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CHARACTERIZATION OF SURFACE PROCESSES ON
MINERAL SURFACES IN AQUEOUS SOLUTIONS

NEPTUNIUM(V) SORPTION ON QUARTZ AND ALBITE IN AQUEOUS SUSPENSION

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1. ABSTRACT

At concentration levels of 10^{-7} M, Np(V) does not adsorb strongly on quartz and albite up to pH values of approximately 9 at solid/solution ratios of 30 to 40 g/l. Significant adsorption (> 20%) occurs on both minerals only at pH > 9. Pretreatment of albite affects the sorption behavior of this mineral at pH > 9, possibly due to the formation of secondary mineral phases at the albite surface. EDTA does not adsorb on quartz at concentrations of 10^{-6} M. In the presence of 50 μM EDTA, Np(V) sorption seems to be restricted. EDTA at the 10^{-6} M level adsorbs onto albite to an appreciable degree at pH values < 7.5. 1 μM EDTA has no effect on Np(V) adsorption onto albite. Carbonate species adsorb on quartz and albite, both cases showing a maximum in sorption at pH 6.5 to 7 where HCO_3^- is the predominant solution species.

2. INTRODUCTION

The behavior of neptunium in the subsurface environment is of interest since neptunium isotopes are included in nuclear waste. One isotope, ^{237}Np has a half life of $2.1 \cdot 10^6$ years. In the last annual report (Kohler et al, 1990), we listed some important issues concerning this isotope. An overview of the behavior of neptunium in the hydrosphere and geosphere and thermodynamic properties such as the chemical speciation of Np as a function of pH and Eh are given by Lieser and Mühlenweg (1988).

Previous work investigated the sorption behavior of Np onto α-Fe_2O_3 (hematite), an accessory mineral of the Yucca Mountain repository. Although the mass contribution of hematite to the total mineralogical composition is minor, strong sorption of Np(V) onto this mineral indicates an important role in the potential geochemistry of migration in a saturated subsurface environment. The work reported herein involves the much more abundant silicate minerals quartz and albite, and is a logical continuation of the ongoing task.

Albite is a more complex mineralogical system than previously studied. Earlier either synthesized minerals, hematite or well characterized ones (e.g., quartz) were studied experimentally. Nevertheless, both albite and quartz are more or less pure mineral phases compared to natural minerals and rock systems.

The modification of natural mineral surfaces (due to weathering or organic coatings, for instance) can have a large effect upon sorption, retardation and migration of radionuclides in the ground water systems. In previous work increased sorption was observed in systems containing hematite and EDTA, a ligand which acts as a surrogate for organic complexing agents. The organic coating blocks sites at the pure mineral surface, making such sites inaccessible for the coordination of a cation such as NpO_2^+. On the otherhand, organics with multiple ligand atoms can provide additional strong binding opportunities when the organics are adsorbed, thus enhancing metal binding overall.

In addition, increased partial pressures of CO_2 are common in many ground waters (Stumm and Morgan, 1981) and the effects of carbonate on sorption of radionuclides have to be studied as well. The formation of strong solution carbonate complexes by many actinide elements is well known (Lieser and Mühlenweg, 1988; Nitsche et al, 1990).

The studies reported here have taken into account the fact that complexing ligands such as EDTA and carbonate species adsorb on mineral surfaces. Often the adsorption of competing ligands is not accounted for in both experimental and modelling studies.

The weathering processes of the minerals under investigation poses a serious problem in planning and conducting sorption experiments because the dissolution processes may interfere with the sorption process. For example, the formation of secondary mineral phases on the surface of the albite can take place. In other words, the sorbing species in solution might be exposed to a slowly altering mineral surface during the sorption process. Such sorption data are difficult to interpret, unless a detailed understanding of the characteristics of the actual surface is available. Such understanding requires a thorough investigation of the weathering processes of albite.

Our experiments on quartz and especially on albite indicate that the history of the sample can have a rather significant influence upon the sorption process. Care should therefore be taken in planning experiments involving minerals such as albite.

3. MATERIALS AND METHODS

Quartz

Quartz was obtained from Pennsylvania Glass Corporation (Pittsburgh, PA) under the brand name "Min-U-Sil 5". It consists of particles of 5 μm median diameter which have a slightly yellow tint due to iron oxide impurities.

The cleaning procedure used to prepare quartz was similar to that of Benjamin (1978). 200 g of quartz were heated to 550°C in a muffle oven for 48 hours to oxidize organic contaminants. It was then refluxed in 4M $HClO_4$ for 4 hours and rinsed with batches of 1500 ml of Milli-Q water until the rinse water was approximately at pH 3. The refluxing and rinse step was repeated several times and each time the suspension was allowed to settle and the supernatant was syphoned off. The pH of the suspension was then brought to 9.15 by addition of 5N NaOH and again, the suspension was washed in Milli-Q water. The pH was then brought to 7.15 by addition of a few drops of 0.05M $HClO_4$. The particle concentration was 205.6 mg/ml.

An aliquot of this stock suspension was exposed to high pH values for a prolonged time in order to allow complete hydrolysis after heating to 550°C. No difference could be detected compared with the aliquot stored at pH 7.15.

X-Ray Diffraction (XRD)

The XRD of the initial quartz material is shown in Figure 1 in which only lines of α-SiO_2 appear. Thus no secondary mineral phases appear to be present at weight concentrations greater than 2 percent.

Specific Surface Area Measurements (BET)

The specific surface area of the quartz was measured using Krypton-adsorption and data were evaluated according to the BET-theory (Brunauer et al, 1938). Part of the Krypton-adsorption isotherm is shown in Figure 2. A specific surface area (A_s) of 5.94 m^2/g was calculated. Spherical particles with a diameter of 5 μm have a specific surface area of A_s of 0.45 m^2/g.

The calculated A_s is much smaller than the measured A_s. We assume that smaller particles are present in our samples which make a large contribution to the total surface area. The particle size
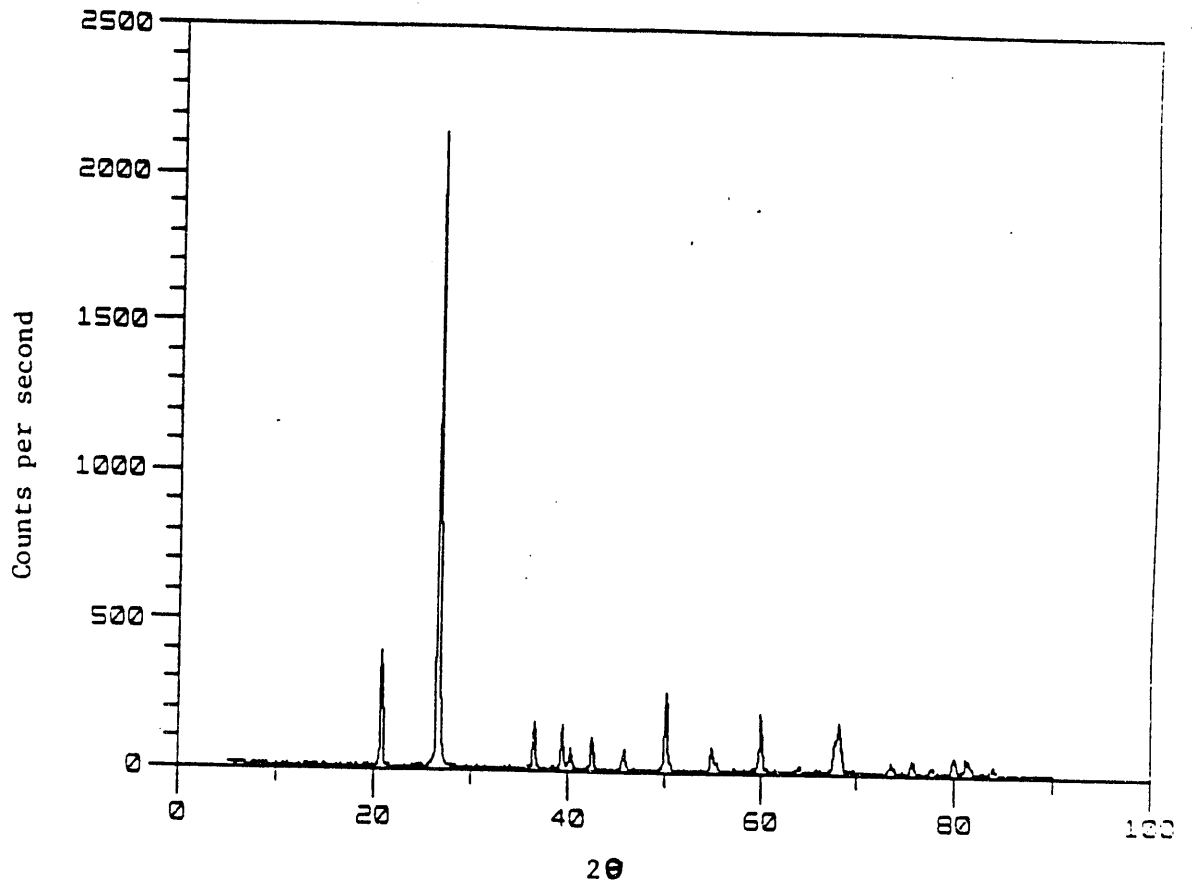
4

