# Study of Ionic Exchanges of Np(V)-ions on Natural Clay Minerals and Goethite, in Carbonate media, by Column Experiments.

**Michel Sardin\*, Jacques Ly, France Lefèvre, Pierre Vitorge**

**\*LSGC-CNRS, ENSIC(INPL),** 1 rue Grandville, BP 451, 54001 Nancy Cedex - France

**CEA DCC/DESD/SESD/Section de Géochimie ,** BP 6, 92265 Fontenay-aux-Roses Cedex - France.pierre.vitorge(at)cea.fr.

## Figure 1: Published Sorption Data

Kd° is experimental Kd value corrected for the influence of Np(V) complexation in aqueous solution: **Kd° = x Kd, where x = [Np(V)]t,aq / [NpO$_2$$^+$].** x is calculated from chemical conditions (typically pH and [CO$_3$]$_{t,aq}$) and known complexation constants. Note that Kd° = Kd in non complexing (typically acidic) media: Kd° is the "partition coefficient of NpO$_2$$^+$", while Kd is the " partition coefficient of total Np(V)".

Depending on pH, clay sorption sites, S, are expected to be in either sodic (SONa) or acidic (SOH) form. These classical **Na$^+$ / H$^+$ cationic exchanges between major cations**, is competing Np sorption. Np is at trace concentration: it cannot modify the heterogeneous equilibria of major ions. According to the ionic exchange theory, the ratio of the sodic to the acidic form of the clay is only dependent on the [Na$^+$]/[H$^+$] ratio. Data are then plotted vs. X = lg([Na$^+$]/[H$^+$]) = pH + lg[Na$^+$].

lg Kd° is expected to be proportional to -lg[M$^+$] (M$^+$ = Na$^+$ or H$^+$), when sorption is due to the **M$_{(f)}$ + NpO$_2$$^+$ <=> M$^+$ + NpO$_{2(f)}$** ionic exchange, **and** when the clay is in M form (i.e SOM predominates). Straightforward calculations using the **ionic exchange theory**, indicate that Kd° [Na$^+$] as well as Kd° [H$^+$] are only dependent on the [Na$^+$]/[H$^+$] ratio. We then plot Y = lg(Kd° [Na$^+$]) = lgKd° + lg[Na$^+$].

Observed **slope 1** is consistent with this representation. See the figures 3 and 4 for more details on the above interpretation in two particular cases. We also add our results (black sqares) taken from the figure 3.
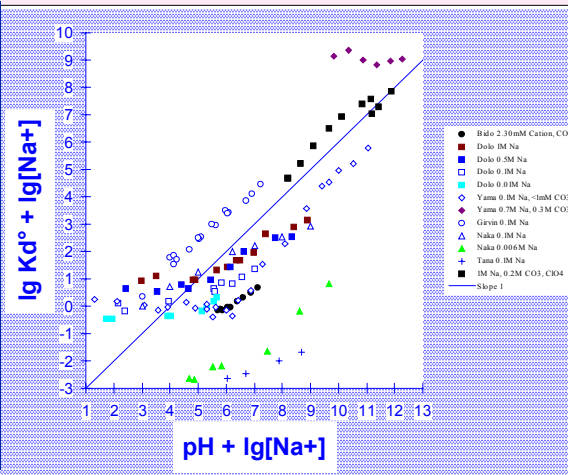


## Figure 2: Typical Chromatograms of Np(V)

**Column** are first **purged with CO$_2$ gas,** and saturated with 0.05 M CaCl$_2$. The **pore volume (Vp = Q µ$_1$)** and the **dispersion of the flow** are deduced from the first moment, µ1, and variance of a **pulse injection of CaCl$_2$** detected by conductivity at the outlet of the column. **Injections of $^{22}$Na at different pH** are interpreted as three exchange capacities. The choice of experimental conditions for injection of Np(V) is determined by theoretical considerations on Kd, that are checked by a priori simulation (not shown on the figure) of the breakthrough curves, with the IMPACT code.

**Experiments:** $^{237}$Np(V) is typically 8µM in ([HCO$_2$$^-$] + [CO$_2$$^{+2}$] = 0.2 M, [Na$^+$] = 1 M, ) aqueous solutions. The response to pulse-injections (0.5 Vp) is counted in each collected fraction, by liquid scintillation (only on the alpha signal). If the recovery is close to 100%, Kd (figure 3) is deduced from the first moment of the recovery peak. Flow rate is Q = 0.5 ml/mn.

