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

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Abstract

The transport properties of Np(V) were studied in a column packed with a mixture of silica sand and natural clay minerals (8% w/w), essentially montmorillonite and kaolinite with goethite (6.5% of clays fraction). The clayey sand packing is 1.6 cm in diameter and 7 cm in length; the pore velocity is 3.6 m/day. Np(V) was injected as a concentration pulse of 8.0 10^{-6} mole/l in a solution containing sodium perchlorate and sodium carbonate at a given pH. Np(V) was detected at the outlet and the distribution coefficient, K_D,was measured from the first moment of peaks. The curve log(K_D) vs pH displays a characteristic shape : Log(K_D) firstly decreases from 1.5 at pH 8.2 to 0.5 at pH 9.8, value for which a minimum is observed. Then, when pH increases from 10.0 to 11.8, log(K_D) value increases to 1.3. The theoritical interpretation of equilibrium properties as a function of pH takes into account $Na^+/H^+/NpO_2^+$ cation exchange on a specific site of clay minerals. Analysis and modelling of peak shapes show that the stronger the retention, the higher the reduced variance of the Np(V) peaks. This behaviour is interpreted in the framework of linear chromatography theory, which leads to attribute the evolution of reduced variance of peaks vs pH to external and/or internal mass transfer limitations. Introducing the characteristic times of a first order kinetics allows one to determine the nature of mass transfer kinetics and the characteristic length of clayey sand aggregates.

1. Introduction

The determination of radionuclide transport properties from column experiments is interesting when it addresses the questions : (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 the mobile phase and the stationary phase containing the solid active for solutes retention.

In the first case, the aim is to interpret the consequences of a compositional disturbance at the system inlet on the composition transition number and position at the system outlet and to deduce the nature of the interactions which are responsible for them (Schweich et al., 1993).

In the second case, one is interested in the location of a concentration front or peak of one single species at the column outlet in a chemically perfectly controlled system and, if possible, in linearly interacting conditions (Sardin et al., 1991).

Numerous works illustrate these two first chromatographic methods (Lefèvre et al., 1993 and 1995, Kohler et al., 1996), but few of them are devoted to the interpretation of the breakthrough curve or peak shape in terms of mass transfer kinetics. Generally, the gaps observed between the theory of local equilibrium transport and experiments are ignored. At most, either one assigns a hydrodynamic dispersion coefficient which is different for the water tracer and the interactive solute, or one uses a first order (linear driving force principle) model which represents the peak or front shape observed at best by means of a parametrical fitting.

This relative lack of interpretation of kinetic effects is due to the fact that they are generally due to the diffusional transport in aggregates and thus strongly depend on the system geometry. Consequently, it is difficult to extrapolate the fitted parameters from the laboratory to the field. Moreover, the relatively slow flow rates in natural porous media have often been a good reason to exclude interpretation in diffusional terms on the small scale (Valocchi, 1985). But, it is now recognised that the local equilibrium assumption can be questionable even at the microscale and that non-equilibrium sorption-desorption might have a significant impact on transport of contaminants in subsurface environment, when these contaminants are strongly adsorbed (Brusseau and Rao, 1989).

Thus, the analysis of breakthrough curves performed using laboratory columns in terms of mass transfer kinetics, may be of great interest (Young and Ball, 1995) and raises questions still poorly resolved. Let us mention the plenary conference of G. De Marsily during the last Migration'95 congress (Harvey and de Marsily, 1995) which was devoted to the possibility of deducing the dispersion coefficient of an interactive solute from the one of the tracer.

Notice that often there is confusion between kinetic and non-linearity effects in the proposed interpretations of curves tailing. The way to discriminate these two effects is to performe experiments at different solute concentrations and/or different flow rates. If the tails of breakthrough curves are superimposable in absolute coordinates at low flow rate and at different solutes concentrations, the adsorption mechanism is non-linear. Contrarily, the independance of the retention time with the injected amount is a sign of linear interactions (Schweich and Sardin, 1981).

Eventually, the study of the solute retention at low concentration submitted to adsorption processes may reveal interactions controlled by a kinetic process and it shows all the stronger that retention is important. The aim of this paper is to show what kind of information can be extracted from retention measurements presenting a kinetic effect at different values of the retention time and what is possible to deduce from it for a heterogeneous field media.

2. Theory

The interpretation of diffusion kinetic effects was widely described in the case of linear processes. The classical example is the one where the column is flushed by a constant flow rate, Q, and where the water velocity distribution can be described by a 1-Dimensional advective-dispersive flow model. The solute partition between the mobile phase (C_m in mol/l) and the stationary phase (C_s in mol/l of stationary phase) is supposed to be governed by a local equilibrium law and/or by a linear mass transfer kinetics (Sardin and al., 1991). Notice that the concentration C_s includes both solute adsorbed on the solid surface and solute dissolved in the immobile water, trapped in the soil aggregates. A classical calculation (Sardin et al., 1991) gives the following formulation :

* *for the mobile phase :*

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

* *for the stationary phase :*

The easiest is to use a first order kinetics (Linear Driving Force or first order model) :

$$\frac{1-\varepsilon}{\varepsilon}\frac{\partial C_s}{\partial t}=k_M\left(C_m-\frac{C_s}{K_d^*}\right) \tag{2}$$

where ε is the volume fraction occupied by the mobile fluid, 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. Notice that K^*_d is a distribution coefficient including the immobile water: $K^*_d = \beta_{im} + \rho_s K_a$, where K_a is the distribution coefficient with respect to the mass of adsorbant ($m^3.kg^{-1}$) and ρ_s ($kg.m^3$), the density of the dry solid.

