Waste/Rock Interaction Technology

Sorption of Redox-Sensitive Elements—Critical Analysis

R. G. Strickert

December 1980

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Pacific Northwest Laboratory
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ABSTRACT

The redox-sensitive elements (Tc, U, Np, Pu) discussed in this report are of interest to nuclear waste management due to their long-lived isotopes which have a potential radiotoxic effect on man. In their lower oxidation states these elements have been shown to be highly adsorbed by geologic materials occurring under reducing conditions.

Experimental research conducted in recent years, especially through the Waste Isolation Safety Assessment Program (WISAP) and Waste/Rock Interaction Technology (WRIT) program, has provided extensive information on the mechanisms of retardation. In general, ion-exchange probably plays a minor role in the sorption behavior of cations of the above three actinide elements. Formation of anionic complexes of the oxidized states with common ligands (OH^- , $\text{CO}_3^{=}$) is expected to reduce adsorption by ion exchange further. Pertechnetate also exhibits little ion-exchange sorption by geologic media. In the reduced (IV) state, all of the elements are highly charged and it appears that they form a very insoluble compound (oxide, hydroxide, etc.) or undergo coprecipitation or are incorporated into minerals. The exact nature of the insoluble compounds and the effect of temperature, pH, pe, other chemical species, and other parameters are currently being investigated.

Oxidation states other than Tc(IV,VII), U(IV,VI), Np(IV,V), and Pu(IV,V) are probably not important for the geologic repository environment expected, but should be considered especially when extreme conditions exist (radiation, temperature, etc.).

Various experimental techniques such as oxidation-state analysis of tracer-level isotopes, redox potential measurement and control, pH measurement, and solid phase identification have been used to categorize the behavior of the various valence states.

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INTRODUCTION

One of the by-products of commercial nuclear power production is radioactive waste consisting of a variety of chemical elements, including actinides, produced by fission and other nuclear reactions. Because several radiotoxic isotopes have long half-lives, such nuclear wastes must be kept isolated from the biosphere for thousands of years. The Department of Energy (DOE), through the National Waste Terminal Storage (NWTs) program, is planning for the isolation of nuclear reactor waste in deep geologic repositories. A broad range of studies have been initiated to investigate the chemical, thermal, and mechanical stability of waste package systems and geologic repositories. Also under investigation are the possible radionuclide transport phenomena which might occur between the repository and the biosphere.

The Waste Isolation Safety Assessment Program (WISAP) was started in 1976 to investigate suitable methodology for evaluating the effectiveness of deep geologic waste disposal. The Waste/Rock Interaction Technology (WRIT) program grew out of WISAP in 1979 and is designed to characterize waste-form radionuclide release and subsequent interactions of radionuclides with engineered barriers and natural geologic materials.

The interactions of the radionuclides with surrounding materials, both near-field and far-field, include a wide range of retention mechanisms (e.g., ion-exchange, precipitation/dissolution, mineral replacement, oxidation-reduction, etc.) which reduce the migration rates of the radionuclides. Empirical methods have been used both in WISAP and WRIT to determine the distribution coefficient (K_d)^(a) of various radionuclides (Brandstetter et al. 1979; Task 4 Proceedings, 1980). The K_d concept was developed in the chromatography field and has been used in various geologic studies where adsorption/desorption equilibrium was achieved within the time frame of interest. However, it has been apparent that the experimental methods used to measure sorption can affect the sorption measurement itself (Relyea 1980). Furthermore,

(a) K_d is the distribution coefficient and is usually defined as $K_d = (\text{milli-moles sorbed per gram of solid})/(\text{millimoles per milliliter of solution})$.

different retention mechanisms (some irreversible) appeared to be important for different radionuclides (Fried et al. 1978). A more complete understanding of the mechanisms controlling migration is needed in order to predict radionuclide concentrations in groundwater solutions throughout a geologic isolation system.

Of particular interest is the experimental research into the retention of radionuclides with multiple oxidation states which could coexist in groundwater environments. In addition to the study of sorption mechanisms of these radioelements there is the need to determine radionuclide oxidation state(s) in groundwater solutions. The dominant oxidation states will be determined by the pH, Eh, complexing ions, and competing ions of the solution itself.

Multivalent radioisotopes which will require long-term isolation from the biosphere are listed in Table 1 along with their half-lives and important valence states. The various uranium isotopes are included for two reasons: 1) the disposal of unprocessed nuclear fuel will involve significant quantities of uranium, and 2) the uranium isotopes listed are alpha-emitting daughter products of other actinides present in nuclear reactor wastes. This report will concentrate on these particular radioelements. A discussion of the redox potential and its measurement and control is also included.

TABLE 1. Multivalent Radioisotopes Which Need Long-Term Isolation from the Environment

<u>Radioisotope</u>	<u>Half-life, yr</u>	<u>Oxidation States of Interest</u>
^{99}Tc	2.14×10^5	(IV), (VII)
^{233}U	1.62×10^5	(IV), (V), (VI)
^{234}U	2.47×10^5	(IV), (V), (VI)
^{235}U	7.08×10^8	(IV), (V), (VI)
^{236}U	2.39×10^7	(IV), (V), (VI)
^{237}Np	2.14×10^6	(III), (IV), (V)
^{239}Pu	2.41×10^4	(III), (IV), (V), (VI)
^{242}Pu	3.87×10^5	(III), (IV), (V), (VI)

SORPTION-PRECIPITATION

The term "sorption" has been used in the past to include a number of different mechanisms which result in the decrease in a nuclide solution concentration and a corresponding increase of the nuclide onto a solid phase. Some researchers (Dosch 1979) have used "sorption" to refer to all possible retention mechanisms including precipitation. Jenne (1977) stated that "sorption and precipitation are in reality different expressions of the phenomenon of the concentrating of solutes on the solid side of the solid-solution boundary." Adsorption, however, is a solid-surface phenomenon. Further complications arise because some experimentalists investigating reversible sorption/desorption mechanisms may have inadvertently exceeded the solubility product of some solid phase containing the nuclide of interest. Thus sorption/desorption may have involved, to some extent, precipitation/dissolution.

Because most of the work discussed in this report deals with sorption, such terms as "sorbed", "desorbed" and so forth will be used in describing the results. When precipitation/dissolution is involved in the retention of a nuclide, it will be identified separately as such. The terms "retention" and "retardation" are more general inclusive terms used to describe all mechanisms which delay the movement of a nuclide in an aquifer.

REDOX POTENTIAL-MEASUREMENT AND CONTROL

An important parameter which must be considered in the study of multi-valent radioelements is the redox potential (Eh). By knowing the Eh value of a system, one may be able to use thermodynamic data to calculate the concentrations (or at least relative concentrations) of the species present.

It is often convenient to discuss the redox potential of a system in terms of the (relative) electron activity, and to define $pe = -\log_{10}(e^-)$ (analogous to pH and the relative hydrogen ion activity). The pe value is related to the Eh value and to the equilibrium constant of the reduction reaction by the following equations:

$$pe = \frac{F \cdot Eh}{RT \ln(10)} = 16.9 \text{ Eh (in volts) (at } 25^\circ\text{C)} \quad (1)$$

$$pe = pe^0 + \frac{1}{n} \log \frac{(ox)}{(red)} \quad (2)$$

$$pe^0 = \frac{1}{n} \log K^0 \quad (3)$$

where F is Faraday's constant ($23.061 \text{ kcal volt}^{-1} \text{ equivalent}^{-1}$), R is the gas constant ($1.987 \text{ cal deg}^{-1} \text{ mole}^{-1}$), T is the temperature in degrees Kelvin ($25^\circ\text{C} = 298.15^\circ\text{K}$), and n is the number of moles of electrons involved in the redox reaction ($\text{oxidized} + ne^- \leftrightarrow \text{reduced}$) where (ox) and (red) are the activities (moles/l) of the oxidized and reduced species, respectively. K^0 is the equilibrium constant of the reaction in terms of activities. Eh and pe will be used interchangeably throughout this report with the above relationship in mind.

The measurement of the redox potential has a number of serious problems which may render meaningless any numbers which are determined. These problems and their effect on Eh measurements, especially of environmental and geologic

systems, have been discussed in detail (Garrels and Christ 1965; Bostrom 1967; Stumm and Morgan 1970). A brief review of the more relevant aspects will be given here.

A major factor in Eh measurement is the kinetics of the electron exchange reaction. Some rate constants may be so small that equilibrium conditions are not reached even on a geologic time scale. A system that is at equilibrium (or a suitably metastable state) must have some buffering capacity (poising) in order that the Eh may be reliably measured. Whether or not a system is poised depends on the exchange current, i_0 , at the redox potential (Morris and Stumm 1967). A low reaction rate constant or low concentrations of reaction species give low exchange currents such that potential measurements are no longer precise. Increasing the electrode surface area will increase the exchange current. Normally, Eh measurements are reliable for exchange currents down to $\sim 10^{-7}$ A, although other effects (such as electrode surface reactions) may require a higher current for the specific redox reaction of interest.