**The variations of dispersion and position of the peak** (and then of Kd) with pH, do not depend on flow rate (this is not shown on the figures). It is then mainly attributed to competing sorption mechanisms of trace (NpO$_2$$^+$) and of major (H$^+$, Na$^+$) cations on the porous medium (see figure 3). **A minimum retention is found at pH 9.65.**
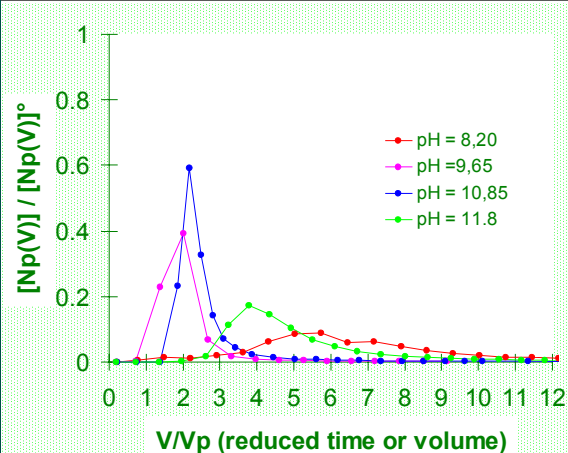
# Abstract

Migration of Np(V) through natural porous media is governed by both the water motion and the heterogeneous and homogeneous reactions, that occur in solution and on the solid. Usually, a lumped coefficient, so-called distribution coefficient, Kd, is used to describe radioelement retention. But, published Kd can vary by up to 6 orders of magnitude with soil and solution compositions (typically pH).

To understand and quantify the mechanisms, that control the transport of neptunium, **transient experiments of Np(V) injection in sodo-carbonated** medium have been performed in **columns packed with a mixture of silica sand and natural clay minerals (6.5%, essentially smectite and kaolinite with 6.5% of goethite)**. The Kd is measured from the mean position of the experimental response at the oulet of the column. The curve lg(Kd) vs. pH displays a characteristic shape, decreasing from 1.5 at pH 8.2 to 0.5 at pH 9.8, value for which a minimum is observed and increasing 1.3 at pH 11.8.

