

FLUORIDE ION LEACHING KINETICS FOR ALKALINE SOILS OF INDIAN ORIGIN

S. SAXENA*, A. RANI

Deptt. of Chemistry, Maa Bharti Girls P.G. College, Kota, Rajasthan, India

ABSTRACT

Aims: The present research study describes leaching kinetics of F^- by loading NaF on undisturbed vertical soil column of the soil collected from Sambhar region of Rajasthan, India.

Place of Study: Government College Kota, University of Kota, Kota, Rajasthan, India.

Methodology: Alkaline soil (pH= 8.2) had 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 leaching kinetics of NaF has been studied by determining the fluoride concentrations in the leachate with time. Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB.

Results: Linear relationship is established between the concentrations of leachable fluoride $[F^-]_i$ and initial 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. While viewing the affect of OH^- ions, the effect of its accompanying cation was also investigated which indicated that maximum $[F^-]_i$ are resulted with addition of NH_4OH in percolating water and minimum with addition of KOH. $[F^-]_i$ is found to decrease with excessive phosphate ions and found to increase with excessive Nitrate and Nitrite ions in percolating water. Total leachable F^- was found to be unaffected by incubation time.

Conclusion:

On the basis of the results, it is concluded that in alkaline soils, fluoride leaching will increase with increase in added NaF salts. An increase in Ca^{2+} levels of extractant has decreased $[F^-]_i$ and LR_{obs} . An increase in Na^+ level of extractant, some of the unleachable fluoride converts into leachable form as $[F^-]_{extra}$. The result of the study are of great significance for developing various mathematical models for salt transport processes in alkaline soil preferable in Sambhar region of Rajasthan and elsewhere in the world.

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

1. INTRODUCTION

Fluoride content in water depends not only on geo-chemical background of the area and climatological factors such as hydrological conditions, land forms, rainfall pattern and evaporation rate but also on the adsorption and leaching of fluoride in soil (Wuyi, W. et al 2002) . The adsorption and leaching processes directly affect fluoride migration and exchange from soil to water. In soil, some of the fluorides get immobilized, taken up by the plants and a part is also carried by the percolating water. All the processes occur simultaneously. Several studies (Barnard, W.R. and D.K. Nordstrom 1982) have been conducted to determine whether fluoride in rainwater was derived from anthropogenic emissions and natural sources such as sea salt cycling. A strong correlation between fluoride and sodium concentration in precipitation samples collected from marine, coastal and inland sites in India has been reported (Neal, C. et al. 1990).

The occurrence of high F^- , a ubiquitous micro pollutant in groundwater and the risk for fluorosis associated with use of such water for human consumption is one of those environmental hazards faced worldwide. At present approximately 29 countries are reported to be affected with severe fluorosis (Agarwal et al., 1997; Apambire et al., 1997). Out of India's 32 states, 17 have been identified as endemic areas for fluorosis with an estimated 25 million people impacted and another 66 million at risk according to a recent survey (<http://www.Fluoridealert.org>). In groundwater fluoride reaches mainly due to its leaching from fluoride rich minerals such as fluorspar CaF_2 , cryolite (Na_3AlF_6), fluoroapatite ($Ca_5F(PO_4)_3$), topaz [$Al_2SiO_4(OH)_2$], sellaite (MgF_2), villianite (NaF). Due to high solubility of NaF , it readily gets adsorbed in human body and hardly after few minutes of its intake plasma F^- concentration rises generating toxicity.

However, besides geochemical background of area and climatological factors leaching and migration depends on nature of leaching salt also. Sambhar region in Rajasthan, India is reported to have groundwater fluoride level in the range 3 to 5 ppm (Agarwal, V., et al. 1997 & Groundwater Atlas of Rajasthan 1999). The soil of the region is old Alluvial Alkaline with Na^+ as high as 3840 meq/lit with pH 8.2. Most of the inorganic salts are either complexed with Fe and Al or remain with soluble ionic form in soil water. At the pH of soil > 7.0 under the alkaline environment, possibility of migration of soluble fluoride to the groundwater is most prominent at all temperature.

In our experimental soil (pH 8.2), the excessive amount of exchangeable Na^+ and K^+ are present naturally hydrolysed to a much greater extent than Ca^{2+} and Mg^{2+} (which are held tightly in the soil), it was interesting to investigate the chemistry of F^- leaching in this soil environment. The soil properties depicts excessive amount of Na^+ ions in comparison to Ca^{2+} and Mg^{2+} which shows that level of exchangeable sodium is high in comparison to that of Ca^{2+} and Mg^{2+} .

The present research study describes leaching kinetics of F^- by loading NaF on undisturbed vertical soil column of the soil collected from Sambhar region of Rajasthan and compared using various kinetic models. Effect of temperature, water filled porosity of the soil, OH^- ions and its accompanied cation, Ca^+ hardness and Na levels of percolating water etc have been investigated in detail on the total leached F^- levels as well as on initial leaching rates.

