STUDY OF IONIC EXCHANGES OF Np(V)-IONS ON NATURAL CLAY MINERALS AND GOETHITE IN CARBONATED MEDIUM BY COLUMN EXPERIMENTS.

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ABSTRACT

Migration of Neptunium(V) through a natural porous media is governed by both the water motion and the heterogeneous and homogeneous reactions that occur in solution and on the solid. Generally, a lumped coefficient, so-called distribution coefficient, K_d, is used to describe the retention of Neptunium in soils. But, when published K_d values are compared as a function of pH, K_d variations of 6 orders of magnitude are observed as a function of soil solutions and composition. To understand and quantify the mechanisms which 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 K_d is measured from the mean position of the experimental response at the oulet of the column. The curve log(K_d) 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. Using an ion exhange modelling, it is shown that, although for the given pH range, the Np(V) is strongly complexed in anionic forms, adsorption is essentially due to its cationic form, NpO_2^+. For pH below 9.8, a contribution of anionic exchange between HCO_3^- and $Np0_2CO_3^-$ is to be considered on anionic sites. The expected anionic exchange is verified by means of migration experiments of ^{14}C labeled carbonated solution.

1.Introduction

Confining of nuclear waste disposal is not only dependent on the container quality, but also on the ability of artificial and natural barriers to retain radionuclides and avoid radioactive leaks in the far field. Predictive calculation of radioelement migration in underground is needed to assess the security of radioactive waste disposals. The main vector of transport in natural porous media is the movement of ground waters, that may transport radionuclides as dissolved solutes or as colloids or pseudo-colloids. The long-distance transport velocity of dissolved radionuclides, is esssentially controlled by the interactions with sites of clays minerals or metal oxydes and by precipitation in contact with minerals. The sorption of ionic species at low concentration, that is the case for radionuclides, is often measured in terms of distribution coefficient K_d. This last one, assumed to be constant in several transport models, is unfortunately dependent on the chemical conditions which usually vary during transport. For neptunium, these variations are essentially due to the competition between the species under study and the major cations in solution at the adsorption sites and the complexation reactions in solution which modify the ionic forms in which the studied element can be found. To take into account the speciation and the competitive adsorption two main models have been developped: the ion exchange model (Dolo, 1991; Gorgeon, 1994), and the model of surface complexation more or less complex (don Girvin.et al.(1991) and Tanaka et al.(1989)). The relatively low velocity of flow in the far field around waste disposals generally leads to assume local equilibrium, but Bidoglio (1987) introduces a model coupling ion exchange and slow kinetics. In two recent papers, Lef□vre et al. (1993, 1995) has been shown relevance of the approach in terms of ion exchange to simulate the transport of strontium in a calcareous clayey sandy soil in a large range of Sr concentrations and experimental conditions. It allows taking into account the competition with major cations and the *a priori* calculation of K_d as a function of the ionic composition. They have displayed and modelled kinectic effects during the adsorption when clay minerals form aggregates between the sand grains.

The aim of this paper is (i) to show the validity of the methodology developed for transient transport on strontium on a case more complex because studying ^{237}Np allows us to introduce the role of speciation in the transport description, and (2) to offer a speciation model including the main mechanisms which control the transport of Neptunium.

2. Methodological approach

In aqueous solution Neptunium is at the oxydation state V. It is stable and has three complexed forms: a neutral complex with hydroxide anion, NpO_2OH, a unique cationic complex, NpO_2^+, and an anionic complex, $NpO_2(OH)_2^-$. In presence of carbonate ions, three other complexes are formed : $NpO_2CO_3^-$, $NpO_2(CO_3^-)_2^{3-}$, $NpO_2(CO_3^-)_3^{5-}$. In a medium low in carbonate and ionic strength, solubility is contolled by the Neptunium hydroxyde, NpO_2OH_s. But, in a sodo-carbonated medium, two hydroxycarbonated mixed precipitates, $NaNpO_2CO_{3s}$ and $Na_3NpO_2(CO_3^-)_{2s}$, have to be accounted for. The consequence of the existence of different forms for Neptunium in solution is that the predominant form of Np in solution is a function of pH.For instance, in a solution $NaClO_4$ 1M, Np(V) 10^{-6}M and carbonate 0.2 M and using the data from table 1, at low pH and until pH 6 , the cationic form, NpO_2^+ is dominant; for pH above 12 that is the anionic form, $NpO_2(CO_3^-)_3^{5-}$. The concentration of NpO_2^+ decreases from pH 6 to pH12 continuously. The analysis of data from recent literature shows that certain authors (Tanaka et al.(1989) and Nakayama et al. (1988)) performed column experiments in conditions where Np was able to precipitate. They observed a complex restitution of Np in the form of several peaks due to the generation of colloids by precipitation.The interpretation of these experiments is not easy and, as most of authors, we performed experiments at concentrations below the solubilty limit to observed only the sorption phenomena.

