

SANDIA REPORT

SAND92-0659 • UC-721

Unlimited Release

Printed July 1992

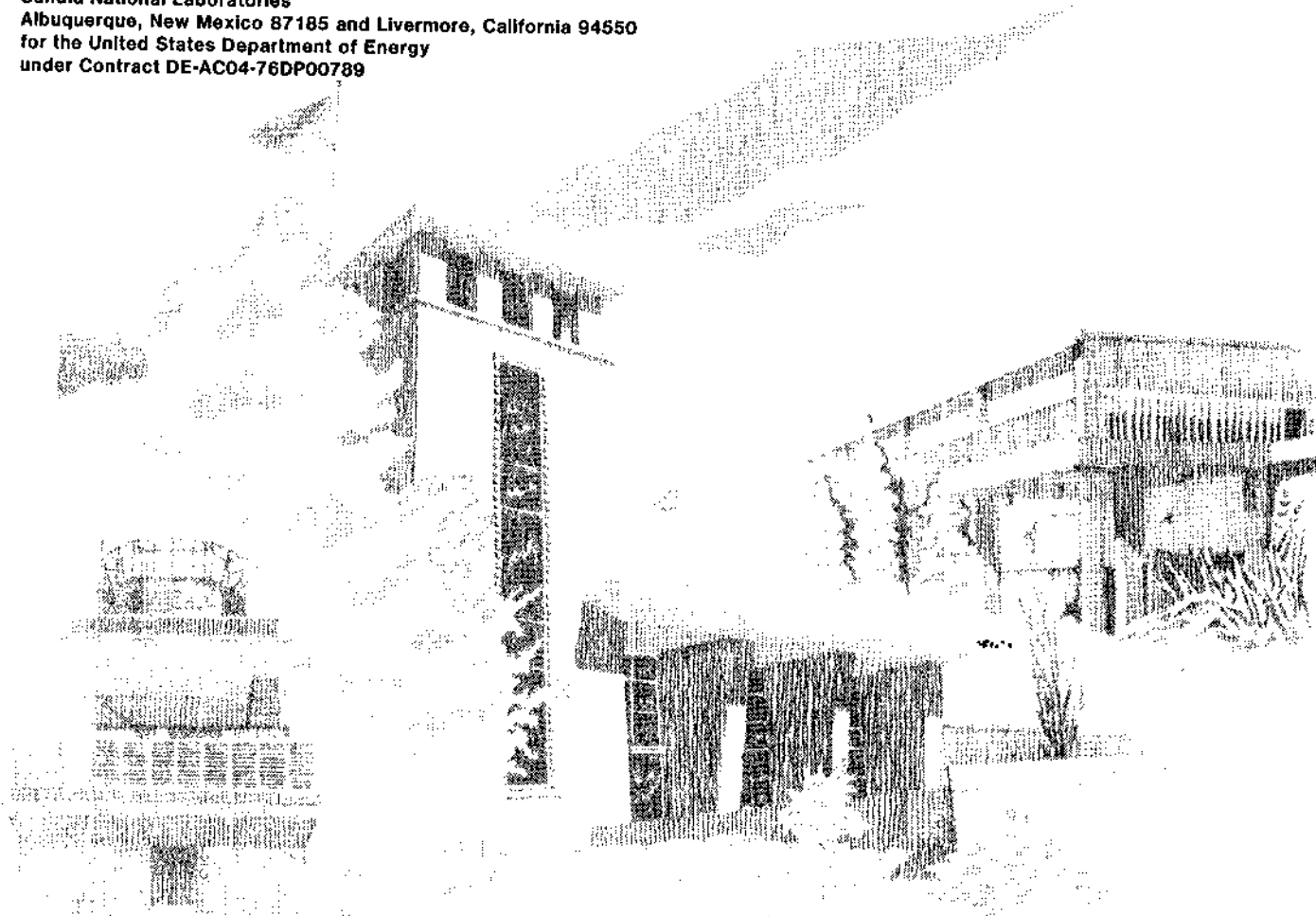
[Handwritten scribbles]

92-0659

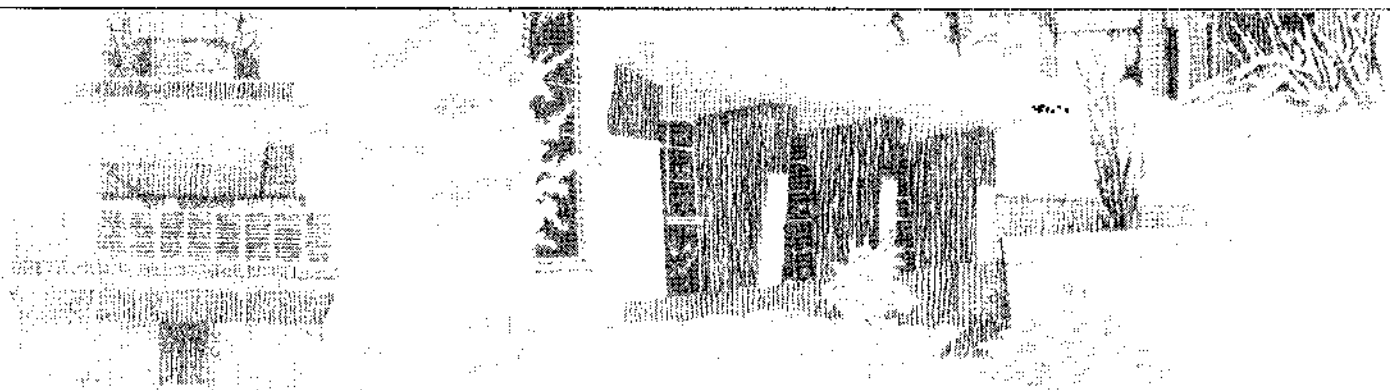
Plutonium Solubility and Speciation Studies in a Simulant of Air Intake Shaft Water from the Culebra Dolomite at the Waste Isolation Pilot Plant

H. Nitsche, K. Roberts, R. C. Gatti, T. Prussin, K. Becraft,
S. C. Leung, S. A. Carpenter, Craig F. Novak

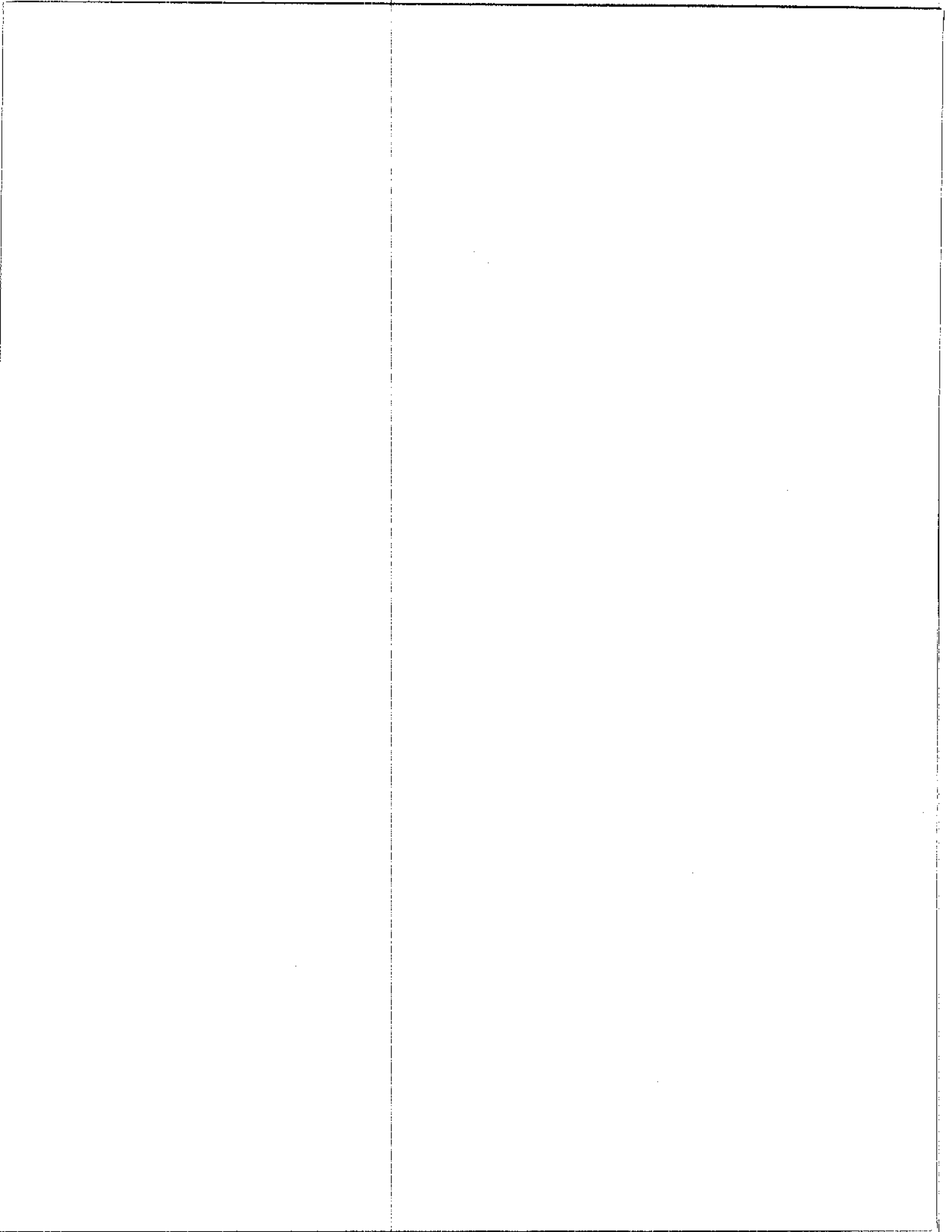
Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-76DP00789



SP 2000078-01



SP 2000078-01



SAND92-0659
Unlimited Release
Printed July 1992

Distribution
Category UC-721

Plutonium Solubility and Speciation Studies in a Simulant of Air Intake Shaft Water from the Culebra Dolomite at the Waste Isolation Pilot Plant*

H. Nitsche, K. Roberts, R.C. Gatti, T. Prussin,
K. Becraft, S.C. Leung, and S.A. Carpenter
Lawrence Berkeley Laboratory
University of California
Earth Sciences Division
Berkeley, California, USA

Craig F. Novak
Fluid Flow and Transport Department 6119
Sandia National Laboratories
Albuquerque, New Mexico, USA

ABSTRACT

The aqueous concentration of a radionuclide is one factor that determines the rate at which the radionuclide might be transported away from a nuclear waste repository should a repository breach occur. This study documents research examining the solubility of plutonium in a brine composition of interest for performance assessment for the Waste Isolation Pilot Plant (WIPP) in southeastern New Mexico. Solutions starting with five different forms of plutonium, Pu(III), Pu(IV), Pu(IV)-polymer, Pu(V), and Pu(VI), were allowed to equilibrate in a brine with composition similar to that measured from the Culebra Member of the Rustler Formation in the Air Intake Shaft to the WIPP. Near-steady-state conditions were reached within a year of reaction time. The resulting concentrations represent an upper bound on the amount of plutonium that can remain dissolved in solution under the experimental conditions (e.g., exclusive of colloids) and can thus be transported with the aqueous phase.

* This work was performed at the Lawrence Berkeley Laboratory for Sandia National Laboratories under Contract No. 40-2516. This report is also published as LBL-30877.

CONTENTS

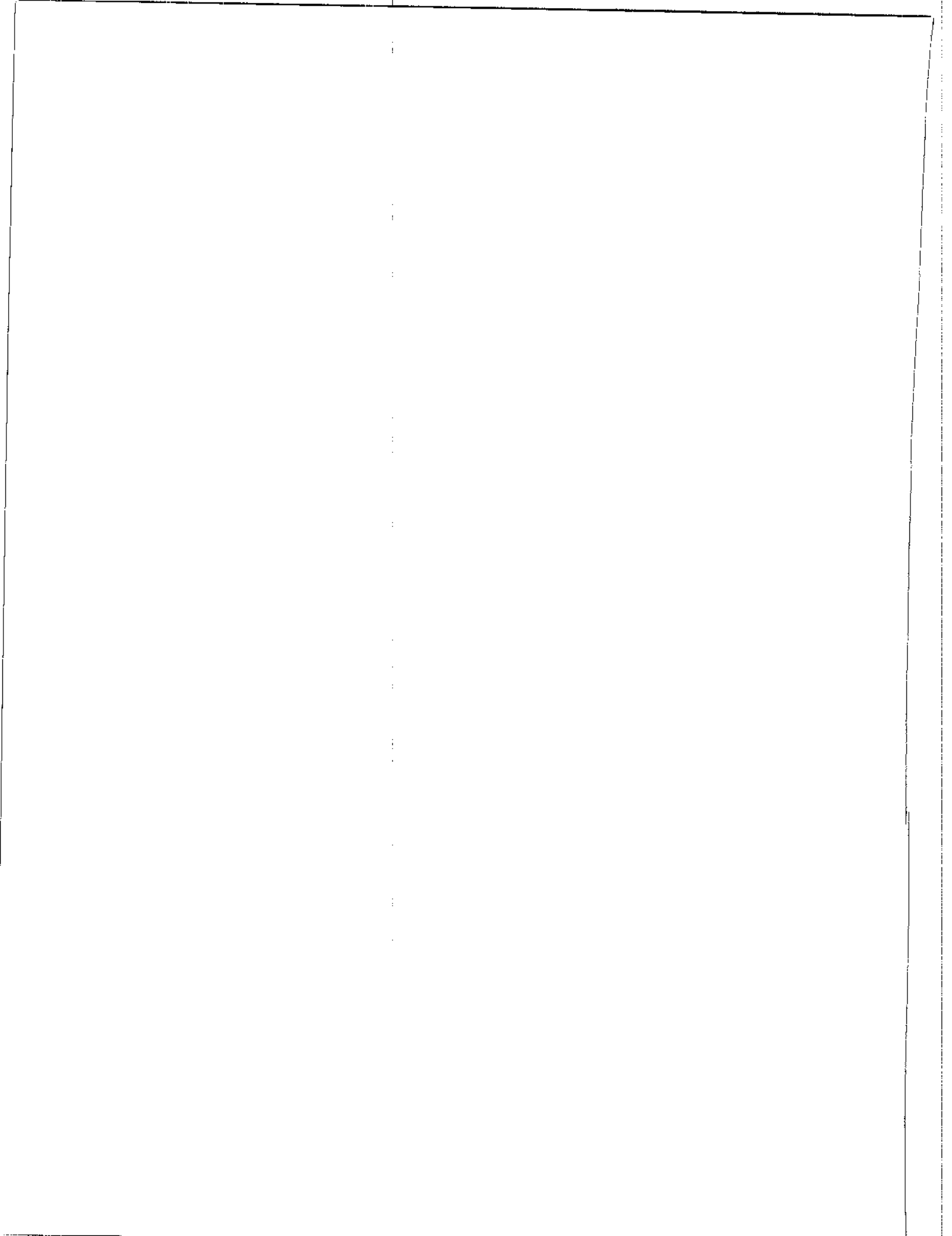
1.	Purpose and Motivation.....	1
2.	Concept of Solubility/Dissolved Concentration Studies.....	3
	2.1 Oversaturation and Undersaturation Experiments	3
	2.2 Phase Separation.....	5
	2.3 Importance of the Solid Phase.....	6
	2.4 Determination of Oxidation States and Speciation.....	7
	2.4.1 Plutonium Oxidation States.....	7
	2.4.2 Plutonium Speciation.....	8
3.	Experimental Details	11
	3.1 Controlled Atmosphere Glove Box	11
	3.2 Water Simulant.....	11
	3.3 Preparation of Experimental Solutions.....	14
	3.3.1 Preparation of Stock Solutions of Plutonium in Single Oxidation States.....	14
	3.3.2 Addition of Stock Solutions to Reaction Vessels	14
	3.4 Phase Separation.....	15
	3.5 Analysis.....	16
	3.6 Oxidation State and Speciation Analysis.....	16
	3.7 Measurement of Oxidation Potential.....	19
	3.8 Identification of Solids.....	19
4.	Results and Discussion	21
	4.1 Dissolved Concentrations	21
	4.2 Oxidation State Determination.....	25
	4.3 Identification of Solids.....	26
5.	Conclusions.....	31
6.	References.....	33

