Leaching Kinetics of Fluoride in Sodic Saline Soil

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Leaching kinetics of fluoride by loading MgF_2 on undisturbed vertical soil columns has been investigated and compared using various kinetic models. Linear relationship is established between the concentrations of leachable fluoride $[F^-]_i$ and rate of leaching (LR_{obs}). $[F^-]_i$ and LR_{obs} are found to decrease with increase in Na^+ and Ca^{+2} levels of extractant, while an increase has been observed with increase in temperature and OH^- ions. Maximum $[F^-]_i$ are resulted with addition of NH_4OH in percolating water and minimum with addition of 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

KEY WORD

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

INTRODUCTION

Today, the problems of high fluoride concentrations in groundwater and the risk of fluorosis associated using such water for human consumption is faced by a large portion of the population all over the world (Sloof et al. 1989). As concentrations of fluoride in the groundwater are greatly affected by the mobility and migration of this contaminant under the influence of adsorption-desorption and cation-anion exchanges within the soil components, it is important to study its migration and leaching. The study become more important in alkaline 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 (Sparks, 1980).

Although the factors that influence the mobility of F^- in the soil are pH and formation of metal fluoride complexes including Al complex (Pickering, 1985), 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, 1984).

In addition to above, quality of percolating water eg., several cations and anions, hardness and sodium absorption ration (SAR) affect the chemical speciation and dissolution of fluoride up to a significant level (Pickering et al., 1988).

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 fluoride endemic areas, if the soil Mg content is increased during liming, leaching of fluoride is lowered due to precipitation of MgF_2.

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.

As our experimental soil is rich in Na^+, Cl^- and F^- ions, efforts has been made to study F^- transport in natural soil environment. Initial leaching rates have been calculated for added MgF_2 and AlF_3 and linear power form equation have been derived. The effect of change in physic-chemical characteristic of percolating water such as Ca^{+2} hardness, Na^+ levels has been discussed in the light of Ca-Mg and Na-Mg exchange. The effect of OH^- ions and its associated cation and temperature on leaching kinetics has been discussed.

Results are fitted to various kinetic models. Results confirmed conversion of leachable fluoride into non leachable form F^- which retained in solution as MgF_2, CaF_2, AlF_3.

MATERIAL & METHOD

Alkaline soil (pH= 8.2) has been collected from Sambhar region of Rajasthaan, 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**.

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

Properties	**Soil**
pH	8.2
ECE	147.6
OC	1.17 %
Na^+	3840 meq/L
Ca^{+2}	5 meq/L
Mg^{+2}	5 meq/L
Colour	Light Grey
Specific Gravity	
Type	
Sand %	
Silt %	
Clay %	

The leaching kinetics of MgF_2 has been studied by determining the fluoride concentrations in the leachate with time. Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB (Rai et al., 2000).

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 cm^3cm^{-3}. The leachate's pore volume was determined using equation (1)

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

where

q' =Volume of effluent collected per unit time i.e. flow rate $cm^3\ h^{-1}$
t =Time that has elapsed since the slug was introduced
θ =water filled porosity cm^3cm^{-3}
V =Total volume of soil column

The flow rate of extractant was found constant (2±0.5 ml/10 min). A fixed volume of aqueous salt solution (slug) with desired anion concentration (NaF or KF) 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. After completely removing the soluble ions the column soil was transferred into the beaker in a known volume of extractant. This salt solution was stirred for 2 hrs. The ion concentration was further determined in the filtrate of the soil suspension to ensure the complete removal of soluble ions from the soil in the column. 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.

RESULT AND DISCUSSION

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.

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

$[F^-]_t$ = 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 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 $[F^-]_{complex}$ is decreased and $[F^-]_i$ increased. $[F^-]_{complex}$ 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 $[F^-]_{complex}$ can be represented as:

$$[F^-]_{complex} = a \times [Mg^{2+}]_{ad} + b \qquad (3)$$

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

Thus equation 3 converts as equation 4

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

A plot of $[F^-]_{complex}$ vs $[F^-]_{ad}$ 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 $[F^-]_{complex}$ value with increase in $[F^-]_{ad}$.