The specific exchange current for the oxygen-water reaction (at 1 atm) is estimated to be 10^{-10} A cm⁻² (Morris and Stumm 1967). Thus it is the redox potential from other reactions which are being measured at the Pt electrode, such as $\text{Pt}(\text{OH}) + e^- \leftrightarrow \text{Pt} + \text{OH}^-$. At lower (reducing) pe values, with the presence of S^{2-} , the formation of platinum sulfide may limit measurements using a platinum electrode because of the surface-sulfide reactions (Brandstetter et al. 1979). Other reactions with solution or suspended material may also coat the Pt electrode and seriously affect the potential measurement by reducing the rate constant or the effective surface area.

There are some techniques which have been used to assure that Eh measurements are more reliable. The use of quinhydrone as an Eh buffer has been discussed extensively (Glasstone 1942; Ives and Janz 1961). The quinhydrone reaction gives $\text{pe} + \text{pH} = 11.82$ at 25°C. Measurements using a pH and Eh electrode in solutions under normal atmospheric or oxic conditions give pe + pH values which indicate that quinhydrone is buffering the system. Because of dissociation of the hydroquinone the pe+pH value above is limited to solutions

where $\text{pH} \leq 8$. Eh indicators such as indigo carmine, nile blue, and 2,6-dichloroindophenol may also be used to determine or control the redox potential of a system (Bondietti 1979). Other inorganic or organic buffers exist and need to be investigated to ascertain whether they have reversible reactions and whether such buffers undergo interfering side reactions with the redox species of interest (e.g., complexation, precipitation, etc.).

A potentiostat has been used previously to maintain a fixed redox potential in a soil-solution suspension (Brandstetter et al. 1979); however, interactions between the soil and working electrode prevented reliable measurements. The use of a potentiostat along with indicator dyes or Eh buffers or in solutions without excessive amounts of soil has not yet been reported.

One of the most commonly used experimental instruments used to control the redox behavior of solutions is the anoxic chamber. Normally, the anoxic chamber is filled with an inert gas (i.e., N_2 , Ar) which is regularly purged or purified to reduce O_2 levels. Oxygen sensors such as those employing an oxygen fuel cell concept are used to monitor the presence of oxygen in the chamber atmosphere. Concentrations of ≈ 1 ppm O_2 in the gas have been obtained. The corresponding reduction in the solution pe value is not great, because $\text{pe} = 13.75 + 1/4 \log p_{\text{O}_2}$ for $\text{pH} = 7$. For $p_{\text{O}_2} = 0.21$ atm, $\text{pe} \approx 13.58$, and for $p_{\text{O}_2} = 10^{-6}$ atm, $\text{pe} \approx 12.25$. Furthermore, the $\text{pe} + \text{pH}$ values for the two oxygen levels (20.58 and 19.25, respectively) are considered greater than the measured $\text{pe} + \text{pH}$ values in some of the experimental work reported below. This is no doubt due to the poorly poised O_2 couple and the fact that O_2 detectors are not available to measure O_2 below about 0.2 ppm in a gas.

The use of redox electrodes at high temperature (100–250°C) has been reported by Danielson (1980). A reference electrode was used which had been constructed for high temperature aqueous environments containing H_2 and H_2S (Danielson 1979). At all temperatures within the range, a potential difference of >1 volt was measured between an oxidizing environment (0.4 ppm O_2) and a reducing environment (0.5 atm H_2). However, experimental results so far indicate that mixed potentials are being measured and that the measured potential is not very sensitive to changes in oxygen concentration.

In summary, the redox potential may be used along with other thermodynamic data to determine the maximum concentration (solubility) of a radionuclide in solution. However, accurate measurements of Eh (or pe) are difficult because:

- Equilibrium conditions may not exist for the redox system.
- The reaction rate may result in a low exchange current, i_0 , at equilibrium.
- Contamination of the electrode surface may reduce the Eh response.

At present, it appears that redox buffers can provide the poised potentials likely to be found under reducing conditions in geologic environments.

Although quinhydrone has been shown to be an effective Eh buffer, other compounds with lower Eh values should be tested to determine their suitability as buffering agents in specific solutions.

NEPTUNIUM SORPTION/DESORPTION

The limited thermodynamic data which are known for neptunium have been reviewed previously (Ames and Rai 1978; Rai and Serne 1978; Onishi et al. 1979). It is known that for pe values less than ~ 12.8 , NpO_2 should be the most stable compound. In acidic and oxidizing conditions, NpO_2 is soluble. However, in neutral pHs, the solubility of NpO_2 is quite low ($< 10^{-5}\text{M}$), especially under redox conditions which simulate geologic environs. From thermodynamic considerations, NpO_2^+ would be the dominant species in solution at low and middle pH ranges. As the pH increases, bicarbonate, hydroxyl, and phosphate complexes may occur if the anions are available. The sorption affinity of NpO_2^+ is not large (Routson et al. 1977). Solubility of specific neptunium compounds are important in determining the concentration of solution species. The solubility of neptunium compounds will involve oxidation-reduction potentials in some cases.

EXPERIMENTAL STUDIES

Bondietti and Francis (1979) investigated the sorption of neptunium using different basalt, granite, or shale rocks in a deoxygenated (< 1 ppm O_2) nitrogen-purged system. Both pH and redox potentials were monitored. From the Eh-pH data, it has been calculated that $\text{pe} + \text{pH} \sim 10$ for the shales and $\text{pe} + \text{pH} \sim 7$ for the granites and basalts. Their Eh measurements indicated that Np(V) should be unstable in the presence of the igneous rocks (basalt and granite) and possibly in the presence of unweathered shales. In the neptunium sorption studies, it was found that Np(V) was being removed from solution by the rocks. After seven days of equilibration, both the neptunium remaining in solution and the neptunium extracted from the igneous (basalt and granite) rocks was 60 to 80% Np(IV) . On the other hand, sorption experiments with the shale, although more rapid in removing neptunium from solution, resulted in little or no reduction to Np(IV) . Basalt which had been pretreated with NaOCl to oxidize the iron also failed to reduce any significant quantities of Np(V) to Np(IV) , even though more than 80% of the neptunium was removed from solution. This would seem to indicate two different mechanisms for neptunium

sorption—one of which involves a redox [$\text{Np(V)} \rightarrow \text{Np(IV)}$] reaction. It was noted that basalts, granites, and unweathered shales also reduced Pu(V) to Pu(IV) in experiments similar to those performed with neptunium (Bondietti and Sweeton 1977).

Culebra dolomite and Magenta gypsum were used in batch sorption-desorption experiments of $^{239}\text{Np(V)}$ (Francis and Bondietti 1980). Under oxic conditions, the Np(V) K_d values were approximately 6.6 ml/g and 200 ml/g for the dolomite and gypsum, respectively. Sorption and desorption values were essentially the same and the valence state was stable, indicating a reversible ion-exchange mechanism. No redox potential measurements were available to determine if Np(V) reduction was contributing to the sorption.

Neptunium sorption as a function of pH was investigated by Allard et al. (1980) using the batch sorption technique. Various minerals (quartz, biotite, bytownite, albite, microcline, olivine, hornblende, and augite) were used. The ^{235}Np tracer was added to the pH adjusted groundwater in a stock solution rather than drying the tracer and redissolving it in groundwater. After 5 days, the Np solution concentration was measured. The results were similar for all minerals in that there were low K_d values (10 to 100 ml/g) for low pHs and a sharp increase in the K_d values at pH ~ 7 to 8 to give K_d values of 1000 ml/g at pH 9. The initial ^{235}Np solution concentration was 2×10^{-11} M. Sorption studies with a brine solution (4 M NaCl) showed only slightly higher distribution coefficients suggesting that the mechanism was not an ion-exchange process. Competition for exchange sites in the brine would be expected to lower K_d values for an ion-exchange process. Similar increases in K_d values for neptunium sorption in 5.13 M NaCl were reported by Relyea and Rai (1980). Hydrolysis and bicarbonate complexing will occur as the pH increases, but it is not known whether these reactions were involved in the sorption process. It has been suggested that at the higher pH values, neptunium solubility may become the limiting factor. Whether pe values decreased as pH values increased was not reported.

Barney and Brown (1979) reported on the reversibility of neptunium sorption from Umtanum basalt, NTS granite, and NTS argillite. The spiked solutions

were made from dried Np-237 tracer and filtered through 0.3 μm membranes prior to use. No Np concentrations were reported. It is anticipated that Np(V) would be the predominant species under oxic conditions. Desorption Kd values after a 5-week period were compared to sorption values after a 2-week period (Table 2). Desorption values were still decreasing after 5 weeks but were expected to approach sorption Kd values with time.