Figure 1

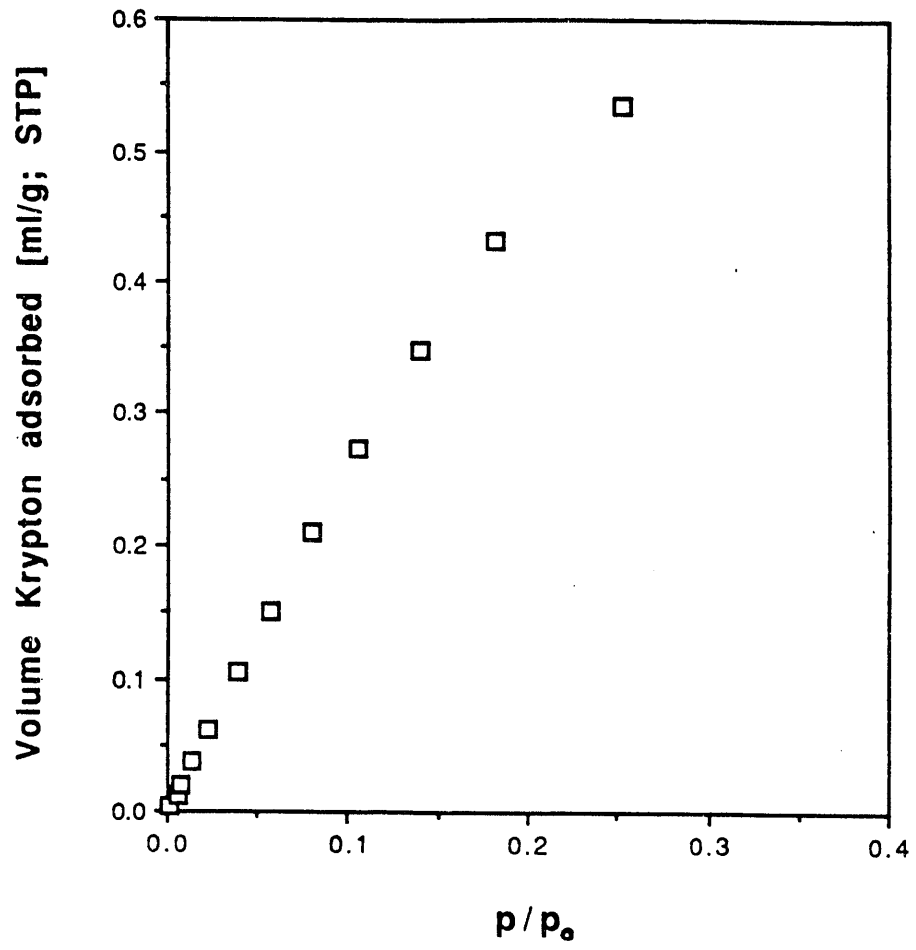# Krypton Adsorption Isotherm on Quartz

Figure 2

distribution of our sample is unknown. Assuming a number of 4.5 surface functional groups per $100A^2$ [a value which is commonly used for silica gels (Gregg and Sing, 1982)] the number of sites is 10^{-5} mol/g. For the number of silanol groups per surface area see also (Gregg and Sing, 1982).

Albite

Albite from Banccroft, Ontario was obtained from Wards Natural Science Establishment Inc., Rocherster, N.Y. After a first size reduction (grinding between metal plates) the albite was ground in a shatterbox to further increase the specific surface area. Batches of 10 to 20 g were ground for 1.5 minutes with a tungsten-carbide grinder. Three batches of 60 g were then suspended in pyrex glass beakers with 2 liters of Milli-Q water and stirred vigorously. Settling times of 3 to 4 days were allowed after which 15 cm of the water column was syphoned off. According to Stoke's law, most of the particles with diameters, d < 0.7 μm should therefore be removed. The process of suspension in Milli-Q water and syphoning was repeated 6 times adding 400 ml of fresh Milli-Q water each time. Removing the smallest particles is important, since they contribute a large fraction to the total surface area and are also more readily dissolved. Dissolution of the solids can interfere with sorption reactions.

The cycle was repeated three more times with 200 instead of 400 ml volumes. The batches were then left in Milli-Q water. One batch was exposed to pH 5 solution. A small amount of magnetic material which was removed after being concentrated was identified by XRD as elemental iron and probably entered the sample during the crushing and first grinding process.

X-Ray Diffraction (XRD)

The X-ray diffraction pattern of the solid confirms the presence of albite as the major mineral phase as shown in Figure 3.

Specific Surface Area Analysis (BET)

Krypton gas adsorption and the BET-theory (Brunauer et al, 1938) were used to measure the specific surface area, A_s, of albite. A value of 1.2 m^2/g was found. Part of the krypton adsorption isotherm on albite is shown in Figure 4. The albite was kept in Milli-Q water at a particle concentration of 108 mg/ml.
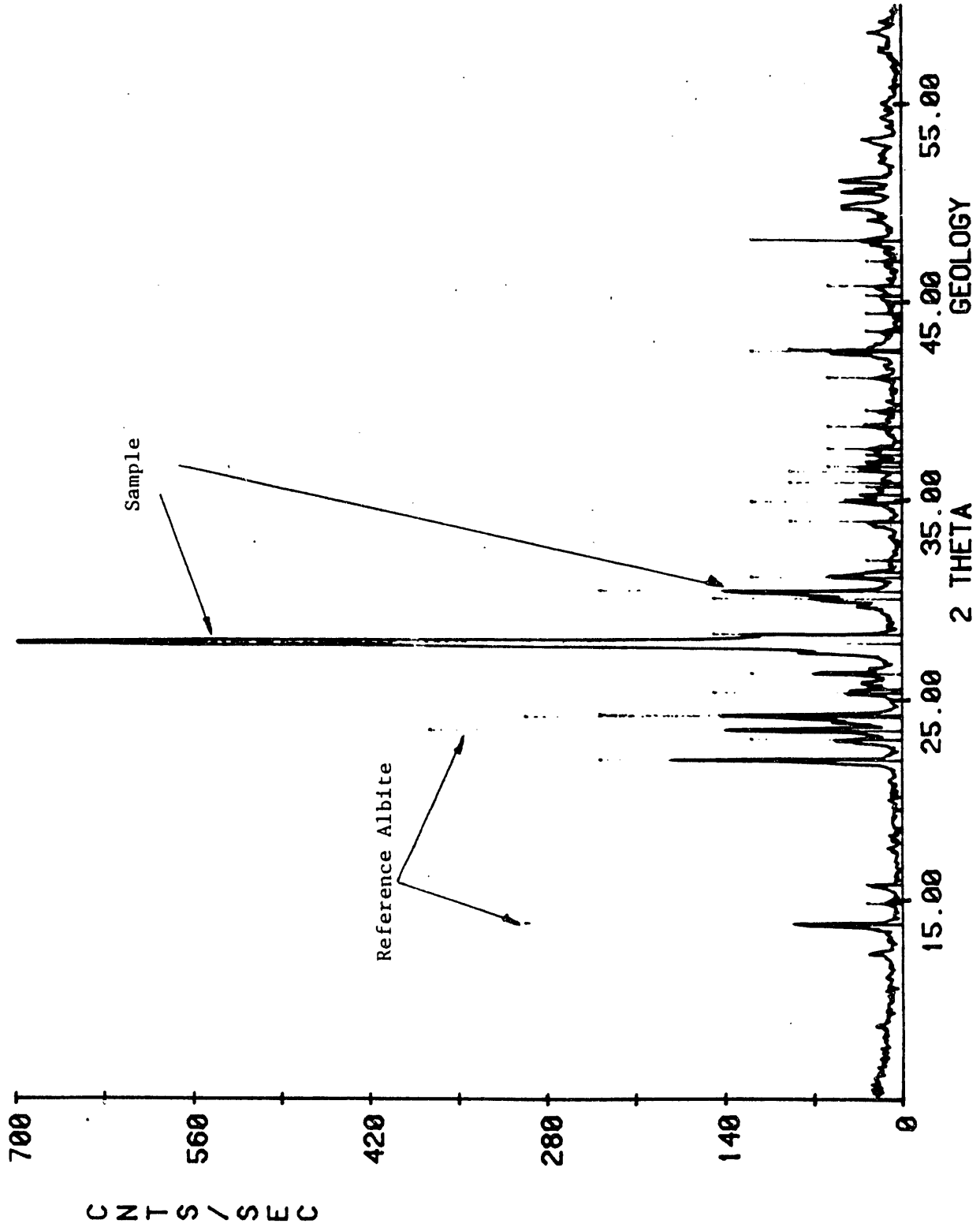
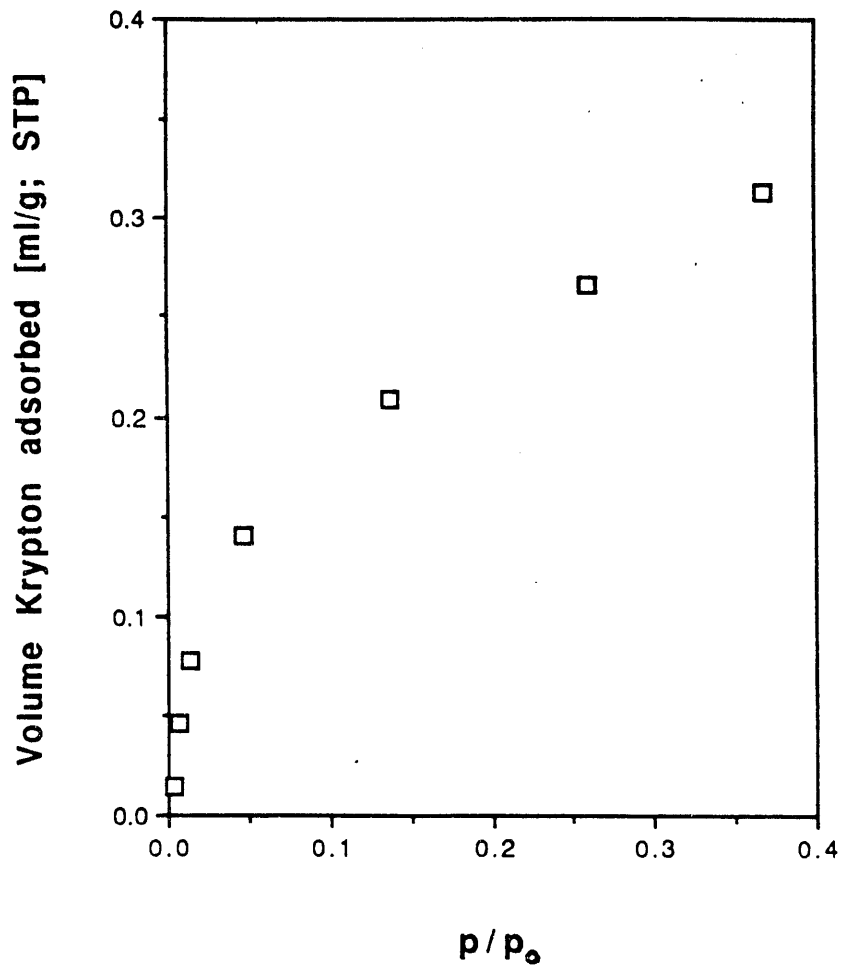Figure 3

Krypton Adsorption Isotherm on Albite

Figure 4

Determination of Neptunyl Concentration

Preparation of Neptunium for Subsequent Sorption and α-Counting

The source of ^{237}Np is described in the 1990 annual report (Kohler, et al, 1990) as well as the ion exchange separation of ^{233}Pa and ^{237}Np. A volume of 2-2.5 ml of Np-stock solution were separated prior to each experiment. In some experiments involving quartz, no separation was performed because sorption occurred at pH > 8 where all ^{233}Pa is sorbed onto the solid and therefore no interference from ^{233}Pa β-particles occurs with the ^{237}Np α-particles during counting of the supernatant. No difference could be found compared to those experiments where the separation of ^{233}Pa was performed. In experiments involving albite, the separation was always performed. Radiochemical purity was always checked by measuring the 311keV Gamma-line of ^{233}Pa. A 4.0 ml aliquot of the sample to be measured was mixed with 15.0 ml Ecolite(+). Measurements were performed on a Beckmann Liquid Scintillation Counter, equipped with a multi channel analyzer. α-peaks were integrated and concentrations calculated assuming 100% counting efficiency (Horrocks, 1974).