The flow method for studying leaching kinetics in saturated flow conditions as desorbed species has its own obvious importance over other kinetic methods i.e. mixed batch (Ogwada and Sparks, 1986), infinite sink (Pavlatou and Polyzopoulous, 1988) in addition to its being pioneer attempt for studying leaching of $[F^-]$ as literature has cited leaching studies of Cl^- , SO_4^{2-} , PO_4^{3-} only (Sharma, B. et al 2009).

2. MATERIAL & METHOD

Alkaline soil (pH= 8.2) had 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 1.1.

Table 1.1: Some physico-chemical characteristics of the column soil

Soil Parameters	Value
pH	8.2
ECE	4 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 gcm ⁻³
Type	Loamy sand
Sand %	21.9%
Silt %	10.7%
Clay %	6.8%

The leaching kinetics of NaF has been studied by determining the fluoride concentrations in the leachate with time as reported earlier (Saxena, S. et al. 2011). Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB (Rai et al., 2000).

2.1 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 cm³cm⁻³. The leachate's pore volume was determined using equation (2) (Ghiedyal, B.P., and R.P. Tripathi .1987.)

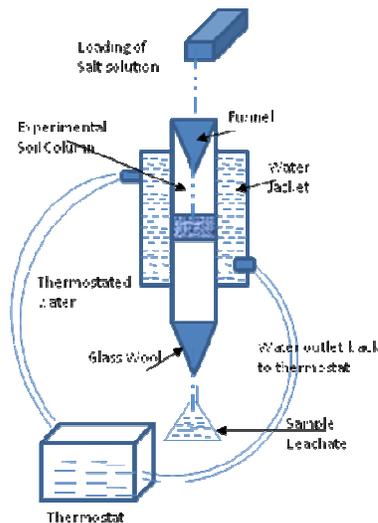
$$Pv = \frac{q' t}{\theta V} \quad (2)$$

where

q' =Volume of effluent collected per unit time i.e. flow rate cm³ h⁻¹

t =Time that has elapsed since the slug was introduced

θ =water filled porosity cm³cm⁻³ V =Total volume of soil column



Schematic Diagram

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) 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 were 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.

3. RESULT AND DISCUSSIONS

3.1 Nomenclature

The concentration terms used for presenting the analytical results are:

$[F]_s$ = leachable fluoride present in column soil, 210 mg/kg

$[F]_{ad}$ = F^- concentration introduced in the soil column

$C_o = [F]_i$ = total leachable content present initially

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

i.e. $[F]_{complex} = \{[F]_s + [F]_{ad}\} - [F]_i$ **When $\{[F]_s + [F]_{ad}\} \geq [F]_i$**

$[F]_{extra}$ = concentration of unleachable fluoride converting into leachable fluoride

$= [F]_i - \{[F]_s + [F]_{ad}\}$ **When $\{[F]_s + [F]_{ad}\} < [F]_i$**

$C_t = [F]_t$ = leached concentration at time 't'

$C_o - C_t = [F]_i - [F]_t$

= Leachable concentration remaining at time 't'

LR_{obs} = Leaching rate

3.2 Leaching Rate Profiles

Initial rate of leaching, LR_{obs} represents the rate of change in leachable concentration with time. LR_{obs} values are obtained from the initial slopes of the plots between $[F]_i$ and time as shown in Figure 1.1.

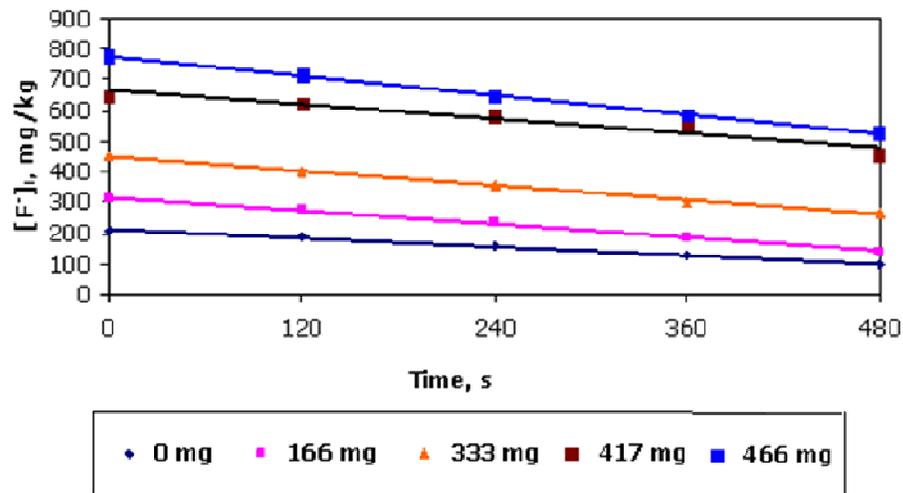


Fig 1.1: Initial leaching rate profiles for F^- leaching for added salt NaF at $30^\circ C$. Soil=30 g, $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$.

