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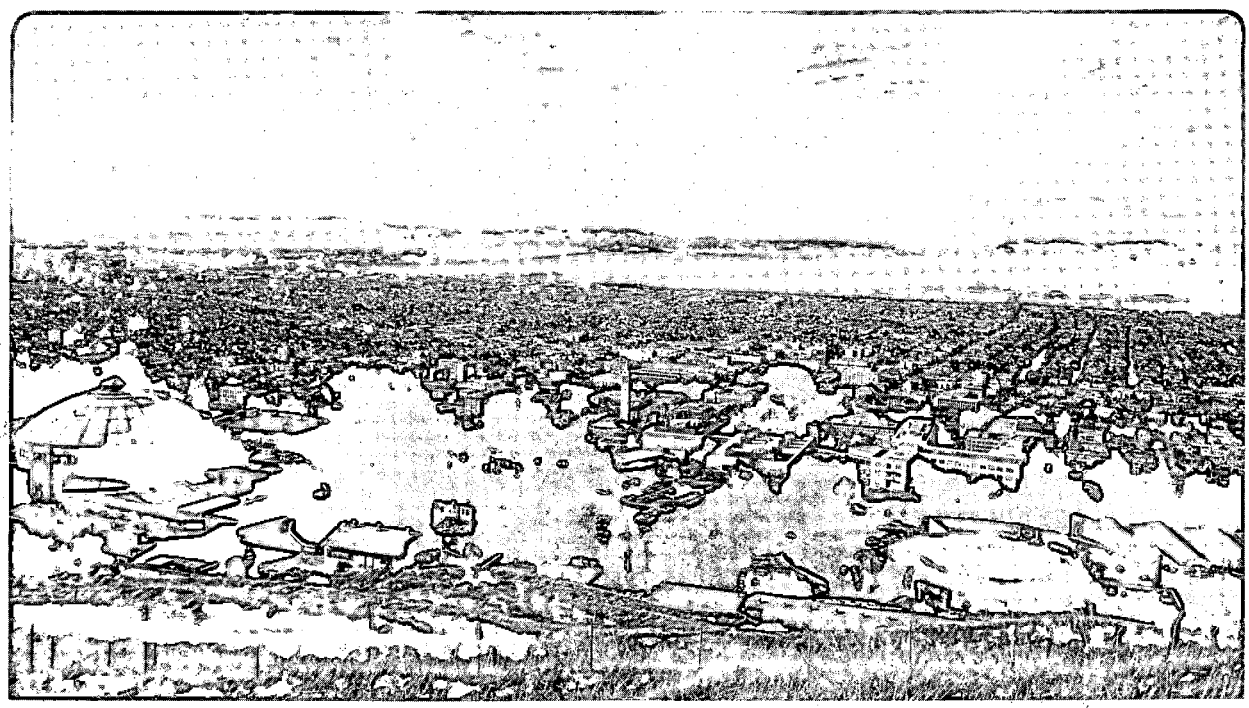

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Temperature Effects on the Solubility and Speciation of Selected Actinides

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ABSTRACT

To meet the requirements for licensing a high-level radioactive waste repository in the U.S., reliable predictions are needed on the solubility of actinide elements and the speciation of the solution complexes formed with groundwater from a prospective repository site (NRC 1984). The migration of contaminated groundwater is considered as one principal mechanism for the transport of radionuclides from the storage location to the accessible environment. The solubility and speciation predictions for actinide waste elements are made by utilizing thermodynamic solution data. Since elevated temperatures are expected in the repository and little or no information is available on thermodynamic solution data at temperatures above 25°C, one common method of prediction is to extrapolate thermodynamic functions to elevated temperatures from available data or reasonable estimates for 25°C.

The objective of this study was to determine experimentally the trends in the temperature dependence of the solubilities and speciation of neptunium, plutonium, and americium. In groundwaters hydroxide and carbonate anions are considered to play a most important role in the formation of insoluble precipitates and soluble complexes of actinides (ALLARD 1982, NRC 1984). Therefore, solubility measurements were made in 0.01 M noncomplexing $NaClO_4$ solution at pH 6.0 and 8.5 at both 25°C and 60°C. The total carbonate concentration was held constant at 120 ppm, a value close to that found in some groundwaters.