Figures

1.	Solubility of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in sodium chloride solutions.....	4
2.	Filtration experiments, at the beginning of the dissolved concentration experiments, to determine the sorption behavior of different plutonium solutions on Centricon-30 filters.....	17
3.	Filtration experiments, at the end of the dissolved concentration experiments, to determine the sorption behavior of different plutonium solutions on Centricon-30 filters.....	17
4.	Total dissolved plutonium concentrations versus time in AISinR at 25°C for five initial forms of aqueous plutonium.....	21
5.	Time-averaged near steady-state aqueous plutonium concentration in AISinR at 25°C for five different initial forms of aqueous plutonium.....	22
6.	Eh values in AISinR at 25°C for five different initial forms of aqueous plutonium, measured at the conclusion of the experiments.....	23
7.	Results of different separation methods for size determination of Pu(IV)-polymer.....	24

Tables

1.	Composition of synthetic Culebra reference Water AISinR at 25°C.....	12
2.	Required and weighed quantities of chemicals to prepare 1000 mL AISinR brine.....	12
3.	Comparison of elemental concentration of AISinR brine determined by chemical analysis with calculated concentrations.....	13
4.	Methods to determine oxidation states in plutonium solutions.....	18
5.	Steady-state solution concentrations and Eh values for plutonium in AISinR brine simulant at 25°C.....	22
6.	Distribution of plutonium oxidation states in AISinR brine simulant at 25°C before reaching steady state.....	27
7.	Distribution of plutonium oxidation states in AISinR brine simulant at 25°C and steady state.....	27
8.	X-ray powder diffraction patterns of plutonium solid phases formed in AISinR brine simulant solutions at 25°C and pH 7.5 compared with the pattern of PuO ₂	29
9.	X-ray powder diffraction patterns of plutonium solid phases formed in AISinR brine simulant solutions at 25°C and pH 7.5 compared with the pattern of KPuO ₂ CO ₃ and NH ₄ PuO ₂ CO ₃	30



1. PURPOSE AND MOTIVATION

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy facility intended to demonstrate safe containment of transuranic (TRU) nuclear waste. The WIPP is located in Southeastern New Mexico within thick halite beds chosen for geologic stability, low porosity and permeability, and the lack of groundwater in the area. The Culebra Dolomite Member of the Rustler Formation is a water-bearing unit overlying the repository. Hydrologic testing has indicated that the Culebra is the most transmissive unit above the repository (Lappin et al., 1989). Calculations assessing the performance of the repository with respect to environmental regulations indicate that should a repository breach occur (e.g., during prospecting for natural resources), radionuclides might reach the accessible environment through transport in the Culebra (Bertram-Howery et al., 1990).

In the absence of colloids, the rate of transport during groundwater flow is limited by the dissolved concentration of an element in the groundwater. Elements identified as being of particular concern with respect to radionuclide release include americium, Am; neptunium, Np; plutonium, Pu; thorium, Th; and uranium, U (Appendix A in Novak, 1992). Measured groundwater compositions in the Culebra in the vicinity of the WIPP range from dilute potable water through ~3 molal ionic strength brines (Novak, 1992). The solubilities of the elements of concern must be quantified in waters with these compositions to estimate transport rates. Radionuclide dissolved concentrations in brines represent a very specialized system for which little data exist. This report documents efforts to quantify maximum plutonium aqueous concentrations in brine of one composition of interest to the WIPP system. Prior to the work presented in this report, dissolved concentrations for plutonium in WIPP Culebra brines were estimated. This report documents studies measuring aqueous plutonium concentrations, providing hard data for use in further repository performance assessment calculations.

In addition to providing the total dissolved concentration of plutonium, this study also quantifies the oxidation state distribution of the plutonium. Aqueous plutonium can exist as Pu(III), Pu(IV), Pu(V), and Pu(VI), and each of these oxidation states behaves differently with respect to interaction with other dissolved

species and with mineral phases. Information on how plutonium is distributed among its oxidation states is necessary for developing models to describe plutonium behavior in transport systems such as the Culebra. The dissolved concentration provides an upper bound on the transport rates, and the oxidation state distribution goes toward describing how plutonium can interact with the mineral phases to undergo chemical retardation.

Chemical speciation (complexation) is due to interactions among dissolved components. Radionuclides can form complexes with both inorganic and organic constituents of ground waters, although the amount of naturally occurring organic material in the Culebra is negligible. Complex formation can add to the stability of radionuclides in the aqueous phase, increasing the dissolved concentration of radionuclides in solution. Because the aqueous concentration limits the maximum rate at which radionuclides in noncolloidal form can be transported in ground waters, the dissolved concentration limit, and the speciation that causes this limit, is essential knowledge for calculations of repository performance assessment.

2. CONCEPT OF SOLUBILITY/DISSOLVED CONCENTRATION STUDIES

Complete solubility/dissolved concentration experiments should provide detailed knowledge of:

- (1) the nature and chemical composition of the solid controlling the aqueous concentration,
- (2) the concentration of the species in the aqueous phase, and
- (3) the identity and electrical charge of the species in the aqueous phase.

Meaningful, thermodynamically defined dissolved concentration studies must satisfy four criteria:

- (1) equilibrium conditions,
- (2) accurate measurement of solution concentrations,
- (3) a well-defined solid phase, and
- (4) knowledge of the speciation and oxidation state of the soluble species at equilibrium.

Only after these conditions are met can the data be called solubility data, and then, not the solubility of element X, but the solubility of mineral Y in water of composition Z.

The dissolved concentration studies discussed here are empirical in the sense that the results are only strictly applicable at the experimental conditions (e.g., temperature, pressure, compositions, etc.) used for the experiments. Mineral solubilities can vary in a nonlinear fashion, as is illustrated in Figure 1 for gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in sodium chloride solutions (Linke, 1958), so extrapolation and interpolation must be done cautiously. This study provides data applicable to WIPP Culebra-specific conditions—data that did not exist previously.

2.1 Oversaturation and Undersaturation Experiments

The ideal solubility/dissolved concentration experiments approach solution equilibrium from both oversaturated and undersaturated conditions. The approach from oversaturation consists of adding an excess amount of an element in dissolved form to an aqueous solution of the composition under study, and then monitoring the precipitation of insoluble material until equilibrium is reached.

The precipitate is then isolated and characterized. The approach from undersaturation consists of dissolving a well defined solid in an aqueous solution of the composition under study until equilibrium is reached. In both cases, the solution concentration is measured as a function of time.

Chemical kinetics controls the rate of approach to equilibration in dissolved concentration experiments. Some solutions equilibrate rapidly, while others equilibrate slowly. Equilibrium conditions are demonstrated experimentally for both oversaturation and undersaturation experiments by monitoring the solution concentration as a function of time until the concentrations remain constant. Because this assumption is based on judgment, the term "steady state" instead of "equilibrium" is more precise. The U.S. Nuclear Regulatory Commission defines "steady state" as "the conditions where measurable changes in concentrations are not occurring over practical experimental times" (Brooks and Corrado, 1984). At steady state as defined above, thermodynamic forces may still change the solution composition, and solids may become less soluble as they change from a disordered, amorphous, or metastable state with higher free energy to an ordered or crystalline state with lower free energy. The changes can occur very slowly and may require very long or even infinite experimental times. Even if equilibrium is not reached, time-limited laboratory supersaturation experiments

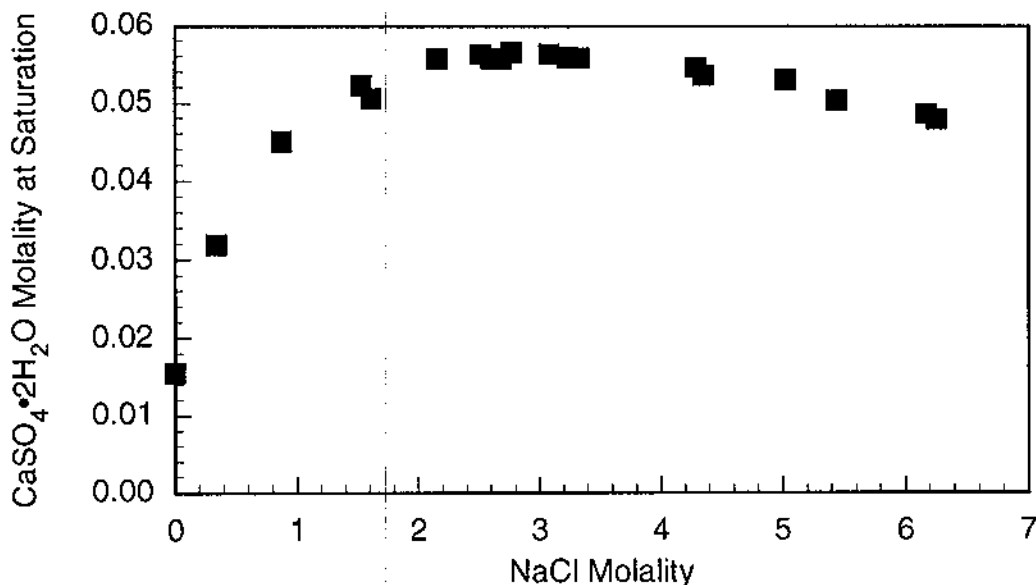


Figure 1. Solubility of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in sodium chloride solutions.

can supply valuable information by providing good estimates on the upper limit of radionuclide dissolved concentrations. Because supersaturation experiments approach the equilibrium concentration from above, measured steady-state concentrations are higher than the equilibrium concentrations.

The combined results from supersaturation and undersaturation experiments should bracket the equilibrium concentration. Supersaturation experiments provide the upper bound, while undersaturation experiments provide a lower bound for the dissolved concentration. For systems in which the solubility-controlling mineral is unknown, oversaturation experiments will precipitate solubility-controlling minerals. These minerals would then be characterized and synthesized for use in confirmatory experiments that approach steady state from undersaturation. This procedure allows undersaturation experiments to be conducted without any bias or preconception about which minerals control the dissolved concentration. Results from oversaturation experiments are reported in this study.

2.2 Phase Separation

Effective separation of the aqueous and mineral phases is essential for obtaining meaningful values for dissolved concentrations, yet this often represents a significant practical problem. Incomplete phase separation and/or sorption of solute during and after the separation can result in high or low values for dissolved concentrations. Incomplete phase separation (leaving some of the solid with the solution phase) leads to erroneously high radionuclide dissolved concentrations, while sorption onto filters and/or container walls results in erroneously low dissolved concentrations.

The solids and solutions are separated by differences in size via filtration, or by differences in density through sedimentation and/or centrifugation. Filtration is the more commonly applied technique. Ultrafiltration using membranes that pass particles with $\leq 0.1 \mu\text{m}$ effective radius can effectively remove solids and larger colloidal particles from aqueous solution. However, dissolved species can sorb on ultrafiltration membranes. Effective filters for dissolved concentration studies must pass soluble species quantitatively; that is, either the filter should have no active sorption sites, or all sorption sites must be

occupied with the potentially sorbing species so that no additional sorption will occur. Acceptable filters will have a small enough pore size to retain the solids and colloids and will show no sorption or minimal sorption during multiple filtrations.

The sorptive sites on filters and filter housings are usually blocked by preconditioning these materials. Preconditioning is accomplished by filtering a volume of solution and then discarding the filtrate. The volume required for prefiltration is determined experimentally as follows. Normally, 500 microliters are filtered, and the filtrate is collected and acidified to minimize sorption in the collection container. The concentration of the species of interest (plutonium in this case) in the filtrate is determined. Another fixed volume is filtered through the same filter, collected, and assayed, and this procedure is repeated until the assayed filtrate concentration is constant. The volume necessary to block sorption sites and thus precondition the filter is the cumulative volume filtered until the assay concentration remains constant. Because sorption of soluble radionuclide species on filters can depend on the solution pH and the species in solution, it is essential to verify that possible sorption sites are indeed blocked when experimental conditions change.

Experimental details about the filters are given in Section 3.4.

2.3 Importance of the Solid Phase

Dissolved concentrations are controlled by the solubility of the equilibrium solid phase. Thermodynamically meaningful results require the existence of a well defined solid phase, which ideally consists of crystalline material. The solids formed from oversaturation tests must be unambiguously identified through physical and/or chemical characterization methods if they are to be synthesized for use in dissolved concentration experiments from undersaturated conditions. Radionuclide solids formed in laboratory experiments and in nature are often amorphous precipitates that are thermodynamically ill-defined. However, most amorphous solids become more crystalline with time. Freshly precipitated microcrystalline solids can also convert in time to a macrocrystalline material. Improved bonding at the lattice surface results in decreasing surface area. Thus, the crystalline solid of higher free energy changes to one of lower free energy

(Ostwald ripening, Ostwald step rule) and become less soluble (Enüstün and Turkevich, 1960; Voorhees, 1985; Morse and Casey, 1988; Rard, 1989).