3.4 Dependence of LR_{obs} on [F]_i

On increasing [F]_i values, the LR_{obs} values seem to increase linearly (Figure 1.2).

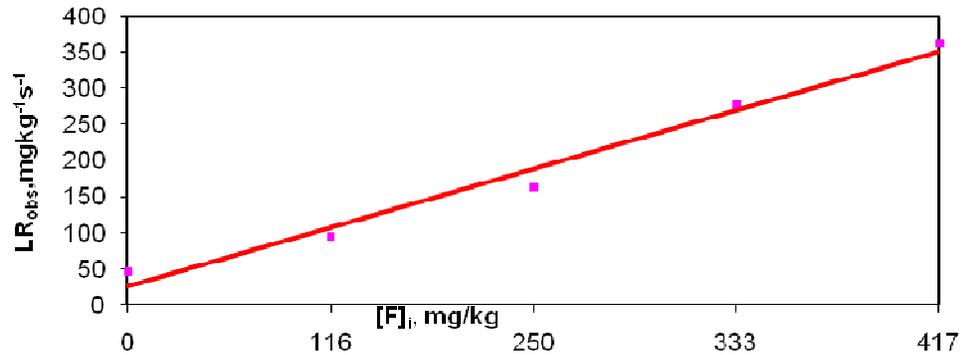


Fig. 1.2: Variation of LR_{obs} with [F]_i for F⁻ leaching during NaF addition at 30° C. Soil=30g, θ=0.315 cm³ cm⁻³.

To estimate fluoride leaching rates The fluoride leaching rates can be fitted in following rate law equation (5):

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

Where C is constant depending upon amount of naturally present leachable fluoride in the soil.

Table 1.2: The values of rate constant (k), order (n) and correlation parameters (r² and SEE) for F⁻ leaching during NaF addition.

Parameter	NaF
10 ⁻³ k	4.14
n	1
r ²	0.99
SEE	0.26
C	35

Unit of 'k' is sec⁻¹

From the Log-Log plots of [F]_i vs LR_{obs}, values of k and n are calculated as 4.14 X 10⁻³ sec⁻¹ and 1.0 respectively.

Our experimental soil is rich in water soluble fluoride (210 mg/kg), however all the adsorption site available for fluoride are not saturated, a portion of the further added fluoride is adsorbed in the column. An order of one with respect to [F]_i for both the salts 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. In some previous studies, a fractional order < 1.0 is obtained for Cl⁻ and SO₄²⁻ and >1.0 for phosphate leaching in clay loam soil of pH 8.2.

3.5 Effect of Temperature

An increase in [F]_i and LR_{obs} is observed with increase in temperature at fixed added concentration of NaF salt. From Arrhenius plot (Figure 1.3) i.e. log k Vs 1/T, the value of activation energy for fluoride releasing is determined. The activation energy is calculated to be 93.41 ± 0.80 kJmole⁻¹.

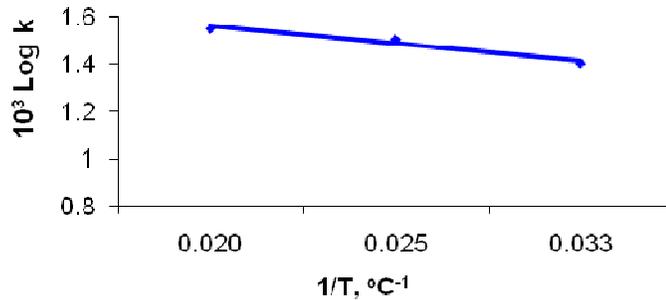


Fig 1.3: Arrhenius plot for the determination of activation energy of F⁻ leaching for NaF added salts. Soil = 30 g. Soil particle size = 500 ≥ r ≥ 250, θ = 0.315 cm³ cm⁻³.

An increase in temperature results in higher leaching rates giving 93.41 ± 0.80 kJmole⁻¹ values of activation energy indicating higher mass transfer due to increase in solubility rather than ion-exchange equilibrium involved in leaching specially in the present case.

At higher column soil temperature, increase can be assigned to increase in rate of solubility of salts which prevents the adsorption of ions on to soil reactive sites (Sardans, J. et al 2008).

3.6 Effect of hardness (Ca²⁺) of extractant

[F]_i and LR_{obs} are found to decrease with increase in Ca²⁺ level of extractant as shown in Figure 1.4.