This study showed no clear change in solubility as the temperature changed from 25°C to 60°C. Many of the solid phases that formed, although crystalline, remain unidentified because of the lack of reference data in the literature. A comparison of the experimental results with solubility predictions from modeling calculations (SILVA 1984) showed significant differences. These differences are probably caused by the existence in the experiment of unknown solubility-controlling solid phases that were not included in the modeling data base. The results of this study demonstrate the need to study radionuclide solubilities experimentally in groundwaters from a prospective repository site to accurately predict the solubility limits needed for licensing a nuclear waste repository.

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1. EXECUTIVE SUMMARY

The objective of this study was to determine experimentally the trends in the temperature dependence of the solubilities and speciation of neptunium, plutonium, and americium. In groundwaters hydroxide and carbonate anions are considered to play a most important role in the formation of insoluble precipitates and soluble complexes of actinides (ALLARD 1982, NRC 1984). Therefore, to keep the task theoretically managable, solubility measurements to steady state were made in noncomplexing perchlorate solution at pH 6.0 and 8.5 at both 25°C and 60°C. The overall carbonate concentration for each case was held constant at 120 ppm, a value close to that found in some groundwaters.

A comparison of the results at the two different temperatures will demonstrate the importance of solubility measurements at elevated temperatures and should assist the NRC in their decision as to whether modeling alone can generally supply satisfactory information on the solubility and speciation of actinide elements at elevated temperatures or if measurements at higher temperatures should be performed. Furthermore, a comparison of the results with modeling calculations for these actinides under conditions similar to the experimental conditions will show for a specific case if the solubility and speciation can be predicted accurately enough by the model alone or if measurements are required for more accurate predictions.

The experimental results are summarized in the table on the following page. No general trend for the solubility was found as the temperature was increased from 25°C to 60°C; i.e.; the neptunium solutions showed increasing solubility, and the plutonium solutions showed decreasing solubility. Many solid phases had to remain unidentified because of the limited time frame and the exploratory nature of this study.

A comparison of the experimental results from this study with solubility predictions from modeling calculations (SILVA 1984) demonstrated the problems of attempting to accurately predict solubility by calculations alone. Many solid phases and solution species formed in the experiment are still unknown and therefore were not included as input for the modeling data base.

The results of this study show the need to determine radionuclide solubilities experimentally using groundwaters from the actual site of a prospective high-level radioactive waste (HLW) repository. Efforts should be spent to increase our knowledge of thermodynamic solution data to improve the accuracy of geochemical data bases. It is advisable to increase efforts to acquire experimental data and to improve the quality of theoretical information on radionuclide solutions at near-neutral pH values. Such an approach will yield scientifically sound and reliable information on the solubilities and speciation of radionuclides. Such information is crucial to the licensing process.

Summary of results for solubility experiment on Np, Pu, and Am in 0.01 M $NaClO_4$, 120 ppm total carbonate concentration, at pH 6 and 8.5, and at 25°C and 60°C.

Np	log steady-state concentration/M		oxidation state in supernatant solution		solid phase	
	25°C	60°C	25°C	60°C	25°C	60°C
pH 6	-(2.66 ± 0.08)	-(2.31 ± 0.09)	V = 100%	V = 100%	amorphous	crystalline unidentified
pH 8.5	-(4.02 ± 0.13)	-(3.80 ± 0.08)	V = 100%	V = 100%	crystalline unidentified	crystalline unidentified

Pu	log steady-state concentration/M		oxidation state in supernatant solution		solid phase	
	25°C	60°C	25°C	60°C	25°C	60°C
pH 6	-(7.72 ± 0.18)	-(8.88 ± 0.28)	V = (56 ± 5)% VI = (44 ± 5)%	V = (59 ± 21)% VI = (30 ± 18)%	crystalline unidentified	Pu(IV)colloid or $PuO_2 \cdot xH_2O$
pH 8.5	-(8.77 ± 0.20)	-(8.92 ± 0.24)	undetermined	IV = (50 ± 8)% V = (32 ± 20)%	amorphous unidentified	Pu(IV)colloid or $PuO_2 \cdot xH_2O$

Am	log steady-state concentration/M		oxidation state in supernatant solution		solid phase	
	25°C	60°C	25°C	60°C	25°C	60°C
pH 6	-(4.51 ± 0.04)	did not reach steady state after 69 days	III = 100%	III = 100%	crystalline[a] unidentified	$AmOHCO_3$
pH 8.5	-(9.21 ± 0.80)		III = 100%	III = 100%	crystalline[a] unidentified	$AmOHCO_3$

(a) Crystal structures are identical at pH 6 and pH 8.5.