β Counting of ^{14}C-EDTA

^{14}C-EDTA was used in most experiments. The source and the procedure for stock solutions are described in the 1990 annual report (Kohler, et al, 1990). For concentration calculations reference samples were prepared. The reference sample were samples containing no solid but the same specific activity of ^{14}C-EDTA. As for ^{237}Np, ^{14}C-EDTA was assayed by liquid scintillation counting.

Double tagged experiments

Experiments involving both nuclides, ^{14}C and ^{237}Np, were performed. The α-spectra and β-spectra of ^{237}Np and ^{14}C, respectively, do not overlap under the chosen conditions. Double tagged experiments can therefore be performed using liquid scintillation counting and the adsorption behavior of both NpO_2^+ and EDTA can be investigated simultaneously.

Carbonate Sorption on Quartz and Albite

The system developed in our laboratory (Van Geen, et al, 1991) to measure the adsorption of carbonate species onto solids is shown in Figure 5. It consists of a main equilibration vessel

equipped with a gas dispersion tube, stir bar, and openings for a microburet and a pH-electrode. A septum plug allows the addition of e.g. acid with a syringe. The volumes of the different parts of the system are given in Figure 5.

First, the solution containing the solid particles is brought to pH < 4 and the system is purged to remove all carbonate species from the volume. A spike of known volume with a known CO_2 concentration (typically 10% CO_2 in N_2) is then injected into the system. After an equilibration time (during which the gas phase is constantly recirculated by pumping) a known volume of the headspace is analyzed for CO_2 by means of an infrared (IR) analyzer. The pH of the suspension is then increased stepwise by adding a few microliters of base (typically 1M NaOH) via the micro-buret, the system is equilibrated and an aliquot of the headspace gas is analyzed for CO_2 as described above. The suspension is titrated in this way to the desired upper pH limit.

The calculations were performed as follows. First, the distribution of CO_2 between headspace and solution as a function of pH is calculated. This is done in a blank system (no solid present, 0.1M $NaClO_4$ only). Corrections are made for each loss of CO_2 during analysis. Data for headspace CO_2 vs pH for systems containing solids are then plotted and in those systems containing the solid it is assumed that the same relationship between headspace CO_2 and solution carbonate as a function of pH is valid. Therefore, measuring headspace CO_2 at a certain pH value gives the solution carbondioxide concentration and knowing the total amount of carbonate in the system, the amount of carbonate adsorbed on the solid can be calculated by taking the difference with respect to the blank-experiment.

Experimental Protocol

Neptunium Sorption on Quartz

Experiments involving quartz were conducted in a 500 ml Pyrex glass batch reactor. Stock suspensions of quartz were added to Milli-Q water, $NaClO_4$ was added to give the desired ionic strength (I). The solid/solution ratio was 30 g/l in all experiments. The suspension was then brought to pH 3 with a few drops of 2M $HClO_4$ and the suspension was purged with argon through a glass fritt for 30 minutes to expel potentially sorbed carbonate species. The separated Np-fraction was then added. By addition of NaOH solution, the pH was raised stepwise and at each step samples of typically 10 ml were pipetted into a 50 ml polycarbonate centrifuge tube (CT), which were then placed onto a rotor for equilibration. During the titration of the suspension an argon head was maintained over the suspension in order to prevent CO_2 from entering.

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Sample loop

By-pass

A

B

Carrier gas →

← to IR analyzer

Standard/spike load

pH probe

Micro-buret

Pump

Septum

V_{total} = 268.5ml

$V_{liquid} = V_L$ = 200 ml

V_{loop} = 3.06 ml

$V_{loop+extra}$ = 4.47 ml

Bubbling sample solution
with metal oxide particles

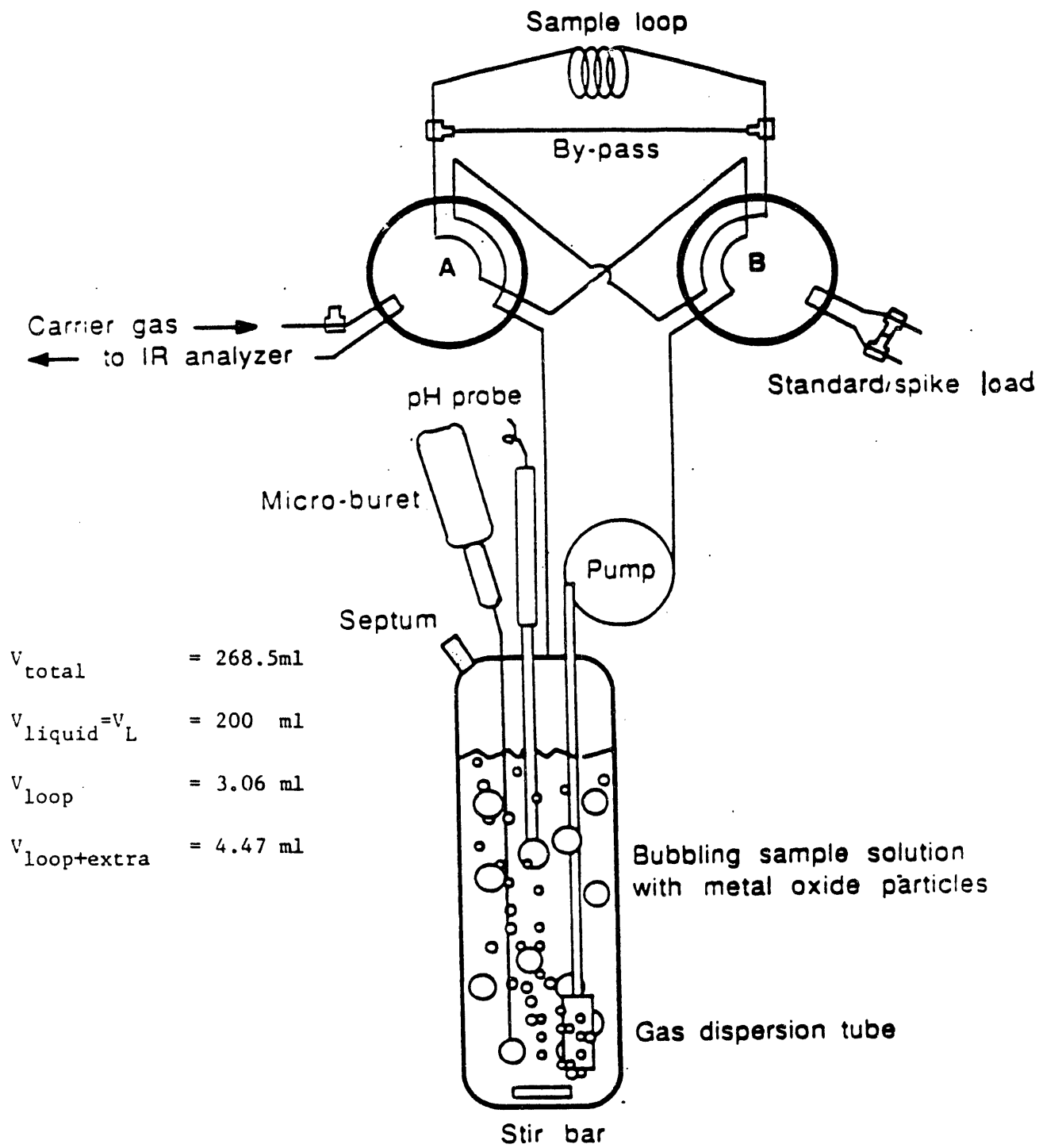Gas dispersion tube

Stir bar

Figure 5

Equilibration times were 16 to 24 hours. After equilibration, the final pH of each sample was measured, the samples were centrifuged on a bench top centrifuge and a 4.0 ml aliquot was pipetted to 15.0 ml liquid scintillation cocktail (LSC) (Ecolite (+)) in a plastic vial.

Mass balance checks were performed occasionally. The supernatant was withdrawn completely, the solid was resuspended in the initial volume of $2M$ $HClO_4$ and the sample rotated or for several hours, centrifuged and 4.0 ml of supernatant were pipetted to 4.0 ml liquid scintillation cocktail for counting.

EDTA Sorption on Quartz

Ethylene Diamine Tetraacetic Acid (EDTA) sorption on quartz was performed in the same type of batch reactor as the neptunium sorption described above. No adsorption of EDTA onto the reactor walls could be measured at $1 \cdot 10^{-6}M$ EDTA over a pH range of 2-10.

Neptunium Sorption on Albite

Experiments on the Np/albite system were conducted in individual polycarbonate centrifuge tubes, each containing the appropriate amount of albite, ionic strength and Np-concentration.

Samples were pretreated in two different ways. Samples prepared by pretreatment A were brought to the pH value of the subsequent sorption and pH was readjusted from time to time. In pretreatment B, the pH value of the solution was again brought to the pH of subsequent sorption, but instead of only readjusting the pH from time to time, samples were centrifuged, the supernatant was withdrawn, new electrolyte solution was added and the pH readjusted to the desired value. Samples with pretreatment A are referred to as weathered samples, whereas samples with pretreatment B are referred to as unweathered.

After the pretreatment, aliquots of separated [237]Np were added to each centrifuge tube, pH was readjusted and the samples were equilibrated for 16 to 20 hours on a rotor. After equilibration the final pH was measured, centrifuged and 4.0 ml aliquots of the supernatant were pipetted into 15.0 ml LSC. Mass balance checks were performed as described above for quartz.

EDTA Sorption on Albite

The same pretreatment of the albite was followed as described above or for the Np/albite system, and aliquots of concentrated EDTA solution were pipetted to each centrifuge tube. Reference samples were run in parallel, containing no solid.

