Temperature influence on ionic exchanges on clayey mineral, deduced from column experiments.

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Abstract

The transient transport of radioelements in clayey porous media had been studied by using chromatographic (column) experiments and 1 M Na^+ + 0.2 M HCO_3^-/CO_3^{2-} aqueous solutions at room temperature. Elution curves of Np(V) and Ca^{2+} at trace concentration had been interpreted by coupling transport equations with mass action law to account for complexation and sorption (ionic exchange on porous media). This allows to measure partition coefficient, $K_{dNp \text{ or } Ca}$, and to model its variations with chemical composition of the aqueous phase. Evidence of three sorption sites, and $H^+/Na^+/(Ca^{2+}$ or $NpO_2^+)$ ionic exchanges had been found in these conditions. H^+/NpO_2^+ ionic exchange equilibrium constant on site 3, $_3K_{H/Np}$, is obtained from K_{dNp} measurements, by using thermodynamic cycles to deduce the contributions of the formation constants of Np(V) carbonate complexes (β_2 and β_3), and of HCO_3^- anion (K_1). The same methodology is here used at 5 to 45°C to estimate enthalpy of reaction, ΔH, from T influence on ionic exchange equilibrium constant. ΔH values are discussed in term of chemical bonding or other interactions of cations with clayey material. As expected, temperature influence on measured K_d is found to be quite small, usually less than experimental reproducibility; but for Np(V) more accurate results are obtained by cancelling systematic errors. Temperature influence on $_3K_{H/Np}$ is smaller than on β_i and K_1. Van't Hoff equation is used to estimate $\Delta H(_3K_{H/Np}) = -2\pm4$ kJ.mol^{-1}.

Introduction

To assess the safety of radioactive waste disposal, the behaviour of radionuclides in porous media has to be known. Solute transport is controlled by hydrodynamics, physico-chemical interactions and aqueous chemistry. When these basic processes are known independently, their coupling can be calculated [1]. This type of prediction was checked experimentally [2] by using column experiments. Sorption properties of the clayey material were [3] characterised by studying Ca^{2+} migration at trace concentration in Na^+/H^+ aqueous solution.

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Taking into account aqueous speciation, experimental results of Np(V) migration (at trace concentration) were interpreted with NpO_2^+/H^+ ionic exchange, while Np(V) anionic carbonate complexes were predominated in the aqueous phase. Since temperature influence on ionic exchange equilibria has seldom been studied, we here focus on this subject, using the same methodology (liquid chromatography and data treatment) as at room temperature: at 5 to 45°C, Na^+, H^+ and Ca^{2+} are used first to characterise each sorption site, Np(V) migration is then measured at three different pH. The flow through the column is characterised by residence time distribution measurements, and modelled using a cell network model [1]. At constant Na^+ concentration, ionic exchange and surface complexation models are equivalent. They both rely on mass action law, hence on Gibbs energy de termination ($\Delta G = - R T \ln K$, where K is the equilibrium constant). Enthalpy of reaction, ΔH, can then be deduced from T influence by using classical thermodynamic equations. ΔH de termination can be useful to (1) compare with theoretical calculations, (2) discuss the type of interactions between species of the studied sorption equilibrium. The aim of the present work is to estimate whether one can deduce ΔH from temperature influence on sorption equilibria. For this, the main chemical equilibria involved in sorption system, are first identified.

Experimental section

Na^+/Ca^{2+} exchange was studied first as a function of pH using trace calcium (^{45}Ca). The material was equilibrated with 1 M Na^+ aqueous solutions. Np(V) migration in 1 M Na^+, 0.2 M (HCO_3^- + CO_3^{-2}), ClO_4^- solutions was then studied. Experiments were performed in liquid chromatography columns (7 cm long for a diameter of 1.6 cm) filled with a sand and Fo-Ca-7 clay (6.5% weight) mixture (typically 20.08 g). Before the first use the column was purged of air with CO_2. Before each experiment it was equilibrated with the working solution. The pore volume and the dispersion of the flow were determined by Residence Time Distribution measurements. For this, the response to a 2 ml pulse injection of a 0.5 M $NaClO_4$ solution was detected by conductivity at the outlet of the column. In our conditions (1 M $NaClO_4$ solutions) this pulse is a tracer of the aqueous electrolyte. All experiments were performed at the same flow rate, 1 ml/min. 2 ml of Np(V) solution at about 5.10^{-6} M were injected through the column. It had the same $Na^+/HCO_3^-/CO_3^{2-}/ClO_4^-$ composition as the eluting one. The solution was collected at the outlet of the column, and the total Np concentration was measured in each fraction by counting its α activity in an α–β discriminating liquid scintillation analyser (LKB-WALLAC 1219 RACKBETA).

For pH measurements, the glass electrode was calibrated in concentration units ($-\lg[H^+]$, not $-\lg(a_{H+})$)

by using HCO_3^-/CO_3^{2-} buffers at I = 1M and the equilibrium constants given in Table 1. More experimental details, eluting curves and other results are given in Ref.[3]. Series of experiments at three different $-lg[H^+]$ (8.76±0.10, 9.53±0.12 and 10.63±0.21, values at 25°C) have been performed at 5 to 45°C (Fig.2 and 3) in the same column, and using the same eluting solution. The difference in $-lg[H^+]$ was then only due to lgK_1 (= lg h + $lg[H^+]$, where h = $[CO_3^{2-}] / [HCO_3^-]$) variations with temperature (Table 1). In these experiments we found 0.1 uncertainty on lg h, that we attributed to pH measurement which were not scattered; but systematically shifted from 5 to 45°C. Typically these shifts were of 0.09 and -0.11 for $-lg[H^+]$ = 8.76 and 9.53 respectively.