2. INTRODUCTION

The storage of high-level radioactive waste (HLW) in repositories located in deep geologic formations is one possible means of permanent disposal in the United States. The waste embedded in several solid containments would be emplaced in the underground repository, where multiple engineered barriers would increase confidence in the long-term performance of the facility. Criteria for overall repository performance are given by the U.S. Nuclear Regulatory Commission (NRC) and the Environmental Protection Agency (EPA) (NRC 1983, EPA 1983).

Although the likelihood of waste form failure is significantly reduced by the use of multiple barriers, the migration of contaminated groundwater must be considered as one principal mechanism for the transport of radionuclides from the storage location to the environment. The magnitude of the groundwater contamination will be controlled by a variety of factors. Some of the major controls are the dissolution rate of the waste package, the formation of solubility controlling solids, and the formation of soluble species. The nature of the compounds and solution species formed will depend on a variety of parameters. They include the oxidation state of the radionuclide, the nature and concentration of the precipitating ions and complexing ligands, and the surrounding geologic host medium, i.e., pH, Eh, and temperature.

In order to develop the information and technology necessary to meet the requirements for licensing a repository, predictions are required on the solubility of actinide elements and the speciation of the solution complexes they will form with the groundwater. The significance of radionuclide solubility and speciation for the assessment of an HLW repository is outlined in detail by an NRC technical position report (NRC 1984).

The solubility and speciation predictions for actinide waste elements are made by utilizing thermodynamic solution data. However, since radiation-induced heat is expected to generate elevated temperature conditions in the repository vicinity (PRESS 1982), the temperature dependence of the thermodynamic constants must also be known. The oxidation state distribution in solution, the solubility product, and the formation constants are all functions of temperature and can be expected to vary with temperature in a rather complex way. Unfortunately, the literature contains little or no information on thermodynamic solution data at temperatures above 25°C. One common way to overcome this lack of data is to extrapolate thermodynamic functions to elevated temperatures from available data or reasonable estimates for 25°C (CRISS 1964A and 1964B, HELGESON 1969, BAES 1976 and 1981, LEMIRE 1980, TURNER 1981, PHILLIPS 1985).

The objective of this study is to experimentally determine trends of the temperature dependance of the solubilities and speciation of neptunium, plutonium, and americium. In groundwaters hydroxide and carbonate anions are considered to play a most important role in the formation of insoluble precipitates and soluble complexes of actinides (ALLARD 1982, NRC 1984). Therefore, to limit the task to hydroxide and carbonate complexation, solubility measurements are made up to steady-state conditions in noncomplexing perchlorate solution at pH 6.0 and 8.5 at 25°C and 60°C. The overall carbonate concentration for each case is held constant at 120 ppm, a value close to that found in some groundwaters.

A comparison of the results at the two temperatures will demonstrate the importance of solubility measurements at elevated temperatures and should help the NRC to decide whether modeling alone can supply satisfactory information on the solubility and speciation of actinide elements at elevated temperatures or whether measurements at higher temperatures should be made.

3. EXPERIMENTAL SECTION

3.1 Radionuclides

All nuclides used in these experiments were obtained through the U.S. Department of Energy's Heavy Element Production Program at Oak Ridge National Laboratory. Throughout these experiments several radioanalytical methods were used for nuclide identification and concentration determination:

a) Alpha energy analysis with a gold-silicon surface barrier detector (Oak Ridge Technical Enterprise Co.) coupled to a low-noise preamplifier, main amplifier, and biased amplifier of LBL design and to a multichannel analyzer (Tracor Northern Inc., Model TN1705).

b) Low-energy gamma ray analysis with two planar intrinsic germanium detectors (LBL design, and Ortec Inc., Model 1513) coupled to amplifiers (LBL design) and to multichannel analyzers (Tracor Northern Inc., Model TN1710 and TN1705).

c) Gross alpha counting with an argon-methane gas proportional counter of LBL design.

d) Alpha counting with a microprocessor-controlled liquid scintillation counter (Packard Instrument Co., Model 460C). A modification of the instrument allowed monitoring the liquid scintillation α-spectrum. A preblend scintillation cocktail was used (Research Products International Corp., complete counting cocktail 3a70B) for sample preparation.

