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Valence Effects on Adsorption

A Preliminary Assessment of the Effects of Valence State Control on Sorption Measurements

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Prepared for the
U.S. Nuclear Regulatory Commission
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ABSTRACT

Estimation of the rates of migration of nuclides from nuclear waste repositories requires knowledge of the interaction of these nuclides with the components of the geological formations in the path of the migration. Determination of these interactions requires that the valence state of the nuclide be known. If the valence state is not known, then there can be no confidence in use of the data for safety analysis. The valence state of some nuclides can be determined by means of solvent extraction techniques. Spectrophotometry can also be used but only at concentrations high enough to give enough absorption of light. The use of Eh-pH diagrams along with an indicator electrode in the solution to predict valence states assumes that the entire system is at equilibrium and that the electrode is at equilibrium with the redox systems in the solution. Attainment of equilibrium is not often attained however, and unless equilibrium can be demonstrated, indicator electrodes along with Eh-pH diagrams must be used with considerable caution. Electrochemical arguments are advanced to illustrate that what is usually measured in practice is a mixed potential determined by the kinetics of the electrode processes occurring at the indicator electrode.

Valence states can be altered electrochemically or by use of added chemical reagents, including redox couples which can hold the potential to relatively specific potentials. The disadvantage of added chemical reagents is that they may alter the characteristics of the sorption reactions by interaction with the sorbent. Electrochemical methods are versatile and do not add reagents, but in some cases the nuclide can adsorb on the electrode itself. A description is given of the application of the electrochemical method of valence control to determination of sorption of Np(V) on alumina.

Valence state control and analysis can be used to study possible redox reactions on materials which might be used as backfill materials. A description is given of survey experiments with a number of sulfides and iron-containing materials. Valence state analysis is used on the initial solutions and leachate from acid leaches of the sorbent after the sorption experiment to help determine whether valence state change is occurring. The preliminary results indicate that on the sulfides tested, sorption occurs both with and without valence state change.

VALENCE EFFECTS ON SORPTION

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1. INTRODUCTION

One of the most critical problems in the safety assessment of proposed nuclear waste repositories is the estimation of the rates of migration of nuclides that might be released in the event of a breach of the repository. There are a number of difficulties in the estimation of these rates, and surely, one of the most critical is the determination of the interaction of the nuclide with the minerals present in the geological formations in the path of the migrating nuclide. Consequently, considerable effort has been expended recently by laboratories in many countries in the study of the sorption behavior of these nuclides. Almost traditionally, these experiments have usually been conducted using a standard batch procedure in which a solution containing the nuclide is contacted with the mineral over a period of time. The reduction in concentration of the nuclide in the solution is measured and the concentration of the nuclide on the mineral is then calculated by use of mass balance. The results have generally been expressed as K_d , which is defined as the quotient of the concentration of nuclide on the mineral divided by the concentration in the solution. If concentration on the mineral is expressed by moles/kg and in the solution by moles/liter, the units will be liters/kg; in many references the essentially equivalent units of cubic centimeters per gram are used. Other methods of measuring K_d have been used, including various column methods. Below we describe a circulating column method.

The validity of this type of measurement is crucial to any reliable estimate of the migration rate. Further, if it could be shown that K_d is high, i.e., that interaction is strong for a given nuclide with almost all minerals, then the other uncertainties in estimating migration rates will be of relatively smaller importance. Unfortunately, there was an early impression that K_d for a given mineral and nuclide was a constant and independent of the many variables that are now known to affect sorption. Early listings of K_d values often included only the mineral and the nuclide and even recent publications sometimes include statements that values of K_d vary from one value to another, without including the many variables which can affect the interaction of nuclides with components of the geological formations.

Most theoretical studies of adsorption have been in the field of physical chemistry, and in this field the term 'distribution coefficient' symbolized by D , has often been used. In chemistry, the use of ' K ' has usually been confined to true equilibrium constants, and this may be the reason that K_d has sometimes been considered a constant for a given system. In this report, we use the term ' K_d ', but we do not imply anything by use of this term other than that it represents the ratio of concentrations on the sorbent and in the solution at the time of measurement. Reversibility is not implied, and no specific mechanism, such as reversible adsorption, is implied.

Extensive research on sorption was supported by the WRIT program (formerly the WISAP program) sponsored by the Office of Nuclear Waste Isolation, DOE, and administered by Pacific Northwest Laboratories. A number of laboratories participated in this program, and although the approaches toward the problem of determining K_d 's varied somewhat from laboratory to laboratory, it was generally realized that a great many factors controlled the value of K_d in a batch-type

experiment. Unfortunately, in the early investigations not all variables were controlled in the experiments, and when an intercomparison of K_d values was attempted (1), there was considerable scatter in the data. In this intercomparison, a number of laboratories received the same rock samples and procedures from the program managers. Groundwater compositions were carefully specified. Among the reasons for the differences were the lack of valence-state control for plutonium, the lack of understanding of the role of speciation on adsorption, and the failure to specify the nuclide concentration to be used. Pertinent results of sorption measurements completed under the sponsorship of the WRIT program have been carefully summarized in recent reports by Serne and Relyea(2) and Strickert(3).

The validity of using values of K_d determined by small scale laboratory experiments in the complex mathematical models designed to predict migration rates is of great concern to safety analysis. In many of the models reversible sorption is assumed, and no attempt is made to allow for change in the value of K_d . However, the various processes that can really occur, such as precipitation or reduction, must be taken into account regardless of the difficulties of doing so. The best way to avoid problems is to understand the basic chemistry of the system well enough to know something of the effects of the changes of the geochemical variables, such as pH, solution composition, temperature, etc.. In this report we consider effects of change of valence state.

The subject of valence state control can really not be separated from consideration of the general chemistry of those nuclides that can exist in various valence states under environmental conditions. Much of our knowledge of the chemistry of the nuclides of interest to waste migration has come from studies relative to the processing of nuclear waste and separation of the transuranium and fission-product elements from the resulting process streams. These separations are generally carried out in acid solutions where many of the problems resulting from hydrolysis, precipitation, and carbonate complexing are avoided. Little research has been carried out in neutral pH ranges, and for good reason. There has been until recently little application for data under these conditions, and research in the neutral pH range is very difficult.

In the absence of valid data concerning the oxidation states and speciation of the nuclides, considerable reliance was and still is placed on so-called Eh-pH diagrams which attempt to map out regions of thermodynamic stability for species of the nuclides. Another type of diagram often used are species-pH diagrams where for a given set of assumptions, plots of pH vs the concentration of the existing species are given. (These are sometimes known as 'spaghetti' diagrams.) Of particular interest to the construction of these diagrams are valid data for solubility products and hydrolysis constants. In fact, the determination of solubilities of the oxides and hydroxides of transuranium elements is still one of the most difficult problems in this type of chemistry because it is so difficult to prepare reproducible crystalline oxides and hydroxides of these elements. In addition, wide variations are reported in hydrolysis constants for many of the elements in question. Also, the presence of complexing ions such as carbonate or fluoride can significantly alter the stabilities of the ions and cause shifts in the lines separating the fields of thermodynamic stability. Despite these limitations, Eh-pH diagrams can be extremely useful if it is realized that they represent only the equilibrium state, that they may be derived from uncertain data, and that the presence of complexing species may considerably alter the diagram as compared to diagrams in the absence of complexing ligands.

Probably the most frequent error in the use of Eh-pH diagrams is confusion of the term Eh as applied to these diagrams and the term 'Eh' as applied to the experimental determination of the electrode potential. For that reason, in this report we will only use 'Eh' to denote a thermodynamic quantity which represents the equilibrium state and can be related to free energies of redox reactions. When we refer to a measured potential, we will use the terms like E (Pt vs SCE) which refers to the potential measured on a platinum electrode with respect to the saturated calomel

electrode. At this time, this may seem like a trivial point, but it is surprising how often the term 'Eh' is used in the same report for both a measured potential and the thermodynamic quantity. This dual use of the 'Eh' has probably also led to a common misconception that what is determined by placing an appropriate electrode into a groundwater and recording the reading of the voltmeter or electrometer is always a thermodynamic quantity. We will discuss below what one actually would be measuring in various hypothetical cases.

If the equilibrium state of a nuclide that can exist in several valence states cannot be determined by placing an electrode in a solution and if the Eh-pH diagrams available are subject to error, then how can the valence state of a nuclide be controlled and identified? In this report, we describe electrochemical and other methods of controlling valence state, give a preliminary assessment of their advantages and disadvantages, and assess the possible errors that can occur in sorption measurements if valence states are not controlled. In this discussion, we describe our own research into valence state control along with examples that we have investigated so far.

2. SPECIATION AND SOLUTION CHEMISTRY

In the Introduction, we mentioned that we cannot really separate the problem of valence state control from that of speciation of the nuclide. With neptunium as an example, we would expect from the literature (4-6) that under conditions likely to be encountered in the geological environment, only the IV and V states would be stable. However, attempts to specify and control the state will depend on the form that may be stable under the conditions of the experiment. In acid solutions the problem is relatively simple; Np(V) is considered to be in the form NpO_2^+ and significant hydrolysis (formation of $\text{NpO}_2(\text{OH})$) does not occur at pH levels below about 8. The IV state of neptunium is generally considered to exist as the Np^{4+} ion in strongly acidic solution. As the pH rises, the IV ion hydrolyses to form a spectrum of hydrolytic species. If other species are present, complex ions of Np may also be present. The important point is that the border between regions of stability will depend on speciation, and one cannot simply state potentials below which a certain reduced form is stable without at the same time making clear what species are present. The term 'regions of stability' when referring to Eh-pH diagrams is probably not a good term because the region is defined for a given set of concentrations and will vary from one set of concentrations to another.

In order to illustrate the dependence of the 'border' between regions of stability on Eh-pH diagrams on chemical factors, we plotted in Fig.1 the calculated border between Np(IV) and Np(V) (equal concentrations of Np(IV) and Np(V) and concentrations low enough to avoid precipitation) using the collected and estimated hydrolysis constants of Allard et al(6). For the calculations shown in Fig.1, we assumed a complete spectrum of possible hydrolytic species of both Np(IV) and Np(V). The dotted lines above and below the line are calculated assuming each hydrolysis constant is in error by a factor of 100. This is a relatively small error because formation constants of hydrolysis products of Np(IV) may be as large as 10^{45} . There is a difference of about 0.2 volts between the upper and lower dotted lines; the upper line corresponds to more stable formation constants of Np(IV). The significance of these differences is that unless hydrolysis constants are known with great precision (they rarely are), the 'borders' between regions of stability will not be known with precision. Therefore, reliance on use of Eh-pH diagrams for exact prediction of speciation would be a mistake.