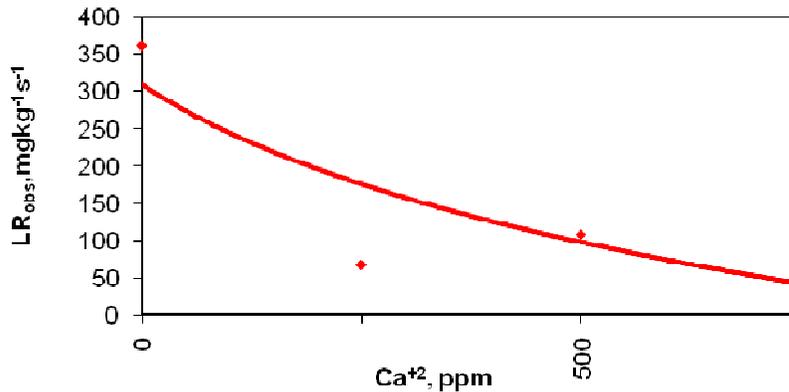


Fig 1.4: Change in LR_{obs} with increase in Ca²⁺ concentration of extractant for F⁻ leaching at different added salts at 30^o C. [F]_{ad} = 466 mg/kg for NaF, [F]_{ad} = 166 mg/kg Soil = 30 g.

The reason for decrease in [F]_i and LR_{obs} with rise in CaCO₃ content of percolating water may be due to possible precipitation of fluorite CaF₂ and fluorapatite [Ca₅(PO₄)₃F] in the column (Bar et al., 1989; Peek and Volk, 1985). Carbonates and bi carbonates are also reported to reduce the ionic fluoride from soil water (Cummings and McIvor, 1988).

3.7 Effect of Sodium Level of Extractant

To witness the role of Na ions present in irrigation water on leaching pattern of fluoride, Na level of extractant was varied detailed results are presented in Figure 1.5.

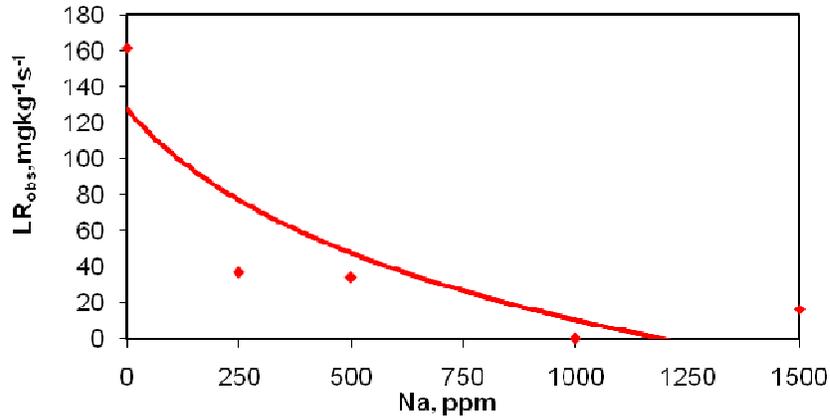


Fig 1.5: Change in LR_{obs} with Na concentration for F⁻ leaching for different concentration of sodium fluoride salts at 30^o C. NaF: [F]_{ad} = 333 mg/kg

It is surprising that an increase in Na levels in extractant water has decreased [F]_i, whereas several previous studies have positively correlated F⁻ (Gupta M.K. et al., 1999) with Na. It seems that in alkaline saline soils, sodium in extractant water has exchanged precipitated Ca²⁺ which subsequently is converted into insoluble CaF₂ lowering the soil solution F⁻ concentration. In an earlier F⁻ adsorption study also, when a sodic slit loam soil was irrigated with high NaCl, high F⁻ geothermal well water, CaF₂ was precipitated restricting the F⁻ leaching (Punia S.R. and Tallibudin, 1977).

3.8 Effect of Incubation time

The results of change in incubation time has shown no significant effect of time on total leachable fluoride. This does not exclude possibility of increased fluoride adsorption with time or with the firmness of the sink between soil and fluoride as observed by Barrow, N.J. and T.C. Shaw 1982, but it shows that prolonged contact between soil and fluoride will not affect the capacity of percolating water to extract fluoride at least for the studied soil. Evidences from literature also support our results as during acid ammonium oxalate extraction of fluoride, F⁻ recovery was unaffected by incubation time (Louis, B., and F. Josee. 2003)

time. However a study of fluoride mobility in entisol has shown decrease in diffusion mobility of F⁻ with rise in incubation period (Rai, K. et al 2000).

3.8 Effect of OH⁻ ions

From Table 1.2 it is evident that [F]_i and LR_{obs} are found to increase with the increase in pH levels of extractant. The order of increase in [F]_i and LR_{obs} is found NH₄OH > NaOH > KOH.

Table 1.2: Change in $[F]_t$, $[F]_i$ and $[F]_j$ with time for F^- leaching during NaF addition at different pH levels of the extractant at 30^o C. $[F]_{ad} = 166 \text{ mg/kg}$, Soil = 30 g, $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$.