Results of radioactive counting are given within a 95.5% confidence interval ($\pm$ 2 σ_R). The following statistical relations were used throughout this study:

a) Count rate: $R = \frac{N}{t}$, N = counts, t = counting time.

b) Standard deviation of count rate: $\sigma_R = \frac{\sqrt{N}}{t}$.

c) Standard deviation of net count rate,

$$2\sigma_N = \sqrt{(2\sigma_t)^2 + (2\sigma_B)^2}$$

σ_t = s.d. of total count rate,

σ_B = s.d. of background count rate.

3.1.1 Neptunium

A purified $^{237}NpO_2^+$ stock solution was prepared from neptunium dioxide. The NpO_2 was dissolved in 8 M HNO_3 containing a trace of NaF to facilitate the dissolution. NaOH was then added to precipitate the hydroxide. After washing, the precipitate was dissolved in 0.1 M HNO_3 and the Np reduced to the +3 state by contacting the solution with zinc amalgam. Purging of the resulting solution with air for a few minutes converted all the Np to the +4 oxidation state. The Np was then purified in the tetravalent state by anion-exchange chromatography (BURNEY 1974). The anion-exchange column

was prepared with 100–200 mesh Biorad AG 1 x 8 resin. Loading and washing was done with 8 M HNO_3 and elution with 0.3 M HNO_3. The elutes were fumed twice with concentrated $HClO_4$ to near dryness. The residue was then redissolved in 10 ml of 0.1 M $HClO_4$. Alpha counting and microtitration with EDTA were used to standardize the stock solution (SMIRNOV 1966). The standardized solution was $(1.17 \pm 0.03) \times 10^{-1}$ M. A 100 μg sample was analyzed by spark emission spectroscopy for metal contaminants. No contaminants were found at levels exceeding the detection limits of the method (CONWAY 1952).

3.1.2 Plutonium

Since the Pu solubility was expected to limit solution concentrations to 10^{-8} M at the experimental pH (NITSCHE 1985), the specific alpha activity of our ^{242}Pu stock solution was increased by spiking with ^{238}Pu, which facilitated concentration measurements at low levels. ^{242}Pu and ^{238}Pu stock solutions were prepared individually from oxide powders. The oxides were dissolved in 6 M HCl and converted to the perchlorate by fuming twice to near dryness with concentrated $HClO_4$. After taking up the residues in perchloric acid, the ^{242}Pu solution was spiked with a small amount of ^{238}Pu solution. The mixture was fumed again with concentrated $HClO_4$ and the residue redissolved in 1 M $HClO_4$. The concentration of this stock solution was determined to be $(2.54 \pm 0.07) \times 10^{-1}$ M from the results of gross alpha counting of dried aliquots with a gas proportional counter and from liquid aliquots with a low-energy gamma counter. Alpha and gamma pulse-height analysis gave the following distribution of alpha activity and composition by weight, respectively, for the mixture: ^{238}Pu, 99.47% and 4.96%; ^{242}Pu, 0.44% and 95.02%; and ^{241}Am, 0.09% and 0.02%. The specific activity of this mixture was 2.07×10^6 dpm/μg. Spectrochemical analysis of a 100 μg sample showed no metal contaminants.

3.1.3 Americium

Since the Am was in solution from a previous experiment, it was cleansed of soluble salts and silica by two NaOH precipitation-dissolution cycles. The resulting tan $Am(OH)_3$ was dissolved in 0.05 M HCl and purified by cation-exchange chromatography on Biorad AG50x8 resin (DIAMOND 1954). The eluate was fumed twice with concentrated $HClO_4$ to near dryness and the residue was redissolved in 2 ml of 0.1 M $HClO_4$. The proportions of nuclides in this solution were found to be 99.998% and 99.878% ^{243}Am, and 0.002% and 0.122% ^{241}Am by alpha activity and weight, respectively. Fifty μg of the sample was analyzed by spark emission spectroscopic analysis for metal impurities. No contaminants were found.

3.1.4 Oxidation State Adjustment

The various oxidation states of Pu and Np in the stock solutions were adjusted by controlled-potential coulometry (STROHMATT 1959, COHEN 1961A). The coulometric cell was a three–electrode setup. A platinum wire counter electrode, a Ag/AgCl/3 M NaCl reference electrode (AgCl), and a platinum gauze working electrode were used. The counter and reference electrodes were separated from the analyte solution by Vycor^R fritted salt bridges that contained 1 M $HClO_4$. Solution purging or blanketing with argon was accomplished through a port in the cell top. Solution stirring was achieved with a magnetic spinbar and an electric stirrer. The neptunium in the stock solution was in the +6 oxidation state after its initial preparation. It was reduced to NpO_2^+ at 645 mV (AgCl).

