

## FLUORIDE RETARDATION FROM QUARTZ SAND-PACKED COLUMN TESTS

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### ABSTRACT

Inasmuch as both low and high concentrations of F<sup>-</sup> in groundwater have different detrimental effects on human health (increased dental caries, and mottled enamel or even severe structural bone deformations, respectively), many efforts have focused on the movement of such anion in aqueous systems. It is so because water drinking is the main intake of F<sup>-</sup> by humans. This paper presents the results of seven dynamic experiments in which solutions of varying [F<sup>-</sup>], pH, and flow velocities circulated through columns packed with clean quartz sand. The breakthrough data were analyzed by means of a computer code adapted to the estimation of equilibrium and non-equilibrium solute transport parameters from miscible displacement experiments in a steady-state, uniform flow field using a pulse-type or continuous source. It was found that larger retardation factors (R) are associated with low pH, low [F<sup>-</sup>] in the feed solutions, and larger flow velocities. Such results appear to be related to the form of the F species, the rather weak bond between the adsorbate and the quartz sand, and stronger anion repulsion at low pore velocities. The estimated values for R vary between 1,22 and 1,50, whereas the distribution coefficients were in the range of 0,1 to 0,05 L kg<sup>-1</sup>. It should be said that the breakthrough curves display hysteresis, leading to a desorption behavior that proceeds faster than the adsorption process.

**Keywords:** column experiments, F<sup>-</sup> adsorption/desorption, retardation

### RESUMEN

Puesto que tanto valores bajos como altos de F<sup>-</sup> en las aguas subterráneas tienen efectos adversos en la salud de los humanos (mayor cantidad de caries, y manchas del esmalte dental e incluso deformaciones óseas, respectivamente), han sido muchos los esfuerzos destinados a dilucidar el movimiento de especies fluoradas en ambientes acuosos. Ello es así porque el consumo de agua por parte de seres humanos representa la mayor fuente de ingreso de F<sup>-</sup>. Este trabajo presenta los resultados de siete experimentos dinámicos en los que soluciones de diferentes [F<sup>-</sup>], pH y velocidades de flujo percolaron a través de columnas empacadas con arena cuarzosa. Los datos de la curva de salida fueron analizados con un programa que permite la estimación de parámetros del transporte de solutos en condiciones de equilibrio o no equilibrio a partir de experimentos de columnas, en un campo de flujo homogéneo y en estado estacionario, creado por un impulso acotado o continuo del trazador de interés. Se halló que los mayores valores del factor de retardo (R) se asociaron a bajos valores de pH, bajas concentraciones de F<sup>-</sup> de las soluciones de inicio, y mayores velocidades de flujo. Los resultados se relacionaron con la forma de las especies de F, el débil enlace entre la especie adsorbida y la superficie de los granos de la arena cuarzosa, y la mayor repulsión aniónica a bajas velocidades porales. Los valores estimados de R variaron entre

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1,22 y 1,50, en tanto que los coeficientes de distribución estuvieron en el rango de 0,1 a 0,05 L kg<sup>-1</sup>. Debe indicarse que las curvas de salida muestran cierto efecto de histéresis, que hace que el fenómeno de desorción se produzca más rápidamente que el de adsorción.

**Palabras clave:** experimentos de columna, adsorción/desorción de F<sup>-</sup>, retardo

## INTRODUCTION

It has been known for a long time that the fluorine (F) content in water supplies and diets has a profound effect in the development of human bones and teeth. The intake of F is mainly determined by the concentration of fluoride ions (F<sup>-</sup>), the most conspicuous fluorine-carrying dissolved species, in the local water supply. One important fact is that both low and high concentrations of F<sup>-</sup> may affect human health. Indeed, F<sup>-</sup> acts as an inhibitor of the bacterial enzymes which, in turn, produce the acid that initiate the enamel caries (Rahamatulla, 1977). Hodge and Smith (1965) show that the absence of F<sup>-</sup> in drinking water or its presence in low concentrations (below 0,5 mg L<sup>-1</sup>) increases remarkably the number of dental caries in children. Gómez Artola et al. (1983) found that the low F<sup>-</sup> content in public drinking water explains the epidemic dental caries in Madrid, Spain. Fabiani et al. (1995) demonstrated that water consumption with an average [F<sup>-</sup>] of 1,54 mg L<sup>-1</sup> reduces notably the risk of osseous fractures, with a considerable saving of public money that can be invested in other sanitary treatments, and that offers a valid alternative to the conventional treatment of the osteoporosis disease.

