in soil fluoride contact time (incubation period) has not affected fluoride leaching and resulted in similar  $[F^-]_i$  and  $\text{LR}_{\text{obs}}$  in different conditions (added and un added columns) which confirms a very fast adsorption-desorption of fluoride in experimental soil.

### B. Dependence of $\text{LR}_{\text{obs}}$ on $[F^-]_i$

The plot between  $\text{LR}_{\text{obs}}$  and  $[F^-]_i$  is given in Figure 4. The fluoride leaching rates can be fitted to following rate law:

$$\text{LR}_{\text{obs}} = k [F^-]_i^n \tag{5}$$

The values of k and n are calculated to be -0.4611 and 1 respectively. The unit of 'k' is  $\text{sec}^{-1}$ .

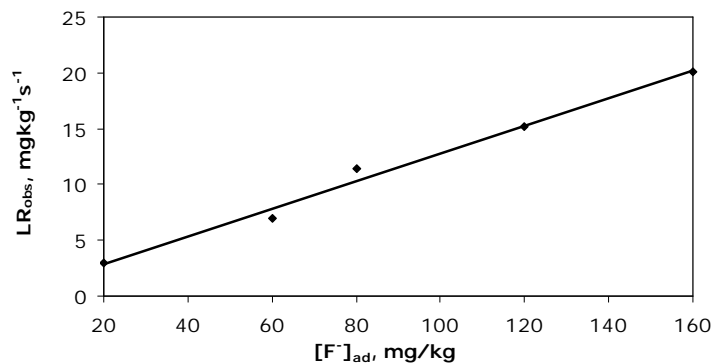


Fig. 4: Variation of  $\text{LR}_{\text{obs}}$  with  $[F^-]_{\text{ad}}$  for  $\text{AlF}_3$  at  $30^\circ \text{ C}$ . Soil= 30 g and  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$ .

### C. Effect of Temperature

An increase in temperature increases  $\text{LR}_{\text{obs}}$  and  $[F^-]_i$  remarkably at all added  $\text{AlF}_3$  concentrations (Figure 5) probably due to increase in solubility of  $F^-$  salts and a very high activation energy has confirmed less mass transfer control during leaching [12]. Value of activation energy as high as  $395 \pm 0.31 \text{ kJ mol}^{-1}$  clearly indicates that the fluoride leaching is controlled by release of  $F^-$  from the saturated soil particles following an ion-exchange reaction mechanism.

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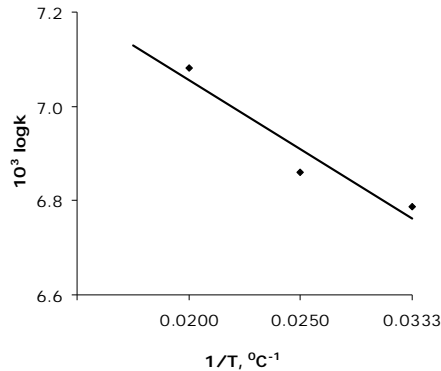


Fig. 5: Arrhenius plot for the determining activation energy of [F<sup>-</sup>] leaching during AlF<sub>3</sub> addition. Soil = 30 g, θ = 0.315 cm<sup>3</sup> cm<sup>-3</sup>.

### D. Effect of hardness (Ca<sup>+2</sup>) of Extractant

[F]<sub>i</sub> and LR<sub>obs</sub> both were found to decrease with increase in hardness of extractant water for blank as well as AlF<sub>3</sub> added columns as shown in Figure 6 and 7. On increasing CaCO<sub>3</sub> level of extractant water, leaching was stopped completely due to formation of CaF<sub>2</sub> in blank and AlF<sub>3</sub> in added columns which remained fixed in the column. Similar to the results of this study, in a previous study [13] too, the addition of gypsum in soil and irrigation water has stopped leaching of F<sup>-</sup> ion into groundwater completely. In presence of higher calcium levels, probability of formation of CaF<sub>2</sub> is more than AlF<sub>x</sub> as Al concentration is much more lower [14] than F<sup>-</sup> and Ca<sup>+2</sup>.