TABLE 2. Sorption-Desorption Values for Np-237
(Barney and Brown 1979)

Rock	Kd (ml/g)	
	2-Week Sorption	5-Week Desorption
Basalt	57	110
Granite	5	120
Argillite	31	100

Barney and Brown (1979) investigated neptunium sorption on fresh and weathered rocks. Basalt, granite, and argillite were artificially weathered by leaching with hot, distilled water for 6 months in flowing N_2 (deoxygenated with pyrogallol) followed by air drying. Kd values for neptunium increased with weathered basalt, remained the same for weathered granite, and decreased slightly for weathered argillite compared to the unweathered rocks (Table 3).

TABLE 3. Comparison of Neptunium Kd Values for Fresh
and Weathered Rock (Barney and Brown 1979)

Rock Type	Kd(a)(ml/g)	
	Fresh	Weathered
Basalt	10 $\pm$ 1	49 $\pm$ 16
Granite	45 $\pm$ 2	39 $\pm$ 3
Argillite	79 $\pm$ 10	56 $\pm$ 16

(a) 14-day equilibration. Error is 1σ .

Changes in the structure of the rocks caused by weathering were discussed, but no clear connection to the small changes in Kd values was evident. It was

stated (Barney and Brown 1979) that ion exchange may be the sorption mechanism for neptunium. This was based on the apparent reversibility of Np sorption and the similar CEC values for both unweathered and weathered rocks. No Eh values were given in the report although sorption experiments were performed in the presence of air.

Neptunium-237 sorption onto rocks was investigated by microautoradiographic techniques (Erdal et al. 1980). In general, the ^{237}Np tended to aggregate on all the materials used (alluvium, NTS tuff, Climax stock granite, and Eleana argillite). The Np appeared to be associated with specific minerals in the thin sections. However, according to the information given, the solutions used in the study was over $1\text{ M }^{237}\text{Np}$. No oxidation state analysis was performed, but Np purification procedures used would tend to establish Np(IV) as the predominant form. It is possible that precipitation may have occurred during these sorption tests.

NEPTUNIUM SUMMARY

Under reducing conditions, such as groundwaters in contact with iron-bearing minerals or old waters within deep aquifers, neptunium (V) appears to be reduced to some undetermined Np(IV) compound. Np(V) itself may undergo reversible ion-exchange sorption/desorption, when it encounters oxidizing conditions. Ion exchange behavior of the NpO_2^+ is not high, as expected, and may be replaced by reduction reactions as the pe value of the solution decreases. Once Np(IV) is formed, it may undergo ion-exchange or more likely precipitation. These areas need to be investigated further. Species identification should be carried out especially at pH values where hydrolysis or carbonate complexes may occur. Uncertainties in the sparse thermodynamic data available in the literature should be improved through experimental measurements of the various reaction constants.

Some requirements in experimental techniques have been made apparent in these studies. The most obvious is the need to analyze for the oxidation states of the neptunium in solution (and solid phase if possible). Solvent extractions or ion exchange techniques can be used (Burney and Harbour 1974).

The solution Eh should be monitored or controlled especially if a particular Np oxidation state is to be maintained. Preparation of the tracers is also important so that one does not reach or exceed the solubility limits at the start of the experiment. This is especially important in using ^{237}Np which has a low specific activity.

PLUTONIUM SORPTION/DESORPTION

The thermodynamics and related chemistry of the various oxidation states of plutonium have been extensively covered (Polzer and Miner 1967; Cleveland 1970; Ames and Rai 1978; Rai and Serne 1978; Onishi et al. 1979). Most studies have involved low pH solutions. At neutral pH values for mildly oxidizing conditions, the solution species of plutonium has been predicted to be Pu(IV) (Cleveland 1970) or Pu(V) (Ames and Rai 1978). Hydrolysis and complexation are expected to be important and may result in anionic species of plutonium. According to Bondietti et al. (1976) the reduction of tetravalent plutonium is unlikely in typical groundwater environments due to the stability of the hydrolyzed or complex species of Pu(IV). However, Rai et al. (1979) showed that, according to thermodynamic data, Pu(III) would be the dominant species under strongly reducing conditions ($p_e + pH < 10$). Pu(V) and Pu(VI) have been shown to be reduced by humic substances (II) (Bondietti et al. 1976).

EXPERIMENTAL STUDIES

Chemical speciation of plutonium was examined by Wilhite (1978) in contaminated soil and water samples from a transuranic burial ground monitoring well and an alpha waste burial trench at Savannah River. Filtration of plutonium contaminated well water (pH 7) through filters finer than $0.45\ \mu\text{m}$ (Table 4) showed that more than half of the plutonium was a soluble species, and that no significant amount of discrete particles $>12\ \text{\AA}$ and $<0.45\ \mu\text{m}$ were present. Using ion exchange columns on $0.45\ \mu\text{m}$ filtered solutions, it was determined that $88 \pm 15\%$ of the soluble plutonium was cationic and $4 \pm 3\%$ was anionic.

TTA, hexone, and xylene extraction procedures were performed with the solutions. About 23% of the plutonium [as Pu(III) or Pu(IV)] was extracted in TTA, 43% [as Pu(V) or Pu(VI)] was extracted in hexone, and less than 2% (as a xylene-soluble plutonium complex) was extracted in xylene. More than 30% remained unextracted.

TABLE 4. Plutonium Concentrations in Various Filtered Solutions (Wilhite 1978)

<u>Filter Size</u>	<u>Total Pu, pC/l</u>
Unfiltered	52.0 $\pm$ 0.6
0.45 μ m	32.2 $\pm$ 3.0
0.1 μ m	26.0 $\pm$ 3.7
10,000 M.W. (a)	23.6 $\pm$ 0.4
1,000 M.W. (a)	27.2 $\pm$ 8.3

(a) Molecular weight.

Analysis of the filtered water and sediment samples from the well resulted in a calculated K_d of $\sim 10^4$ ml/g. Yet when filtered well water was contacted for an unspecified time with uncontaminated burial ground soil, a K_d value of ~ 60 ml/g was determined. It was concluded (Wilhite 1978) that some plutonium species with a "high K_d " value had been retained in the sediments in the past, leaving a more mobile species in solution.

Contaminated soil was examined and it was found that the plutonium was distributed over the sand ($>50 \mu$ m), silt ($>2 \mu$ m, $<50 \mu$ m), and clay ($<2 \mu$ m) fractions, with the clay fraction containing 76% of the soil-bound plutonium. This was due primarily to the greater surface area of the clay particles.

Sequential extractions with 0.1 N $MgCl_2$, dithionite-citrate, and sodium hydroxide solutions showed that an average of 2.5% of the plutonium was ion-exchangeable, 2.5% was organically bound, and 87% was found in the oxide coatings or crystalline phase. It would appear that solubility limits of some Pu compound may be determining the plutonium solution concentration; however, because of the unknown isotopic composition of the Pu ($^{238}, ^{239}, ^{240}Pu$ were present), no concentration values were given.

Extractions at different pH values were performed on Pu-contaminated sediments at Rocky Flats, Colorado (Rees, Cleveland, Gottschall 1978). It was shown that the K_d values decreased as the solution pH increased above 7. K_d values at pH 7 were around 120,000 ml/g after 68 hr of extraction time. The

conclusion was that plutonium dispersed from the sediment as radiocolloids or sorbed onto dispersed colloidal sediment particles. No soluble complexes were found. Such a result is likely because no filtration was done on the extraction solutions used for K_d determination. Another experiment showed that only 5 to 6% of Pu which passed through a 5 μm filter also passed through a 0.2 μm filter.

In four successive 20-hr extractions of particular sediments by pH 9 and pH 11 solutions, a decrease in Pu solution concentration was attributed to variations in the degree with which plutonium was bound to the soils or to the association of some plutonium to smaller sediment particles that were more readily dispersed. The calculated K_d values also decreased with each successive extraction of fresh sediment with a single pond water sample. In all of the extraction experiments, no filtration was done. A TTA extraction was performed on some of the sediments but no oxidation state analysis was reported. The experiments were carried out under oxic conditions. No analysis of pond water was done to see if aluminum hydroxide solubility or other similar reactions may have affected the Pu present in "solution" at the higher pH values.

Coles, Weed, and Tewhey (1980) reported several sorption K_d values for ^{237}Pu on various geologic materials. Coles et al. dried the tracer in a polyethylene bottle before redissolving the tracer in simulated groundwaters. The solutions were then filtered (0.4 μm) before being used in batch sorption experiments. In preparing the spiked groundwater solutions it was found that 25% of the Pu remained on the filter using granitic groundwater (47.7 mg/l HCO_3^- , pH = 7.8), while more than 95% of the Pu remained on the filter using a bicarbonate (153 mg/l HCO_3^- , pH = 8.2) groundwater. Using blank containers as "sorption samples", 97% of the ^{237}Pu sorbed onto the container walls from granitic groundwater and only 45% of the Pu sorbed onto the walls with bicarbonate groundwater. According to the authors the seemingly contradictory results for plutonium behavior on the filter and on the container walls was evidence of the difficulty of working with tracer level amounts of Pu at near-neutral pH values. However, considering filter loss and container wall loss, both groundwaters lost about 98% of the initially available plutonium so that

the final solution concentrations were about the same in both groundwater blanks. The bicarbonate solution appeared to lose Pu at a faster rate than the granitic groundwater. Whether this was due to the small differences in bicarbonate concentration or to the small difference in pH is not known. No oxidation state analysis was performed on the solution plutonium after it had been dried and redissolved. All sorption experiments were carried out under atmospheric conditions, so that Pu(V) might be expected to be the predominant species (Rai, Serne, Swanson 1979).