Treatment of data

The retention volume V_R, was calculated from the measurement of the column response to pulse injections of element X, at steady flow: it is the first moment of the recovery peak. The value of the distribution coefficient,

$$K_{dX} = \frac{[\overline{X}]}{[X]} \qquad (1)$$

was calculated as

$$K_{dX} = \frac{V_p}{M}\left(\frac{V_R}{V_P} - 1\right) \qquad (2)$$

where [X] ($mol.l^{-1}$) and $[\overline{X}]$ ($mol.kg^{-1}$) are the total X concentrations in the aqueous phase and sorbed on the porous medium respectively. The pore volume, V_p, was calculated as the first moment of the recovery peak of a tracer of the aqueous phase. For each site, i, it is assumed that the X^{z+}/Y^+ ionic exchange equilibrium

$$\overline{{}_iX^{z+}} + z\,Y^+ \Leftrightarrow X^{z+} + z\,\overline{{}_iY^+} \qquad (3)$$

(where X^{z+} = (Na^+, Ca^{2+} or NpO_2^+), Y^+ = H^+, Na^+ or NpO_2^+), $\overline{{}_iX^{z+}}$ represents the species X^{z+} sorbed on sites i) is described by mass action law for ideal systems

$${}_iK_{X/Y} = \frac{[\overline{{}_iY^+}]^z[X^{z+}]}{[Y^+]^z[\overline{{}_iX^{z+}}]} \qquad (4)$$

Note that ${}_iK_{Na/Ca} = ({}_iK_{Na/H})^2 / {}_iK_{Ca/H}$, ${}_iK_{X/H} = 1 / {}_iK_{H/X}$, and that ${}_iK_{X/Y}$ is dimensionless for cations of same charge (z = 1), i.e. for $H^+/Na^+/NpO_2^+$ exchanges in our study. Ionic exchange capacity for site i, EC_i, is constant (mass balance equation), and

$$EC_i = [\overline{{}_iNa^+}] + [\overline{{}_iH^+}] \qquad (5)$$

since Ca and Np(V) where used at trace concentrations. The distribution coefficient of X^{z+} relative to site i, is

$$ {}_iK_{dX^{z+}} = \frac{\overline{[{}_iX^{z+}]}}{[X^{z+}]} \qquad (6) $$

Reporting Eq.(4) into Eq.(6) gives

$$ {}_iK_{dX^{z+}} = \frac{\overline{[{}_iY^{+}]}^{z}}{[Y^{+}]^{z}} \;/\; {}_iK_{X/Y} \qquad (6a) $$

Reporting Eq.(6a) for ${}_iK_{Na/Ca}$ and for ${}_iK_{Na/H}$, into Eq.(5) for calcium at trace concentration, gives

$$ {}_iK_{dCa} = \frac{{}_iK_{Na/Ca}\ EC_i^{2}}{[Na^{+}]^{2}(1+{}_iK_{Na/H}\dfrac{[H^{+}]}{[Na^{+}]})^{2}} \qquad (7) $$

At high pH ($[H^+] << [Na^+]\ {}_iK_{H/Na}$), $EC_i \approx [\overline{{}_iNa^{+}}]$ (Eq.5), $lg({}_iK_{dCa}) \approx P_i$ (Eq.7) is constant, where

$$ P_i = lg({}_iK_{Na/Ca}\ EC_i^2 / [Na^+]^2) \qquad (7a) $$

conversely, when $[H^+] >> [Na^+]\ {}_iK_{Na/Ca}$, $EC_i \approx [\overline{{}_iH^{+}}]$ (Eq.7),

$$ lg({}_iK_{dCa}) = lg({}_iK_{H/Ca}\ EC_i)^2 +2\ (-lg[H^+]) \qquad (7b) $$

The intercept of the two above limiting lines (Eq.7a and b), is obtained for $-lg[H^+] = pHi$,

$$ pH_i = 0.5\ lg({}_iK_{Na/H}) - lg[Na^+]) \qquad (7c) $$

The measured K_{dCa} values (Eq.2) were modelled by reporting Eq.(7) into

$$ K_{dCa} = {}_1K_{dCa} + {}_2K_{dCa} + {}_3K_{dCa} \qquad (8) $$

Similar modelling was used for K_{dNp}. At low pH, Ca^{2+} is expected to be sorbed only on site 1, $K_{dCa} \approx {}_1K_{dCa}$ (Eq.8), and lgK_{dCa} is a straight line of slope +2 (Eq.7b) as a function of $-lg[H^+]$. Increasing pH above pH_1 (Eq.7c) a plateau, P_1, is reached (Eq.7a). Increasing again pH, K_{dCa} will increase after the first plateau, to a second plateau corresponding to sorption site 2, and so on. Evidence of 3 ionic exchange sites was found in this way (Fig.1); but the third plateau was not reached because high enough pH could not be used (avoiding clay dissolution).