Hydroxides	NaOH				KOH				NH ₄ OH			
	10.5		12.5		10.5		12.5		10.5		12.5	
Time	$[F]_t$	$[F]_i$	$[F]_t$	$[F]_i$	$[F]_t$	$[F]_i$	$[F]_t$	$[F]_i$	$[F]_t$	$[F]_i$	$[F]_t$	$[F]_i$
0	0	300	0	473	0	250	0	317	0	383	0	433
120	1	299	17	456	3	247	3	313	7	377	15	418
240	3	297	33	440	10	240	10	307	40	343	60	373
360	17	283	50	423	20	230	17	300	73	310	88	345
480	43	257	77	396	33	217	27	290	107	277	119	314
600	77	223	107	366	50	200	37	280	140	243	165	268
720	93	207	130	343	67	183	50	267	173	210	195	238
840	110	190	157	316	83	167	67	250	207	177	225	208
$[F]_i$	300		473		250		317		383		433	
$LR_{obs} \text{ mgkg}^{-1} \text{ s}^{-1}$	44.01		89.63		25.63		24.82		99.38		121.18	

$[F]_t$, $[F]_i$ and $[F]_j$ are in mg/kg

As the radii of F^- and OH^- ions are comparable, an exchange of OH^-F^- is inevitable which showed increased fluoride leaching with increase in OH^- concentrations. Surprisingly the cation attached to OH^- ion which affected F^- leaching significantly, the maximum being with NH_4OH and minimum with KOH . NH_4^+ ions which can carry at least 4 F^- ion through H—F bond (Alvi and Bell, 1998), result in highest $[F]_i$ and LR_{obs} value in our experiment. It seems that replacement of OH^- ion is more in case of $NaOH$ than KOH as the lattice energy of KOH is more because of which availability of free OH^- ions are less in KOH in comparison to $NaOH$.

Unlike other soluble ions, F^- is not leached much from naturally salinized salt affected soil rather it is redistributed within the soil profile. The adsorption of F^- to soil increases with decrease in soil pH in acidic soil while in most of the alkaline soil F^- is replaced by OH^- ion producing high leachable concentration of ionic fluoride (Perrot, K.W. et al 1976). Thus the leaching rate of F^- is always found higher in an alkaline soil. The maximum leaching is observed when NH_4OH is added in percolating water because of H-F bonding with NH_4^+ which can carry more number of F^- ions (at least 4) with single NH_4^+ ion resulting in highest $[F]_i$ and LR_{obs} values. It seems that replacement of OH^- ion is more in case of $NaOH$ than KOH as the lattice energy of KOH is more because of which availability of free OH^- ions are less in KOH in comparison to $NaOH$.

The maximum leaching occurs on adding NH_4OH and minimum with KOH . Some earlier studies on adsorption and desorption of F^- on soil of China interpreted as competing sorption of OH^- in soil solution replacing some F^- from surface of soil colloids resulting in increase in leaching of F^- . The leaching rate of F^- was found higher in alkaline soil than acidic. In some groundwater quality assessment studies F^- was positively correlated with pH (Gupta, M.K. et al. 1999)

3.9 Application to the Kinetic Models

To describe F^- leaching kinetics, several kinetic models were tried and it was observed that First order kinetic model (Jardine, P.M., and L.W. Zelogny .1986 and Sparks, D.L., and P.M. Jardine .1981) is found to be most suitable for leaching of fluoride for NaF salt (Figure 1.6). The concentration terms used in different equations are as follows:

$$[F]_i = C_0; [F]_t = C_t; [F]_l = [F]_i - [F]_t = C_0 - C_t \quad ; \quad \ln(C_0 - C_t) = a - bt$$

Kinetic models tried are as under:

Kinetic Model	Rate Equation
Zero order kinetic model	$C_0 - C_t = a - bt$
First Order Equation	$\ln(C_0 - C_t) = a - bt$
Second Order Equation	$1/C_t = a - bt$
Parabolic Diffusion	$C_t = a - bt^{1/2}$
Elovich Equation	$C_t = a - b \ln(t)$

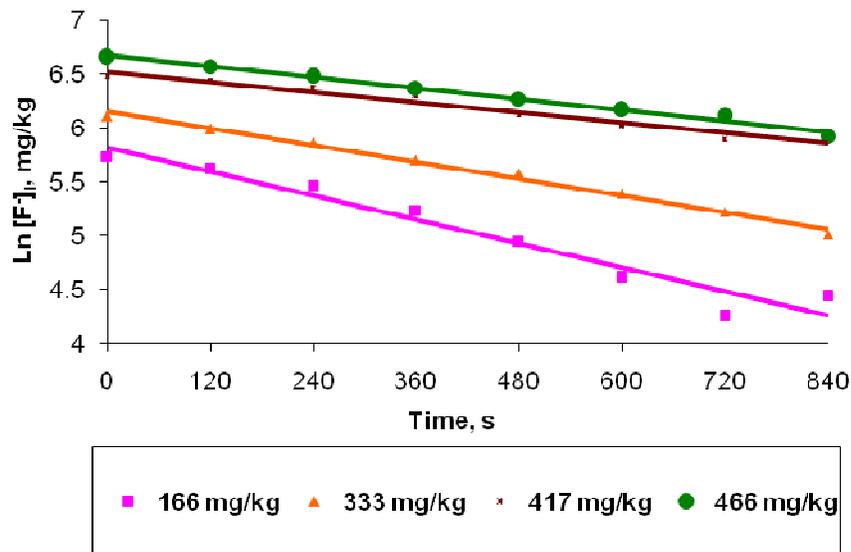


Fig 1.6 : First Order equation profile for F^- leaching during NaF addition at different $[F]_{ad}$ at $30^\circ C$. Soil = 30 g , $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$.