The calculated Kd values were determined by two methods: 1) the calculated Kd value was corrected for container wall sorption by using a blank wall sorption factor, and 2) no wall sorption was included in Kd calculations. For Thirsty Canyon tuff using "granitic" groundwater, method 1 gave a Kd of 190 ml/g (+20%) whereas method 2 gave 8,000 ml/g (+18%). Using Climax Stock granite with simulated granite groundwater, Kd values calculated by method 1 were ≤ 500 ml/g and Kd values calculated by method 2 gave values of 1000 to 20,000 ml/g.

A set of 15 different sandstones were used along with a brine solution to examine the sorption behavior of various radioisotopes (Coles, Weed, and Tewhey 1980). As expected, ^{137}Cs and ^{85}Sr had low Kd values (<1 ml/g) due to competition for exchange sites with Na^+ in the brine. The Kd values for plutonium were still high (63 to 3270 ml/g), and the conclusion was that the unique chemistry of plutonium plays a critical role in its removal from solution under high salt concentration conditions. Ion exchange does not play a major role in the retention of plutonium in the sandstones. Mineral content of the sandstones and particle size did not appear to be correlated to the retention of plutonium.

In sorption-desorption studies of plutonium on basalt, granite and shale, Francis and Bondietti (1980) contacted the rocks with solutions of Pu(V). Although it was not stated in their report whether anoxic conditions were employed, it was presumed that ferrous iron in the rocks would reduce plutonium to Pu(IV) which would then sorb onto the rock. The unreduced Pu(V) was removed from the rocks with two salt solution washes. The rocks were then used in desorption Kd experiments with synthetic groundwater (pH 8.2). The results

(Table 5) indicated that 1) the K_d values are about the same as previously reported K_d values (Rees, Cleveland, Gottschall 1978; Wilhite 1978), and 2) the K_d values are similar for the three successive desorption intervals of one month. Valence analysis showed that the plutonium in solution was Pu(IV). This does not agree with thermodynamic data (Onishi et al. 1980) or with other studies (Rai, Serne, Swanson 1979). Using concentrations of $>10^{-13}$ M would infer that solubility limits of some plutonium compounds may control the plutonium in solution and render any K_d calculations useless.

TABLE 5. Successive Plutonium Desorption K_d Values (1-Month Intervals) (Francis and Bondietti 1980)(a)

Rock	K_d (ml/g)(b)			Log M of Desorbed Pu
	1	2	3	
Basalt	20,000 $\pm$ 10,000	30,000 $\pm$ 7,000	22,000 $\pm$ 12,000	-12.9 to -12.4
Granite	23,000 $\pm$ 23,000	10,000 $\pm$ 5,000	33,000 $\pm$ 28,000	-13.0 to -12.1
Shale	99,000 $\pm$ 110,000	300,000 $\pm$ 230,000	57,000 $\pm$ 22,000	-13.9 to -12.3

(a) The large uncertainties in the K_d values correspond to uncertainties in radioanalytical measurements of solutions with near background levels of activity.

(b) Desorption K_d s were determined following two successive NaCl washes. Desorption solution was synthetic groundwater (pH 8.2).

Surface sorption studies with 10^{-13} M plutonium contacting basalt or granite chips (~ 5 cm² surface area) were performed (Francis and Bondietti 1980) using 10^{-3} M NaHCO₃ solutions (pH 8.4). Surface K_d values of 10 ml/cm² or less were determined. According to the authors, if one corrects for the unreduced Pu(V) in solution, K_d values for Pu(IV) correspond to the 100 ml/cm² values obtained for desorption.

Culebra dolomite and Magenta gypsum were used in batch sorption-desorption experiments of plutonium (Francis and Bondietti 1980). Under oxic conditions, the ²³⁶Pu(V) groundwater solutions were stable. In contact with either the dolomite or gypsum, the Pu(V) showed gradually increasing K_d values (>100 ml/g) over a period of 9 days. Desorption values were still higher (>200 ml/g) after 1 week.

Sorption-desorption experiments were also done using $^{236}\text{Pu(IV)}$ ground-water solutions. For the gypsum, Pu(IV) K_d values were about 4 times greater than those of Pu(V) and still increasing after 9 days. For the dolomite, Pu(IV) K_d values were more than 10 times higher than those of Pu(V) and also were increasing after 9 days. Desorption values for Pu(IV) were still higher for each type of rock.

From further work by Francis and Bondiotti, it was suggested that Pu(V) is being reduced by the materials in the rock to Pu(IV) and that if it were not for the reduction to the highly sorbable Pu(IV) , the Pu(V) should have a similar K_d value to that of Np(V) .

Erdal et al. (1980) initially treated a ^{237}Pu tracer solution (in 3 M HCl) with sodium nitrite so that the plutonium was in the IV oxidation state. The tracer was dried and then dissolved in an appropriate groundwater solution ($\text{pH} \approx 8$). Analysis indicated that following a 1-hr centrifuging, only half of the ^{237}Pu remained in solution at room temperature (22°C). Filtering through a $0.4 \mu\text{m}$ Nucleopore[®] (Nucleopore Corporation, Pleasanton, CA) filter reduced the concentration ($\sim 5 \times 10^{-13}$ M ^{237}Pu) only slightly. At 70°C , however, only 6% of the plutonium remained in solution after centrifuging and filtration.

Ground-water solutions were also prepared (Erdal et al. 1980) using ^{239}Pu . One of the ^{239}Pu groundwater solutions was prepared by adding an aliquot of ^{239}Pu stock solution to the groundwater and then readjusting the groundwater pH by adding sodium hydroxide. The initial concentration of the solutions ($\text{pH} \approx 8$) was estimated to be 10^{-6} M. However, this value exceeds the expected solubility of plutonium at that pH. After centrifuging, the ^{239}Pu concentration was estimated to be $\sim 10^{-7}$ M, although there were indications that with some filtered groundwater solutions, the ^{239}Pu concentration was $\sim 10^{-9}$ M.

No plutonium oxidation state analysis was performed on the spiked ground-water solutions. It was stated later in the report that various species of plutonium could exist in the groundwater solutions due to colloidal formation and hydrolysis, but no data were given.

Plutonium sorption (and desorption) on argillite under oxic conditions has been reported by Erdal et al. (1980). The batch Kd method was used, however, the oxidation state or species of the plutonium was not determined. With argillite, both sorption and desorption Kd values (ml/g) were similar for a given temperature (22°C or 70°C). There was an order of magnitude difference between Kd values for filtered and unfiltered solutions (Table 6). It was suggested (Erdal et al. 1980) that this difference was due to the association of plutonium activity with fine particulates. Whether these particulates were present in the initial groundwater solution or whether they came from the argillite material was not determined. Because of the reduction in solution activity when the initial groundwater tracer solutions were filtered, it is possible that the plutonium species present may contribute to the effect. The ^{239}Pu groundwater solution probably contained some plutonium colloidal or particulate material because the added ^{239}Pu tracer exceeded the expected solubility of plutonium at $\text{pH} \approx 8$.

TABLE 6. Representative Kd Values for Pu on Argillite (Erdal et al. 1980)

	Kd (ml/g)(a)	
	22°C	70°C
^{237}Pu Sorption		
Unfiltered(b)	4,200 (1,100)(c)	2,100 (220)
Filtered	37,000 (12,000)	75,000 (38,000)
^{237}Pu Desorption		
Unfiltered	5,700 (1,400)	2,000 (250)
Filtered	34,000 (3,700)	37,000 (50,000)
^{239}Pu Sorption		
Unfiltered	25,000 (9,000)	--

(a) Pu groundwater solutions prepared with dried tracers. Solution/solid ratio = 20.

(b) Indicates whether final solutions were filtered after centrifuging and before counting.

(c) Values in parentheses are standard deviations of the mean (absolute values).

Another indication that tracer preparation may affect the speciation of plutonium came from the tuff sorption data (Erdal et al. 1980). Under oxic conditions at 22°C, typical batch K_d values for sorption on different tuff samples (solution/solid ratio = 20.0) ranged from 100 ml/g to 200 ml/g for plutonium groundwater solutions prepared from dried Pu tracer. For plutonium groundwater solutions prepared by adding acidic Pu (presumably IV) tracer solution to the groundwater solution and adjusting the pH, batch K_d values ranged from 1000 ml/g to over 3000 ml/g. Variations in different tuff samples or differences in some of the experimental methods (as discussed by Relyea 1980) may account for the K_d effects noted, but it is also apparent that there needs to be an awareness of what particular species of plutonium exists in the solutions which are being used for sorption studies, and the effects of different spiking (dilution) techniques.

