

LEACHING KINETICS OF AMMONIUM FLUORIDE IN ALKALINE SOIL USING PERCOLATION

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Abstract- Aims: The present research study describes leaching kinetics of F^- by loading NH_4F on undisturbed vertical soil column of the soil collected from Sambhar region of 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 has been studied by determining the fluoride concentrations in the leachate with time. Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB.

Results: Initial leaching rate has been calculated and linear power form equation has been derived. Results are fitted to various kinetic models. Results confirm the increase in leaching due to bonding of free fluoride with NH_4^+ ions through H-F bonds.

Conclusion: The fact that NH_4F adopts the structure with an increased degree of hydrogen bonding between NH_4^+ and F^- ions., The leaching of fluoride will be more in presence of NH_4^+ ions. On the basis of the results of this study, this can be concluded that in an agriculture field, if the added fertilizers rich in ammonium ions and fluoride is present simultaneously, the leaching of F^- will be more.

Index Terms- First Order Kinetic Model, Fluoride, Ion Exchange, Leaching Kinetics, TISAB, Pore Volume, Saturated Flow, Alkaline Soil

I. INTRODUCTION

Fluoride ions find their way in the agriculture field soil from diverse sources i.e. weathering of rocks, use of phosphatic fertilizers, sewerage sludge, pesticides etc [1]. Infact phosphatic fertilizers are the major source of fluoride contamination of agricultural soil as they are manufactured from rock phosphate which generally contain around 3.5% Fluorine[2].

In an earlier report on fluoride, an average annual addition of fluoride to soil through fertilizers has been estimated to be 1.1 kg/ha[3].

In fluoride rich soil, application of ammonium containing fertilizers or of urea which can quickly hydrolyze to ammonia or can produce NH_4^+ ions can result in formation of NH_4F up to a significant level[4]. Loss of ammonium ions through irrigation water from agricultural field soil is most serious. With rise in the atmospheric fluoride concentration together with atmospheric ammonia, possibility of wet and dry precipitation of fluoride as NH_4F increases. Loss of ammonium ions through irrigation water from agricultural field soil is most serious, if the ideal soil

temperature, soil pH and moisture conditions are not available for nitrification specially where adequate ammonium ions are available specially in excess to the needs to the crop plant[5].

NH_4F is hazardous in case of eye and skin contact. Over exposure can result even in death. Inflammation of the eye is characterized by redness, watering and itching. Skin inflammation is characterized by itching, scaling, reddening or occasionally blistering.

By looking deep into the toxic effect of ammonium fluoride. the leaching kinetics of NH_4F in fluoride endemic saline soil (pH 8.2) has been investigated in undisturbed vertical column under saturated flow by further adding known concentration of ammonium fluoride in soluble form.

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. MATERIALS & METHOD

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 as under:

pH = 8.2; ECe = 4 dsm^{-1} ; OC = 1.17 %;
 Na^+ = 3840 meq/l ; Ca^{+2} = 5 meq/l; Mg^{+2} = 5 meq/l;
Sand = 21.9%; Silt = 10.7%; Clay = 6.8 %
Colour = Light Grey; Bulk Density = 1.48 gcm^{-3} ;
Type = Loamy Sand

The leaching kinetics of NH_4F has been studied by determining the fluoride concentrations in the leachate with time as reported earlier[6]. Fluoride was estimated using Fluoride Ion Selective Electrode with TISAB[7].

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 $0.315 cm^3 cm^{-3}$. 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 $\text{cm}^3\text{cm}^{-3}$

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 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 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. $[F^-]_{complex} = \{[F^-]_s + [F^-]_{ad}\} - [F^-]_i$

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

$$= [F^-]_i - \{[F^-]_s + [F^-]_{ad}\}$$

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

$C_o - C_t = [F^-]_I - [F^-]_t$

= Leachable concentration remaining at time 't'

LR_{obs} = Leaching rate

$[NH_4F]_{add} = [F^-]_{ad}$ = F^- concentration introduced in the soil column as soluble NH_4F .

3.2 Total Leachable Fluoride, $[F^-]_i$ and Extra Fluoride, $[F^-]_{extra}$

The values of total leachable fluoride $[F^-]_i$ and extra fluoride $[F^-]_{extra}$ for NH_4F are given in Table 1.