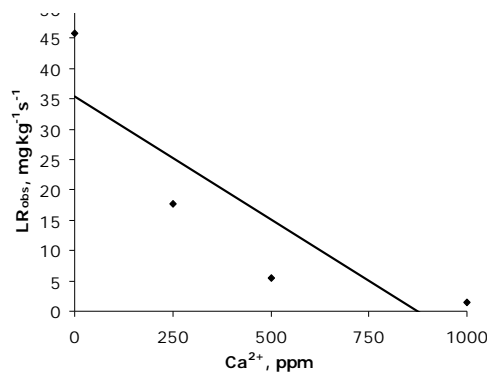
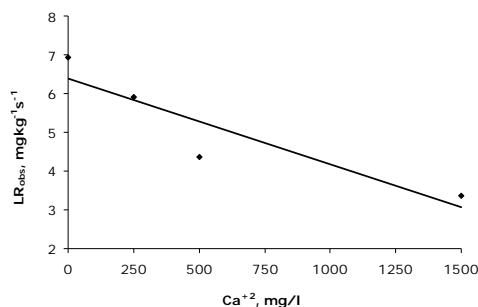


Fig. 6: Change in LR<sub>obs</sub> with increase in Ca<sup>+2</sup> concentration of extractant for F<sup>-</sup> leaching in blank soil column at 30<sup>0</sup> C. [F]<sub>ad</sub> = 0 mg/kg and Soil=30 g, θ = 0.315 cm<sup>3</sup> cm<sup>-3</sup>.

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**Fig 7:** Change in LR<sub>obs</sub> with increase in Ca<sup>2+</sup> concentration of extractant for F<sup>-</sup> leaching during AlF<sub>3</sub> addition at 30<sup>o</sup> C. [F]<sub>ad</sub> = 50 mg/kg, Soil=30 g, θ =0.315 cm<sup>3</sup> cm<sup>-3</sup>.

### E. Effect of Sodium Level of Extractant

An increase in Na level in percolating water has increased [F]<sub>complex</sub> thereby reducing [F]<sub>i</sub> in blank as well as in AlF<sub>3</sub> added columns. The decrease in [F]<sub>i</sub> and LR<sub>obs</sub> in blank columns is attributed to the release of calcium and magnesium ions from the soil matrix during Na-Ca, Na-Mg exchanges which precipitate ionic fluoride as CaF<sub>2</sub> and MgF<sub>2</sub> in the column. When significant amount of Al<sup>3+</sup> is added, a good concentration of free aluminium ions are also supposed to be present in soil water or matrix which may bind free F<sup>-</sup> present in the soil and convert it into unleachable form as cryolite (Na<sub>3</sub>AlF<sub>6</sub>) as both Al<sup>3+</sup> and Na<sup>+</sup> remain in very high concentrations in the column.

The limiting nature of plot reflects that formation of fluoride complex depends upon soil type and size of the column along with added salt concentration.

Our results reveal the fact that in soil rich in Sodium and Aluminium, fluoride leaching will be decreased due to formation of CaF<sub>2</sub>, AlF<sub>3</sub> and Na<sub>3</sub>AlF<sub>6</sub>. Ionic fluoride is either not formed or even if, it is formed in small amount, immediately releases F<sup>-</sup> in soil-water which again gets precipitated as stable Al or Ca complexes limiting the leaching of fluoride from the column soil.

### F. Effect of pH of Extractant

[F]<sub>i</sub> and LR<sub>obs</sub> are found to increase with increase in pH levels of extractant in AlF<sub>3</sub> added columns.

The order of increase in [F]<sub>i</sub> and LR<sub>obs</sub> values are NH<sub>4</sub>OH > NaOH > KOH as shown in Table 3. Release of F<sup>-</sup> in the soil solution is possible during replacement of fixed fluoride by [OH]<sup>-</sup> ions which increases the concentration of leachable fluoride. The reason for maximum leaching during NH<sub>4</sub>OH addition is the formation of 4H-F bonds with ammonium ions to carry more fluorides which increases [F]<sub>i</sub> and LR<sub>obs</sub> in comparison to Na<sup>+</sup> and K<sup>+</sup> [15].