Rai, Serne, and Swanson (1979) investigated air-equilibrated solutions in contact with ²³⁹Pu(IV) hydroxide. A combination of solvent extraction and spectrophotometric techniques were used to determine the oxidation states of plutonium in solutions of different pH values. Redox potentials were also monitored. The data showed that Pu(V) is the dominant species in solutions in equilibrium with Pu(IV) hydroxide.

Measurements were also made (Rai, Serne, and Swanson 1979) on species of plutonium in solutions contacting ²³⁹PuO₂(c). In these solutions it was shown that Pu(IV) were not present in solutions under relatively oxidizing environmental conditions. It was also shown that a rapidly oxidizable species of plutonium [going to Pu(VI)] is present in solution. Because the oxidation of Pu(IV) [or Pu(III)] to Pu(VI) has been shown to be slow (~4 hours) (Rai, Serne, and Swanson 1979; Cleveland 1970), the conclusion was that Pu(V) is the dominant species in this solution.

The experimental results obtained in this study agree with the oxidation state of plutonium expected from an Eh-pH diagram (Rai et al. 1979) constructed from thermodynamic data (Figure 1). Under reducing conditions (e.g., pe + pH ≲ 10), it is expected that Pu(III) would be the dominating species. It

FIGURE 1. Equilibrium Diagram of Potential (Eh), with Respect to Standard Hydrogen Electrode, Versus pH at 25°C Showing Stability Fields of Different Aqueous Pu Species. Dashed lines represent 1 atm O_2 (upper) and 1 atm H_2 (lower). Shaded areas represent broad boundaries, between stability field, due to errors in the thermodynamic data. [Hydrolyzed species of Pu(IV) may be important, but because reliable formation constants are not available at environmental pH values, their relative stability fields are impossible assess.] [From Rai, Serne, and Swanson (1980)].

should be pointed out that the stability fields of Pu(IV) species are not well known; this could influence the interpretation based upon presently available thermodynamic data.

The concept of comparing the solubility of plutonium compounds as a means of possibly identifying the Pu solid phases in sediments was explored by Rai, Serne and Moore (1980). Three different contaminated Hanford soils were

suspended in solutions of different pH and the Pu solution concentration was plotted (Figure 2) along with the solubility lines of $\text{PuO}_2(\text{c})$ and $\text{Pu}(\text{OH})_4(\text{am})$ determined previously (Rai, Serne, and Swanson 1980). The Z9-4-11A and Z9-4-5A soil samples appear to contain $\text{PuO}_2(\text{c})$ [or perhaps a Pu species with similar solubility as $\text{PuO}_2(\text{c})$]. The presence of $\text{PuO}_2(\text{c})$ was confirmed in the Z9-4-11A soil by X-ray diffraction analysis. The Pu concentration characteristics of the Z-12-1D soil implies that no PuO_2 exists in the soil.

FIGURE 2. Log Concentration of Pu from Solutions Contacting Contaminated Soil as a Function of pH (Rai, Serne, and Moore 1980)

The plutonium concentration in all the solutions contacting the contaminated soils were much lower than the $\text{Pu}(\text{OH})_4(\text{am})$ solubility line, implying that none of the hydroxide compound exists in the soils.

Rai et al. (1980) have carried out a detailed study into the possible mechanisms for the sorption of Pu(VI) by various clays and rocks using batch sorption techniques, with periodic sampling of the solutions. Pu oxidation state analyses were performed to distinguish between Pu(III)/Pu(IV) and Pu(V)/Pu(VI). Fe(II) and Fe(III) weight percentages, surface areas, cation exchange capacities, and X-ray diffraction analysis of the clays and rocks were also done. Only small amounts of impurities were found in any of the clays, such that any plutonium sorption mechanism could be considered to be associated with the characteristics of that particular mineral. At pH ~ 4, the percent of ^{239}Pu (initially $7.3 \times 10^{-9} \text{ M}$) sorbed by the different minerals was plotted (Figure 3) as a function of time (corresponding K_d values are ~34 times the percentage value). No correlation was found between CEC and the Pu adsorbed, thus ion exchange was not a major sorption mechanism. Essentially all of the solution Pu was in the oxidized state [Pu(V) or Pu(VI)]. The presence of ozone lowered the sorption of plutonium by vermiculite and biotite to ~50%, but did not affect the adsorption by kaolinite. Vermiculite, biotite, and hematite, which had large amounts of Fe(II), also adsorbed large fractions of Pu(VI). Kaolinite and gibbsite had relatively little structural Fe(II) and also sorbed only a small fraction of the plutonium. Both montmorillonite and nontronite had low amounts of Fe(II); however, montmorillonite had relatively high exchangeable Pu while nontronite had only a small amount of exchangeable Pu. The reasons for this difference are not known; especially since both clays are similar in structure.

At pH ~ 7 (a value more typical of repository groundwaters than pH 4) all minerals exhibited high sorption values (>93%) for Pu initially at $7.3 \times 10^{-9} \text{ M}$. Desorption of Pu decreased for kaolinite and montmorillonite. Hydrolysis of Pu(VI) and subsequent sorption may be an important mechanism at pH ~ 7, especially with minerals having low sorption in pH 4 solutions.

FIGURE 3. Adsorption of $^{239}\text{Pu(VI)}$ by Aerated Mineral Suspensions at pH 4. Averages of duplicate samples are plotted. (○ = <7%, □ = 7-15%, and Δ = 15-30% difference between the replicates). (Rai et al. 1980).

Relyea et al. (1979, 1980) investigated the sorption of plutonium-237 under oxic ($p\text{O}_2 \sim 0.7$) and anoxic ($p\text{O}_2 \sim 2.7$) conditions using twelve selected minerals and four solutions in a series of batch K_d experiments. For the 5.13 N NaCl and 0.03 N CaCl_2 solutions, the K_d values were higher under anoxic than under oxic conditions in agreement with thermodynamic expectations. Lower K_d values were obtained for anoxic conditions with 0.03 N NaHCO_3 and no significant differences were observed between the anoxic and oxic conditions with the 0.03 N NaCl solution. An explanation for the results using the last two solutions was not available. For all permutations of experimental conditions, the plutonium sorption K_d value was large (>1000 ml/g in all but 14 cases, and >500 ml/g in all but 5 cases). No oxidation state analysis was reported.

The extent of Pu(IV) polymer in environmental solutions is important in estimating the migration potential of Pu. Rai and Serne (1978) have looked at the available literature data on Pu(IV) polymer formation. The pH and Pu concentrations obtained from the data are approximate, but cover a range of pH values. The concentration data have been plotted (Figure 4) as a function of pH, along with the $\text{Pu}(\text{OH})_4(\text{am})$ solubility line (Rai, Serne, and Swanson 1979). Because the data appear to coincide with the $\text{Pu}(\text{OH})_4$ solubility line, it was concluded that the Pu(IV) polymer and $\text{Pu}(\text{OH})_4$ are similar in their solubilities. However, recent values (Rai and Swanson 1980) of Pu concentration in pH 4 and pH 7 solutions contacting Pu(IV) polymer fall slightly below the $\text{Pu}(\text{OH})_4(\text{am})$ solubility line but above the $\text{PuO}_2(\text{c})$ solubility line.

PLUTONIUM SUMMARY

The oxidation/reduction behavior of plutonium is difficult to elucidate from the reported studies due to relatively few analyses of oxidation states or measurements of redox potentials. However, certain general patterns are indicated.

Preparation of tracer solutions will affect the oxidation state of plutonium present in solution. When Pu(IV) solutions are dried and redissolved in near neutral groundwaters under oxic conditions, it is likely that the soluble species will be Pu(V). This was shown clearly in the study of Erdal et al. (1980) and may account for some of the "unusual" results of other investigators.

Pu(IV) and Pu(V) appear to be the two important oxidation states which are encountered (at least in laboratory conditions). Pu(VI) was observed or measured (Wilhite 1978); however, Rai, Serne, and Moore (1980) have clearly indicated that the extraction procedures used to identify Pu(VI) will not distinguish between Pu(V) and Pu(VI). From the study of Erdal et al. (1980) it may be concluded that Pu(IV) sorbs onto rocks and minerals (and filters and container walls) to a greater extent than Pu(V). Pu(IV) desorption is slow while Pu(V) desorption may be reversible (Francis and Bondietti 1980).

FIGURE 4. Log Concentration of Pu in Solutions as a Function of pH. A-Solutions in equilibrium with Pu(OH)_4 . B-Comparison of Pu(IV) polymer formation or solubility conditions with the Pu(OH)_4 solubility. (Rai and Serne 1978).