2.4 Determination of Oxidation States and Speciation

2.4.1 Plutonium Oxidation States

The oxidation state of an element refers to the number of electrons gained or lost relative to a defined reference state. Some elements have only one oxidation state in solution, others have several. The reference state for plutonium is plutonium metal, Pu^0 or $\text{Pu}(s)$. Aqueous plutonium occurs in four different oxidation states: Pu(III), Pu(IV), Pu(V), and Pu(VI), represented by aqueous species such as Pu^{3+} , Pu^{4+} , PuO_2^+ , and PuO_2^{2+} , respectively. There is also a polymeric form of plutonium, Pu(IV)-polymer, that can exist in solution. Plutonium is unusual in that all aqueous plutonium oxidation states have comparable redox potentials, meaning that the conversion from one oxidation state to another is relatively easy. As a consequence, it is possible for all four plutonium oxidation states to exist in solution at the same time.

Knowledge of oxidation states is important because the charge on an ion determines in part the affinity of that ion for the mineral phase, and it is this affinity that determines chemical retardation in a transport system. Also, the knowledge of the oxidation state distribution is essential for developing and confirming conceptual models of the behavior of aqueous plutonium and developing mathematical descriptions of this behavior.

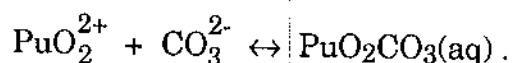
Oxidation states in solution are commonly determined by ion exchange chromatography, solvent extraction, coprecipitation, or electrochemistry. These methods detect oxidation states indirectly, and can detect concentrations as small as 10^{-10} Molar and below, making them useful for radionuclide dissolved concentration studies. Solvent extraction and coprecipitation are often used successfully to determine the oxidation states of ions present in very low concentration (Nitsche et al., 1988). Ion exchange chromatography can be less reliable because the exchange resin may reduce the ions in solution, giving the wrong results for the oxidation state distribution. Electrochemical methods identify individual ions by measuring the electrical potential required to reduce or

oxidize the ions. Electrochemistry works best for oxidation or reduction reactions that are thermodynamically reversible and have fast reaction kinetics. Because many radionuclide oxidation/reduction reactions are irreversible and slow (e.g., the reactions of $\text{PuO}_2^+/\text{Pu}^{4+}$), the utility of electrochemical techniques for determining radionuclide oxidation states in these experiments is limited.

In the studies documented in this report, the oxidation states of plutonium species in solution were determined by a solvent extraction and coprecipitation technique (Nitsche et al., 1988).

2.4.2 Plutonium Speciation

The speciation of plutonium in solution refers to the complexation of the various plutonium oxidation states with other solution constituents. For example, the plutonyl ion, PuO_2^{2+} , can react with carbonate, CO_3^{2-} , to form a plutonylcarbonato species as given by the reaction



Speciation, like oxidation state distribution, is a controlling factor in transport behavior because it influences both the forms of plutonium in solution and the extent to which the plutonium can interact with the mineral phases and thus undergo chemical retardation. As in the case of oxidation state distribution, knowledge of aqueous speciation is essential for developing and confirming conceptual models of the behavior of aqueous plutonium and developing mathematical descriptions of this behavior.

The speciation of elements in solution is commonly determined by adsorption spectrophotometry. Most aqueous plutonium species with concentrations greater than $\sim 10^{-5}$ M can be detected by absorption spectrophotometry. Because the aqueous plutonium concentrations observed in dissolved concentration studies are usually lower than this limit, application of spectrophotometry for speciation determination is generally not possible for these experiments. Photoacoustic spectroscopy (PAS) provides much greater sensitivity, approaching 10^{-8} to 10^{-9} M (Stumpe et al., 1984; Ewart et al., 1988; Cross et al., 1989; Torres et al., 1989; Doxtader et al., 1987). Both conventional

spectrophotometry and photoacoustic spectroscopy measure the energy absorbed when light passes through a sample; the difference between the methods lies in the means for measuring the absorbed energy. Spectrophotometry compares the light intensity of a beam passing through the sample with a beam passing through a reference solution. PAS measures the pressure wave in solution caused by the absorption of energy. This pressure wave is generated when excited 5^n electrons in dissolved actinide ions undergo non-radiative decay to the ground state; the pressure is proportional to the absorbed energy. The majority of aqueous plutonium concentrations in this and other WIPP brine simulants under study by Nitsche and coworkers is too low to be detected by conventional spectrophotometry but could be detected by using photoacoustic spectroscopy.

3. EXPERIMENTAL DETAILS

This section discusses the experimental details of conducting the dissolved concentration studies, including the composition of the brine simulant, preparing the plutonium stock solutions, etc.

3.1 Controlled Atmosphere Glove Box

Actinide elements such as plutonium pose a radiation hazard, requiring all experimental work to be performed in glove boxes. Because control of the external carbon dioxide gas composition was also part of the experimental protocol, all experiments were conducted in a controlled-atmosphere glove box.

3.2 Water Simulant

The composition of the synthetic brine used in these experiments, given in Table 1, is based on chemical analyses of brine taken from the Culebra Dolomite Member of the Rustler Formation in the AIS (Appendix B in Novak, 1992). The measured brine composition was modified by addition of $\text{CO}_2(\text{g})$ until the solution was in equilibrium with calcite, $\text{CaCO}_3(\text{s})$. The calcium concentration was then reduced by 25% to minimize the possibility for gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$, or calcite precipitation. These calculations were done assuming a temperature of 16.6°C (although the experiments were conducted at 25°C) using the computer code PHRQPITZ (Plummer et al., 1988) by M.D. Siegel of Sandia National Laboratories. The resulting brine composition was given the name Air Intake Shaft in-situ Reference brine (AISinR).

One liter of AISinR was prepared using weighed amounts of the analytical grade reagents $\text{KCl}(\text{s})$, $\text{NaCl}(\text{s})$, $\text{CaCl}_2(\text{s})$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$, $\text{Na}_2\text{SO}_4(\text{s})$, $\text{NaHCO}_3(\text{s})$, and $\text{H}_3\text{BO}_4(\text{s})$. The calculated quantities required and the weighed amounts are shown in Table 2. $\text{Na}_2\text{SO}_4(\text{s})$, $\text{CaCl}_2(\text{s})$, and $\text{NaCl}(\text{s})$ were dried for six hours at 110°C before use. The chemicals were dissolved in deionized-distilled water to make 1000 mL solution. The solution was filtered through a $0.05 \mu\text{m}$ filter membrane (Nuclepore Corporation, Pleasanton, CA). All operations were carried out in a glove box under inert (argon) atmosphere.

Table 1. Composition of Synthetic Culebra Reference AlSinR brine at 25°C

	Molarity	g/L	ppm
Ca ²⁺	0.0171	0.6854	685.4
Mg ²⁺	0.0215	0.5226	522.6
Na ⁺	0.6434	14.792	14792
K ⁺	0.0082	0.321	321
Cl ⁻	0.5678	20.130	20130
SO ₄ ²⁻	0.0796	2.552	255.2
B	0.00279	0.0316	30.16
TIC (total inorganic carbon), as HCO ₃	0.00178		
pH = 7.46			
log(p _{CO2(g)} , ATM) = -2.707			
Ionic Strength = 0.844 molal			

Table 2. Required and Weighed Quantities of Chemicals to Prepare 1000 mL AlSinR Brine

	Required (g)	Weighed (g)
NaHCO ₃	0.1495	0.1480 ± 0.0004
NaSO ₄	11.31	11.31 ± 0.01
H ₃ BO ₄	0.1731	0.1725 ± 0.0004
KCl	0.6103	0.6110 ± 0.0004
NaCl	28.19	28.19 ± 0.01
CaCl ₂	1.90	1.8990 ± 0.0004
MgCl ₂ · 6H ₂ O	4.37	4.3710 ± 0.0004

Samples of AISinR were analyzed by induced coupled plasma with atomic emission spectroscopy (ICP-AES) analysis (Plasma Spectrometer, Applied Research Lab Inc., Model 3510) to determine the actual solution composition. These results are compared with the target concentrations for the AISinR brine in Table 3.

Table 3. Comparison of Elemental Concentration of AISinR Brine Determined by Chemical Analysis with Calculated Concentrations

	Calculated (ppm)	Analysis (ppm)
Ca	685.4	613.2 ± 61
Mg	522.6	576.0 ± 5.8
Na	14792	14613 ± 438
K	321	307.7 ± 154*
S	2552	2561 ± 127
B	30.16	28.4 ± 1.4

* high error due to nonoptimal concentration range for potassium to optimize the accuracy for all other elements

Because the concentration of total inorganic carbon (TIC) in solution can change in response to the carbon dioxide content of gas over the solution, special care was taken to preserve the intended TIC concentration of AISinR. This was accomplished by equilibrating the solutions with gas mixtures of 1963 ± 27 ppm CO_2 . In addition to carbon dioxide, the gas mixtures contained $20.9 \pm 0.1\%$ oxygen, with the balance made up of argon. Thus, the experiments were conducted in an oxidizing environment. The AISinR equilibrated with the gas had a measured operational pH of 7.47. The hydrogen concentration, or p cH , had a value 0.42 ± 0.09 units higher than the measured operational pH, determined spectrophotometrically with phenol red using the methods reported by Robert-Baldo et al., (1985). The dissociation constant for phenol red in AISinR brine necessary for this procedure was determined by potentiometric titration to be $\text{pK} = 7.94 \pm 0.21$.

3.3 Preparation of Experimental Solutions

3.3.1 Preparation of Stock Solutions of Plutonium in Single Oxidation States

The ^{239}Pu stock solution was prepared by dissolving plutonium metal in 6 M hydrochloric acid, HCl. The solution was purified from possible metal contaminants by anion exchange chromatography. The purity of the stock solution was tested by spark emission spectroscopy and no contaminants were present above the detection limit of the method, which ranges from less than 1 to less than 0.01 weight percent. The oxidation states Pu(III), Pu(IV), Pu(V), and Pu(VI) were prepared by electrochemical adjustment of the plutonium stock solution (Cohen, 1961a; Newton et al., 1986). The presence of a single oxidation state was verified by absorption spectrophotometry (Cohen, 1961b). Before use, all stock solutions were filtered through 0.22 μm polyvinylidene difluoride syringe filter units (Millipore Corporation, Bedford, MA) to remove possible suspended particles (e.g., dust or silica) that could sorb the plutonium to form pseudocolloids.

The Pu(IV) polymer solution was prepared by precipitating plutonium(IV) from an acidic solution with sodium hydroxide, NaOH. The hydroxide precipitate was dissolved in 1 M HCl, reprecipitated and dissolved again in 1 M HCl. The pH was adjusted to ~ 2.5 by dilution with water. An adsorption spectrum of the solution showed the presence of polymer and ionic plutonium. The Pu(IV) polymer was separated from the ionic plutonium using a cation exchange column, which traps the ionic species while allowing the uncharged polymer to run through the column. The polymer was then sized by filtration through a 220 nm pore-size filter. The sole presence of Pu(IV) polymer in the filtrate was verified by adsorption spectrophotometry.

3.3.2 Addition of Stock Solutions to Reaction Vessels

The equilibration vessels were 90 mL Teflon perfluoralkoxy (PFA) cells (Saville Corporation, Minnetonka, MN) with ports at the top to accommodate a pH electrode, a 1/16"-diameter Teflon line for the gas mixture, and an opening for

withdrawing samples. Five individual reaction vessels were prepared to accommodate the five forms of plutonium stock solution to be studied.

Approximately 0.5 to 1 mL of each stock solution was added to 70 mL AISinR at the start of the experiment. To compensate for the change in pH caused by the addition of the acid plutonium stock solutions, a small amount of CO₂(g)-free sodium hydroxide solution was added to the AISinR in the reaction vessels just before the plutonium stock solutions were added. The experiment was performed in this way so that concentrated base would not need to be added after plutonium was already in each reaction vessel. The addition of strong base to a solution containing plutonium can result in unpredictable and irreversible microprecipitation and formation of microcolloids, a situation to be avoided. The operational pH of the solubility solutions was maintained at 7.47 ± 0.10 unit, measured twice weekly using Ross combination glass electrodes (Orion Research Incorporated, Boston, MA). The electrodes were calibrated with NIST traceable standard buffers of pH 7 and 10. When required, the pH in the reaction vessels was adjusted with small amounts (usually between 30 and 300 μ L) of dilute (0.05-0.1 M) HCl or NaOH solutions. The electrodes were removed from the plutonium solutions after each pH measurement.

3.4 Phase Separation

Sampling aliquots of the solution phases were withdrawn, suspended/colloidal material was separated, and the remaining aqueous phase was analyzed for dissolved plutonium. Samples were withdrawn periodically to obtain dissolved concentration data as a function of time and to show the approach to steady state.

As discussed in Section 2.2, the efficiency of phase separation can have a large impact on measured dissolved concentrations. To study phase separation within the context of these experiments, Centricon-30 centrifugal filters (Amicon Corporation, Danvers, MA) were used to separate the phases of the plutonium solutions. The filters contain a YM-type membrane with a calculated pore size of 4.1 nm. To minimize possible plutonium absorption on the filters, the filters were presaturated with the solution to be separated. Filters were tested for plutonium sorption by filtering 500 μ L aliquots of the test solution and counting the filtrates

until a total volume of 2000 μL had passed through the filter. The results of these tests, conducted soon after experiment initiation, are shown in Figure 2 and at the end of the experiments in Figure 3. It is important to perform these tests at different times because the plutonium sorption behavior may change due to changes in plutonium speciation. Because the plutonium concentration did not increase with increasing filtered volume, negligible sorption on the filters can be assumed. Sorption onto the filters would be indicated by increasing concentrations with increasing filtered volumes. Routine separations were carried out by presaturating the filters with 500 μL of solution.