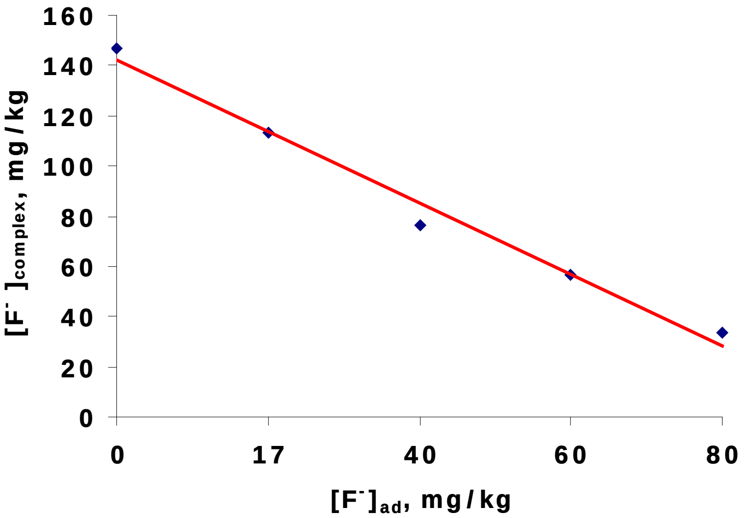


Fig1: Variation of $[F^-]_{complex}$ with $[F^-]_{ad}$ for leaching of MgF_2 at 30° C. Soil= 30 g, θ =0.315 cm^3cm^{-3}.

In the present case the cation, Mg^{2+}, being bivalent is calculated to be half of $[F^-]_{ad}$. 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 $Na\text{-}Mg^{+2}$ exchange is also increased which increases $[F^-]_i$ in the soil solution decreasing $[F^-]_{complex}$ because the complexed fluoride in this case remains mainly as MgF_2.

Variation of Incubation period

Variation of incubation period (soil-added fluoride interaction time) was done from 0 hrs to 4 days on blank soil columns and at $[F^-]_{ad}$ = 40 mg/kg. The values of $[F^-]_i$ as well as LR_{obs} were found same at all varied values of incubation time (Louis, B. and F. Josee. 2003).

Leaching Rate Profiles

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

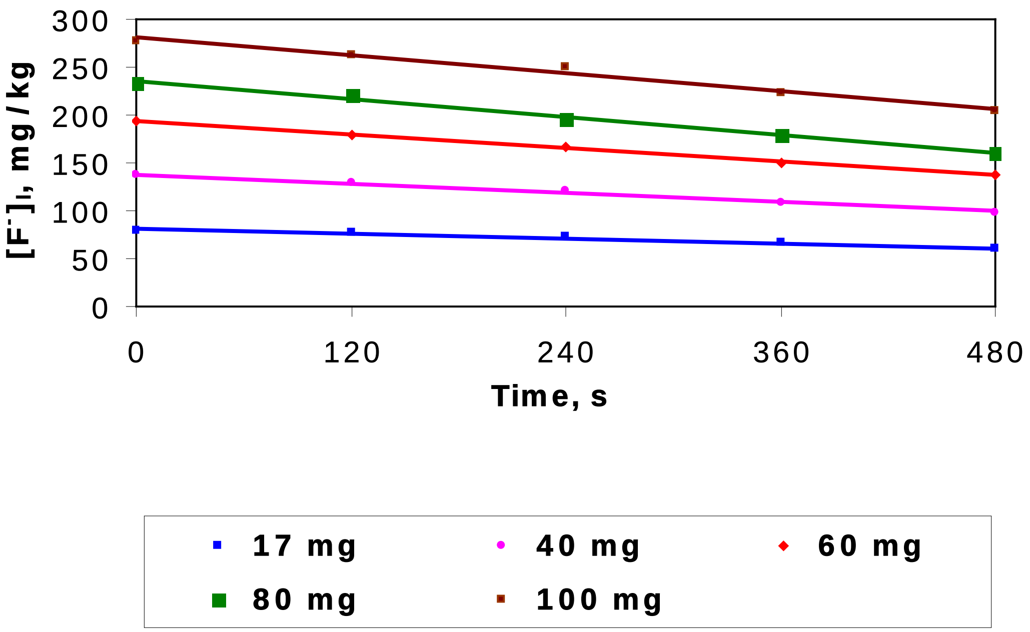


Fig.2: Initial leaching rate profiles for F^- leaching for MgF_2 addition at 30^0 C. Soil= 30 g, θ =0.315 cm^3cm^{-3}.