Another difficulty that can occur deals with the solubility of the various valence states. For many cases, the lower valence state is said to be very insoluble. Examples are the oxides of the IV states of Np and Tc. The usual thermodynamic solubilities may not necessarily be relevant here, because they refer to well-defined crystalline forms that may not be formed under environmental conditions. In our experience, when we form Np(IV) in a glass cell at concentration levels far below the

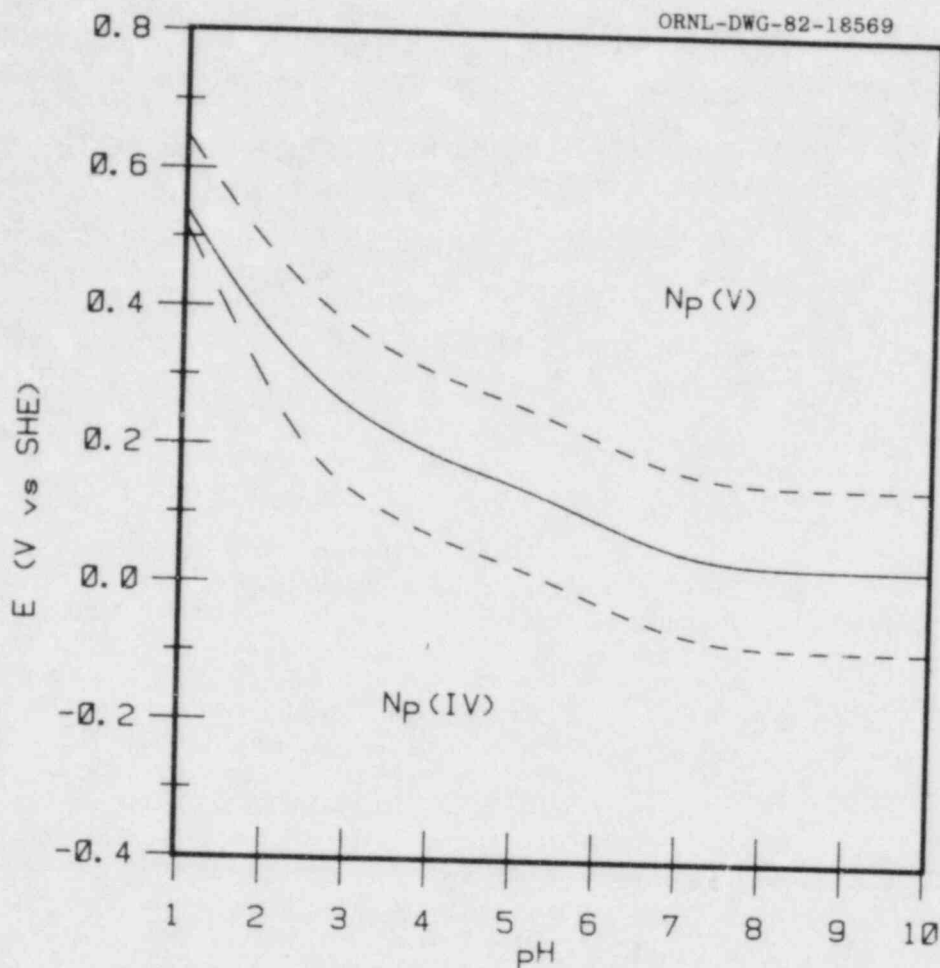


Fig. 1. Electrode potential boundaries for Np at 50% IV and 50% V. Dashed lines indicate uncertainties in hydrolysis constants. See text for conditions. Total [Np] = $1E-12$ Molar.

estimated thermodynamic solubilities, Np(IV) disappears from solution even at pH 3, where it is predicted that species like $Np(OH)^{3+}$ and $Np(OH)_2^{2+}$ are formed. Presumably these species are adsorbed by the electrode or other surfaces, and although Eh-pH diagrams for Np (4-6) predict solubility at the concentration level that we used, in the actual experiment, Np did not remain in solution. One must also remember that common complexing agents like fluoride, phosphate, and carbonate ion, if present in a certain quantity, can solubilize certain nuclides at concentration levels where precipitation might be expected.

The problem of determining the species and the oxidation state in these types of studies is probably the most difficult aspect of this project. If species are present in relatively large concentrations e.g., $\sim 10^{-5}$ to 10^{-4} M, it is possible to characterize the species by their absorption spectra provided their molar extinction coefficients are large enough (i.e., if enough light is absorbed at a convenient wavelength). Fortunately, aqueous technetium species generally have very high extinction coefficients in the UV region, and it is possible to deal with fairly low concentration levels. With neptunium it is also possible to determine speciation by spectrophotometry(7), but only by increasing the concentration of alpha-emitting isotopes to the point where special facilities are needed for reasonable solution volumes. For low to moderate concentrations of neptunium, solvent

extraction methods may be used to determine the valence state. In this technique, it may be necessary to adjust the acidity of the solution in order to produce an extractable species. For example, an extractant such as TTA in benzene may be used to extract one valence state in the presence of the other valence states where favorable distribution coefficients exist. Of course, it is difficult to confirm directly that the desired valence state is present. However, by carrying out a number of experiments in which Np is either oxidized or reduced by reagents which are known to react at high concentrations, one can develop a pattern of chemical evidence that is convincing as to which valence states are present.

3. ELECTROCHEMISTRY

Because many chemists and geologists are not familiar with electrochemical kinetics, we present here a brief introduction to the discussions that follow, so the reader can appreciate the difficulties in interpreting measured electrode potentials. Good introductions to the subject are available.(8-11). Ref. 8 is an especially good concise introduction to electrode kinetics.

Electrode kinetics differ from kinetics in bulk solutions in two important respects. First, reactions are surface reactions and therefore are dependent upon concentrations of species at the electrode surface. These concentrations may or may not be the same as the concentration in the bulk of the solution. A second difference is that rates of electrode reactions are functions of electrode potential, and rates may therefore be varied over many orders of magnitude merely by changing the electrode potential. Various forms of fundamental rate equations are given in the literature. For our purpose, the following equation is most useful:

$$I = n \cdot F \cdot A \cdot C \cdot k \cdot \exp[a \cdot z \cdot F \cdot (E - E_{ref}) / (R \cdot T)] \quad (3.1)$$

where I is the net rate expressed in amperes, n is the number of electrons transferred per mole of reactant, F is Faraday's constant (96,500 Coulombs/equivalent), A is the surface area of the electrode in cm^2 and C is the concentration of the reactant in moles/ cm^3 . Thus, the units of k for this case are cm/sec. (In this report, we use the symbol '*' to signify multiplication as is done in common computer languages.) In Eq.1 we assume only a single reactant with a first order dependence upon the reactant. In the general case, the current will be dependent on the product of all of the reactants, each raised to the appropriate power. In the exponent, T is the temperature in Kelvins, R the gas constant, $a \cdot z$ is a kinetic factor composed of the transfer coefficient 'a' and a charge number 'z', numbers which have mechanistic significance. When expressed in volts, RT/F is equal to about 0.0256 at 25 C, and therefore, the rate will change by a factor of 2.72 for every change of 0.0256 volts, or a factor of ten for every $2.303 \cdot 0.0256 = 0.0591$ volts if $a \cdot z = 1$. The potential of the electrode, E, referred to a reference electrode, and the rate constant k are related in that the choice of reference is arbitrary, but once chosen the value of k will depend on which reference electrode is selected. In practice, most electrochemical measurements are referred to the saturated calomel electrode (SCE) and most thermodynamic potentials to the standard hydrogen electrode (SHE). However, it is convenient in tabulating electrochemical rate constants to refer the measured potential to the standard potential (unit activities of all reactants and referred to SHE) of the redox couple in question.(12)

Eq. (3.1) may refer to cathodic reactions (reduction of oxidized species) or anodic reactions (oxidation of reduced species). As in much of electrochemistry, it is important to maintain appropriate sign conventions in electrochemical kinetics. For cathodic reactions, the term in the exponent is negative and for anodic reactions it is positive. Thus, as the electrode becomes more positive with respect to a reference electrode, anodic currents increase and cathodic currents decrease. Some investigators prefer to consider cathodic currents negative and anodic currents positive. For convenience in plotting logarithms of currents; however, it is usual to consider all currents as positive.

At any electrode in which oxidation and reduction are both occurring, the net current will be the difference between the anodic and cathodic currents. At equilibrium the two currents will be equal and the net current will be zero. It is important to realize that, although the net current is zero, oxidation and reduction are both occurring. For a redox couple, the rate at equilibrium of the oxidation and reduction reactions is called the exchange current.

As mentioned above, Eq. (3.1) refers to concentrations at the electrode surface. If reactions at the surface are very fast, the rate of mass transfer (diffusion and convection) to the surface may not be fast enough to maintain the concentration at the bulk level. As the potential is changed and the rate of the electrode reaction increased, a limiting current will be reached corresponding to the maximum rate of mass transfer to the electrode surface. A simple test for mass transfer limitation on an electrode reaction is to vary the amount of stirring or convection (e.g., flow rate past the electrode), and any dependence of the current on stirring or convection indicates that the reaction is at least partially under mass transfer control.

There are many ways to represent the net current as a function of potential taking mass transfer into account (9). For our purposes, we will use the expression:

$$i = n \cdot F \cdot A \cdot C \cdot k \cdot [(1 - i/i_{la}) \cdot \exp(a \cdot z \cdot S) - (1 - i/i_{lc}) \cdot \exp(-(1 - a) \cdot z \cdot S)] \quad (3.2)$$

where i is called the current density and is equal to I/A , and $S = (E - E_{ref}) \cdot F / (R \cdot T)$. Eq. (3.2) refers to a case where there is a single oxidized and a single reduced species at equal concentrations, e.g., the Fe^{2+}/Fe^{3+} redox couple. This equation is formed by including two terms representing the anodic and cathodic partial currents. The net current is the difference between these currents. Mass transfer is taken into account by the terms $(1 - i/i_{la})$ and $(1 - i/i_{lc})$. Here i_{la} and i_{lc} refer respectively to anodic and cathodic limiting currents that can be supported by the mass transfer conditions of the system. For the case represented by Eq. (3.2), the exchange current density is equal to $n \cdot F \cdot C \cdot k$. In the general case, when the concentrations of the oxidized and reduced species are not equal, the exchange current is given by a more complex expression which is dependent on the kinetic constants.