3.5 Analysis

The solution and the solid phases were separated and analyzed independently. Concentration measurements of the aqueous portions were made by counting with either a germanium low-energy counting system of LBL design, or with a liquid scintillation counter (Pharmacia LKB Nuclear Incorporated, Gaithersburg, MD, Model Rackbeta 1219).

With the germanium counter, plutonium was analyzed for the uranium *L* x-rays coming from the α -decay of the plutonium. Possible contributions to the *L* x-rays from the decays of other radionuclides, also present in small amounts, were corrected by subtraction (Nitsche et al., 1991). (When plutonium decays to uranium through α -decay, the uranium formed is in an excited state. The internal rearrangement of the electrons of the uranium atom to a more stable configuration releases the characteristic *L* x-rays.)

The liquid scintillation counter (LSC) can discriminate between possible β -emitting solution contaminants and the plutonium α -radiation. The LSC was calibrated with plutonium standard solutions that had compositions similar to the plutonium assays.

3.6 Oxidation State and Speciation Analysis

Table 4 lists the methods used to determine the distribution of plutonium oxidation states. Each of the five methods was carried out independently of the

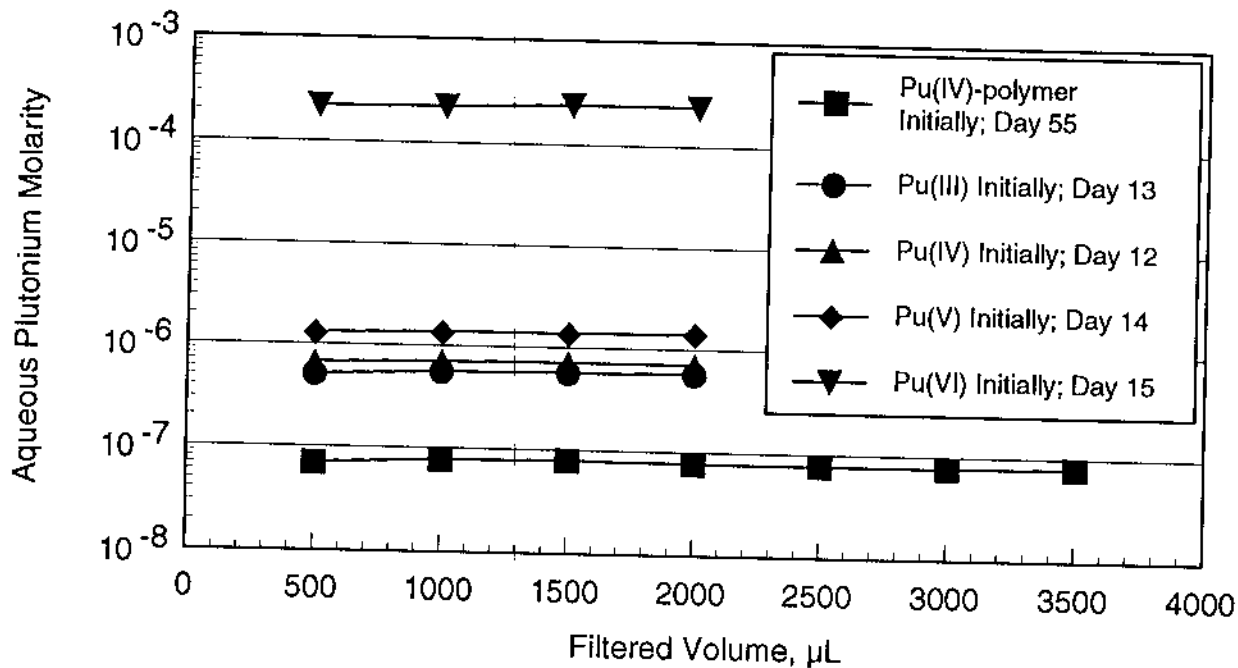


Figure 2. Filtration experiments, at the beginning of the dissolved concentration experiments, to determine the sorption behavior of different plutonium solutions on Centricon-30 filters.

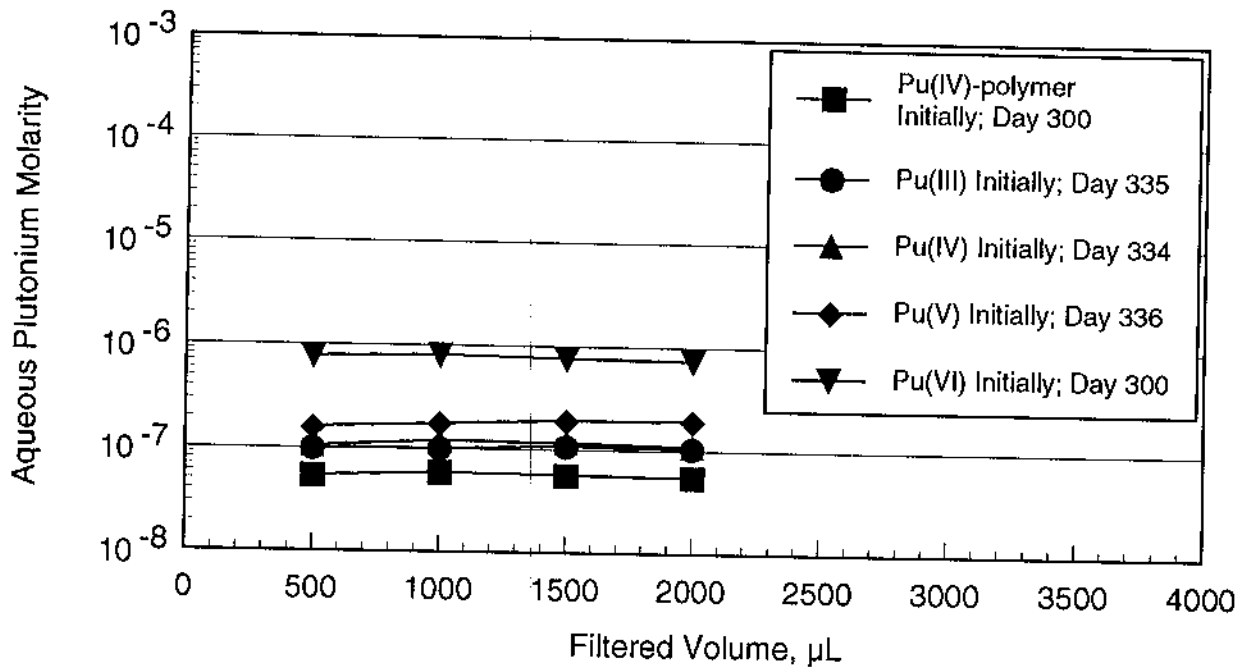


Figure 3. Filtration experiments, at the end of the dissolved concentration experiments, to determine the sorption behavior of different plutonium solutions on Centricon-30 filters.

Table 4. Methods to Determine Oxidation States in Plutonium Solutions

Method	Oxidation State Distribution	
	Organic Phase	Aqueous Phase
TTA* extraction at pH = 0	+4	+3, +5, +6, Pu(IV) polymer
TTA extraction at pH = 0 with Chromate	+3, +4	+5, +6, Pu(IV) polymer
HDEHP† extraction at pH = 0	+4, +6	+3, +5, Pu(IV) polymer
HDEHP extraction at pH = 0 with Chromate	+3, +4, +5, +6	Pu(IV) polymer
LaF ₃ precipitation with Chromate	+3, +4, Pu(IV) polymer in precipitate	+5, +6 in supernatant

* thenoyltrifluoroacetone
† di(2-ethylhexyl)phosphoric acid

others. These methods were successfully tested on 3.5 M NaCl solutions containing plutonium in known oxidation states (adjusted electrochemically) at concentrations of 10^{-4} M and 10^{-7} M. Combining the individual results yields the amount of each oxidation state present in each solution. The oxidation state determination for each plutonium solution required that 33 samples be counted in the LSC including standards and background blank, a total of 165 LSC samples for a complete experiment.

Much time was spent in setting the parameters on the LSC to accommodate counting samples from the plutonium oxidation state determination. This was necessary because the different chemical components of the samples cause quenching and shift the plutonium alpha spectra.

Difficulties were experienced with the above scheme for determining plutonium oxidation states at the conclusion of the AISinR experiments. Some of the extractions that used dichromate as an oxidant produced unusable results for various reasons. First, with time the dichromate is reduced to Cr(III), which has a very deep green color that caused tremendous quenching problems for liquid scintillation counting of plutonium samples. Second, the dichromate appears to have oxidized some Pu(IV) to Pu(VI) during the separation. Third, the extractant thenoyltrifluoroacetone (TTA) was found to be sensitive to oxidants such as dichromate. This is a difficult problem to solve because it requires either finding a colorless oxidant strong enough to oxidize Pu(III) to Pu(IV) and Pu(V) to Pu(VI) in a relatively short time while not oxidizing Pu(IV) to Pu(VI), or finding a new separation scheme that does not require the use of an oxidant. The dichromate method worked in 3.5 M NaCl solutions without carbonate or other ligands present yet did not work in AISinR at the conclusion of the experiments.

3.7 Measurement of Oxidation Potential

At the end of each solubility experiment, the oxidation potential, E_h , of each solution was measured with a platinum electrode versus a Ag/AgCl/saturated NaCl reference. The platinum electrode was cleaned with 6 M nitric acid before and after each measurement. Readings were stable within 30 to 60 minutes. The electrode setup was checked with "Zobell's Solution" before and after each measurement (Garrels, 1960; Langmuir, 1971).

3.8 Identification of Solids

The solid compounds were analyzed by x-ray powder diffraction measurements. A few micrograms of each actinide precipitate were placed in a 0.33-mm diameter quartz capillary tube, and the tube was sealed with an oxybutane microtorch. The tube was mounted in an 11.46-cm diameter Debye-Scherrer camera and then irradiated with x-rays from a Norelco III x-ray generator (Phillips Electronics, Inc.). Copper K_α radiation filtered through nickel was used.

4. RESULTS AND DISCUSSION

4.1 Dissolved Concentrations

Results of the plutonium dissolved concentration studies are shown in Figure 4. The plutonium was initially introduced as Pu(III), Pu(IV), Pu(V), Pu(VI), and Pu(IV) polymer to AISinR. The steady-state concentrations and the solutions Eh values are given in Table 5 and plotted in Figures 5 and 6,

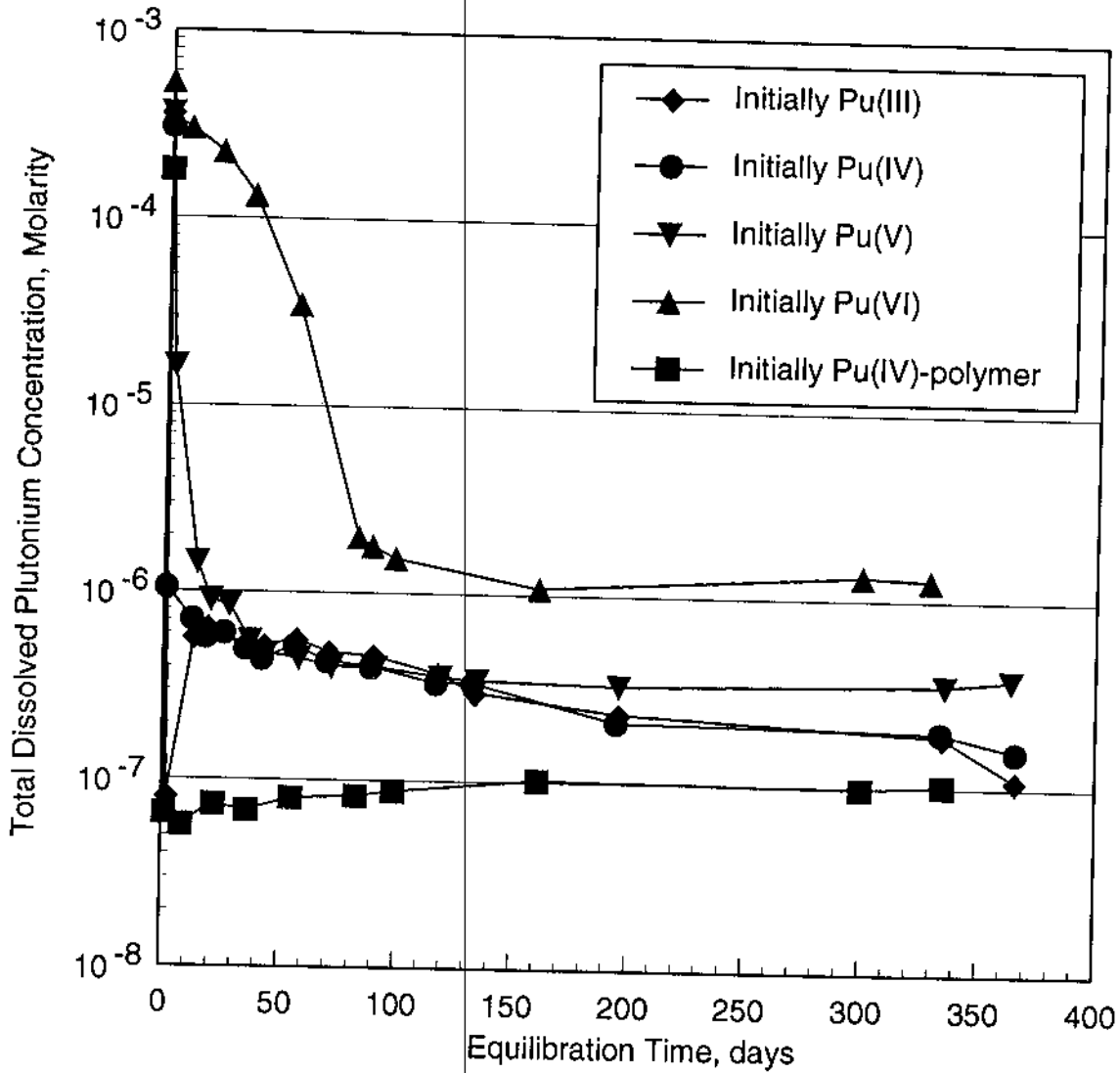


Figure 4. Total dissolved plutonium concentrations versus time in AISinR at 25°C for five initial forms of aqueous plutonium.