On the other hand, the ingestion of excess F<sup>-</sup> (1-4 mg L<sup>-1</sup>) is responsible for the disease known as fluorosis (mottled enamel), characterized by a brownish-yellow discoloration of teeth (Hodge and Smith, 1965). Waters containing high F<sup>-</sup> (above 4-5 mg L<sup>-1</sup>), if consumed for a long time, can produce severe structural deformations of human bones (Krishnamachari, 1977).

Assuming that most of water supplies rely on groundwater resources, and given the limitations pointed out above, the purpose of this paper is to present and discuss dynamic laboratory experiments data where solutions of varying [F<sup>-</sup>], pH, and *v* (mean pore velocity) percolated columns packed with clean quartz sand. The final goals were to observe the adsorption-desorption behavior, and to estimate the retardation factor, *R* (i.e., a dimensionless quantity that indicates whether the solute travels with the same velocity of the water).

## MATERIALS AND METHODS

### Quartz sand preparation

To eliminate impurities, the quartz sand samples, commercially known as bond sand, were boiled in 10% HCl for ten minutes and then washed with excess distilled water until the pH of the leachate equalled that of the distilled water. The samples were then oven-dried at 105 °C and kept in close containers.

### [F<sup>-</sup>] and pH measurements

The F<sup>-</sup> concentrations were measured with a Fisher Accumet pH/mV (model 620) meter and a specific electrode (Orion, model 94-09). Before measuring a given set of samples, fresh solutions of known [F<sup>-</sup>] were prepared to obtain the calibration curve, and a recheck of such a curve was done between samples measurements, following the guidelines given by Orion Research Inc. (1973) and by the U.S. Environmental Protection Agency (1979). Both samples and standards were mixed in proper amounts with TISAB, a commercially available solution designed to partially buffer the pH between 5 and 6, and to provide a high total ion strength background that swaps out

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variations in total ion strength between samples (Orion Research Inc., 1973). For the pH measurements, the pH meter mentioned above was used with a standard glass-combination electrode, which was calibrated against commercial buffer solutions of known pH. All [F<sup>-</sup>] and pH readings were taken at 23 ± 1 °C.

#### **Column preparation**

A plexi-glass column was packed with the quartz sand above mentioned. Because of the many precautions involved in the packing tasks and the tests needed before launching the experiments, the reader is referred to Usunoff (1993) for further details. Suffice to say that the following data were measured/obtained: Column length: 30,48 cm, Column internal diameter: 3,15 cm, Mass of quartz sand in column: 369,5 g.  $\theta$  (porosity): 39% (estimated at packing time)

#### **Dimensionless variables**

$C_i/C_0$  (relative concentration): ratio between the outlet concentration at time  $i$  and the input concentration of tracer ( $C_0$ ),  $T$  (pore volume or PV) =  $v t / L$ , where  $v$  is the mean pore velocity ( $L T^{-1}$ ),  $t$  is the time for  $C/C_0 = 0,5$ , and  $L$  is the column length

#### **Experimental mechanics**

The flow, which took place from bottom to top, was driven by a peristaltic pump connected through a two-way valve to two containers with fluids at the same pH (one carrying the F<sup>-</sup> solution, and the other distilled water).

Typically, a run proceeded as follows: distilled water was circulated until the effluent pH stabilized, time at which the two-way valve was switched and the circulation of the tracer solution (F<sup>-</sup>) started. Samples of the effluent were taken until their [F<sup>-</sup>] was about the same as the input [F<sup>-</sup>]. Then, the double-position valve was switched to allow the entrance of the pH-adjusted distilled water. Sampling continued until the effluent [F<sup>-</sup>] was negligible.