Np(V) sorption was interpreted as NpO_2^+ ionic exchange on the third site (i = 3), hence ${}_3K_{dNp} = K_{dNp}$ (Eq.8). $K_d°$ notation is used for ${}_3K_{dNpO_2^+}$ (Eq.6).

$$ K_d° = \alpha\ K_{dNp} \qquad (9) $$

is deduced from K_{dNp} definition (Eq.1), where

$$ \alpha = 1 + \sum_{j=1}^{3}\beta_j[CO_3^{2-}]^j + \sum_{j=1}^{2}{}^*\beta_j[H^+]^{-j} + {}^*\beta_{2,2}\,[CO_3^{2-}]^2 / [H^+]^2 \qquad (10) $$

is Np(V) complexation coefficient (calculated with the constants of Table 1). When $-\lg[H^+] << 10$, $EC_3 \approx [\overline{{}_3H^+}]$ (Eq.5), using this approximation and Eq.(9) gives similarly as Eq.(7b)

$$\lg K_d^\circ \approx \lg({}_3K_{H/Np}\ EC_3) + (-\lg[H^+]) \tag{11}$$

Hence, the curve $\lg K_d^\circ$ vs. $-\lg[H^+]$ is a straight line of slope +1, and this was used as evidence of the

$$\overline{{}_iNpO_2^+} + H^+ \Leftrightarrow NpO_2^+ + \overline{{}_iH^+} \tag{12}$$

ionic exchange equilibrium (Fig.2). Conversely, when site 3 is under Na^+ form, $K_d^\circ \approx ({}_3K_{Na/Np}\ EC_3) / [Na^+]$: the curve $\lg K_d^\circ$ vs. $-\lg[H^+]$ is expected to be a horizontal line (Fig.3). In chemical conditions where $[\overline{{}_3Na^+}] << [\overline{{}_3H^+}] \approx EC_3$, $[CO_3^{2-}] << [HCO_3^-] \approx [CO_3]_t = 0.2\ mol.l^{-1}$ and $[Np(V)] \approx [NpO_2(CO_3)_3^{5-}] = [NpO_2^+]\ \beta_3\ [CO_3^{2-}]^3 = [NpO_2^+]\ \beta_3\ (K_1\ [HCO_3^-]/[H^+])^3 \approx [NpO_2^+]\ \beta_3\ K_1^3\ [CO_3]_t^3/[H^+]^3$ (Eq.1, 6a and 9)

$$\lg K_{dNp} \approx \lg({}_3K_{H/Np}\ EC_3 / (\beta_3\ K_1^3\ [CO_3]_t^3)) - 2\ (-\lg[H^+]) \tag{11a}$$

where EC_3 is a constant, $({}_3K_{H/Np} / K_1^3\ \beta_3)$ is the constant of the equilibrium

$$\overline{{}_iNpO_2^+} + 3\ HCO_3^- \Leftrightarrow NpO_2(CO_3)_3^{5-} + 2\ H^+ + \overline{{}_iH^+} \tag{12a}$$

and $[CO_3]_t$ was constant in our experiments. The constant of equilibrium(12), ${}_3K_{H/Np}$, is then calculated by using K_1 and β_3 auxiliary data. This is implicitly a thermodynamic cycle from equilibrium (12a) to equilibrium (12). For temperature influence we rather used

$$\overline{{}_iNpO_2^+} + HCO_3^- + 2\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + \overline{{}_iH^+} \tag{12b}$$

equilibrium, because $[HCO_3^-]$ and $[CO_3^{2-}]$ did not vary with temperature in each set of experiments (their derivative with T is zero), while pH (as $\lg K_1$) did vary with T. Using the above approximations, equilibrium (12b) corresponds to

$$\lg K_{dNp} \approx \lg({}_3K_{H/Np}\ EC_3 / (\beta_3\ K_1)) - \lg[HCO_3^-] - 2\ \lg[CO_3^{2-}] \tag{11b}$$

Temperature influence on equilibrium constant was interpreted [4] with series expansion

$$R \ln K(T,I) \approx R \ln K(T^\circ,I) - \Delta H(T^\circ,I)\ \Delta(1/T) + T^{\circ 2}\ \Delta C_p(T^\circ,I)\ (\Delta(1/T))^2 / 2 \tag{13}$$

where $\Delta(1/T) = 1/T - 1/T^\circ$, and $T^\circ = 298.15$ K. Heat capacity contribution was neglected, this is equivalent to the Van't Hoff equation

$$\Delta H = -R \ln 10 \left(\frac{\partial \lg K}{\partial \frac{1}{T}} \right)_P \tag{14}$$

Parameters needed for I corrections at T≠T° are poorly known, using ΔH minimises the corresponding uncertainty [4]. Deriving Eq.(11b) gives

$$\Delta H({}_3K_{H/Np}/(\beta_3\ K_1)) = -\ R\ \ln 10\ \left(\frac{\partial \lg K_{dh}}{\partial \frac{1}{T}}\right)_P \tag{15}$$

where K_{dh} is K_{dNp} and $\Delta H({}_3K_{H/Np}/(\beta_3\ K_1)) \approx \Delta H_h$ is the enthalpy reaction (Eq.12b), both in chemical conditions where approximations leading to Eq.(11b) are valid, and for a set of experiments where $[HCO_3^-]$ and $[CO_3^{2-}]$ did not vary with T (corresponding to $-\lg[H^+] = h$ at 25°C). Hence (Eq.15)

$$\Delta H_h \approx \Delta H({}_3K_{H/Np}) - \Delta H(K_1) - \Delta H(\beta_3) \tag{15a}$$

This is an approximation since partial dissociation of the Np(V) limiting complex, and partial deprotonation of site 3 are neglected in Eq.(15a). Actually the more general equation (also valid in other chemical conditions)

$$\Delta H_h = \Delta H({}_3K_{H/Np}) - y\ \Delta H(K_1) - x\ \Delta H(\beta_3) - (1 - x)\ \Delta H(\beta_2) + (1 - y)\ \Delta H({}_3K_{Na/H}) \tag{16}$$

was used where $x = [NpO_2(CO_3)_3^{5-}] / [Np]_t \approx 1 / (1 + 1 / k_3\ [CO_3^{2-}])$, $k_3 = \beta_3/\beta_2$, $y = [\overline{{}_3H^+}] / CE = 1 /(1 + {}_3K_{H/Na}\ [Na^+] / [H^+])$. x was constant in a set of experiments, (1 - y) variations with T, were small. The systematic error of 0.09 and -0.11 for $-\lg[H^+] = 8.76$ and 9.53 respectively during Np(V) migration study (see Experimental Section) induces an error on $\lg({}_3K_{H/Np})$ determination, which in turn induces -4.5 and 2.7 kJ.mol^{-1} shifts on $\Delta H({}_3K_{H/Np})$ determinations (Eq.16).