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**TABLE III**  
CHANGE IN  $[F]_i$  AND  $LR_{OBS}$  FOR F LEACHING DURING  $AlF_3$  ADDITION AT DIFFERENT PH LEVELS OF THE EXTRACTANT AT  $30^0 C$ .  
SOIL=30,  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$ .

| Hydro-<br>-xides                                 | NaOH |      |      |      | KOH  |      |      |      | NH <sub>4</sub> OH |      |      |      |
|--------------------------------------------------|------|------|------|------|------|------|------|------|--------------------|------|------|------|
|                                                  | 10.5 |      | 12.5 |      | 10.5 |      | 12.5 |      | 10.5               |      | 12.5 |      |
| pH                                               | 10.5 |      | 12.5 |      | 10.5 |      | 12.5 |      | 10.5               |      | 12.5 |      |
| $[F]_{ad}$<br>mgkg <sup>-1</sup>                 | 0    | 80   | 0    | 80   | 0    | 80   | 0    | 80   | 0                  | 80   | 0    | 80   |
| $[F]_i$<br>mgkg <sup>-1</sup>                    | 235  | 165  | 270  | 190  | 220  | 140  | 230  | 155  | 258                | 210  | 300  | 230  |
| $LR_{obs}$<br>mgkg <sup>-1</sup> s <sup>-1</sup> | 53.7 | 15.5 | 63.8 | 22.5 | 44.8 | 12.1 | 50.2 | 14.3 | 62.5               | 28.1 | 80.5 | 35.3 |

### G. Application to the Kinetic Models

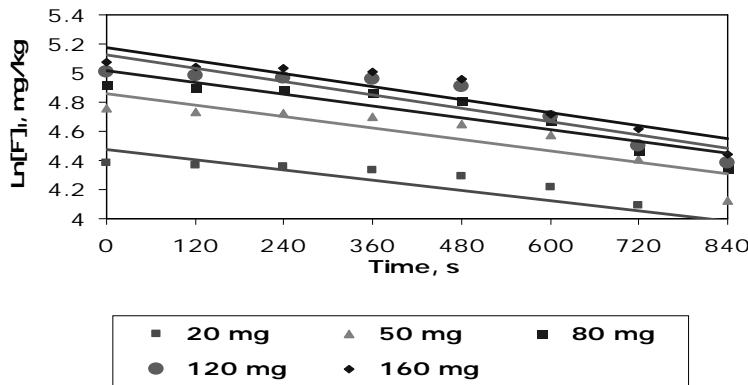
The results of the leaching of fluoride on adding  $AlF_3$  in saline soil are fitted to various kinetic models. While applying the integrated equations of different kinetic models, the concentration of leachable fluoride is assumed to be the maximum initially. The concentration terms used in different equations are defined as:

$$[F]_i = C_0 \quad ; \quad [F]_t = C_t; \quad [F]_i - [F]_t = C_0 - C_t$$

All the models were tested with least square regression analysis. On the basis of high  $r^2$  and low SEE, first order kinetic model is found to be best fit for representing fluoride leaching in saline soil.

$$\ln(C_0 - C_t) = a - bt \tag{6}$$

An order of one with respect to  $[F]_i$  for  $AlF_3$  proved that rate of  $[F]$  leaching depends only upon the concentration of the total soluble fluoride available for leaching and equilibrium between the ionic and fixed fluoride is achieved very fast.(Figure 8).



**Fig 8:** First Order Kinetic Equation profile for  $AlF_3$  leaching at different  $[F]$  at  $30^0 C$ . Soil=30g,  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$ .

## IV. CONCLUSION

The present study concludes that in fluoride rich saline soil with pH 8.2, leaching of  $F^-$  will be decreased on adding  $AlF_3$ .  $Ca^{+2}$  ions will impose negative effects on  $F^-$  leaching while temperature will increase leaching. It is suggested that in saline soils of fluoride endemic areas, leaching of fluoride from soil to subsurface or groundwater can be controlled by increasing the hardness, SAR and aluminium content of the irrigation water or directly amending the soil with



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gypsum and water soluble aluminium salts eg  $\text{AlCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$  etc. The result of this study of fluoride leaching from saline soils causing groundwater pollution can be applied to develop fluoride risk assessment models for fluoride pollution areas.

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