Because the $Fe(II)/Fe(III)$ couple is so important to geochemistry, we will use it as an example to illustrate these equations. In Fig.2 we show experimental current voltage curves for the case of millimolar $Fe(II)$ and $Fe(III)$ in hydrochloric acid. A planar platinum electrode (area = 1.5 cm^2) was used and current-potential curves were taken with a potentiostat. The calculated curves were computed from Eq. (3.2) assuming a limiting current of 5×10^{-4} amperes and a rate constant of 0.001 cm/sec . This gives an exchange current density of 0.1 amperes/cm^2 for this system (at 10^{-3} M $Fe(II)$ or $Fe(III)$).

Under environmental conditions (intermediate pH values and realistic iron concentrations) the concentration of iron will be much lower and may be determined by the solubility of hydroxides or other compounds. In Fig.3 we show an example which assumes that the concentration of Fe^{3+} is 10^{-9} M and Fe^{2+} is 10^{-6} M . (Here we refer to the actual ions; hydrolyzed iron or complexed iron could also be present). The open squares represent calculated current-voltage curves for these conditions. Note that the equilibrium potential is about 0.6 volts (0.594 to be exact). We do not show an experimental curve for this case because it would be a very difficult experiment to maintain Fe^{3+} at this level and eliminate all other redox reactants, especially oxygen. The exchange current density is very low in this case $\sim 10^{-10} \text{ amperes/cm}^2$.

It is of considerable interest to inquire as to the effect of a second redox system and again taking an

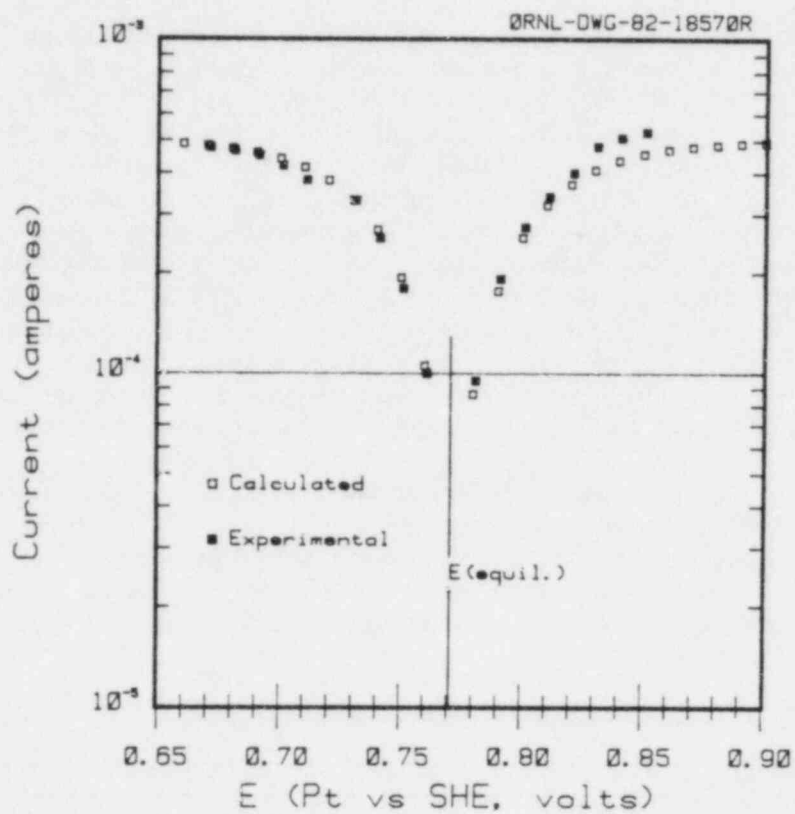


Fig. 2. Calculated and experimental current-potential curves for 0.0001M (Fe)II - 0.001M Fe(III), 0.1N HCl.

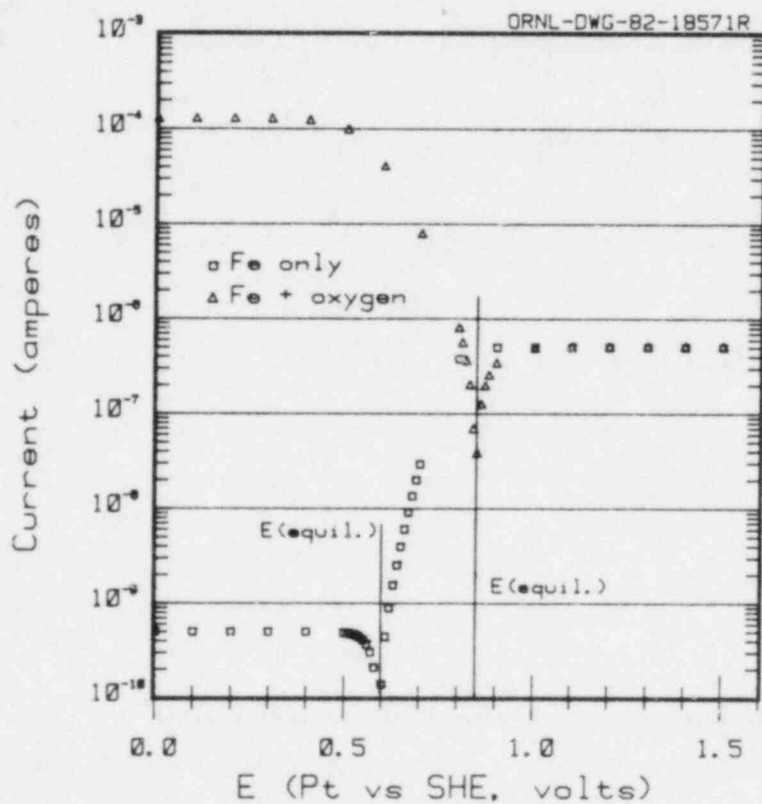


Fig. 3. Calculated and experimental current-potential curves for 1E-6M Fe(II) - 1E-9M Fe(III), 2 ppm oxygen (25% saturation).

example of interest to geochemistry, we use the example of oxygen. Because oxygen evolution from water is extremely unlikely except in the presence of extremely strong oxidizing potentials, we need consider only the reduction of any oxygen present. We will assume an initial oxygen content of about 2 ppm which corresponds to about 25% air saturation. The triangles in Fig.3 represent the calculated current for this case and the equilibrium potential will be 0.846 volts (SHE), which largely represents the equality of the reduction of oxygen and the oxidation of Fe(II). If oxygen concentration is reduced the equilibrium potential will be reduced according to the relation shown in Fig 4. Thus, even at oxygen concentrations of 0.001 ppm, the potential of an electrode will not indicate the equilibrium conditions of the iron redox couple but will be shifted (polarized) to a higher potential. In this calculation, we have assumed a value of k for oxygen reduction of 2×10^{-11} , a standard potential of 1.2 volts, and $n = 4$. These numbers are consistent with experimental values observed for oxygen reduction on a platinum electrode; however, the value of k is quite sensitive to experimental conditions and might show considerable variation in practice.

In Fig.4, it is shown that for a change of oxygen concentration of five orders of magnitude the potential changed about 0.24 volts. A change of a factor of 100,000 in oxygen concentration is a really significant change in the oxidizing power of the solution; yet the potential changed less than a quarter of a volt. Thus the electrometric method of determining solution concentrations is not a really sensitive method because response tends to be logarithmic with respect to concentrations.

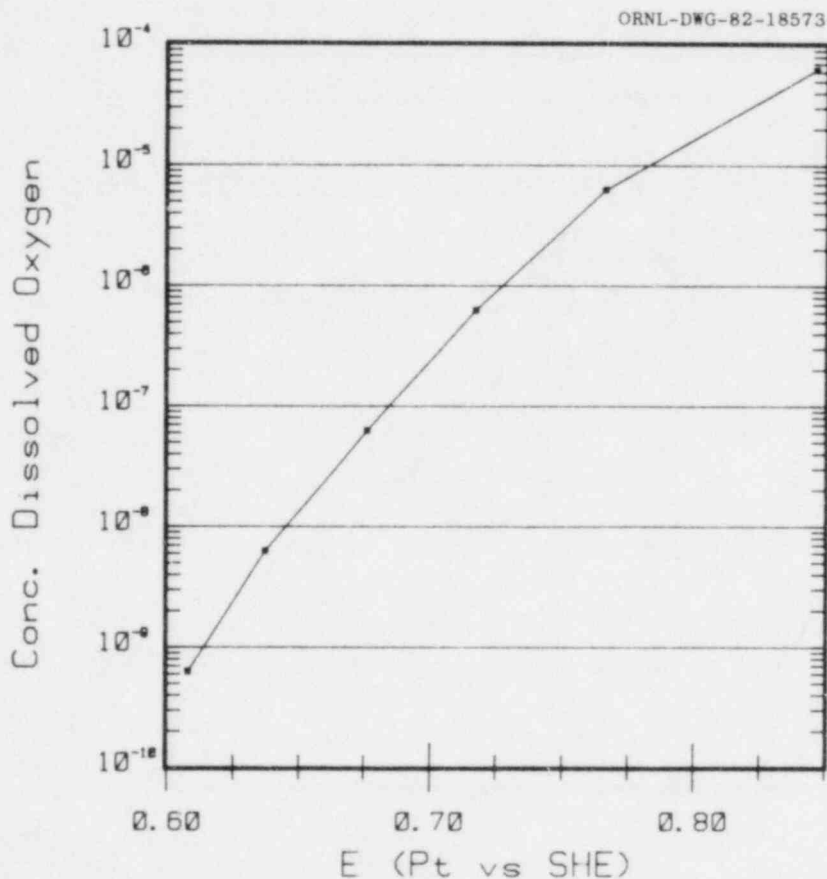


Fig. 4. Electrode potential vs concentration of oxygen for solutions with $1E-6M$ Fe(II) and $1E-9M$ Fe(III).

In general for natural systems there will be more than one redox couple present. Under these conditions the potential that one would measure on an indicating electrode placed in the groundwater would usually be a mixed potential as illustrated by the iron-oxygen system in Fig. 3. The only cases where they might indicate a true equilibrium potential will be (1) where only a single redox couple is present and is at equilibrium and (2) where multiple redox couples are present and the concentrations of each couple are such that each redox couple is at the same equilibrium potential. Thus, for most practical cases, the potential read by an indicating electrode will not be an equilibrium potential but a mixed and kinetically derived potential. It is therefore generally invalid to use measurements derived from indicating electrodes in conjunction with Eh-pH diagrams to predict the course of geochemical reactions.

