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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.

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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, $CaSO_4 \cdot 2H_2O$, 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
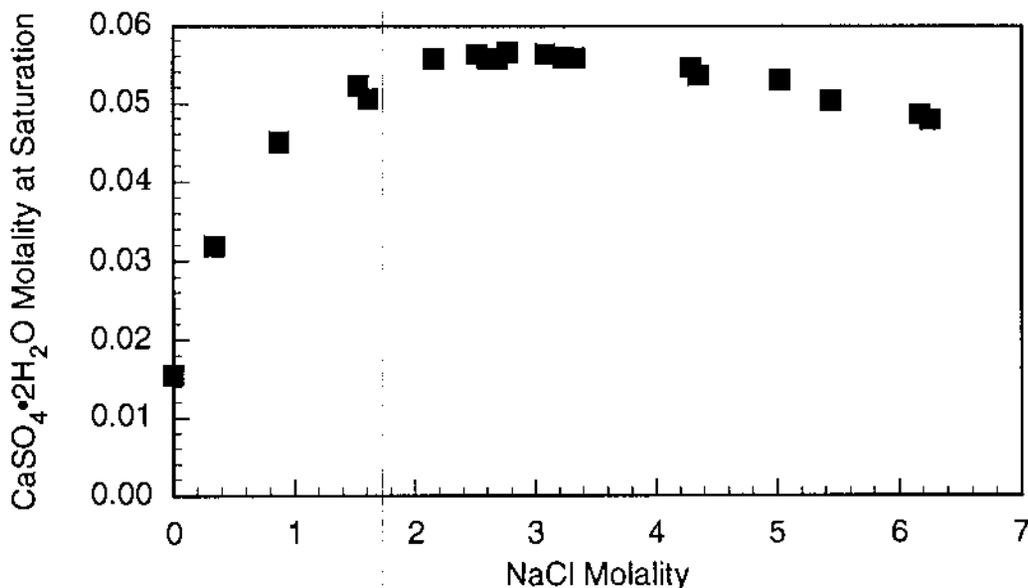
Figure 1. Solubility of gypsum, $CaSO_4 \cdot 2H_2O$, in sodium chloride solutions.

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 ≤ 0.1 μm 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

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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 $Pu(s)$. 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 PuO_2^+/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

$$PuO_2^{2+} + CO_3^{2-} \leftrightarrow PuO_2CO_3(aq) \,.$$
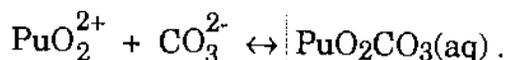
Speciation, like oxidation state distribution, is a controlling factor in transport behavior because it influences both the forms of plutonium in solution and the extent to which the plutonium can interact with the mineral phases and thus undergo chemical retardation. As in the case of oxidation state 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 ~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

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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 $CO_2(g)$ until the solution was in equilibrium with calcite, $CaCO_3(s)$. The calcium concentration was then reduced by 25% to minimize the possibility for gypsum, $CaSO_4 \bullet 2H_2O(s)$, 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 KCl(s), NaCl(s), $CaCl_2(s)$, $MgCl_2 \bullet 6H_2O(s)$, $Na_2SO_4(s)$, $NaHCO_3(s)$, and $H_3BO_4(s)$. The calculated quantities required and the weighed amounts are shown in Table 2. $Na_2SO_4(s)$, $CaCl_2(s)$, and NaCl(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 μm filter membrane (Nuclepore Corporation, Pleasanton, CA). All operations were carried out in a glove box under inert (argon) atmosphere.

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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_3BO_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
$MgCl_2 \cdot 6H_2O$	4.37	4.3710 ± 0.0004

Samples of AlSinR 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 AlSinR brine in Table 3.