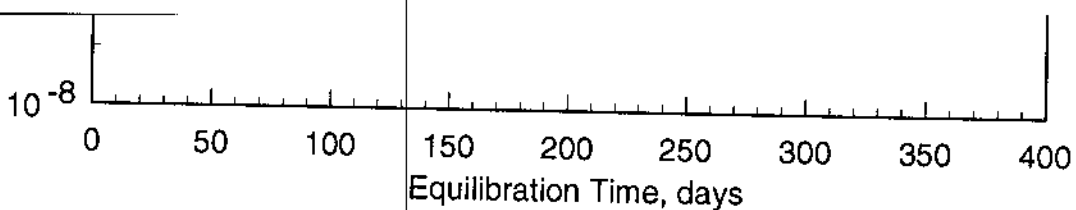


Figure 4. Total dissolved plutonium concentrations versus time in AISinR at 25°C for five initial forms of aqueous plutonium.

Table 5. Steady-State Solution Concentrations and Eh Values for Plutonium in AlSinR Brine Simulant at 25°C

Initial Oxidation State	pH	Concentration (M)	Eh (mV)
Pu ³⁺	7.45 ± 0.11	(3.75 ± 1.58) × 10 ⁻⁷	431 ± 15
Pu ⁴⁺	7.45 ± 0.11	(3.54 ± 1.29) × 10 ⁻⁷	401 ± 15
PuO ₂ ⁺	7.45 ± 0.09	(3.88 ± 0.48) × 10 ⁻⁷	427 ± 15
PuO ₂ ²⁺	7.46 ± 0.04	(1.24 ± 0.13) × 10 ⁻⁶	417 ± 15
Pu(IV) polymer	7.45 ± 0.04	(8.21 ± 1.60) × 10 ⁻⁸	439 ± 15

respectively. The individual measurements are listed in Appendix A. The concentration errors are 2σ overall errors including errors due to multiple pipettings, counter calibrations, and counting statistics. The Eh values were measured to supply future chemical modeling efforts with a reference value. Without modeling, however, the Eh measurements are only of limited value

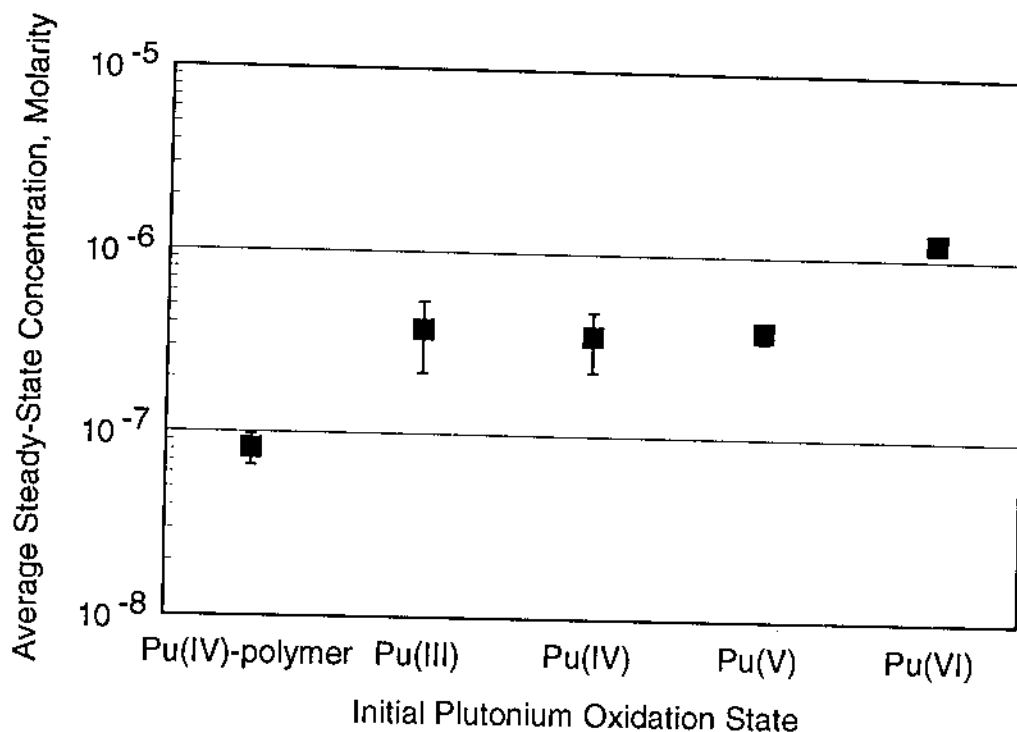


Figure 5. Time-averaged near steady-state aqueous plutonium concentration in AlSinR at 25°C for five different initial forms of aqueous plutonium.

because they may represent a combination of many different reduction-oxidation (redox) reactions for each solubility experiment.

As Figure 4 shows, the aqueous plutonium concentrations in the solutions initially containing Pu(III), Pu(IV), and Pu(V) decrease steadily with time, but no real steady-state conditions were reached even after more than 360 days. However, the changes between two adjacent plutonium concentration measurements are relatively small. Therefore, the upper limit of dissolved concentration was determined by averaging the concentration data collected between days 36 and 366 for Pu(III), between days 35 and 365 for Pu(IV), and between days 44 and 364 for Pu(V). Considering the error intervals of the average values, the plutonium shows the same dissolved concentration for these three solutions, $\sim 3.7 \cdot 10^{-7}$ M, as shown in Figure 5. The plutonium solubility of the solution initially containing Pu(VI) is about a factor of three higher than the above mentioned solutions. Again, no real steady-state conditions were reached after 329 days. For the first 36 days, the plutonium concentration remained high at

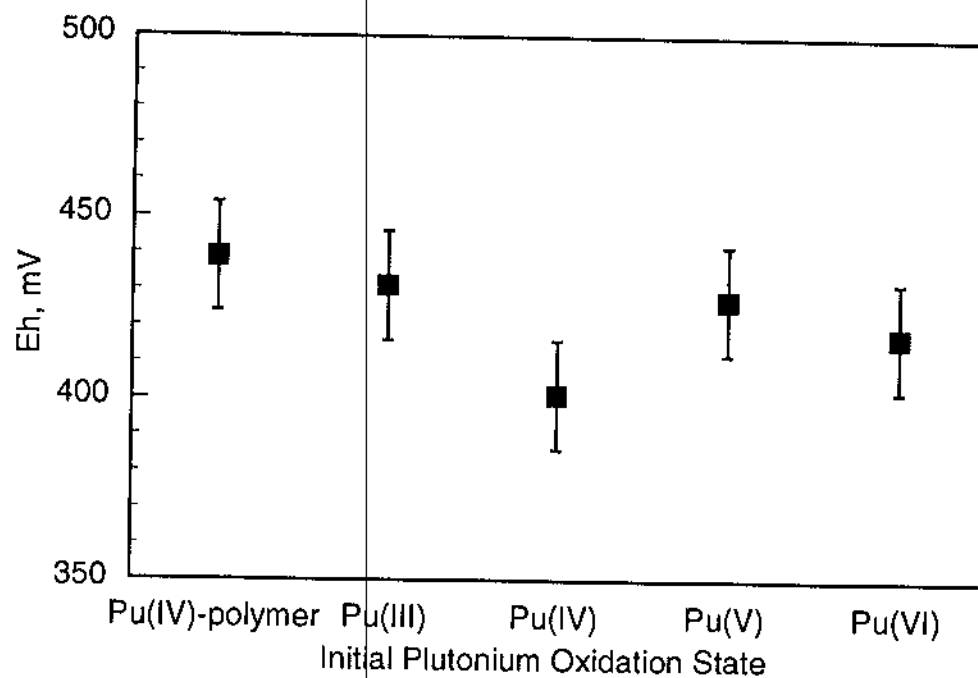


Figure 6. Eh values in AISinR at 25°C for five different initial forms of aqueous plutonium, measured at the conclusion of the experiments.

about $2 \cdot 10^{-4}$ M, but then dropped within fifty days by about two orders of magnitude. After this, the concentration decreased much more slowly. The average solubility value, $\sim 1.2 \cdot 10^{-6}$ M, was calculated from the measurements taken between 161 and 329 days of reaction time.

The plutonium(IV) polymer solution showed the lowest dissolved concentration, $8 \cdot 10^{-8}$ M, and did not significantly vary in concentration over the course of the experiment. The size of the Pu(IV) polymer after 37 days was determined by comparing the concentration remaining in solution after phase separation by three different methods: gravity settling, centrifugation, and filtration. The results in Figure 7 show that most of the Pu(IV) polymer was sedimented by centrifugation under these conditions and is estimated to be larger than about $0.1 \mu\text{m}$ (Svedberg and Pederson, 1940). Only a small fraction of the Pu(IV)-polymer was in the 4-100-nm size range, with the rest of the polymer fraction remaining in solution, which by the definition used in this study means material that passes through a 4.1-nm filter.

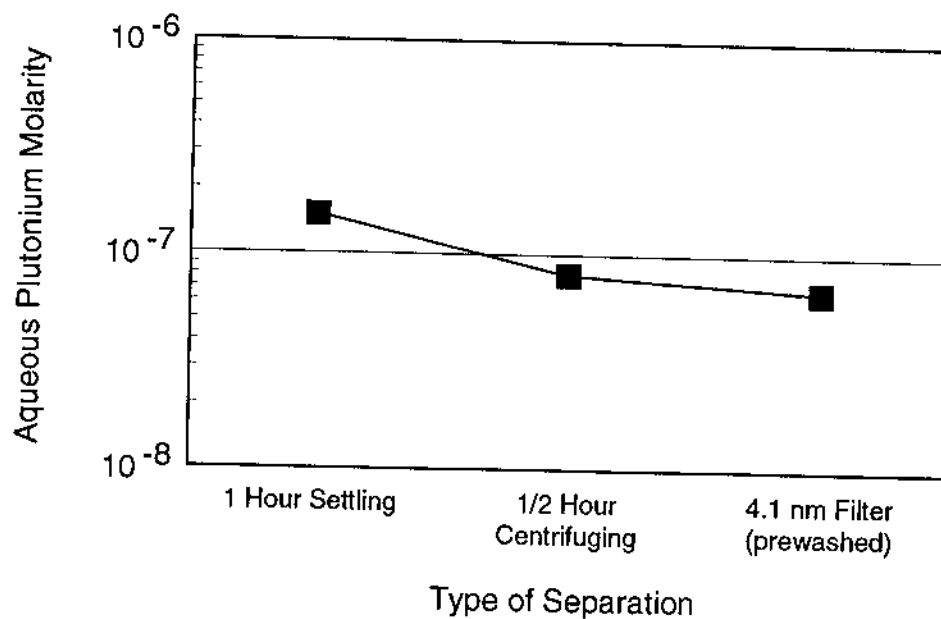


Figure 7. Results of different separation methods for size determination of Pu(IV)-polymer.

4.2 Oxidation State Determination

The plutonium supernatant solutions were analyzed after about 127 days and at the end of the experiments for their oxidation state distributions. The speciation studies are made difficult by the low aqueous concentrations of plutonium. The plutonium concentrations lie below the sensitivity range of methods such as absorption spectrophotometry, which would allow the direct measurement of the species present. Therefore, we used the method that is outlined in Section 3.6 to determine the oxidation states indirectly. Results of the two studies are given in Tables 6 and 7.

After 127 days, all solutions contained predominantly Pu(V) and Pu(VI), whereas Pu(III), Pu(IV), and Pu(IV) polymer are present in small or insignificant quantities. These observed valence distributions cannot be explained by disproportionation equilibria and complex stabilization (Silver, 1972). It is possible that reaction products formed by α -radiolysis of AISinR may cause the predominance of high oxidation states in the plutonium solutions. It is noteworthy that the solutions were filtered through a 4.1-nm filter before the oxidation state determination because we wanted to determine only the true soluble plutonium fraction without any colloidal or polymeric plutonium being present. This treatment separates all Pu(IV) polymer larger than 4.1 nm from the solution. Therefore, we refer to Pu(IV) polymer in the context of this determination only to the fraction that is smaller than 4.1 nm.

As discussed in Section 3.6, there were some problems with the oxidation state determination of the end of the experiments. The separation schemes that enable discrimination between the +III and +V oxidation states did not work properly for the solutions containing initially Pu(III), Pu(V), and Pu(VI). Therefore, only the sum of these oxidation states can be quoted. For the initially Pu(IV) solution, the separation between Pu(V) and Pu(VI) failed, and only this sum can be reported. The reason for these failures is not yet understood; it is possible that ionic constituents present in the AISinR brine interfered with the scintillation counting. The oxidation state determination scheme for plutonium was developed in solutions of dilute acid or 3.5 M NaCl without carbonate and other ligands present that are in the AISinR brine. The dissolved concentration experiments were terminated before the data from redox state determination was

completely analyzed. Thus, the oxidation state determinations could not be repeated when the problem was discovered. By comparing the results from the end of the experiments with the 127-day determination, the conclusion can be drawn that the predominant oxidation states in all solutions are +III, +V and +VI. Between day 127 and the end of the experiment, Pu(III) was possibly formed by reduction of Pu(V) and Pu(VI). The alpha-radiolysis of AISinR may have formed the reducing agent for such a reduction reaction, however there is no confirmatory evidence for the reduction at this time.

4.3 Identification of Solids

The plutonium precipitates in each of the reaction vessels were collected by centrifugation and dried under an argon jet. All precipitates had a dark green appearance similar to that of Pu(IV) polymer. D-spacings and relative intensities of the x-ray powder diffraction patterns from the precipitates are listed in Tables 8 and 9. All precipitates were crystalline, except the solid formed in the Pu(IV)-polymer solutions. The precipitate from the Pu(IV)-polymer solution showed only two diffraction lines, indicating at most a low degree of crystallinity. We compared the x-ray powder diffraction patterns with reference patterns published in the literature to assign the lines. They were compared to patterns of crystalline PuO₂ (Mooney and Zachariasen, 1949), PuO₃·0.8H₂O (Bagnall and Laidler, 1964), KPuO₂CO₃ (Ellinger and Zachariasen, 1954), NH₄PuO₂CO₃ (Ellinger and Zachariasen, 1954), and PuO₂CO₃ (Navratil and Bramlet, 1973). The crystalline precipitates from the brine simulant solutions containing initially PuO₂⁺ and PuO₂²⁺ had x-ray diffraction patterns that compare to patterns of KPuO₂CO₃ and NH₄PuO₂CO₃. Considering that the sodium content in AISinR brine is about 55 times greater than the potassium content, we conclude that these solids are likely sodium plutonyl(V) carbonates, NaPuO₂CO₃(s). Further characterizations to confirm this identification are planned. The plutonium oxidation state of the solid formed in the initially hexavalent plutonium solution was reduced to the pentavalent state. This agrees well with the results from the oxidation state analysis of the respective supernatant solutions that also showed Pu(V) as the major oxidation state.