In the assumption of local equilibrium, $C_s = K^*_d\, C_m$ and the system can be reduced to a single equation :

$$u\frac{\partial C_m}{\partial x}+\frac{\partial C_m}{\partial t}\left(1+\frac{1-\varepsilon}{\varepsilon}K^*_d\right)=D_A\frac{\partial^2 C_m}{\partial x^2} \tag{3}$$

Introducing the reduced variables, $t_m = \dfrac{L}{u}$, the capacity factor K_d' and $Pe = \dfrac{uL}{D_A}$, we can show that the mean retention time of the solute, t_R, and the variance, σ^2, are respectively equal to

$$t_R = t_m\left(1+\frac{1-\varepsilon}{\varepsilon}K^*_d\right) = t_m\left(1+K_d'\right) \tag{4a}$$

$$\sigma^2 = \frac{2t_R^{\ 2}}{Pe} \tag{4b}$$

whatever the boundaries conditions, , as soon as Pe is greater than 20 (Sardin et al., 1991). In presence of kinetics, one shows that t_R is not modified, but the variance becomes

$$\sigma^2 = \frac{2t_R^{\ 2}}{Pe} + 2K_d'\, t_M t_m \text{ where } t_M = \frac{K_d'}{k_M} \tag{5}$$

and the reduced variance σ'^2, obtained by dividing σ^2 by t_R^2 is :

$$\sigma'^2 = \frac{\sigma^2}{t_R^{\ 2}} = \frac{2}{Pe} + \frac{2K_d'}{1+K_d'}\frac{t_M}{t_R} \tag{6}$$

The kinetic model is so defined by four parameters : t_m, Pe, K_d' and t_M. . Assuming the local equilibrium ($t_M = 0$) and the reduced variance is equal to $2/Pe$ (eq.6) and is independent of the capacity factor K_d'. The reduced variance is then theoretically the same for the interactive solute and the tracer.

The interpretation of the characteristic time, t_M, can be done in two ways. One is in terms of external diffusion assuming the presence of immobile water around the aggregate. The characteristic transfer time is thus expressed as :

$$t_e = K_d'\frac{\delta l}{D_{mol}} \tag{7}$$

where δ is the boundary layer thickness, l is the ratio between the volume and the surface area of the aggregate in contact with the mobile water. If the aggregate can be simulated by to sphere (diameter, d_p), $l = d_p/6$. D_{mol} is the molecular diffusion coefficient. The other way is in terms of internal diffusion in the porous matrix where immobile water and porous matrix are in equilibrium. The characteristic transfer time is expressed as :

$$t_i = K_d'\frac{\mu l^2}{D_e} \tag{8}$$

where μ is a shape factor, equal to 3/5 for sphere, D_e is the effective diffusion coefficient, which depends on both internal porosity and tortuosity. D_e is often between $0.2D_m$ and $0.1D_m$.

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

3. Methodology

3.1 Column experiments

Experiments were performed using a chromatographic column filled with a sand and clay minerals (Fo-Ca-7) mixture with 6.5% clay. The mineral composition of clays is 84%, kaolinite and smectite, 6% quartz and 6.5% goethite. Average sand grain diameter is 200 µm. The column contained 20.08 g of mixture and was 7 cm in length. The column was saturated with a conditioning solution ($NaClO_4 + NaHCO_3$). The pH is adjusted using NaOH or $HClO_4$. The concentration of carbonate is sufficient to assure a good buffering effect. The pH is constant inside the column. The pore volume and the flow dispersion were determined by Residence Time Distribution (RTD) measurements using a water tracer : a brief change in the $NaClO_4$ concentration was simply used to performed an input signal, the response of which is measured by conductivity at the outlet of the column. All the experiments were performed at the same flow rate, 1 ml/min. For the Np(V) transport experiments, the column was first equilibrated with the working solution. Then 2 ml of Np(V) 5.10^{-6}M solution was passed through the column, i.e. an amount $n_0=10^{-8}$ mole. The solution was collected at the outlet of the column and the total neptunium concentration measured in each fraction by counting its α activity in an α–β discriminating liquid scintillation analyser (LKB-WALLAC 1219 RACKBETA).

3.2 Working equations

The pore volume, V_p, and the Péclet Number, Pe, were obtained from the experimental first moment, μ_1, and variance, σ^2, of the residence time distribution of the water tracer.

$$V_p = Q.\mu_1 \text{ and } Pe = \frac{2.\mu_1^2}{\sigma^2} \tag{9}$$

The Np(V) peaks were normalized and were presented by the product $E(t).V_p$ as a function of V/Vp (V, the eluted volume). E(t) (= $C(t)*Q/n_0$) is the retention time distribution . From the Np(V) transport experiments (figure 1), the zero-moment and first-moment of the elution peak are calculated. The zero-moment gives the amount of Np(V) recovered and is compared to the injected amount. For all experiments, the recovered percentage is close to 100% indicating a reversible adsorption. Thus, the first moment allows the calculation of the mean retention volume V_R which is related to the capacity factor by the relationships

$$K_d' = \frac{V_R}{V_P} - 1 \text{ and } K_d = K_d'\frac{V_p}{M} \tag{10}$$

The mass transfer time was obtained by using the transport model described below. Pore volume, Péclet number and capacity factor were a priori determined (relationships 9 and 10); the fittings were performed on t_M only.

4. Results and interpretation

Experiments were performed in solution containing sodium perchlorate and bicarbonate/carbonate such as $[Na^+]$=1M and $[CO_3]_t$=0.2M. The DTS measurements led to a pore volume of 7.5 cm^3 and a Péclet number of 130. The results of K_d measurement as a function of pH are given in table 2. The value of lg(K_d) vs pH first decreases from 1.83 at pH 8 to 0.4 at pH 10, then increases to 1.2 at pH 12 (see K_d values in Table 2).