A lot of experiments have been performed to measure the adsorption of main radionuclides present in nuclear waste on different minerals. Only studies, for which the experimental data are sufficient (*i.e.* pH and ionic composition of the aqueous phase known) and obtained in conditions where the Np(V) does'nt precipitate have been analyzed. All these experiments have been performed with Np(V) concentration below 10^{-6} M and with a liquid volume and soil mass ratio such as the total amount of Np(V) is low with respect to the sorption capacity of the soil. To compare these experiments, performed in a large range of experimental conditions, in a same diagram, we use the theory of ion exchange. In the sodium chlorate solution and in presence of ionizable sites on materials two cationic exchanges on each site have to take into account : Na^+/NpO_2^+ and Na^+/H^+. Preliminary experiments have been shown that the variation of exchange capacity of FOCA7 is perfectly described as a function of pH with 3 sites (Gorgeon 1994). The third at high pH is amphoteric and due to the presence of goethite in the clay composition. The selectivity coefficient between the two homoionic species, Na^+ and NpO_2^+, in solution and these, $\overline{Na}_j$, and $\overline{Np}_j$, adsorbed on a site j of a natural ion exchanger is written,

$$K^{j}_{Na/NpO_2} = \frac{\left[\overline{NpO_{2j}}\right]\left[Na^+\right]}{\left[\overline{Na_j}\right]\left[NpO_2^+\right]} \qquad (1a)$$

The same relationship can be written for the exchange Na/H. The selectivity coefficient are dimensionless. Np(V) being at trace level, its total concentration in solution, [Np], is linked to $[NpO_2^+]$ by the complexation coefficient α_{Np},

$$[Np] = \alpha_{Np}[NpO_2^+] \qquad (2)$$

where, $\alpha_{Np} = 1 + ...$ (3)

The distribution coefficient of total Np between the solution and the surface is by definition,

$$K_{dNp} = \frac{\left[\overline{Np}\right]}{\left[Np\right]} \qquad (4)$$

where $\left[\overline{Np}\right]$ and $\left[Np\right]$ are the concentrations in mole per liter of solution on the surface of FOCA7 (three sites) and and in solution. K_{dNp} is dimensionless in the chosen units. Using the relationships (1) to (4), it is possible to link the distribution coefficient K_{dNp}, the selectivity coefficients of cationic exchanges, the concentrations of mains cations in solution and the exchange capacity of the 3 sites, Nej (j=1 to 3) by the relationships,

$$Y_C = \lg\left(K_{dNp}.\alpha_{Np}\right) - pH = \sum_j \frac{K^{j}_{Na/Np}Ne_j}{\left\{K^{j}_{H/Np} + 10^{X_C}\right\}} \qquad (5a)$$

with $X_C = \lg\left[Na^+\right] + pH$ (5b)

Y_C and X_C can be calculated from experimental data for K_{dNp}, measurement of pH and complexation constant calculation in solution. Plotting Y_C as a function of X_C allows us to show the stoichiometry of adsorption reaction. If $Y_C = f(X_C)$ is a decreasing linear function with a slope between 0 and -1, NpO_2^+ is the fixed species. The same kind of calculation can be done for anions using the same definition for the selectivity coefficient substituting cationic species by anionic complexes and H^+ by OH^- in competition with carbonate species (The detail of calculations is given in Lef□vre (1995)). In figure 1 we have plotted the literature results in (Y_C, X_C) coordinates. The comparison with the (-1)-slope straighline shows that (1) for the sets of data performed with clay minerals or quartz, the slope is close to -1 if X_C is below 6. Above this value, the slope is comprise between -1 and 0; (2) From the differences between the sets of point associated to different materials, it is possible to deduce an order of affinity for Np on differents minerals: quartz<clays<ferrous oxides. This affinity order is partially confirmed by the works of Keeney-Kennicut and Morse (1984) who purpose the following order : clay <goethite<calcite<aragonite.

As conclusion of this section, it seems to be reasonable on the basis of ion exchange theory, Np(V) speciation in solution, and literature data analysis to assume that below $X_C = 6$, (pH = 6 in $NaClO_4$ 1M and pH = 8 in $NaClO_4$ 0.01M), the adsorption of Np is mainly governed by the adsorption of $Np0_2^+$ on ionized sites of minerals. Above $X_C = 10$ (basic pHs), there is the unique adsorption of cationic species because the amphoteric sites are totally in anionic form. Between 6 and 10, anionic exchange with carbonate complexes and cationic exchange with NpO_2^+ coexist. These asumptions will be discussed in the last section of this paper after the presentation of experimental result.