III. RESULT AND DISCUSSIONS

3.1 Nomenclature

**Table 1: Values of $[F^-]_i$ and $[F^-]_{extra}$ at different F^- added for leaching of NH_4F at $30^\circ C$.
Soil = 30g, $\theta = 0.315 \text{ cm}^3\text{cm}^{-3}$.**

$[F^-]_{ad}$, mg/kg	$[F^-]_i$, mg/kg	$[F^-]_{extra}$, mg/kg
0	210	-
116	435	109
166	520	144
233	610	167
300	836	326
416	976	350

An increase in the concentration of NH_4F or $[F^-]_{ad}$ increased $[F^-]_i$ and LR_{obs} when deionized water is used for percolation. This increase is attributed not only to an increase in free F^- level of the soil but also to an increase in NH_4^+ ion concentration which significantly increased F^- leaching by converting fixed fluoride into leachable form and is given as $[F^-]_{extra}$. $[F^-]_{extra}$ is determined using equation 2:

$$[F^-]_{extra} = [F^-]_I - \{[F^-]_{ad} + [F^-]_s\} \quad (2)$$

$[F^-]_{extra}$ is found to depend largely on concentration of the NH_4 ion added as well as exchangeable cations present naturally in the soil. Thus $[F^-]_{extra}$ can also be represented as given in equation 3:

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

For monovalent salt $[NH_4^+] = [F^-]_{ad}$, thus equation (3) can be written as equation (4):

$$[F^-]_{extra} = a \times [F^-]_{ad} + b \quad (4)$$

A plot of $[F^-]_{ad}$ vs $[F^-]_{extra}$ is given in Figure1. The values of 'a' and 'b' are determined from the Figure 1 and reported as 0.88 and 420.88 mg/kg respectively.

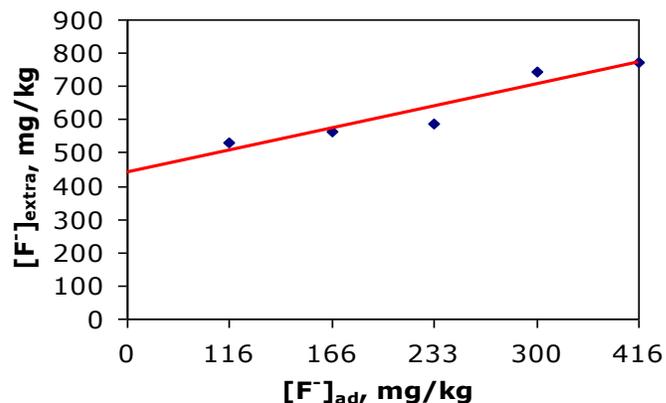


Fig 1. Variation of $[F^-]_{extra}$ with $[F^-]_{ad}$ for leaching of NH_4F at $30^\circ C$. Soil = 30g, $\theta = 0.315 \text{ cm}^3\text{cm}^{-3}$.

In the sequential calculations, the total leachable content has been taken to be equal to the leachable content present initially for the determination of initial leaching rates.

It is assumed that increase in $[F^-]_i$ is due to high affinity of fluoride for NH_4^+ ion. It seems that NH_4^+ ion does not remain in isolation rather it associates atleast four F^- through all four H atoms present in it. This high association of F^- with NH_4^+ ion resulted in moderate increase in fluoride leaching. On comparing the values of $[F^-]_i$ and LR_{obs} at fixed $[F^-]_{ad}$ for different added salts, the order of increase in $[F^-]_i$ and LR_{obs} are found $NH_4F > NaF > KF > MgF_2 > AlF_3$. It is confirmed that cation NH_4^+ assist leaching due to H-F bonding whereas Al^{+3} stops due to complexation of ionic F^- as AlF_3 . Mg^{+2} ions whereas complex F^- as MgF_2 , Na-Mg exchange in soil increase free Na in soil water which assist in F^- leaching.

Initial rate of leaching, LR_{obs} and F^-_i remain unaffected by the change in incubation time which confirms the fast adsorption & desorption of fluoride in experimental soil.

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

The dependence of LR_{obs} on $[F^-]_i$ is shown in Figure 2. The fluoride leaching follows first order path and rates can be fitted to the following rate law equation (6):

$$LR_{obs} = k [F^-]_i^n + C \tag{6}$$

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

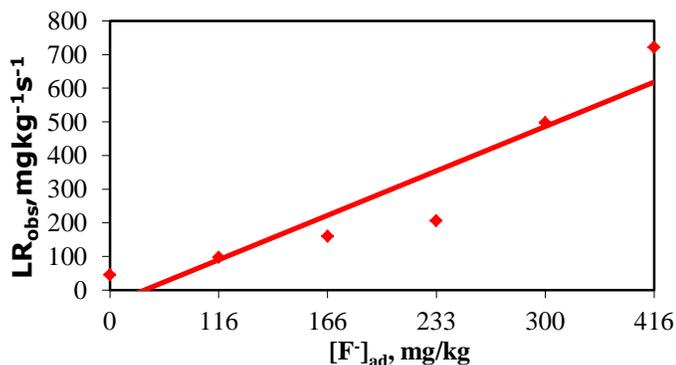


Fig. 2: Variation of LR_{obs} with added concentration for NH_4F at $30^\circ C$. Soil = 30g, $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$.

From the log-log plots of equation (6), values of k and n are calculated to be 4.067 and 1.0 respectively. The unit of 'k' is sec^{-1} .