The Np(V) retention has been interpreted as a competitive adsorption of the three cations Na^+,H^+ and NpO_2^+ on clays minerals in reports presented elsewhere [André 1997]. This interpretation shows the following : (1) the description of the adsorption properties of clay minerals over a large range of pH needs to take into account three sites, the first one is active from low pH; the second is ionized from pH 6 and higher, the last one from pH 10 and higher; (2) NpO_2^+ is the unique fixed species of Np(V); (3) only the third site is active for the Np(V) retention; (4) The minimum in the Np(V) capacity factor values when the pH increases is due to the competition between the sorption on the third site and the neptunium complexation by carbonate anions in solution. The expression of the neptunium distribution coefficient is given by (André, 1997) :

$$\lg K_{dNp} = \lg K_{H/Np} + \lg C_E + pH - \lg \alpha_c - \lg\left(1 + K_{H/Na}\frac{[Na^+]}{[H^+]}\right) \qquad (11a)$$

where α_c is the neptunium complexation coefficient,

$$\alpha = 1 + \beta_1\left[CO_3^{2-}\right] + \beta_2\left[CO_3^{2-}\right]^2 + \beta_3\left[CO_3^{2-}\right]^3 + \frac{{}^*\beta_1}{\left[H^+\right]} + \frac{{}^*\beta_2}{\left[H^+\right]^2} + \frac{{}^*\beta_{22}\left[CO_3^{2-}\right]^2}{\left[H^+\right]^2} \qquad (11b)$$

C_E = 0.08 meq.g^{-1} is the exchange capacity of the third sorption site (11% of total sites). The constants of equations (11a&b) are defined and their values are given in table 1.

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 the experimental curves with a higher maximum (Figure 1). The variations of the characteristic transfer time (t_M) vs K_d' (Figure 2 and Table 3) is a straight line through the origin with a slope t_C= 38 s. The theoretical calculation of t_C in terms of mass transfer time leads to use the relationships (7) and (8) where

$$t_C = \frac{\delta l}{D_{mol}} \text{ and } t_C = \frac{\mu l^2}{D_e} \qquad (12a\&b)$$

respectively. Tsukamoto et al. (1994) give a value of the molecular and effective diffusion coefficients of Np(V) in loosely compacted clays, D_{mol} = 7 10^{-10} m^2/s and D_e = 1.8 10^{-10} m^2/s. δ may be evaluated using the correlation of Wilson and Geankoplis (1966)

$\frac{D_{mol}}{\delta} = 1.09u\left(Pe_{mol}\right)^{-2/3}$ with $Pe_{mol} = \frac{u\,d_c}{D_{mol}} = \frac{Qd_c}{\varepsilon\Omega D_{mol}}$. Notice, we use in this relationship the characteristic diameter but not the diameter of sand particle directly. This correlation is valid for $1.6 < Pe_{mol} < 55\,000$ and $0.35 < \varepsilon < 0.75$. In the experimental conditions, Q = 1 ml/min, Ω = 2.01 cm^2, and ε = 0.40, from which we deduce $u = \frac{Q}{\varepsilon\Omega}$ = 2.0710^{-4} m/s and Pe_{mol} is about 150 . The main difficulty now is to evaluate the dimension scale, l or d_C,(If the aggregates are assumed to be spherical $l = \frac{d_c}{6}$) of the diffusion process. Three assumptions can be made (see table 4) : (1) the characteristic dimension is the mean sand particle diameter, d_p. The grain is not porous and the clay mineral is deposited on the external surface. Only external diffusion is needed to account for in this case. (2) The characteristic dimension can be deduced from the dispersivity of the packing, $\alpha = L/Pe$,or (3) viewed in terms of Height Equivalent to a Theoretical Plate, $h=L/J$ where J is the number of mixing cells in series from the linear chromatographic theory (Sardin et al., 1991). $J = Pe/2$ for a pure dispersive process. In the cases (2) and (3) we consider aggregates as a set of sand particles containing clays minerals. To reach the adsorption sites, the solute must diffuse through the clayey sand particles.

In case (1), we deduced from (12a) that t_C = 2.2 s, i.e. one order of magnitude less than the experimental value. These assumption can be rejected.

The values of t_C given by the assumptions (2) and (3) are more or less of the same order of magnitude. A good compromise can be found assuming a coupling between both internal and external mass transfer kinetics in aggregates between 500 and 1000 µm. But it is not possible to discriminate between the two diffusionnal processes. As suggested by Sardin et al. (1991), solutions to resolve the problem could be to change either the aggregate characteristic length or the fluid velocity. The second solution is easy to perform, but the first one is more complex and needs to a specific method of packing.

On the basis of the data used in this paper, it is possible to given the evolution of t_C for different characteristic lengths. This behavior is given in the figure 4 where we show that an increase in the characteristic length leads to an increase in the gap between the internal and external diffusion processes. At a high value of the characteristic length, the internal diffusion kinetics becomes dominating. Consequently, in the field the kinetics of the process is certainly controlled by the internal diffusion in the aggregates, the size of which can be very large (from some centimeters to one meter). For instance, if the aggregates are 20 cm the characteristic times for internal and external diffusion kinetics are 0.42 day and 0.055 day, respectively. Assuming a retention factor $K'_d = 10^2$ for Np(V) in an aquifer less carbonated in contact with clayey sand, the mass transfer time, $t_M = K_d'.t_C$ is about 50 days. This simple calculation reveals the important role played by the kinetic processes when the flow in porous media is ill-controlled (bypass or aggregates formation) and the radionuclides are strongly fixed. Notice we have used a simple first order model to take into account the diffusion into aggregate. More complex models can be used accounting for aggregates geometry and solving the diffusion equations. The simple model presented above becomes questionable in a weakly dispersive systeme when internal diffusion is dominant ($t_i > t_m$) (Sardin et al, 1991). In the other cases the results are of the same order of magnitude.

5. 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 perchlorate in solution, the column experiments performed at different pH values display a characteristic behaviour of the retention time which can be modeled taking into account carbonic equilibria and $H^+/Na^+/NpO_2^+$ cation exchange on a third clays site. If the location of the Np-peaks vs pH may be well represented by a transport model coupling the equilibrium model and convective-dispersive flow, the representation of their shape needs to take into account kinetics. Using the classical first order approximation, we have shown that the characteristic time of adsorption is proportional to the retention factor. This property agrees with the theory of mass transfer 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.