Table 6. Distribution of plutonium oxidation states in AISinR brine simulant at 25°C before reaching steady state

	Initial Oxidation State	Pu (III) Day 127	Pu (IV) Day 127	Pu (IV) polymer Day 91	Pu (V) Day 128	Pu (VI) Day 127
Final Oxidation State (%)						
Pu (III)		0	0	0	0	0
Pu (IV)		2.3 ± 0.3	0	1.5 ± 0.3	1.3 ± 0.2	0
Pu (IV) polymer		2.3 ± 0.2	2.0 ± 0.2	51.1 ± 5.2	4.8 ± 0.4	11.2 ± 1.5
Pu (V)		27.9 ± 2.2	12.6 ± 1.2	41.8 ± 11.6	20.8 ± 1.9	72.8 ± 7.1
Pu (VI)		67.4 ± 4.9	85.4 ± 6.4	5.6 ± 1.0	73.1 ± 5.4	16.1 ± 1.2
Total Pu		99.9 ± 7.6	100.0 ± 7.8	100. ± 18.1	100.0 ± 7.9	100. ± 9.8

Table 7. Distribution of plutonium oxidation states in AISinR brine simulant at 25°C and steady state

	Initial Oxidation State	Pu (III) Day 366	Pu (IV) Day 366	Pu (IV) polymer Day 335	Pu (V) Day 364	Pu (VI) Day 329
Final Oxidation State (%)						
Pu (III)			15.5 ± 2.1	13.4 ± 2.3		
Pu (IV)		2.3 ± 0.8	1.5 ± 0.3	3.4 ± 0.6	3.2 ± 0.5	3.0 ± 0.8
Pu (IV) polymer		1.4 ± 0.6	1.6 ± 0.3	1.3 ± 0.4	3.5 ± 0.6	0
Pu (V)				69.8 ± 9.9		
Pu (VI)		6.6 ± 3.0		12.1 ± 1.8	24.3 ± 4.0	21.2 ± 5.7
Pu (III + V)		89.7 ± 29.6			69.0 ± 10.4	75.7 ± 20.1
Pu (V + VI)			81.4 ± 9.3			
Total Pu		100.0 ± 34.0	100.0 ± 12.0	100.0 ± 15.0	100.0 ± 15.5	99.9 ± 26.6

The precipitates formed in the solutions with initially Pu(III) and Pu(IV) are microcrystalline but are only partially identified. The plutonium is predominantly in the +IV oxidation state, and the minerals do contain carbonate. The microcrystallinity of these solids is noteworthy because these results are quite different from the results of solubility experiments at near-neutral pH (in J-13 reference groundwater from the Yucca Mountain region) where solutions initially containing Pu(IV) formed amorphous Pu(IV) polymer precipitates (Nitsche, 1991).

Table 8. X-ray powder diffraction patterns of plutonium solid phases formed in AlSinR brine simulant solutions at 25°C and pH 7.5 compared with the pattern of PuO₂ (Mooney and Zachariasen, 1949)

Pu ³⁺ solution		Pu ⁴⁺ solution		Pu(IV) polymer solution		PuO ₂	
d(Å)	I ^a	d(Å)	I ^a	d(Å)	I ^a	d(Å)	I ^b
		4.73	m				
		3.10	m			3.08	100
2.81	m	2.71	w			2.67	20
2.66	t	1.99	s				
1.99	s	1.95	t	1.93	t		
		1.91	t			1.89	80
1.73	w	1.73	w	1.70	t		
1.64	t	1.63	t			1.62	80
						1.55	20
1.26	t						
1.24	t	1.24	t			1.23	50
		1.22	t			1.20	50
						1.10	50
						1.04	50
						0.96	20
						0.91	80
						0.90	50
						0.85	50
						0.82	50
						0.81	50
						0.78	20

(a) Relative intensities visually eliminated: vs = very strong, s = strong, m = medium, w = weak, t = trace.

(b) Relative intensities in percent.

Table 9. X-ray Powder Diffraction Patterns of Plutonium Solid Phases Formed in AlSinR Brine Simulant Solutions at 25°C and pH 7.5 Compared with the Pattern of KPuO_2CO_3 and $\text{NH}_4\text{PuO}_2\text{CO}_3$ (Ellinger and Zachariassen, 1954)

PuO_2^+ solution		PuO_2^{2+} solution		KPuO_2CO_3		$\text{NH}_4\text{PuO}_2\text{CO}_3$	
d(Å)	I ^a	d(Å)	I ^a	d(Å)	I ^b	d(Å)	I ^b
5.02	m	5.04	m	4.93	40	5.08	50
4.39	t	4.43	w	4.43	15	4.39	30
4.02	m+	4.03	s	4.03	100	4.01	100
3.31	m-	3.31	m	3.29	40	3.34	40
2.66	t	2.67	w	2.63	16	2.71	25
2.53	m	2.55	m	2.55	40	2.58	15
		2.52	w	2.46	14	2.54	50
2.27	t	2.27	w	2.27	18	2.28	30
				2.21	4	2.23	5
2.14	w+	2.15	m	2.15	45	2.19	5
1.98	s	2.02	w	2.01	20	2.14	50
		1.99	m-			2.02	20
1.84	t	1.84	w	1.83	18	1.87	15
		1.83	w			1.85	25
1.79	t	1.79	w	1.79	8	1.81	30
1.73	t			1.77	20	1.73	6
1.64	t	1.65	m	1.64	35	1.68	6
						1.67	4
						1.64	40
				1.58	10	1.61	8
						1.58	10
1.49	t	1.50	t	1.53	6	1.51	17
		1.48	t	1.49	16	1.50	20
				1.47	20	1.47	17
				1.41	10	1.43	15
						1.41	18
				1.38	10	1.40	12
				1.34	4	1.36	10
		1.29	t	1.31	6	1.30	25
		1.28	t	1.27	25	1.28	17
				1.26	14	1.27	17
				1.23	14		

(a) Relative intensities visually estimated: vs = very strong, s = strong, m = medium, w = weak, t = trace.

(b) Relative intensities in percent.

5. CONCLUSIONS

These studies demonstrate good methodology for determining the solubility or dissolved concentration of plutonium in brines. The measurement of dissolved concentrations in solubility studies is not a "quick and dirty" process. The experiments documented here required on the order of three to four months to reach an approximate steady state; true steady state was not achieved after a year of reaction time.

The oxidation state determinations were not entirely successful for discriminating among all oxidation states. However, the oxidation state determinations include some of the first work for measuring relative proportions of oxidation states in complicated brine solutions. Valuable experience was gained and is being used to design effective separations for future studies.

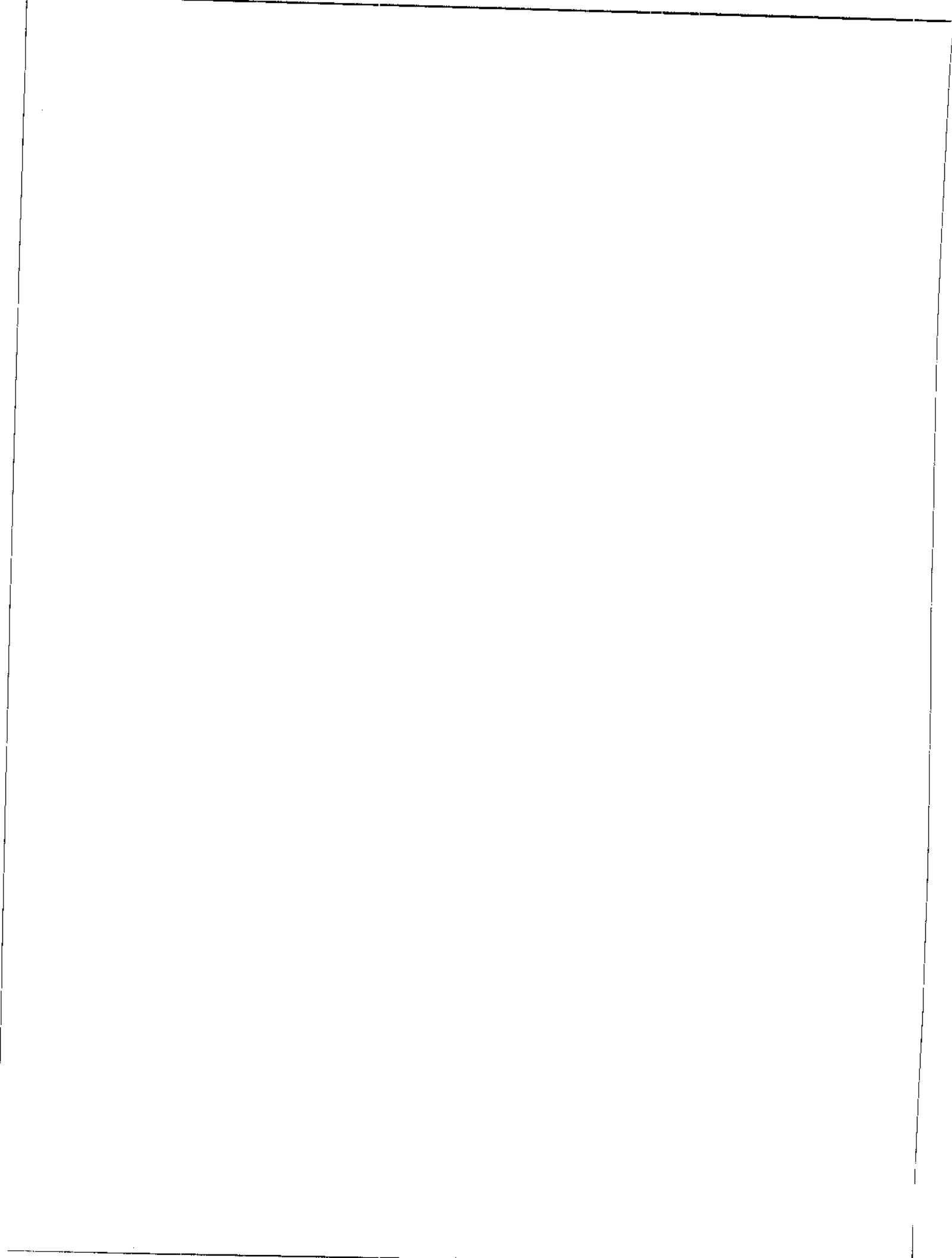
These studies show that aqueous plutonium in solution, initially added in the +III, +IV, +V, and +VI oxidation states, changed with time during these studies. The solubility-controlling mineral was the same for the initially Pu(V) and Pu(VI) solutions and appears to be $\text{NaPuO}_2\text{CO}_3(\text{s})$. Similarly, the solubility-controlling mineral was the same for the initially Pu(III) and Pu(IV) solutions. This mineral remains unidentified, but is known to contain both carbonate and plutonium in the +IV oxidation state.

6. REFERENCES

- Bagnall, K.W., and J.B. Laidler. 1964. "Neptunium and Plutonium Trioxide Hydrates," *Journal of the Chemical Society*. August 1964, 2693-2696.
- Bertram-Howery, S.G., M.G. Marietta, R.P. Rechard, P.N. Swift, D.R. Anderson, B.L. Baker, J.E. Bean, Jr., W. Beyeler, K.F. Brinster, R.V. Guzowski, J.C. Helton, R.D. McCurley, D.K. Rudeen, J.D. Schreiber, and P. Vaughn. 1990. *Preliminary Comparison with 40 CFR Part 191, Subpart B for the Waste Isolation Pilot Plant, December 1990*. SAND90-2347. Albuquerque, NM: Sandia National Laboratories.
- Brooks, D.J., and J.A. Corrado. 1984. *Determination of Radionuclide Solubility in Groundwater for Assessment of High-Level Waste Isolation*. Technical Position. Washington, DC: U.S. Nuclear Regulatory Commission. (Available from NRC Public Document Room, Washington, DC).
- Cohen, D. 1961a. "Electrochemical Studies of Plutonium Ions in Perchloric Acid Solution," *Journal of Inorganic and Nuclear Chemistry*. Vol. 18, 207-216.
- Cohen, D. 1961b. "The Absorption Spectra of Plutonium Ions in Perchloric Acid Solution," *Journal of Inorganic and Nuclear Chemistry*. Vol. 18, 211-218.
- Cross, J.E., D. Crossley, J.W. Edwards, F.T. Ewart, M. Liezers, J.W. McMillan, P.M. Pollard, and S. Turner. 1989. *Actinide Speciation. Further Development and Application of Laser Induced Photoacoustic Spectroscopy and Voltammetry*. NSS/R-119. Harwell, England: United Kingdom Nirex, Ltd.
- Doxtader, M.M., V.A. Maroni, J.V. Beitz, and M. Heaven. 1987. "Laser Photoacoustic Spectroscopy for Trace Level Detection of Actinides in Groundwater," *Scientific Basis for Nuclear Waste Management X, Boston, MA, December 1, 1986*. Eds. J.K. Bates and W. B. Seefeldt. Pittsburgh, PA: Materials Research Society. 173-184.
- Ellinger, F.H., and W. H. Zachariassen. 1954. "The Crystal Structure of $KPuO_2CO_3$, $NH_4PuO_2CO_3$ and $RbAmO_2CO_3$," *Journal of Physical Chemistry*. Vol. 58, no. 5, 405-408.
- Enüstün, B.V., and J. Turkevich. 1960. "Solubility of Fine Particles of Strontium Sulfate," *Journal of the American Chemical Society*. Vol. 82, no. 17, 4502-4509.
- Ewart, F.T., J.W. McMillan, H.P. Thomason, M. Liezers, and P.M. Pollard. 1988. *Development of a Laser-Induced Photoacoustic Facility for Actinide Speciation*. NSS/R-103. Harwell, England: United Kingdom Nirex, Ltd.
- Garrels, R.M. 1960. *Mineral Equilibria at Low Temperature and Pressure*. New York: Harper and Brothers.