Ion exchange may be one of the mechanisms involved in Pu(V) sorption; salt solution extractions have been used to remove Pu(V) from a rock suspension (Francis and Bondietti 1980). Clays do not exhibit a large ion exchange sorption affinity for Pu(VI), and presumably Pu(V) (Rai, Serne, and Moore 1980).

If ion exchange is a mechanism for the sorption of Pu(IV), it is a strong one and not easily reversible. Rai and coworkers have shown that Pu(IV) oxide and hydroxide have low solubility which limits the concentration of plutonium species in solution; the plutonium in solution exist as Pu(V). Complexation of Pu(V) is expected to be insignificant.

Temperature is important in the sorption of plutonium. A 48°C rise in temperature reduced, down to a few percent, the amount of plutonium passing through a filter. The increase in temperature could have speeded up (by perhaps 30 times) slow colloidal formation which would then be filterable. In addition, from thermodynamics, as the temperature increases, PuO₂ solubility will decrease.

The small differences between K_d values under oxic or anoxic conditions (Relyea et al. 1980) are not unexpected from the discussion of pe values in a previous section (The experiments described had only a small range in pe values).

Colloidal formation of Pu(IV) including the frequently discussed Pu polymer was observed in several references. Filtration was the standard procedure in removing the polymer from solution (Erdal et al. 1980). The identification of Pu polymer (Rai and Serne 1978) with Pu(OH)₄ (at least according to solubilities) should simplify Pu studies. It may also explain the temperature effects of filtered plutonium mentioned above. Rai and Swanson (1980) have shown that Pu(IV) polymer behaves as a solid and has a solubility under environmental conditions which is intermediate between Pu(OH)₄(am) and PuO₂(c).

The needed improvements in experimental techniques for plutonium chemistry are basically the same which were listed for neptunium. Oxidation state

analysis and Eh measurement (or control) must be done. It would be useful if a reliable (and relatively simple) technique were developed for distinguishing between Pu(V) and Pu(VI) oxidation states under typical groundwater conditions.

Finally, it should be noted that the higher specific activity of ^{239}Pu over ^{237}Np or ^{238}U may result in greater alpha radiolysis effects in solution (Rai, Strickert and Ryan 1980). Work could be done in an inert (argon) glove box to eliminate the radiolysis of dissolved oxygen and nitrogen in solutions which produces nitric acid.

TECHNETIUM SORPTION/DESORPTION

The thermodynamics and related chemistry of technetium has been reviewed extensively (Boyd 1959; Anders 1960; Cobble 1964; Rulfs et al. 1967; Ames and Rai 1978; Rai and Serne 1978; Onishi et al. 1979). The environmental chemistry of technetium was recently reviewed by McFadden (1980). In aqueous solutions Tc(VII), as pertechnetate anion (TcO_4^-), is stable over broad pH and ionic strength ranges, including those of natural groundwater solutions. It can be reduced in solution by hydrazine, hydroxylamine, SnCl_2 , and other reductants to form the hydrated Tc(IV) species, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$. Tc(IV) may be oxidized by H_2O_2 , air, MnO_4^- , or Cl_2 to Tc(VII).

EXPERIMENTAL STUDIES

In the lower oxidation states, technetium may form strong complexes. The order of hydrolysis for the various Tc oxidation states is expected to be $\text{IV} > \text{II} > \text{V} > \text{VI} > \text{VII}$ (McFadden 1980). Thus the redox potential of natural groundwater systems and the presence in the groundwaters of complexing agents will determine the technetium species formed.

The sorption of TcO_4^- was studied using twenty-two different soils, representing a broad range of physical-chemical properties (Wildung et al. 1974). Performed under oxic conditions, K_d values ranged from 0.007 to 2.8 ml/g. The K_d values increased with increasing organic carbon content and decreased with increasing pH. Retention of pertechnetate was associated with the positive charge on the organic fraction and amorphous oxides.

A study (Francis and Bondietti 1980) was done to investigate the effects of ferrous ion concentration and pH on the concentration of pertechnetate in both basalt suspension and simulated groundwater solutions. These experiments were carried out under anoxic conditions.

In one set of experiments it was concluded that Fe^{2+} added to a stirred cell before the addition of TcO_4^- had little or no effect on the sorption of TcO_4^- , while adding the Fe^{2+} to the suspension at pH 8 containing TcO_4^- did reduce the TcO_4^- concentration.

In another experiment, the pH of the basalt suspension was raised which resulted in a reduction in the concentration of both TcO_4^- and Fe^{2+} .

It is most probable that at least two reactions are involved in these experiments: 1) reduction of pertechnetate to (possibly) TcO_2 by the ferrous ion, and 2) coprecipitation of the reduced Tc species by ferrous carbonate or ferrous or ferric hydroxide.

Several problems prevent further meaningful conclusions from these ferrous-pH experiments. The large dependence of pertechnetate concentration on both pe and pH as shown in equation (4), for the reaction: $\text{TcO}_4^- + 4\text{H}^+ + 3\text{e}^- \leftrightarrow \text{TcO}_2 + 2\text{H}_2\text{O}$,

$$\log [\text{TcO}_4^-] = 4 \text{ pH} + 3 \text{ pe} - \log K^\circ \quad (4)$$

requires very precise measurements of concentration, pe, and pH. Some of the ferrous ion concentrations (which presumably affect pe) used in (Francis and Bondietti 1980) experiments are below the minimum concentration needed to reliably measure oxidation potentials with the platinum electrode (Stumm and Morgan 1970). Mixed oxidation potentials result from contributions of several reactions. Unless the system is well-poised (i.e., buffered), Eh measurements may drift. Furthermore, there is the problem of coating the platinum electrode surface with material from the basalt suspension. This can result in differences between the local measured potential and the actual bulk potential. Finally, the controlled Eh-pH stirred cells were never shown to be controlled. No dissolved oxygen concentration measurement was made. In fact, the (pe + pH) sum, as determined from the data given, varied over a wide range (7 to 15).

Studies (Francis and Bondietti 1980) on the desorption of technetium retained on basalt showed that TcO_4^- slowly came back into solution when air was bubbled through the reaction cell. The rate of release ($0.01 \mu\text{M}/\text{day}$) was slower than the removal of TcO_4^- from a groundwater solution in contact with basalt ($3.8 \mu\text{M}/\text{day}$).

Francis and Bondietti (1980) performed a series of measurements of TcO_4^- concentration, Fe^{2+} concentration, pH, and Eh as a function of time for

anoxic stirred reactors containing suspensions of basalt (solution/solid ratios varied from 15 to 100). After adding basalt, the pH of each suspension was adjusted until stable.

A linear regression analysis was performed on the data to find an equation relating the logarithm of the rate of change in technetium sorption with the difference between a calculated and measured potential. According to the results, the technetium sorbs [presumably as Tc(IV)] at a higher redox potential than predicted (Pourbaix 1966). There are some doubts about the conclusions, however. The $(\text{pH} + \text{pe})$ values for the reactors range from 5.7 to 17.2, indicating that the platinum electrode may not be measuring realistic redox potentials. It is likely that the surface of the platinum electrode may have been affected by the basalt in suspension. The logarithmic equation was arbitrarily chosen and was not related to kinetic properties of the chemical reactions which may be involved.

The removal of trace level amounts of $^{95\text{m}}\text{TcO}_4^-$ from solution by various minerals and chemical reagents was investigated (Strickert, Friedman and Fried et al. 1978) by batch techniques. The solutions used for each sample were made from distilled water which had been equilibrated with an excess of similar material. The solution to solid ratio varied from 2 to 5 ml/g. In general, silicates and other minerals such as apatite and anhydrite removed little technetium ($\lesssim 10\%$) while minerals containing copper or iron (e.g., bournonite, pyrite, chrysocolla, galena and tetrahedrite) removed between 50 and 100%. Using a variety of sulfides, oxides and other chemical reagents, it was shown that compounds containing multivalent metal ions in the highest oxidation state were not effective in removing of pertechnetate tracer from solution. In the specific case of copper sulfide, it was Cu_2S which removed 99+% of TcO_4^- while CuS removed only a few percent. CdS , HgS , and ZnS removed less than 10% of the pertechnetate; FeS removed 99+%. Apparently the sulfide has little effect in any reduction which may occur, although the sulfide could be the (or one of the) insoluble Tc compounds formed after reduction. Iron and lead granules also removed large fractions (99+ and 80%, respectively) of the pertechnetate in solution. The experiments were carried out under atmospheric

conditions; however, due to the small solution to solid ratio and the fact that the vials were sealed during the sorption time with little air in the vial, the redox potential of the solution was probably dependent on the material used rather than the O_2 present in the lab. No Eh readings were taken of the solutions prior to the addition of tracers or during the sorption experiment.