Results and interpretation

The curve representing the $\lg K_{dCa}$ vs. $-\lg[H^+]$ shows two plateaux; a third one is not reached (Fig.1). Each plateau corresponds to one sorption site saturated by Na^+. Its height (P_i in Fig.1) is given (Eq.7a) by the exchange capacity (CE_i), $[Na^+]$ (constant in this study) and the Na^+/Ca^{2+} exchange constant (${}_iK_{dCa}$). Before the ith plateau, the site i is saturated by H^+ and $\lg({}_iK_{dCa})$ vs. $-\lg[H^+]$ has a slope of 2 (Eq.7b). Front position (pH_i on Fig.1) is given by $[Na^+]$ and ${}_iK_{Na/H}$ (Eq.7c). Calcium sorption was modelled with three sorption sites. ${}_iK_{Na/H}$ and ${}_iK_{H/Ca}$ values (Table 2) were then deduced by using were determined by curve fitting Eq.(7), CE_i was independently known [3]. Protonation of site 1 was hardly detected, and ${}_1K_{Na/H}$ could not be estimated accurately. Saturation of site 3 by Na^+ cation, could only be obtained at high pH where clay could be altered. For this reason uncertainties on ${}_3K_{Na/Ca}$ and ${}_3K_{Na/H}$ were increased. Uncertainty on ${}_2K_{Na/H}$ was quite important for unexplained reason. The data on Na^+/H^+ exchange were too scattered to detect temperature influence and this is reflected on pH_i position (Fig.1), and on uncertainty attributed to ΔH values (Table 2). Ca^{2+} sorption on site 2 slightly increases with temperature, while on site 1, Ca^{2+} sorption is not temperature dependent within experimental uncertainty. The values of the (dimensionless) ${}_2K_{Na/H}$ and ${}_3K_{Na/H}$ constants are much bigger than 1, which indicates H^+ is more strongly bounded on sites 2 and 3 than Na^+. While H^+ interaction with site 1 is hardly detected (pH_1 is not detected on Fig.1) and ${}_1K_{Na/H}$ value could not be measured: this is consistent with a ${}_1K_{Na/H}$ value of about 1, and (Na^+ or H^+) ion pairing with site 1. Determinations of the corresponding $\Delta H({}_iK_{Na/H})$ values are not accurate enough to confirm or not these interpretations.

Ca^{2+} sorption on site 1 is again weaker than on site 2, and $\Delta H({}_2K_{Na/Ca}) = 12 \pm 6$ kJ.mol.$^{-1}$ seems to be consistent with stronger interaction of Ca^{2+} than Na^+: it is of the order of magnitude of enthalpy of reaction in aqueous solutions involving chemical bound (and not only ion pairing).

In 1 M $NaClO_4$, 0.2 M total carbonate concentration media, the curve lgKd° (= $lgK_{dNpO_2^+}$) vs. -lg[H^+] has a slope of +1 for -lg[H^+] < 10.5, beyond the slope decreases (Fig.2). Np(V) sorption is then interpreted (Eq.11) as a simple H^+/NpO_2^+ ionic exchange (Eq.12). In pH conditions used in this Np(V) study, sites 1 and 2 were clearly saturated by Na^+, hence H^+/NpO_2^+ ionic exchange can only be attributed to a third site corresponding to lgK_{dCa} increase at -lg[H^+] > 10 on Fig.1. H^+ from the third site of the clayey material is exchanged with aqueous NpO_2^+ although it is not the Np(V) main species in solution. This interpretation is quite straightforward because we have used lgK_d° (Eq.9 and 11). This is a way to eliminate the coupling of Np(V) aqueous speciation, that is independently known (and calculated), and that explains the shape of the raw lgK_d curve (Fig.2). Typically for -lg[H^+] ≈ 9.2 the approximations leading to Eq.(11a) are valid, and a slope of about -2 is indeed observed for the experimental results. In other chemical conditions other approximations are used taking into account the changes of Np(V) and carbonate aqueous speciation, and eventually Na^+/H^+ exchange on site 3. The main Np(V) carbonate aqueous complex containing the NpO_2^+ cation exchanged for H^+ (or eventually Na^+), is written on Fig.2 together with the compensating anion (HCO_3^- or CO_3^{2-}) in each pH domain and the slope of lgK_{dNp} vs. -lg[H^+]. Each point of the upper curve, lgK_d°, was deduced from a point of the lower curve, lgK_{dNp}, by a vertical translation of lgα (Eq.9), which is calculated (Eq.10) from known parameters (Table 1) and chemical conditions: Figure 2 shows the dramatic effect of aqueous speciation on the shape of lgK_d curve as compared to the H^+/NpO_2^+ ionic exchange process (lgK_d° curve). Series of experiments at three different -lg[H^+] (8.76, 9.53 and 10.63, values at 25°C) have been performed at 5 to 45°C (Fig.2 and 3). As for Ca^{2+}, temperature influence on Np(V) migration is small. lgK_d° nearly fall on a single line while lgK_d ones are not: temperature influence is more important on aqueous speciation, than on the H^+/NpO_2^+ ionic exchange process. Aqueous speciation contribution to ΔH_h is (Eq.16) indeed more important than the contribution of ionic exchange reaction, $\Delta H({}_3K_{H/Np})$. Typically $\Delta H_{8.76} = -4.6\pm7.2$ kJ.mol^{-1} and $\Delta H_{9.53} = 0.5\pm1.8$ kJ.mol^{-1} were measured (Fig.3), while $\Delta H(K_1) = 14.7\pm0.3$ kJ.mol^{-1} is balanced (in Eq.16) by $\Delta H(\beta_3) \approx -15.1\pm1$ kJ.mol^{-1} (Table 1). From $\Delta H_{8.76}$ and $\Delta H_{9.53}$, $\Delta H({}_3K_{H/Np}) \approx -5.5\pm7.3$ and -2.1 ± 2.5 kJ.mol^{-1} are deduced (Eq.16) where uncertainty is 1.96 standard deviation. Taking into account the +4.5 and -2.7 kJ.mol^{-1} shifts induced by the pH measurements (see Section treatment of data), these two values are closer and in agreement with $\Delta H({}_3K_{H/Np})$ 2±4 kJ obtained by using the Van't Hoff equation on ${}_3K_{H/Np}$ determined (Table 2) at each temperature (from the three K_d measurements performed at each temperature). The most accurate $\Delta H({}_3K_{H/Np})$ determination,