After the fuming procedure the plutonium stock contained only PuO_2^{2+}. The reduction from the plutonium-dioxo-cations to Pu^{4+} cannot be performed directly. Because of the irreversibility of the reaction PuO_2^+ to Pu^{4+}, a large overpotential must be applied. This leads to the formation of Pu^{3+}. Therefore, all PuO_2^+ was reduced at –100 mV (AgCl) to Pu^{3+} and then oxidized at 1100 mV (AgCl) to Pu^{4+}.

Purity control for each valence state was established by absorption spectrophotometry utilizing a recording spectrometer (Varian Instruments Division, Cary Products, Model 17). A minicomputer (Digital Equipment Corp., Model MINC-11-B, LSI-11/2) was interfaced to the spectrometer to allow digital data collection and manipulation, e.g., background subtraction and data smoothing. For molar absorptivities with values below 100 $M^{-1}cm^{-1}$, cells of 100 mm pathlength were utilized; for solution ions with higher molar absorptivities, a 10 mm cuvette gave sufficient response at given concentration levels. For all measurements, solutions corresponding to the analytical solution without radionuclides were used as reference. The spectra were taken in the range 350–1250 nm. Spectra obtained for each individual oxidation state were identical with published data (HAGAN 1966, SHILOH 1969), with the exception of the Pu(IV) spectrum (COHEN 1961B). The absorption peak maxima agreed well with COHEN's Pu(IV) spectrum, but no "background sloping" toward higher absorbance values was observed at frequencies below 460 nm.

3.2 Solutions

All solutions were prepared with deonized, distilled, CO_2-free water under an inert-gas atmosphere. The water was taken from the distillation apparatus while it was still hot and was stored in an inert-gas glove box to eliminate CO_2 uptake. Prior to being used, the solutions were filtered through a 0.05 μm polycarbonate membrane filter (Nuclepore Corp.) to remove suspended particulate material, e.g., dust or silica, that could absorb the actinide ions to form pseudocolloids. The total carbonate concentration ($c_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$) of 120 ppm at the different pH values and temperatures was achieved by saturating the solutions with Ar-CO_2 gas mixtures of specified composition. The partial CO_2 pressures were calculated utilizing literature values for the equilibrium quotients of the carbonate system (PHILLIPS 1985). Values not listed at the appropriate ionic strength or temperature were derived from linear extrapolation of data most closely representing the desired conditions. The nominal partial CO_2 pressures were maintained at all times above the solutions' surface. Reagant grade $NaClO_4$ (G. F. Smith Chemical Company) was recrystallized twice from H_2O before it was used to make the 0.01 M $NaClO_4$ noncomplexing supporting electrolyte solution.

3.3 Procedures and Equipment

3.3.1 Solubility Measurements

The solubility measurements were made in an inert-atmosphere box (Vacuum Atmospheres Co., Model HE-43-2) to avoid contamination of solutions by CO_2 and O_2. A computer-controlled pH-stat was used to maintain the experimental pH values. A laboratory computer (Laboratory Data Control, Milton Roy Company, Model CCM) control system was used to sense any one of six microcombination pH electrodes (Beckman Instr., Inc., Model 39522) via a pH-electrode switch (Orion Research, Inc., Model 605, modified for remote control) and a pH meter (Radiometer America, Inc., Model pHm 84). If the pH of the selected solution was not within the preselected range, 5μl of dilute $HClO_4$ or NaOH was dispensed on computer command to the appropriate solution through a computer-selectable, six-position solvent-delivery valve (Eldex Laboratories, Inc., Model SV 1062) by a digital diluter (Hamilton Company, Model 100000). All solutions were continuously monitored and pH corrections made as required. The diluter,

associated electronics, and acids and bases are contained in a separate argon-atmosphere glove box (Labconco Corp.) adjacent to the inert-atmosphere box to avoid radioactive contamination.

To avoid clogging of the pH electrode's electrolyte bridge by formation of insoluble $KClO_4$, the KCl/AgCl bridge electrolyte was replaced with a concentrated NaCl solution, which was saturated with AgCl. The pH electrodes were calibrated with buffers at least twice every week to correct for possible electrode drift. Phosphate was used for pH 6 and borax for pH 8.5 to prepare buffer solutions with nominal pH values of 6.00 and 8.50, respectively, at 25°C (BATES 1973). Nominal pH values for the buffers at 60°C were calculated from their temperature coefficients (phosphate, dpH/dt = –0.0028 unit °C; borax, dpH/dt = –0.008 unit °C).