Experiments at Controlled Atmospheres

Exclusion of CO_2: Suspensions were brought to pH values <4 and purged with argon to remove all carbondioxide. During the experiments an argon head was kept over the suspension in the case of experiments performed in batch reactors or the suspensions in the centrifuge tube's were purged with argon while the centrifuge tubes were open for pH measurements. Samples were rotated in a glove bag, purged with air that was filtered through an ascarite filter to remove CO_2. No attempts were made in experiments with albite to exclude atmospheric CO_2-gas.

Controlled CO_2 Atmosphere:

In experiments conducted at atmospheric P_{CO_2} ($P_{CO_2} = 10^{-3.5}$ atm) compressed air was purged through the suspension and at pH > 9 , $NaHCO_3$ was added allowing much shorter equilibration times.

At increased partial pressures of $CO_{2(g)}$ ($p_{CO2} = 2 \cdot 10^{-2}$ atm) a gas mixture was used (1.95% CO_2 in N_2). Again, samples were purged with the gas-mixture and 0.1M, 1M or solid $NaHCO_3$ was added as a carbonate source for the same reason stated above. Samples were rotated over night in a glove bag that was constantly purged with the gas mixture.

4. RESULTS AND DISCUSSION

An overview of neptunium chemistry in the hydrosphere and in the geosphere is given by Lieser and Mühlenweg (1988). A stability diagram of the different Np-species is shown (Figure 6) as a function of pH and Eh (from Lieser and Mühlenweg, 1988) which shows that under laboratory conditions (aerobic conditions) Np is present as Np(V), mostly as NpO_2^+.

Quartz

Standard Adsorption Edges

Figure 7 shows adsorption edges (fraction Np(V) adsorbed vs. pH) of Np(V) onto quartz at different sorption times ranging from 54 to 111 hours. No difference in adsorption was observed over this time period within experimental error. Sorption starts to become significant only at pH > 8. We used 30 g/l quartz, assuming 2.31 sites per nm^2 and with 5.9 m^2/g we calculate a site concentration of $6.8 \cdot 10^{-4}M$. 2.31 sites/nm^2 is a low value but is in accordance with the suggestions proposed by Davis and Kent (1990). Site concentrations of silica gels are reported to be 4.5 to 5 sites/nm^2 (Gregg and Sing, 1982), which would lead to a site concentration of $1.5 \cdot 10^{-3}M$. In the iron oxide experiments a site concentration of approximately $2 \cdot 10^{-4}M$ was used and the adsorption edge was at lower pH values indicating stronger adsorption of Np(V) onto the iron oxides.

The experimental design included calculations to assure that precipitation of $NpO_2OH(s)$ did not occur for the experimental conditions in this study. Figure 8 shows data for the pH adsorption edges of NpO_2^+ on quartz up to pH 12. Significant adsorption occurs only above pH 10 and no precipitation is evident up to pH 12. Precipitation would result in a step function going to 100 percent removal. Lieser and Mühlenweg (1988) reported a range of solubility products for $NpO_2OH(s)$ (log K_{so} = -8.81 to -9.73). Since experiments were conducted at $Np_T = 1.4 \times 10^{-7}$ M and calculations showed no precipitation would occur until pH > 13 because the formation of hydrolysis products $(NpO_2(OH)_2^-)$ lowers the activity of NpO_2^+.

The Effect of Ionic Strength

Figure 9 shows no measurable effect on the adsorption edge at increasing ionic strength. However, errors at low fractional uptake are relatively large. Binding constants will be derived at 0.1M $NaClO_4$ using a surface complexation model. The adsorption edge for 0.001M $NaClO_4$ will
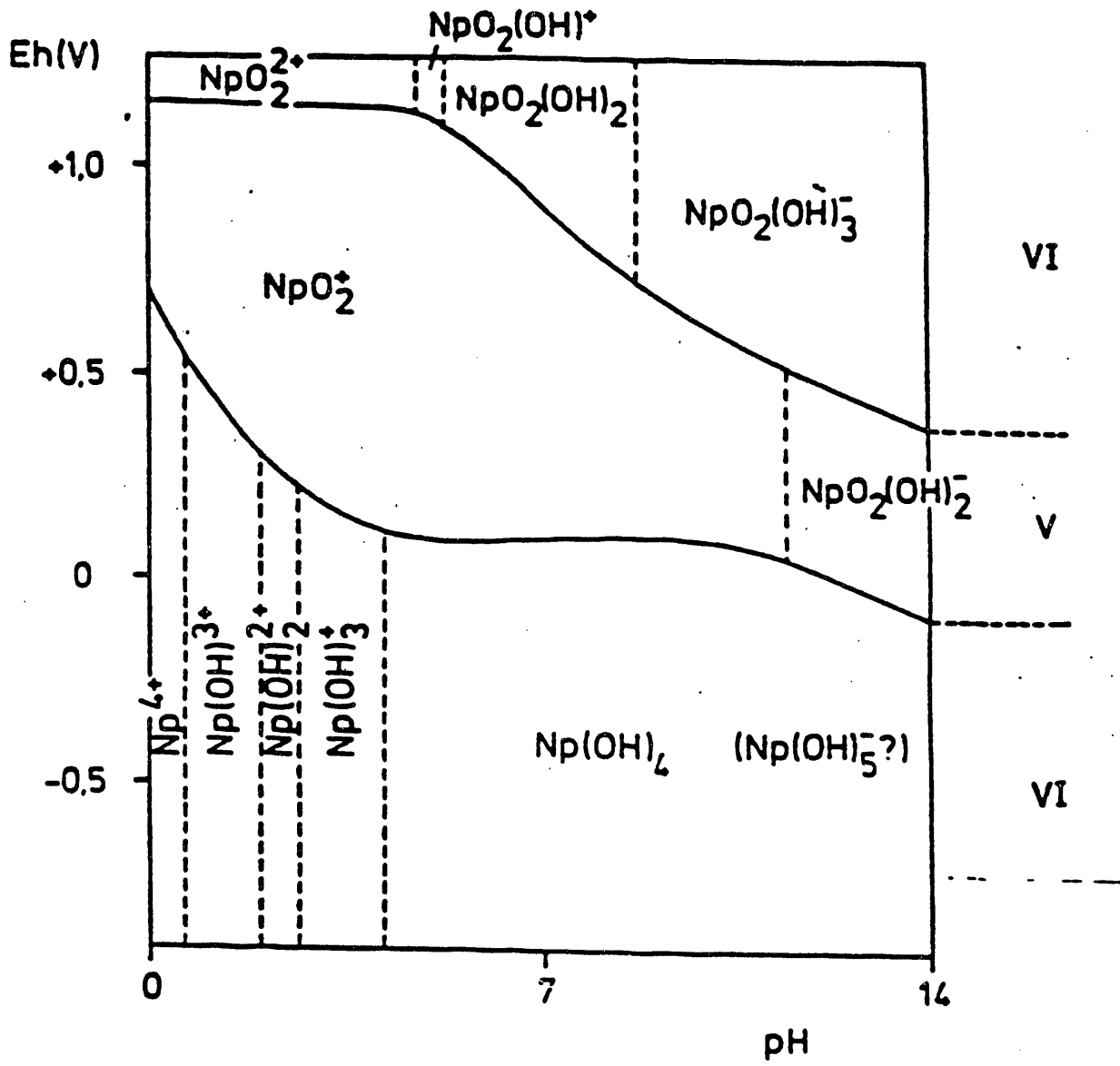
Figure 6

Sorption of Np(V) onto Quartz
I = 0.1M NaClO4,   S/L = 30 g/l
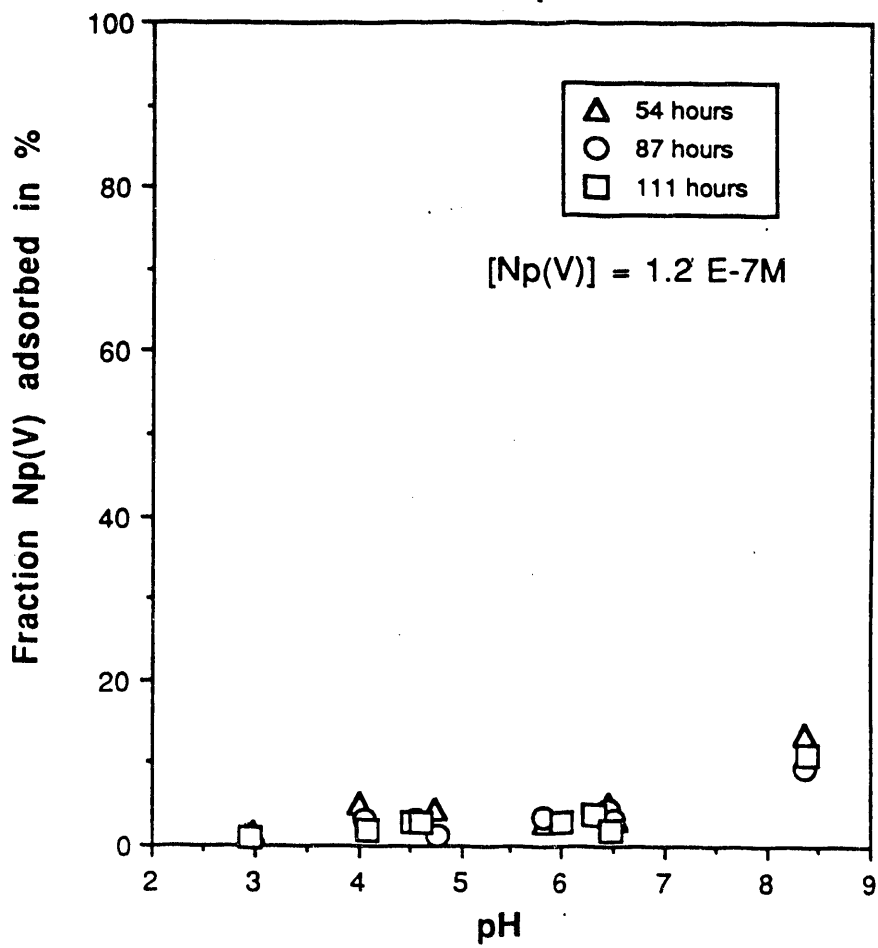# Variation of Sorption Time