6. Notations

C_m, C_s, $C(t)$	concentrations in the mobile phase (mol.l^{-1}), in the stationary phase (mol.l^{-1}), measured at the outlet (mol.l^{-1})
C_E	exchange capacity of the third site (meq.g^{-1})
D_{mol}, D_e	molecular diffusion, coefficient effective diffusion coefficient (m^2.s^{-1})
D_A	Axial dispersion (m^2.s^{-1})
d_p, d_c, l	particle diameter, characteristic length (µm)
$E(t)$	Residence Time Distribution (s^{-1})
h	Height Equivalent to a Theoretical Plate (m)
$J=Pe/2$	number of mixing cells
k_M	mass transfer coefficient (s^{-1})
K_d, K^*_d, K_a, K_d'	distribution coefficient (l/kg of stationary phase), distribution coefficient (l/l of stationary phase), distribution coefficient (l/kg of dry solid), dimensionless distribution coefficient
$l(=d_c/6)$	particle volume/particle surface (m) (spherical assumption)
L	column length (cm)
M	clayey sand mass (g)
n_0	injected amount (mole)
Pe, Pe_{mol}	Péclet number of column, molecular Péclet number
Q	Flow rate (ml.mn^{-1})
t, t_m, t_R	time, travel time in mobile phase, mean retention time (s)
t_e, t_i, t_M	external, internal and global mass transfer times (s, min, day or year)
u	pore velocity (m.s^{-1})
V_p, V_R	pore volume, retention volume (ml)
α, α_C	dispersivity (µm), complexation coefficient (eq.11b)
δ	boundary layer thickness (µm)
μ, μ_1	shape factor, first moment of the RTD (s)

ρ,ρ_s	water density, solid density (kg.m^{-3})
σ^2, σ'^2	variance (s^2) and reduced variance
Ω	column section area (m^2)