Solubility measurements were made in 100 ml polypropylene cells with sealed ports at the top to allow permanent emplacement of a pH electrode, introduction of Ar-CO_2 gas, addition of 0.05 M $HClO_4$ or 0.05 M NaOH for pH correction, and sampling. The cells were placed in close-fitted openings inside a hollow brass block to achieve the experimental temperatures of 25 ± 1°C or 60 ± 1°C. From a circulating thermostat (Haake Inc., Model KT 33) located outside the inert-atmosphere glove box, thermostated water was pumped in a closed circuit through the core of the brass block and back to the thermostat. The $HClO_4$ was made from doubly distilled concentrated stock (G. F. Smith Chemical Company); NaOH pellets "low in carbonate" (J. T. Baker Chemical Co.) were used to prepare the NaOH solution. Solutions were prepared as described previously. Samples were shaken at 80 rpm with an automatic shaker (Lab-Line, Inc., Model Junior Orbit).

Because of the exploratory character of this project, solubilities were measured only from the supersaturation direction. Approaching solubility measurements in this way allows an upper limit to be determined for the material of interest (NRC 1984). Aliquots of NpO_2^+, Pu^{4+}, and Am^{3+} stock solutions were placed in pre-leached (1:1 HCl, 1:1 HNO_3, H_2O), separate polypropylene cells with 50 ml of the aqueous phase at 25 ± 1°C or 60 ± 1°C. The initial solution concentrations are given in Table 1. The pH of the supporting electrolyte was kept slightly basic to compensate for the amount of acid introduced by adding the actinide stock solution. Special care was taken not to allow the pH to drop below the experimental values of 6 or 8.5, which would have necessitated addition of base to readjust the pH. Addition of base can result in unpredictable microprecipitation and formation of polymers.

Achievement of steady-state conditions for the solubility measurements was monitored by sampling aliquots of the solution phases and analyzing for the respective radioisotope as a function of time. The efficiency of the separation of solid and solution phase is strongly dependent on the method of separation. The effects of various separation methods for neptunium, plutonium, and americium have been investigated by several researchers (RAI 1982, BERNKOPF 1984, NITSCHE 1985).

The studies show that ultrafiltrations with Centricon Microconcentrators (Amicon Corp., MW cutoff 30,000, calculated pore size 4.1 nm) provide the most effective separation. For all filtrations, possible absorption of soluble material on the filters was minimized by first filtering an aliquot of the sample and discarding the filtrate before filtering a second sample for analysis. A sufficient amount of 9 M HCl (15–100 μl) was always added to the filtrate-collecting vial to acidify the filtrate. This prevents possible absorption of radioactive material on the container walls, which would lead to erroneous results for the concentration determination of the solution phase.

After separation of solution and solid phase, the two components were analyzed separately. Concentration measurements of the supernatants were made by counting liquid aliquots with the germanium low-energy counting system. For ^{237}Np and ^{243}Am the 29.34 keV and the 74.67 keV γ-ray lines were used, respectively. Plutonium was

Table 1.
Initial solution concentrations for NpO_2^+, Pu^{4+}, and Am^{3+}.

	$\frac{c_{NpO_2^+}}{M}$	$\frac{c_{Pu}^{4+}}{M}$	$\frac{c_{Am}^{3+}}{M}$
pH 6, 25 °C	2.95×10^{-3}	3.2×10^{-4}	4.1×10^{-4}
pH 6, 60 °C	6.55×10^{-3}	6.4×10^{-4}	2.1×10^{-4}
pH 8.5, 25 °C	1.95×10^{-3}	3.2×10^{-4}	2.6×10^{-4}
pH 8.5, 60 °C	2.40×10^{-3}	3.9×10^{-4}	1.1×10^{-4}

assayed by utilizing the uranium $L\beta_1$ (17.22 keV) and $L\beta_2$, (16.43 keV) X-rays. At ultra-trace levels the sum of the $UL\alpha_1$ (13.61 keV), $UL\alpha_2$ (13.46 keV), $L\beta_1$, $L\beta_2$, and $L\gamma_1$ (20.16 keV) uranium X-rays was used to minimize the statistical counting error.

