

## LEACHING KINETICS OF FLOURIDE FROM FLOURIDE CONTAMINATED SOIL OF SAMBHAR REGION BY LOADING MAGNESIUM FLOURIDE SALT

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### ABSTRACT

The present research study describes leaching rate profile of  $F^-$  by loading  $MgF_2$  on undisturbed vertical soil column of the soil collected from Sambhar region of Rajasthan, India. Alkaline soil (pH= 8.2) had been collected from Sambhar region of Rajasthan, India. Linear relationship is established between the concentrations of leachable fluoride  $[F^-]_i$  and rate of leaching ( $LR_{obs}$ ). With increase in added  $Mg^{2+}$  concentration, the  $Na^+$ - $Mg^{+2}$  exchange is also found to increase which increases total leachable  $F^-$  initially present in the soil solution. First order model is found to be best fit for representing fluoride leaching in the present experimental conditions.

**Keywords:** First Order Kinetic Model, Fluoride, Ion Exchange, Leaching Kinetics, TISAB, Saturated Flow, Alkaline Soil

### INTRODUCTION

Magnesium is an important mineral present in soil, responsible for plant nutrition as well as in maintaining the pH of the soil. The role of Mg is in producing the hardness in water and in the ion exchange reactions occurring in the soil is very well known. In soils, the exchangeable magnesium is in water soluble form. The nonexchangeable magnesium remains precipitated in the soil and can be released by ion exchange when large quantities of chlorides and sulphates are present which enhances its removal in percolating water and develops Mg deficiency in the soil (Selim *et al.*, 1975). In agricultural fields, Mg is a required component of fertilizer for certain crops grown in coarse textured soil in humid region and  $F^-$  is added as an impurity of added fertilizer. Thus the simultaneous occurrence of  $Mg^{+2}$  and  $F^-$  becomes inevitable phenomenon in agriculture fields. As  $MgF_2$  can reach in soil naturally or anthropogenically it has drawn the attention of the researchers investigating the fluoride speciation and chemistry in soil. Our experimental soil was rich in  $Na^+$ ,  $Cl^-$  and  $F^-$  ions, efforts has been made to study  $F^-$  transport in natural soil environment. Although the factors that influence the mobility of  $F^-$  in the soil are pH and formation of metal fluoride complexes including Al complex, the fate of these inorganic fluoride complexes depends on their chemical nature, deposition in soil matrix, interaction with soil and soil-water component and climate (Davison, 1983). Initial leaching rates have been calculated for added  $MgF_2$  and linear power form equation have been derived. Results are fitted to 5 different kinetic models viz Zero Order, First Order, Second Order, Parabolic and Ellovich Equation. First order kinetic model is found to be best suitable for representing leaching kinetics of fluoride by adding  $MgF_2$  salt. Results confirmed conversion of leachable fluoride into non leachable form  $F^-$  which retained in solution as  $MgF_2$ ,  $CaF_2$ ,  $AlF_3$ .

### MATERIALS AND METHODS

Alkaline 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  $NH_4F$  has been studied by determining the fluoride concentrations in the leachate with time as reported earlier (Saxena *et al.*, 2011). Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB (Rai *et al.*, 2000).

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**Table 1: Some physico-chemical characteristics of the column soil**

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

### Procedure of Leaching Studies:

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)

$$Pv = \frac{q't}{\theta v} \quad \dots(1)$$

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

The flow rate of extractant was found constant ( $2 \pm 0.5 \text{ ml/10 min}$ ). 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.

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

$[F^-]_s$  = Leachable fluoride present in column soil, 210 mg/kg.

$[MgF_2]_{add} = [F^-]_{ad}$  =  $F^-$  concentration introduced in the soil column as soluble  $MgF_2$ .

$[F^-]_i$  = total leachable content present initially.

$[F^-]_{complex}$  = Complexed fluoride i.e.  $F^-$  concentration retained in column.

$$\text{i.e. } [F^-]_{complex} = \{[F^-]_s + [F^-]_{ad}\} - [F^-]_i \quad \dots(2)$$

$[F^-]_t$  = leached concentration at time 't'.

$[F^-]_l$  =  $[F^-]_i - [F^-]_t$

= Leachable concentration remaining at time 't'.

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

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

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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 (Tracy *et al.*, 1984).