Such experiments yielded data to construct the BTC (breakthrough curve).

#### **Breakthrough curve data handling**

The adsorption-desorption data were the input of the computer program CFITIM (van Genuchten, 1981), which was later included as one of the options of the more robust set of programs STANMOD (Simunek et al., 1999).

CFITIM is a program for estimation of equilibrium and non-equilibrium solute transport parameters from miscible displacement experiments in a steady-state, uniform flow field using a pulse-type or continuous source. Such estimations use a non-linear, least-squares curve fitting procedure.

If the relationship between the solute adsorbed and its concentration in solution can be described by a linear isotherm, the one-dimensional convective-dispersive equation of solute transport in saturated porous media can be written as:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

where  $R$  is the retardation factor (dimensionless),  $C$  is the solute concentration ( $ML^{-3}$ ),  $t$  is the time ( $T$ ),  $D$  is the longitudinal dispersion coefficient ( $L^2T^{-1}$ ),  $x$  is the space ( $L$ ), and  $v$  is the pore velocity ( $LT^{-1}$ ). The retardation factor  $R$  is given by (Freeze and Cherry, 1979):

$$R = 1 + \rho_b K_d / \theta \quad (2)$$

where  $\rho_b$  is the bulk mass density ( $ML^{-3}$ ), and  $K_d$  is the distribution or partition coefficient ( $L^3M^{-1}$ ).

One of the advantages of using CFITIM is that it estimates  $R$ , which can be plugged directly into equation 1. Moreover, given that values of  $\rho_b$  and  $\theta$  are available,  $K_d$  can be calculated. Notice that if  $R = 1$ , the solute travels with the same velocity as the carrier

fluid, whereas if  $R > 1$ , the solute interacts with the solid, and its movement is said to be retarded with respect to the bulk flow.

## RESULTS

Seven runs were carried out, numbered 1 to 7, in which the  $[F^-]$  and the pH of the input solutions were varied, as well as the flow velocity. Such values are shown in Table 1. As for the breakthrough data (measured and fitted), their graphical display is shown in Figures 1 (1through 7).

Runs 1, 2, and 3 were designed to assess the relationship between  $F^-$  adsorption and pH. Runs 4, 5, and 6 were to test the degree of  $F^-$  adsorption as the  $[F^-]$  in the feed solutions was varied. Finally, runs 1, 4, and 7 were intended to reveal the influence of the mean pore velocity in the adsorption phenomenon.

## DISCUSSION OF RESULTS

**Comments on the retardation factor values** As presented in the Material and Methods section of this paper, the estimation of the retardation factor  $R$  made use of the fitting capabilities of the program CFITIM (van Genuchten, 1981) to BTC data. Although it is a well-known program developed by a notorious scientist, the reader may like to have an independent check on how trustable those values are. Bovin (2008) indicated that when

the BTC data are plotted in the conventional way of  $C/C_0$  (relative concentration) vs. dimensionless time  $T$  (pore volume), the  $T$  value on the x-axis is equal to  $R$  for  $C/C_0 = 0,5$ . By looking at Figure 1 (1-7) one may conclude that the so-estimated values for  $R$  resemble quite well the fitted values shown in Table 1, which reinforces the suitability of Bovin's rule of thumb.

**$[F^-]$  and flow velocity (almost) constant, pH varied** Taking the retardation factor  $R$  as the diagnostic variable,  $R$  is seen to increase as the pH of the input solutions decreases. Notice, also, the slight increment of the effluent pH. That is to say, low pH values would enhance the  $F^-$  adsorption on the quartz sand particles. Such observations may be related to at least two factors:

(1) The zero point charge of quartz, for which Stumm and Morgan (1981) have given a value of 2. Indeed, as the pH increases above 2, the surface of quartz particles becomes negatively charged, with a corresponding decrease in anion sorption.