7. References

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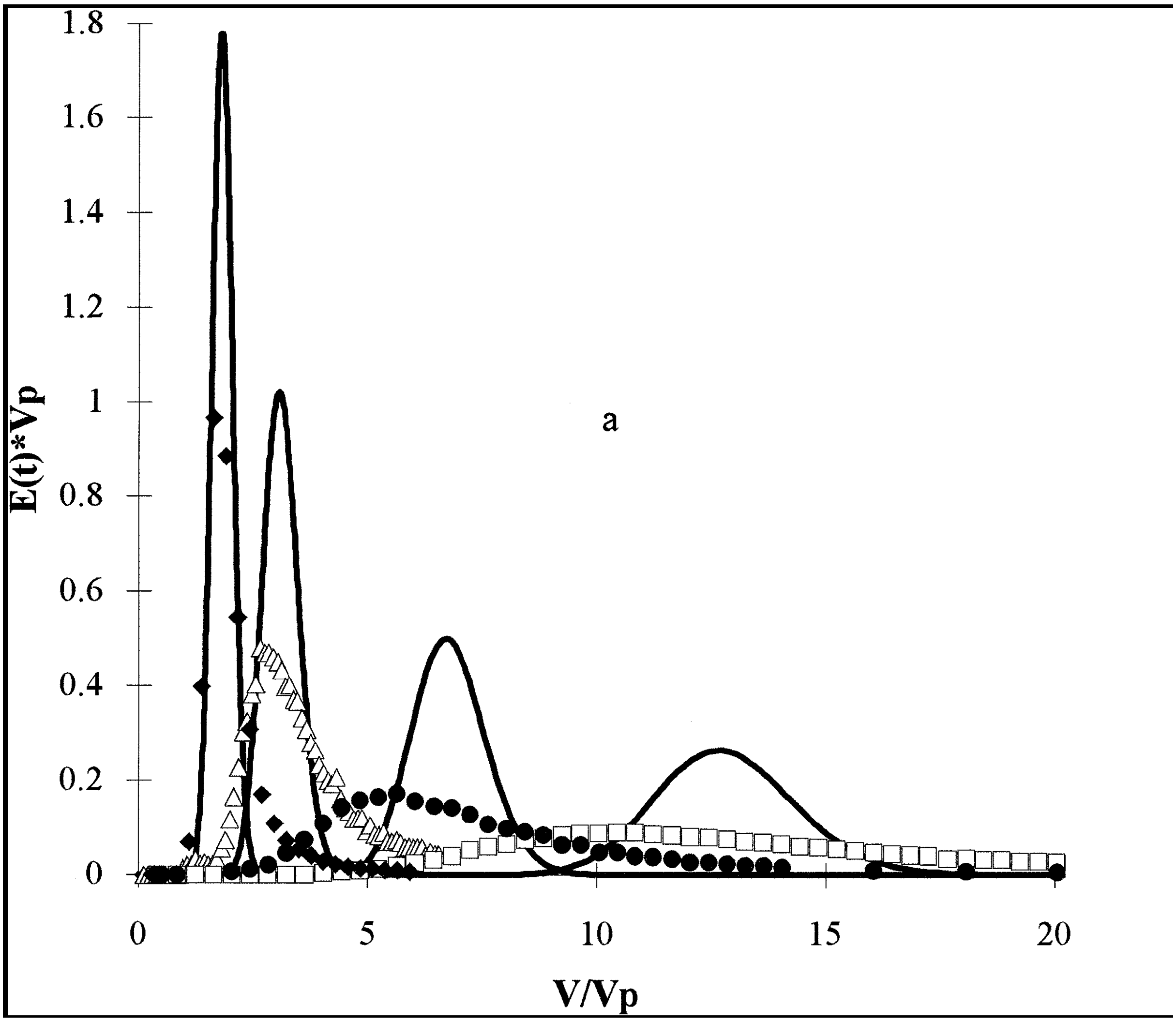
1.8
1.6
1.4
1.2
1
0.8
0.6
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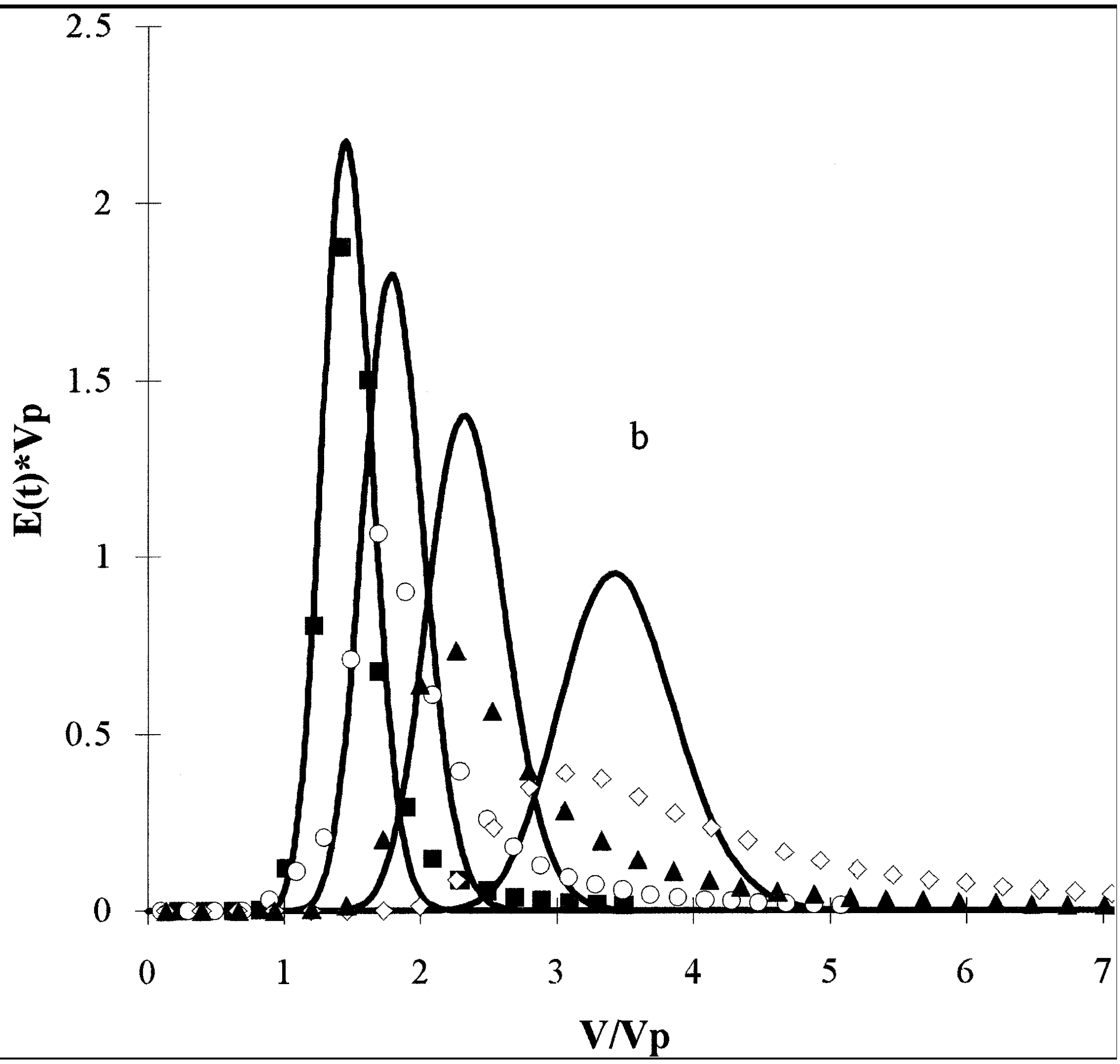
E(t)*Vp
a
0
5
10
15
20
V/Vp