Figure 7

Sorption of Np(V) onto Quartz
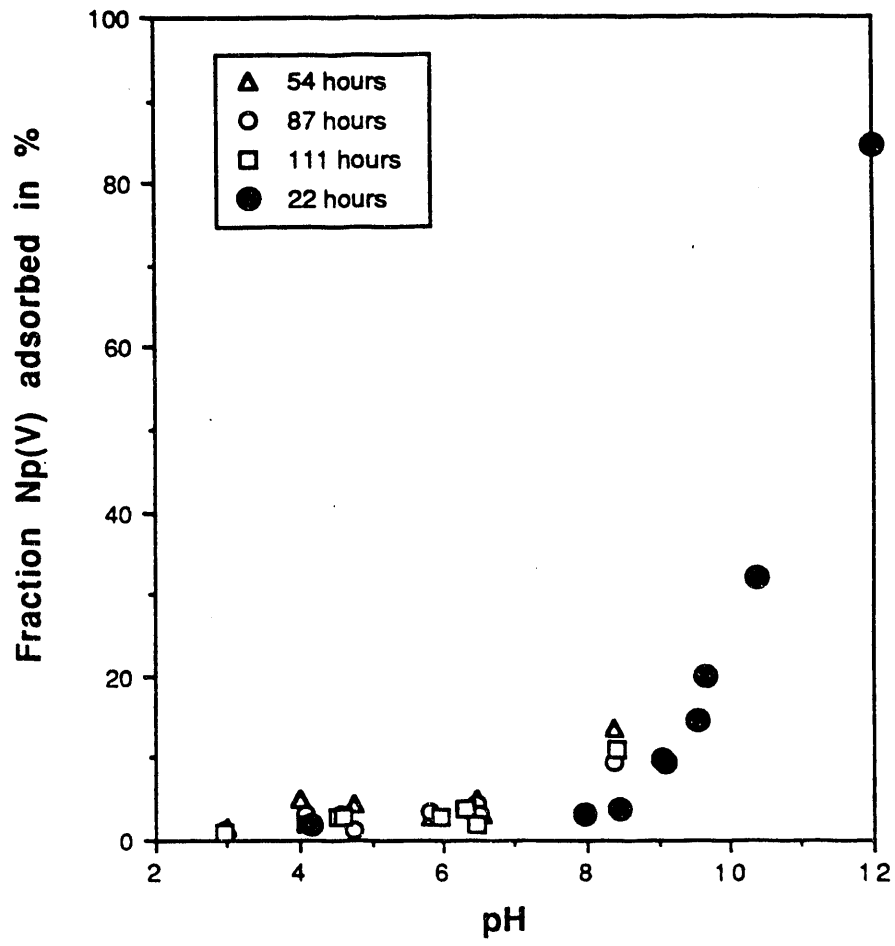## I = 0.1M NaClO4,   S/L = 30 g/l

Figure 8

Sorption of Np(V) onto Quartz
I = 0.1 and 0.001M NaClO4
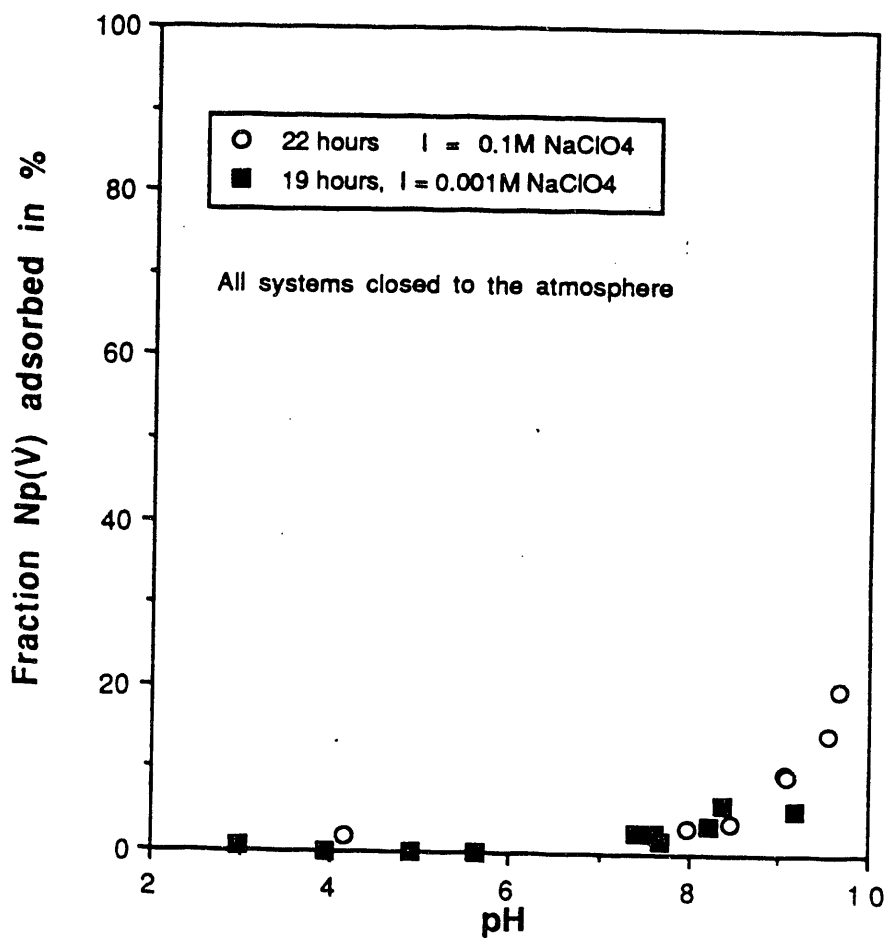S/L = 30 g/l,   [Np(V)] = 1.4E-7M

Figure 9

be estimated using the binding constant derived at the higher ionic strength. Also, a literature review of adsorption of metal cations onto Si-OH bearing minerals such as quartz or silica gels might give some insight into whether inner- or outer-sphere bonding can be expected for NpO_2^+.

Variation of the Ratio Np_T/Solid

Figure 10 shows two adsorption edges at different Np(V) concentrations at the same solid/liquid ratio. As expected, the edge for the lower concentration starts at lower pH. Again, it is possible that modeling of both adsorption edges can be accomplished with one single set of binding constants, since the number of surface sites is much greater than total Np ($1.5 \cdot 10^{-3}$M) $>>$ (10^{-7}, 10^{-8}M). Sorption equilibration times were very similar, so that no kinetic effects are apparent.

Effect of CO_2 upon Np(V) Sorption

The effect of CO_2 on the adsorption edges of Np(V) in the presence of carbonate species is summarized in Figure 11. The formation of Np-carbonato complexes in solution is well known and complex formation constants are established (Nitsche and Standifer, 1990). The data in Figure 11 suggest that at pH > 8 where edges in the presence of carbonate are lower than in absence of carbonate, carbonato complexes of Np(V) in solution prevent the adsorption of the actinide ion. Furthermore, as shown later, carbonate itself does not adsorb strongly onto quartz at pH > 8, therefore, ternary complexes of the form $Si\text{-}OH\text{---}HCO_3^-\text{---}NpO_2^+$ are not likely to be formed.

EDTA Sorption

No significant adsorption (> 5%) of EDTA at $1.0 \cdot 10^{-6}$ M over the pH range 2.08 to 9.41 was observed. In this pH range, EDTA is in the form of a divalent and trivalent anion, whereas the quartz surface is predominantly negative.

Effect of EDTA at 50 μm upon NpO_2+ Adsorption

Figure 12 shows adsorption edges in the presence and absence of 50 μM EDTA. As can be seen, virtually no uptake of NpO_2^+ takes place at 50 μM EDTA over a pH range from 3 to 10. This is explained by the formation of solution species such as NpO_2EDTA^{3-} and NpO_2HEDTA^{2-} which are non-adsorbing. EDTA itself is not adsorbed and the formation of ternary surface complexes as in the case of hematite (Kohler et al, 1990) can be excluded.

11

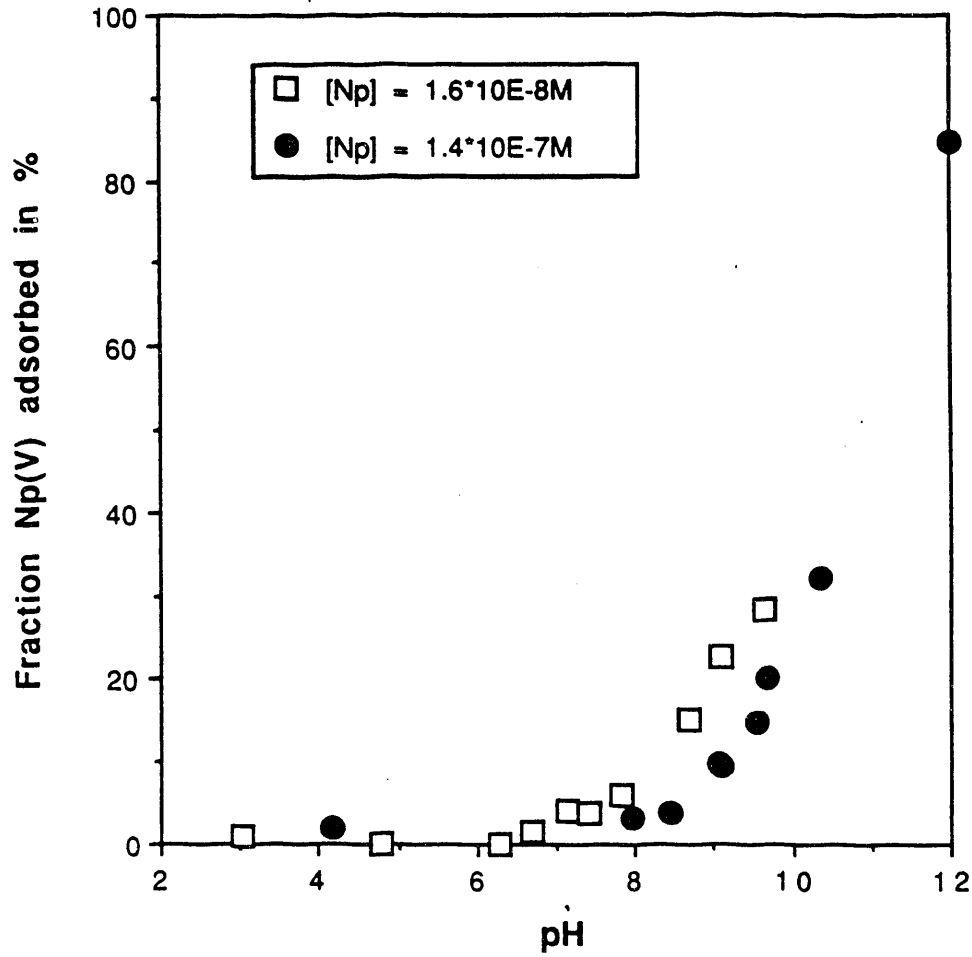## Sorption of Np(V) onto Quartz
I = 0.1M NaClO4, S/L = 30 g/l

