

Fluoride Transport and Adsorption/desorption Processes with Different Flow Rates

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1. INTRODUCTION

Fluorine is the lightest element of the halogen group and the most electronegative element^[1] that constitutes about 0.06-0.09 percent of the earth's crust^[2]. F⁻ ions have the same charge and almost same radius as hydroxide ions and therefore can possibly replace each other in mineral structures or form complexes with aluminum and ferric ions^[1]. Fluoride in soil can be derived both from natural sources, through geochemical processes and anthropogenic sources such as fertilizers containing phosphate^[3], phosphate mines and aluminum smelters^[4]. Consuming proper amount of fluoride can be beneficial to dental health had help strengthen bones but overdosing of can cause diseases such as fluorosis and osteosclerosis^[5].

In many developing countries, people depend on high fluoride concentration groundwater as drinking water, and the removal of fluoride is realized by first pumping out then either adsorbed by absorbent or form sediment by adding chemicals^[6]. During pumping, there is a chance for deep, old high-fluoride groundwater to contaminate shallow low-fluoride

groundwater^[6]. Also, in contaminant remediation procedure, "pump and treat" is a common way to remove fluoride from soil. The efficiency of these methods using pumps can be affected by pumping rates, higher pumping rate means higher flow rate in the soil.

2. OBJECTIVES

1) To develop a numerical model describing fluoride adsorption/desorption and transport behaviors and compare the result with laboratory experiments;

2) To investigate fluoride adsorption/desorption and transport behaviors at different flow rates.

3. THEORY BACKGROUND

Fluoride sorption process can be explained by the different kinds of models such as isotherm models and the surface complexation models. The isotherm models, for example, the linear Kd model and the Langmuir-Freundlich model, are empirical based models that limited to experiment conditions such as pH^[7]. However, fluoride sorption process depends on pH^[8] which makes the isotherm model less appropriate for explaining fluoride sorption behaviors. The

surface complexation models are more theoretical based and considered surface charges resulting from protonation, dissociation reactions, and surface complexation reactions at mineral surfaces^[9]. It can be used when changes during sorption reaction and has been proved to be in good consistent with numbers of experimental data^[10].

The transport process of fluoride can be described by the advection-dispersion equation with physical nonequilibrium process. This process happens when heterogeneity exists, and the solute transport is not in equilibrium with some regions act as sink/source components affecting transport behavior^[11]. One of the widely used model for physical nonequilibrium process is the two-region model^[12]. It divided the water in the porous medium according to mobility, one is the primary region the solute transports by advection and dispersion and the other is a relative stagnant region where the solute only transports by diffusion (Figure 1). The two-region model has turn out to be able to fit the experimental data well^[13].

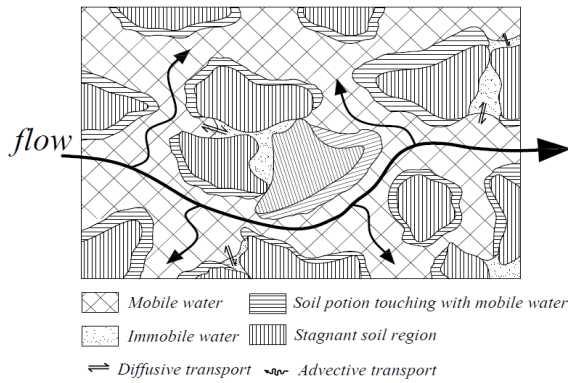


Figure 1. A schematic of the Two-region model

4. NUMERICAL SIMULATIONS OF THE EXPERIMENTAL DATA

To accomplish objectives mentioned above, a numerical model based on laboratory column experiments with flow interruptions^[14] is built. The experiment set and the conceptual model is shown in Figure 2 and the experiment procedures are shown in Figure 3.

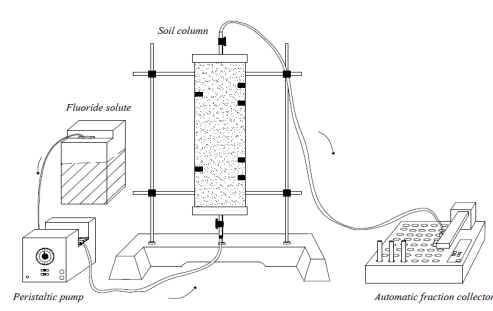


Figure 2. A schematic of the Two-region model

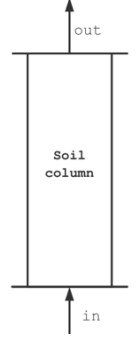


Figure 3. A schematic of the conceptual model

① The governing equations based on mass balance is (1) to (3)^[15].