Even when Np(V) anionic complexes are predominant in the aqueous solution, **adsorption should essentially be attributed to its cationic form, NpO$_2$$^+$. Kd variations are modelled by using aqueous speciation, and ionic exchange equilibria** on the porous medium involving Np(V) at trace concentration **and several** major aqueous ions. The **two sites of Na$^+$ / H$^+$ cationic exchange**, found in neutral to acidic media are attributed to clay minerals. In neutral to basic media a third site, S, is probably amphoteric. It is completely anionic above pH 11. At pH less than 9 HCO$_3$$^-$/OH$^-$ anionic exchange is suspected on the same site S. For these two reasons, S is attributed to goethite.
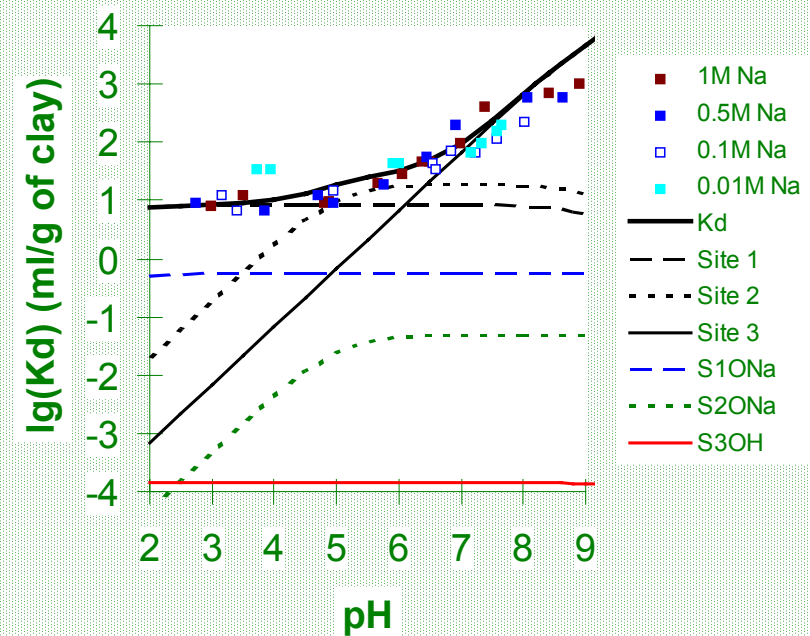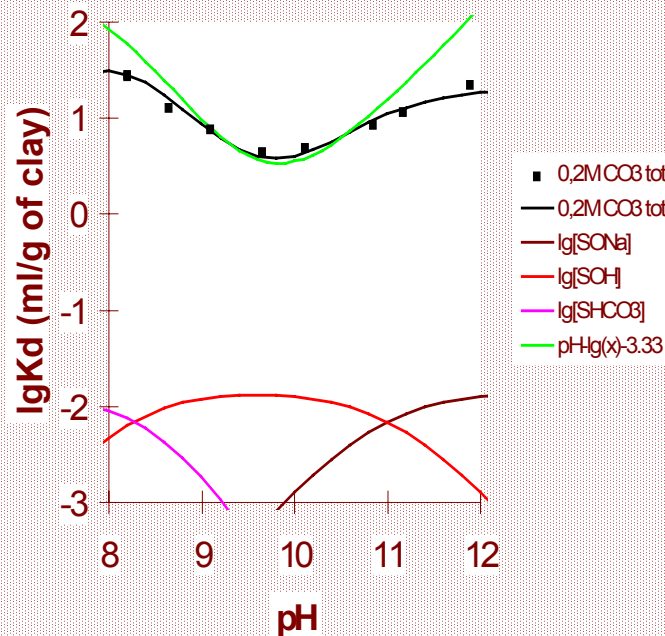
# Figure 3: Kd variations with pH in 0.2 M $HCO_3^-/CO_3^{2-}$ media

Kd are deduced from column experiments (figure 2). $[CO_3]_{t,aq}$ = 0.2 M, [Na] = 1 M, $ClO_4^-$. All the curves are calculated.

lg Kd **black curve** is nearly parallel to the (pH - lg x) **green one**, (where x = $[Np(V)]_{t,aq}/[NpO_2^+]$ is calculated from Np(V) aqueous speciation): following ionic exchange theory, this indicates that Np(V) sorption is mainly due to $H^+/NpO_2^+$ cationic exchange on one site, S. x variations are here mainly due to carbonate complexation of Np(V). x decreases with pH as long as $HCO_3^-$ is titrated into $CO_3^{2-}$.

Acidic basic titration (these experimental data are not shown here) of the porous medium can be interpreted with three sorption sites, $S_i$ (i = 1 to 3, see also figure 4). Here S is $S_3$, that is enough to interpret Np(V) fixation. SOH starts to be partially transformed into SONa only **at pH more than 10** (curves at the bottom of the figure), where **lg[SONa] curve is parallel to the lg Kd data**: this SONa/SOH cationic exchange explains that the deviation of the **black lgKd curve**, from the **(pH - lgx) green one**.

**At pH less than 9** SOH/SOHCO$_3$ anionic exchange is suspected on the same site (curves at the bottom of the figure). This equilibrium between major cations would then now explain the deviation of the **black lgKd curve**, from the (pH - lgx) **green one**. This amphoteric behaviour and the 0 charge point suggest that S should be attributed to goethite.



Figure 3 (left graph) legend:
- 0,2M CO3 tot
- 0,2M CO3 tot
- lg[SONa]
- lg[SOH]
- lg[SHCO3]
- pH-lg(x)-3.33



Figure 3 (right graph) legend:
- 1M Na
- 0.5M Na
- 0.1M Na
- 0.01M Na
- Kd
- Site 1
- Site 2
- Site 3
- S1ONa
- S2ONa
- S3OH

# Figure 4: Kd variations with pH (Dolo's data)

At least two of the three exchange capacities (see figure 3) are needed to model Kd variations.

The first site, $S_1$, is always sodic ($S_1$ONa) in Dolo's chemical conditions, and at **pH less than 5**, Np(V) sorption could be attributed to the $S_1$ONa/$S_1$ONpO$_2$ cationic exchange.