Figure 10

Adsorption of Np(V) onto Quartz
Effect of p(CO2)
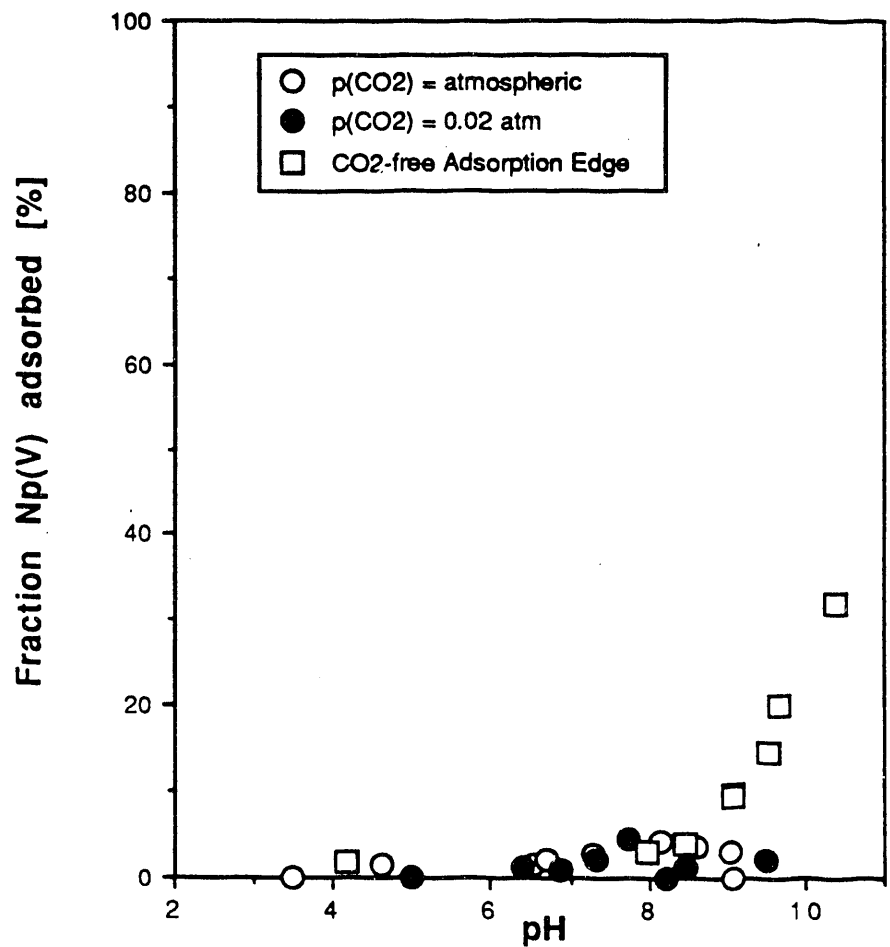## [Np]=1.4E-7M, 30g/l, 0.1M NaClO4

Legend:
- ○ p(CO2) = atmospheric
- ● p(CO2) = 0.02 atm
- □ CO2-free Adsorption Edge

Y-axis: Fraction Np(V) adsorbed [%]
X-axis: pH

Figure 11

Sorption of Np(V) onto Quartz
I = 0.1 M NaClO4, [EDTA] = 50 uM
S/L = 30 g/l, [Np(V)] = 1.4E-7M

All systems closed to the atmosphere

△	Absence of EDTA
O	Absence of EDTA
●	50 uM EDTA

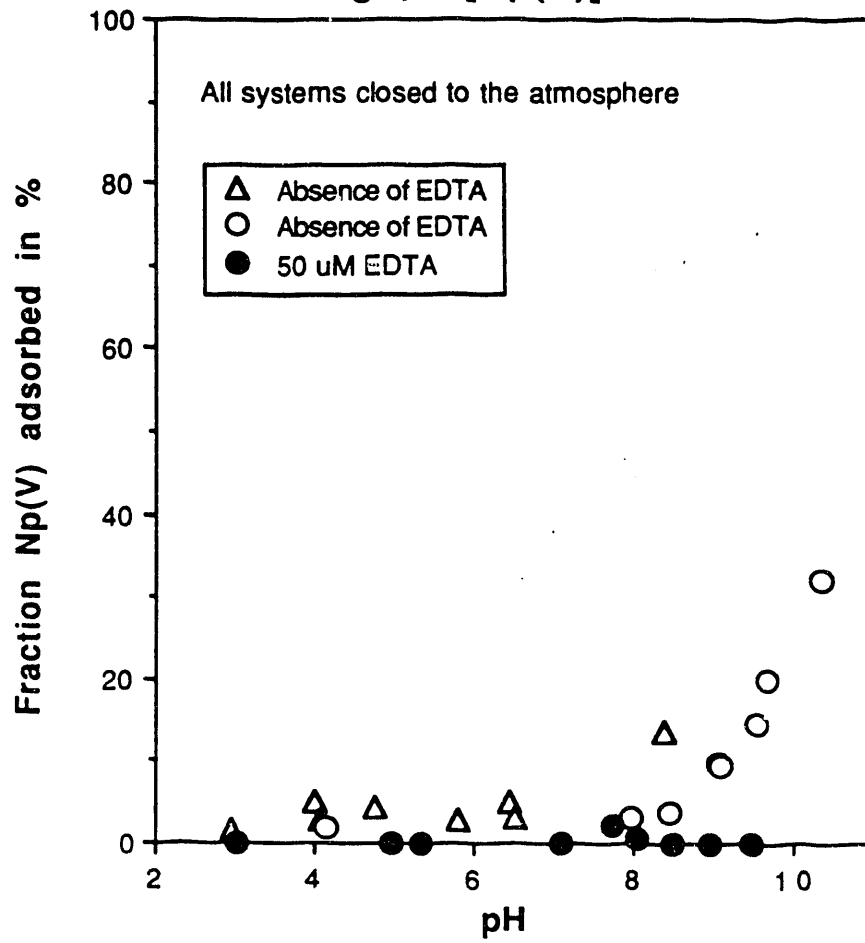Fraction Np(V) adsorbed in %

pH

Figure 12

Reversibility of NpO₂+ Adsorption

Reversibility in this context means that the equilibrium composition of the system does not depend on the initial conditions and that it should not matter from which side the final pH is reached. Therefore the pH history of the system must not play a role.

In the reversibility study, the pH of the suspensions were raised initially to approximately 10, to adsorb Np(V) for varying times, then pH was lowered to the desired value where the samples were equilibrated for different times. Figure 13 summarizes the results. Two cases are distinguished: Case 1, where we adsorbed NpO_2^+ at pH 10 for minutes, brought the pH down and equilibrated for 20 hours. Case 2, in which the samples were kept at pH 10 for 20 hours, followed by lowering pH and equilibrating for minutes.

Case 1 shows no difference within experimental errors to the adsorption edges without ligands (Figure 12). Case 2 shows significant differences with respect to the normal adsorption edge in the pH range $3 < pH < 8$ in that a significant fraction of NpO_2^+ which seems to be almost independent of pH remains sorbed.

A possible explanation for this behavior is that the 20 hours exposure of the quartz to pH 10 solutions dissolved significant amounts of quartz as $H_3SiO_4^-$ (Stumm and Morgan, 1981). When the pH is lowered precipitation and recrystallisation or formation of amorphous SiOH can occur at the quartz surface burying underlying sorbed NpO_2^+.

Albite

In the following discussion weathered albite refers to pretreated albite with 0.1M $NaClO_4$ where the pH was adjusted only, whereas unweathered albite implies a pretreatment of albite with 0.1M $NaClO_4$ in which the solution was replaced and pH adjustment was done. Normally, under a chosen set of experimental conditions, adsorption edges were measured including a sample series that underwent both pretreatments.

Figure 14 shows the data of normal adsorption edges, including weathered and non weathered samples. The specific surface area is approximately 50 m²/l, which is equiv· .nt to $1.9 \cdot 10^{-4}$ M in sites. Within experimental error, no difference in the curves were observed up to pH values of approximately 8 to 9. Above pH 9 a distinct and reproducible difference occurs in the edges, depending on the pretreatment of the solids. The weathered samples show a sharp increase in

"Reversibility" of Np(V) Adsorption onto
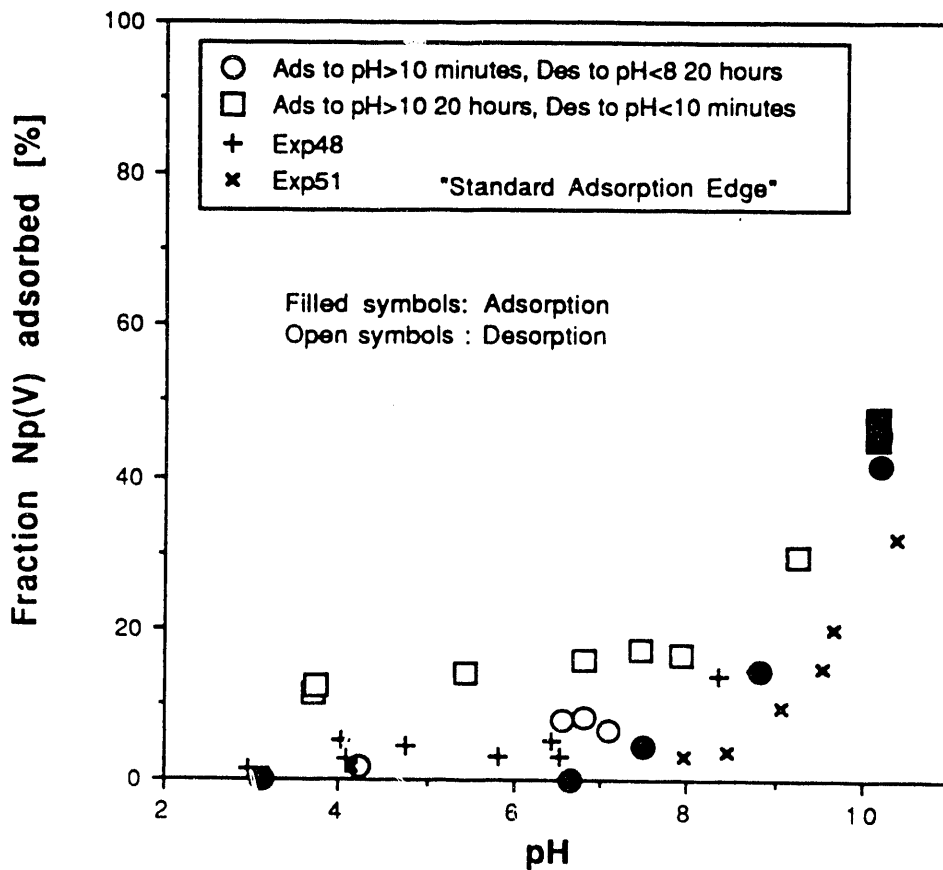Quartz with Respect to pH
[Np] = 1.4E-7M, 30g/l, 0.1M NaClO4