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + \rho_b \frac{\partial s}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial z^2} - v_m \theta_m \frac{\partial C_m}{\partial z} \quad (1)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + \rho_b \frac{\partial s_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (2)$$

$$\theta = \theta_m + \theta_{im} \quad \theta_v = \theta_m v_m \quad \theta D = \theta_m D_m \quad s = s_m + s_{im} \quad (3)$$

C_m : the concentration of solute in the immobile regions (ML^{-3});
 C_{im} : the concentration of solute in the immobile regions (ML^{-3});
 v_m : the average pore-water velocity in the mobile region (LT^{-1});
 D_m : coefficient of longitudinal hydrodynamic dispersion in the mobile region ($L^2 T^{-1}$);
 θ : volumetric water content ($L^3 L^{-3}$);
 θ_m : volumetric mobile water content ($L^3 L^{-3}$);
 θ_{im} : volumetric immobile water content ($L^3 L^{-3}$);
 ρ_b : dry soil bulk density (ML^{-3});
 s : the solid phase concentration of total solute (MM^{-1});
 s_m : the solid phase concentration of solute from the mobile region per mass of dry soil (MM^{-1});
 s_{im} : the solid phase concentration of total from the immobile region per mass of dry soil (MM^{-1});
 α : mass transfer coefficient between mobile and immobile region (T^{-1});
 z : distance (L);
 t : time (T)

② Boundary conditions: the upper boundary condition for inlet is the constant concentration boundary with a fixed NaF concentration of 50 mg/L of fluoride, and the lower boundary for outlet is a flux boundary. ③ Parameters used are listed in table 1. ④ Reactions for fluoride sorption are as follows:

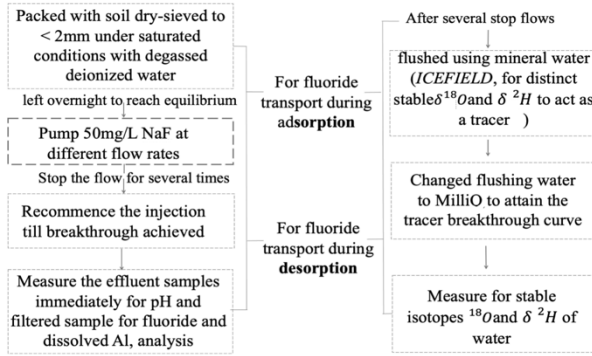
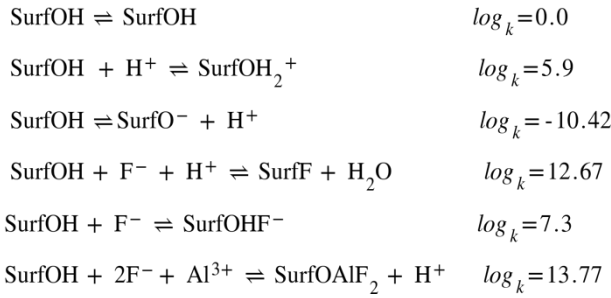


Figure 4. Procedure of the experiment that the numerical model based on

4. RESULTS

Several numerical simulation cases are performed to discuss how transport under different flow rates and the ratio of immobile zone in the total porosity contributes to fluoride transport and sorption processes in the modeled porous medium. The processes considered were, advection-dispersion (ADE) and advection-dispersion including physical nonequilibrium (PNE) process for transport, and linear sorption and surface complexation model (SCM) for sorption desorption processes.

CASE 1 Impact of different physical nonequilibrium transport and sorption processes on fluoride breakthrough curves (Figure 5. and Figure 6.).

When physical nonequilibrium is included, the breakthrough curves are right-shifted the tailing is more obvious during both adsorption and desorption. There is a plateau exists at high

flow rate, at low flow rate, an obvious right-shift occurs.

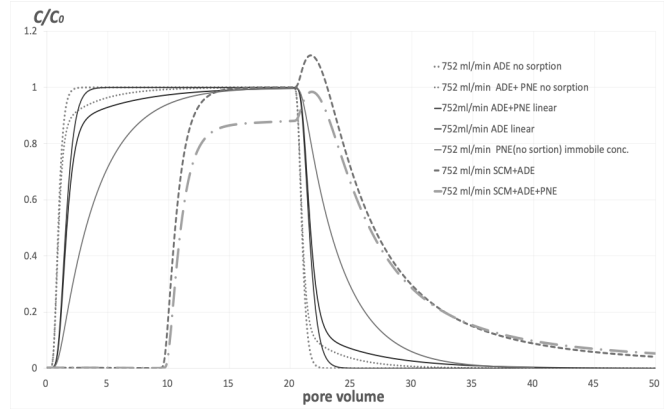


Figure 5. Fluoride relative concentration in the mobile zones versus pore volume at a high flow rate with different transport and sorption processes

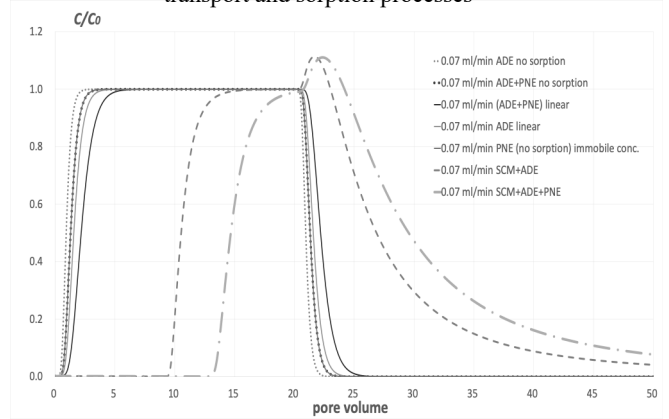


Figure 6. Fluoride relative concentration in the mobile zones versus pore volume at a low flow rate with different transport and sorption processes

CASE 2 Impact of different flow rates on fluoride breakthrough curves when physical nonequilibrium is included in transport and surface complexation model for sorption processes (Figure 7. and Figure 8.).

