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LETTER REPORT

TITLE: Plutonium Chemistry and Migration Behavior in High-Level Waste Repository Environments

AUTHORS: J. C. Mailen and J. T. Bell

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PROJECT MANAGER: G. K. Jacobs

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SUMMARY AND RECOMMENDATIONS

The chemistry of plutonium and its effect on the migration behavior of plutonium in geologic repositories has been surveyed. As a part of this survey, the experimental approaches being used to estimate the migration of plutonium in geologic repositories have been evaluated.

Several major questions need consideration and, if possible, a general scientific consensus regarding the current studies of plutonium behavior in geologic repositories. The major question is, "Are the experimental studies answering the proper questions?" In order to predict the migration of plutonium within the repository, the solubility of plutonium in the geologic system and the behavior of colloids and pseudocolloids under realistic conditions must be known. The solubility of plutonium appears to be the simplest of these variables to measure, but what the investigators mean by "solubility" is not well defined. In virtually all cases the plutonium in solution is measured in such a way as to include colloidal material. This presents difficulties in obtaining reproducible measurements of solubilities and behavior when in contact with minerals. It would be better if the soluble plutonium was limited to the monomeric and small agglomerated species (trimeric and tetrameric hydrolyzed plutonium, for instance) in solution; the behavior of these species should be more predictable in both dissolution and sorption. The behavior of colloids and pseudocolloids could then be studied separately. However, studies such as these are extremely difficult and it may be impossible to realistically duplicate the solutions, colloids, and pseudocolloids which will form in the real system. One is then left with the option of trying to duplicate the repository system, as nearly as possible, in any experiment. This would require using a closely simulated waste form, groundwater, and repository minerals. The entire system would have to be coupled together so that dissolved plutonium would circulate over the minerals. Aqueous flow rates and any periods of drying (in the case of the Yucca Mountain system) should be simulated as nearly as possible. The aqueous flow rates may be so slow that they cannot be simulated in realistic experimental times. If so, several aqueous flow rates should be

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examined and the results extrapolated to the expected repository flow rates. The effects of temperature, atmosphere, and radiation should be examined or simulated. Some efforts are currently underway using this approach [SEITZ (1984)] [SCHRAMKE (1984)] [WILSON (1985)].

The described ideal experiments appear to be very difficult and time consuming. Is it really necessary to perform such difficult experiments? This brief assessment cannot answer that question, but it seems to these reviewers that the current, less complicated experiments are failing to lay all the questions to rest. It may be argued that, even though the current data are not completely correct for a repository, it represents a worst case. This is likely the case for colloidal material since, at the lower flow rates in a repository, the colloids would have more opportunity to deposit on surfaces. The argument for a worst case for all the plutonium species is not simple.

A clear plan needs to be formulated to address the questions regarding plutonium behavior in a geologic repository. If new experiments or a continuation of the current studies are to be undertaken, there should be general agreement among experts in the area as to the questions to be answered and the approaches which will be fruitful. An important area is the application of realistic models to the repository to define "how low is low enough." It may be that the current data can be used to show that plutonium migration is or is not a serious problem. It may be that plutonium chemistry in the aqueous phase is not important if the leach rates from waste forms and transport of groundwater to the accessible environment are low enough. It also appears that information may be available from cases in which plutonium has been released to the environment; models of plutonium migration should adequately explain these observations. Of particular interest would be the behavior of plutonium at Oklo [BROOKINS (1976)], at the Rocky Flats plant, at Hanford Engineering Development Laboratory, and at underground nuclear testing sites. Of course, the geological variables at these sites are not the same as those for the geologic repositories, but any realistic model should be capable of reasonable agreement with these relatively (to laboratory experiments) long-term experiences of plutonium migration.

The chemical conditions in a repository rock/groundwater system are complex and difficult to duplicate in experiments, making it questionable whether all aspects of plutonium migration behavior over geologic time scales can be predicted from basic laboratory experiments alone. Such experiments, however, can be useful in defining the mechanisms of important chemical interactions and in determining limiting constants. Agreement among investigators, modelers and those responsible for evaluation of the overall system is needed in order to establish accepted experimental methodology for plutonium migration prediction. If knowledge of the chemical behavior of plutonium is essential for satisfactory prediction of repository performance it may be necessary to investigate its chemical behavior in integrated rock/groundwater systems which attempt to duplicate the expected repository environment to the greatest possible degree.

1.0 PLUTONIUM CHEMISTRY AND MIGRATION BEHAVIOR IN HIGH-LEVEL WASTE GEOLOGIC REPOSITORY ENVIRONMENTS

This report is a survey of the experimental techniques being used and data which have been obtained regarding the migration behavior of plutonium in geologic repositories proposed in basalt or tuff. The chemistry relevant to the behavior of plutonium in such repositories is summarized and the important factors in simulation of plutonium migration behavior will be discussed. Results obtained by various investigators will be summarized with recommendations for additional work.

The operation of commercial light water reactors (LWRs) generates spent fuel consisting of uranium oxide (UO_2) with bred plutonium oxide (PuO_2) plus fission products. The fuel is contained in Zircaloy tubes and is currently stored under water at the reactor sites. Options for its future handling include reprocessing to recover and recycle the uranium and plutonium, and direct disposal of the spent fuel. If the fuel is reprocessed, the fission products and small fractions of the uranium and plutonium will be incorporated into a low-solubility waste form for disposal; the current indications are that this waste form will be a glass matrix. The waste material will be encapsulated in metal canisters and stored in a deep geologic waste repository. [CRWMP (1985)(b)]

The quantities of material to be handled depend on the future development of the nuclear industry in the U.S.; estimates of spent fuel discharged from commercial reactors range from 48,000 to 427,000 metric tons of heavy metal (MTHM) by the year 2040 [DOE/EIS (1980)]. LWRs typically operate with a burnup of ~30,000 MWD/MTHM and, at discharge, the UO_2 fuel contains ~1wt% plutonium [CAMPBELL (1981)]. Thus, the plutonium content of the spent fuel in 2040 A.D. may be between ~500 and 4300 metric tons. Additional waste material from reprocessing of military fuels will need storage; this material likely will be in the form of glass.

The plutonium isotopes in reactor fuel include those of atomic weights between 238 and 242. Their long-term hazard results from the long half-lives of the 239 (24,360 y), 240 (6580 y) and 242 ($\sim 5 \times 10^5$ y) isotopes. Plutonium is a heavy-metal poison and can, if ingested, concentrate in the bones. Inhalation is a particular hazard with deposition of particles of plutonia in the lung tissue leading to severe local damage and the potential for producing lung cancer.

The proposed repository in basalt at the Hanford Site (Basalt Waste Isolation Project; BWIP) would store waste in basalt beds. These beds were laid down 17 to 6 million years ago and extend to more than 10,000 feet in depth. These beds underlie portions of three states and are the second largest basalt formation in the world. The candidate repository location is between ~2500 feet and 3700 feet below the surface in the Grande Ronde Basalt formation [CRWMP (1985a)].

The proposed storage site in tuff is beneath Yucca Mountain in Nye County, Nevada. Yucca Mountain is located adjacent to the south-western boundary of the Nevada Test Site ~100 miles northwest of Las Vegas. The mountain is a long narrow ridge generally running north and south with a steep western slope and a gentler eastern slope. The underlying strata are inclined at three to eight degrees to the east. The ridge stands from about 1000 to 1200 feet above the surrounding alluvial flats. Characteristics that make Yucca Mountain attractive for waste storage include the thick deposits of highly sorptive tuff, the deep static water table which is more than 1700 feet below the land surface and the low average rainfall of ~5 inches per year. The stratigraphic horizon under study is a densely welded unit of the Topopah Spring tuff about 1200 feet below the land surface and about 550 feet above the static water table [CRWMP (1985b)].

2.0 CHEMISTRY OF PLUTONIUM

2.1 Oxidation States

Excellent reviews of plutonium chemistry are given by [WICK (1980)], [CLEVELAND (1980)], AND [KELLER (1971)]. Plutonium is highly unusual in being able to simultaneously exist in four oxidation states, from (III) to (VI), in aqueous solutions. This behavior is unique to plutonium of all the elements of the periodic table and is allowed by the tendency of Pu^{4+} and Pu^{5+} to disproportionate coupled with the relatively slow rates of subsequent reactions which require rupture of the plutonium-oxygen bonds of the PuO_2^{2+} and PuO_2^+ ions.

Pu(IV) disproportionates to yield Pu(III) and Pu(VI) ;



The equilibrium constant for this reaction at 25°C in acid perchlorate solutions of unit ionic strength (0.2 to 1.0 M H^+ , 1.0 M ClO_4^-) is given by:

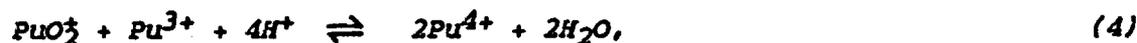
$$K = [\text{Pu(III)}]^2[\text{Pu(VI)}][\text{H}^+]^4/[\text{Pu}^{4+}]^3 = 0.0089, \quad (2)$$

where the terms in square brackets are molar concentrations. The value of the equilibrium constant is quite temperature sensitive and is strongly influenced by complexing which stabilizes the Pu^{4+} state.

Pu(V) can disproportionate according to the overall reaction;



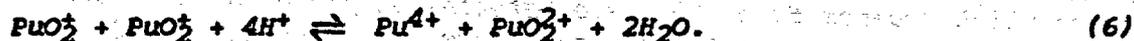
The actual mechanism requires reaction with Pu(III) ;



with Pu(IV) ;



or with Pu(V);



The rate of disproportionation of Pu(V) is proportional to the hydrogen ion concentration, and in very low acid concentrations, in the absence of Pu(III) and Pu(IV), Pu(V) is quite stable.