With increase in  $F^-$ , the value of  $[F^-]_{\text{complex}}$  is decreased and  $[F^-]_i$  increased.  $[F^-]_{\text{complex}}$  is found to depend upon two important factors (i) Exchangeable cations naturally present in soils (ii) Nature and concentration of cation of the added fluoride salt.

Thus  $[F^-]_{\text{complex}}$  can be represented as:

$$[F^-]_{\text{complex}} = a X [Mg^{2+}]_{\text{ad}} + b \quad \dots(3)$$

$$\text{But } [Mg^{2+}]_{\text{ad}} = [F^-]_{\text{ad}}/2$$

Thus equation 3 converts as equation 4

$$[F^-]_{\text{complex}} = \frac{a[F^-]_{\text{ad}}}{2} + b \quad \dots(4)$$

A plot of  $[F^-]_{\text{complex}}$  vs  $[F^-]_{\text{ad}}$  is given in Figure 1. The values of 'a' and 'b' are determined from the slope and intercept of Figure 1 and calculated to be -1.38 and 167 respectively. The negative value of 'a' corresponds to continuous decrease in  $[F^-]_{\text{complex}}$  value with increase in  $[F^-]_{\text{ad}}$ .

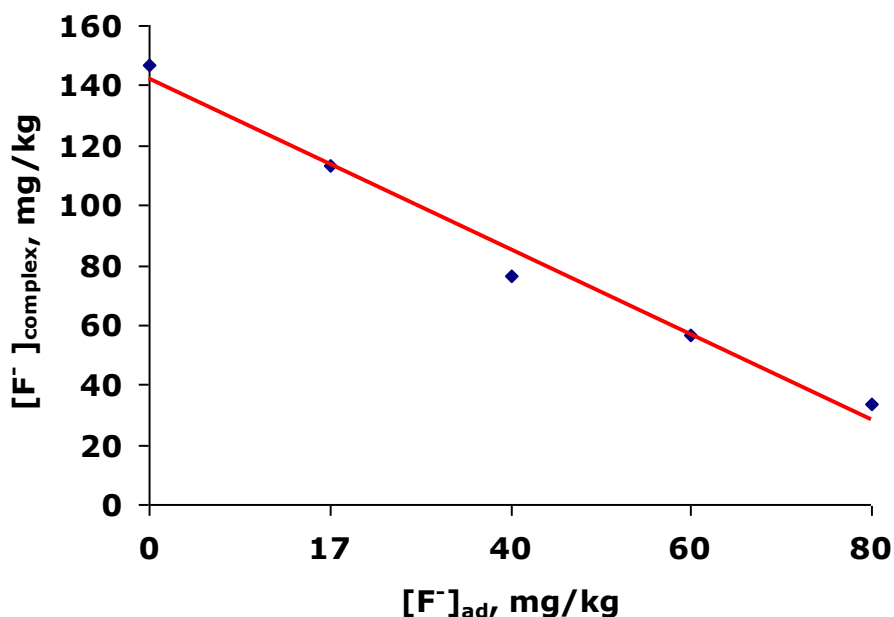


Figure 1: Variation of  $[F^-]_{\text{complex}}$  with  $[F^-]_{\text{ad}}$  for leaching of  $MgF_2$  at 30° C. Soil= 30 g,  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$

## RESULTS AND DISCUSSION

In the present case the cation,  $Mg^{2+}$ , being bivalent is calculated to be half of  $[F^-]_{\text{ad}}$ . While increase in  $Mg^{2+}$  content of soil column increases the possibility of conversion of leachable fluoride into unleachable  $MgF_2$ , the  $Mg$ - $Na$  exchange further releases unleachable fluoride into soil water as ionic fluoride. Thus with increase in  $Mg^{2+}$  concentration, the  $Na$ - $Mg^{+2}$  exchange is also increased which increases  $[F^-]_i$  in the soil solution decreasing  $[F^-]_{\text{complex}}$  because the complexed fluoride in this case remains mainly as  $MgF_2$ .

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### Leaching Rate Profiles

Initial rate of leaching,  $LR_{obs}$  are obtained from the initial slopes of the plots between  $[F^-]_i$  and time as shown in Figure 2.