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

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

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

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 s^{-1} and 1.0 respectively.

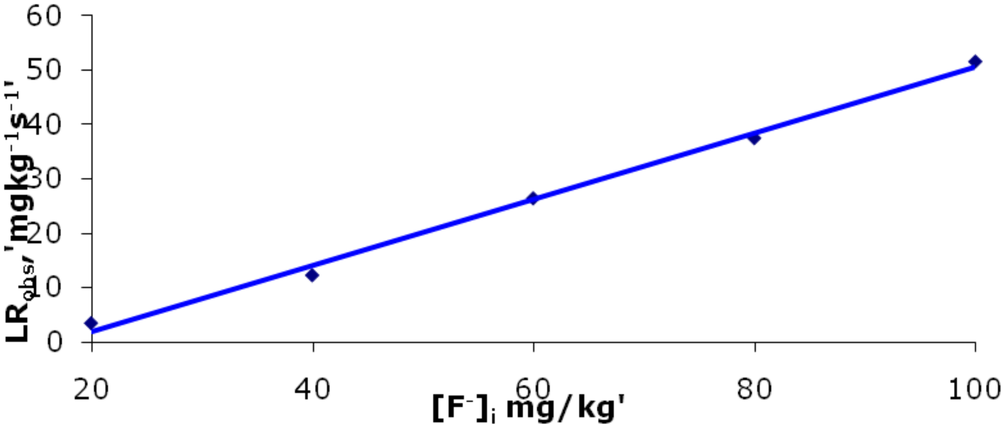


Fig 3: **Variation of LR_{obs} with added fluoride concentration $[F\text{-}]_i$ for MgF_2 addition at 30^0 C. Soil= 30 g, θ =0.315 cm^{3}cm^{-3}.**

Effect of Temperature

Only a slight increase in leaching rate of fluoride is observed with increase in the temperature which is resulted probably due to increase in the solubility of naturally present fluoride salts and added MgF_2 at higher temperature.

From Arrhenius plot (Figure 4) i.e. log k Vs 1/T, the value of activation energy is determined to be 240 ± 0.61 kJ mol^{-1}.

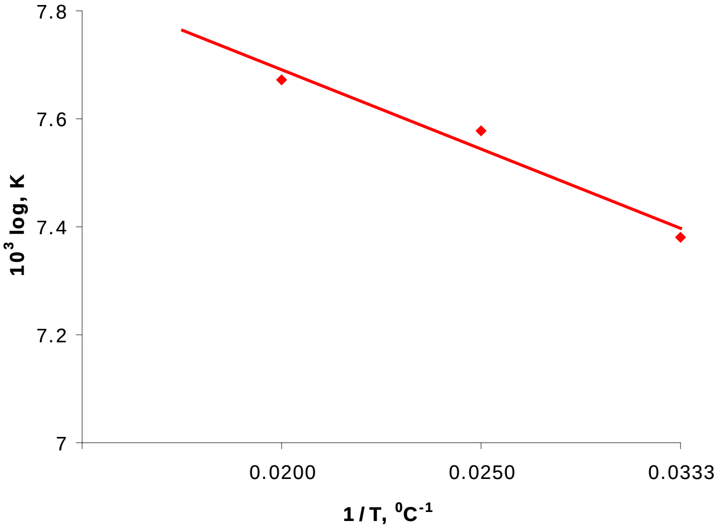


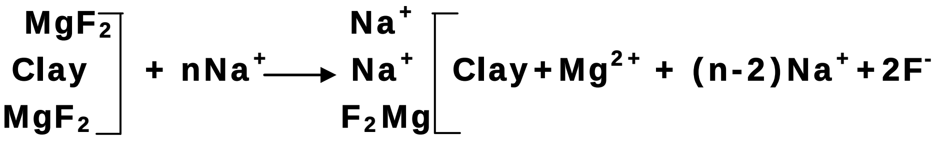
Fig 4: Arrehenius plot for the determination of activation energy of F^- leaching during MgF_2 addition. Soil = 30 g. Soil particle size = 500 ≥ r ≥250, θ= 0.315 cm^3 cm^{-3}.