$$\Delta H({}_3K_{H/Np}) \qquad = -2\pm4 \text{ kJ.mol}^{-1}$$

is the one obtained from $\Delta H_{9.53}$, because uncertainty due to pH measurement is smaller and systematic error cancels since the same buffering HCO_3^- and CO_3^{2-} concentrations in the same column, were used in a set of experiments at 5 to 45°C. $\Delta H({}_3K_{H/Np}) = -2\pm3$ kJ.mol^{-1} value indicates H^+ and NpO_2^+ interactions with site 3 have similar energy.

Finally cationic exchange equilibria on clayey material from aqueous solutions at fixed Na^+ concentration, could be described by using the mass action law for ideal systems. The equilibrium constants (Table 1) for ions of same charge are dimensionless and their relative values can then be used to compare their relative affinity for the third site of the Fo-Ca-7 clayey mineral: $H^+ > NpO_2^+ >> Na^+$. This suggests that Na^+ weak interaction to this third site could be of ion-pairing type, while H^+ and NpO_2^+ much stronger interaction to the third site would rather be similar to chemical bounding.

Let us point out that temperature influence on ionic exchange equilibrium constant is usually smaller than many possible systematic errors and than temperature influence on auxiliary data used in thermodynamic cycles. Reliable data could only be obtained by using the same column and the same eluting solution that was buffered, to cancel some of the systematic errors. Reasonable accuracy might alternatively be obtained by using temperature gradient.

Notations

EC_i	exchange capacity of the site i (meq/100g), in the theoretical formula, SI units (eq/kg) are used
${}_iK_d$, ${}_iK_{dX}$	distribution coefficient (ml/g) (it is equivalent to the SI units, l/kg) of element X sorbed on site i
K_{dX}	distribution coefficient (ml/g) of element X, X=Np or Ca
$K_d°$	NpO_2^+ distribution coefficient (ml/g) (Eq.9) on site 3

K_{dh}	K_{dNp} for a set of experiments where $[HCO_3^-]$ and $[CO_3^{2-}]$ did not vary with T ($-lg[H^+] = h$ at 25°C)
M	clay mass (g)
V_p	pore volume (ml)
V_R	retention volume (ml)
$\overline{{}_iX^{z+}}$	species X sorbed on site i
$[\overline{{}_iX^{z+}}]$	concentration of X sorbed at the solid surface (mol/kg)
[X]	concentration of X in aqueous solution (mol/l)
$\Delta H(K)$	enthalpy change corresponding to the equilibrium constant, K (Eq.13 and 14)
ΔH_h	enthalpy change measured at $-lg[H^+] = h$ (Eq.16)

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Captions to the figures

Figure 1: $\mathrm{lgK_{dCa}}$ values at different temperatures measured by column experiments with Fo-Ca-7 clayey mineral and 1 M $NaClO_4$ aqueous solutions. The curves were drawn by using the ion exchange theory (mass action law for ideal system) with three sorption sites (Eq.7), the numerical values of the exchange capacities, EC_i, and of the constants at 25°C, $\mathrm{lg}({}_iK_{Na/H})$ and $\mathrm{lg}({}_iK_{Na/Ca})$, given in Table 1. Each plateau, P_i (Eq.7a), and "front", slope 2 and pH_i (Eq.7b and c), is interpreted as evidence of a sorption site (see text).

Figure 2 : Np(V) and NpO_2^+ distribution coefficients, K_{dNp} (squares) and $K_d°$ (circles) respectively, with Fo-Ca-7 clayey mineral and 1 M Na^+, $[CO_3]_t$ = 0.2 M, ClO_4^- aqueous solution. The slope +1 (upper curve) for $\mathrm{lg}K_d°$ (at $-\mathrm{lg}[H^+] < 10.5$), is interpreted as ionic exchange between H^+ and NpO_2^+ (Eq.11). $\mathrm{lg}K_d°$ is calculated as $\mathrm{lg}\,\alpha + \mathrm{lg}K_{dNp}$ (Eq.9), where K_{dNp} is measured by column experiments, and α is Np(V) complexation coefficient (Eq.10). Hence each $\mathrm{lg}K_d°$ point is translated vertically by $\mathrm{lg}\alpha$ from the corresponding $\mathrm{lg}K_{dNp}$ one. For $\mathrm{lg}K_{dNp}$, the slopes are due to the aqueous speciation(α) and eventually Na^+/H^+ exchange on site 3 of the clay (as written on the figure). Lines are calculated with equilibrium constants of Tables 1 and 2. Data (+, x) at 25°C were taken from various experiments in different columns, while the other ones (at 5 to 15°C) were obtained from 3 series in the same column (where $-\mathrm{lg}[H^+]$ = 8.76±0.10, 9.53±0.12 and 10.63±0.21, values at 25°C) using the same eluting solution for each series. Only the data for these three series were used for curve fitting.