The equilibrium ratios of the various plutonium oxidation states are controlled by Eq. 5. The rate of reaction has been shown to be first order with respect to each reactant;

$$-d[\text{Pu}^{4+}]/dt = -d[\text{PuO}_2^+]/dt = k_1[\text{Pu}^{4+}][\text{PuO}_2^+] - k_2[\text{Pu}^{3+}][\text{PuO}_2^{2+}]. \quad (7)$$

The value of the first rate constant decreases slowly with decreasing acidity and that of the second rate constant remains constant. At the very low expected concentrations ($<10^{-6}$ M) of these ions in groundwater the rates of reaction predicted by Eq. 7 would be small but should require times only on the order of hours to attain equilibrium. However, adsorption of the various species on surfaces could retard the approach to equilibrium.

The various methods which can be used to determine the oxidation state of plutonium in solution are listed below with the lowest concentrations for which they are applicable [KIM (1982a)]:

- Optical spectrometry: $> 10^{-6}$ M
- Polarography: $> 10^{-6}$ M
- Laser induced spectrophotometry: $> 10^{-8}$ M
- Solvent extraction: unlimited
- Coprecipitation: unlimited

Solvent extraction and coprecipitation are listed above as having no lower limit of applicability (other than counting sensitivity). Unfortunately, the speciations determined by these two techniques are open to doubt. Separation of the extractable or precipitateable species may shift the equilibrium among the species leading to erroneous results. Foreign ions present in the groundwater may interfere with the extraction; examples are sulfate and fluoride which form strong complexes with Pu(IV) and will retard its extraction. Precipitations may remove polymeric species and colloids by adsorption on the precipitate. Thus, completely satisfactory methods for determining speciation of plutonium in groundwater solutions at concentrations of importance to repository assessments are not available.

2.2 Reduction/Oxidation by Radiation

The primary effect of gamma radiation and the portion of the alpha radiation which escapes from the waste material on plutonium chemistry will be redox products of radiation-induced reactions of the local aqueous environment. Such radiation products can react with plutonium to change the usually-expected plutonium chemistry.

Free radicals produced by the radiolysis of water include powerful reductants such as $e^-(aq)$ and powerful oxidants such as OH [SULLIVAN (1983)]. Interactions of plutonium with these species may include catalysis of the initial dissolution of the oxide and oxidation/reduction of species in solution or adsorbed on surfaces. Additionally, in the presence of nitrogen, radiolysis can produce nitric acid and change the pH of the groundwater [RAI (1980a)]. The degree of change of the groundwater pH depends on the content of buffering species; significant decreases in pH could increase the dissolution rate of oxide and the solubility of plutonium in the groundwater. Alpha radiolysis also contributes to a decrease in the crystallinity of PuO_2 by causing the dissolution of the plutonium followed by rapid reprecipitation of amorphous material [RAI (1981a)].

2.3 Hydrolysis and polymerization

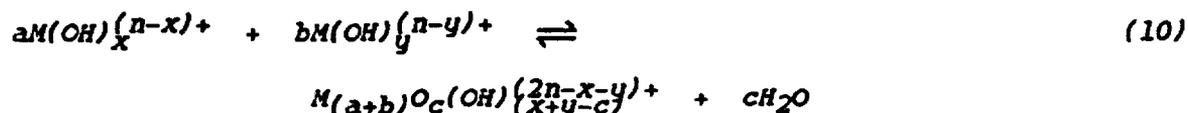
Metal cations in low acidity aqueous solutions react with water to form acid and hydrolyzed metal species (Eq. 8).



The extent to which such hydrolysis reactions will occur depends primarily on pH, temperature, complexing anions and hydrolysis species interactions. Parameters of lesser importance include ionic radius of the metal ion, ionic strength and pressure. The equilibrium constant for equation 8 is generally called the hydrolysis constant. Multivalent metal cations may react with more than one water molecule per cation, equations 8 and 9.



The number of water molecules that can react with a metal is generally limited to the oxidation state of the non-complexed metal cation. Thus a trivalent or tetravalent cation could react with 3 or 4 water molecules, respectively, and when no other reactions occur the cations would have 3 or 4 hydrolysis constants, respectively. However, hydrolysis chemistry is not so simple. Partially hydrolyzed multivalent cations can interact to form dimers, trimers, and on to polymer species (Eq. 10).



This general hydrolysis equation applies to the hydrolysis of all metal cations, and also applies to oxymetal cations such as $VO(2+)$ and $UO_2(2+)$. Polymeric metal hydrolysis species can be further stabilized by aging or by elevated temperature. This aging was first described by [THOMAS (1963)] as an intramolecular reaction to form water and to change hydroxyl-bridging bonds into oxo-bridging bonds (Eq. 11).



Hence, hydrolysis of metal cations is the first part of the progression of aqueous cations to hydroxides and polymers and metal oxides.

Aqueous plutonium chemistry includes four oxidation states (III, IV, V, and VI). The (IV) and (VI) states are the generally stable states in macro-systems. The (III) state is stable only in systems that are chemically reducing or have redox potentials less than 0.98v. The (V) state is generally unstable and may disproportionate according to Eqs. (3 to 6) [CLEVELAND (1970)]. Conditions that favor stability of the (V) state include high concentrations of the (VI) and (IV) states to reverse the disproportionation reaction, high concentrations of (VI) and (III) to reverse the reaction of (V) and (IV), and systems with very low concentrations of total plutonium and acid.

The first hydrolysis constants for the four non-complexed aqueous plutonium states are 5×10^{-2} , 5×10^{-5} , 7×10^{-8} and 2×10^{-10} for Pu(IV), (VI), (III), and (V), respectively [CLEVELAND (1970)]. The magnitude of these values suggest that hydrolysis of Pu(IV) can significantly affect plutonium chemistry in a system with pH of zero, with increasing effects at higher pH. Hydrolysis of Pu(VI) can be important at a pH of 2 with increasing effects at higher pH. Hydrolysis of Pu(III) can be significant at a pH of 6 or higher, and hydrolysis of Pu(V) occurs only for pH >7.

The second stage hydrolysis of plutonium cations occurs at corresponding higher pH values. These constants for Pu(IV), (VI), and (III) indicate that second stage hydrolysis becomes significant at respective pH values of 1, 4, and 6. The most significant hydrolysis reactions after the first stage hydrolysis is formation of a Pu(IV) polymer. The equilibrium constant for the second stage Pu(IV) hydrolysis has been difficult to determine because polymeric Pu(IV) begins to form concurrently with the second stage hydrolysis [BELL (1973)]. The Pu(VI) and (III) second stage hydrolysis also leads to dimer and trimer species, but not to stable polymeric materials.

The Pu(IV) polymer is formed by nucleation of the hydrolysis products. Plutonium (IV) at macroconcentrations in low acid will disproportionate reversibly to form Pu(III), (V) and (VI) before hydrolysis and

polymerization begin [BELL (1973)]. Therefore, the kinetics of the Pu(IV) polymer formation can depend on the concentrations of the other oxidation states as well as that of the (IV) state and the acid.

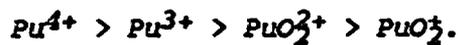
The polymerization rate for 0.009 M Pu in HNO₃ was determined to be first power dependent on the Pu(IV) concentration. However, studies with higher concentrations of plutonium, 0.05 M, indicate that the polymerization kinetics were 1.5 power dependent on the Pu(IV) concentration when the initial polymerization was observed and the Pu(IV) concentration was the same as the total concentration of Pu [TOTH (1980)]. It would be presumptuous and probably erroneous to extrapolate the known polymerization rate data to concentrations less than 1 x 10⁻⁶ M.

An induction period preceding observable polymerization was also reported by [TOTH (1980)]. That induction period is explained as the time that initial hydrolysis species interact and nucleate into small prepolymer units. The kinetics for formation of the prepolymer units cannot be determined. However, one can assume that the rates of formation during the induction period would depend on the Pu(IV) concentration to the second or greater power. This leads us to conclude that Pu(IV) at concentrations less than 1 x 10⁻⁶ M in low acid solutions would exhibit very long polymer induction times. And at concentrations less than 1 x 10⁻⁸ M the stable Pu(IV) polymer species probably would never form, and the hydrolysis species would adsorb onto contaminants.

2.4 Inorganic Complexes

Interactions of plutonium with complexing agents can be very intricate in the groundwater/rock environment; such agents may sorb on mineral surfaces where they can then sorb plutonium in addition to direct complexation in the aqueous phase. This section will discuss the aqueous chemistry of plutonium with complexing agents and the possible complications in the groundwater/rock environment.

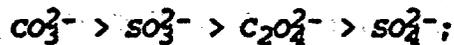
Tetravalent plutonium ions form complexes readily due to their small size and high charge. The order of decreasing complex-forming ability of plutonium ions is:



Formation of complexes by Pu(IV) tends to stabilize and solubilize this species when proper anions are available in the groundwater. Among monovalent inorganic anions the order of decreasing strength of complexes with Pu(IV) is:



Among divalent inorganic anions the order of decreasing strength of complexes with Pu(IV) is:



the complexes with the divalent anions are stronger than those with the monovalent anions. Another inorganic anion, present at low concentrations in some groundwaters and which forms complexes with Pu(IV), is phosphate.