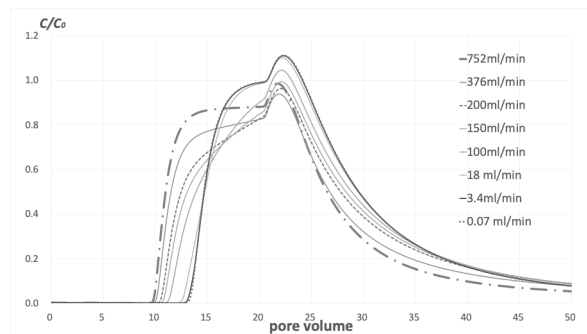


Figure 7 Fluoride relative concentration in the mobile zones versus pore volume at different flow rates. Immobile zone is included in transport and surface complexation model for sorption process

For different flow rates, when flow rate is low, the solute concentration difference between the mobile and immobile zone is small because the resident time is long, and the mass transfer is more sufficient. When flow rate is high, there is an obvious time lag and concentration difference between the mobile and immobile zones because the resident time is short for mass to transfer as soon as contacting the immobile zone.

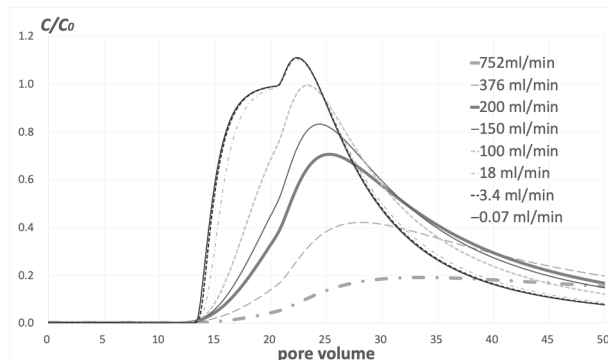


Figure 8. Fluoride relative concentration in the immobile zones versus pore volume at different flow rates. Immobile zone is included in transport and surface complexation model for sorption process

At low flow rate, the peak concentration is not changed much if sorption is included, but at high flow rate, the peak largely decreased from 1 to 0.88. Tailing is more obvious when sorption is included, and tailings of BTCs using surface complexation model is heavier than those using linear model

CASE 3 Impact of immobile zone ratio on breakthrough curves with physical nonequilibrium transport process and surface complexation model for sorption process.

With the ratio of immobile zone increasing, the shape of BTCs at lower flow rates changed remarkably than those of higher flow rates. When the ratio equals 0.7, the desorption half of the BTCs are not observable within 50 pore volumes.

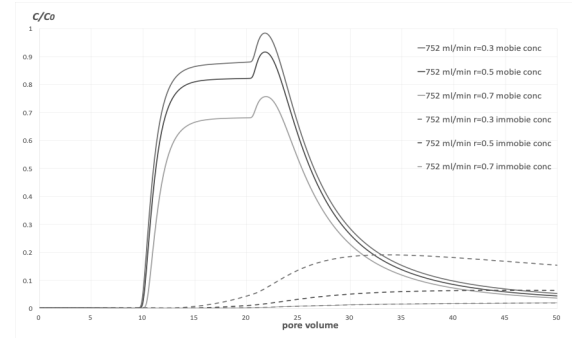


Figure 9. Fluoride relative concentration versus pore volume at different immobile zone ratios a high flow rate

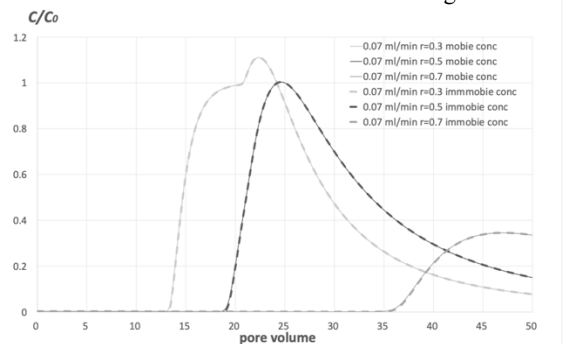


Figure 10. Fluoride relative concentration versus pore volume at different immobile zone ratios a low flow rate

5. DISCUSSION AND IMPLICATIONS

The results of this study show that high flow rate may lead to a higher residual fluoride concentration in the fraction of water that solute can only transported in by diffusion (immobile water), which can be applied during pumping high-fluoride concentration groundwater. The pumping rate should not be too high in order to avoid the solute in the immobile zones diffuse back in to the low-fluoride concentration water.

When the immobile zone in the soil occupies a higher ratio in total porosity, the pumping rate should be higher since the ratio impacts less on concentration at higher flow rates.

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