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 alkaline soil, if added salt is NaF. 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.

4.0 CONCLUSION

The present study throws light on the leaching behaviour of soluble ionic salt in saturated flow condition in alkaline soil and its migration to groundwater. Interesting results about the effects of various factors such as decrease in $[F]_i$ and LR_{obs} with increase in Na^+ and Ca^{2+} levels of the extractant and increase in the same with temperature and OH^- ion. These can be used for estimating leaching rate of F^- from contaminated soil of fluoride endemic areas and thus are of great significance for developing various mathematical models for salt transport processes in alkaline soil preferable in Sambhar region of Rajasthan and elsewhere in the world.

5.0 REFERENCES

1.	Agarwal, V., A.K.Vaish, and P. Vaish.1997. Groundwater quality on fluoride and fluorosis in Rajasthan. Curr. Sci. 73(9):743-64.
2.	Alvi, A. and R.M. Lynden Bell.1998. Displacement and distortion of the ammonium ion in rotational transition states in ammonium fluoride and ammonium chloride. J. Chem. Phys. 110(12):5861-5865.
3.	Apambire, W.B., D.R. Boyle, and F.A. Michael.1997. Geochemistry, genesis and health implication of fluoriferous groundwater in the upper region of Ghana. Environ. Geol. 33(1):13-24.
4.	Bar Yusef, B., I. Afik and R. Rosenberg.1989. Ecological studies, 74. Inorganic contaminants in the Vodase Zone. Springer Verlag , New York. 75-85.
5.	Barnard, W.R., and D.K. Nordstrom.1982. Fluoride In precipitation. II. Implication for the geochemical cycling of fluoride. Atmos Environ. 16(1):10-11.
6.	Barrow, N.J., and T.C. Shaw.1982. Effect of ionic strength and nature of the cation on the desorption of fluoride from soil. J. Soil Sci. 33:219-231.
7.	Cummings, C. and M. McIvor.1988. Fluoride-induced hyperkalemia: the role of Ca ²⁺ -dependent K ⁺ channels. Am. J. Emerg. Med. 6: 1-3.
8.	Ghiedyal, B.P., and R.P. Tripathi .1987. Salt Transport in Soil Physics . Wiley Eastern, 614 - 643.
9.	Groundwater Atlas of Rajasthan.1999. By State Remote Sensing Application Centre, Deptt. of Science and Technology, Govt. of Rajasthan, Jodhpur.
10.	Gupta, M.K., V. Singh, P. Rajwanshi, M. Agarwal, K. Rai, S. Srivastava and S. Das.1999. Groundwater quality assessment of tehsil Khergarh, Agra (India) with special reference to fluoride: Env. Monitoring and assessment , 59:275-285.
11.	http://www.fluoridealert.org .
12.	Jardine, P.M., and L.W. Zelogny .1986. Mono nuclear and polynuclear aluminium speciation through differential kinetic reactions. Soil. Sci. Soc. Am. J. 50:895 -900.
13.	Louis, B., and F. Josee.2003. Vadose Zone process and chemical transport. J. Environ. Qual. 32:662-673.
14.	Neal, C., C.J. Smith, J. Walls, P. Willingham, S. Hills, and M. Neal.1990. Comments on the hydrological regulation of the halogen elements in rainfall streamflow, throughfall and stream waters at an acidic forested area in mid-Wales Sci. Total Environ. 91:1-11.
15.	Ogwada, R.A., and D.L. Sparks.1986. Kinetics of ion exchange on clay minerals and soil. Evaluation of Methods. Soil Sci. Soc. Am. J. 50: 1158- 1162.
16.	Pavlatou, A., and N.A. Polyzopoulos.1988. The role of diffusion in the kinetics of phosphate desorption, the relevance of the Elovich Equation J. Soil. Sci. 39:425 - 436.
17.	Peek, D.C., and V.V. Volk.1985. Fluoride sorption and desorption in soils. Soil Sci Soc. Am. J. 49:583-586.
18.	Perrot, K.W., B.F.L. Smith and R.H.E. Inkson.1976. The reaction of fluoride with soil and soil minerals. J. Soil Sci. 27:58-67.
19.	Punia, S.R. and O. Tallibudin. 1977. Sodium calcium exchange equilibria in salt affected and normal soil. J. Soil. Sci. 28:276-288.
20.	Rai, K., M. Agarwal, S. Dass and R. Shrivastava.2000. Fluoride diffusive mobility in soil and some remedial measures to control its plant uptake. Current Sci. 79(9):1370-1373.