We have presented this electrochemical section as an introduction to the discussions and assessments that follow. However, before proceeding with the assessment section, the ultimate objective of this program, we will present the experimental portion of this program. We do not include all of the experimental work we have done under this program, for much of it is still in progress. We do indicate some of the preliminary results of these experiments in progress below, but we wish to emphasize that conclusions from these must be considered tentative.

4. EXPERIMENTAL

We present here the results of experimental work that was performed under this contract since its initiation, July 1, 1981. We also present some work done with technetium prior to that date. Because we had obtained a supply of ^{95m}Tc ($t_{1/2} = 65\text{d}$) from our previous sponsors, and because it was decaying to a point where it could no longer be used, we began methods development and preliminary Tc measurements on materials that might reduce Tc before the July initiation date of this project. The materials chosen might be useful as backfill materials if substantial sorption can be shown to occur.

In fact, the availability of isotopes has to some extent determined the sequence of our experimental work. Thus we have concentrated on neptunium in the current fiscal year because we were able to get some ^{235}Np (the convenient 396d x-ray emitter) which was a byproduct of a cyclotron irradiation carried out in the isotopes section here at ORNL. Ordinarily the cost of the isotope would have been over \$10K but we were able to obtain it by carrying out the separation of the Np ourselves. In the course of developing the separation scheme, we also developed some of our techniques of valence state adjustment and analysis.

We present below in this section (1) a discussion of the circulating column method with electrochemical control, (2) some results on Tc that are relevant to this discussion, and (3) results on Np. In the last section, we then present a preliminary assessment of valence state control based on the experiments and analyses we have performed so far.

4.1 The Circulating Column Method As we indicated above in the electrochemical section, the rate of an electrochemical reaction may be increased or decreased by varying the potential. As the rate is increased, control of the rate of the reaction may pass then to mass transfer control and further increase of the potential will not cause an increase in rate. In order to increase the effectiveness of a cell in carrying out a reaction, it is possible to use very high surface area electrodes such as porous electrodes. Some of the limitations of mass transfer control are overcome by use of this technique and essentially quantitative electrolysis can be carried out. If the reaction is slow, a recycle through the cell improves the possibility of complete reaction.

Our apparatus is shown schematically in Fig.5. We used a PAR (Princeton Applied Research, P.O. Box 2565, Princeton, NJ 08540) Model 173 potentiostat with a PAR Model 376 Current Converter. The cell top is a 5 port plastic cell available from PAR (Part No. K66) as are special

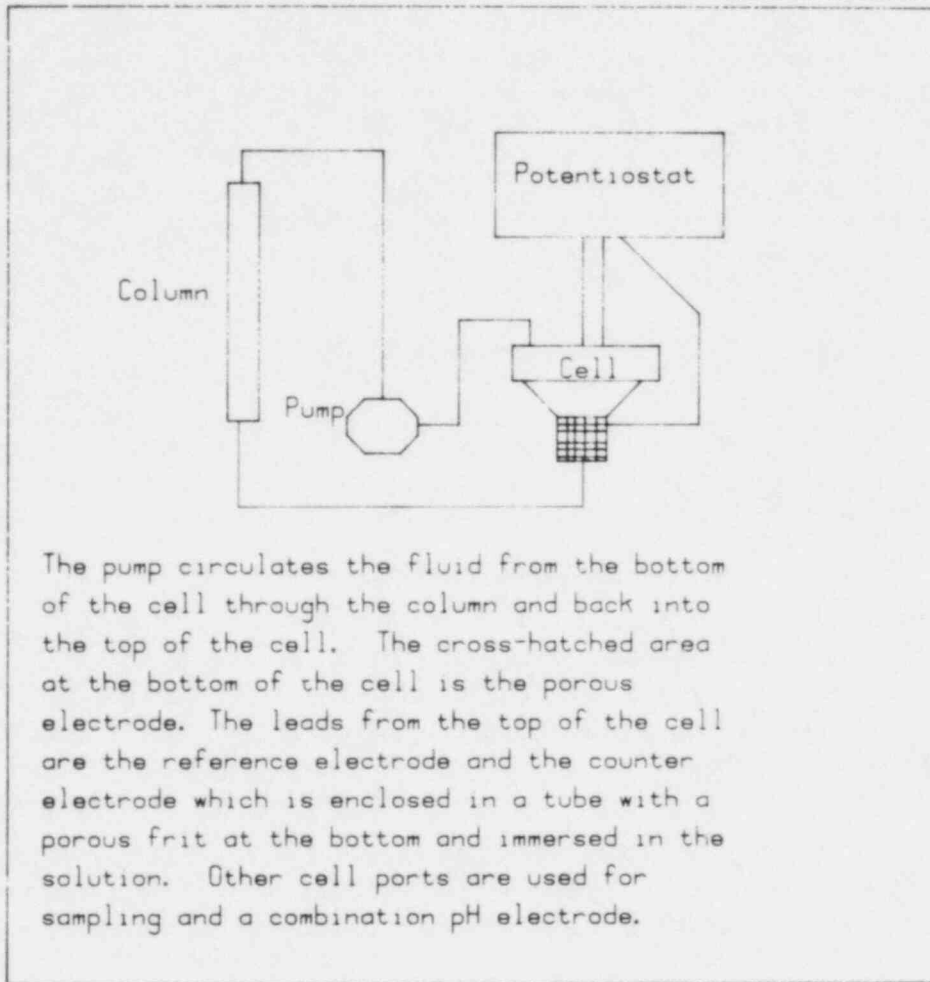


Fig. 5. Schematic drawing of cell with circulating column.

reference electrodes for this cell top (Part No. K0077 used with bridge tube K0065). Any standard tubing pump which pumps in the range of a few milliliters per minute may be used. Our columns were very small and usually contained approximately a gram of sorbent. We have used various filter materials to prevent the adsorbent from escaping the column. The material must be just fine enough to prevent escape. A blank experiment was always run without adsorbent to make sure the materials in the column did not adsorb the nuclide in question. We have used both a platinum screen rolled into a cylinder or granular silver in which the particle size is on the order of 0.5 mm as an electrode. We usually immersed a combination pH electrode in the solution through one of the ports of the cell. For work in anoxic conditions, argon was bubbled through the solution in the cell. When it was desired to count the tracer in the solution, an aliquot was drawn using the house vacuum into a small chamber above the cell. This chamber was maintained under an argon or nitrogen atmosphere.

Distribution coefficients are calculated as in the batch method by the relation

$$K_d = (N_i - N_f) * V / (N_i * W_t) \quad (4.1.1)$$

where K_d is the distribution coefficient, N_f is the counting rate of the tracer after equilibration (per unit time and volume), N_i is the initial counting rate, V the total volume, and W_t the weight of the sample. This same equation is used in the batch methods where separation of the solid and liquid phase is achieved by centrifugation, except that allowance must be made for a slight dilution of the initial tracer concentration by the solution present with the solid after the centrifugation following the final preequilibration with unlabelled electrolyte solution. Our normal procedure in the batch method is to preequilibrate the solids three times with the solution for periods of about three days each, while adjusting the pH to the value desired. The circulating column method simplifies this procedure since we merely recirculate the solution through the column until the pH has stabilized and the period is as long as we want it to be.

We have found that Np(IV) is difficult to produce at normal potentials that one might encounter in environmental situations. In acid solution (pH 1-2) where it should be easiest to produce (cf. Fig.1), potentials of about $-0.6V$ vs SCE ($\sim -0.35V$ vs SHE) to even lower potentials were required to begin producing Np(IV). Initially we were unable to produce Np(IV) on platinum at higher pH values, i.e., greater than about 2, but recently we have indications that Np(IV) can be produced at these pH values. We then switched to a silver electrode and were more successful in producing what we believe to be Np(IV), for when electrolysis was carried out, the tracer gradually disappeared from solution. Probably Np(IV) was produced, and it is immediately adsorbed onto the electrode and other surfaces. The overall concentration of Np in these experiments was less than $5 \times 10^{-11} M$. These results suggest that it is quite difficult to produce a soluble Np(IV) species for sorption study by this technique, because Np will immediately tend to adsorb on any surface available including the electrode.

The difficulty that we have had in producing Np(IV) suggests that its removal by reduction may not be a very probable process in a natural situation except for very strongly reducing conditions. On the other hand, we have observed very high distribution coefficients for sorption of Np on alumina and other oxides, and these experiments suggest that Np may be easily sorbed by natural oxides or hydrous oxides which are very prevalent in many natural environments. Without knowing the valence state distribution of the Np in the solution it is not certain whether the oxides adsorb the IV or the V state of Np from the solution. We therefore carried out experiments by the circulating column method which incorporated an electrochemical cell adjusted to insure that the Np in the solution was Np(V). Results are shown in Fig.6 for experiments with Np(V) sorption on gamma-alumina in $0.1M$ NaCl from pH 4.6 to pH 7.8. This use of the cell was especially convenient, because we have found that Np tracer as originally obtained is often a mixture of valence states, and some means must be used to convert it to a pure valence state. This electrolytic method is the most convenient method we have found so far. (The reason that Np is often found in several valence states is that in the preparation of the tracer, acid solutions are generally used and Np(V) will tend to disproportionate to Np(IV) and Np(VI) giving a mixture of all three states (5).) The results in Fig.6 show that the distribution coefficients are very high at high pH as we originally determined in batch experiments (14). There is still the possibility that the adsorbed Np is in the IV state. However, when we change the pH to lower values the sorption is reversible, and the Np readily desorbs. This suggests that the Np is present as Np(V). In order to demonstrate this, we are experimenting with rapid leaching of the mineral in oxygen-free atmospheres, followed by immediate valence state analysis in an attempt to find any evidence of reduction.

Valence state analysis is a very important part of all of these procedures, and we use solvent extraction to check for the presence of a particular valence state. We use thenoyltrifluoroacetone (TTA), $0.5M$, in xylene to check for the presence of Np(IV), which is extracted from $1M$ solutions with very high distribution coefficients. The presence of Np(VI) is determined by solvent extraction with tri-n-octylamine (TOA), 10% by volume in xylene, from $4M$ HCl. We have spent considerable time testing and confirming these procedures, the bases of which are described or referenced in Ref.5.