Table 3. Comparison of Elemental Concentration of AlSinR 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 AlSinR. 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 AlSinR equilibrated with the gas had a measured operational pH of 7.47. The hydrogen concentration, or pcH, 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 AlSinR brine necessary for this procedure was determined by potentiometric titration to be pK=7.94 ± 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 (Savillex 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 $CO_2(g)$-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 µL) 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 µL 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

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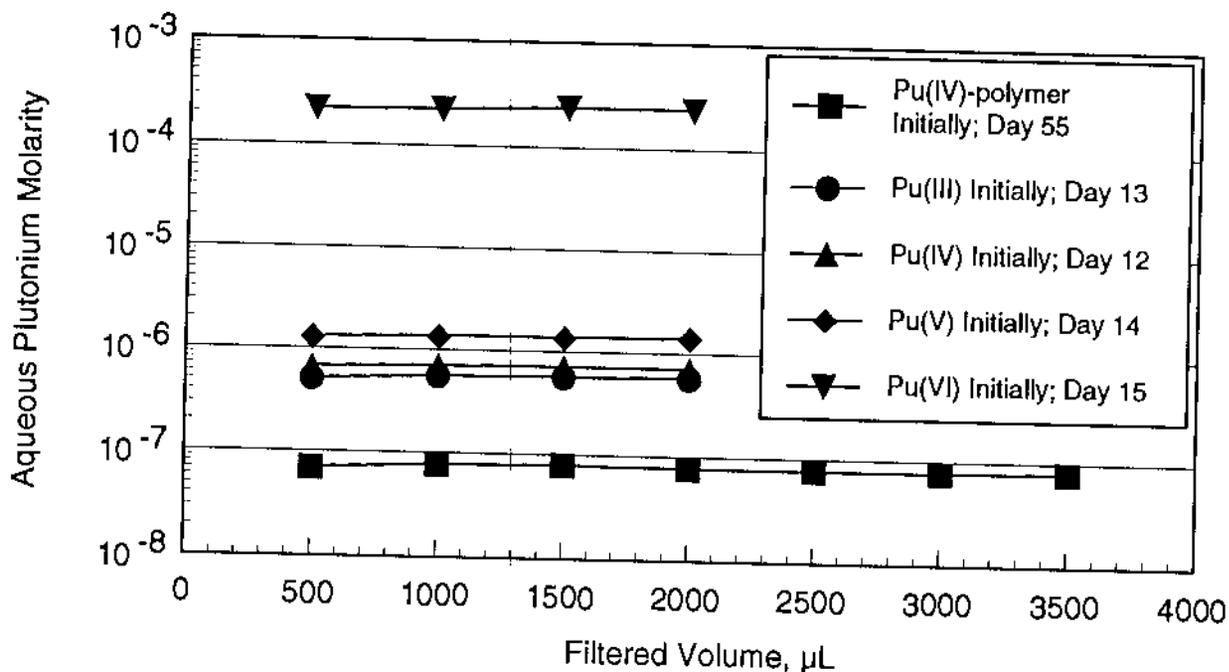
Figure 2. Filtration experiments, at the beginning of the dissolved concentration experiments, to determine the sorption behavior of different plutonium solutions on Centricon-30 filters.
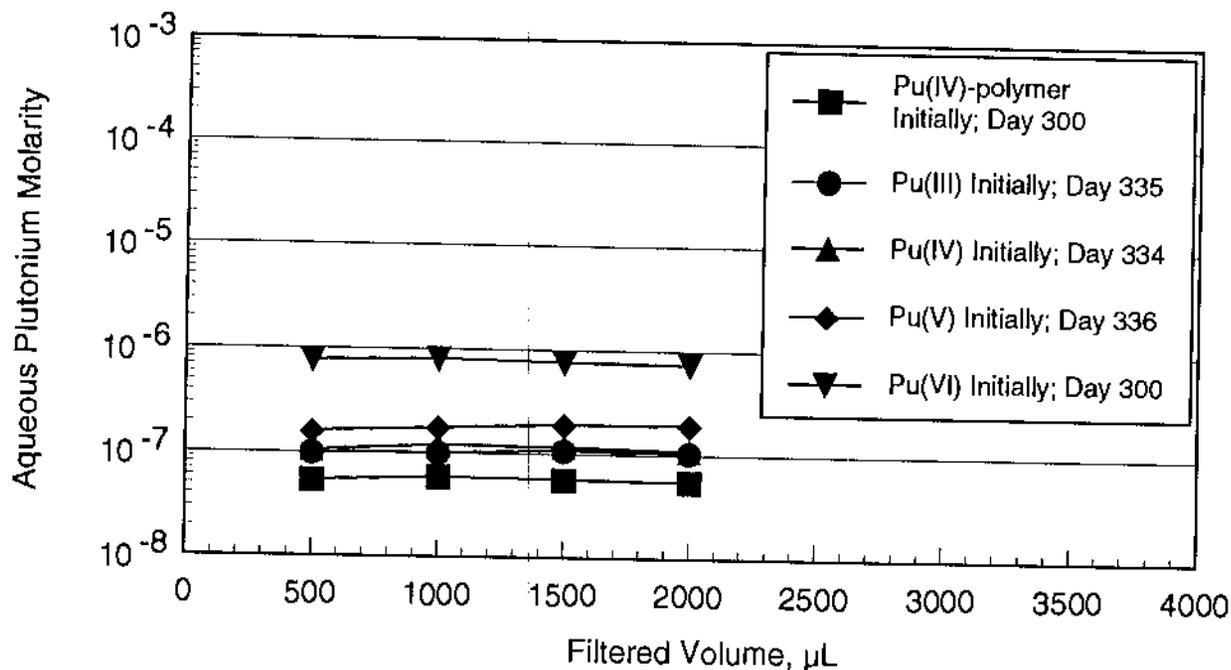
Figure 3. Filtration experiments, at the end of the dissolved concentration experiments, to determine the sorption behavior of different plutonium solutions on Centricon-30 filters.

