Analysis of breakthrough curves of Np(V) in clayey sand packed column in terms of mass transfer kinetics.

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1. INTRODUCTION

The determination of radionuclide transport properties from column experiments shows its interest when it is question

(1) to display coupling between various retention mechanisms such as precipitation, ion exchange, surface complexation ;

(2) to measure adsorption equilibrium properties in a chemically perfectly controlled medium (control of the pH, ionic composition, etc.);

(3) and/or to determine the mass transfer kinetics in the presence of flow between a mobile phase and a stationary phase containing the solid active for solutes retention.

If numerous works illustrate these two first chromatographic methods few of them are devoted to the interpretation of the breakthrough curve or peak shape in terms of mass transfer kinetics.

d_p

d_c

Internal diffusion

External diffusion

CAPTION

Stagnant water

Sand grain covered with clay minerals

Mobile water

The porous medium with aggregates and stagnante zones
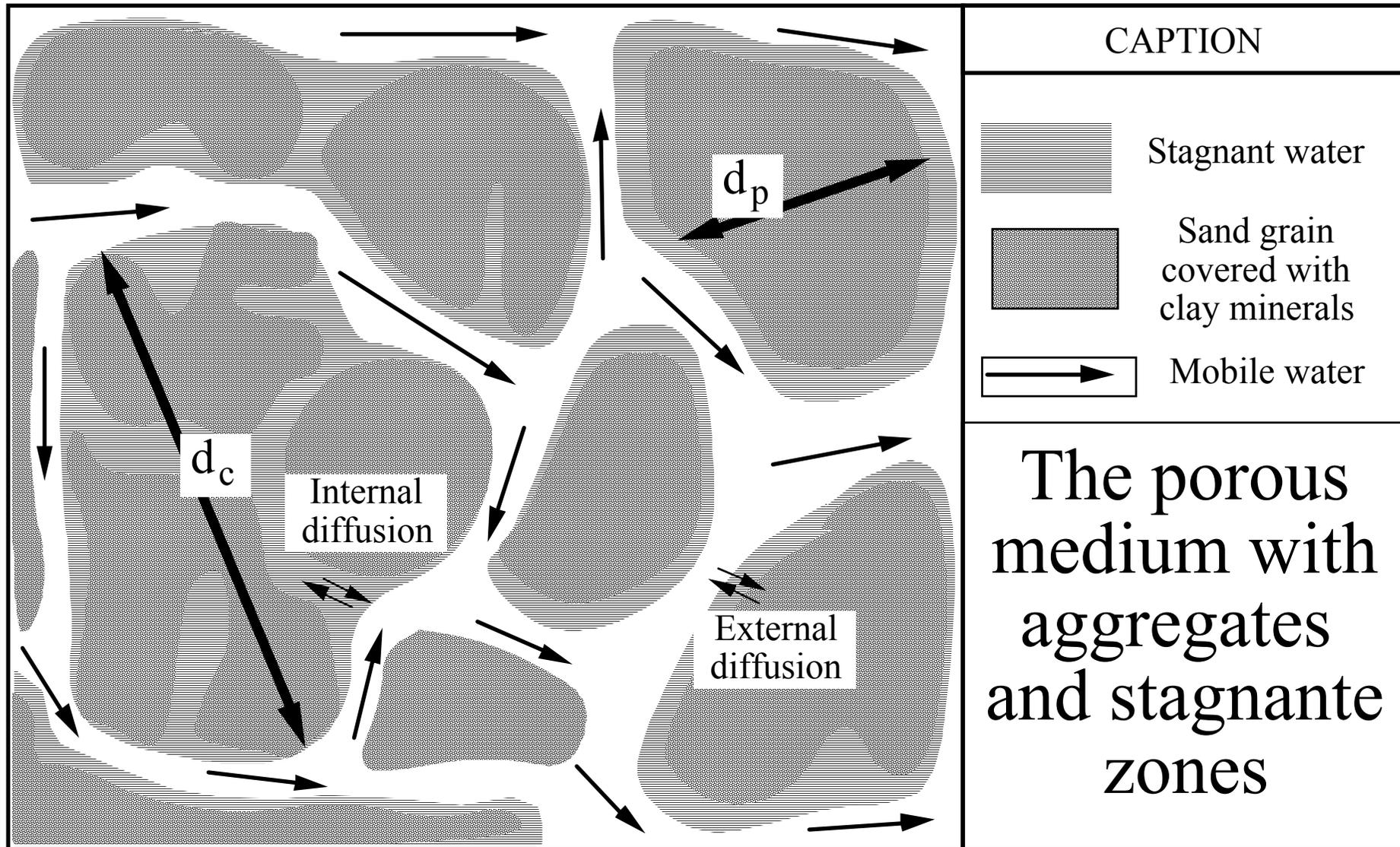
2. THEORY(1)