An increase in temperature of the soil column has increased the leaching of $[F^-]_i$ and LR_{obs} values due to high solubility of precipitated fluoride and the activation energy is calculated as 240.01± 0.61 k J mol^{-1}. A high value of activation energy again reported to true ion-exchange during leaching.

Effect of Sodium Level of Extractant

Na level of extractant is varied by adding appropriate amount of NaCl in deionized water. NaCl salt is chosen because of (i) high solubility of the salt in H_2O (ii) the column soil is saturated with Na^+ and Cl^- ions and leached without affecting leaching rate of fluoride.

An increase in Na level of percolating water has increased $[F^-]_i$ as well as LR_{obs}. Figure 5 clearly show that $[F^-]_{complex}$ decreases remarkably with increase in Na level of percolating water. This increase in $[F^-]_i$ and LR_{obs} is attributed to the Na-Mg and Na-Ca exchange on the soil colloids which releases Mg^{2+} in the soil solution from the adsorption sites of MgF_2. The equation 6 represents probable exchange reaction on the clay surface.



$$\left.\begin{matrix}MgF_2\\ Clay\\ MgF_2\end{matrix}\right] + nNa^+ \longrightarrow \begin{matrix}Na^+\\ Na^+\\ F_2Mg\end{matrix}\left[Clay + Mg^{2+} + (n-2)Na^+ + 2F^- \right. \quad (6)$$

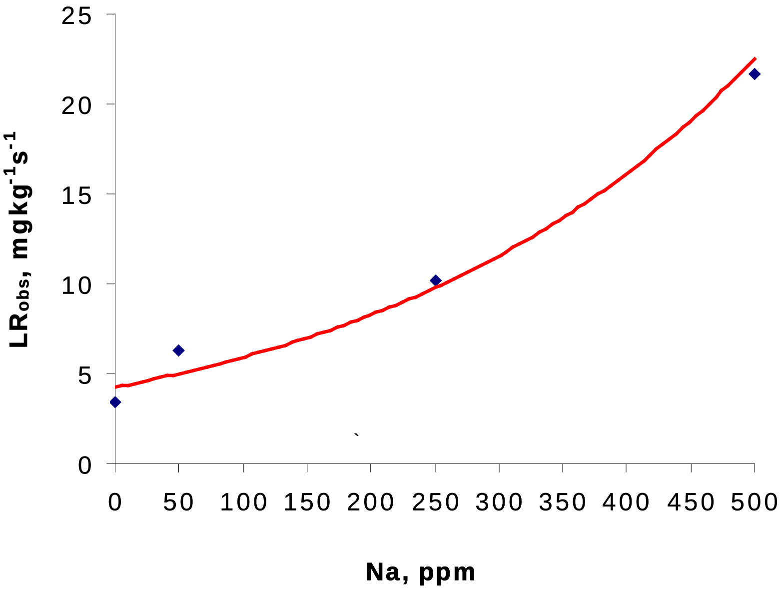


Fig 5: Change in LR_{obs} with increase in Na concentration for F^- leaching during MgF_2 addition at 30^0 C. $[F^-]_{ad}$ = 17 mg/kg, Soil=30 g, θ=0.315 cm^3cm^{-3}.

Effect of Change in Hardness (Ca^{+2}) of Extractant

Hardness level of extractant (deionized H_2O) was varied by adding Ca^{+2} in the form of $CaCO_3$.