In column flow experiments with crushed material (Strickert et al. 1978) an initial, small Tc peak within the first few free column volumes was the only major contribution to the eluted activity for copper-bearing minerals. Despite a range of sorption values for different minerals, no delayed peak (typical of an ion-exchange process) was observed, even with poorly sorbing materials.

The mechanism which is responsible for Tc retention was associated with the mineral surface itself rather than colloidal material suspended in rock-equilibrated solutions. This was concluded from batch experiments (Strickert et al. 1978) in which low Tc sorbing material was added to solutions equilibrated with high sorbing material prior to the addition of the pertechnetate tracer. No significant removal of Tc from the solution occurred. Using a saturated salt solution, the removal of the pertechnetate ion from solution was only slightly less than in the lower ionic strength rock-equilibrated groundwaters. This is another indication that ion-exchange is not a significant retention mechanism of Tc, because a more dramatic decrease in the removal of Tc sorption from saturated brine solutions would have been expected.

Allard et al. (1979) investigated the batch sorption of technetium on various minerals and rocks including granite, biotite, pyrite, and magnetite. No pH or Eh values were reported. After contact times of around 24 hr, they observed sorption ($K_d \sim 50$ ml/g) with granitic material in contact with deaerated solution. The solution was deaerated by adding Fe(II). An aerated solution contacting granite produced a low K_d value (<1 ml/g) for technetium. The other minerals had K_d values of 1 to 6 ml/g; however, this could also be due to excess Fe(II) in solution and not Fe(II) present in the mineral. The exact form of the sorbed Tc was not determined. It was speculated (Allard et al. 1979) that TcO_2 or $TcO(OH)_2$ may be present, or that Tc(IV) was

sorbed onto the rock after being reduced in solution. The qualitative nature of these experiments should be investigated in more detail to determine the particular mechanisms which may be involved.

Using stirred cells which were continuously purged with deoxygenated (<1 ppm O_2) nitrogen, technetium-99 sorption was studied using basalt, granite and some shales (Bondiotti and Francis 1979). Eh and pH measurements of the different rock suspensions indicated that the igneous rock suspensions (solution/solid ratio ~ 6) ($pe + pH \approx 7$) should reduce TcO_4^- to TcO_2 while the shale suspensions (solution/solid ratio ≈ 15) ($pe + pH \approx 10$) should not. In the batch experiments, the igneous rocks did remove 99% of the ^{99}Tc (initially TcO_4^- , 0.11 μM) from solution; weathered shale removed ^{99}Tc at a slow but measurable rate. It was suggested (Bondiotti and Francis 1979) that anionic sorption by iron sesquioxides may be the mechanism for such removal by shale. Unweathered shales did not remove any ^{99}Tc from solution. When basalt was pretreated with $NaOCl$ (to oxidize the iron) before the sorption experiment, no technetium was removed from solution. The rock-sorbed technetium was not removed by a solution of 2 M $NaCl$. However, by adding bromate solution, a good oxidizing agent, TcO_4^- was regenerated and released from the rock. In column flow experiments using fractured basalt and unsaturated flow conditions, technetium desorption was also studied. Again, Tc was not released by leaching with 2 M $NaCl$ but was partially removed by a bromate (oxidizing) solution.

The apparent reduction of TcO_4^- by the various rocks also occurred under anoxic conditions when $^{95m}TcO_4^-$ was used at concentrations of 10^{-11} M. However, under normal atmospheric conditions no significant $^{95m}TcO_4^-$ was reduced.

Technetium sorbed on small columns of crushed basalt was not removed by simulated groundwater solutions (Francis and Bondiotti 1980) under oxic conditions. A 5% hydrogen peroxide solution rinse resulted in elution of technetium from the column. Although the most likely oxidation state for the sorbed Tc is Tc(IV) it is not known whether the actual bound species is TcO_2 or $TcO(OH)_2$.

Using the measured ^{95m}Tc concentration ($2.4 \times 10^{-13} \text{ M}$) of a solution in contact with an anoxic crushed basalt column, it was calculated (Francis and Bondietti 1980), based on thermodynamic data (Pourbaix 1966), that the Eh value corresponding to a TcO_2 solubility of this concentration should be around -0.160 V . This is lower than the approximately 0.1 V measured in a stirred cell system (Bondietti and Francis 1979). Use of a different radioactive tracer which is not isotopically pure may contribute to an error in the calculated concentration.

Attempts (Francis and Bondietti 1980) to investigate the temperature and time dependence of the Tc removal were inconclusive. Sorption at 72°C and at 22°C was higher than at 0°C , but large variations in sorption at the first two temperatures make interpretation impossible. K_d values (ml/g) after 7 days were 106 ± 31 at 72°C , 312 ± 403 at 22°C , and 2.0 ± 1.7 at 0°C . It was felt that better control of possible oxygen contamination was needed in order to adequately measure temperature effects.

Relyea and Washburne (1979) compared the technetium sorption behavior of kaolinite, montmorillonite, and vermiculite from various salt concentrations, under anoxic conditions and with or without a hydrogen peroxide pretreatment of the solids. The H_2O_2 pretreatment resulted in a decrease in sorption of Tc by the three clays although no significant differences in pH or pe were apparent between the treated and untreated clay suspensions. It is possible that the clay suspensions reacted with the Pt electrode to mask the true bulk redox potential. Similar experiments with Sr-85 showed no effect of H_2O_2 pretreatment and the Sr-85 sorption behavior was that expected from ion-exchange theory.

TECHNETIUM SUMMARY

The relationship of oxidation state and sorption behavior is perhaps more clearly understood for technetium than for the multivalent actinides. The pertechnetate ion is the stable ionic species under oxic conditions and has only a very small anion exchange behavior with various rocks or minerals. The pertechnetate ion is capable of being reduced to Tc(IV) by ferrous iron present

in geologic media. The Tc(IV) species either forms a highly insoluble species or coprecipitates with iron hydroxide or some other compound. Because Tc(IV) sorption was only slightly affected by a saturated salt solution, Tc(IV) apparently shows little ion exchange behavior. The reduction of Tc(VII) to the lower oxidation state can be lessened by partially destroying the ferrous concentration in the rock with a hydrogen peroxide treatment of the crushed material. Release of the bound Tc(IV) can be initiated by oxidizing the suspension with air or H_2O_2 .

Attempts to measure the redox potential at which pertechnetate reduction would occur (Bondiotti and Francis 1979; Relyea and Washburne 1979) were hampered by erratic or inconsistent Eh measurements, perhaps due to the erratic behavior of the Pt electrode. Platinum interactions with suspended material is suspected. This problem will require further study.

Two important goals for future technetium solid phase retention studies are to: 1) identify by oxidation state analysis the presence of Tc(IV) in the solid or solution phase; and 2) identify the solid phase(s) of Tc(IV) and determine the solubility limits for the Tc(IV) compound(s).

URANIUM SORPTION/DESORPTION

The thermodynamics and related chemistry of the various oxidation states of uranium in groundwater systems have been extensively reviewed (Ames and Rai 1978; Rai and Serne 1978; Langmuir 1978; Onishi et al. 1979). U(IV) and U(VI) are the stable states in solution. Hydrolysis and complexation are important and can result in anionic species of uranium.

Under oxidizing conditions, UO_2^{++} is the controlling species, though in the presence of carbonates or phosphates $\text{UO}_2(\text{HPO}_4)_2^=$, UO_2CO_3 , or $\text{UO}_2(\text{CO}_3)_2^=$ may form in neutral or near-neutral solutions. Uranium fluoride complexes may also form. The solubility of uranium is typically 10^{-8} M or greater depending upon the degree of complexation (Langmuir 1978).

Under reducing conditions, USiO_4 (Coffinite) and UO_2 (uraninite) are predicted to be the stable solids. At pH 4-7 the solubilities of these minerals are $<10^{-12}$ M (Langmuir 1978). Phosphate or carbonate complexes may increase solubility by several orders of magnitude. At the lower Eh values, UO_2^+ may also exist as a solution species.

EXPERIMENTAL STUDIES

A number of recent studies have looked at the sorption/desorption behavior of uranium on various geologic media.

The migration (and leachability) of uranium isotopes depends upon the oxidation state of the uranium. Kobashi et al. (1979) looked at the radioactive disequilibrium of uranium isotopes in a naturally occurring mineral, euxenite. ^{238}U decays through two short-lived daughters to form ^{234}U . Examining the $^{234}\text{U}/^{238}\text{U}$ ratios as a function of valence state showed that, for the euxenite mineral, the ratio was greater for the tetravalent state than for the hexavalent state. However, in leaching studies the $^{234}\text{U}/^{238}\text{U}$ ratio was similar to the ratio for the hexavalent state. Using the experimental data given, it can be calculated the U(VI) is preferentially leached three times more than U(IV). These studies were performed under atmospheric conditions.