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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(lV) polymer
HDEHP† extraction at pH = 0	+4, +6	+3, +5, Pu(lV) polymer
HDEHP extraction at pH = 0 with Chromate	+3, +4, +5, +6	Pu(lV) polymer
LaF$_3$ precipitation with Chromate	+3, +4, Pu(lV) 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, Eh, 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 oxy-butane 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.

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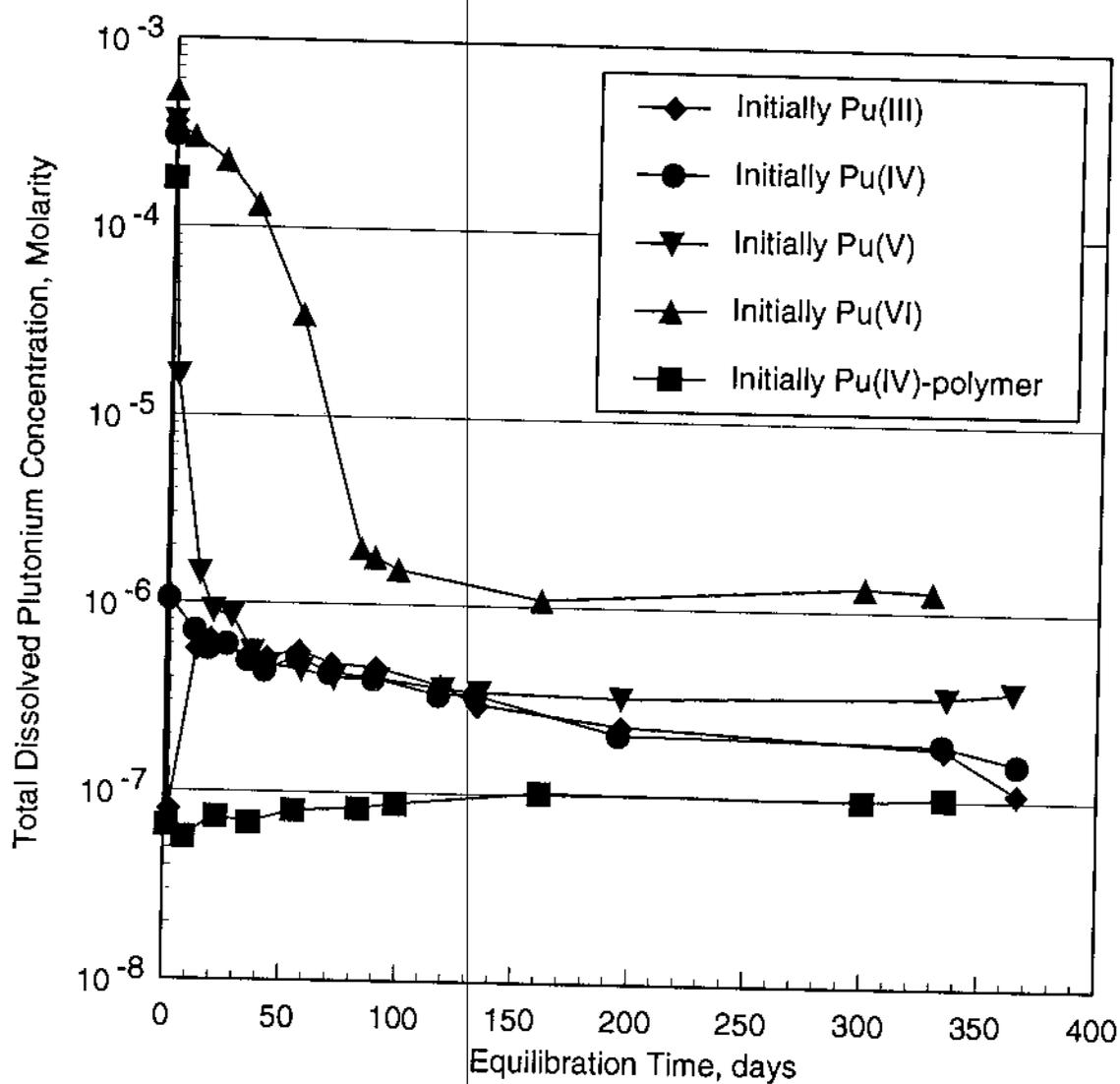
Figure 4. Total dissolved plutonium concentrations versus time in AISinR at 25°C for five initial forms of aqueous plutonium.