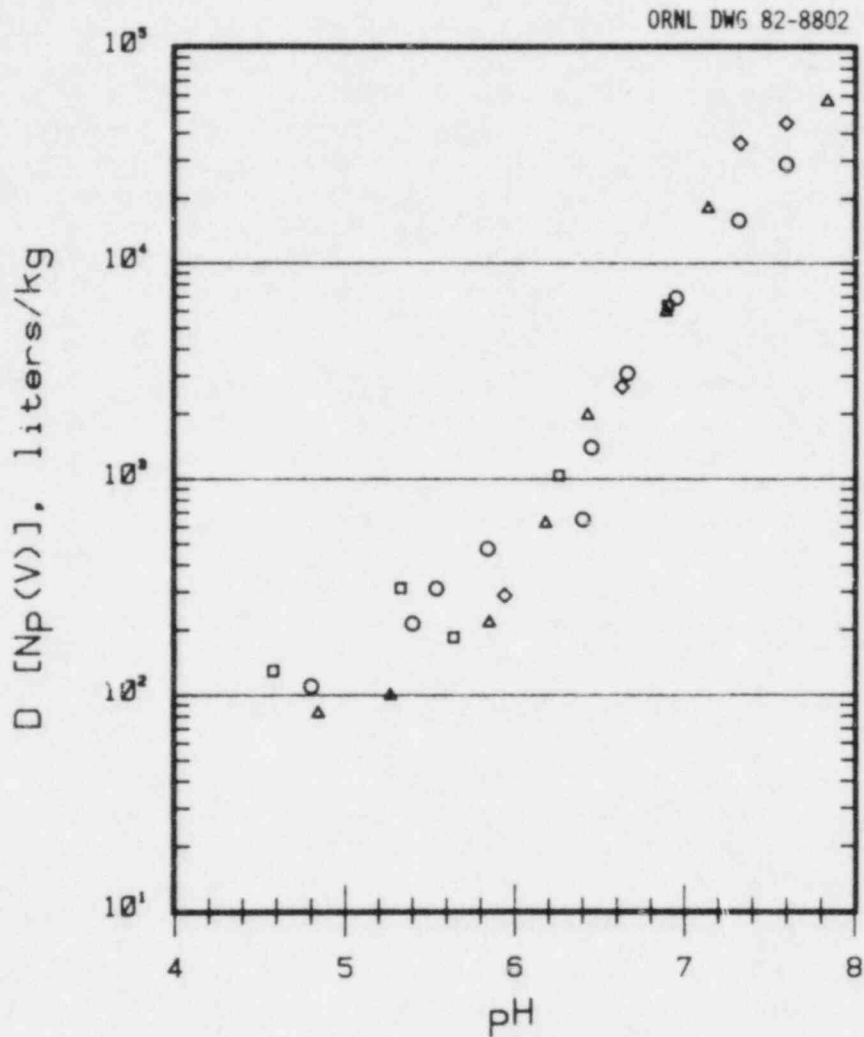


Fig. 6. Adsorption of Np(V) on alumina. Recirculating column method. 0.1M NaCl. $1E-12M$ Np-235. Circles, pH increasing, diamonds, decr.; triangles, pH incr., squares, decr.

4.2 Tc and Np Adsorption

4.2.1 Methods

Measurement of sorption under anoxic conditions involves the development of an adequate technique for handling separation and tracers in a controlled atmosphere box with a very low partial pressure of oxygen environment. Separation of the solution from the adsorbent is particularly difficult if centrifugation is selected, for the samples must be removed, centrifuged, and placed back in the controlled atmosphere box without introducing oxygen. Rather than attempt to use centrifugation, we decided to use a dialysis membrane to separate the adsorbent and the solution in all of our detailed studies of the interaction of nuclides with minerals under anoxic conditions. This method gives excellent separation, but attainment of equilibrium may be slow because of the length of time to reach equilibrium through the membrane. This method consisted of the following steps: (1) The solutions and adsorbents were introduced into a controlled atmosphere chamber after they were treated to remove oxygen. (2) The adsorbents were put into the dialysis bags along with a small amount of solution, and the bags were then placed into containers containing the solution. (3) The adsorbents were allowed to preequilibrate for several days. (4) Tracer was introduced into the

chamber containing the dialysis bag. (5) Periodically small aliquots of solution were taken out and counted. (6) The distribution coefficient was then calculated.

The controlled atmosphere box is a Model HE 43-2 DRI-LAB with a HE-493 DRI-TRAIN, Vacuum Atmospheres Company, Hawthorne, California. Because we use aqueous solutions, this box also is fitted with an extra container for removal of moisture before the gas within the box flows through the oxygen getter. It is difficult to determine the ultimate oxygen and carbon dioxide content of the box, for we have not found a satisfactory way either of monitoring carbon dioxide or low levels of oxygen. Our meters and tests simply indicate no oxygen, but they are not sensitive enough to indicate levels less than about 100 ppb oxygen (about 1% air saturation).

Two methods have been used to remove oxygen from solutions before introducing them into the atmosphere box. For the early technetium work the solutions were first degassed by passing pure argon through them and then frozen. While frozen they were placed into house vacuum for a while and then allowed to thaw. They were then refrozen and evacuated several times. Finally they were introduced into the atmosphere box while frozen. The solids were simply evacuated for a while and then introduced into the box under vacuum. Later the procedure was modified to eliminate the freezing step, and solutions were introduced into the box in containers that could be evacuated. (When materials are put into the box they are first placed into an antechamber that is evacuated.) Solutions were made up in the box.

The dialysis membrane is a standard laboratory item, cellulose dialyzer tubing. The solid was placed into the tubing, and the tubing was folded over and tied much like a double tea bag.

During the equilibration period, the pH of the solution was monitored and in most cases the potential of a platinum electrode immersed in the solution was monitored also.

4.2.2 Technetium

Under BES sponsorship in 1980 we investigated adsorption of TcO_4^- on various minerals under both aerated and deaerated conditions. The work on aerated solutions has been published (13). Some initial work was also done in the atmosphere box under reduced oxygen conditions. Several of the minerals which showed moderate to high sorption of technetium under anoxic conditions were selected for further study using the techniques described in Section 4.2.1. Experiments were carried out for periods of from one to two weeks. Results of these studies are shown in Figs. 7 and 8. For biotite and galena, sorption increased for several days and then levelled to relatively steady values. For the basalts and pyrite, values increased with time and did not come to a steady value within the duration of the experiment (up to 17 days).

These experiments with technetium were terminated when the supply of technetium was exhausted. A few observations are worth noting however. One of the basalts used in these studies was obtained from the WRIT program and was contaminated with iron from the grinding process. When this basalt was used for sorption studies under anoxic conditions using the dialysis tubing techniques described above, it appeared that iron hydroxide, presumably ferrous hydroxide, was deposited on the walls of the container and that the iron hydroxide adsorbed a considerable amount of technetium. The mechanism of this sorption is not known. It is tempting to say that Tc is reduced by the ferrous iron and then precipitated. However there is no direct proof that this occurs, and the fact that the reaction is favored by thermodynamics does not mean that it does occur. There is still the possibility of adsorption of Tc(VII), and the course of the reaction must be determined by experiment.

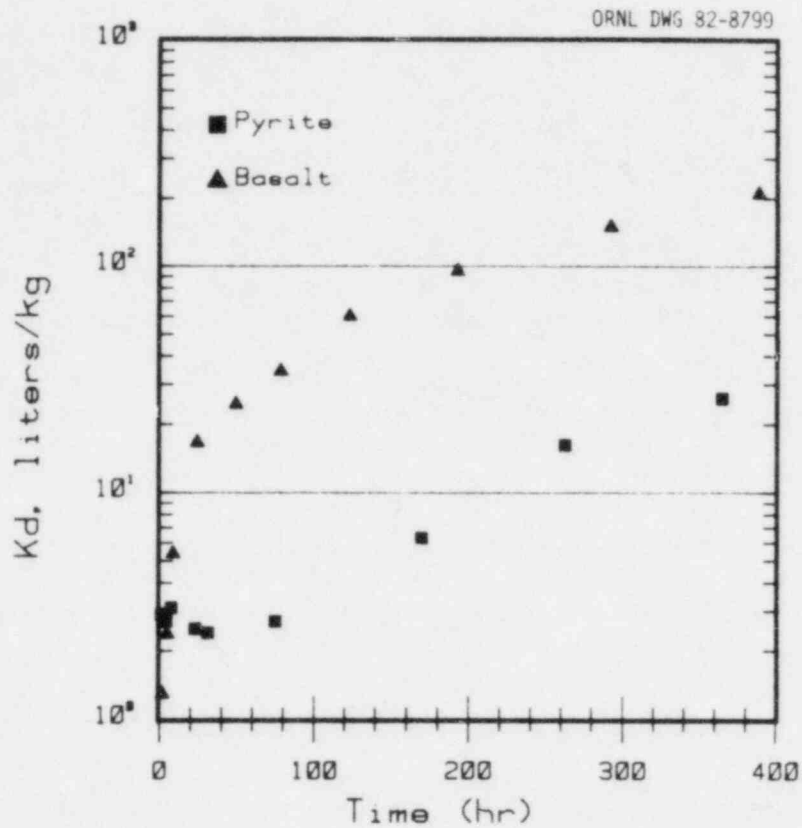


Fig. 7. Variation with time of K_d for sorption of Tc(VII) on pyrite and basalt. Anoxic 0.1M NaCl. Pyrite, pH 4. Basalt, pH 8.8.