- Jones, L.H., and R.A. Penneman. 1953. "Infrared Spectra and Structure of Uranyl and Transuranium (V) and (VI) Ions in Aqueous Perchloric Acid Solution." *Journal of Physical Physics*. Vol. 21, no. 3, 542-544.
- Keenan, T.K., and F.H. Kruse. 1964. "Potassium Double Carbonates of Pentavalent Neptunium, Plutonium, and Americium," *Inorganic Chemistry*. Vol. 3, no. 9, 1231-1232.
- Langmuir, D. 1971. "Eh-pH Determination," *Procedures in Sedimentary Petrology*. Ed. R. E. Carver. New York: Wiley-Interscience. 597-635.
- Lappin, A.R., R.L. Hunter, D.P. Garber, and P.B. Davies, eds. 1989. *Systems Analysis, Long-Term Radionuclide Transport, and Dose Assessments, Waste Isolation Pilot Plant (WIPP), Southeastern New Mexico; March 1989*. SAND89-0462. Albuquerque, NM: Sandia National Laboratories.
- Linke, W.F. 1958. *Solubilities: Inorganic and Metal-Organic Compounds*. Washington, DC: American Chemical Society. Vols. 1-2.
- Mooney, R.C.L., and W.H. Zachariasen. 1949. "Crystal Structure Studies of Oxides of Plutonium," *The Transuranium Elements. Research Papers*. Eds. G.T. Seaborg, J.J. Katz, and W.M. Manning. New York: McGraw-Hill. Part II, 1442-1447.
- Morse, J.W., and W.H. Casey. 1988. "Ostwald Processes and Mineral Paragenesis in Sediments," *American Journal of Science*. Vol. 288, 537-560.
- Nakamoto, K. 1986. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. New York: Wiley.
- Navratil, J.D., and H.L. Bramlet. 1973. "Preparation and Characterization of Plutonyl(VI) Carbonate," *Journal of Inorganic and Nuclear Chemistry*. Vol. 35, no. 1, 157-163.
- Newton, T.W., D.E. Hobart, and P.D. Palmer. 1986. *The Preparation and Stability of Pure Oxidation States of Neptunium, Plutonium, and Americium*. LAUR-86-967. Los Alamos, NM: Los Alamos National Laboratory. (Copies of paper available from authors).
- Nitsche, H. 1991. "Basic Research for Assessment of Geologic Nuclear Waste Repositories: What Solubility and Speciation Studies of Transuranium Elements Can Tell Us," *Scientific Basis for Nuclear Waste Management XIV, Boston, MA, November 26-29, 1990*. Eds. T.A. Abrajano, Jr. and L.H. Johnson. Pittsburgh, PA: Materials Research Society. 517-529.
- Nitsche, H., S.C. Lee, and R.C. Gatti. 1988. "Determination of Plutonium Oxidation States at Trace Levels Pertinent to Nuclear Waste Disposal," *Journal of Radioanalytical and Nuclear Chemistry*. Vol. 124, no. 1, 171-185.

- Nitsche, H., R.C. Gatti, and S.C. Lee. Unpublished. "Low-level Determination of Plutonium by Gamma and L- X-ray Spectroscopy," *Proceedings of International Topical Conference on Methods and Applications of Radioanalytical Chemistry-II*, Kona, HI, April 21-27, 1991.
- Novak, C.F. 1992. *An Evaluation of Radionuclide Batch Sorption Data on Culebra Dolomite for Aqueous Compositions Relevant to the Human Intrusion Scenario for the Waste Isolation Pilot Plant*. SAND91-1299. Albuquerque, NM: Sandia National Laboratories.
- Plummer, L.N., D.L. Parkhurst, G.W. Fleming, and S.A. Dunkle. 1988. *A Computer Program Incorporating Pitzer's Equations for Calculation of Geochemical Reactions in Brines*. Water-Resources Investigations Report 88-4153. Denver, CO: U.S. Geological Survey.
- Rard, J.A. 1989. *The Effect of Precipitation Conditions and Aging Upon Characteristics of Particles Precipitated From Aqueous Solutions*. UCID-21755. Livermore, CA: Lawrence Livermore National Laboratory.
- Robert-Baldo, G.L., M.J. Morris, and R.H. Byrne. 1985. "Spectrophotometric Determination of Seawater pH Using Phenol Red," *Analytical Chemistry*. Vol. 57, no. 13, 2564-2567.
- Silver, G.L. 1972. "Suggestion for the Determination of Plutonium Valencies in Aqueous Solutions," *Radiochemistry and Radioanalytical Letters*. Vol. 9, nos. 5-6, 315-320.
- Stumpe, R., J.I. Kim, W. Schrepp, and H. Walther. 1984. "Speciation of Actinide Ions in Aqueous Solution by Laser-Induced Pulsed Photoacoustic Spectroscopy," *Applied Physics B*. Vol. 34, no.4, 203-206.
- Svedberg, T., and K.O. Pederson. 1940. *The Ultracentrifuge*. Oxford: Clarendon Press. 5-66.
- Torres, R.A., C.E. Palmer, P.A. Baisden, R. E. Russo, and R. J. Silva. 1990. "A Comparison of Photoacoustic Spectroscopy, Conventional Absorption Spectroscopy, and Potentiometry as Probes of Lanthanide Speciation," *Analytical Chemistry*. Vol. 62, no. 3, 298-303.
- Voorhees, P.W. 1985. "The Theory of Ostwald Ripening," *Journal of Statistical Physics*. Vol. 38, nos. 1-2, 231-252.



APPENDIX A:
Tables of Dissolved Plutonium Concentration Measurements

Table A-1. Results of Plutonium (III) Dissolved Concentration Experiments in AlSinR Simulant at 25°C

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	—	$(3.59 \pm 0.18) \times 10^{-4}$
4W1A2S2	2	7.44	$(8.18 \pm 0.81) \times 10^{-8}$
4W2A4S2	13	7.47	$(5.74 \pm 0.57) \times 10^{-7}$
4W3A1S2	19	7.49	$(6.44 \pm 0.63) \times 10^{-7}$
4W5A1S2	36	7.49	$(5.16 \pm 0.51) \times 10^{-7}$
4W6A1S2	43	7.44	$(5.21 \pm 0.51) \times 10^{-7}$
4W7A1S2	57	7.40	$(5.62 \pm 0.55) \times 10^{-7}$
4W8A1S2	71	7.46	$(4.82 \pm 0.47) \times 10^{-7}$
4W9A1S2	90	7.48	$(4.64 \pm 0.46) \times 10^{-7}$
4W10A7S2	118	7.50	$(3.75 \pm 0.37) \times 10^{-7}$
4W11A1S2	134	7.49	$(2.98 \pm 0.29) \times 10^{-7}$
4W12A1S2	196	7.49	$(2.35 \pm 0.13) \times 10^{-7}$
4W13A1S2	335	7.49	$(1.88 \pm 0.13) \times 10^{-7}$
W9Pu932	366	7.46	$(1.11 \pm 0.06) \times 10^{-7}$
average 4W5A1S2 through W9Pu932			$(3.75 \pm 1.58) \times 10^{-7}$

Table A-2. Results of Plutonium (IV) Dissolved Concentration Experiments in AISinR Simulant at 25°C

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	—	$(3.04 \pm 0.15) \times 10^{-4}$
5W1A2S2	1	7.46	$(1.05 \pm 0.10) \times 10^{-6}$
5W2A4S2	12	7.47	$(7.11 \pm 0.70) \times 10^{-7}$
5W3A1S2	18	7.36	$(5.76 \pm 0.57) \times 10^{-7}$
5W4A1S2	26	7.52	$(6.05 \pm 0.59) \times 10^{-7}$
5W5A1S2	35	7.47	$(5.00 \pm 0.49) \times 10^{-7}$
5W6A1S2	42	7.43	$(4.44 \pm 0.44) \times 10^{-7}$
5W7A1S2	56	7.43	$(5.18 \pm 0.51) \times 10^{-7}$
5W8A1S2	70	7.48	$(4.35 \pm 0.43) \times 10^{-7}$
5W9A1S2	89	7.38	$(4.06 \pm 0.40) \times 10^{-7}$
5W10A7S2	117	7.50	$(3.35 \pm 0.33) \times 10^{-7}$
5W11A1S2	133	7.46	$(3.35 \pm 0.33) \times 10^{-7}$
5W12A1S2	195	7.48	$(2.12 \pm 0.11) \times 10^{-7}$
5W13A1S2	334	7.49	$(1.98 \pm 0.14) \times 10^{-7}$
W9Pu898	366	7.46	$(1.58 \pm 0.09) \times 10^{-7}$
average 5W5A1S2 through W9Pu898			$(3.54 \pm 1.29) \times 10^{-7}$

Table A-3. Results of Plutonium(V) Solubility Experiments in AISinR Brine Simulant at 25°C

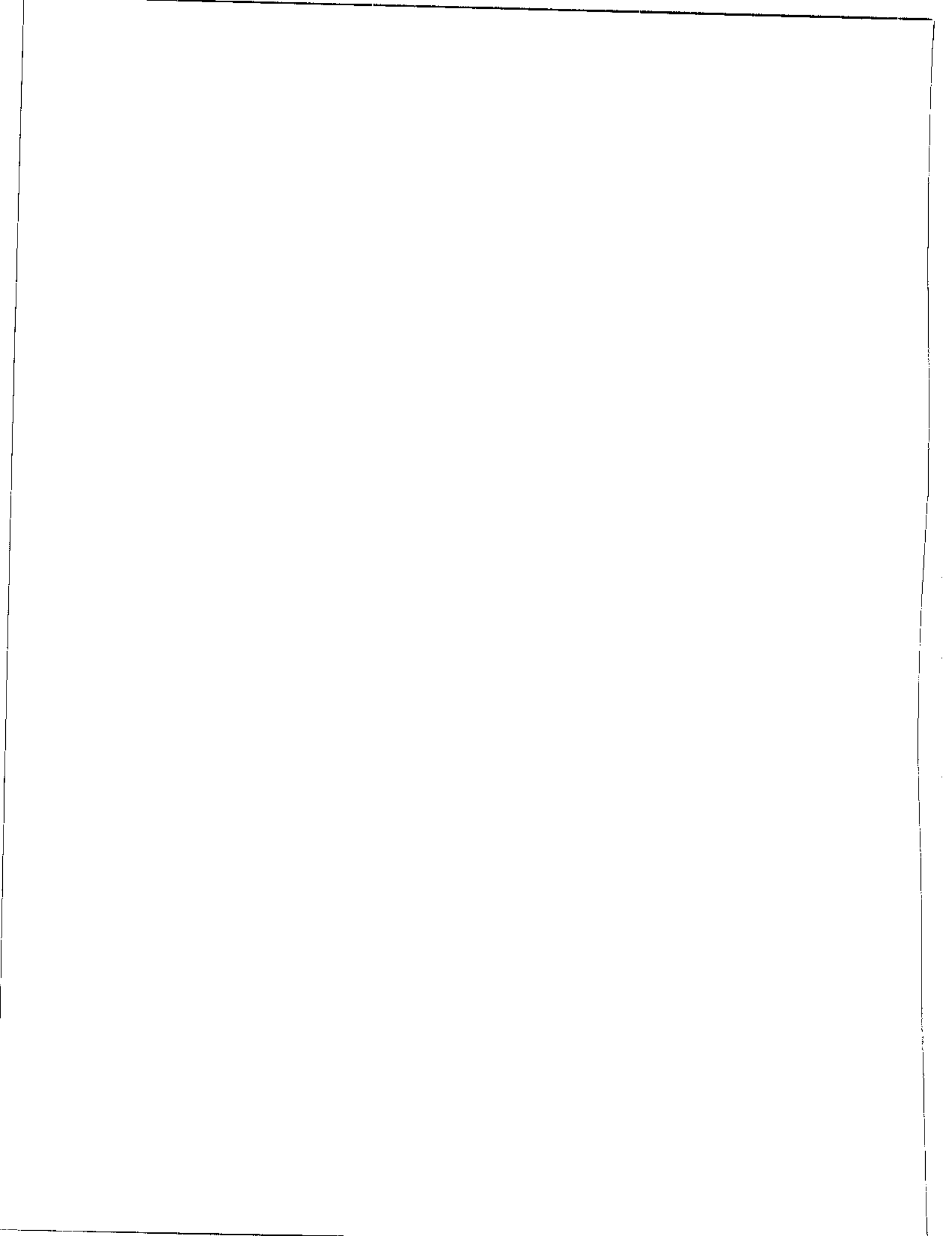
Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	-	$(3.58 \pm 0.18) \times 10^{-4}$
2W1A2S2	3	7.30	$(1.64 \pm 0.16) \times 10^{-5}$
2W2A4S2	14	7.44	$(1.43 \pm 0.14) \times 10^{-6}$
2W3A1S2	20	7.38	$(9.01 \pm 0.89) \times 10^{-7}$
2W4A1S2	28	7.53	$(8.49 \pm 0.83) \times 10^{-7}$
2W5A1S2	37	7.41	$(5.48 \pm 0.54) \times 10^{-7}$
2W6A1S2	44	7.43	$(4.73 \pm 0.46) \times 10^{-7}$
2W7A1S2	58	7.40	$(4.48 \pm 0.44) \times 10^{-7}$
2W8A1S2	72	7.44	$(4.04 \pm 0.40) \times 10^{-7}$
2W9A1S2	91	7.45	$(4.05 \pm 0.40) \times 10^{-7}$
2W10A7S2	119	7.47	$(3.61 \pm 0.36) \times 10^{-7}$
2W11A1S2	135	7.47	$(3.46 \pm 0.34) \times 10^{-7}$
2W12A1S2	196	7.49	$(3.31 \pm 0.18) \times 10^{-7}$
2W13A1S2	336	7.50	$(3.51 \pm 0.22) \times 10^{-7}$
W9Pu829	364	7.46	$(3.77 \pm 0.20) \times 10^{-7}$
average 2W6A1S2 through W9Pu829:			$(3.88 \pm 0.48) \times 10^{-7}$
average pH:			7.45 ± 0.09

Table A-4. Results of Plutonium(VI) Solubility Experiments in AISinR Brine Simulant at 25°C