3. Column experiments

Thanks to the assumptions developed in the previous section it is possible to develop a speciation model to deduced the values of the Np(V) distribution coefficient at different carbonate and $NaClO_4$ concentrations. The operative conditions in column impose to performed experiments with low Kd's, both to reduce the time of an experiment and to have a measurable signal with the ^{237}Np.The experiments have been performed on one column that were filled with **XXX** (Table 2). Before being used, the column has been purged of air with CO_2 as purging gas and saturated with 0.05 M $CaCl_2$ solution to put the exchange sites of the clays in calcium form. The response to step or pulse injections of $CaCl_2$, which is well suited to trace the flow in the given experimental conditions (Lefevre et al., 1993), is measured by conductivity at the outlet of the column. First moment, μ_1, and variance, σ^2, of this response give access to the pore volume ($V_p = Q.\mu_1$) and the dispersion of the flow (number of mixing cell $J= Pe/2 = uL/D = \mu_1{}^2/\sigma^2$, and the dispersivity, $\alpha = L/J$). Injections of ^{22}Na is then performed at different pH to measured the three exchange capacities, Ne_j. Finally, the choice of experimental conditions for injection of Np(V) has been determined by the theorical considerations extracted from the data analysis presented above. To show the role played by $NpO_2{}^+$ in the retention Np(V) with respect to the anionic carbonated forms it was necessary from an experiment to another one to vary the pH. All the experiments have been performed at the same flow rate, 0.5 ml/mn, except two experiments for which the flow rate was ten times lower to exhibit some kinetic limitations in mass transfer.

The values of K_d are calculated from the measurement of the column answer to pulse-injections ($0.5V_p$) of a Np(V) 10^{-6}M solution at given pH and salt concentration at steady flow. At the outlet of the column, the effluent is collected and the total concentration of Np(V) is measured in each fraction by **XXX**. The total recovered amount of Np(V) is then compared to the injected amount. If the recovery is close to 100%, the retention volume at a given pH of the Np(V), $V_R(pH)$, is calculated as the first moment of the recovery peak. Finally K_d' is obtained from the relationship,

$$K_d' = K_d \backslash F(V_p;M) = \backslash F(V_p;M) \left(1- \backslash F(V_R;V_p)\right) \tag{6}$$

4. Experimental results.

The exchange capacity of the soil is measured by interpreting the elution curve of a injection pulse of ^{22}Na tracer in a column fed with sodium chloride only. The injected tracer solution is of the same chemical composition as the pre-equilibrating solution and the eluant. The pH of feeding solutions is fixed by addition of NaOH or HCl.

Three sites are so shown. The first one, which appears at low pH is negatively charged and completely ionized below pH 5. The second, negatively charged too, appears at pH 5 and is completely ionized at pH 7. These two types of sites represent 90% the number of sites (65,7 meq/100g) and are essentially due to the clay minerals. The last one, which represent 10% of the set (6.5 eq/100g), is amphoteric and can be attribuated to the Goethite present in the FOCA clay (see table 2). It is ionized between pH's 9 and 12.

In table 4 are presented the experimental results as a function of main parameters of the experimental system. All the experiments have been performed at the same sodium chlorate concentration. The carbonate concentration is different for the three first experiments. Examples of chromatograms obtained at different pH are presented in figure 2. They show a notable influence of the retention on the peak dispersion which is not compatible with a linear adsorption and/or with the local equilibrium adsorption. The experiments 2 and 12 performed at a ten time lower flow rate do not show an important kinetic effect. Although the injected amount is low with respect to the sites concentration, the non-linearity of adsorption seems to be the main reason of the observed dispersion.

Plotting lg(K_d) as a function of pH shows a singular behaviour: above pH 9.8, value for which a minimum is observed, Kd decreases. Then, when pH increases to 11.8, log(Kd) value increases to 1.3. This behaviour indicates a modification in the adsorption mechanism around pH 9.8.

To test if the nature of adsorption is changed on the surface around pH9.8, two kinds of experiments have been performed with ^{14}C-labeled carbonate. The first ones (13 & 15) consist in the injection of a pulse of ^{14}C-carbonate with carbonate but without Np(V) in order to evaluate the distribution of carbonate between surface and solution by measurement of the distribution coefficient of ^{14}C at two pH's around 9.8, 11.05 and 8.2. In the second ones (14 &16), performed in the same conditions, Np(V) is added in the pulse to see if the Np carbonate complexes are adsorbed. At a pH above 11 no adsorption of carbonate is measurable. Contrarly at 8.2 the adsorption is sensitive but independante of the Np concentration.

5. Interpretation and discussion

In the figure 4 the pH-evolution of the Np(V) speciation is represented by the variation of lg(a_{Np}), the logarithm of the complexation coefficient (3) and the ionization of sites by the Na-saturation. The lower is lg(a_{Np}), the lower is the concentration of NpO_2^+ in solution. Below pH 6, NpO_2^+ is the main Np(V)-species in solution. It controls the adsorption on negatively charged sites. Between 6 and 10 the NpO_2^+ concentration decreases and carbonate complexes become dominant. Above pH 10, the main Np(V)-species is $NpO_2(CO_3)_3^{5-}$ (10^{-6} mole/l), and NpO_2^+ is at a very low concentration (10^{-12} mole/l)). The experiments with ^{14}C-labeled carbonate show that only at a pH below 9 adsorption of anions is observed. Above 11 all the sites are negatively charged and behave as cation exchangers. Consequently, the adsorption of Np(V) above pH11 can be only attributed to NpO_2^+ adsorption. The increase of adsorption above pH10 is the consequence of the negative ionization of the third amphoteric site which can be attribuated to the goethite. The adsorption constant on this site must be very high indicating a modification of the type of interaction : from ion exchange on clays minerals at low pH to complexation reaction on goethite at high pH.