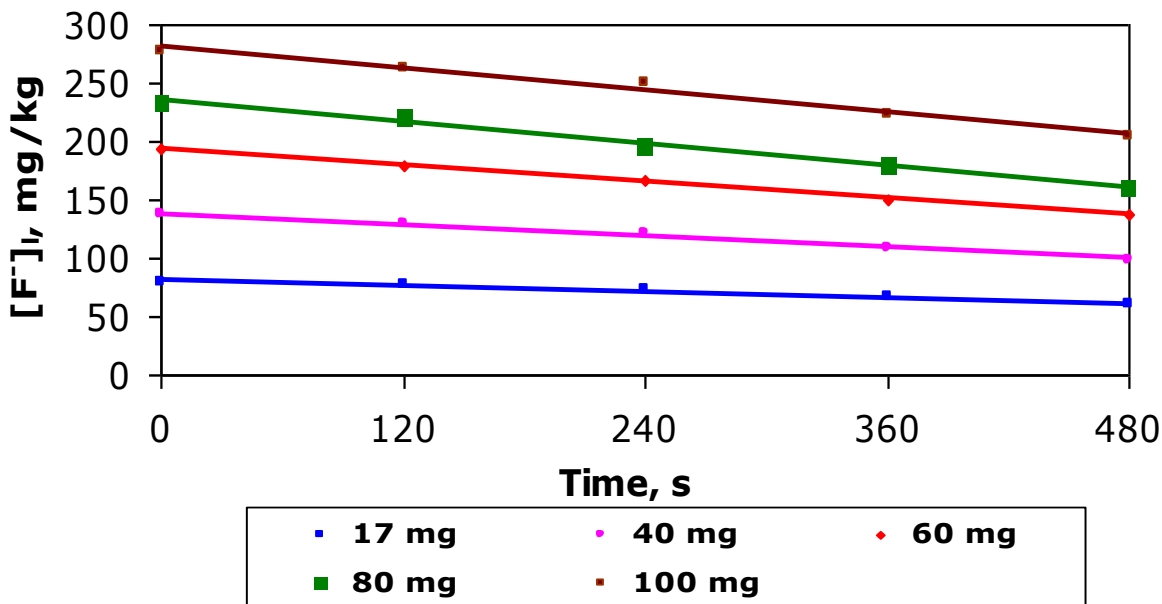


Figure 2: Initial leaching rate profiles for  $F^-$  leaching for  $MgF_2$  addition at  $30^\circ C$ . Soil= 30 g,  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$

### Dependence of $LR_{obs}$ on $[F^-]_i$

The fluoride leaching rates can be fitted to the following rate law equation (5):

$$LR_{obs} = k [F^-]_i^n \quad \dots(5)$$

From the log-log plots of  $LR_{obs}$  and  $[F^-]_i$  (Figure 3), the values of  $k$  and  $n$  are calculated to be  $0.9495 \text{ s}^{-1}$  and 1.0 respectively.

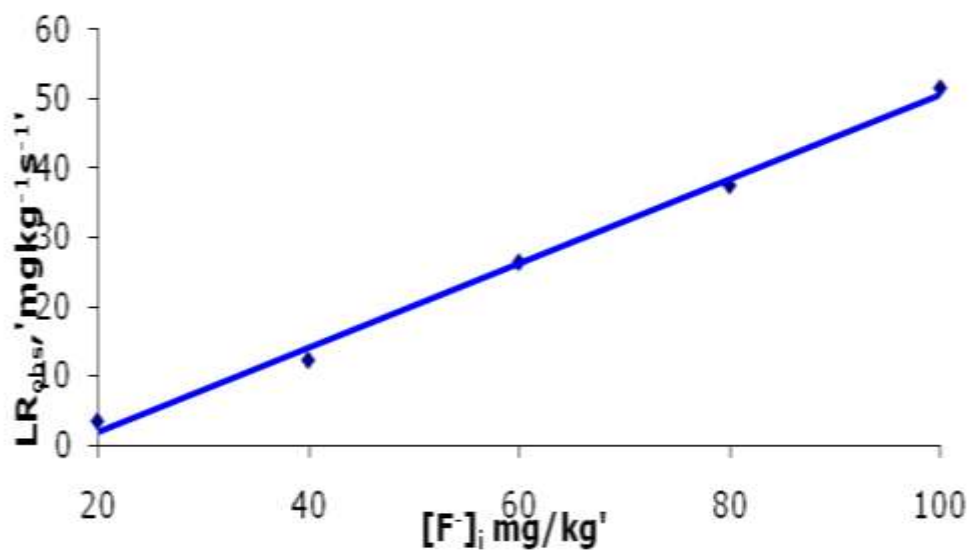


Figure 3: Variation of  $LR_{obs}$  with added fluoride concentration  $[F^-]_i$  for  $MgF_2$  addition at  $30^\circ C$ . Soil= 30 g,  $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$