3.3 Application to the Kinetic models

While applying various integrated equations of different kinetic models, the concentration of leachable fluoride was assumed to be maximum initially i.e. at $t=0$. The concentration terms used in different equations are as follows:

$$[F^-]_i = C_0; [F^-]_t = C_t; [F^-]_t = [F^-]_i - [F^-]_t = C_0 - C_t$$

All the models were tested with least square regression analysis. On the basis of high r^2 and low SEE, first order model was found suited to represent leaching in our experimental conditions.

To describe F^- leaching kinetics, several kinetic models were tried and it was observed that First order kinetic model[8,9] is found to be most suitable for leaching of fluoride for NaF salt (Fig. 1.6). The concentration terms used in different equations are as follows:

$$[F^-]_i = C_0; [F^-]_t = C_t; [F^-]_t = [F^-]_i - [F^-]_t = C_0 - C_t; \text{Ln}(C_0 - C_t) = a - bt$$

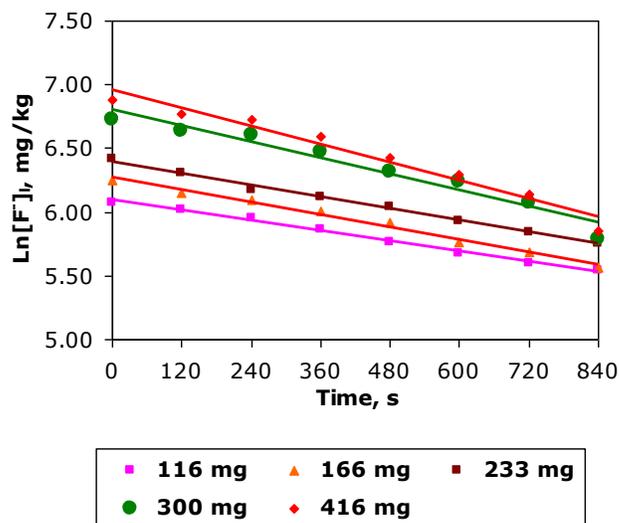


Fig 4.9: First Order equation profile for NH_4F leaching at different $[F^-]$ at $30^\circ C$. Soil = 30 g, $\theta = 0.315 \text{ cm}^3 \text{ cm}^{-3}$.

Kinetic models tried are as under:

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

IV. CONCLUSION

The fact that NH_4F adopts the structure with an increased degree of hydrogen bonding between NH_4^+ and F^- ions including the low NH stretching frequency and the high activation energy

for rotation[10], the leaching of fluoride will be more in presence of NH_4^+ ions. On the basis of the results of this study, this can be concluded that in an agriculture field, if the added fertilizers rich in ammonium ions and fluoride is present simultaneously, the leaching of F^- will be more.

The method adopted for estimating F⁻ leaching during this work can effectively estimate F⁻ leaching rates from soil of fluoride endemic area and can develop control strategy to stop leaching by changing the quality of irrigation water and soil thermal properties. It is suggested that for developing ion leaching models besides soil physico-chemical characteristics, thermal properties should also be taken into account. Irrigation water quality should also be monitored regularly to check fluoride leaching from agriculture fields rich in nitrogenous fertilizers.

REFERENCES

- [1] Oelschalager, W.. Fluoride uptake in soil and its depletion. *Fluoride*.**4**:80-84. (1971)
- [2] Hart, E.B., P.H. Phillips and G. Boshstedt.. Relationship of soil fertilization with superphosphates and rock phosphate to the fluorine content of plants and drainage waters. *Am J. Public Health*.**24**:936-940. (1934)
- [3] Mclaughlin, M.J., K.G. Tiller, R. Naidu and D.P. Stevens.. Review: The behaviour and environmental impact of contaminants in fertilizers. *Aust J. Soil Res.* 34:1-54. (1996)
- [4] Nyle C. In: The nature and properties of soils. Brady Macmillan Publishing Company New York.
- [5] Dick, W.A.. Organic carbon, nitrogen and phosphorus concentrations and pH in soil profile as affected by soil tillage. *Soil Sci. Soc. Amer. J.* **47**: 102-107. (1983)
- [6] Saxena, S., U. Chandrawat, A. Rani.. Leaching Kinetics of fluoride in sodic saline soils. *J. Industrial Pollun. Control* : **27(2)** :127-132 (2011)
- [7] Rai, K., M. Agarwal, S. Dass and R. Shrivastava. Fluoride diffusive mobility in soil and some remedial measures to control its plant uptake. *Current Sci.* **79(9)**:1370-1373.(2000)
- [8] Jardine, P.M., and L.W. Zelogny. Mono nuclear and polynuclear aluminium speciation through differential kinetic reactions. *Soil. Sci. Soc. Am. J.* 1986; 50:895 -900.
- [9] Sparks, D.L., and P.M. Jardine. Thermodynamics of potassium exchange in soil using a kinetic approach. *Soil Sci. Soc. Am. J.* 1981; 45:1094-1099.
- [10] Alvi, A. and R.M. Lynden Bell. Displacement and distortion of the ammonium ion in rotational transition states in ammonium fluoride and ammonium chloride. *J. Chem. Phys.* 110(12):5861-5865(1998).

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