Using the complete speciation of Np(V) in presence of carbonate and the existence of three sites on the surface, one of which amphoteric, we have simulated the results of sorption of Dolo (1991) and these from the present work (figure 4). The adsorption mechanism is represented by reactions involving 8 equilibrium constants (values in the caption of figure 4) : three set of two cationic equilibrium constants (1a) and (1b) and 2 anionic equilibrium constants for the third amphoteric sites involving OH^-, HCO_3^- and $NpO_2CO_3^-$ as main anionic species at pH 9.

Conclusions

The results presented above are an attemp to elucidate the retention mechanisms of Np(V) on clayey sandy soil. They partially show that, if at low pH the adsorption on clay minerals by electrostatic process is the main mechanism, at pH above 8 the mechanism is more complex and is notably influenced by the presence of ferrous oxyde as goethite. The affinity of NpO_2^+ on this mineral is very strong and adsorption occurs although the concentration of $NpO_2^+$is very low at high pH. These interpretation and modelling have to be confirmed by other experiments, but they have the interest to show that as a function of pH the nature of adsorption mechanism can change and have to be attributed at different minerals : At low pH clays minerals are the main adsorbant and the adsorption is governed by ion exchange, at high pH the metal oxydes plays the main role and the adsorption is governed by surface complexation. The set of results can be interprated by both ion exchange or surface complexation theories.

References

Allard B. and Beall G. W., 1980. Actinide-retaining backfill materials in underground repositories for a-contaminated wastes. IAEA-SM-246/13 Report.

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 materiau 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 ˆ la modélisation physicochimique de la rétention de radioéléments ˆ vie longue par des matériaux argileux.

Jauzein M., André C., Margrita R., Sardin M., 1989. A flexible computer code for modelling transport in porous media : Impact. Geoderma, 44 : 95-113.

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., Sardin M., Vitorge P., 1995. XXX. Journal of Contaminant Hydrology, XXX.

Lefèvre F., XXX, Thèse INPL, Nancy-France, 1995.

Maya et al., XXX

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

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

Riglet C. Chimie du Neptunium., XXX

Sardin M., Schweich D., Leij F.and M. Van Genuchten, 1991. Modeling the nonequilibrium transport of linearly interacting solutes in porous media : a review. Water Resources Research, 27 n¡ 29 : 2287-2307.

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.

Table 1: Mineral composition of soil

Soil composition	% weight	Clays (< 2µm) composition	% weight
silica (sand RF)	93.45	quartz	5.9
Clays (FOCA7)	6.55	goethite	5.7
		calcite	1
		kaolinite	4.6
		(50 % kaolinite, 50 % smectite)	82.1

Table 2 : 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 : $\alpha = L/2J$ (cm)	
Flow rate ($cm^3 .mn^{-1}$)	0.5
Exchange capacity (µ eq/g) (pH=9.22)	48.5

TABLE 3 : description of reactions and equilibrium constants used in aqueous phase. Equilibrium constants are given at two Ionic Strength, 0 and 1M.

Reac. #	**Chemical equilibrium**	**lg(K) I=0 M**	**lg(K) I=1 M**	**Ref.**
	Water dissociation			
R1	$H_2O = H^+ + OH^-$	-13.99	-13.83	Riglet et al.(1990)
	Calcocarbonic equilibria			
R2	$CO_{2aq} + H_2O = HCO_3^- + H^+$	-6.35	-6.18	Riglet et al.(1990)
R3	$CO_{2aq} + 2H_2O = CO_3^{--} + 2H^+$	-16.68	-15.7	"
	Complexes with NpO_2^+			
R13	$NpO_2^+ + H_2O = NPO_2OH + H^+$	-11.50	-11.33	Maya et al.(1983)
R14	$NpO_2^+ + 2H_2O = NpO_2(OH)^{2-} + 2H^+$	-23.00	-22.44	ib.
R15	$NpO_2^+ + CO_3^{2-} = NpO_2CO_3^-$	4.70	4.56	ib.
R16	$NpO_2^+ + 2CO_3^{2-} = NpO_2(CO_3)_2^{3-}$	6.39	7.13	ib.
R17	$NpO_2^+ + 3CO_3^{2-} = NpO_2(CO_3)_3^{5-}$	5.52	8.54	ib.
	Precipitation reactions in carbonate solution			
R22	$NpO_2(OH)_s + H^+ = NPO_2^+ + H_2O$	5.12	4.95	
R23	$NaNpO_2(CO_3)_s = Na^+ + NpO_2^+ + CO_3^{2-}$	-11.00	-10.06	ib.