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	-	$(5.28 \pm 0.24) \times 10^{-4}$
1W5A1S2	1	7.35	$(3.36 \pm 0.03) \times 10^{-4}$
1W6A1S2	8	7.44	$(2.99 \pm 0.29) \times 10^{-4}$
1W7A1S2	22	7.45	$(2.24 \pm 0.22) \times 10^{-4}$
1W8A1S2	36	7.47	$(1.32 \pm 0.13) \times 10^{-4}$
1W9A1S2	56	7.51	$(3.50 \pm 0.35) \times 10^{-5}$
1W10A1S2	83	7.48	$(1.98 \pm 0.19) \times 10^{-6}$
1W11A1S2	89	7.48	$(1.77 \pm 0.17) \times 10^{-6}$
1W12A1S2	99	7.49	$(1.53 \pm 0.15) \times 10^{-6}$
1W13A1S2	161	7.48	$(1.09 \pm 0.06) \times 10^{-6}$
1W14A1S2	300	7.46	$(1.34 \pm 0.08) \times 10^{-6}$
W9Pu795	329	7.46	$(1.29 \pm 0.07) \times 10^{-6}$
average 1W13A1S2 through W9Pu795:			$(1.24 \pm 0.13) \times 10^{-6}$
average pH:			7.46 ± 0.04

Table A-5. Results of Plutonium(IV) -Polymer Solubility Experiments in AlSinR Brine Simulant at 25°C

Sample I.D.	Days	pH	Concentration (M)
Initial amount added	0	-	$(1.79 \pm 0.11) \times 10^{-4}$
6W1A1S2	1	7.32	$(6.60 \pm 0.65) \times 10^{-8}$
6W2A1S2	8	7.43	$(5.74 \pm 0.56) \times 10^{-8}$
6W3A1S2	22	7.40	$(7.40 \pm 0.69) \times 10^{-8}$
6W4A1S2	36	7.47	$(6.82 \pm 0.67) \times 10^{-8}$
6W5A1S2	55	7.47	$(8.01 \pm 0.79) \times 10^{-8}$
6W6A1S2	83	7.46	$(8.30 \pm 0.82) \times 10^{-8}$
6W7A1S2	99	7.44	$(8.81 \pm 0.87) \times 10^{-8}$
6W8A1S2	161	7.46	$(1.03 \pm 0.06) \times 10^{-7}$
6W9A1S2	300	7.48	$(9.82 \pm 0.81) \times 10^{-8}$
W9Pu864	335	7.48	$(1.03 \pm 0.06) \times 10^{-7}$
average 6W1A1S2 through W9Pu864:			$(8.21 \pm 1.60) \times 10^{-8}$
average pH:			7.45 ± 0.04



DISTRIBUTION

Federal Agencies

US Department of Energy, (5)
Office of Civilian Radioactive Waste
Management
Attn: Deputy Director, RW-2
Associate Director, RW-10
Office of Program
Administration and
Resources Management
Associate Director, RW-20
Office of Facilities
Siting and Development
Associate Director, RW-30
Office of Systems
Integration and
Regulations
Associate Director, RW-40
Office of External
Relations and Policy
Forrestal Building
Washington, DC 20585

US Department of Energy (4)
WIPP Project Integration Office
Attn: W.J. Arthur III
L.W. Gage
P.J. Higgins
D.A. Olona
PO Box 5400
Albuquerque, NM 87115-5400

US Department of Energy
Attn: National Atomic Museum Library
Albuquerque Operations Office
PO Box 5400
Albuquerque, NM 87185-5400

US Department of Energy (4)
WIPP Project Site Office (Carlsbad)
Attn: R. Becker
V. Daub
J. Lippis
J.A. Mewhinney
PO Box 3090
Carlsbad, NM 88221

US Department of Energy
Research & Waste Management Division
Attn: Director
PO Box E
Oak Ridge, TN 37831

US Department of Energy
Attn: E. Young
Room E-178
GAO/RCED/GTN
Washington, DC 20545

US Department of Energy
Office of Environmental Restoration
and Waste Management
Attn: J. Lytle, EM-30 (Trevion II)
Washington, DC 20585-0002

US Department of Energy (3)
Office of Environmental Restoration
and Waste Management
Attn: M. Frei, EM-34 (Trevion II)
Washington, DC 20585-0002

US Department of Energy
Office of Environmental Restoration
and Waste Management
Attn: S. Schneider, EM-342
(Trevion II)
Washington, DC 20585-0002

US Department of Energy (3)
Office of Environment, Safety
and Health
Attn: C. Borgstrom, EH-25
R. Pelletier, EH-231
Washington, DC 20585

US Department of Energy (2)
Idaho Operations Office
Fuel Processing and Waste
Management Division
785 DOE Place
Idaho Falls, ID 83402

US Environmental Protection
Agency (2)
Radiation Programs (ANR-460)
Attn: R. Guimond
Washington, DC 20460

US Geological Survey (2)
Water Resources Division
Attn: R. Livingston
Suite 200
4501 Indian School, NE
Albuquerque, NM 87110

US Nuclear Regulatory Commission
Attn: H. Marson
Mail Stop 623SS
Washington, DC 20555

NM Environment Department
WIPP Project Site
Attn: P. McCasland
PO Box 3090
Carlsbad, NM 88221

Boards

Defense Nuclear Facilities Safety
Board
Attn: D. Winters
Suite 700
625 Indiana Ave., NW
Washington, DC 20004

Nuclear Waste Technical Review
Board (2)
Attn: D.A. Deere
S.J.S. Parry
Suite 910
1100 Wilson Blvd.
Arlington, VA 22209-2297

Advisory Committee on Nuclear Waste
Nuclear Regulatory Commission
Attn: R. Major
7920 Norfolk Ave.
Bethesda, MD 20814

State Agencies

Environmental Evaluation Group (3)
Attn: Library
Suite F-2
7007 Wyoming, NE
Albuquerque, NM 87109

NM Bureau of Mines and Mineral
Resources
Socorro, NM 87801

NM Energy, Minerals, and Natural
Resources Department
Attn: Library
2040 S. Pacheco
Santa Fe, NM 87505

NM Environment Department (3)
Secretary of the Environment
Attn: J. Espinosa
1190 St. Francis Drive
Santa Fe, NM 87503-0968

Laboratories/Corporations

Lawrence Berkeley Laboratory (30)
Attn: H. Nitsche
Mailstop 70A-1115
1 Cyclotron Rd.
Berkeley, CA 94720

Battelle Pacific Northwest
Laboratories (2)
Attn: H.C. Burkholder, P7-41
R.E. Westerman, P8-37
Battelle Blvd.
Richland, WA 99352

Savannah River Laboratory (3)
Attn: N. Bibler
M.J. Plodinec
G.G. Wicks
Aiken, SC 29801

INTERA Inc.
Attn: J.F. Pickens
Suite 300
6850 Austin Center Blvd.
Austin, TX 78731

INTERA Inc.
Attn: W. Stensrud
PO Box 2123
Carlsbad, NM 88221

IT Corporation
Attn: R.F. McKinney
Regional Office - Suite 700
5301 Central, NE
Albuquerque, NM 87108

Los Alamos National Laboratory
Attn: B. Erdal, CNC-11
PO Box 1663
Los Alamos, NM 87544

RE/SPEC, Inc.
Attn: W. Coons
Suite 300
4775 Indian School, NE
Albuquerque, NM 87110-3927

RE/SPEC, Inc.
Attn: J.L. Ratigan
PO Box 725
Rapid City, SD 57709

Southwest Research Institute (2)
Center for Nuclear Waste
Regulatory Analysis
Attn: P.K. Nair
6220 Culebra Road
San Antonio, TX 78228-0510

SAIC
Attn: G. Dymmel
101 Convention Center Dr.
Las Vegas, NV 89109

SAIC
Attn: H.R. Pratt,
10260 Campus Point Dr.
San Diego, CA 92121

SAIC (2)
Attn: M. Davis
J. Tollison
2109 Air Park Rd., SE
Albuquerque, NM 87106

Tech Reps Inc. (3)
Attn: J. Chapman
R. Jones
E. Lorusso
5000 Marble, NE
Albuquerque, NM 87110

Westinghouse Electric Corporation (5)
Attn: Library
C. Cox
L. Fitch
R. Kehrman
L. Trego
PO Box 2078
Carlsbad, NM 88221

Universities

University of New Mexico
Geology Department
Attn: Library
Albuquerque, NM 87131

University of Washington
Attn: G.R. Heath
College of Ocean
and Fishery Sciences
583 Henderson Hall
Seattle, WA 98195

Individuals

P. Drez
8816 Cherry Hills Rd., NE
Albuquerque, NM 87111

D.W. Powers
Star Route Box 87
Anthony, TX 79821

Libraries

Thomas Brannigan Library
Attn: D. Dresp
106 W. Hadley St.
Las Cruces, NM 88001

Hobbs Public Library
Attn: M. Lewis
509 N. Ship St.
Hobbs, NM 88248

New Mexico State Library
Attn: N. McCallan
325 Don Gaspar
Santa Fe, NM 87503

New Mexico Tech
Martin Speere Memorial Library
Campus Street
Socorro, NM 87810

New Mexico Junior College
Pannell Library
Attn: R. Hill
Lovington Highway
Hobbs, NM 88240

WIPP Public Reading Room
Carlsbad Public Library
Attn: Director
101 S. Halagueno St.
Carlsbad, NM 88220

Government Publications Department
General Library
University of New Mexico
Albuquerque, NM 87131

**National Academy of Sciences,
WIPP Panel**

Charles Fairhurst, Chairman
Department of Civil and
Mineral Engineering
University of Minnesota
500 Pillsbury Dr., SE
Minneapolis, MN 55455-0220

Howard Adler
Oak Ridge Associated Universities
Medical Sciences Division
PO Box 117
Oak Ridge, TN 37831-0117

John D. Bredehoeft
Western Region Hydrologist
Water Resources Division
US Geological Survey (M/S 439)
345 Middlefield Road
Menlo Park, CA 94025

Fred M. Ernsberger
250 Old Mill Road
Pittsburgh, PA 15238

Rodney C. Ewing
Department of Geology
University of New Mexico
Albuquerque, NM 87131

B. John Garrick
PLG, Inc.
Suite 400
4590 MacArthur Blvd.
Newport Beach, CA 92660-2027

Leonard F. Konikow
US Geological Survey
431 National Center
Reston, VA 22092

Jeremiah O'Driscoll
Jody Incorporated
505 Valley Hill Drive
Atlanta, GA 30350

Christopher G. Whipple
Clement International
Suite 1380
160 Spear St.
San Francisco, CA 94105

Peter B. Myers
National Academy of Sciences
Board on Radioactive
Waste Management
2101 Constitution Ave.
Washington, DC 20418

Ina Alterman
Board on Radioactive
Waste Management
GF456
2101 Constitution Ave.
Washington, DC 20418

Foreign Addresses

Studiecentrum Voor Kernenergie
Centre D'Energie Nucleaire
Attn: A. Bonne
SCK/CEN
Boeretang 200
B-2400 Mol, BELGIUM

Atomic Energy of Canada, Ltd. (3)
Whiteshell Research Estab.
Attn: B. Goodwin
M. Stevens
D. Wushke
Pinewa, Manitoba, CANADA ROE 1LO

Francois Chenevier, Director (2)
ANDRA
Route du Panorama Robert Schumann
B.P.38
92266 Fontenay-aux-Roses Cedex
FRANCE

Jean-Pierre Olivier
OECD Nuclear Energy Agency
Division of Radiation Protection
and Waste Management
38, Boulevard Suchet
75016 Paris, FRANCE

Claude Sombret
Centre D'Etudes Nucleaires
De La Vallee Rhone
CEN/VALRHO
S.D.H.A. BP 171
30205 Bagnols-Sur-Ceze, FRANCE

Bundesministerium fur Forschung und
Technologie
Postfach 200 706
5300 Bonn 2, GERMANY

Gesellschaft fur Reaktorsicherheit
(GRS) (2)

Attn: B. Baltes
W. Muller

Schwertnergasse 1
D-5000 Cologne, GERMANY

Bundesanstalt fur Geowissenschaften
und Rohstoffe

Attn: M. Langer
Postfach 510 153

3000 Hanover 51, GERMANY

Hahn-Meitner-Institut fur
Kernforschung

Attn: W. Lutze

Glienicker Strasse 100
100 Berlin 39, GERMANY

Institut fur Tieflagerung (2)

Attn: K. Kuhn

Theodor-Heuss-Strasse 4
D-3300 Braunschweig, GERMANY

Physikalisch-Technische Bundesanstalt

Attn: P. Brenneke

Postfach 3345
D-3300 Braunschweig, GERMANY

D.R. Knowles

British Nuclear Fuels, plc
Risley, Warrington, Cheshire WA3 6AS
1002607 UNITED KINGDOM

AEA Technology

Attn: J.H. Rees

D5W/29 Culham Laboratory
Abington, Oxfordshire OX14 3DB
UNITED KINGDOM

AEA Technology

Attn: W.R. Rodwell

O44/A31 Winfrith Technical Centre
Dorchester, Dorset DT2 8DH
UNITED KINGDOM

AEA Technology

Attn: J.E. Tinson

B4244 Harwell Laboratory
Didcot, Oxfordshire OX11 0RA
UNITED KINGDOM

Nationale Genossenschaft fur die
Lagerung Radioaktiver Abfalle (2)

Attn: S. Vomvoris
P. Zuidema

Hardstrasse 73
CH-5430 Wettingen, SWITZERLAND

Shingo Tashiro

Japan Atomic Energy Research
Institute

Tokai-Mura, Ibaraki-Ken
319-11 JAPAN

Netherlands Energy Research
Foundation ECN

Attn: L.H. Vons

3 Westerduinweg
PO Box 1
1755 ZG Petten, THE NETHERLANDS

Svensk Karnbransleforsorjning AB

Attn: F. Karlsson

Project KBS
Karnbranslesakerhet
Box 5864
10248 Stockholm, SWEDEN

Sandia Internal

1502

3141

3145

3151

6000

6119

6119

6119

6121

6121

6300

6302

6303

6303

6341

6341

6341

6342

6342

6343

6343

6345

6345

6347

8523-2

9300

J.C. Cummings

S.A. Landenberger (5)

Document Control (8) for
DOE/OSTI

G.C. Claycomb (3)

D.L. Hartley

E.D. Gorham

C.F. Novak (20)

Staff (10)

J.R. Tillerson

Staff (7)

D.E. Miller

T.E. Blejwas, Acting

W.D. Weart

S.Y. Pickering

A.L. Stevens

Staff (6)

WIPP Central Files (10)

D.R. Anderson

Staff (20)

T.M. Schultheis

Staff (2)

R.C. Lincoln

Staff (9)

D.R. Schafer

Central Technical Files

J.E. Powell