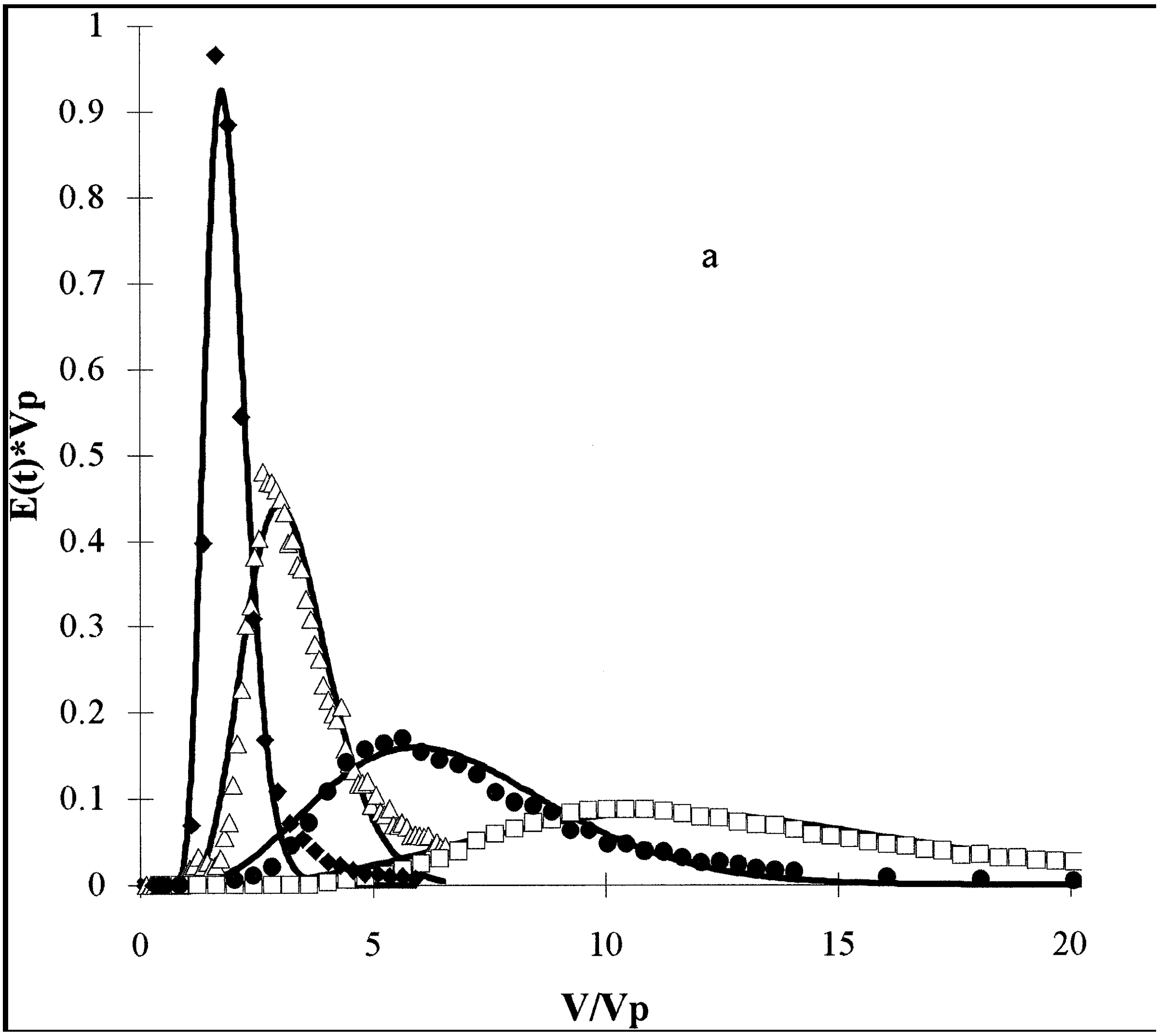


Figures 1 : **breakthrough curves of Np(V)** in 1M $NaClO_4$ with 0.2 M $[CO_3]_t$.

a) pH<10 : □ : pH=7.95 - ● : pH=8.3 - △ : pH=9.0 - ◆ : pH=9.2

b) pH>10 : ■ : pH=10.0 - ○ : pH=11.0 - ▲ : pH=11.4 - ◇ : pH=11.9.

Continuus curves are obtained by means of simulation with a transport model assuming local equilibrium . (Pe = 130, V_p = 7,5 cm^3, flow rate = 1 cm^3/mn). The $E(t).V_p$


1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
E(t)*Vp
a
0
5
10
15
20
V/Vp

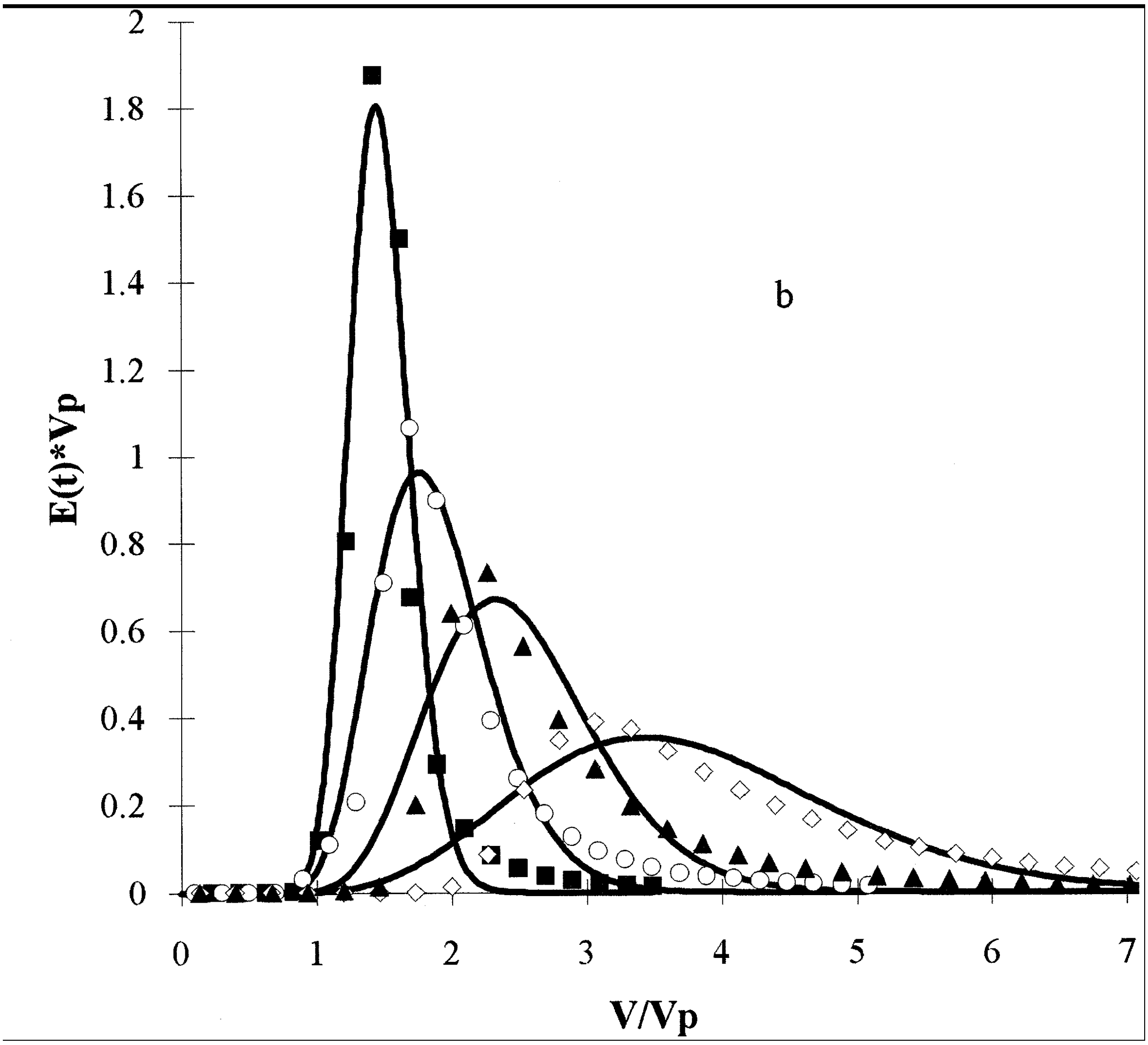


Figure 2 : **Characteristic transfer time** vs dimensionless distribution coefficient of Np(V).