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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	$(3.75 \pm 1.58) \times 10^{-7}$	431 ± 15
Pu^{4+}	7.45 ± 0.11	$(3.54 \pm 1.29) \times 10^{-7}$	401 ± 15
PuO_2^{+}	7.45 ± 0.09	$(3.88 \pm 0.48) \times 10^{-7}$	427 ± 15
PuO_2^{2+}	7.46 ± 0.04	$(1.24 \pm 0.13) \times 10^{-6}$	417 ± 15
Pu(IV) polymer	7.45 ± 0.04	$(8.21 \pm 1.60) \times 10^{-8}$	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
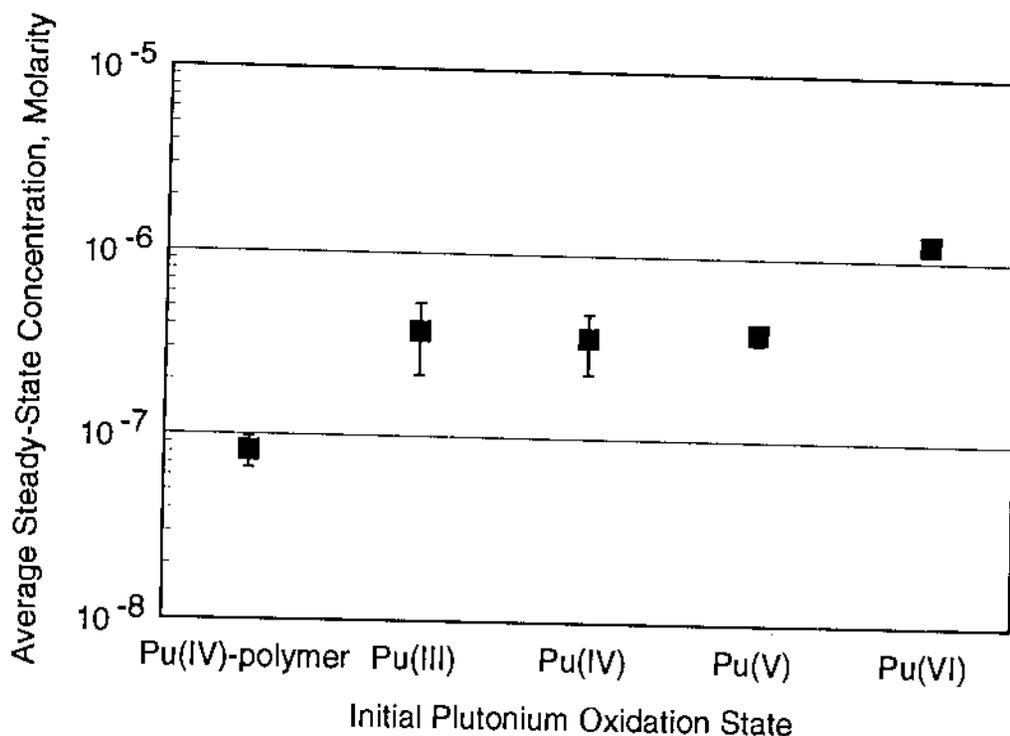
Figure 5. Time-averaged near steady-state aqueous plutonium concentration in AlSinR at 25°C for five different initial forms of aqueous plutonium.

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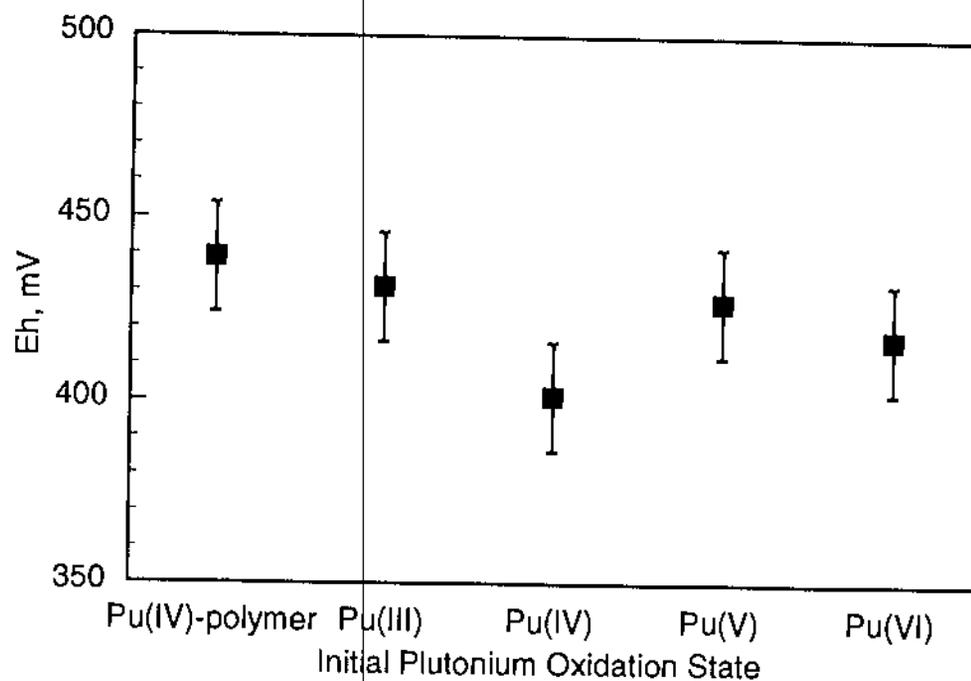
Figure 6. Eh values in AISinR at 25°C for five different initial forms of aqueous plutonium, measured at the conclusion of the experiments.