Fig.3: Temperature influence on $\mathrm{lgK_{dNp}}$ values for $-\mathrm{lg}[H^+]$ = 8.76±0.10, 9.53±0.12 and 10.63±0.21. The experimental data are taken from Fig.2. The slopes (lines) are used (Eq.15) to calculate ΔH_h corresponding approximately to reaction (12.b). $\Delta H({}_3K_{H/Np})$ was then calculated (Eq.16) from ΔH_h, $\Delta H(\beta_3)$ and $\Delta H(K_1)$ (Table 2).

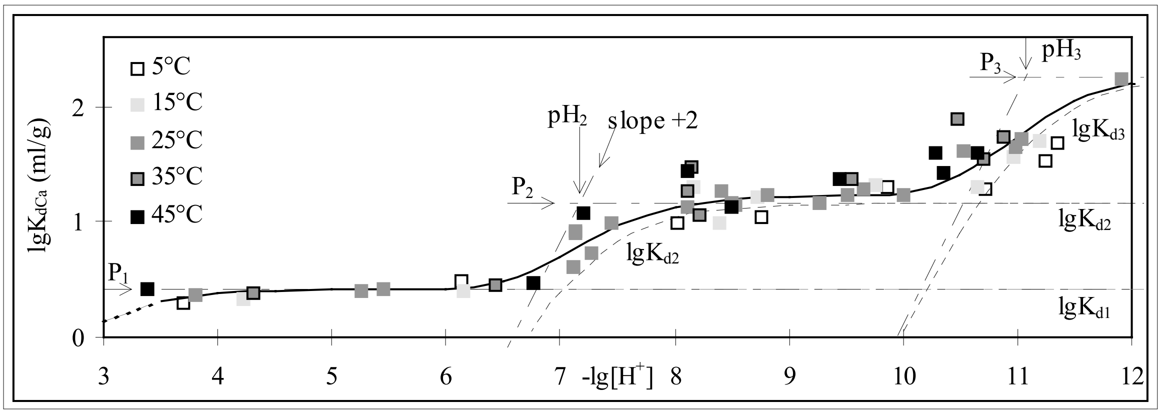

Fig1

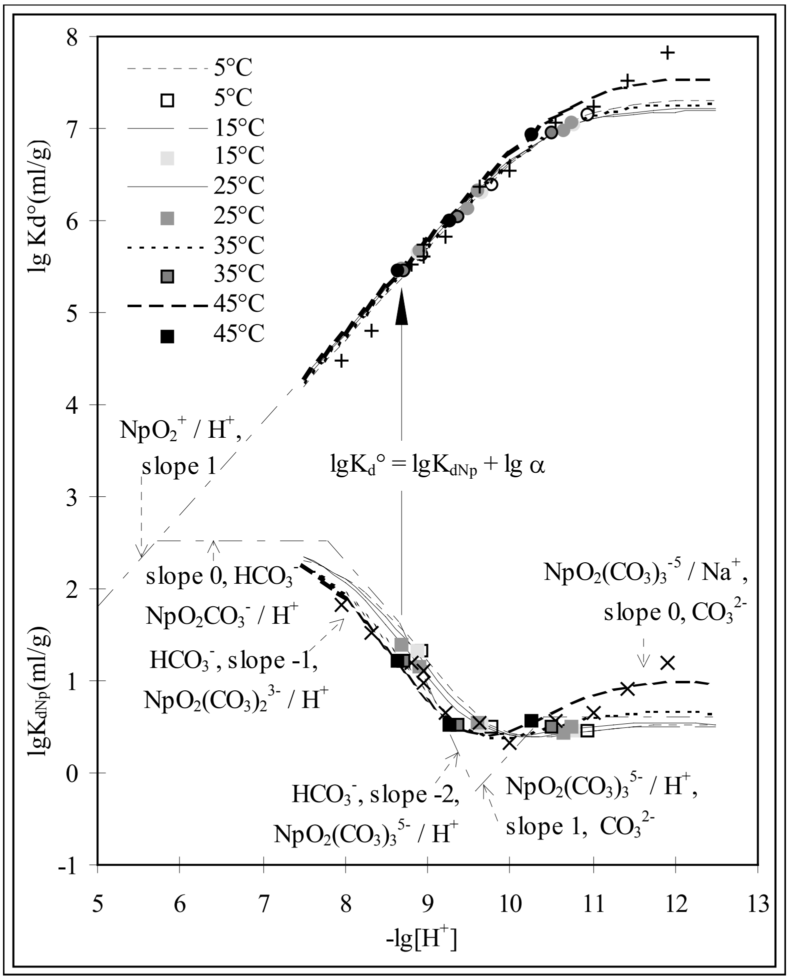

Fig.2

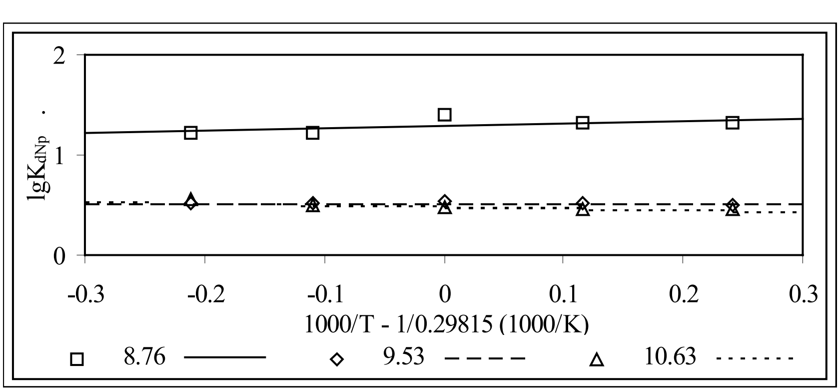

Fig.3

K definition	medium	lgK(5°C)	lgK(15°C)	lgK(25°C)	lgK(35°C)	lgK(45°C)	ΔH(25°C)
$K_w = [H^+]\,[OH^-] / a_{H_2O}$	I = 0	-14.704 ± 0.014	-14.340 ± 0.014	-14.001 ± 0.014	-13.684 ± 0.014	-13.386 ± 0.014	$55.81_5 \pm 0.05_7$
	1 M $[NaClO_4]^{(a)}$	$-14.55_1 \pm 0.03_5$	$-14.18_2 \pm 0.02_9$	$-13.83_8 \pm 0.02_7$	-13.51	-13.22	$55.82_0 \pm 0.05_7$
	1 M $[NaClO_4]^{(b)}$	-14.59	-14.19	-13.83	-13.51	-13.22	
$K_p = [H^+]\,[HCO_3^-] / (P_{CO_2}\, a_{H_2O})$	I = 0			$-7.82_6 \pm 0.02$			
	1 M $[NaClO_4]^{(a)}$			$-7.62_1 \pm 0.03_6$			
$K_1 = [H^+]\,[CO_3^{2-}] / [HCO_3^-]$	I = 0	$-10.51_4 \pm 0.02$	$-10.41_8 \pm 0.02$	$-10.32_9 \pm 0.02$	$-10.24_5 \pm 0.02$	$-10.16_7 \pm 0.02$	14.7 ± 0.3
	1 M $[NaClO_4]^{(a)}$	$-9.79_6 \pm 0.05_2$	$-9.66_9 \pm 0.05$	$-9.59_1 \pm 0.04_8$	$9.49_6 \pm 0.04_9$	$-9.40_2 \pm 0.05_2$	$14.7_1 \pm 0.3_2$
$K_{12} = [H^+]\,[HCO_3^-] / ([CO_{2(aq)}] + [H_2CO_{3(aq)}])$	I = 0			$-6.35_4 \pm 0.02$			
	1 M $[NaClO_4]^{(a)}$			$-6.14_9 \pm 0.03_6$			