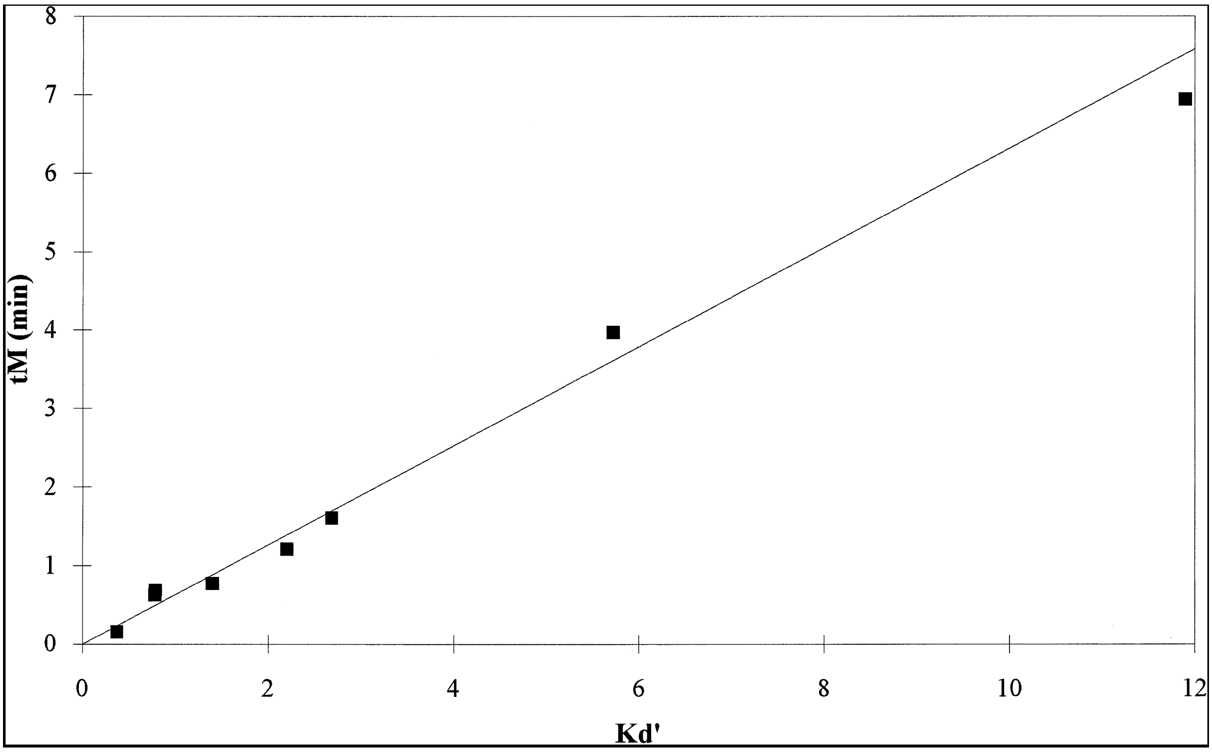


Figure 3 : breakthrough curves of Np(V) in 1M $NaClO_4$ with 0.2 M $[CO_3]_t$.

a) pH<10 : □ : pH=7.95 - ● : pH=8.3 - △ : pH=9.0 - ◆ : pH=9.2

b) pH>10 : ■ : pH=10.0 - ○ : pH=11.0 - ▲ : pH=11.4 - ◇ : pH=11.9

Continuous curves represent adjustments with a model of mixing cells in series with first order kinetics. (Pe = 130, V_p = 7,5 cm^3, flow rate = 1 cm^3/mn).