R24	$Na_3NpO_2(CO_3)_{2s} = 3Na^+ + NpO_2^+ + 2CO_3^{2-}$	-13.66	-11.45	ib.

TABLE 4 : Experimental conditions and measured Kd values. $[Na^+]$ = 1 mole/l. In the experiments #13 to #16 carbonates are labeled with ^{14}C.

Run #	**Total Carbonate (mole/l)**	**Total Np(V) (µmole/l)**	**pH (measured)**	**injected volume (Vp)**	**flow rate ml/mn**	**capacity factor**	**distribution coefficient (l/kg)**
1	0.1	12.6	11.19	0.51	0.5	8.81	47,1
2	0.1	13.0	11.19	0.52	0.5	-	-
3	0.15	8.34	11.43	0.50	0.5	4.91	26,2
4	0.2	8.46	11.89	0.49	0.5	3.51	18.8
5	0.2	8.64	11.17	0.50	0.5	2.19	11.7
6	0.2	8.6	10.11	0.50	0.5	0.9	4.9
7	0.2	8.55	9.09	0.49	0.5	1.43	7.6
8	0.2	8.51	9.65	0.49	0.5	0.84	4.5
9	0.2	8.42	10.85	0.51	0.5	1.57	8.4
10	0.2	8.34	8.65	0.50	0.5	2.42	12.9
11	0.2	3.68	8.2	0.50	0.5	5.16	27.6
12	0.2	3.68	8.2	0.51	0.05	5.22	27.9
13	0.01	0	11.05	0.50	0.5	0.	0
14	0.001	2.7	11.51	0.50	0.5	0.	0
15	0.001	0	8.2	0.50	0.5	0.73	67
16	0.001	2.7	8.2	0.53	0.5	0.71	65