21.	Sardan, J., J. Penuelas, P. Prieto and M. Estiarta (2008), J. of Geo-physical Res. 113,11 pp.
22.	Saxena, S., U. Chandrawat, A. Rani. 2011. Leaching Kinetics of fluoride in sodic saline soils. J. Industrial Pollun. Control : 27(2) :127-132
23.	Sharma, B., S. Saxena, M. Vijay, A. Rani. 2009. Leaching mechanism of alkaline soils under Phosphate application: A Kinetic Approach. Environ. Sci. 4(5): 208-213
24.	Sparks, D.L., and P.M. Jardine .1981. Thermodynamics of potassium exchange in soil using a kinetic approach. Soil Sci. Soc. Am. J. 45:1094-1099.
25.	Wuyi, W., R.Li. J. Tan, K. Luo, L. Yang, H.Li. and Y. Li. 2002. Adsorption and leaching of fluoride in soils of China. Fluoride 35 (2):122-129.

REVIEWER NO.1

PART 2: Review Comments

	Reviewer's comment	Author's comment
Compulsory REVISION comments	<ol style="list-style-type: none">1. Sufficient details of the methods/process should be provided so that another researcher is able to reproduce the experiments described in the manuscript. It is better to provide a schematic drawing of the experimental apparatus used for the kinetic research.2. In line 32-33, the conclusion is related to the PO_4^{3-}, NO_3^- and NO_2^- ions, however, there seems to be no narrative or corresponding research in the body of the manuscript.3. What about the repetition and repeatability error of the experimental data? If possible, please give more kinetic data in the manuscript to support the results, if possible.	<ol style="list-style-type: none">1. Incorporated in the text with schematic diagram.2. The effects of PO_4^{3-}, NO_3^- and NO_2^- ions is part of another fluoride salt & by mistake it was included in the conclusion part. Now, it has been removed from conclusion.3. The kinetic data in the form of coefficient of R^2, slope & SEE for studied kinetic model is enclosed in the paper at Table No.
Minor REVISION comments	<ol style="list-style-type: none">1. Some sentences are too long to understand, for instance, the sentence of line 31 to 37 is very long and difficult to understand.2. There are some typing errors in the manuscript such as Line 160 and line 227.3. Line 208-209, more explanation may be needed.4. Line 229, the figure caption is wrong. I think, it is not "different added salts" but "different concentration of sodium".5. Line 248-249, is the acid ammonium oxalate extraction of fluoride similar to the case studied in the manuscript?6. Line 273-274, the reason may not be enough for the explanation of the maximum leaching of fluoride when the cation of NH_4^+ attached to OH^-. Similar is that in line 286-288.	<ol style="list-style-type: none">1. Necessary modifications have been incorporated in the revised paper.2. Typing errors have been corrected.3. Explanation with reference is enclosed in paper4. Corrected5. Yes
Optional/General comments	The leaching kinetics of fluoride ion for alkaline soil is very important. The obtained kinetic model may be used for estimating leaching rate of F^- from contaminated soil of fluoride areas and thus is of great significance for developing various mathematical models for salt transport processes in alkaline soil preferable in Sambhar region of Rajasthan.	

PART 8: Reviewer Details:

Name:	Qiusheng ZHOU
Department, University & Country	Central South University, P. R. China

Reviewer 2**PART 2: Review Comments**

	Reviewer's comment	Author's comment
<u>Compulsory REVISION</u> comments		
<u>Minor REVISION</u> comments	<p>1). At page 5, line 188 – 194, the whole paragraph needs to be explained. Why all the adsorption sites available are not saturated?</p> <p>2). What is the role and significance of the values of k & n calculated using Eq. (5)?</p> <p>3). Authors need to explain the significance of n=1, n >1 and n < 1 regarding the adsorption and/or leaching phenomena of the concerned ions.</p>	<p>1. If all available sites are saturated, the added concentration of fluoride salt will totally leach out and not remain in the form of $[F^-]_{\text{complex}}$.</p> <p>2. The 'k' represent the rate constant & 'n' represent order of reaction. Detailed table has been incorporated in paper.</p> <p>3. The mathematical equation represents the leaching phenomenon. n=1 represents uniform leaching rate while n > 1 represents desorption and <1 represent adsorption.</p>
<u>Optional/General</u> comments	Authors should revise it in accordance with the format of the Journal, where it is required.	