Fluoride is present in the groundwaters associated with basalt and tuff to levels of up to ~30 mg/L [KELMERS (1984)] and about 1.0-2.3 mg/L [REES (1984)], respectively. Fluoride forms strong mono- and di-fluoro complexes with Pu(IV); their overall stability constants are $\sim 10^8$ and 10^{14} , respectively [CLEVELAND (1979)]. The effect of fluoride is generally to promote the formation of Pu(IV) and to increase the solubility of the plutonium [CLEVELAND (1983a)]; fluoride at the levels in the groundwaters could complex a significant fraction of the plutonium. These effects depend, however, on the "free fluoride"; that fluoride not associated with other cations and available to form complexes with plutonium. For instance, the divalent ions such as Ca(II) and Mg(II) compete for fluoride ions and the fluoride may sorb on the surface of minerals. Complexes of Pu(IV) with chloride are too weak and the chloride concentrations too low to influence the plutonium chemistry in the groundwaters being considered here. The association constant for the Pu(IV) monosulfate complex is about 3×10^2 [WICK (1980) p 447]. Sulfate concentrations in groundwaters associated with tuff and basalt can range from a few to ~200 mg/L [KELMERS (1984)] [CLEVELAND (1979)]. At the 100 mg/L level of sulfate up to ~30% of the plutonium could be present as sulfate complexes. Again, other cations and sorption on minerals may compete for sulfate. Phosphate is known to form complexes with Pu(IV), but their stoichiometry and significance in near-neutral solutions have not been defined. The low concentrations of phosphate in groundwaters (<0.1 mg/L) [CLEVELAND (1983a)] make the significance of phosphate complexing with Pu(IV) low. Carbonate complexes are known to increase the solubility of plutonium hydroxide [WICK (1980) p 450]. Few values for complexation constants of plutonium with carbonate ions exist [LEMIRE (1980)] [KIM (1983a)] and significant doubt exists concerning their validity [RAI (1985)]. RAI (1985) indicates that the best value for the stability constant of PuCO_3^+ is about 1×10^{12} . This value indicates that formation of carbonate complexes in groundwater, which can contain ~60 mg/L of carbonate (~0.001 M) [KELMERS (1984)] can be significant.

2.5 Organic Complexes

Organic compounds are commonly present in natural groundwaters from the biodegradation of plant and animal matter and from methane dissolved in Hanford groundwater. The resulting compounds are called humic substances and are subdivided, by solubility, into other sub-classes. For instance, humic acid is soluble in alkali but not in acid, and fulvic acid is soluble in both alkali and acid. Further subdivision is possible, but will not be considered here. The various classes of humic substances differ mainly in molecular weight and in degree of

oxidation. Humic substances vary greatly in composition depending on the initial source material but they generally contain phenolic, carboxylic acid and hydroxyl groups which result in significant ability to complex metal ions. The humic substances from the 3,690-3,720 foot interval within research well DC-6 (Grande Ronde Formation of the Columbia River Basalt Group) at Hanford, Washington have been characterized [MEANS (1982a)]. The total dissolved organic content (DOC) content of the groundwater was found to be 0.3 ppm; the major portion of the compounds were low-molecular-weight fulvic acids with molecular weights of ~700-1000. This data implies a concentration of humic substances in the groundwater of $<0.0004 \text{ M}$.

Actinides form complexes with humic and fulvic acids whose strengths are comparable with those of the hydroxide and carbonate complexes [OLOFSSON (1983)]. Thus, it is expected that humic substances can have a significant effect on the behavior of plutonium in groundwater. Studies of the solubility of plutonium as a function of pH in the presence and absence of humic and fulvic acids showed significantly greater solubility of plutonium in the presence of the organic acids [MEANS (1982b)]. For instance, with an initial plutonium concentration of 0.54 ppm, in the absence of humic and fulvic acids at a pH of ~8 only ~3% of the plutonium remained in solution. The presence of 41.6 ppm of humic acid retained 100% of the plutonium in solution and the presence of 51.3 ppm of fulvic acid retained ~90% of the plutonium in solution. It was further observed that the precipitating plutonium, when more plutonium was present, carried a significant fraction of the humic and fulvic acids, indicating the presence of insoluble complexes [MEANS (1982b)]. Further, it is known that the presence of humic and fulvic acids in a medium affects the nucleation of crystallites, probably by adsorption on the surface of the particles [WEBER (1985)]. This behavior could affect precipitation rates and the sizes of particulate material formed.

2.6 Chemical State of Plutonium in Waste Forms

The average valence of plutonium in spent fuel depends on the equilibrium pressure of oxygen in the gas phase of the fuel pin. LWR fuel initially has a stoichiometry of $\sim \text{UO}_2.002$ [CUBICCIOTTI (1978)]. During reactor operation oxygen is freed by fission of uranium and is apportioned to the fission products and to the Zircaloy cladding. In general, the oxygen potential will be buffered by the Mo/MoO₂ couple. This couple is oxidizing enough to maintain all the plutonium as PuO₂. The PuO₂ will exist in the spent fuel as a dilute solid solution in the bulk UO₂ phase.

The grain size in fabricated reactor fuel can vary with the fabrication parameters, and the grain size will change during reactor operations. Fine-grained fuels dissolve more rapidly than coarse-grained fuels [WILSON (1985)].

If the fuel is exposed to air the thermodynamically stable oxide for uranium is UO_3 and a slow conversion from UO_2 can be expected. PuO_2 is not oxidized under these conditions. The UO_2 oxidation is not observed at room temperature in ordinary time periods, but may occur during geologic times. The oxidation results in major changes in the crystalline structure of the material and will generate a finely divided solid with a high surface area. If this should happen the leach rate of the fuel would be greatly increased.

When plutonium oxide is incorporated in glass it can react with silica to form plutonium silicate. It is known that the pure compounds can be reacted to form $PuSiO_4$ if they are heated to $\sim 1100^\circ C$ (by analogy to the preparation of $PuGeO_4$) and can possibly be prepared at lower temperatures [WICK (1980) p347]. Any unreacted plutonium would likely be present as dispersed, partly-reacted, PuO_2 particles.

2.7 Waste Form Dissolution

Reactor fuel: Actinide dioxides are normally quite insoluble in aqueous solutions. Dissolution requires either oxidation to a higher valence state, reduction to a lower valence state or formation of a strong complex with the tetravalent ion. During the dissolution of oxide fuel in a repository, with low water flow rates, a saturated thin layer of water should exist on the surface of fuel exposed to water. Additional dissolution of the fuel surface would be controlled by diffusion of the dissolved species from the saturated layer into the bulk aqueous phase. It is observed that UO_2 dissolves readily in HNO_3 , while PuO_2 is essentially insoluble; this results from the ability of HNO_3 (and HNO_2) to oxidize UO_2 but not PuO_2 . Plutonia can be dissolved in nitric acid by using stronger oxidizing agents such as Ce^{4+} [HORNER (1977)] or by addition of fluoride, which forms a strong complex with Pu^{4+} [TALLENT (1977)]. Plutonia is also readily dissolved by HI solutions where the HI acts as a strong reducing agent [TALLENT (1977)].

Groundwater can contain both sulfate and fluoride which can participate in dissolution of PuO_2 . All types of radiation; alpha, beta, and gamma; interact with water to produce free radicals. Atomic hydrogen, hydrated electrons and HO_2 radicals can act as powerful reducing agents and may participate in the dissolution of PuO_2 . Hydrogen peroxide is produced from reactions of the primary free radicals and can also act as a reductant. The OH radicals can act as powerful oxidizing agents. While the combination of oxidation and reduction can dissolve some of the PuO_2 , the dissolved plutonium may not remain in solution. Hydrolysis can cause reprecipitation and may generate colloidal material. The colloidal, hydrolyzed plutonium should have a higher solubility than either crystalline PuO_2 or PuO_2-UO_2 solid solution. A further retardation of the dissolution of uranium oxide fuels could probably be obtained by a local backfill (perhaps in the primary fuel containers) with UO_2 . This would assure that any groundwater which reached the fuel would be presaturated with UO_2 and would decrease the driving force for dissolution.

Glass Waste: Groundwaters would be expected to be relatively saturated with silica leached from the surrounding rock strata. Thus dissolution of glass would eventually be accompanied by deposition of silica [COHEN (1985)], although the elevated temperature near the glass would increase the local solubility. The initial stages of leaching include selective removal of the alkali-metal ions from the surface of the glass; this process is controlled by diffusion through a progressively thicker layer of porous material which is silica-enriched. Transport of plutonium from the glass is, initially, further retarded by adsorption of the plutonium on the hydrated silica-rich layer. After all available sites in the layer have been saturated the plutonium would be released at increasing rates until, at equilibrium, the plutonium release rate would be expected to be equivalent to the penetration rate of the glass surface [BARKATT (1981)]. Reprecipitation of plutonium from the groundwater, either on the surface of the glass or as particulate material, may occur.

3.0 GEOLOGICAL FACTORS

3.1 Groundwater

Groundwaters contain numerous inorganic anions and cations and also organic materials which can affect the solubility of plutonium in groundwaters [ALLARD (1982)]. Typical groundwater compositions in basalt and tuff are given in Table 1. Here we see significant amounts, in some cases, of fluoride, sulfate, and carbonate; all these anions form strong complexes with tetravalent plutonium. The stabilities of the various complexes have been discussed in the section on plutonium complexes. Disagreement exists between various authors regarding the importance of carbonate complexes in the behavior of plutonium in groundwaters. [KIM (1983a)] indicates that, in groundwater associated with tuff ($\text{pH} < 8$ and low carbonate concentrations), Pu(IV) hydroxide species predominate; in basaltic groundwaters ($\text{pH} > 8$ and carbonate $> 10^{-4} \text{ M}$) the formation of hydroxycarbonate and carbonate complexes may take place. [SULLIVAN (1982)] indicates that in sea water ($\text{pH} = 8.8$, ionic strength = 0.1 M , $\text{HCO}_3^- = 0.1 \text{ M}$) that Pu(VI) exists about equally as $\text{PuO}_2(\text{OH})_2$ and as $\text{PuO}_2(\text{OH})_2(\text{HCO}_3)^-$ with a small quantity of $\text{PuO}_2(\text{CO}_3)_2^{2-}$. However, in basaltic groundwaters where the pH and carbonate concentrations are sufficient to form such complexes, the basaltic rock is reducing (in a sealed repository) giving Pu(III) as the predominant species [SEITZ (1982a)] [SALTER (1981)]. In tuff waters which are oxygenated, the predominant species is expected to be Pu(V) [RAI (1980b)]. The presence of strong complexing agents will tend to stabilize the Pu(IV) species [CHOPPIN (1983)]. It has been stated that the solubility and behavior of plutonium is dominated by the hydroxide and carbonate complexes [KIM (1982a)]. Others have found no evidence of major effects from carbonate in experimental studies [OLOFSSON (1983)] [BARNEY (1982)] [CLEVELAND (1983a)]. This behavior suggests that the solubilities are not very different for the solids formed when carbonate is present or absent. Carbonate is said to be important in determining the solubility of neptunium [BARNEY (1982)]; if

the above references are correct, this must be due to differing importance of the hydroxide and carbonate complexes for the plutonium and neptunium cases.