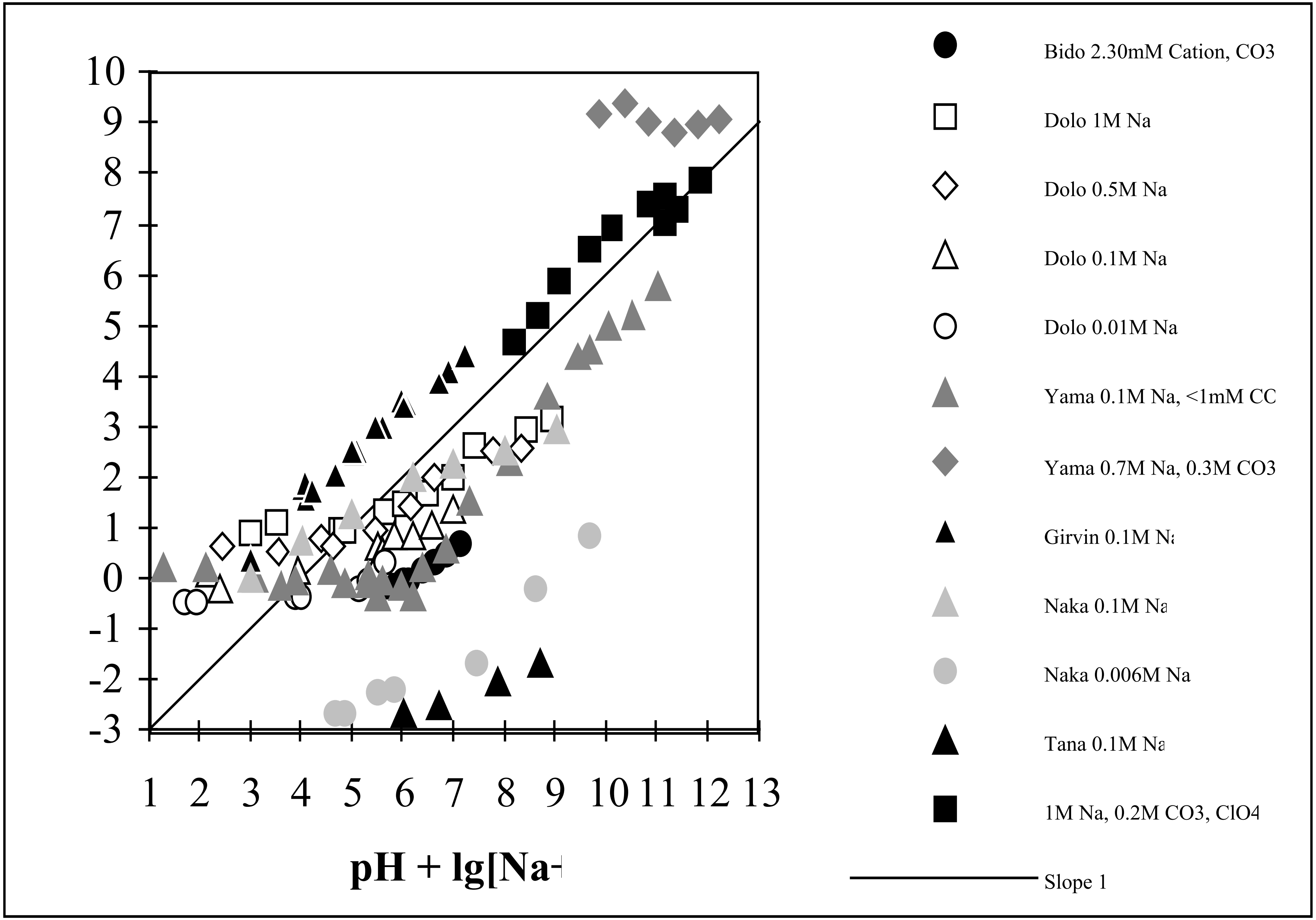
Captions of the figures

Figure 1: Comparison of literature adsorption data in terms of cation exchange : Y_C vs X_C . The slope -1 is displayed. The points parallel to this slope are the consequence of a ionic competition between major cation in solution (often Na^+) and NpO_2^+. When the set of experimental data is parallel to X_C-axis, exchange between H^+ and NpO_2^+ occurs. Higher is the Y_C value for a given X_C, higher is the affinity of Np for materials. The Kd values for quartz are very low for pH below 10.

Figure 2: Examples of chromatograms of Np vs pH. Total carbonate = 0.2M. Flow rate 0.5 ml/mn. See table 4.The shape of peaks reflect both interactions and collect mode.

Figure 3: Lg(Kd) as a function of pH. The speciation in terms of $-\lg(\alpha_{Np})$ and the sites saturation by sodium is given.