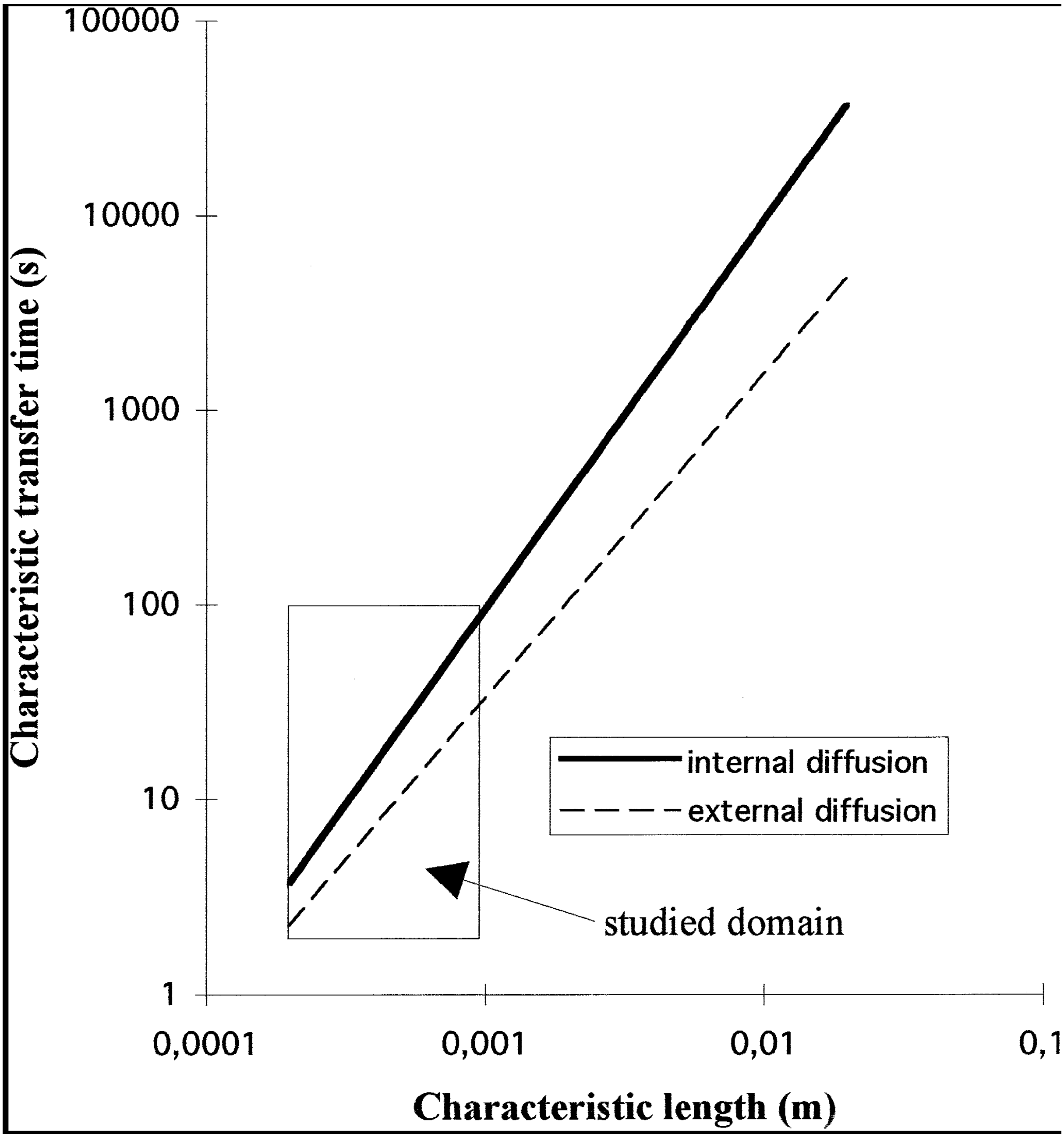


Figure 4 : Influence of the characteristic dimension of aggregates
on both external and internal transfer times.

Table 1: Aquatic chemistry constants in 1M $NaClO_4$ used in this work.

These constants are obtained from a literature critical review (Vitorge, 1998). Equilibrium constants for the carbonate system are calculated from (5) values at I=0 calculated to 1M $NaClO_4$ by using the Specific Interaction Theory.

Equilibrium	Constant	lg K I=1 M (25°C)
$H_2O \Leftrightarrow H^+ + OH^-$	Ke	-13.83
$NpO_2^+ + CO_3^{2-} \Leftrightarrow NpO_2CO_3^-$	β_1	4.29
$NpO_2^+ + 2\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{\ 3-}$	β_2	6.64
$NpO_2^+ + 3\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{\ 5-}$	β_3	8.29
$NpO_2^+ + H_2O \Leftrightarrow NpO_2OH + H^+$	$^*\beta_1$	-11.35
$NpO_2^+ + 2\ H_2O \Leftrightarrow NpO_2(OH)_2^- + 2\ H^+$	$^*\beta_2$	-22.48
$NpO_2^+ + 2\ CO_3^{2-} + 2\ H_2O \Leftrightarrow NpO_2(OH)_2(CO_3)_2^{\ 5-} + 2\ H^+$	$^*\beta_{22}$	-18.78
$CO_{2g} + H_2O \Leftrightarrow H^+ + HCO_3^-$	K_p	-7.61
$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$	K_1	-9.60
$CO_{2aq} + H_2O \Leftrightarrow H^+ + HCO_3^-$	K_{12}	-6.12
$\overline{H} + NpO_2^+ \Leftrightarrow H^+ + \overline{NpO_2}$	$K_{H/N\,p}$	-2.66
$\overline{Na} + H^+ \Leftrightarrow \overline{H} + Na^+$	$K_{Na/H}$	11.07

$\overline{X}$ = adsorbed species

Table 2: Distribution coefficient of Np(V)

measured and calculated using equation (11), $NpO_2^+/H^+/Na^+$ ion exchange in 1M $NaClO_4$ with 0.2 M $[CO_3]_t$ on the third site.

pH	lg(K_d) measured (ml/g)	lg(K_d) from equations 11 a&b (ml/g)
7.95	1.83	1.92
8.3	1.51	1.65
8.8	1.21	1.14
8.95	0.98	0.98
8.96	1.10	0.96
9.2	0.66	0.70
9.63	0.54	0.43
10.0	0.33	0.38
10.54	0.56	0.56
11.0	0.66	0.78
11.43	0.91	0.93
11.9	1.19	1.02

Table 3: Characteristic transfer time and dimensionless distribution coefficient

of Np(V) at different pH.

pH	K_d’	t_M (mn)
7,95	11,90	6,94
8,3	5,72	3,97
9,0	2,2	1,2
9,2	0,79	0,69
10,0	0,37	0,16
11,0	0,79	0,63
11,4	1,40	0,77
11,9	2,69	1,6

Table 4 :Influence of the choice of the characteristic dimension and of the diffusion process on the value of the characteristic time t_C.

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			
δ (µm)	50	90	140
$t_C\,(\mathrm{s}) = \dfrac{\delta d_c}{6D_{mol}}$	2.2	10.3	32.8
Internal transfer assumption			
$t_C(\mathrm{s}) = \dfrac{d_c^2}{60D_e}$		23.1	92.6