Sulfate and fluoride form strong complexes with Pu(IV) and are present in significant quantities in groundwaters (Table 1). Sulfate has been observed to increase the apparent solubility of plutonium in groundwater, but its effect may be due to enhanced aggregation of plutonium polymers into larger, more easily removed (by adsorption or filtration) agglomerates [CLEVELAND (1983a)] [CLEVELAND (1982)]. Fluoride tends to increase the solubility of plutonium in deionized water, but not consistently in groundwaters [CLEVELAND (1983a)] [CLEVELAND (1982)]. It appears that the effects of fluoride and sulfate, to some extent, are due to effects on plutonium present as colloids or pseudocolloids.

Cations which are present in groundwaters can affect the availability of anions which could otherwise complex plutonium. This is particularly true of alkaline earths which form strong complexes with fluoride and sulfate and effectively decrease their available concentrations.

As was discussed in the section on organic complexes, humic substances in the groundwater can directly complex the plutonium species or can sorb on surfaces and affect their sorption properties for plutonium.

The species present in any particular groundwater depend on the oxidation/reduction potential of the system, the pH and the presence of complexing agents; ionic, polymeric and colloidal forms are possible. In a sealed repository in basalt the presence of ferrous ion in the rock results in a strongly reducing system and Pu(III) would predominate [SEITZ (1982a)] [SALTER (1981)]. In tuff, where the water is more likely to be oxygenated, the plutonium will be in a higher oxidation state and the predominate species has been experimentally determined to be Pu(V) [RAI (1980b)]. Note, however, that the methods used to determine oxidation states are open to some question [KIM (1982a)].

The solubility-determining solids in solutions with pH > 7 are likely to be hydroxides, hydrous oxides or possibly hydroxycarbonates. The quantities of these materials in solution may be decreased by sorption on the surfaces of various solids.

Plutonium can be present as colloids, such as those formed by Pu(IV) hydroxide, in addition to ionic forms. These colloids as well as pseudocolloids (ionic forms or polymers sorbed on other colloids) can undergo stable or unstable physical sorption on the surface of solid matrices [KIM (1982b)]. In experimental systems these colloids are difficult to separate from ionic species and without elaborate chemical means solubility data obtained by different phase separation methods can vary by orders of magnitude [KIM (1982a)]. In filtrations of groundwaters saturated with americium, significant solubility differences were found between solutions filtered through 0.22 μm and

1.8 nm filters [KIM (1982a)]. Examinations by microautoradiography of sorption membranes showed the presence of large complex species, polymers, or colloids in so-called solutions, even after multiple centrifuge stages, indicating the difficulty of separating particulates from ionic species [ERDAL (1982)]. Studies of sorption of plutonium from tuff groundwater onto thin sections of tuff showed that the plutonium was rather uniformly sorbed on the rock sections and indicated the presence of aggregated species [VINE (1980)]. The uniformity likely indicates physical adsorption. In these same studies the plutonium was shown to settle out in a Teflon container, also consistent with the formation of aggregates. In scanning electron microscope (SEM) photographs of crushed basalt micron-sized fine particles that were electrostatically attached to larger basalt particles were observed; these small particles could provide sites for adsorption of plutonium [SCHRAMKE (1985)]. This is likely a phenomenon caused by crushing the basalt; thus, the small particles present in tests using crushed basalt are not representative of the geologic system far from the excavation. Pseudocolloids formed by sorption of plutonium on the small particles may be a more significant phenomenon than is the case in an actual repository. The waste form itself can also contribute colloidal particles; dissolution of glass generates silica particles [CLEVELAND (1983b)]. These particles of hydrated silica likely are highly sorptive and may have properties similar to silica gel.

3.2 Properties of Tuff and Basalt

Tuff is a highly sorptive rock composed of solidified and welded volcanic ash plus rock fragments and other loose material. Each layer of tuff at the Yucca Mountain Site is generally hundreds of feet thick [CRWMP (1985b)]. The immediate repository area contains "dry" material since the permanent water table is ~550 feet below. This unsaturated zone is of primary interest in retardation of transport of radionuclides, but the water-saturated formations nearer the water table can be important if significant transport occurs. In the water-saturated zone the tuff is highly zeolitized [OGARD (1984)]. Even the unsaturated zone may be penetrated by water due to slow seepage from the surface. Transporting radionuclides would then be exposed to alternate aqueous transport and drying on mineral surfaces.

Water flow in basalt occurs primarily through cracks in the basalt. Retardation of radionuclide transport can occur by precipitation of insoluble compounds, settling of particulates and sorption on the surface of interbedded solids. Chemical adsorption of transported radionuclides occurs primarily on secondary minerals contained within the cracks. The secondary minerals in the basalt have been characterized [SALTER (1981)]. The basalt formation is below the water table and transport depends upon flow rates of water within the formation and the various retardation mechanisms.

3.3 Sampling of Geological Materials

It is quite difficult to take and maintain samples removed from geologic repository sites. Great care must be taken that the sampling position has not been contaminated by water from other positions in the borehole or by drilling fluids. When aqueous samples are taken, relief of pressure allows dissolved gases, for example, CO₂, to escape and can cause precipitation of materials such as calcium carbonate [SEITZ (1982b)]. All the conditions initially pertaining to the sample should be determined such as temperature, electrical conductivity, pH, redox potential, and gas overpressure and composition. Proper determination of these values would require removing pressurized samples and examining them without depressurization; obviously, a very difficult undertaking. After samples are taken they must be protected from interactions with air and microbial agents [BRUHL (1982)]. Storage of samples in plastic bottles (except Teflon) should be avoided due to gas permeability through the plastic.

Representative rock samples are similarly hard to obtain and maintain. This is particularly true for rocks such as basalt which contain reduced (relative to air) species such as Fe(II) and Mn(II). These materials, when stored in air or in containers permeable to oxygen, are converted to oxidized forms which will not possess the same properties as were present at the repository. Handling of rock samples would require storage and handling in an inert atmosphere or in an atmosphere typical of the geologic repository. In particular, grinding, crushing and handling of high-surface-area materials in air should be avoided [BRUHL (1982)].

3.4 Sorptive Capacities of Minerals

Sorption capacities of mineral samples can be characterized by standard sorption tests using, for example, cesium and strontium [SALTER (1981)] [VINE (1980)] [JOHNSTONE (1980)] [WOLFSBERG (1979)]. This allows easy comparison of capacities and distribution coefficients between different specimens.

4.0 EXPERIMENTAL METHODS

Experimental tests which have been made to characterize migration of plutonium in geologic repositories can be classified as (1) solubility tests, (2) sorption tests and (3) leaching tests. The latter two categories include both static and flow testing.

4.1 Solubility Determinations

NRC position: The NRC has developed a technical position document on solubility measurements [NRC (1984)] and the Statement of Position is quoted here:

"It is the position of the NRC that any site program that elects to take credit for solubility-limited release rates, should design a set of experiments to determine radionuclide solubilities applicable to the site-specific conditions. In designing this set of experiments, the site program should:

- 1) Develop a matrix of experiments in which the selection of starting materials is based on the anticipated range of proportions and compositions of phases under the various physicochemical conditions expected for a nuclear waste repository;
- 2) Determine experimental run product compositions for liquids and, where feasible, solids using analytical methods that include state-of-the-art techniques;
- 3) For the experimental matrix, determine radionuclide solubilities from undersaturation and oversaturation (experimental reversal) or, if this is impractical or impossible, from oversaturation where the concentration of radionuclide in the liquid decreases as the system approaches equilibrium;
- 4) Document the magnitudes of experimental and conceptual uncertainties from all anticipated sources; and
- 5) Use geochemical modeling only for interpreting experimental results and for planning experiments.

The NRC staff considers that this approach of experimental determination of solubilities will provide reasonable but conservative estimates of solubility under repository conditions. When combined with a judicious choice of "key" radionuclides, this approach will maximize the usefulness of the information obtained from a minimum number of experiments."

In solubility determinations the most defensible values are obtained by approaching saturation from both dissolution of the characteristic solid and by precipitation of the characteristic solid from saturated solutions. While this is the most desirable experimental approach it requires significant experimental time and ingenuity. This approach makes it less likely that a slow approach to equilibrium is mistaken for true equilibrium and also less likely that colloidal material in solution will be mistaken for truly dissolved species (amounts of and type of colloid are unlikely to be the same for both directions of approach to equilibrium). Solubilities are often measured from only one direction with the equilibrium concentration being determined as the solution concentration which remains constant over some period of time. Solubilities may be determined in water, simulated groundwater or natural groundwater. The solubilities determined should be larger than the final concentrations of plutonium in solution found in either corresponding sorption or leaching experiments since, in those types of tests, the plutonium is present in or on solids with lower plutonium chemical activities.

4.2 Sorption Determinations

Sorption experiments can be either static or flowing. In either case a solution of the radionuclide is contacted with the mineral and the removal of the radionuclide by sorption is determined. In the static system the final concentration gives a sorption ratio and in the flowing system the depletion of the radionuclide in the stream after passage through the bed and the breakthrough curve can be interpreted in terms of a sorption ratio.

4.3 Dissolution Determinations

Leaching tests involve examination of the removal of the radionuclide from a particular waste form such as spent fuel or glass. These tests can involve leaching with a solution (real or simulated groundwater) or, in the most complicated and realistic tests, can also have present representative minerals to equilibrate with the leach solution. In the most elaborate systems, the leach solution flows from the solid being leached to the mineral to be contacted.