Figure 4 : Modelling of Kd values by ion exchange theory using at low pH the data of Dolo (1991)
site 1 : $K_{Na/H} = 10$, $K_{Na/NpO2} = 15$ (from DOLO, 1991); site 2 : $K_{Na/H} = 10^5$, $K_{Na/NpO2} = 400$ (from Dolo), site 3 (amphoteric): $K_{Na/H} = 10^{11}$, $K_{Na/NpO2} = 9.0\ 10^8$, $K_{OH/HCO3} = 10^9$, $K_{OH/NpO2CO3} = 10^{14}$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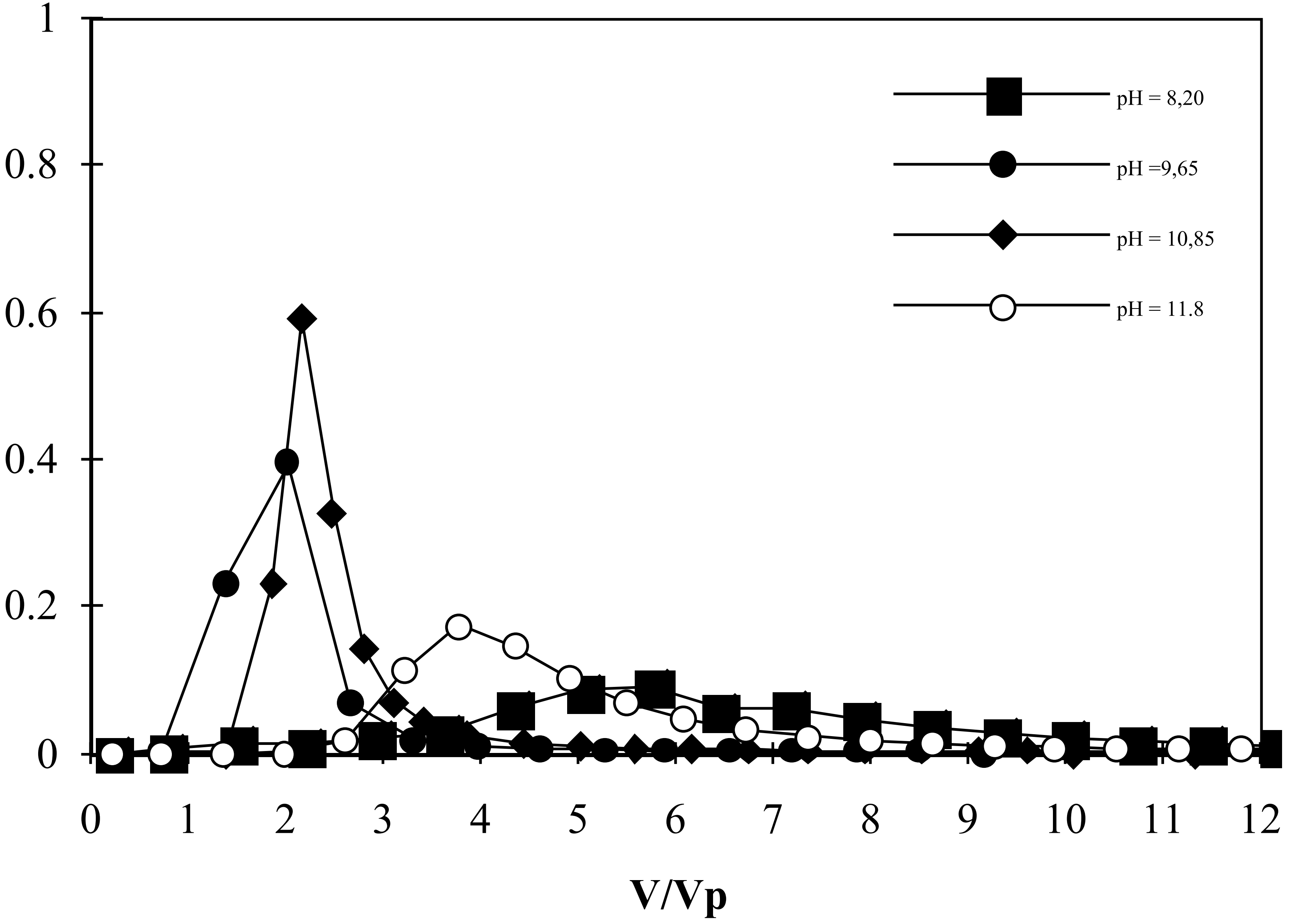
11
12
13
pH + lg[Na+
● Bido 2.30mM Cation, CO3
□ Dolo 1M Na
◇ Dolo 0.5M Na
△ Dolo 0.1M Na
○ Dolo 0.01M Na
▲ Yama 0.1M Na, <1mM CC
◆ Yama 0.7M Na, 0.3M CO3
▲ Girvin 0.1M Na
▲ Naka 0.1M Na
● Naka 0.006M Na
▲ Tana 0.1M Na
■ 1M Na, 0.2M CO3, ClO4
Slope 1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V/Vp
pH = 8,20
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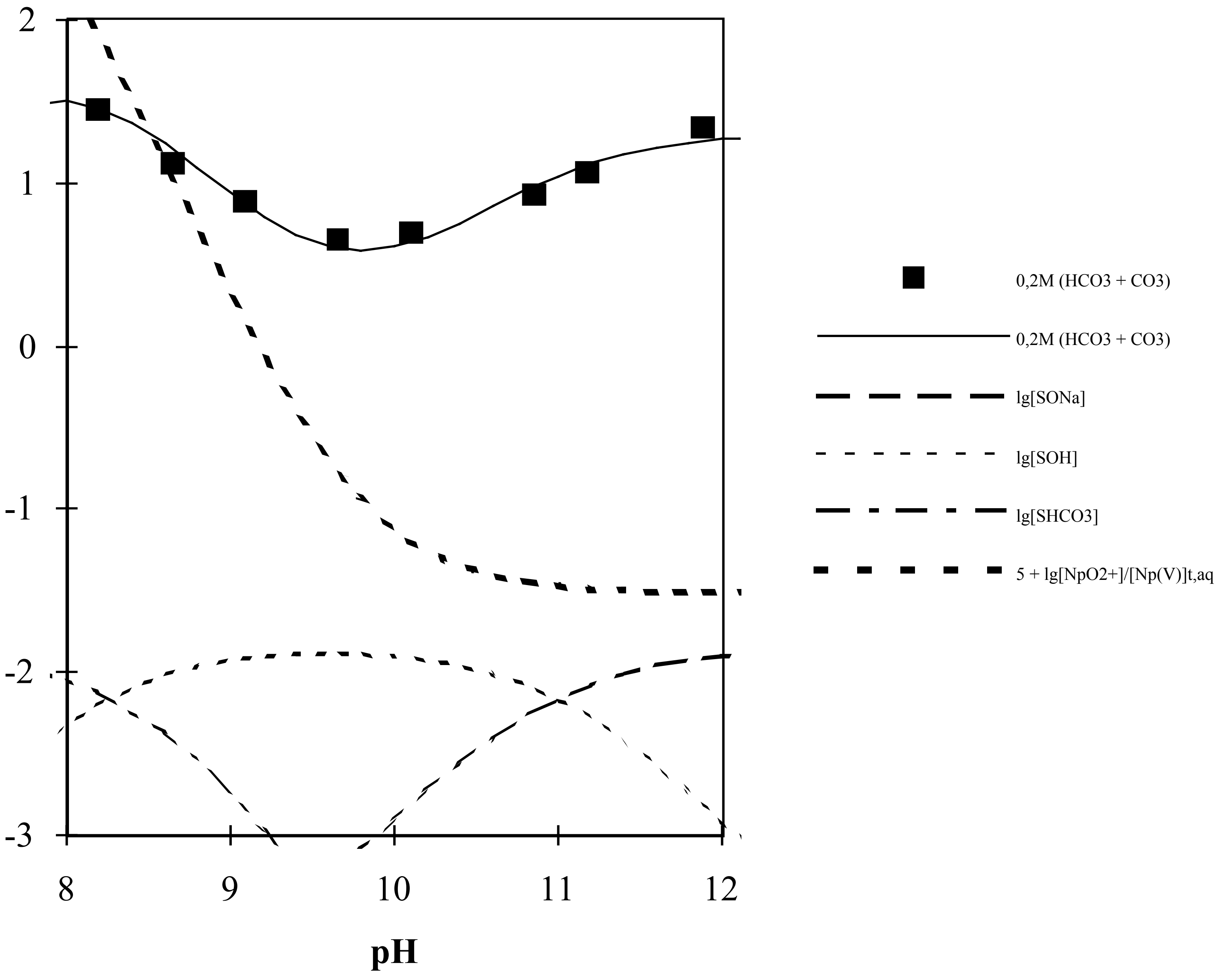
pH = 10,85
pH = 11.8