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### Application to the Kinetic Models

The result of the leaching of fluoride salt in alkaline soils are fitted to various kinetic models viz Zero Order, First Order, Second Order, Parabolic and Ellovich Equation represented in Figure 4.

By 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:

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

**Zero Order Kinetic Model:** This model utilizes the equation 6 as shown under:

$$C_0 - C_t = a - bt \quad \dots(6)$$

The zero order plots were drawn with  $(C_0 - C_t)$  and  $t$ . Zero order reaction have been applied to describe adsorption of potassium by Burns and Burber (1961), Chromium by Amachar and Baker (1982) and nitrogen reaction by Keeney (1973) in soils.

**First Order Equation:** This model is based on the use of equation (7);

$$\ln(C_0 - C_t) = a - bt \quad \dots(7)$$

The first order plots were drawn between  $\ln(C_0 - C_t)$  and  $t$ . The application of first order reaction to soil chemical process have been observed for potassium by Jardine and Sharps (1984) and Ogwada and Sharks (1986), for nitrogen by Carski and Sparks (1987), for phosphorous by Vig *et al.*, (1979) and for chloride by Mianaxi (2005).

**Second Order Equation:** This model is based on the use of equation (8) or (9) given as;

$$1/C_t = 1/C_0 + kt \quad \dots(8)$$

or

$$1/C_t = a - bt \quad \dots(9)$$

The second order plots were drawn between  $1/C_t$  and  $t$ . Phosphate reaction on calcite by Greffin and Jurinuk (1974) and Al reaction in soil by Jardine and Zelazny (1986) are described by second order kinetic model.

**Parabolic Diffusion:** The parabolic diffusion plots were drawn using equation 10;

$$C_t = a - bt^{1/2} \quad \dots(10)$$

Plots are drawn between  $C_t$  and  $t^{1/2}$ . This model assumes that the reaction rate is controlled by diffusion of ions either from or to the reactive sites. This equation has been used to study the kinetics of reaction on soil constituents, by Sparks and Jardine (1981) and Hodge and Johns (1987) and for pesticide reactions by Weber and Geould (1966).

**Elovich Equation:** Another Kinetic model widely applied for the adsorption of various cations, anions and organic substances in soil system is elovich equation. The plots are drawn with  $C_t$  and  $\ln t$  according to equation (11):