5.0 EXPERIMENTAL REQUIREMENTS

5.1 Available Experimental Time

Many difficulties are encountered when attempting to simulate the conditions which would exist in a geologic repository. In reality, the actual conditions cannot be duplicated experimentally due to the long geological times of importance in the repository. In particular, plutonium with its many valence states and the probable colloidal and adsorbed states may require very long times to reach complete species equilibrium. In experimental flow systems, the flow rates will usually be much larger than those which will exist in the repository since the time available for an experiment will be limited. As a consequence the small colloids and particulates will not have as much time to contact surfaces (by Brownian motion) and sorb there or settle out. The actual volume of water per volume of rock will likely be larger and the content of radionuclides may be larger, to make analyses easier, in experimental systems than in the repository.

5.2 Handling of Rock Samples

Preparation of the rock samples is an important experimental area and one for which many variables are hard to control. As pointed out earlier the rocks must be protected from non-representative atmospheres during procurement and handling. In many cases, the rock should not be exposed to air. A particular concern would be grinding and sieving operations. If these are carried out in air significant surface oxidation can occur which will change the oxidation/reduction balance during subsequent experiments. Control of particle size distribution used in experiments is necessary to specify the surface area of the rocks. Particles ranging down to 10^{-4} microns exist in groundwater

from basaltic formations [SEITZ (1982b)]. These very fine particles will contribute to the formation of pseudocolloids; their removal by dry sieving or wet sieving will be incomplete and difficult to duplicate in different tests. This may be one source of the variation of results in inter-laboratory testing [RELYEA (1979)]. Another concern is the condition of freshly broken rock as compared to the aged rock in the repository. Duplication of the geologic aging process is impossible and is complicated by the problems of oxidation if the freshly exposed (and presumably highly reactive) rock surfaces are exposed to air.

5.3 Handling of Water

The difficulty of obtaining representative groundwater specimens was mentioned earlier. For this reason many investigators have chosen to use synthetic groundwaters which more or less completely duplicate the composition of the true groundwaters (see Table 1). Unfortunately, it is quite difficult to duplicate the true groundwater in all respects. Significant areas in which the true groundwaters have generally not been duplicated are in the overpressure of CO₂ which occurs in the tuff formations and in the content of humic substances; the overpressure of CO₂ is also seldom maintained in tests with true groundwaters. The former would require operation in an inert atmosphere with a proper CO₂ overpressure; this approach has been taken by several authors [NITSCHKE (1985)] [JACOBS (1985)]. Duplication of the humic substance content is quite difficult due to their complex nature and variability depending on their source. Groundwaters are expected to be largely saturated with silica from the surrounding rocks; it is not clear that this saturation has been duplicated in all synthetic groundwaters. This is particularly important for studies of leaching of glass where the silica content will affect the leach rates of the glass. The content of colloidal particulates in groundwater is not duplicated in any case. Complete duplication of all components in natural groundwaters is not attempted in any case with the experimenter either relying on his or others judgement(s) as to the relative importance of each component; a process which can lead to doubts regarding the applicability of the experimental results.

5.4 Introduction of Plutonium

Introduction of the plutonium spike into the aqueous solution is a difficult procedure to completely defend except where the plutonium is leached from a representative waste form. The plutonium can be added in an acid solution and then the pH adjusted by adding base. The worry here is that the local basic condition where the basic solution is added may give a local change in the character of the plutonium. Another procedure dries the plutonium and then dissolves the precipitated plutonium in the aqueous solution, sometimes followed by filtration to remove any particulates larger than the filter cutoff. The concern here is that in drying the plutonium a concentrated solution and solid are formed. Then, when the solid is contacted with the groundwater, the plutonium is locally concentrated and will tend to form agglomerates;

this would be unlikely in the very dilute solutions which would actually be present in the repository. Many of these non-representative agglomerates would not be removed by filtration and could perturb the experiment.

5.5 Control of Equilibration

The equilibration conditions should be carefully controlled in temperature, total pressure, cover gas composition, pH, Eh and in-growth of microorganisms. All of these requirements are significantly difficult with the exception of temperature control. Total pressure control, necessary where systems at elevated temperature are studied, requires operation in an autoclave with the accompanying difficulties in addition and removal of materials. Control of the cover gas, largely through elimination of oxygen and addition of CO₂ where necessary, requires operation in closed equipment or in an "inert gas" box. Control of pH may require operation with a CO₂ overpressure; even this may not be sufficient since radiolysis can affect the pH. If the periodic addition of basic or acidic solutions is required to maintain a constant pH the worry arises of the generation of local regions where the pH is different than the bulk solution. Control of Eh where sufficient quantities of mineral surface are present and in the absence of oxygen may not be difficult. If necessary, electrochemical or chemical control may be used, although interaction of the plutonium with the electrode surface or with the chemical control agent may be a problem. Chemical oxidation/reduction control agents can also interact with mineral surfaces to change their sorption properties. Control of bacterial contamination is a very difficult, but possibly important problem. Numerous varieties of bacterial are present in any experimental facility and will be quite difficult to exclude from the experiment. However, bacteria can act to change the character of surfaces and increase the sorption (actually sticking) of particulates to the surfaces [MEYER (1977)]. Microbial growth has been reported in experimental systems in which sorption ratios were being determined [JACOBS (1985)]; The reported ability of microbes to take up particulate plutonium from solution and the likelihood that much of the plutonium in groundwater is particulate in form makes the validity of such results doubtful.

5.6 Sampling of Experiments

Sampling and handling of aqueous samples from groundwater experiments is an area of significant uncertainty. The large amount of particulate material present in groundwaters and available from crushed rocks give significant surface for plutonium to sorb to form pseudocolloids. The presence of very small particles makes it likely that some of these pseudocolloids will not be removed by the centrifugation and filtration procedures used by experimenters to separate the "solution" from the solid phase. It is likely that much of the plutonium concentrations for these solutions are not present as ionic species. This makes interpretation of data very difficult since the behavior of colloids can

vary markedly with relatively small changes in solution variables. Certainly, a simple distribution coefficient cannot represent the complex behavior of a system such as this.

6.0 RECOMMENDED EXPERIMENTAL TECHNIQUES

Earlier discussion has indicated the difficulty and, indeed, the impossibility of duplicating the conditions of a geologic repository in an experimental system. Does this mean that experimental testing is impossible or useless? Not necessarily. In order to furnish conservative values for the migration of plutonium, it is only necessary to be convinced that the predicted migration rates are at least as large as will occur in the real system. In such a complex system it is difficult to delineate the requirements of more defensible experiments, but based on the literature surveyed and particularly on the joint U.S./FRG workshop [CONF-821053] which addressed many of these problems the following list of recommendations and justifications is presented.

- (1) The experiments should use real groundwaters if at all possible. At the very least, selected tests with natural groundwaters should confirm more complete testing using synthetic waters. The major reason for this recommendation is the possibility that the presence of humic acids in natural groundwaters can affect the behavior of plutonium both by complexing the plutonium and by modifying the sorptive properties of mineral surfaces. Particulates in natural groundwater may sorb plutonium. Natural groundwater samples should be handled and stored in a manner designed to preserve their original composition. This will require sealing in air-tight containers and prevention of microbial contamination.
- (2) Abnormal microbial growth should be prevented in the experimental system. This is a very difficult requirement since addition of biocides could alter the behavior of plutonium. It might be possible to sterilize the system by heating before the test and using care in removing samples to prevent contamination. This requirement is necessary since it is well documented that microbes accumulate plutonium and alter the sorptive properties of surfaces for particulates.
- (3) The minerals to be tested should be handled in such a way as to preserve their condition, as nearly as possible, as it existed in the proposed repository. In some cases this will require storage and handling in an inert atmosphere. This is particularly important where the minerals are reducing. Improper storage may render them non-reducing and can result in unrealistic valences of plutonium. For instance if the plutonium is not reduced to the trivalent state, but remains tetravalent, the effect of anion complexing will be greatly enhanced. If mineral samples are pulverized their surface should be conditioned by preexposure to the groundwater; it is not clear what time of exposure would be required to return freshly fractured surfaces to a state such as existed for old surfaces in the repository. In

fact, the surface of pulverized rock, even after lengthy contact with groundwater, may still be significantly different from the initial dense rocks in the repository.

- (4) The atmosphere above the experiment should approximate that in the repository as nearly as possible. It is particularly important to maintain the proper CO₂ partial pressure to assure the correct carbonate and bicarbonate concentrations in the water. While there is evidence that carbonate content is not very important, the large stability constants for complexes of plutonium with carbonate make it advisable to simulate this aspect as closely as possible. Oxygen partial pressure should also be maintained at the value expected for the particular condition being simulated. Maintaining total pressure should not be important except in cases where elevated temperatures generate high water partial pressures.
- (5) A justifiable standard for separation of solids from the aqueous phase by filtration or centrifugation should be adopted. It appears that total removal of all particulates from the solutions is nearly impossible. The aim of the filtration and/or centrifugation should be to remove any particulates large enough to settle by gravity given sufficient time. Note that this does not remove all particulates which will eventually be removed by attachment (sorption) on solid surfaces; it does give an upper limit to the plutonium in solution which can be expected to transport for any significant distance.
- (6) It must be recognized that simple distribution coefficients do not adequately represent the complex behavior of an element such as plutonium, which exists in several valence states, and as colloids and pseudocolloids.

Care must be taken that the species in the aqueous phase are those which will exist in the groundwater and sufficient time must be allowed for complete equilibrium to be attained.

7.0 CURRENT SOLUBILITY DATA

The solubility of plutonium, from plutonia, in the repository aqueous phase is the highest level of soluble plutonium which can conceivably occur. The facts that the plutonium is being leached from a waste form with a diluted form of plutonia and that the dissolved plutonium will adsorb on mineral phases must lead to lower dissolved plutonium levels. However, some plutonium can exist as colloids in the repository water and be transported, at least over some distance.