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 11.4 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 Ni was used.

4. EVALUATION OF SOME TECHNIQUES FOR THE DETERMINATION OF OXIDATION STATES IN PLUTONIUM SOLUTIONS

The determination of oxidation states in the solution phase is most important to thorough studies of solubility if the metal ion involved can potentially be present in several different oxidation states. The most common methods for the determination of oxidation states in Pu solutions are absorption spectrophotometry, ion exchange chromatography (on either organic or inorganic substrates), solvent extraction and coprecipitation techniques.

4.1 Absorption Spectroscopy

Conventional absorption spectroscopy can be applied only to solutions of rather high concentration. The $5f^n$–$5f^n$ transitions in Pu are weak, and therefore the observable differences in light absorption are not very pronounced. Table 2 lists the most prominent absorption bands for Pu, the molar absorptivity for each band, and a meaningful detection limit, where a clear distinction between signal and noise is still possible (signal: noise = 10:1). In order to reach these limits, a double beam UV-VIS-NIR spectrometer with digital output capability is required. The digitalization will allow background subtraction and data smoothing through the application of mathematical data processing (i.e., Fourier Transformation). Also an optical pathlength of 100 mm is to be used. If an ion is present in several oxidation states in one solution, the sensitivity limits may be even higher because of the overlap of absorption bands from different oxidation states.

Despite the limitations to relatively high solution concentrations, absorption spectroscopy provides a versatile method for solution speciation at these levels. Cation-complexation of actinide metal ions exert small shifts in the $5f^n$–$5f^n$ electron transition, which can be observed as shifts in wavelength and intensity of the absorption signal. When these parameters are determined experimentally, it is possible to gain qualitative and quantitative information on the speciation of a given complex in solution. However, for Pu solutions containing ligands with either unknown or nonestablished Pu-complexation characteristics, no conclusion can be drawn for the speciation by this experimental technique. Both the spectral shift as a function of ligand complexation and the complex stability constants must be well established for each individual Pu complex. This information can then help to identify the speciation in a multiligand solution with one or several strong complexing ligands.

Recently, photoacoustic spectroscopy (PATEL 1981) was used for the oxidation-state-specific detection and speciation of actinide ions in aqueous solution (STUMPE 1984A and 1984B, BUCKAU 1985). As in absorption spectrophotometry this technique measures the energy absorbed when light passes through the sample. The difference is in the determination of the absorbed energy: In conventional spectroscopy the difference is determined by comparing the light intensity of a sample beam with a reference beam, whereas in photoacoustic spectroscopy the absorbed energy is measured directly in the form of a pressure wave in the solution. The pressure wave is generated by the nonradiative decay of the $5f^n$ electrons to the ground state and is proportional to the absorbed energy. The detection limit is improved by two to three orders of magnitude compared with conventional absorption spectrophotometry.

4.2. Ion Exchange

Cation exchange chromatography on organic resins exploits the different adsorption and desorption behavior of the Pu ions in each individual oxidation state (DIAMOND 1954, SPECHT 1969, NEWTON 1982, 1983A, and 1983B, GEHMECKER 1985). Most cation exchange resins exhibit reducing properties. This can change the oxidation state

Table 2.
Absorption parameters for Pu[a].

valence	wavelength / nm	molar absorptivity(ϵ) / $M^{-1}cm^{-1}$	sensitivity(c)[b] / M
Pu^{3+}	600	38	1.3×10^{-5}
Pu^{4+}	470	55	9×10^{-6}
PuO_2^{+}	569	18	1.8×10^{-5}
PuO_2^{2+}	831	555	9×10^{-7}
Pu(IV) colloid	613	12-18	4×10^{-5}

(a) COHEN 1961B, CONSTANZO 1973.

(b) The sensitivity is determined by the minimum absorbance of A = 0.005 for a given concentration, expressed as $c = \frac{A}{\epsilon \cdot l}$ (ϵ = molar absorptivity, l = optical path-length).

distribution of the analytical Pu solution and will result in misleading data at trace levels.

Inorganic exchange material is considered to be less reducing than organic resins. For zirconium phosphate as matrix material contradictory results are reported in the literature (NEWTON 1983 A, GEHMECKER 1985). GEHMECKER successfully separated mixtures of Pu^{3+}, Pu^{4+}, and PuO_2^+, whereas NEWTON reported partial oxidation of plutonium.