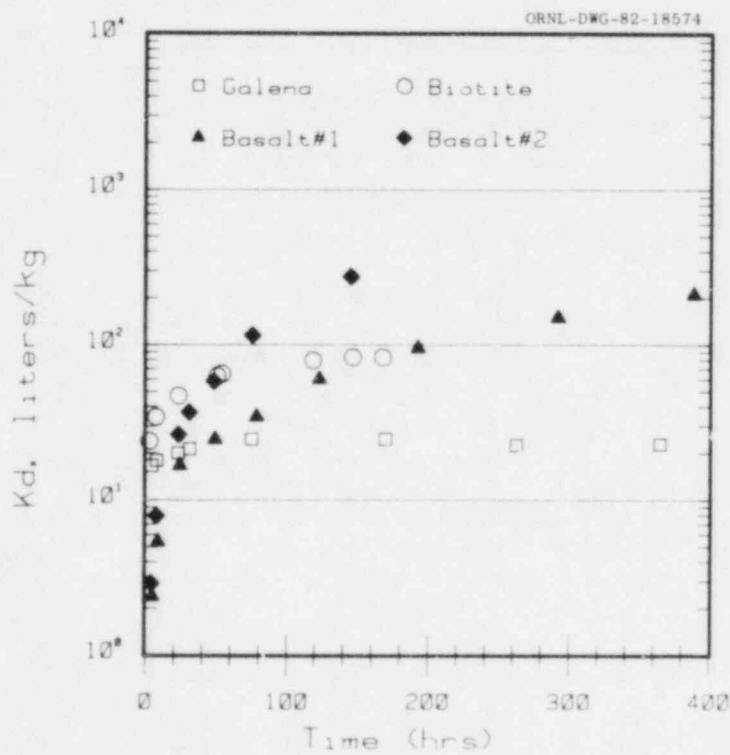


Fig. 8. Variation with time of K_d for sorption of Tc(VII) on various minerals. 0.1M NaCl.

4.2.3 Neptunium

If neptunium is removed from solution when in contact with a mineral or rock several processes can be postulated for its removal. One of the more frequently cited is reduction of the normally stable Np(V) to Np(IV) followed by precipitation or sorption of Np(IV). Another possibility is sorption of Np(V) without valence change. Reduction of Np(V) may occur either through a solution reaction or a surface reaction in which Np(V) interacts directly with reducing materials at the mineral surface. Distinguishing these two modes of reduction is quite important, for if reduction occurs through a solution mechanism, then an analysis of groundwater might suffice to predict whether reduction might occur in a geological formation for a given set of conditions. If reduction is a surface reaction, it will be specific to certain minerals and it will be necessary to characterize both the formation and the groundwater. Characterization of the groundwater would be necessary in this latter case because the surface reaction will normally depend also on the solution composition.

As on our studies on Tc, we first performed a large number of batch survey experiments both under oxic and anoxic conditions. Our aim was to look for significant differences between oxic and anoxic conditions. The oxic experiments were normal batch experiments using normal air-saturated solutions. The anoxic experiments were carried out with all equilibrations in the controlled atmosphere box. The samples were only removed for centrifugation, and they were carefully sealed before removal. After removal for centrifugation, they were returned to the atmosphere box before opening them to remove tracer for counting. In each case, the solid adsorbents were preequilibrated several times with the solution before tracer was added. Then a series of determinations at varying pH were completed. The anoxic measurements were then compared to the similar series of experiments under oxic conditions. Results are shown in Figs. 9 to 17. In each experiment the starting material was essentially >98% Np(V) at a concentration of $\sim 4 \times 10^{-11}$ M and the solution

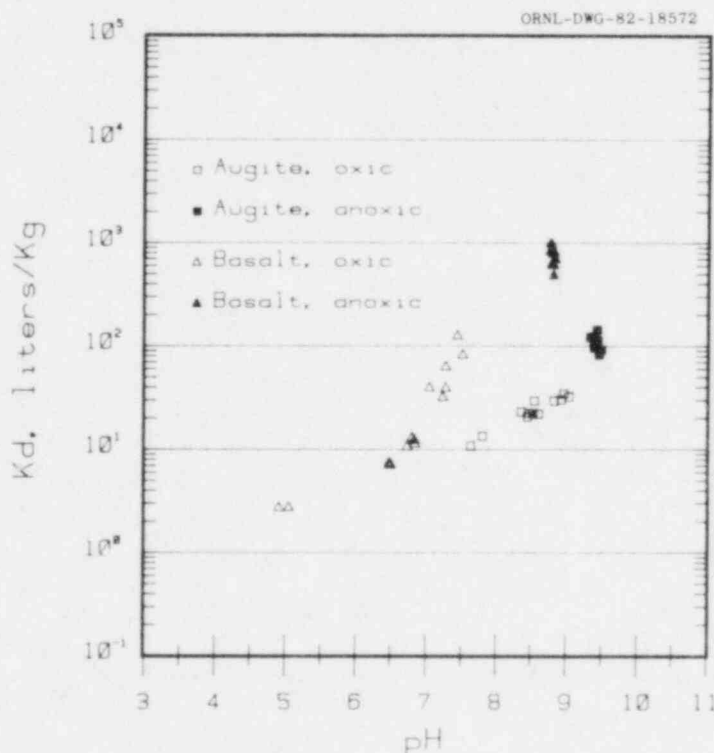


Fig. 9. Adsorption of Np(V) from 0.1M NaCl on basalt and augite.

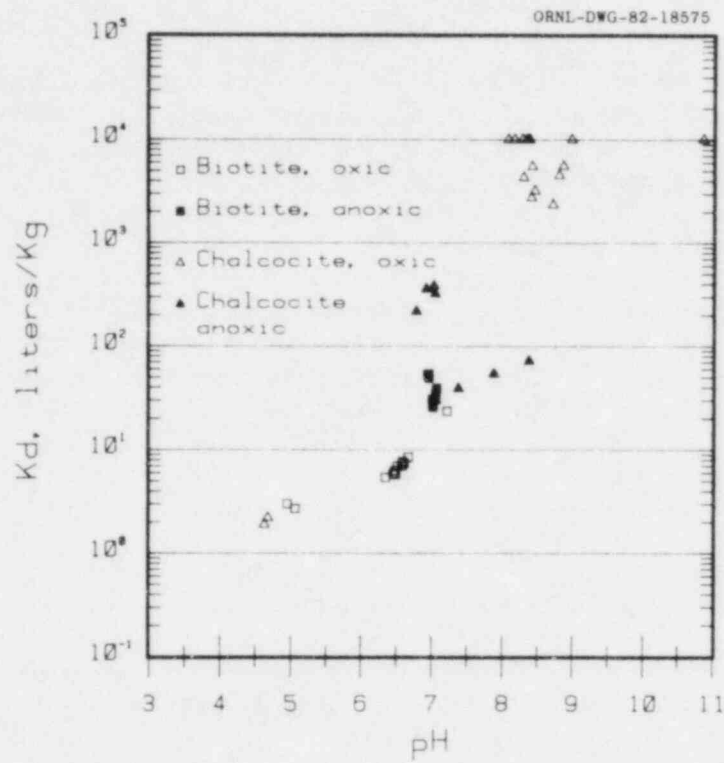


Fig. 10. Adsorption of Np(V) from 0.1M NaCl on biotite and chalcocite.

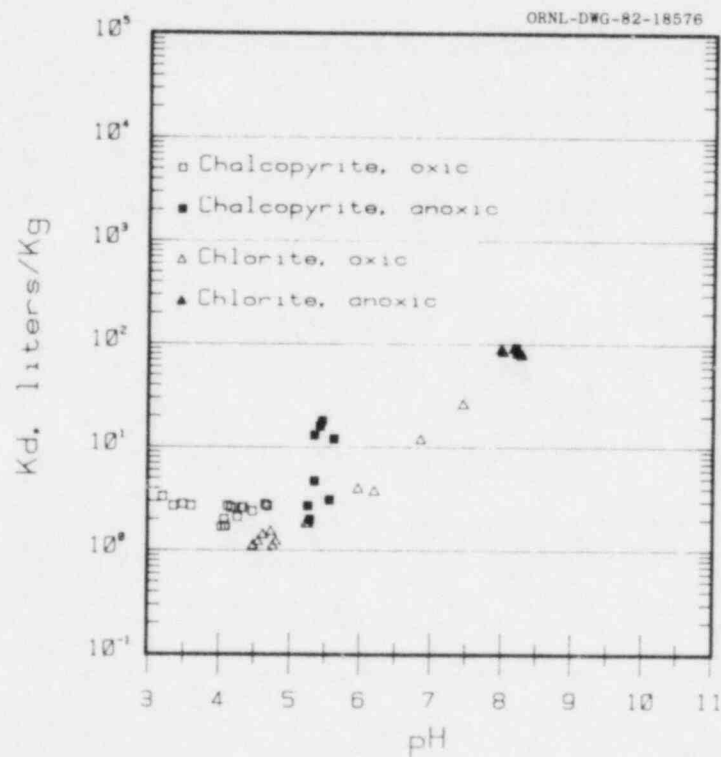


Fig. 11. Adsorption of Np(V) from 0.1M NaCl on chalcopyrite and chlorite.

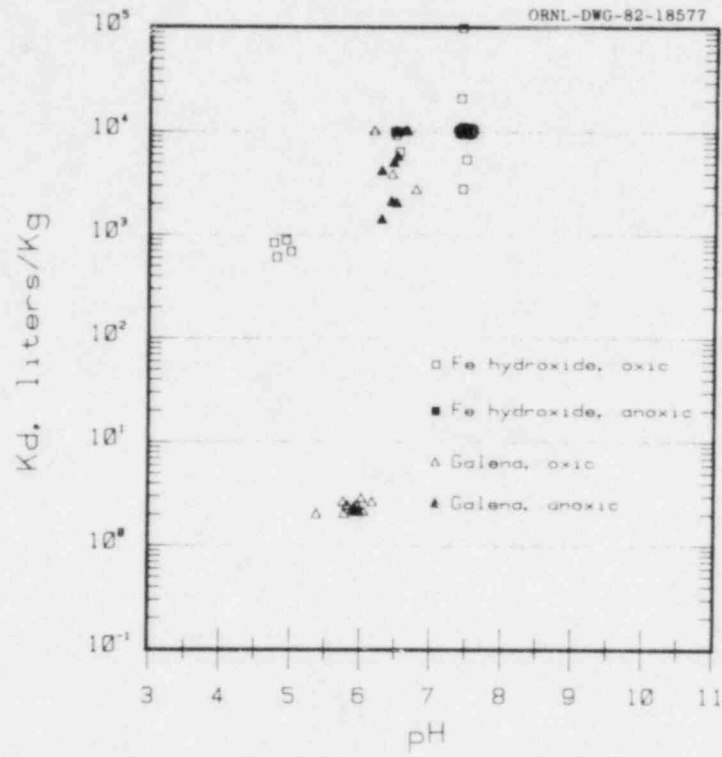


Fig. 12. Adsorption of Np(V) from 0.1M NaCl on ferrous hydroxide and galena.