Table 2 contains values of the solubility of plutonium for various solutions at pH values above 7. In the absence of carbonate and other complexing anions the solubility of plutonium from plutonia has been calculated [ALLARD (1982)] as $\sim 2.5 \times 10^{-9}$ M at a pH of 7 and with only a slight increase with increasing pH above 9. The first three solubilities listed in Table 2 [NITCHE (1985)] show that the initial plutonium valence state can influence

the solubility attained by precipitation from a supersaturated solution. Initial valences of +4 and +6 gave solubilities higher than those found with an initial valence of +5; the solubility with an initial valence of +5 was similar to that calculated [ALLARD (1982)]. Solubilities in pure water were found to be lower if the initial valences of the plutonium were +3 and +4 than if they were +5 and +6 [CLEVELAND (1983a)]. The solubilities determined in both cases [CLEVELAND (1983a)] were lower than those predicted [ALLARD (1982)]. Solubilities in J-13 water where the CO₂ overpressure and pH were controlled [NITSCHKE (1985)] were all higher than that predicted for pure water, probably due to complexation or formation of pseudocolloids. In experiments using J-13 water where the CO₂ overpressure and pH were not controlled [CLEVELAND (1983a)] the plutonium solubilities were lower than predicted [ALLARD (1982)] and considerably lower than those found in tests where the CO₂ overpressure and pH were controlled [NITSCHKE (1985)]. Solubilities can depend significantly on the plutonium solid phase; solubilities found with Pu(OH)₄ were significantly higher than those found with PuO₂ [RAI (1981a)] [RAI (1980a)] [RAI (1980b)]. The solubility found for PuO₂ solid is in good agreement with the calculated value. Note however that if the solid being leached is a diluted PuO₂ (as in reactor fuel or glass) the solubility of the Pu(OH)₄ will not be attained unless there is a large difference in temperatures in the regions where the oxide is being dissolved and the region of precipitation. As was discussed in the section on the chemistry of plutonium in groundwater, the solubility of plutonium can also be affected by the presence of complexing agents such as sulfate and fluoride; these effects have been studied [CLEVELAND (1983a)]. The major effect of carbonate/bicarbonate on the solubility of plutonium is illustrated by the last three sets of data in Table 2; solubilities are increased by 2-3 orders of magnitude by introduction of carbonate and bicarbonate.

8.0 CURRENT DATA ON SORPTION ON BASALT

Plutonium will be adsorbed on various secondary minerals within the basalt. The data on sorption of these minerals found in this brief survey [BARNEY (1982)] [SALTER (1981)] is somewhat sketchy but indicates K_d values of a few hundred to a few thousand. Of the composition variables of Grande Ronde groundwater studied (Na⁺, Ca²⁺, K⁺, Mg²⁺, Cl⁻, F⁻, CO₃²⁻, HCO₃⁻, SO₄²⁻ and oxidizing potential), the most important variable appears to be the oxidizing potential [BARNEY (1982)], with Pu(IV) being the most strongly adsorbed. In actuality the valence of the plutonium may not really be a variable since the Fe(II)/Fe(III) couple may control the valence of the plutonium except during the period where the repository is filled with air. According to [SEITZ (1982a)] and [SALTER (1981)] predominant plutonium oxidation state in contact with basalt will be Pu(III).

9.0 CURRENT DATA ON SORPTION ON TUFF

Much more data is available on the sorption of plutonium on tuff minerals [JOHNSTONE (1980)] [VINE (1980)] [SALTER (1981)] [WOLFSBERG (1979)] [RELYEA (1979)]. In fact the volume of data and the complexity of the system preclude an adequate evaluation of the data in this review. We present here

portions of the general conclusions of [VINE (1980)] as a summary of the observed behavior of plutonium. "The sorptive properties tend to vary with the mineralogy; the R_d values are highest for the zeolitized tuff (JA-37). At least qualitatively the (... plutonium values show) a slight decrease (with increasing particle size). The R_d values show very little increase with longer contact times; the plutonium values tend to increase more than do the americium values. The method of preparing the traced feed solutions appears to have influenced the observed sorption ratios... However, the improved procedure used in Experiment 4 for centrifuging and transferring solutions after contact may have resulted in the removal of more particulates from solution, which would result in the observation of higher R_d values... Also, for ^{239}Pu the sorption R_d values are greater than the desorption but for ^{237}Pu the desorption R_d values are greater than the sorption." These conclusions illustrate several points made earlier in this review regarding the difficulty of performing this type of experiment; difficulties in preparing tracer feeds, separation methods of solids, and difficulty in obtaining reproducible data due to the many variables over which the experimenter has only moderate control. For instance the conclusion that the two plutonium isotopes gave different behaviors is likely an experimental artifact.

10. CURRENT INTEGRATED STUDIES

The difficulties of simulating, in a simple experiment, the plutonium species which will be present in the repository environment make it attractive to more completely simulate the entire system. If the waste form is actually dissolved in the groundwater or a closely simulated water, the proper plutonium species should be present. These could then interact in the correct manner with minerals. This approach is being examined with studies in which glass dissolves and the species interact with basalt [SEITZ (1984)] [SCHRAMKE (1984)], and in dissolution tests with irradiated reactor fuel [SCHRAMKE (1984)] [WILSON (1985)]. Tests such as these could lead to improved definitions of the behavior of plutonium in the actual repository system. Two of these studies [SEITZ (1984)] [SCHRAMKE (1984)] used simulated groundwater; this approach has possible problems particularly in the duplication of particulates and humic substances contained in natural groundwater. The other study [WILSON (1985)] used both natural groundwater and simulated groundwater; this appears to be a better approach. [WILSON (1985)] has not incorporated, at this time, minerals to examine interactions with the dissolved species. Note that this type of experiment still requires resolution of questions concerning the various species of plutonium in solution; truly dissolved species and colloidal species.

The current observations from these studies are the following. In studies using glass waste forms plutonium in the aqueous phase was much below the quantity calculated by the quantity of glass dissolved whether basalt was present or not [SCHRAMKE (1984)]. The pH was observed to be lowered by the presence of fuel in the simulated dissolution, probably due to metal-ion hydrolysis reactions [SCHRAMKE (1984)]. Plutonium and other actinides dissolved from a glass waste form were found to migrate more rapidly through aged basalt than through fresh materials [SEITZ (1984)]. In tests with

irradiated reactor fuel the concentrations of plutonium in solution agreed with those calculated from the quantity of fuel dissolved [SCHRAMKE (1984)] [WILSON (1985)]. In tests comparing dissolution of actinides from bare fuel pellets and from fuel pins with holes or slits, the total measured fractional actinide releases were much greater with bare fuel [WILSON (1985)].

11.0 CONCLUSIONS

This brief review of the current knowledge of the behavior of plutonium in geologic repositories has shown that the simulation of the repository system in experiments is very difficult due to the complexity of plutonium behavior. This is the likely explanation of any disagreements observed in experimental data from the various investigators. Such a brief review can only point out possible problem areas; it cannot give specific directions for future efforts. It does appear that current experiments are not likely to completely define all areas for which data are desired. A more integrated approach appears desirable to limit efforts to critical areas. This will require a stronger interaction between experimental and modeling efforts. Testing of models using data obtained over a number of years where plutonium has been transported in the ground would be useful.

Table 1. Groundwater compositions

Reference	1	2	3	4	5
Synthetic?	No	No	No	No	No
Location	NTS	NTS: J-13	NTS	NTS	NTS: J-13
Medium	Tuff	Tuff	Tuff	Tuff	Tuff
Al (mM)		0.001			
B (mM)					0.0015
Ba (mM)					0.3244
Ca (mM)	0.2495	0.29	0.2495	0.2495	0.0000
Fe (mM)	0.0001	0.0008	0.0001	0.0001	0.0823
Mg (mM)	0.1234	0.072	0.1234	0.1234	
Mn (mM)	.0000	0.00002	.0000	.0000	
K (mM)	0.1074	0.136	0.1074	0.1074	0.1202
Li (mM)		0.009			0.0072
Na (mM)	2.1739	1.96	2.1739	2.1739	2.0435
Sr (mM)	0.0006		0.0006	0.0006	0.0007
Si (mM)	1.1647	1.07	1.1647	1.1647	
Tl (mM)					
V (mM)					
Cl (mM)	.1975	0.18	0.1973	0.1973	0.2172
F (mM)	0.1211	0.11	0.1211	0.1211	0.0895
NO ₃ ⁻ (mM)	0.16				
PO ₄ ⁻ (mM)	<.0001		<.0001	<.0001	
SO ₄ ⁻ (mM)	0.1978	0.19	0.1978	0.1978	0.2186
Alkalinity (meq)	1.958	2.34	1.9580	1.9580	
CO ₃ ²⁻ (mM)					0.0000
HCO ₃ ⁻ (mM)					2.1311
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)				2.1311	
Total Carbon (mM)					
Ionic Strength					
pH	7.8	7	7.8	7.8	7.3
Eh(mV)		700			
Diss. Org C (ppm)					

References

1. [CLEVELAND (1983a)]
2. [NITSCHKE (1985)]
3. [REESE (1985)]
4. [CLEVELAND (1983b)]
5. [WOLFSBERG (1979)]
6. [OGARD (1984)]
7. [KNIGHT (1985)]
8. [BARNEY (1982)]
9. [SEITZ (1984)]
10. [SCHRAMKE (1984)]
11. [SALTER (1981)]
12. [RELYEA (1979)]
13. [KELMERS (1984)]
14. [MEANS (1982)]

Table 1. Groundwater compositions (Cont.)