- constant flow rate
- 1-D advective-dispersive flow.
- mobile phase (C_m in mol/l) and stationary phase (C_s in mol/kg)

for the mobile phase :

$$u\frac{\partial C_m}{\partial x} + \frac{\partial C_m}{\partial t} + \frac{1-\varepsilon}{\varepsilon}\rho_a\frac{\partial C_s}{\partial t} = D_A\frac{\partial^2 C_m}{\partial x^2}$$

for the stationary phase :

$$\frac{1-\varepsilon}{\varepsilon}\rho_a\frac{\partial C_s}{\partial t} = k_M\left(C_m - \frac{C_s}{K_d}\right)$$

ε is the volume fraction occupied by the mobile fluid,
ρ_α is the density of the stationary phase,
D_A represents the axial dispersion, u is the pore velocity,
k_M is the mass transfer coefficient and
K_d the distribution (or partition) coefficient.

3. THEORY(2)

Local equilibrium assumption , $C_S = K_d\, C_m$

Mean retention time of the peak   *variance*   *with*

$$t_R = t_m\left(1 + \frac{1-\varepsilon}{\varepsilon}\rho_a\, K_d\right) = t_m\left(1 + K_d'\right) \qquad \sigma^2 = \frac{2t_R^{\,2}}{Pe} \qquad t_m = \frac{L}{u} \text{ and } Pe = \frac{uL}{D_A},$$

First order kinetics : $\dfrac{1-\varepsilon}{\varepsilon}\rho_a\dfrac{\partial C_s}{\partial t} = k_M\left(C_m - \dfrac{C_s}{K_d}\right)$

Reduced variance   *Characteristic transfer time*

$$\sigma'^2 = \frac{\sigma^2}{t_R^{\,2}} = \frac{2}{Pe} + \frac{2K_d'}{1+K_d'}\frac{t_M}{t_R} \qquad\qquad t_M = \frac{K_d'}{k_M}$$

Kinetic model ======>four parameters : t_m, Pe, K_d' and t_M.

4. DEFINITION OF THE MASS TRANSFER TIME

External diffusion assumption

$$t_e = K_d' \frac{\delta l}{D_{mol}}$$

δ : boundary layer thickness, D_{mol} is the molecular diffusion coefficient;

l : ratio between the volume and the surface area of the aggregate in contact with the mobile water. sphere (diameter, d_p), $l = d_p/6$.

External diffusion assumption

$$t_i = K_d' \frac{\mu l^2}{D_e}$$

μ : shape factor, equal to 3/5 for sphere, D_e : effective diffusion coefficient,

In both cases, the expression of the characteristic transfer time proportionally depends on the adsorption capacity, K_d'. If the internal or external diffusion processes control the kinetics, an increase in the retention capacity at a given flow rate must lead to a proportional increase of the characteristic transfer time. This property is experimentally explored.

5. METHODOLOGY

Chromatographic column filled with a sand and clay minerals (Fo-Ca-7) mixture with 6.5% clay. Average sand grain diameter is 200 μm.