about 2 • 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, ~1.2 • 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 • 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 μm (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.
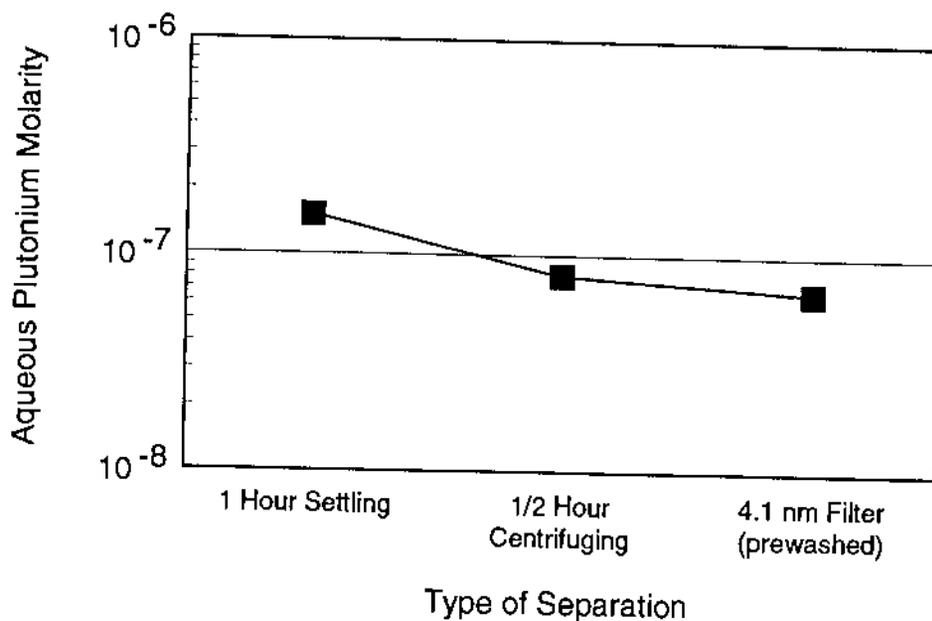
Figure 7. Results of different separation methods for size determination of Pu(IV)-polymer.

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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 PuO_2 (Mooney and Zachariasen, 1949), $PuO_3 \cdot 0.8H_2O$ (Bagnall and Laidler, 1964), $KPuO_2CO_3$ (Ellinger and Zachariasen, 1954), $NH_4PuO_2CO_3$ (Ellinger and Zachariasen, 1954), and PuO_2CO_3 (Navratil and Bramlet, 1973). The crystalline precipitates from the brine simulant solutions containing initially PuO_2^+, and PuO_2^{2+} had x-ray diffraction patterns that compare to patterns of $KPuO_2CO_3$ and $NH_4PuO_2CO_3$. 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, $NaPuO_2CO_3(s)$. 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 PuO_2 (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 $NH_4PuO_2CO_3$ (Ellinger and Zachariasen, 1954)

PuO$_2^+$ solution		PuO$_2^{2+}$ solution		KPuO$_2$CO$_3$		NH$_4$PuO$_2$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
						2.19	5
2.14	w+	2.15	m	2.15	45	2.14	50
1.98	s	2.02	w	2.01	20	2.02	20
		1.99	m−				
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
				1.53	6	1.51	17
1.49	t	1.50	t	1.49	16	1.50	20
		1.48	t	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 $NaPuO_2CO_3(s)$. 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.