Reference	5	6	6	6	6
Synthetic?	No	No	No	No	No
Location	NTS: J-13	NTS: VH-1	NTS: H-6	NTS:H-3	NTS:H-5
Medium	Tuff	Tuff	Tuff	Tuff	Tuff
Al (mM)			0.004	0.019	0.006
B (mM)					
Ba (mM)	0.0015				
Ca (mM)	0.3244	0.25	0.14	0.02	0.03
Fe (mM)	0.0000		0.002	0.002	0.0002
Mg (mM)	0.0823	0.06	0.009	0.0002	0.001
Mn (mM)		0.0007	0.0002		0.0004
K (mM)	0.1202	0.049	0.053	0.038	0.059
Li (mM)	0.0072	0.013	0.014	0.032	0.006
Na (mM)	2.1739	3.48	3.22	5.39	2.35
Sr (mM)	0.0005				
Si (mM)		0.83	0.71	0.6	0.62
Ti (mM)					
V (mM)					
Cl (mM)	0.2116	0.28	0.22	0.23	0.16
F (mM)	0.0895	0.14	0.22	0.28	0.07
NO ₃ ⁻ (mM)			0.09	0.003	0.14
PO ₄ ³⁻ (mM)					
SO ₄ ²⁻ (mM)	0.2082	0.47	0.29	0.32	0.15
Alkalinity (meq)			2.75	4.72	2.0
CO ₃ ²⁻ (mM)	0.0000				
HCO ₃ ⁻ (mM)	2.1311				
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)	2.1311				
Total Carbon (mM)					
Ionic Strength					
pH	7.3	7.5	7.4	9.4	7.1

Table 1. Groundwater compositions (Cont.)

Reference	6	6	6	6
Synthetic?	No	No	No	No
Location	NTS:G-4	NTS:H-1	NTS:H-4	NTS:25b#1-I
Medium	Tuff	Tuff	Tuff	Tuff
Al (mM)	0.0007		0.001	0.001
B (mM)				
Ba (mM)				
Ca (mM)	0.23	0.15	0.27	0.49
Fe (mM)	0.0007		0.0005	0.0007
Mg (mM)	0.007	<.004	0.008	0.028
Mn (mM)				
K (mM)	0.064	0.041	0.066	0.084
Li (mM)	0.012	0.006	0.023	0.04
Na (mM)	2.43	2.22	3.65	2.43
Sr (mM)				
Si (mM)	0.7	0.67	0.92	1.12
Ti (mM)				
V (mM)				
Cl (mM)	0.16	0.16	0.17	0.2
F (mM)	0.13	0.05	0.24	0.06
NO ₃ ⁻ (mM)	0.09		0.08	0.01
PO ₄ ⁻ (mM)				
SO ₄ ⁻ (mM)	0.16	0.2	0.25	0.21
Alkalinity (meq)	2.34		2.82	2.2
CO ₃ ⁻ (mM)				
HCO ₃ ⁻ (mM)				
CO ₃ ⁻ + HCO ₃ ⁻ (mM)				
Total Carbon (mM)				
Ionic Strength				
pH	7.1	7.5	7.4	7.7

Table 1. Groundwater compositions (Cont.)

Reference	6	6	6	6
Synthetic?	No	No	No	No
Location	NTS:25b#1-4	NTS:25b#1-28	NTS:J-13	NTS:29a#2
Medium	Tuff	Tuff	Tuff	Tuff
Al (mM)	0.001	0.002	0.001	0.001
B (mM)				
Ba (mM)				
Ca (mM)	0.46	0.45	0.29	0.28
Fe (mM)	0.012	0.001	0.0008	0.0009
Mg (mM)	0.028	0.027	0.072	0.014
Mn (mM)	0.006	0.001	0.00002	0.0005
K (mM)	0.064	0.077	0.136	0.031
Li (mM)	0.043	0.024	0.009	0.014
Na (mM)	2	1.61	1.96	2.22
Sr (mM)				
Si (mM)	1.02	1.03	1.07	0.92
Ti (mM)				
V (mM)				
Cl (mM)	0.28	0.19	0.18	0.23
F (mM)	0.08	0.06	0.11	0.03
NO ₃ ⁻ (mM)	0.03	0.07	0.16	0.3
PO ₄ ⁻ (mM)				
SO ₄ ⁻ (mM)	0.22	0.21	0.19	0.24
Alkalinity (meq)	2.41	2.13	2.34	1.77
CO ₃ ²⁻ (mM)				
HCO ₃ ⁻ (mM)				
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)				
Total Carbon (mM)				
Ionic Strength				
pH	7.2	7.3	6.9	7

Table 1. Groundwater compositions (Cont.)

Reference Synthetic?	6 No	6 No	7 No	7 No
Location	NTS:J-12	NTS:25p#1	NTS:J-13	NTS:25p#1
Medium	Tuff	Tuff	Tuff	Tuff
Al (mM)		0.003	0.0009	0.0051
B (mM)				
Ba (mM)			0.0000	0.0019
Ca (mM)	0.35	2.19	0.2869	2.1520
Fe (mM)		<.002	0.0002	0.0008
Mg (mM)	0.086	1.312	0.0724	1.3122
Mn (mM)		0.002	0.0002	0.0019
K (mM)	0.13	0.343	0.1345	0.3427
Li (mM)		0.046	0.0086	0.1037
Na (mM)	1.65	7.43	1.9609	4.7826
Sr (mM)			0.0004	0.0045
Si (mM)	0.9	0.62	1.1317	0.6192
Ti (mM)			0.0006	0.0008
V (mM)			0.0004	0.0005
Cl (mM)	0.21	1.04	0.1805	1.0437
F (mM)	0.13	0.18	0.1105	0.1842
NO ₃ ⁻ (mM)		<.002	0.1629	<.002
PO ₄ ⁻ (mM)				
SO ₄ ⁻ (mM)	0.23	1.34	0.1884	1.3429
Alkalinity(meq)	11.44			
CO ₃ ⁻ (mM)				
HCO ₃ ⁻ (mM)			2.3443	11.3115
CO ₃ ⁻ + HCO ₃ ⁻ (mM)				
Total Carbon (mM)				
Ionic Strength				
pH	7.1	6.7	6.9	6.7
Eh(mV)			300	

Table 1. Groundwater compositions (Cont.)

Reference	7	2	8	9
Synthetic?	No	No	Yes	Yes
Location	NTS:H-3	GR	GR #2	GR; DC-6
Medium	Tuff	Basalt	Basalt	Basalt
Al (mM)	0.0041			
B (mM)				0.1324
Ba (mM)	~0			
Ca (mM)	0.0257	<.0025	0.0252	0.032
Fe (mM)	0.0040	0.0054		
Mg (mM)	0.0013	<.04		0.00073
Mn (mM)	0.0005	0.0001		
K (mM)	0.0473	0.0767	0.0642	0.048
Li (mM)	0.0291			
Na (mM)	5.1739	13.0435	10.6957	13.1262
Sr (mM)	.0000	0.0001		
Si (mM)	0.6868	1.6639	0.8623	2.01
Ti (mM)	<.0001			
V (mM)	0.0001			
Cl (mM)	0.2285	3.9492	4.2877	6.04
F (mM)	0.2632	2.7368	1.9526	1.95
NO ₃ ⁻ (mM)	<.008			
PO ₄ ⁻ (mM)		0.0011		
SO ₄ ⁻ (mM)	0.3144	0.7808	1.1243	1.1767
Alkalinity (meq)		2.9180		
CO ₃ ²⁻ (mM)				
HCO ₃ ⁻ (mM)	4.0164			
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)		109		
Total Carbon (mM)				
Ionic Strength				
pH	8.7	9.3	10	
Eh (mV)	-123			

Table 1. Groundwater compositions (Cont.)

Reference	10	10	3	4	11
Synthetic?	Yes	Yes	No	No	Yes
Location	GR3	GR3	GR	GR	GR-1
Medium	Basalt	Basalt	Basalt	Basalt	Basalt
Al (mM)					
B (mM)					
Ba (mM)					
Ca (mM)	0.0696	0.0798	<.0025	<.0025	0.1622
Fe (mM)			0.0054	0.0054	
Mg (mM)	0.0014	0.0015	<.04	<.04	0.0411
Mn (mM)			0.0001	0.0001	
K (mM)	0.0818	0.1458	0.0767	0.0767	0.2302
Li (mM)					
Na (mM)	16.3913	16.9565	13.0435	13.0435	1.3348
Sr (mM)			0.0001	0.0001	
Si (mM)	~1.266	~1.266	1.6639	1.6639	0.4160
Ti (mM)					
V (mM)					
Cl (mM)	9.9577	9.9859	3.9459	3.9459	0.3977
F (mM)	1.7263	1.7158	2.7368	2.7368	
NO ₃ ⁻ (mM)					
PO ₄ ⁻ (mM)			0.0011	0.0011	
SO ₄ ⁻ (mM)	1.7489	1.5199	0.7808	0.7808	0.1156
Alkalinity (meq)			2.9180	2.9180	
CO ₃ ²⁻ (mM)					
HCO ₃ ⁻ (mM)					
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)				1.3361	
Total Carbon (mM)	0.9417	0.9500			
Ionic Strength					0.002
pH	~9.7	~9.7	9.3	9.3	8

Table 1. Groundwater compositions (Cont.)

Reference	11	12	13	13	13
Synthetic?	Yes	Yes	Yes	Yes	Yes
Location	Gr-2	GR?	GR-1	GR-2	GR-3
Medium	Basalt	Basalt	Basalt	Basalt	Basalt
Al (mM)					
B (mM)					
Ba (mM)					
Ca (mM)	0.0260	0.33	0.1622	0.0264	0.0699
Fe (mM)					
Mg (mM)	0.0029	0.08	0.0411	0.0029	0.0012
Mn (mM)					
K (mM)	0.0639	0.23	0.2302	0.0639	0.0870
Li (mM)					
Na (mM)	9.7826	1.3	1.3348	9.7826	15.5652
Sr (mM)					
Si (mM)	1.7970		0.4160	1.7970	1.2679
Ti (mM)					
V (mM)					
Cl (mM)	3.6953	0.46	0.4062	9.3371	8.8011
F (mM)	1.5263	0.04	0.0000	1.5263	1.7579
NO ₃ ⁻ (mM)					
PO ₄ ³⁻ (mM)					
SO ₄ ²⁻ (mM)	0.7495	0.48	0.1156	0.7495	1.8010
Alkalinity (meq)					
CO ₃ ²⁻ (mM)			0.0000	0.9833	
HCO ₃ ⁻ (mM)		0.95	1.3361	1.2295	
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)	2.2128				0.8869
Total Carbon (mM)					
Ionic Strength	0.014				
pH	10		8	10	9.77

Table 1. Groundwater compositions (Cont.)