Figure 13

Np(V) Adsorption onto Albite
I = 0.1M NaClO4, 40g/l, [Np] =(1.3-1.4)E-7M
Different Pretreatment of Solid

Solution not replaced
during pretreatment

Previous Experiments

New Experiments,
extended, diff.
pH range

Solution replaced
during pretreatment

Open Symbols: Liquid Phase Measurement
Closed Symbols: Solid Phase Measurement
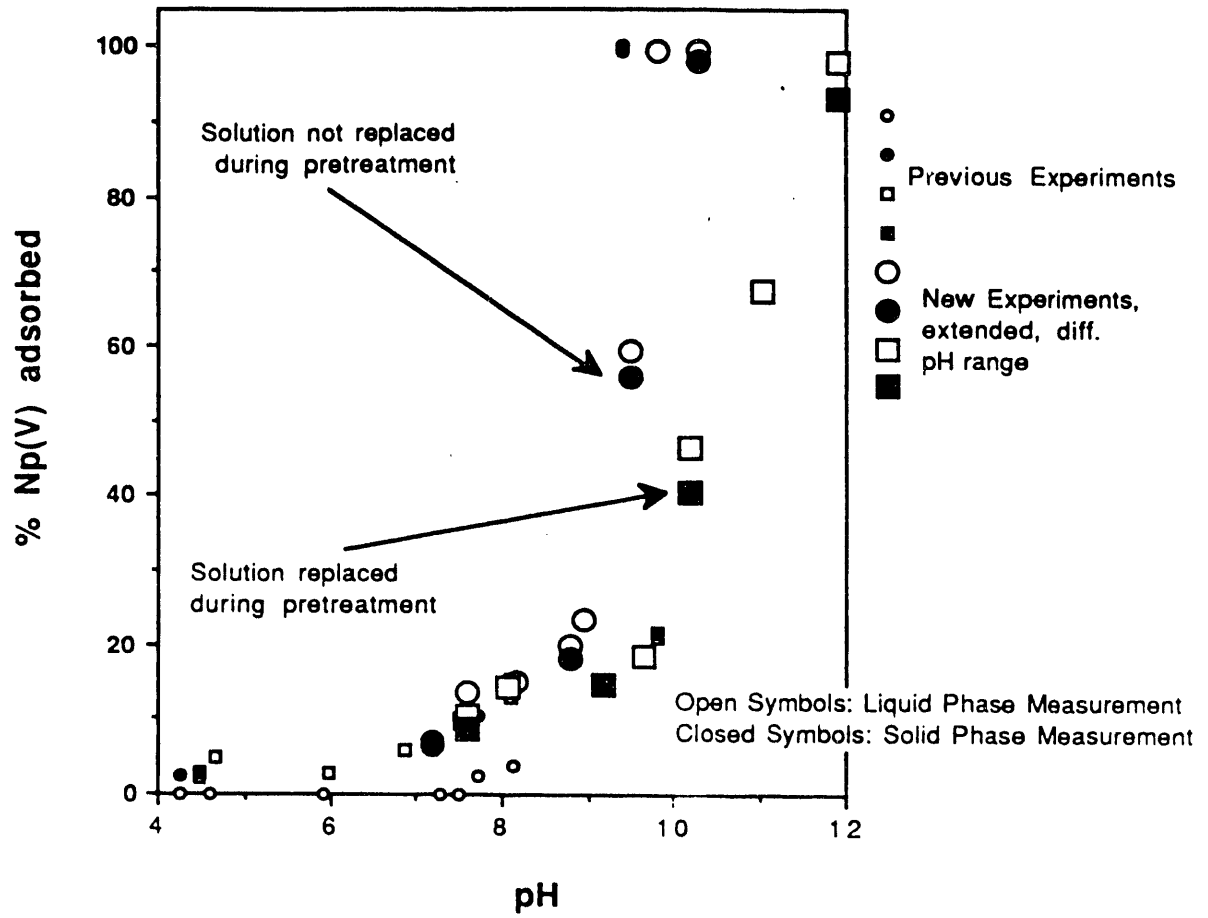
% Np(V) adsorbed

pH

Figure 14

sorption from approximately 20% to 100% in a small pH interval of < 0.3 pH units, whereas the unweathered samples show normal behavior which is a gradual increase of sorption with increasing pH. The adsorption edge of the latter indeed resembles the one of quartz (compare with Figure 7), notice although that the site concentration was larger for quartz.

When solutions are replaced during pretreatment, Al^{3+} may be removed from the top layer of the albite surface, leaving a silicon enriched surface behind, consisting mainly of surface silanol groups, Si-OH, as in quartz. When the solutions are not replaced, samples are weathered, Al^{3+} precipitated, forming secondary Al-phases such as gibbsite ($Al(OH)_3$) which sorb NpO_2^+ stronger than quartz. Experiments conducted on pure gibbsite minerals showed that the adsorption edge of NpO_2^+ on gibbsite was indeed at approximately pH 6 (Wieland, personal communication).

A better understanding of the processes going on at the albite surface will require a more detailed and time consuming study involving analysis of the solution compositions with respect to the major cations constituting albite and possibly spectroscopic techniques to get a clearer picture of the surface composition. As can be seen from Figure 15 weathering times of up to two weeks have no effect on the NpO_2^+ adsorption.

EDTA Adsorption onto Albite

The results of EDTA adsorption at [EDTA] = $1.0 \cdot 10^{-6}$M onto albite are shown in Figure 16. Pretreatment (weathered/non-weathered) has no measurable influence on the adsorption behavior. Total site concentration was approximately $2 \cdot 10^{-4}$M. The coverage of the albite surface with EDTA is therefore below 1 percent. The adsorption behavior is typically anionic in that there is relatively high adsorption at low pH and low sorption at high pH. There is virtually no sorption at pH > 8 unlike the case for iron oxides (Kohler et al, 1990). Since there was no sorption of EDTA on quartz, we assume that sites other than SiOH are responsible for the sorption of EDTA, possibly Al-OH.

NpO2+/EDTA/Albite

A comparison of Figure 14 with Figure 16 shows that there is almost no overlap of the EDTA and NpO_2^+ adsorption edges on albite. The formation of ternary complexes is unlikely. Figure 17 gives experimental proof, that 1µM EDTA has no effect on NpO_2^+ sorption under the chosen conditions.

Np Adsorption onto Albite
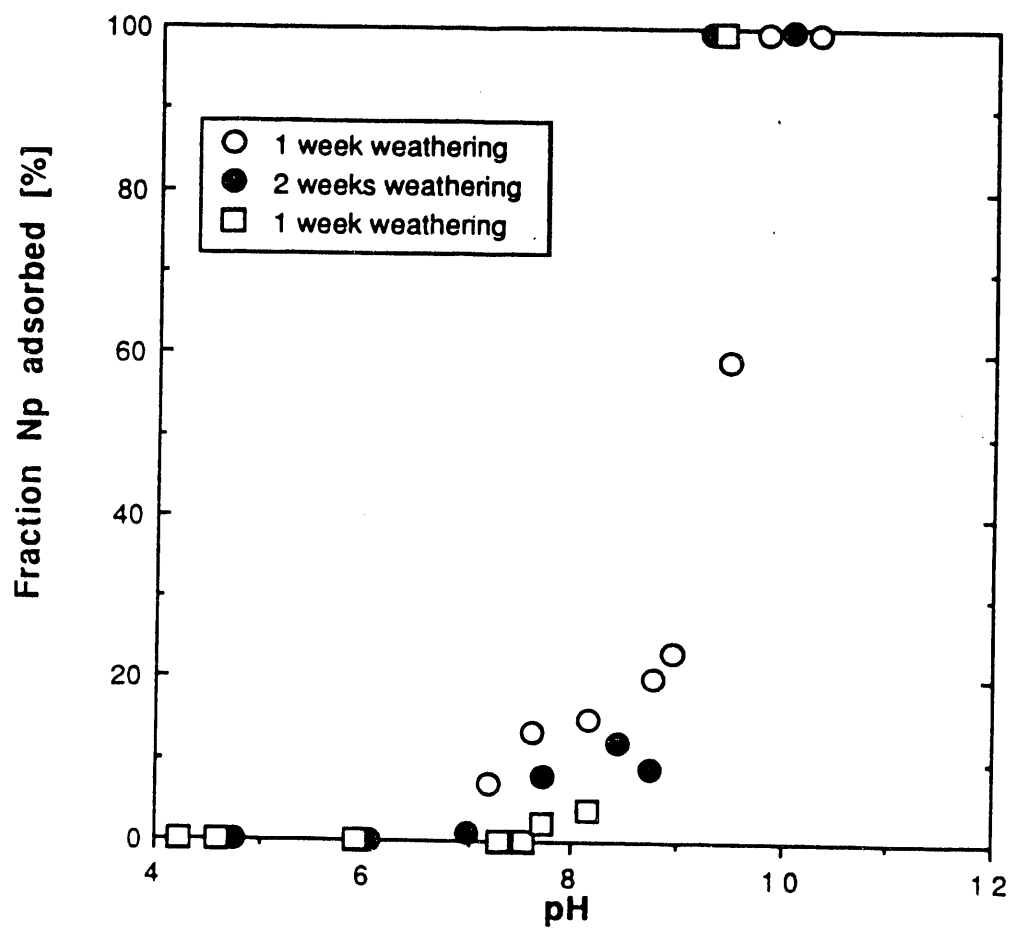## Influence of Pretreatment Time
[Np] = (1.1-1.3)E-7M, I = 0.1M NaClO4

Figure 15

EDTA Adsorption onto Albite
[EDTA] = 1E-6M, I = 0.1M NaClO4, 40g/l
Different Pretreatments of Albite

□ Solution not replaced
■ during pretreatment
○ Solution replaced
● during pretreatment