**At pH 5 to 6** $S_2$ONa/$S_2$ONpO$_2$ cannot now be neglected, this is partially due to the $S_2$OH/$S_2$ONa titration.

**At pH more than 6**, Kd increase is attributed to the same site, $S_3$, as in our (figure 3) work (but here $S_3$HCO$_3$ is not formed since $[CO_3]_{t,aq}$ is too low). For this we assume, that the clay mineral was not completely purified from goethite. We then fit the concentration of this impurity.

For clarity, **curves are drawn only in 1 M Na conditions**. When [Na] is decreased by 1 order of magnitude, lg[$S_i$ONa] and then lg Kd (if due to site i) are shifted by 1 unit toward high pH values. lg Kd is also shifted up vertically by 1 unit, if the Np(V) sorption is mainly due to the $S_i$ONa/$S_i$ONpO$_2$ cationic exchange.

## Mineral composition of soil

| Soil composition | % weight |
| --- | --- |
| silica (sand RF) | 93.45 |
| Clays (FOCA7) | 6.55 |

| Clays (< 2mm) composition | % weight |
| --- | --- |
| quartz | 5.9 |
| goethite | 5.7 |
| calcite | 1 |
| kaolinite | 4.6 |
| (50 % kaolinite, 50 % smectite) | 82.1 |

## Soil Column characteristics

| Column | 4C2 |
| --- | --- |
| Inner diameter (cm) | 1.6 |
| Length of bed (cm) | 8.0 |
| Type of sand | RF70 250µ + FOCA7, 6.55%w/w |
| Mass of sand mixture(g) | 22.1 |
| Pore Volume (cm$^3$) | 7.75 |
| Porosity | |
| Number of mixing cells : J (water tracer) | 100 |
| Dispersivity : a = L/2J (cm) | |
| Flow rate (cm$^3$.mn$^{-1}$) | 0.5 |
| Exchange capacity (m eq/g) (pH=9.22) | 48.5 |

## References

**Bidoglio G., Offermann P., and Saltelli A., 1987**. Neptunium migration in oxidizing clayey sand. *Applied geochemistry, 2, 275-284.*

**Dolo J.M., 1991**. Etude de la rétention de l'Americium III, du Neptunium V et de l'Uranium IV par un matériau argileux. *Thèse CNAM, Paris, june, 14.*

**don Girvin C., Lloyd L.A., Allen P. S., and McGarrah J.E., 1991**. Neptunium adsorption on synthetic amorphous iron oxyhydroxide. *J. of Colloid and interface Science, 141,(1),67-76.*

**Gorgeon L., 1994**. Contribution à la modélisation physicochimique de la rétention de radioéléments à vie longue par des matériaux argileux. *Thèse Université Paris 6*

**Keeney-Kennicutt W.L. and Morse J.W., 1984**. The interactions of Np(V)0$_2^+$ with common mineral surfaces in dilute aqueous solutions and seawater. *Marine Chemistry, 15, 133-150.*

**Lefèvre F., Sardin M., Schweich D., 1993**. Migration of strontium in clayey and calcareous sandy oil : precipitation and ion exchange. *Journal of Contaminant Hydrology, 13 : 215-229.*

**Lefèvre F**., Thèse INPL, Nancy-France, to be presented.

## References (continued)

**Nakayama S., Arimoto H., Yamada N., Moriyama H. and Higashi K., 1988**. Column experiments on migration behavior of neptunium (V), *Radiochimi. Acta, 44/45, 179-182.*

**Nakayama S. and SakamotoY., 1991**. Sorption of neptunium on naturally-occuring iron-containing minerals, *Radiochim. Acta, 52/53, 153-157.*

**Tanaka S., Nagasaki S., Itagaki H., and Yamawaki M., 1989**, Speciation and retardation phenomena of neptunium in underground environnements, *Saclay T7435.*

**Yamaguchi T., Pratopo M.I., Moriyama H. and Higashi K., 1991.** Adsorption of Caesium and neptunium(V) on bentonite. *In proceeding of the third international conference on nuclear fuel reprocessing and waste management, RECOD 91, Sendai, Japan, 2,999-1004.*