Reference	13	14
Synthetic?	Yes	No
Location	GR-4	GR:DC-6
Medium	Basalt	Basalt
Al (mM)		
B (mM)		
Ba (mM)		
Ca (mM)	0.0539	0.0549
Fe (mM)		
Mg (mM)	0.0000	0.0016
Mn (mM)		
K (mM)	0.3529	0.0716
Li (mM)		
Na (mM)	14.5217	9.8696
Sr (mM)		
Si (mM)	1.6023	NA
Ti (mM)		
V (mM)		
Cl (mM)	11.4245	3.1876
F (mM)	1.0474	
NO ₃ ⁻ (mM)		
PO ₄ ⁻ (mM)	0.0026	
SO ₄ ⁻ (mM)	0.0416	1.1868
Alkalinity(meq)		
CO ₃ ²⁻ (mM)		1.5500
HCO ₃ ⁻ (mM)	<.016	
CO ₃ ²⁻ + HCO ₃ ⁻		
CO ₃ ⁻ (mM)	1.5082	
Total Carbon (mM)		
Ionic Strength		
pH	9.7	10.2
Eh(mV)		
Diss. Org C (ppm)	0.34	

Table 2. Selected Solubilities of Plutonium at pH \geq 7

Reference	1	1	1	1
Water Type	0.1 M NaClO ₄	J-13	J-13	J-13
Init. Ox. St.	+4	+4	+5	+6
Temp (°C)	25	25	25	25
Al (mM)		0.001	0.001	0.001
B (mM)				
Ba (mM)				
Ca (mM)		0.29	0.29	0.29
Fe (mM)		0.0008	0.0008	0.0008
Mg (mM)		0.072	0.072	0.072
Mn (mM)		0.00002	0.00002	0.00002
K (mM)		0.136	0.136	0.136
Li (mM)		0.009	0.009	0.009
Na (mM)		1.96	1.96	1.96
Sr (mM)				
Si (mM)		1.07	1.07	1.07
Ti (mM)				
V (mM)				
Cl (mM)		0.18	0.18	0.18
F (mM)		0.11	0.11	0.11
NO ₃ ⁻ (mM)		0.16	0.16	0.16
PO ₄ ³⁻ (mM)				
SO ₄ ²⁻ (mM)		0.19		0.19
0.19				
Alkalinity (meq)		2.34	2.34	2.34
CO ₃ ²⁻ (mM)				
HCO ₃ ⁻ (mM)				
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)				
Total Carbon (mM)				
Ionic Strength				
pH	7	7	7	7
Eh (mV)		700	700	700
Diss. Org C (ppm)				
Pu Solubility (M)	(3±2)E-8	(1.6±0.2)E-6	(8±3)E-6	(3±2)E-5

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1. [NITSCHÉ (1985)]
2. [RAI (1981a)]
3. [RAI (1981b)]
4. [RAI (1980c)]
5. [CLEVELAND (1983c)]
6. [KIM (1983)]

Table 2. Selected Solubilities of Plutonium at pH ≥ 7 (Cont.)

Reference	2 ^a	2	3 ^b	4 ^b
Water Type	Pure	Pure	<0.001 M Cl ⁻	0.0015 M CaCl ₂
Init. Ox. St.	+4;PuO ₂	+4;Pu(OH) ₄	+4;poly	+4;PuO ₂
Temp (°C)				
Al (mM)				
B (mM)				
Ba (mM)				
Ca (mM)				
Fe (mM)				
Mg (mM)				
Mn (mM)				
K (mM)				
Li (mM)				
Na (mM)				
Sr (mM)				
Si (mM)				
Ti (mM)				
V (mM)				
Cl (mM)				
F (mM)				
NO ₃ ⁻ (mM)				
PO ₄ ⁻ (mM)				
SO ₄ ⁻ (mM)				
Alkalinity(meq)				
CO ₃ ²⁻ (mM)				
HCO ₃ ⁻ (mM)				
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)				
Total Carbon (mM)				
Ionic Strength				
pH	7	7	7	7.3
Eh(mV)				
Diss. Org C (ppm)				
Pu Solubility (M)	4E-9	1.4E-7	1.6E-8	2.2E-9

^aMore data at other pH values.

^bMore data at lower pH values.

Table 2. Selected Solubilities of Plutonium at pH ≥ 7 (Cont.)

Reference	4 ^b	4 ^b	5
Water Type	0.0015 M CaCl ₂	0.0015 M CaCl ₂	DC-15(Basalt)
Init. Ox. St.	+4;Pu(OH) ₄	+4;Pu(OH) ₄	+3,+4
Temp (°C)			
Al (mM)			
B (mM)			
Ba (mM)			
Ca (mM)			<.0025
Fe (mM)			0.00537
Mg (mM)			<.04
Mn (mM)			0.00009
K (mM)			0.07673
Li (mM)			
Na (mM)			13.04348
Sr (mM)			0.00011
Si (mM)			1.66389
Ti (mM)			
V (mM)			
Cl (mM)			3.94589
F (mM)			2.73684
NO ₃ ⁻ (mM)			
PO ₄ ³⁻ (mM)			0.00105
SO ₄ ²⁻ (mM)			0.78076
Alkalinity(meq)			2.91800
CO ₃ ²⁻ (mM)			
HCO ₃ ⁻ (mM)			
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)			
Total Carbon (mM)			
Ionic Strength			
pH	7.5	7.7	9.3
Eh(mV)			
Diss. Org C (ppm)			
Pu Solubility (M)	2.6E-8	1.6E-8	\geq E-9

^bMore data at lower pH values.

Table 2. Selected Solubilities of Plutonium at pH ≥ 7 (Cont.)

Reference	5	5	5	5
Water Type	DC-15(Basalt)	Pure	Pure	J-13
Init. Ox. St.	+5,+6	+3,+4	+5,+6	+3,+4
Temp ($^{\circ}$ C)				
Al (mM)				
B (mM)				
Ba (mM)				
Ca (mM)	<.0025			0.24950
Fe (mM)	0.00537			0.00013
Mg (mM)	<.04			0.12341
Mn (mM)	0.00009			0.00002
K (mM)	0.07673			0.10742
Li (mM)				
Na (mM)	13.04348			2.17391
Sr (mM)	0.00011			0.00057
Si (mM)	1.66389			1.16473
Ti (mM)				
V (mM)				
Cl (mM)	3.94589			0.19729
F (mM)	2.73684			0.12105
NO ₃ ⁻ (mM)				
PO ₄ ³⁻ (mM)	0.00105			<.0001
SO ₄ ²⁻ (mM)	0.78076			0.19779
Alkalinity(meq)	2.91800			1.95800
CO ₃ ²⁻ (mM)				
HCO ₃ ⁻ (mM)				
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)				
Total Carbon (mM)				
Ionic Strength				
pH	9.30			7.8
Eh(mV)				
Diss. Org C (ppm)				
Pu Solubility (M)	9.8E-10	9E-11	9.6E-10	4.4E-10

Table 2. Selected Solubilities of Plutonium at pH ≥ 7 (Cont.)

Reference	5	6 ^c	6 ^c
Water Type	J-13	CO ₃ ²⁻ /HCO ₃ ⁻	CO ₃ ²⁻ /HCO ₃ ⁻
Init. Ox. St.	+5,+6	+4;PuO ₂	+4;PuO ₂
Temp (°C)			
Al (mM)			
B (mM)			
Ba (mM)			
Ca (mM)	0.24950		
Fe (mM)	0.00013		
Mg (mM)	0.12341		
Mn (mM)	0.00002		
K (mM)	0.10742		
Li (mM)			
Na (mM)	2.17391		
Sr (mM)	0.00057		
Si (mM)	1.16473		
Ti (mM)			
V (mM)			
Cl (mM)	0.19729		
F (mM)	0.12105		
NO ₃ ⁻ (mM)			
PO ₄ ³⁻ (mM)	<.0001		
SO ₄ ²⁻ (mM)	0.19779		
Alkalinity(meq)	1.95800		
CO ₃ ²⁻ (mM)		3.2E-8	1E-5
HCO ₃ ⁻ (mM)		1.6E-4	1.6E-3
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)			
Total Carbon (mM)			
Ionic Strength			
pH	7.8	7	8
Eh(mV)			
Diss. Org C (ppm)			
Pu Solubility (M)	8.4E-10	4E-6	3.2E-6

^cMore data at other pH values; solutions prepared by adding carbonate and bicarbonate to obtain pH; ionic strength = 1.0.

Table 2. Selected Solubilities of Plutonium at pH ≥ 7 (Cont.)

Reference	6 ^c
Water Type	CO ₃ ²⁻ /HCO ₃ ⁻
Init. Ox. St.	+4; PuO ₂
Temp (°C)	
Al (mM)	
B (mM)	
Ba (mM)	
Ca (mM)	
Fe (mM)	
Mg (mM)	
Mn (mM)	
K (mM)	
Li (mM)	
Na (mM)	
Sr (mM)	
Si (mM)	
Ti (mM)	
V (mM)	
Cl (mM)	
F (mM)	
NO ₃ ⁻ (mM)	
PO ₄ ³⁻ (mM)	
SO ₄ ²⁻ (mM)	
Alkalinity (meq)	
CO ₃ ²⁻ (mM)	1.3E-3
HCO ₃ ⁻ (mM)	2E-2
CO ₃ ²⁻ + HCO ₃ ⁻ (mM)	
Total Carbon (mM)	
Ionic Strength	
pH	9
Eh (mV)	
Diss. Org C (ppm)	
Pu Solubility (M)	3.2E-7

^cMore data at other pH values; solutions prepared by adding carbonate and bicarbonate to obtain pH; ionic strength = 1.0.

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