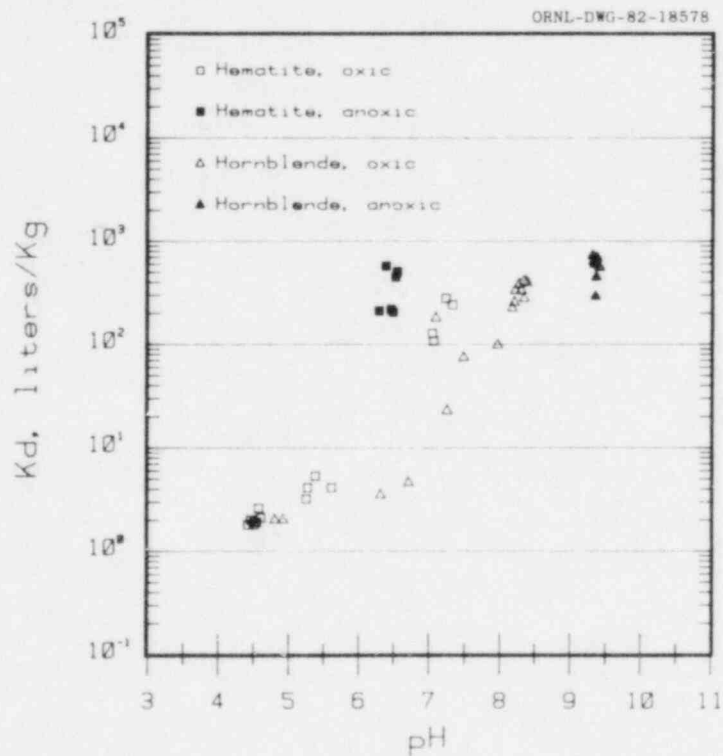


Fig. 13. Adsorption of Np(V) from 0.1M NaCl on hematite and hornblende.

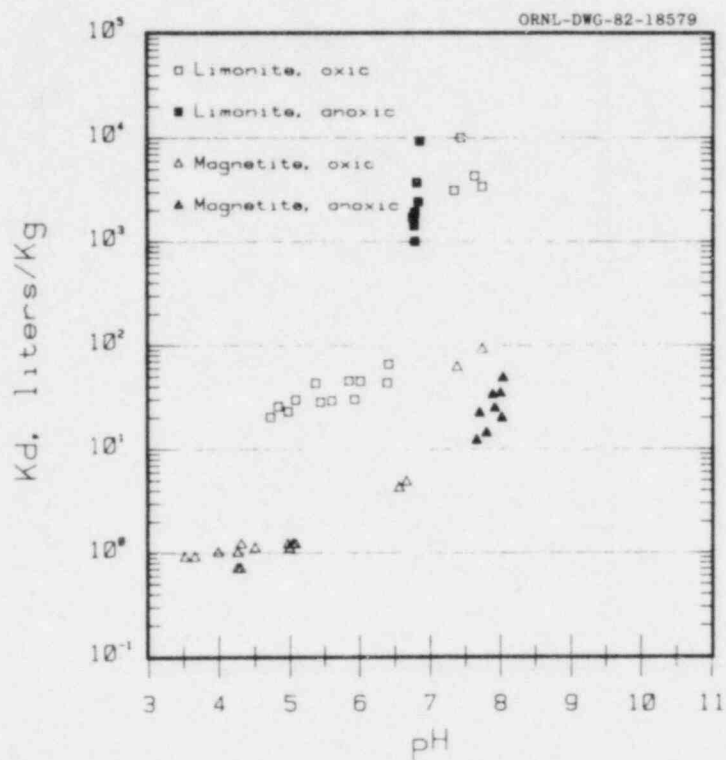


Fig. 14. Adsorption of Np(V) from 0.1M NaCl on limonite and magnetite.

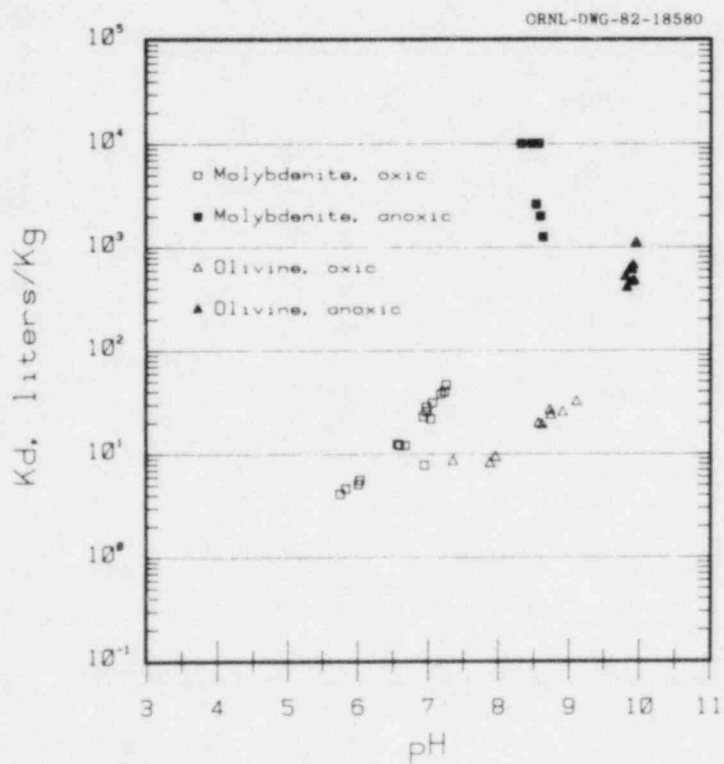


Fig. 15. Adsorption of Np(V) from 0.1M NaCl on molybdenite and olivine.

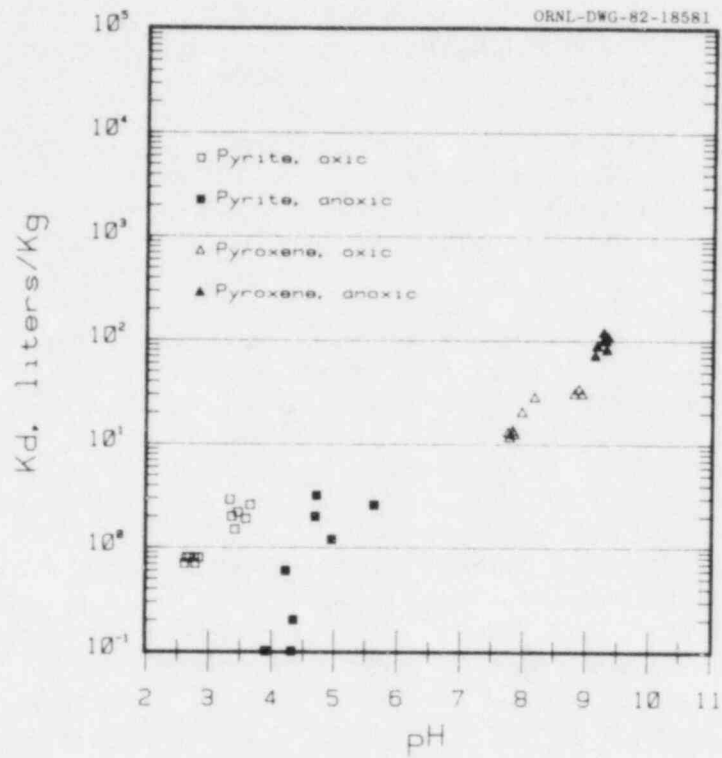


Fig. 16. Adsorption of Np(V) from 0.1M NaCl on pyrite and pyroxene.

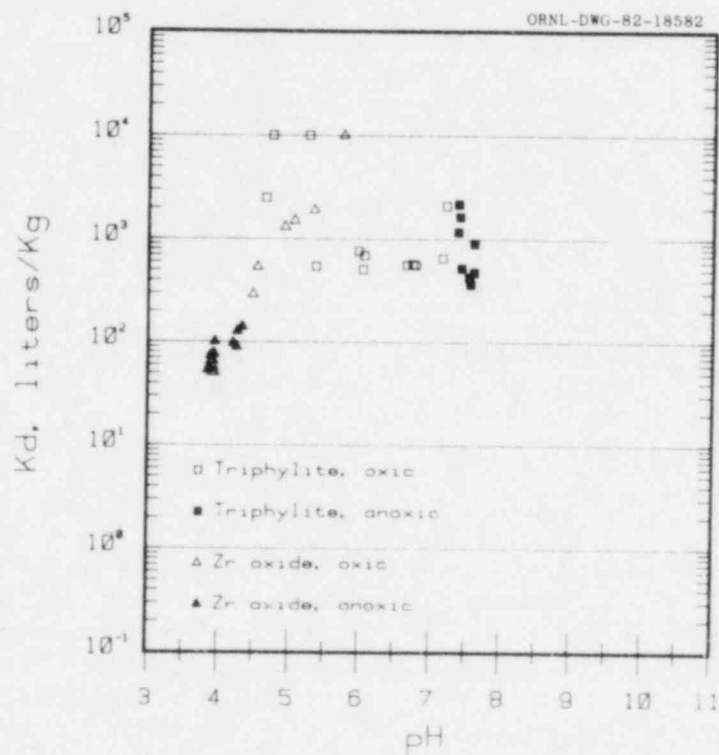


Fig. 17. Adsorption of Np(V) from 0.1M NaCl on triphylite and zirconium oxide.

was 0.1M NaCl. (We generally use 0.1M NaCl for our first solution, but we plan use of simulated groundwaters in later experiments.) Examination of these data show that in most cases the differences in the K_d 's between the oxic and anoxic determinations could be accounted for by differences in pH. That is, if a line is drawn roughly through the data, all data, oxic or anoxic, will fall approximately on this line for a given sorbent. From this one might infer that reduction leading to precipitation is not a significant mechanism for removal. However further study will be necessary before this can be inferred from the data. In particular, evidence for the presence of Np(IV) must be obtained. As we mentioned above at the concentration levels with which we work, the evidence can only be indirect.