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-1
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11
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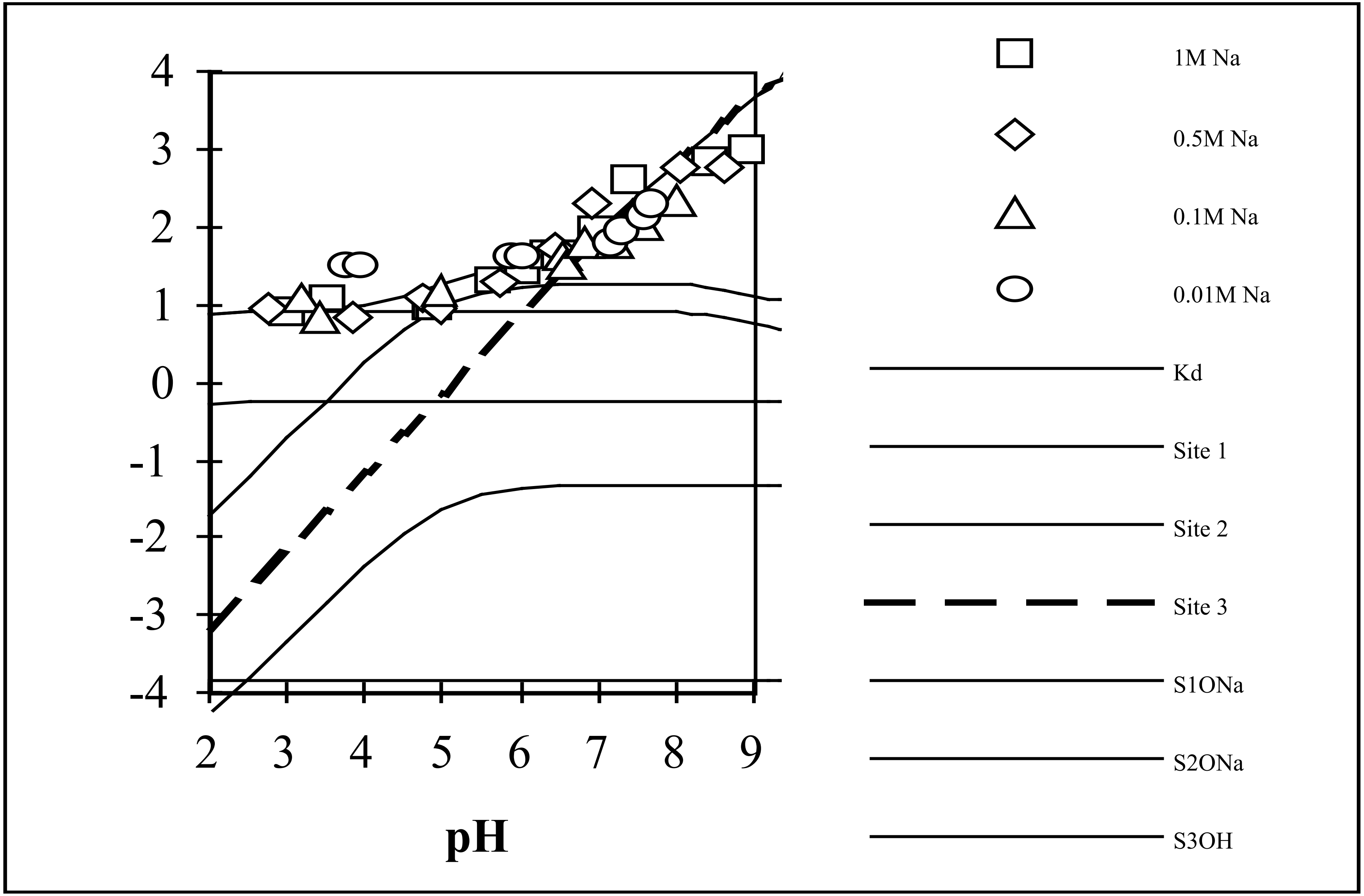
pH
0,2M (HCO3 + CO3)
0,2M (HCO3 + CO3)
lg[SONa]
lg[SOH]
lg[SHCO3]
5 + lg[NpO2+]/[Np(V)]t,aq


4
3
2
1
0
-1
-2
-3
-4
2
3
4
5
6
7
8
9
pH
1M Na
0.5M Na
0.1M Na
0.01M Na
Kd
Site 1
Site 2
Site 3
S1ONa
S2ONa
S3OH