On increase in Ca^{+2} concentration of extractant water, $[F^-]_i$ and LR_{obs} are increased slightly due to Na-Ca and Ca-Mg exchange. Addition of Ca^{+2} forms both monovalent and heterovalent exchange where most of the exchange sites are occupied by Na^+ ions surrounded by F^-. During Ca-Mg exchange, free Mg ions are replaced in soil solution. From the soil solution free Mg^{2+} again precipitate on soil surface as MgF_2. During Na-Ca exchange, the Ca ions from the soil solution are precipitated on clay surface releasing Na^+ ions thus increasing the formation of soluble NaF.

It is interesting to note that all the $[F^-]_i$ and LR_{obs} values are much less than the $[F^-]_s$, (our experimental soil is rich water soluble fluoride 210 mg/Kg) which confirms that even on increasing Ca^{+2} ions, only a slight decrease in the $[F^-]_{complex}$ values occur (Figure 6). Thus it is clear that hardness of irrigation water up to 1500 ppm of Ca^{+2} will not stop $[F^-]$ leaching in the endemic areas if Mg^{+2} ions are also present in large amount in the soil. The dosing of Ca^{+2} is essential to stop fluoride leaching from such polluted sites.

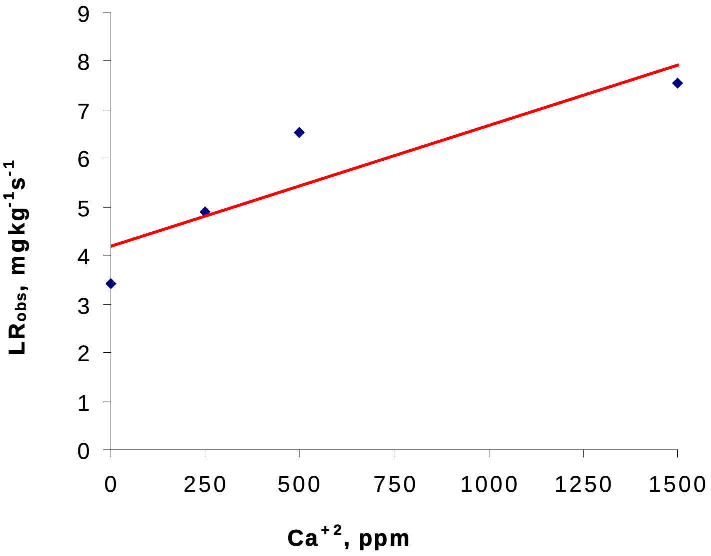


Fig 6: Change in LR_{obs} with increase in Ca^{+2} concentration of extractant for F^- leaching during MgF_2 addition at 30^0 C. $[F^-]_{ad}$ =80 mg/kg, Soil = 30 g, θ= 0.315 cm^3 cm^{-3}.

Effect of OH^- ions

The pH of the extractant water was varied from 7.0 – 12.5 using NaOH, KOH and NH_4OH. $[F^-]_i$ and LR_{obs} are found to increase with the increase in pH levels of extractant water. The order of increase in $[F^-]_i$ and LR_{obs} values are NH_4OH > NaOH > KOH. The detailed results are tabulated and presented in Table 2.

Table 2: Change in $[F^-]_t$, $[F^-]_l$ and $[F^-]_i$ with time for F^- leaching during MgF_2 addition at different pH levels of the extractant at 30^0 C. $[F^-]_{ad}$ = 17 mg/kg, Soil = 30 g, θ= 0.315 cm^3 cm^{-3}.

Hydroxide	**NaOH**				**KOH**				**NH_4OH**			
pH	**10.5**		**12.5**		**10.5**		**12.5**		**10.5**		**12.5**	
Time	**$[F^-]_t$**	**$[F^-]_l$**	**$[F^-]_t$**	**$[F^-]_l$**	**$[F^-]_t$**	**$[F^-]_l$**	**$[F^-]_t$**	**$[F^-]_l$**	**$[F^-]_t$**	**$[F^-]_l$**	**$[F^-]_t$**	**$[F^-]_l$**
0	0	90	0	98	0	83	0	89	0	96	0	103
120	3	87	5	93	2	81	3	86	4	92	6	97
240	7	83	10	88	5	78	6	83	9	87	11	92
360	13	77	16	82	11	72	15	74	15	81	18	85
480	20	70	23	75	18	65	22	67	22	74	25	78
600	28	62	32	66	22	61	27	62	28	68	31	72
720	38	52	42	56	28	55	32	57	36	60	38	65
840	48	42	53	45	37	46	41	48	44	52	47	56
$[F^-]_i$	**90**		**98**		**83**		**89**		**96**		**103**	
LR_{obs}	**5.18**		**6.11**		**3.70**		**4.43**		**5.10**		**5.70**	