(2) The fluorine complexation as the pH is lowered. At pHs below neutrality and in the absence of cations such as  $Al^{3+}$  and  $Fe^{3+}$ , the  $F^-$  species able to be present are  $HF^0$ ,  $HF_2^-$ , and  $F^-$  (Hem, 1968; Roberson and Barnes, 1978). The concentrations of  $HF^0$  and  $HF_2^-$  (at 25 °C) can be calculated from (Broene and De Vries, 1947):

$$[HF^0] = [H^+] [F^-] 10^{3,17}, \text{ and } [HF_2^-] = [H^+] [F^-]^2 10^{3,76}$$

Hence, unless the pH is extremely low and the total  $[F^-]$  is very high, the amount of  $HF_2^-$  in solution can be neglected. Of importance, however, are  $HF^0$  and  $F^-$ , whose percentages for runs 1, 2, and 3 were as follows:

Run 1: almost all added  $F^-$  is in the  $F^-$  form

Run 2:  $[HF^0] H^+$  93% of total  $F^-$ , and  $[F^-] H^+$  7% of total  $F^-$

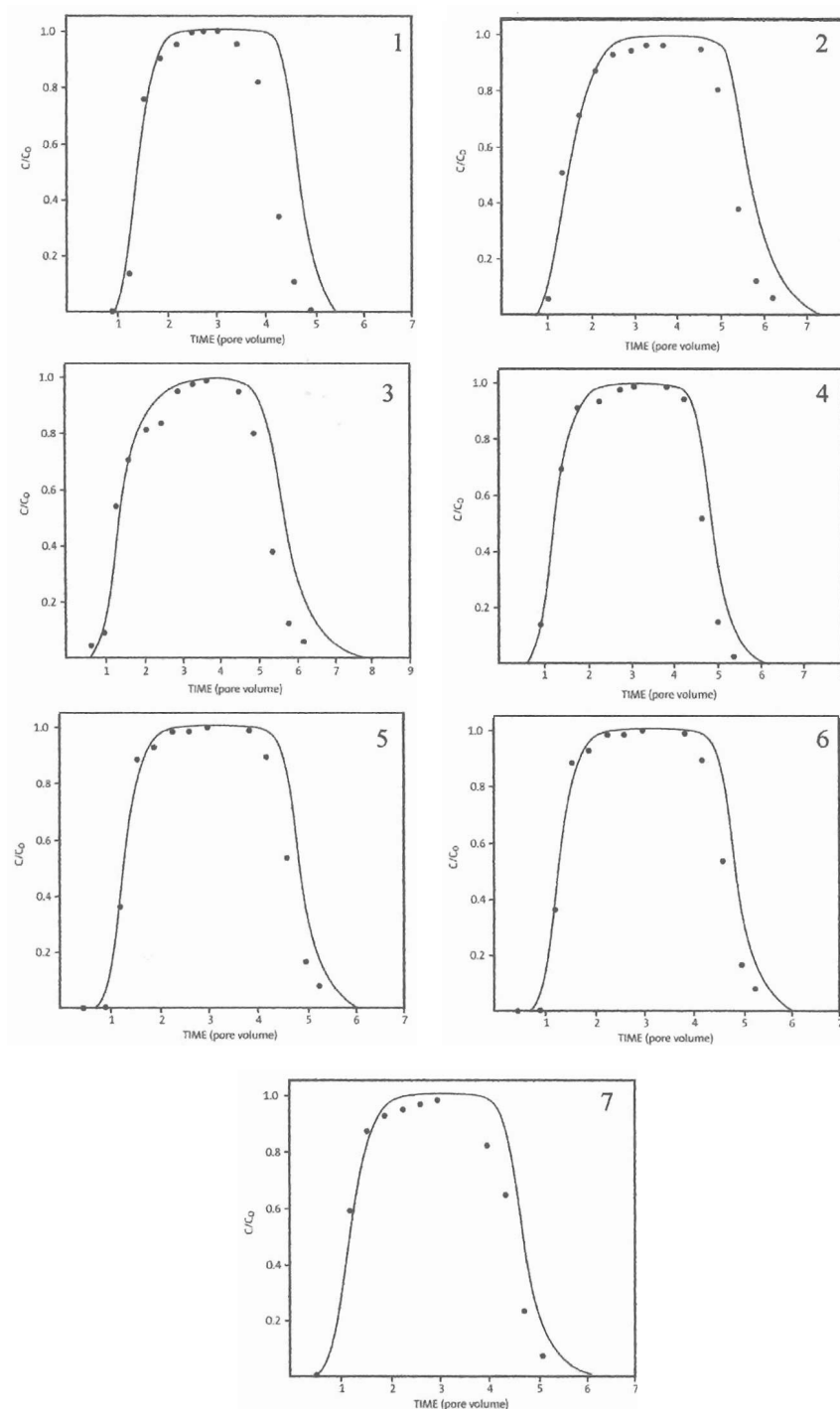
Run 3:  $[HF^0] H^+$  1,5% of total  $F^-$ , and  $[F^-] H^+$  98,5% of total  $F^-$