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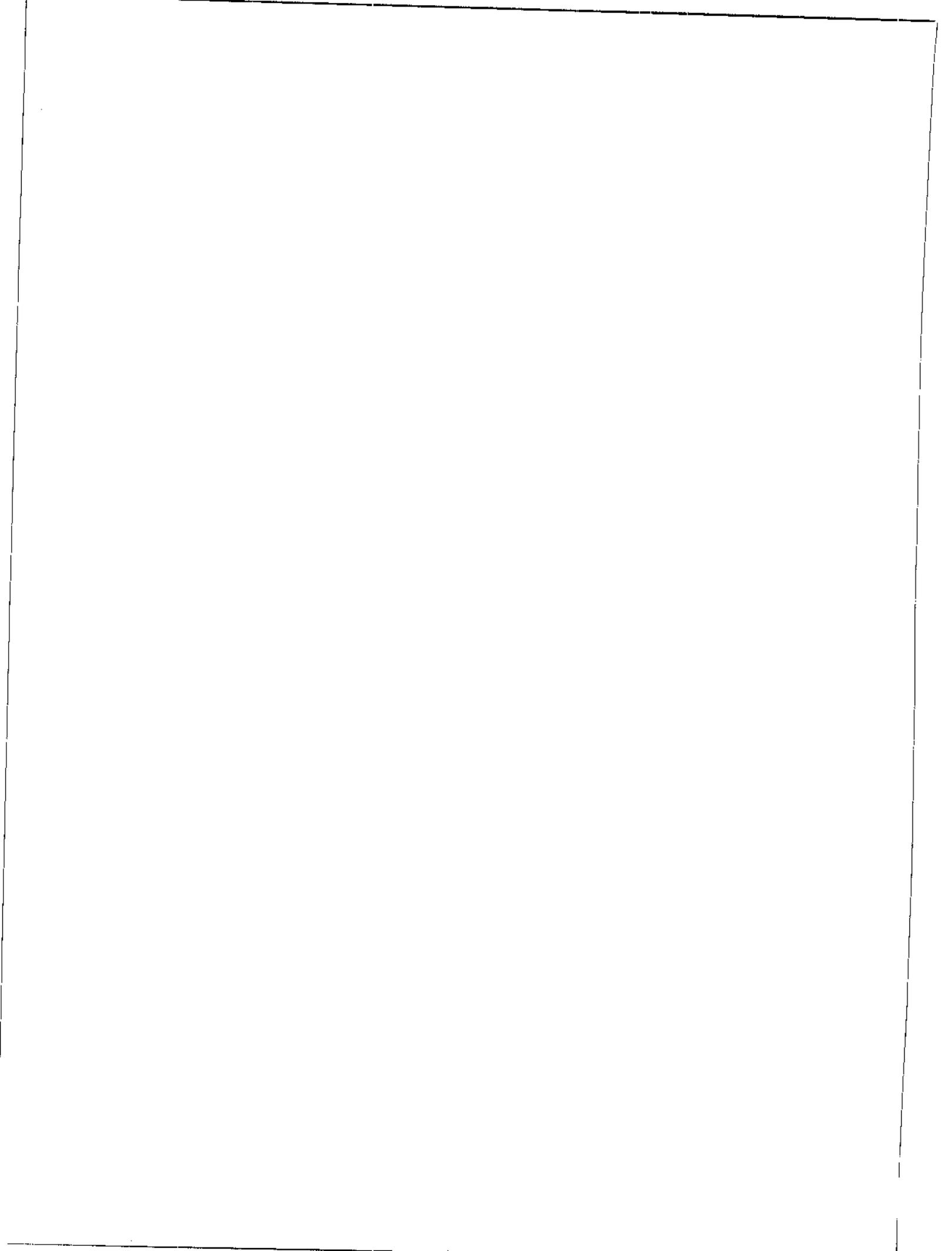
APPENDIX A:
Tables of Dissolved Plutonium Concentration Measurements