Mineral composition of the clay material Fo-Ca-7.

Table 1

Clay composition	% weight
Kaolinite and Smectite	84
Quartz	6
Goethite	6.5

Pore volume = 7.5 cm3
Péclet number = 130

The column contained 20.08 g of mixture and is 7 cm in length. The column is saturated with a conditioning solution ($NaClO_4$ + $NaHCO_3$). The pore volume and the flow dispersion were determined by Residence Time Distribution (RTD) measurements of a water tracer.

Flow rate, 1 ml/min.

Injection : 2 ml of Np(V) $5.10^{-6}M$

Total neptunium concentration is measured in each fraction by counting the α activity in an $\alpha-\beta$ discriminating liquid scintillation analyser (LKB-WALLAC 1219 RACKBETA).

6. RESULTS AND INTERPRETATION

The value of K_d vs pH first decreases from 1.83 at pH 8 to 0.4 at pH 10 (figure 2a), then increases to 1.2 at pH 12 (figure 2b).

(1)The Np(V) retention is interpreted by a competitive adsorption of the three cations Na^+, H^+ and NpO_2^+ on clays minerals.

(2) adsorption properties of clay minerals in large range of pH = three sites; The first one is active only at low pH; the second is ionized from pH 6 and the last one from pH 10.

(3) NpO_2^+ is the unique fixed species of Np(V);

(4) Only the third site is active for the Np(V) retention;

(5) The decrease of Np(V) capacity factor when pH increases is due to the neptunium complexation by carbonate anions, and the increase below pH 10 is due to the fact that the carbonate anion is more important in solution than the bicarbonate.

7. ANALYSIS OF NP-PEAKS IN TERMS OF MASS TRANSFER KINETICS

The analysis of the breakthrough curves shape shows that the reduced variance increases with the capacity factor.

When the retention increases, the peak maximum decreases and the curve becomes less symmetrical. This is attributed to mass transfer limitations.

The breakthrough curves are well simulated with the advective-dispersive model with first order kinetics described below (Figure 3), whereas the simulations with a model with local equilibrium lead to curves more symmetrical than experimental curves with a higher maximum (Figure 2).

The variations of the characteristic transfer time (t_M) vs K_d' (Figure 4) is a straight line through the origin with a slope $t_C = 38$ s

Characteristic dimension	Sand particle: particle diameter	aggregate : dispersivity	Height Equivalent to a Theoretical Plate
d_c (µm)	$d_p = 200$	$\alpha = L/Pe = 500$	$h = L/J = 1000$
External transfer assumption			
$t_C(s) = \dfrac{\delta d_c}{6D_{mol}}$	**2.2**	**10.3**	**32,8**
Internal transfer assumption			
$t_C(s) = \dfrac{d_c^{2}}{60D_e}$		**23.1**	**92.6**

Influence of the choice of the characteristic dimension and of the diffusion process on the theoretical value of the characteristic time t_C.

8. CONCLUSIONS

- The retention of Np(V) in a clayey sand is mainly controlled by the equilibrium properties of the homogeneous and heterogeneous reactions which occurs in the system.

- In the presence of a constant excess of sodium carbonate and sodium chlorate in solution, the experiments performed in column at different pH display a characteristic behaviour of the retention time which can be modeled taking into account calcocarbonic equilibria and $H^+/Na^+/NpO_2^+$ cation exchange on the third site of clays.

- If the location of Np-peaks vs pH is well represented by a transport model coupling the equilibrium model and convective-dispersive flow, the representation of their shape needs to take into account a kinetic model.

- Using the classical first order approximation we have shown that the characteristic time of adsorption is proportionnal to the retention factor. This property agrees with the theory of mass tranfer kinetics. If the aggregate volume increases the internal diffusion becomes preponderant and when neptunium retention increases (for instance in less carbonated media), t_M becomes drastically high leading to a control of radionuclide transport by kinetic processes.