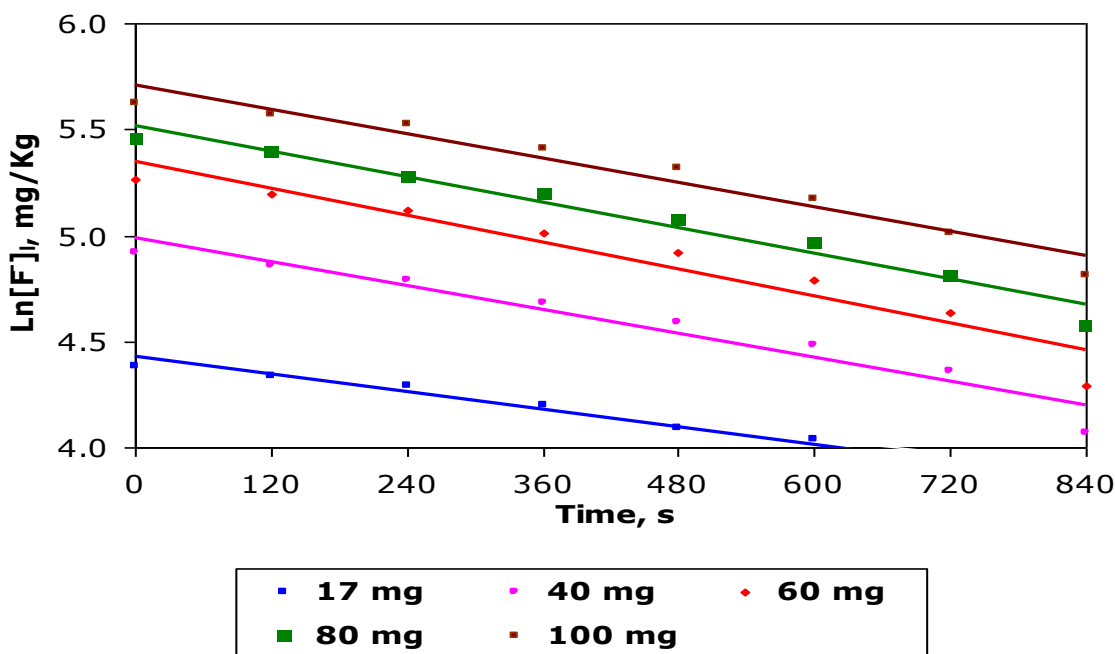
$$C_t = a - b \ln(t) \quad \dots(11)$$

This equation have been used to describe the kinetics of phosphate sorption and adsorptions on soils and soils minerals by Sharpley (1983) and Sulphur Sorption and adsorption Kinetics by Hodges and Jone (1987). This equation assumes heterogeneous distribution of adsorption energies where the  $E$  increase linearly with surface coverage, Low (1960).

### Statistical Interpretation

The rate laws by suitable rearrangements were brought in the linear form and the best fit least square lines were obtained in each case. Thus in all  $y = mx + c$  type plots, the straight lines shown are the best fit least square lines. Statistical parameters were calculated using computer program. Studies on soil systems are known to have only satisfactory reproducibility due to very complex and inhomogeneous nature of the soil. To overcome this difficulty to the extent possible, soils of similar type with similar physico-chemical characteristic have been used in columns. The result were reproducible within  $\pm 10\%$ .

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**Figure 4:** First Order equation profile for  $\text{MgF}_2$  leaching at different  $[\text{F}^-]$  at  $30^\circ\text{C}$ . Soil = 30 g,  $\theta = 0.315\text{ cm}^3\text{ cm}^{-3}$

The values of  $r^2$  and low SEE decides the criteria for best fit model. The values of  $r^2$  and SEE for the First Order equation at different added Magnesium Fluoride are given in Table 2.

**Table 2:** Coefficient of Determination ( $r^2$ ), Standard Error Estimate (SEE) and Slope for First Order kinetic models applied on  $\text{F}^-$  leaching for  $\text{MgF}_2$  addition at different  $[\text{F}^-]_{\text{ad}}$  at  $30^\circ\text{C}$ . Soil = 30 g,  $\theta = 0.315\text{ cm}^3\text{ cm}^{-3}$

$[\text{F}^-]_{\text{ad}}\text{ mg/l}$	$r^2$	Slope $\times 10^{-3}$	SEE
17	0.96	-0.69	1.84
40	0.94	-0.94	3.40
60	0.93	-1.06	5.37
80	0.97	-1.00	3.21
100	0.96	-0.95	6.75

On the basis of high  $r^2$  and low SEE, Zero and First order kinetic models are found to be best fit for representing fluoride leaching in the present experimental conditions.

### Conclusion

In undisturbed alkaline soil column, the leaching of fluoride mainly depends on ion exchange capacities of different mono and hetro valent ions present in the soil column. As with increase in added fluoride co-cation concentration, the value of  $[\text{F}^-]_{\text{complex}}$  decreases. Out of 5 different kinetic models, first order kinetic model is the best suited one. Thus the order using integrated rate equation as well as initial rate equation is identical for  $\text{F}^-$  leaching in alkaline soil, if added salt is  $\text{MgF}_2$ . The results of the present study can be utilized for developing  $\text{F}^-$  leaching models in fluoride endemic areas and measuring groundwater pollution due to fluoride leaching. It is conclude and suggested that in Na and Mg rich soils, liming is not the only remedy to retard groundwater fluoride contamination. The only remedy to retard the groundwater contamination rather defluoridation of groundwater should essentially be adopted before using groundwater in such areas.



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