Open Symbols: Liquid Phase Measurement
Closed Symbols: Solid Phase Measurement

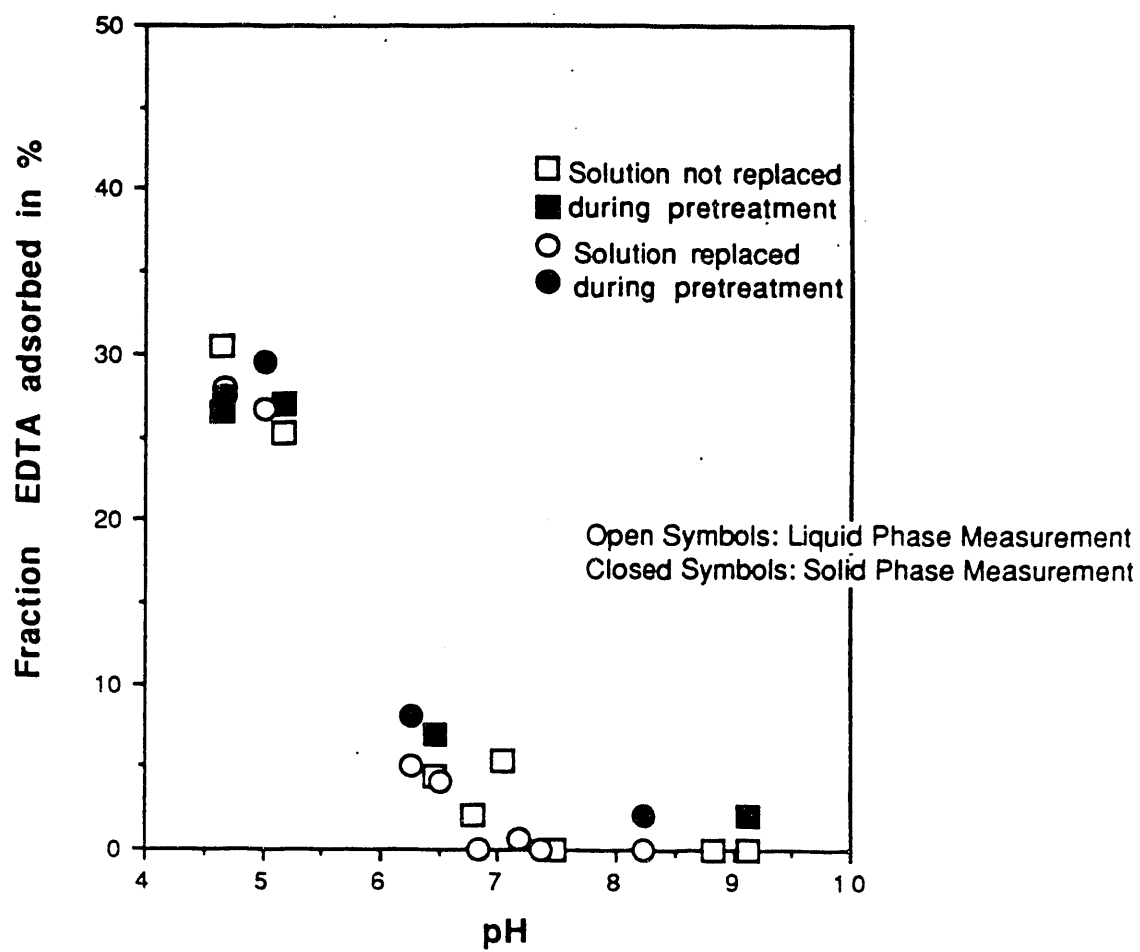Fraction EDTA adsorbed in %

pH

Figure 16

Adsorption of Np onto Albite in Presence of
EDTA; [Np] = 1.2E-7M, [EDTA] = 1μM
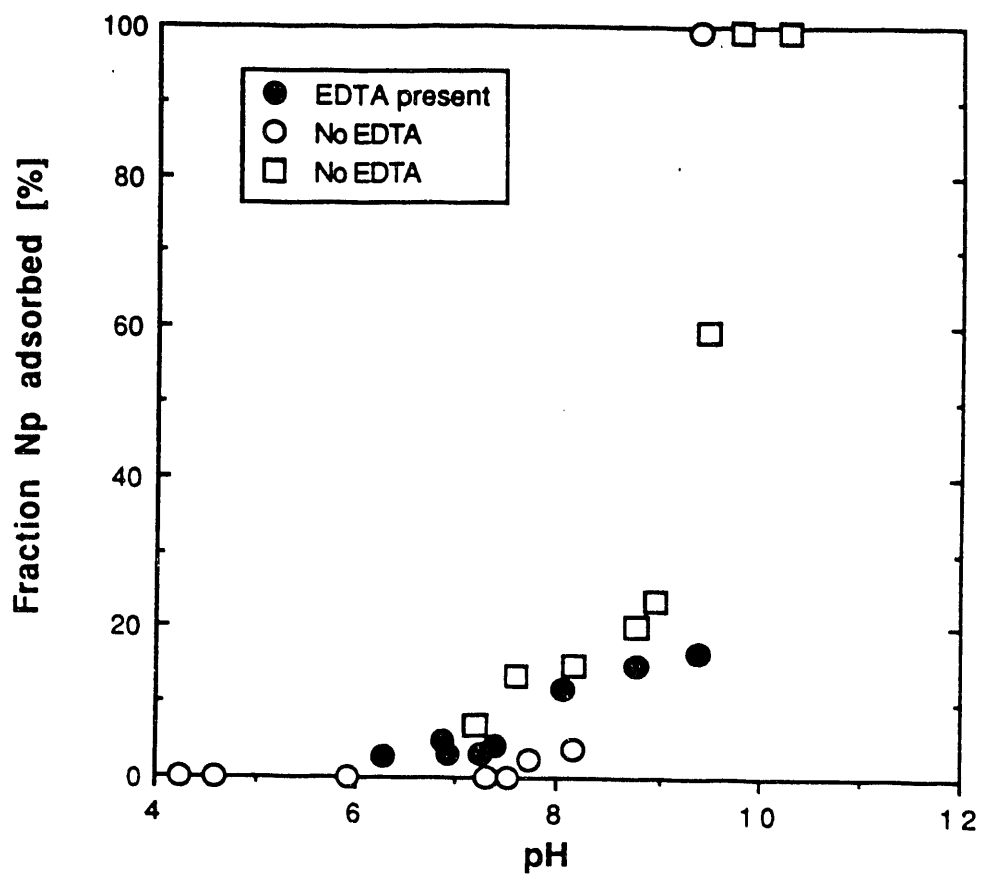I = 0.1M NaClO4, S/L appr. 40g/l

Figure 17

Carbonate Adsorption onto Quartz and Albite

The adsorption behavior of CO_2-species on quartz and albite is depicted in Figure 18. Both curves show the same general behavior found for the iron oxides, little sorption at low pH, maximal sorption at pH 6.5 to 7 followed by weak sorption at pH > 8. pH 6.5 to 7 is the main dominance of the species HCO_3^- which can adsorb as an anion onto positively charged surface sites such as $AlOH_2^+$ forming surface complexes of the form $AlOH_2^+$---HCO_3^-. For both solids, the possibility of the formation of complexes such as S-OH---H_2CO_3 exists where S = Si, Al.

Adsorption of Carbonate Species onto Albite and Quartz
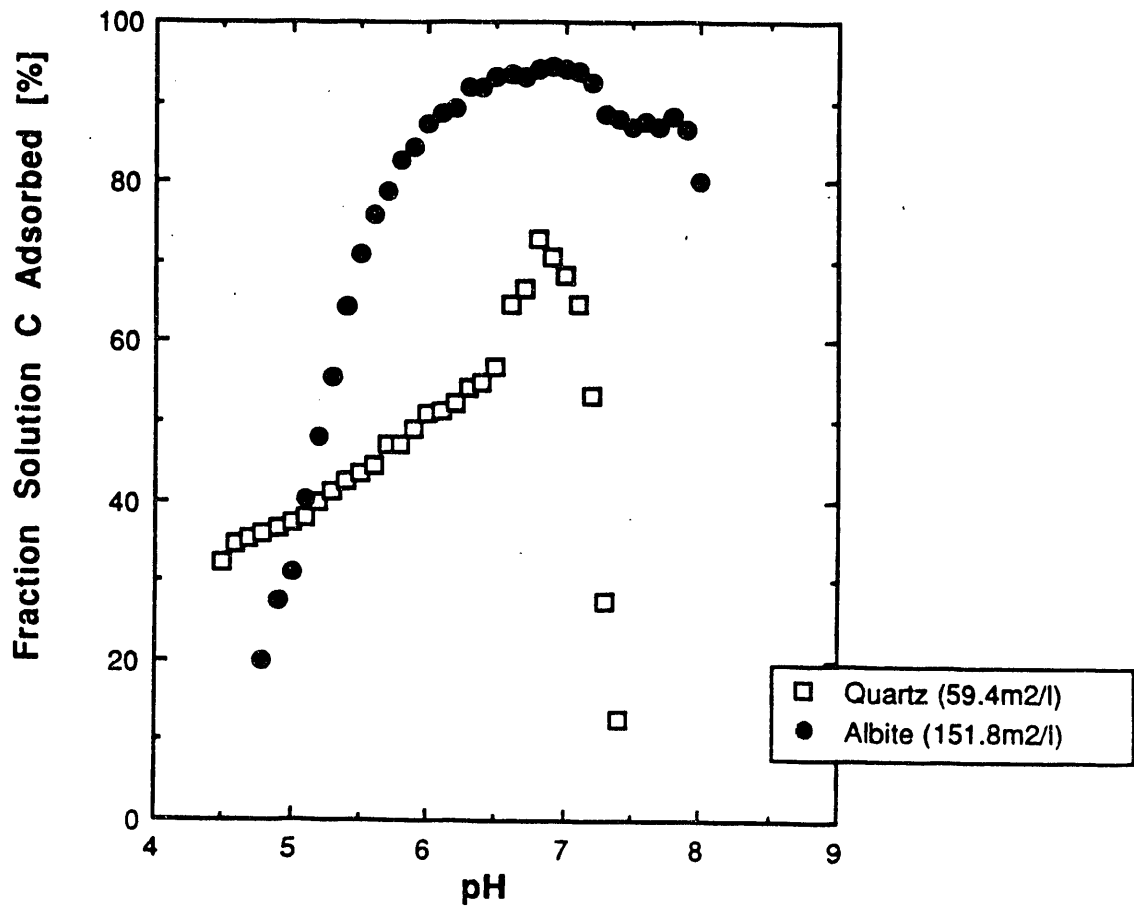**I = 0.1M NaClO4**

Figure 18

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