$\beta_1 = [NpO_2CO_3^-] / ([NpO_2^+]\,[CO_3^{2-}])$	I = 0	$5.14_8 \pm 0.04_9$	$5.04_5 \pm 0.04_9$	$4.94_8 \pm 0.04_9$	$4.85_8 \pm 0.04_9$	$4.77_3 \pm 0.04_9$	$-15.9_1 \pm 0.5_2$
	1 M $[NaClO_4]^{(a)}$	$4.78_4 \pm 0.27_1$	$4.67_1 \pm 0.20$	$4.56_4 \pm 0.17_0$	$4.46_1 \pm 0.20$	$4.36_1 \pm 0.27_1$	$-15.8_3 \pm 0.5_2$
	1 M $[NaClO_4]^{(c)}$			$4.5_7 \pm 0.3_5$			
$\beta_2 = [NpO_2(CO_3)_2^{3-}] / ([NpO_2^+]\,[CO_3^{2-}]^2)$	I = 0	$6.71_3 \pm 0.19_4$	$6.61_2 \pm 0.19_4$	$6.51_7 \pm 0.19_4$	$6.42_9 \pm 0.19_4$	$6.34_6 \pm 0.19_4$	$-15.5_6 \pm 0.5_2$
	1 M $[NaClO_4]^{(a)}$	$7.2_{64} \pm 0.3_{34}$	$7.1_{62} \pm 0.2_{79}$	$7.0_{67} \pm 0.2_{59}$	$6.9_{79} \pm 0.2_{79}$	$6.8_{96} \pm 0.3_{34}$	$-15.4_8 \pm 0.5_2$
	1 M $[NaClO_4]^{(c)}$			$7.0_3 \pm 0.2_4$			
$\beta_3 = [NpO_2(CO_3)_3^{5-}] / ([NpO_2^+]\,[CO_3^{2-}]^3)$	I = 0	$5.67_1 \pm 0.16_5$	$5.57_2 \pm 0.16_4$	$5.47_9 \pm 0.16_4$	$5.39_2 \pm 0.16_4$	$5.31_1 \pm 0.16_4$	$-15.2_4 \pm 1.0_3$

	1 M [$NaClO_4$](a)	$8.8_{18} \pm 0.3_{63}$	$8.7_{46} \pm 0.3_{14}$	$8.6_{85} \pm 0.2_{96}$	$8.6_{35} \pm 0.3_{14}$	$8.6_{0} \pm 0.3_{63}$	$-15.1_{4} \pm 1.0_{3}$
	1 M [$NaClO_4$](c)			$8.5_{2} \pm 0.4_{1}$			
$^*\beta_1 = [NpO_2OH_{(aq)}]\,[H^+] / ([NpO_2^+]\,a_{H_2O})$	1 M [$NaClO_4$](a,d)			-11.7 ± 0.9	$-11.7 \pm 0.6_{2}$		
$^*\beta_2 = [NpO_2(OH)_2^-]\,[H^+]^2 / ([NpO_2^+]\,a^2_{H_2O})$	1 M [$NaClO_4$](a,d)			$-23.1_{1} \pm 1.0$	-23.11 ± 0.05		
$^*\beta_{22} = [NpO_2(OH)_2(CO_3)_2^{5-}]\,[H^+]^2 / ([NpO_2^+]\,[CO_3^{2-}]^2\,a^2_{H_2O})$	1 M [$NaClO_4$](a)			$-22.3_{1} \pm 1.6_{8}$ -18.15 ± 1.42			

(a) Calculated by using the SIT formula, excepted for $^*\beta_i$, and used in the present work.