PART 8: Reviewer Details:

Name:	Anonymous Reviewer:- Reviewer does not want to disclose his/her identity
Department, University & Country	

REVIEWER NO 3: **PART 2: Review Comments**

	Reviewer's comment	Author's comment
COMPULSORY REVISION comments	<p>L. 90 and others: Ca^{2+} instead of Ca^{+2} etc. L.90: "present naturally hydrolyzed" is unclear L.96: Ca^+ is incorrect L.131-134: the pre-sorption of NaF was done at static or dynamic conditions? Was the uniformity of adsorption verified? L.141-158: I am rather confused by nomenclature and fluorides "balance". Where did the value of 210 mg/kg (l.152) come from? What is the difference between this value and total leachable content (l.154)? Is C_o sum of F_s and F_{ad}? From l.156 and l.158 it follows that $F_{complex} = -F_{extra}$ which seems to be strange. I highly recommend to clearly state which quantities were really measured and which were calculated from laboratory data and to add units into the nomenclature list. L.160: Should F_i be $C_o - C_i$? L.183: Eq. (5) implies zero leaching rate at zero F_i which contradicts to data given both in Fig. 1.1 and Fig. 1.2. L.311: I do not understand which are the five different kinetic models. Was the model discrimination done in the present work? There are no details on this analysis and no model parameters are reported.</p>	<p>L90: Corrected. L90: Clarifications included in paper. L96: Corrected L131-134: Static . Yes. L141-158: 210 mm/kg of fluoride is naturally present in soil of Sambhar region of Rajasthan India and estimated in blank soil column. Total leachable content is the sum of amount of naturally present fluoride and added fluoride in the form of sodium salts. Yes. The equations to be used are having boundary conditions which are now incorporated in paper. L160: Typographical Corrections have been made. L 183: Again, the represented equation have boundary conditions which are mentioned in paper. L 311: All the kinetic models used are now mathematically represented in the paper.</p>
Minor REVISION comments	<p>L. 76-77: consistent use of capital letters in mineral names L. 93 (and 9): should "by loading NaF" mean that first NaF was loaded and then leaching was studied? Please clarify. L.162 v. l.166: LR_{obs} is leaching rate or just initial leaching rate? L.169: Please place 417 mg before 466 mg Figs. 1.4, 1.5: I suggest to remove the curve which does not fit data and does not aid eyes. Figs. 1.1 and 1.6 are very similar and could be merged into one figure.</p>	<p>L 76-77: Corrected. L93& 9 : Yes L162 -166: From the initial rate plots, LR_{obs} have been calculated L169: Corrected Fig 1.4, 1.5: On doing so r^2 & SEE will not depict true picture & it will be difficult to select appropriate kinetic model. Figs 1.1 and 1.6: Scales are different</p>
Optional/General comments	<p>What about statistical characteristics of experimental data? E.g. number of replicates, standard deviations etc. Despite of some critical remarks I like this work and encourage authors to go on improving the text. Generally, the problem and methodology are clearly stated and adequately selected.</p>	<p>Enclosed in the paper</p>

PART 8: Reviewer Details:

Name:	Miloslav Pekař
Department, University & Country	Faculty of Chemistry, Brno University of Technology, Czech Republic

REVIEWER NO 4

PART 2: Review Comments

	Reviewer's comment	Author's comment
<p>COMPULSORY REVISION comments Abstract: Rephrasing of last part is needed. Conclusion needs modification and addition of more information.</p>	<p>Abstract: In the conclusion part, the role of PO₄ and NO₂ fertilizer ions is given, but it is not discussed in the text. Conclusion: There is no reference of fluoride ion in the first sentence.</p>	<p><i>Necessary corrections have been made in the paper.</i></p>
<p>Minor REVISION comments Citation of references in the text needs improvement.</p>	<p>Following are minor mistakes</p> <ol style="list-style-type: none"> 1. Line 59: Replace Et by et 2. Line 60: Full stop is far 2002) . by 2002). 3. Line 72: Reference is without initial name 4. Line 75: Replace reaches by contaminated 5. Line 76: Replace cryolite by Cryolite 6. Line 84: Replace full stop after Rajasthan 7. Line 102: References are without initial names 8. Line227: Replace Detailed by detailed 9. Line 234: Reference is without initial name 10. Line 239: Reference is without initial name 11. Line 246: Reference is without initial name 12. Lines 249-251: correct the sentence. 13. Line 252: Reference is without initial name 14. Line 274: Reference is without initial name 15. Line 285: Kindly check "ion³⁹" 16. Line 361: Remove b from 1986 	<ol style="list-style-type: none"> 1. Complied with 2. Complied with 3. Complied with 4. Complied with 5. Complied with 6. Complied with 7. Complied with 8. Complied with 9. Complied with 10. Complied with 11. Complied with 12. Complied with 13. Complied with 14. Complied with 15. Complied with 16. Complied with
<p>Optional/General comments <i>Title shows the work is related to soils of India, but they used only one soil sample of Rajasthan, India.</i></p>	<p>Line 2: Soil of Rajasthan, India</p>	<p>Every where it has been mentioned that soli is collected form Sambhar region of Rajasthan, India.</p>

PART 8: Reviewer Details:

Name:	Dr. Shahid Naseem
Department, University & Country	Department of Geology, University of Karachi, Karachi, Pakistan