The sorption behavior of uranium [presumably as the (VI) state] on argillite under oxic conditions has been measured (Erdal et al. 1980) for different particle sizes and sorption times at ambient temperature. For particle sizes greater than 106 μm , K_d values range from 1 ml/g to 7 ml/g. No significant increases in sorption were noticed between sorption times of 6 days and 21 days. For the argillite particle fraction less than 75 μm , sorption K_d values ranged from about 15 ml/g to 100 ml/g. Complexing with the carbonate found in argillite groundwater is expected for the uranium (VI); this would tend to reduce sorption. The higher sorption values reported for the smaller particle size material are probably due to the increased number of exchange sites (increased surface area) per gram of material. It was not stated whether a metal grinder was used to grind the argillite to less than 75 μm . Metal flakes from the grinder could reduce U(VI) in solution.

Culebra dolomite and Magenta gypsum were used in batch sorption-desorption experiments of $^{237}\text{U(VI)}$ (Francis and Bondietti 1980). Under oxic conditions, the $^{237}\text{U(VI)}$ K_d values were 2.4 ml/g and 14 ml/g for the gypsum and dolomite, respectively. Sorption and desorption values were essentially the same and the valence state was stable. The low K_d values compared to the corresponding Np(V) values were attributed to stronger carbonate complexes for U(VI).

Anoxic sorption measurements with $^{236,237}\text{U}$ were made using granite and argillite materials (Erdal et al. 1980). The uranium tracer solution was dried before being put into the anoxic chamber. Over a period of 20 days contact time, uranium K_d values were around 1 ml/g for the granite samples and around 7 ml/g for the argillite fractions. No apparent reducing potentials exist in these materials to change uranium to U(IV). The effect of the anoxic chamber on carbonate concentration in the argillite samples was not discussed. No reports of measurements of redox potentials have been made in these studies.

The batch sorption of uranium on granite under oxic and anoxic condition was studied (Francis and Bondietti 1980). At 72°C under anoxic conditions the average uranium K_d value was 32 ± 13 ml/g, while under oxic conditions the average uranium K_d value was 7 ± 5 ml/g. The data appeared to suggest that some U(VI) is reduced to U(IV) under anoxic conditions. However, because of

the N_2 purging of groundwater, a reduction in dissolved CO_2 may have affected $CO_3^{=}$ complexation of U(VI). The pH of the groundwater solution was raised from 8.0 to 9.1 in 20 hr of N_2 purging. Desorption under oxic conditions after 5 days gave average Kd values of 22 ml/g and 28 ml/g for the two sets of granite material, anoxic and oxic, respectively, used in the earlier sorption work.

The sorption of uranium by salt dome materials was investigated by Erdal et al. (1980). Two different mixtures of material (referred to as 'aquifer' material and 'aquitard' material)^(a) were used along with two different groundwater compositions, one representing the Wilcox aquifer (1,260 ppm $NaHCO_3$ and 7 ppm $CaSO_4$) and the other representing a brine (containing 10,000 ppm NaCl and 7 ppm $CaSO_4$). Batch Kd values were determined under both oxic and anoxic [<0.2 ppm $O_2(g)$] conditions using a $^{236,237}U$ tracer at $\sim 10^{-7}$ M concentration. The tracer stock solution consisted initially of U(VI). Results (Table 7) show that Kd values are somewhat lower under anoxic conditions. One noticeable result is the much higher Kd values with brine under either oxic or anoxic conditions than with the bicarbonate groundwater. In control samples of the two uranium groundwater solutions, only 35 to 40% of the uranium was recovered from the brine solution under anoxic conditions, and 78 was recovered under oxic conditions; the remainder apparently was sorbed onto the container walls. The bicarbonate solution retained essentially all of the uranium in the control samples.

URANIUM SUMMARY

Sorption behavior of uranium involves the U(VI) and U(IV) oxidation states. U(VI) is more soluble especially when complexed with the carbonate ion. This results in lower Kd values, due to the formation of the anionic soluble carbonate complex of uranium.

(a) The aquifer material was a 50/50 mixture of the Calvert Bluff and Carrizo strata from the Hainesville salt dome area in East Texas; the aquitard sample was a 50/50 mixture of Hooper and Simsboro materials. Preliminary mineralogy indicated that both mixtures were mainly quartz with minor amounts of secondary clays.

TABLE 7. Average pH and Uranium Kd Values for Hainesville Salt Dome Materials and Simulated Groundwater Under Oxidic and Anoxic Conditions

<u>Solid</u>	<u>Ground Water</u>	<u>Oxidic pH</u>	<u>Anoxic pH</u>	<u>Average Kd (ml/g)(a)</u>	
				<u>Oxidic</u>	<u>Anoxic</u>
Aquifer	Wilcox	8	9	118 (29)	7.2 (22)
Aquitard	Wilcox	9	9	3.34 (43)	1.44 (92)
Aquifer	Brine	8	6	9200 (8.3)	5730 (10)
Aquitard	Brine	7	4	577 (4.4)	237 (6.4)

(a) Value in parentheses is the percent error from the standard deviation of the mean for three replicate measurements.

Carbon dioxide concentrations in anoxic chambers are often much lower than in the atmosphere. This may lead to a decrease in the concentration of the U(VI) carbonate complexes, or an increase in pH, and contribute to an increase in U(VI) sorption under anoxic conditions. These mechanisms should be explored further.

Reduction of U(VI) to U(IV) under anoxic conditions results in an increase in uranium retention on geologic materials. This retention may be primarily due to the extremely low solubility (10^{-12} M) of uranium under reducing conditions. The U(IV) solid phase species is not known and will need to be identified. Dissolution behavior should also be investigated. Such studies will probably require uranium isotopes of high specific activity (e.g., ^{230}U , ^{232}U) in order to measure uranium at the expected low concentrations.

As with other multivalent elements, oxidation state analysis and Eh and pH measurements should be conducted for uranium sorption/desorption studies.

CONCLUSIONS

The redox-sensitive elements (Tc, U, Np, Pu) discussed in this report are of interest to nuclear waste management due to their long-lived isotopes which have a potential radiotoxic effect on man. Long-term geologic isolation is a suitable means of preventing migration of these isotopes to the biosphere. One of the most important barriers for effective isolation is the sorption of any migrating radioactive species by geologic materials present between the repository and the biosphere. In their lower oxidation states the redox-sensitive elements in this report have been shown to be highly retained by geologic materials under anoxic or reducing conditions.

A complete understanding of the mechanisms responsible for the retention of these multivalent elements does not yet exist; however, experimental research conducted in recent years, especially through the WISAP and WRIT programs, has provided extensive information toward such an understanding. In general, ion-exchange probably plays a minor role in the sorption behavior of cations of the three actinide elements. Formation of anionic complexes of the oxidized states reduces ion exchange further. Pertechnetate also exhibits little ion-exchange sorption.

Plutonium appears to be removed readily from neutral or near neutral solutions even under oxic conditions. This may be due to either exceeding the solubility limit in solution or to some surface reduction process. Under similar conditions, Np(V) is the dominant oxidation state in solution with a solubility in the range of 10^{-5} M. NpO_2^+ is not highly adsorbed. Uranium [as U(VI)] can readily form anionic complexes with phosphate or carbonate which are not retarded by geologic media. Oxidizing conditions result in technetium forming highly soluble TcO_4^- which migrates with the groundwater.

In the reduced (IV) state, all four of the elements are highly charged and it appears that they form very insoluble compounds (oxide, hydroxide, etc.) or undergo coprecipitation or mineral incorporation. The exact nature of the insoluble compounds and the effect of temperature, pH, pe, other chemical species, and other parameters are now being determined.

Oxidation states other than Tc(IV,VII), U(IV,VI), Np(IV,V), and Pu(IV,V) are probably not as important for the geologic environments expected, but should be considered especially when extreme conditions exist (radiation, temperature, etc.).

Under any specific groundwater conditions, it is paramount that the solubility limits of the radioactive species be determined, preferably experimentally; past thermodynamic data have been shown to be erratic especially for very insoluble actinide compounds. In some cases, solubility limits may fall below maximum permissible concentrations (MPC). When the solubility exceeds the MPC, other sorption mechanisms (ion exchange, mineral replacement, etc.) will need to be studied to measure their retardation effects. In addition, experimentally determined stability constants are needed for various actinide complexes which may exist under geologic conditions.

It is doubtful, however, that all possible groundwater scenarios could be measured or even duplicated. For this reason, it is particularly vital that the reaction mechanisms and chemical species are clearly understood and that thermodynamic measurements are accurately determined in those groundwaters which are examined. Such knowledge would then allow the concentrations in other groundwaters to be estimated.

Various experimental techniques such as oxidation-state analysis of tracer-level isotopes, redox potential measurement and control, understanding of radiolysis effects, and solid phase identification are being developed to fit the specific conditions of a geochemical system.

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Sandia Laboratories
Division 4512
Albuquerque, NM 87185

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Office of Nuclear Waste
Isolation
Battelle Memorial Institute
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Department of Energy
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