Run N°	pH of input solution	pH of effluent solution	$[F^-]$ in input solution $mg L^{-1}$	Mean flow velocity $cm min^{-1}$	Retardation factor (*)
1	6,75	7,05	6,00	0,5589	1,43
2	3,11	3,20	5,45	0,5133	1,50
3	4,88	5,00	6,00	0,5403	1,49
4	6,09	6,44	6,00	0,4179	1,30
5	6,13	6,22	4,00	0,4086	1,35
6	6,08	6,12	2,00	0,4020	1,41
7	6,31	6,54	6,00	0,2894	1,22

(\*) CFITIM estimation

**Table 1.** Column experiments: measured and estimated data.

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**Figure 1.** (1-7) .1. Breakthrough curve for column experiment 1, 2 .Breakthrough curve for column experiment 2, 3. Breakthrough curve for column experiment 3, 4. Breakthrough curve for column experiment 4, 5. Breakthrough curve for column experiment 5, 6. Breakthrough curve for column experiment 6, 7. Breakthrough curve for column experiment 7 (dots: data; solid line: fitted by CFITIM).

As for the possible species that F can form with silicon, Roberson and Barnes (1978) concluded that  $\text{SiF}_6$  is the most important one. However, the solubility of quartz at 25 °C is so low (6 mg L<sup>-1</sup>) (Morey et al., 1962; Marion et al., 1976; Roberson and Barnes, 1978) that, even for the column run at the lowest pH (run 2), the  $[\text{SiF}_6]$  barely exceeds 10<sup>-8</sup> M, and it can safely be disregarded.

Based on (1) or (2) above, or on both, the conclusion is that the F<sup>-</sup> adsorption depends on the type of F species present, which, in turn, are linked to the prevailing pH in the system, with low pH values (below 4,5 or 5) promoting the formation and adsorption of HF<sup>0</sup>. It may be pertinent to recall that Hingston (1981) suggested the consideration of the role of both anion (F<sup>-</sup>) and conjugated acid (HF) in adsorption studies.

**pH and flow velocity (almost) constant, [F<sup>-</sup>] varied**

The observed trend indicates that adsorption occurred, with R values becoming smaller as the input [F<sup>-</sup>] was increased (Table 1). Such results are rather puzzling because, in general terms, the adsorption of inorganic species onto mineral surfaces has been found to increase with the concentration of adsorbate in solution. Inasmuch as [HF<sup>0</sup>] should have been minimal at the pH of the three input solutions, the conclusion is that the F<sup>-</sup> ion did not interact much with the mineral surface, or that the adsorption process was overcome by the highly dynamic nature of the experiment. It may be interesting to add that Fluhler et al. (1982) reported that an earlier breakthrough of F<sup>-</sup> at the top of columns as the [F<sup>-</sup>] of the feed solutions was increased could be interpreted as the non-linear nature of the adsorption isotherm.

**pH and [F<sup>-</sup>] (almost) constant, flow velocity varied** Although care was taken to select velocities so that the flow would be laminar, the results indicate that larger retardation factors are associated with faster

flow velocities (Table 1). Again, this finding is contrary to the expected outcome. It can be thought, at least theoretically, that an enlarged time of contact between the adsorbate and the adsorbent (i.e., lower velocities) would result in better chances for the species in solution to attach to the mineral surface. Such an explanation, however, ignores the status of the surface charge of the adsorbent when adsorption takes place. As stated earlier, the quartz particles are negatively charged above a pH of 2, which would certainly inhibit anion adsorption. If so, and in the light of the results already discussed, such repulsion seems to be more effective at lower pore velocities.