(b) Calculated from values at I = 0 taken from Ref.[7].

(c) Calculated in Ref.[8] from published measurements in 1 M [$NaClO_4$].

(d) Published measurements in 1 M [$NaClO_4$], were uncertainty has been re-evaluated [8].

Table 1: Aquatic chemistry constants at 25°C in molar unit. Np(V) data were obtained from our literature critical review [8]. Equilibrium constants for other systems are calculated in 1 M [$NaClO_4$] medium by using the SIT [5,9], from data at I = 0 [5]. For comparison, selected experimental data in 1 M $NaClO_4$ medium for Np(V) carbonate [10] and hydroxide [11] complexes are tabulated as recalculated in our review [8]. For K_w and K_1, corresponding ΔH (kJ.mol.$^{-1}$) of reaction are calculated from standard (I = 0) enthalpy of formation [5], and then calculated at I = 1 M by using the SIT formula [4]. For Np(V) constants, similar ΔH calculations are performed from original data [6] measured at I = 0.1 M.. Temperature influence on SIT coefficient, Δε, was neglected. For this approximation, uncertainty on Δε/ΔT have been arbitrary increased by 0.001 kg.mol.$^{-1}$.K^{-1} for K_w and K_1, and by 0.01 kg.mol.$^{-1}$.K^{-1} for Np(V) carbonate complexes. Heat capacity contribution was neglected when calculating (Eq.13) temperature influence on equilibrium constants.

Constant	lgK(5°C)	lgK(15°C)	lgK(25°C)	lgK(35°C)	lgK(45°C)	lgK$^{(a,b)}$	ΔH$^{(a)}$ (kJ.mol.$^{-1}$)	ΔG$^{(a)}$ (kJ.mol.$^{-1}$)	ΔS$^{(a)}$ (J.K^{-1}.mol.$^{-1}$)
${}_1K_{Na/Ca}{}^{(b)}$	0.91 ± 0.15	0.78 ± 0.15	0.84 ± 0.15	0.84 ± 0.15	0.89 ± 0.15	**0.85 ± 0.1**	**-2 ± 6**	-4.8 ± 0.9	17 ± 20
${}_2K_{Na/Ca}{}^{(b)}$	3.5$_1$ ± 0.30	3.58 ± 0.15	3.6$_0$ ± 0.20	3.8$_0$ ± 0.35	3.7$_6$ ± 0.4	**3.66 ± 0.1**	**12 ± 6**	-20.9 ± 0.9	112 ± 20
${}_3K_{Na/Ca}{}^{(b)}$	3.7$_1$ ± 0.4	3.7$_2$ ± 0.4	4.4$_3$ ± 0.4	4.0$_7$ ± 0.4	4.1$_5$ ± 0.4	4.0 ± 0.3$_4$	17 ± 50$^{(e)}$	-23.$_1$ ± 2.$_3$	136 ± 170$^{(e)}$
${}_2K_{Na/H}{}^{(c)}$	7.5$_7$ ± 0.5	6.9$_1$ ± 0.5	7.1$_6$ ± 0.5	7.4$_2$ ± 0.5	7.1$_7$ ± 0.5	**7.24 ± 0.2$_6$**	-6 ± 31$^{(e)}$	-41.3 ± 1.1	120 ± 100$^{(e)}$
${}_3K_{Na/H}{}^{(c)}$	10.6 ± 0.5	10.5 ± 0.5	10.4 ± 0.5	10.5 ± 0.5	10.8 ± 0.5	10.6 ± 0.4	6 ± 15$^{(e)}$	-60.$_3$ ± 2.$_9$	224 ± 51$^{(e)}$
${}_3K_{H/Np}{}^{(c)}$	-2.2$_0$ ± 0.4	-2.1$_4$ ± 0.4	-2.1$_4$ ± 0.4	-2.1$_7$ ± 0.4	-2.1$_2$ ± 0.4	**-2.1$_5$ ± 0.3**	2 ± 4	12.$_3$ ± 2.$_3$	-33 ± 34
${}_3K_{H/Np}{}^{(c,d)}$							**-2 ± 4**		

$^{(a)}$constants at 25°C, determined from experimental data at 5 to 45°C, by using Van't Hoff equation (Eq.13 neglecting heat capacity contribution).

$^{(b)}{}_iK_{Na/Ca}$ unit is (kg/l).

$^{(c)}{}_iK_{Na/H}$ and ${}_iK_{H/Np}$ are dimensionless.

$^{(d)}$Preferred value determined from Fig.3 to minimise error from pH measurement (see text).

$^{(e)}$lgK determinations were not accurate enough to detect temperature influence, hence corresponding ΔH and ΔS values could not really be determined.

Table 2: Thermodynamic data for ionic exchange equilibria as determined in the present work in 1 M $NaClO_4$ media from the experimental data shown in Fig.1 and 2. The most reliable values are bolded. Enthalpies of reactions (mean value about 25°C) are calculated by using series expansions (Eq.13 and 14), from experimental data shown in Fig.1 for Na^+/Ca^{2+} and Na^+/H^+ exchanges, and similarly for $H^+/NpO_2{}^+$ exchange. $\Delta G = -R\ T° \ln K$ and $\Delta S = (\Delta H - \Delta G) / 298.15$ are also tabulated, where K is the value at 25°C obtained by linear regression from data at 5 to 45°C (footnote$^{(a)}$). Ionic exchange capacities, EC_i = 61, 6 and 8 meq/100g for site i (i = 1, 2 and 3 respectively) are taken from [3].