These data shown in Figs. 9 to 17 are good examples of K_d 's which should not be used in any final safety analysis of migration rates. We can not tell what processes are occurring and whether, for example, reduction is occurring or whether the sorption is reversible. These experiments were simply scoping experiments where we were looking for possible effects of presence and absence of oxygen. For this reason, some of the adsorbents were selected for further study. These include iron-containing minerals, sulfides, and basalt. Most of these minerals were chosen because of the possibility of the occurrence of redox reactions on their surfaces, and they might therefore be used as a component of backfill. The dialysis technique described above for Tc was used and both the pH and the potential on a platinum electrode were monitored. At the conclusion of the experiment, the adsorbent was removed and treated with 1N HCl without exposure to air. The leachate was then subjected to valence state analysis and the proportions of Np(IV), Np(V), and Np(VI) determined both in the solution and in the extractant for the mineral. Results are shown in Table 1 for the proportions in the extractant; in the solution valence state analysis showed almost 100% Np(V). The

Table 1. Np valence distribution from leachate*

Mineral		Valence Distribution (%)		
		IV	V	VI
Biotite	#1	10.6	87.7	1.7
	#2	12.1	86.7	1.2
Chalcopyrite	#1	93.4	6.0	0.6
	#2	92.1	6.9	1.0
Galena	#1	18.2	81.1	0.7
	#2	17.9	81.3	0.8

*Sample extracted with 1M HCl under Ar atmosphere immediately after removal from sorption cell. Duplicate samples (#1, 2) from leachate.

final values of the pH, K_d , and the potential of the platinum electrode (in volts vs SHE) are given in Table 2. Note that the final values of the potentials for all three minerals were above the line of stability shown in Fig.1. Yet the neptunium leached from the chalcopyrite was almost entirely Np(IV) and that from the biotite largely Np(V). At present we are repeating these experiments. We are also trying to improve these techniques for analysis of the leachate from the minerals on which the neptunium is adsorbed, for it should be quite useful in analysing the course of the reaction. We need to insure that in the course of leaching the mineral, the valence state of the neptunium does not change.

Table 2. Final Kd, pH, E (Pt vs SHE) for Np Sorption

Mineral	Parameters		
	Kd	pH	V vs SHE
Biotite	22.6	6.97	0.448
Chalcopyrite	6.3	6.26	0.280
Galena	18000	8.79	0.281

5. ASSESSMENT OF TECHNIQUES OF VALENCE CONTROL

In this section, we give the following preliminary conclusions concerning valence state determination and control. These conclusions are based partly on our experiments and partly on general considerations.

- For those nuclides which can exist in several valence states under environmental conditions, the validity of sorption measurements from solutions in which the valence state is not known is highly questionable and therefore should never be used in any estimate of migration rate for safety analysis.
- Measurement of the potential at an indicating electrode, which some investigators incorrectly identify as the Eh of the solution, will not give any definitive information regarding whether a given nuclide will undergo a redox reaction. Such measurements can however be indicative of general oxidizing or reducing conditions. It can never be assumed that these measurements indicate true thermodynamic potentials.
- The electrochemical method can be a useful method of controlling valence state. However, reduced forms of pertinent nuclides may sorb or precipitate on the electrode.
- Use of chemical reagents such as redox buffers can be a valid method but only if it is shown that the chemicals will not affect the sorption characteristics of the sorbent.
- In sorption experiments which may involve valence change, there is no substitute for a detailed investigation of the reaction in order to find out what is the nature of the sorption process.

5.1 Use of Kd Data obtained without Valence Analysis

The fundamental principle to keep in mind when considering the use of Kd data obtained without knowing the valence state distribution is that a change of valence state for any element must be considered as seriously as a change of element. In fact, for the actinides different elements with the same valence state, e.g., U(V)-Np(V), will behave chemically more similarly than the same element in different valence states. Hydrolysis constants of U(V) and Np(V) have quite similar values(6); the same applies to the pairs U(VI)-Np(VI) and U(IV)-Np(IV). This point is really self-evident to chemists who have worked with the lanthanides and the actinides, for in the case of these elements the similarities between elements are sometimes remarkable.

The corollary to this should be obvious. If the valence state of an adsorbing nuclide is unknown, the data are essentially worthless for use in any final safety analysis. This is a strong statement, and we make it so intentionally. We do not imply by this that a Kd experiment done without valence state control should never be done, since such experiments can be valuable preliminary experiments. Nor do we imply that some method of valence state control must be used in the experiments to determine Kd, but we do say that the valence state in the groundwater must be known during the

experiment. It is also extremely desirable to know what the process of removal is, for example, whether the nuclide is simply adsorbed or whether it is reduced as it is adsorbed. Therefore, we conclude that no sorption data should be used for safety assessment unless the valence state of the adsorbing species is known with reasonable certainty. If the valence state is known, the validity of the data then is dependent on the proper technique in measuring the extent of sorption, but that question is beyond the scope of this project.

5.2 The 'Eh' Method of Valence State Analysis

We have indicated above in the section on electrochemistry that the potential measured on a platinum electrode immersed in a solution containing ferrous and ferric iron and oxygen will be determined by a kinetic balance between the reduction reactions and the oxidation reactions. The correlation between the observed potential (usually called a "mixed potential") and the thermodynamic potential is complex. In fact, the literature of electrochemistry is filled with complex analyses of the reactions that take place on various electrodes. Thus, the first and most important point to keep in mind is that rarely will an indicating electrode indicate a true thermodynamic potential. The only cases where a measured potential might be close to the thermodynamic potential would be the case of only one redox couple present at equilibrium, provided that this couple interacted enough with the indicating electrode to control its potential. If there is more than one redox couple present, then each must be at equilibrium, and that would be exceptional.

On the other hand, as the example given above shows, the potential of a platinum electrode will tend to become more positive as the concentration of oxygen increases (Fig.3) and to become more negative if the concentration of ferrous ion increases. Thus the potential read on a platinum electrode can only be a rough indication of oxidizing and reducing conditions in the groundwater. The electrode, however, will not indicate whether a mineral could cause reduction, unless that mineral is at complete equilibrium with the groundwater. In the case of iron-containing minerals, equilibrium implies that the ferrous and ferric concentrations in the groundwater would be at equilibrium with the mineral, and if more than one iron-containing mineral were present, then the minerals would both have to be at equilibrium with each other and with the groundwater.

Thus use of the so-called 'Eh' probe will not indicate whether oxidation or reduction will occur but it will give an approximate indication of oxidizing or reducing conditions. Its use in connection with an analysis of the groundwater, particularly the oxygen content and the iron ion composition, could be helpful in prediction of redox reactions.

The experiments which we described above in section 4.2.3 concerning sorption of Np on several minerals in a controlled atmosphere box illustrate the difficulties that might be encountered with use of an indicating electrode. In each of these experiments, the potential of a Pt electrode was monitored. Yet, in each case the potential was in a region where reduction would not normally be expected to occur. The data however indicate that for chalcopyrite, reduction of Np(V) to Np(IV) was essentially the only mechanism of removal; with the other minerals it appears that several mechanisms are occurring including reduction.

5.3 Electrochemical Methods

The porous electrode technique which we described above can be useful for some purposes, but, as its application to Np showed, it also has limitations. If the species to be formed or stabilized at its present valence state is very soluble and does not tend to adsorb on glass, plastic, or the electrode, then it can be used in a circulating column method. However, with Np(IV), all of the nuclide apparently disappeared from solution as soon as electrochemical conditions were sufficiently reducing to form it. Although we have only done very preliminary experiments with Tc, we suspect

that a similar situation might exist with it also, and we are looking further into the chemistry of Tc and Np to see if under environmental conditions there might be sufficient complexing agents, e.g., carbonate species, to keep low levels of reduced Tc and Np in solution.

The porous electrode technique was very useful in the experiments with neptunium solution on oxides, for it insured that the neptunium was solely in the V state under the conditions of the experiment. Although the V state is considered to be the stable state in normal aerated solutions, we have found in our experiments that when Np tracer is prepared by standard methods given in the literature, it is difficult to prepare 100% pure Np(V). The porous electrode technique was also used to show that when Np(IV) was formed, the resulting Np adsorbed on just about every component of the cell including the electrode.

5.4 Chemical Methods of Valence Control

We have not yet attempted any experiments with redox buffers. By the term 'redox buffer' we mean pairs of reagents like Fe(II)-Fe(III) that can poise the potential of a solution to a value determined by the equilibrium potential of the pair. There are two fairly obvious difficulties with use of redox buffers that in our opinion greatly limit their usefulness. Firstly, any individual redox buffer will have a limited range of potentials of usefulness. The potential can be varied to some extent by changing the ratio of the oxidized and reduced forms or the pH, but in order to get a wide range of potentials and pH's, a number of buffers must be used. Perhaps the most serious difficulty is the possibility that the buffer introduces a new variable into the adsorption experiment, and therefore it must be demonstrated that the presence of the buffer does not alter the characteristics of the sorbent with respect to the particular adsorption reaction under study. To be specific, if the sorption of lower valence states of Tc is under study, then a strong reducing agent may be placed into the solution; the question then is how does one demonstrate that this reducing agent will not affect the surface of the mineral, perhaps by reducing any ferric ions in the surface to ferrous. Before using Kd data obtained with redox buffers, it must be demonstrated that the buffer does not affect the adsorbent. We see no definitive way of doing this.

These same considerations apply to the use of single reagents like powerful redox reagents (hydrazine, ozone, etc.) which are often used to insure that a nuclide is in an upper or lower valence state. Again one must demonstrate that they do not alter the mineral, or they must be removed prior to contact with the mineral.

5.5 Preliminary Recommendations

Probably the most important consideration from these studies is that the valence state, or distribution of valence states, must be known prior to studies of sorption of the nuclide in question. Secondly, there is much more confidence in sorption data if methods have been established to find out whether a reduction or oxidation occurs in the sorption reaction.

The electrochemical method, especially when a porous electrode is utilized, can be used to adjust and stabilize a valence state for a sorption experiment provided that valence state is soluble under the conditions of the experiment. Otherwise the nuclide may simply precipitate on the electrode. The great advantage of the electrochemical method is that its use does not introduce unwanted chemical species into the solution as the redox buffer method often does. Chemical oxidizing and reducing agents can be used to adjust the valence state, but only if it is demonstrated that the species present do not affect the adsorbent. The 'Eh' method of determining what valence states should be present can be suggestive, but must be used with great caution because electrode potentials of indicator electrodes rarely indicate equilibrium potentials in complex systems.

Use of sorption data for safety analysis is always contingent upon careful experimentation in which the process is understood with sufficient clarity to identify the valence state of the adsorbing species. Unfortunately many data in the literature are not presented with this information. When examining data for use in predicting migration rates, it must be realized that it will be of little value to safety analysis if valence effects are not known, and it must always be kept in mind that a change of valence can be and usually is a more significant change in chemical properties than a change of the nuclide; this is especially true of the actinides.

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