**Changes in pH and the adsorption-desorption behavior** Two common characteristics were found in the column experiments, namely, an increase in the pH of the effluent solutions as compared to the pH of the input solutions (Table 1), and the existence of hysteresis in the otherwise reversible adsorption process. Allowance was not made to account for the buffering effect of quartz, although it is assumed to be negligible at the pHs used in the experiments. Therefore, the observed systematic increase in pH can be ascribed to the release of OH<sup>-</sup> from the exchange sites on the sand particles.

The recession limb of the BTC indicates that, for all cases, desorption proceeded at a faster pace than adsorption. Such an effect may represent the lack of equilibrium during washing (Hingston et al., 1974) and, at the very least,

Run N°	K <sub>d</sub> (L kg <sup>-1</sup> )
1	1,04 x 10 <sup>-1</sup>
2	1,18 x 10 <sup>-1</sup>
3	1,21 x 10 <sup>-1</sup>
4	7,24 x 10 <sup>-2</sup>
5	8,44 x 10 <sup>-2</sup>
6	9,89 x 10 <sup>-2</sup>
7	5,31 x 10 <sup>-2</sup>

**Table 2.** Estimated distribution coefficients for the column experiments.

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gives a clear indication of the weak bond between the adsorbed species and the sand particles.

**The distribution or partition coefficient  $K_d$**   
Inasmuch as the distribution coefficient  $K_d$  is embodied in the definition of the retardation factor  $R$  (equation 2), the fitted values for the latter can be used to calculate the magnitude of the former. If the assumption is made that the mass density of the quartz sand is  $2,65 \text{ g cm}^{-3}$ , then the bulk mass density  $\rho_b$  that corresponds to a porosity  $\theta$  of 39% is around  $1,62 \text{ cm}^{-3}$ , and the distribution coefficient can be calculated from the expression for  $R$ . Having done so, the figures shown in Table 2 were obtained for the various runs.

The underlying assumption in estimating  $K_d$  is that the values for both  $R$  and  $\theta$  are correct and, hence, not subject to uncertainties. However, that may not be strictly so. If, instead a porosity of 39%, a range of porosities between 35 and 45% is considered (i.e., a change of 29%) with other variables remaining constant, a 52% change in the values for  $K_d$  is calculated. On the other hand, when  $\theta$  is kept constant and  $R$  is varied between 1,1 and 1,6 (i.e., a 45% change), the corresponding values for  $K_d$  change by 400%. Such a simple exercise demonstrate quite explicitly the important effect that uncertainties in the measured values of  $\theta$  and the fitted values for  $R$  can have on the estimation of the distribution coefficient. Extreme care, therefore, should be taken by those applying values for  $K_d$  reported in the literature, particularly when those values are to be used in environmental-impact studies.

### CONCLUSIONS

Solutions of variable pH, concentration of  $F^-$ , and mean flow velocity were forced to circulate through columns packed with quartz sand, which provided data for estimating the retardation factor  $R$  (fitted by means of a non-

linear, least-squares curve fitting procedure). The outlet measurements indicate that a weak interaction between the solute and the quartz sand takes place, and that the early breakthrough of outflowing  $F^-$  (hysteresis) could point out to a lack of equilibrium during the displacement of the adsorbate species. It would appear that lower pH input solutions enhance the adsorption of  $F^-$  species, most probably in the  $HF^0$  form. Surprisingly enough, increased amounts of  $F^-$  in the input solutions did not result in increased adsorption, which indicates a hardly noticeable interaction between the adsorbent and the adsorbate and the non-linear nature of the adsorption phenomenon. Increased flow velocities resulted in larger retardation factors, suggesting that longer contact times between the adsorbent and the adsorbate promote anion repulsion.

The estimated values for  $R$  vary between 1,22 and 1,50, whereas the distribution coefficients were in the range of 0,1 to 0,05  $\text{L kg}^{-1}$ .

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