LR_{obs} mg kg^{-1} s^{-1}: $[F^-]_t$,$[F^-]_l$ and $[F^-]_i$ are in mg/kg

Release of F^- in the soil solution is possible during replacement of fixed fluoride by $[OH^-]$ ions which increases the concentration of leachable fluoride. The reason for maximum leaching during NH_4OH addition is the formation of 4H-F bonds with ammonium ions (Alvi, A. and Lynden Bell. 1998) to carry more fluorides which increases $[F^-]_i$ and LR_{obs}.

Application to the Kinetic Models

The result of the leaching of fluoride salt in sodic saline soils are fitted to various kinetic models. 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:

$[F^-]_i = C_o$; $[F^-]_t = C_t$; $[F^-]_l = [F^-]_i - [F^-]_t = C_o - C_t$

First order model is found to be best fit for representing fluoride leaching in the present experimental conditions as shown in Figure 7.

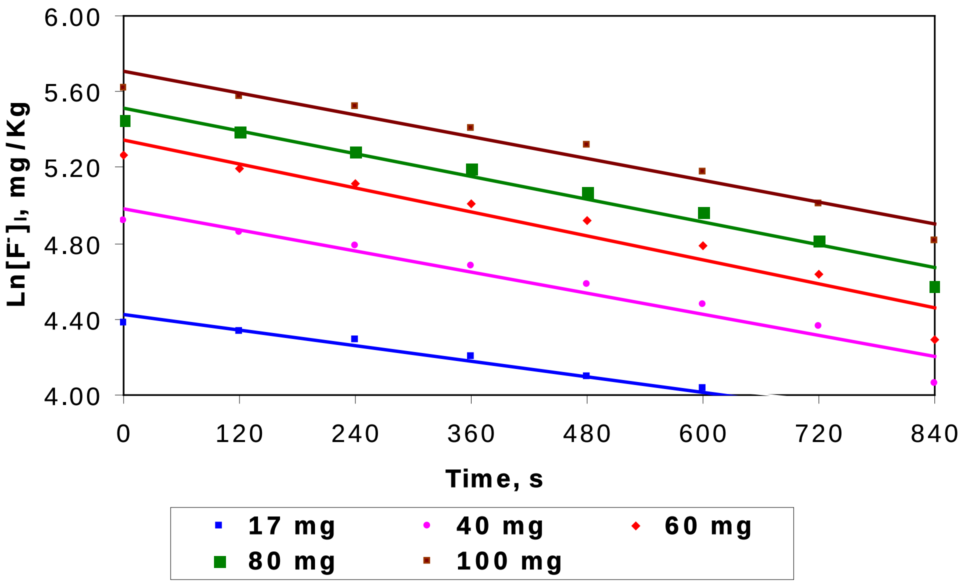


Fig 7 : First Order equation profile for MgF_2 leaching at different $[F^-]$ at 30^0 C.

CONCLUSION

In undisturbed sodic 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 $[F^-]_{complex}$ decreases. When we increase the concentration of Ca^{+2} and Na^+ ions, there is slight decrease in amount of $[F^-]_{complex}$ is observed. A high value of activation energy indicates a lower mass transfer but true ion exchange affecting the fluoride leaching in our experimental conditions. 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 F^- leaching in sodic saline soil, if added salt is MgF_2. The results of the present study can be utilized for developing 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 top retard the groundwater contamination rather defluoridation of groundwater should essentially be adopted before using groundwater in such areas.

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