Table A-1. Results of Plutonium (III) Dissolved Concentration Experiments in AISinR 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 6W1AlS2 through W9Pu864: $(8.21 \pm 1.60) \times 10^{-8}$

average pH: 7.45 ± 0.04
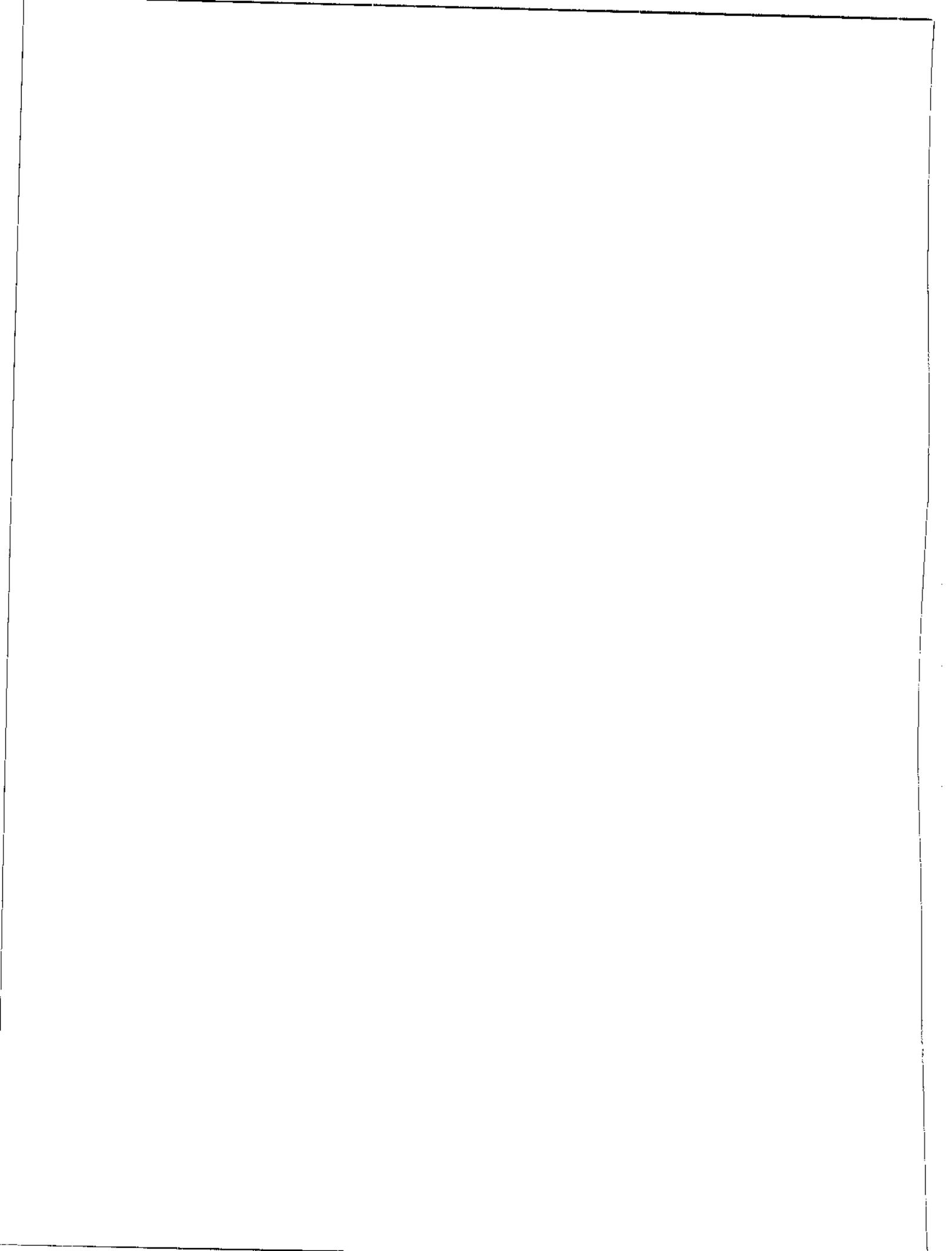
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