4.3 Extraction and Coprecipitation Techniques

Solvent extraction is widely used for Pu separations (GMEHLIN 1975). Thenoyltrifluoro-acetone (TTA), methyl-isobutyl-ketone (Hexone), and di(2-ethylhexyl) phosphoric acid (HDEHP) are most commonly utilized for oxidation state determinations (FOTI 1964, CVJETICANIN 1975, BONDIETTI 1976, BERTRAND 1982, NITSCHE 1985, GEHMECKER 1985). TTA extracts by chelation, Hexone by the formation of ion associates, and the strongly acidic HDEHP acts as a "liquid cation exchanger."

Coprecipitation methods employ the similarity in precipitation behavior of a so-called carrier ion with the solution species, which, alone, would not form a significant precipitate because of their low concentration (HYDE 1954). In a previous study (NITSCHE 1985), a scheme was derived to determine quantitatively trace amounts of plutonium ions of different oxidation states. In this report this method was extended and refined. Two HDEHP extraction steps at pH 0 and pH 1 were added. Table 3 surveys the methods used and their selectivity for specific oxidation states.

TTA (Alfa Products, M. Thiokol, Inc.) was recrystallized twice from cyclohexane. It was dissolved in xylene to make a 0.5 M solution. The extractant was presaturated with 1 M HCl or pH 4 acetate buffer prior to its use. 0.5 ml aliquots of the test solution were adjusted (HCl for pH 0, actetate buffer and HCl for pH 4) to make 1 ml, which was extracted for 5 min with an equal volume of TTA utilizing a vortex mixer (VWR scientific, model K-550-G). The phases were separated and subjected to a second extraction. The combined organic phases were "back-washed" with equal volumes of aqueous solution (1 M HCl for pH 0, acetate buffer for pH 4). After phase separation, the back-wash solution was combined with the remaining aqueous solutions. The organic raffinate and the aqueous solution were assayed by γ counting.

The methyl-isobutyl-ketone used for the Hexone extractions was doubly distilled and acid presaturated (1 M HNO_3) prior to its use. Solid $Ca(NO_3)_2 \cdot 4H_2O$ and 1 M HNO_3 were added to 0.5 ml aliquots to make the solution 4 M in $Ca(NO_3)_2$. The extraction was done twice in the manner described for TTA; the back-wash was 4 M in $Ca(NO_3)_2$ and 1 M in HNO_3.

The TTA and the Hexone extractions have been tested in a previous study (NITSCHE 1985) individually on a Pu^{4+} solution and on Pu^{3+}/Pu^{4+} and Pu^{4+}/PuO_2^{2+} mixtures. TTA extractions at pH 0 yielded 98 $\pm$ 2% Pu^{4+}, whereas extractions at pH 4 yielded 96 $\pm$ 4% for Pu^{3+} and Pu^{4+}. Hexone extractions were sometimes burdened by a relatively large error. On the average 90 $\pm$ 20% Pu^{4+} and PuO_2^{2+} could be found in the organic raffinate. This may be due to unsatifactory phase separations, since the boundary between the Hexone and the aqueous solution is formed by two colorless solutions and therefore is not very distinct.

To overcome this problem two HDEHP extractions were tested for their potential of being a useful addition to the scheme for the determination of oxidation states. 0.5 ml aliquots of the test solution were acidified with HCl to make 1 ml of solution of either pH 0 or pH 1. The extraction was performed twice with equal volumes of 0.5 M HDEHP (Alfa Products, M. Thiokol, Inc.) in toluene. The unified organic raffinates were

Table 3.
Methods to determine the oxidation state in plutonium solutions.

method	oxidation state distribution	
	organic phase	aqueous phase
TTA extraction at pH 0	+4	+3,+5,+6,colloid[a]
TTA extraction at pH 4	+3,+4	+5,+6,colloid[a]
HDEHP extraction pH 0	+4,+6,	+3,+5,colloid[a]
HDEHP extraction pH 1	+3,+4,+6	+5,colloid[a]
Hexone extraction	+4,+6	+3,+5,colloid[a]
LaF_3 precipitation[b]	+3,+4,colloid[a] in precipitate	+5,+6 in supernatant

(a) Pu(IV) colloid.
(b) Method with "holding oxidant."

back-washed with HCl of appropriate concentration, and then the phases were separated and counted individually.

The coprecipitation was performed as follows: 0.5 ml of the analyte solution was made 1 M in HNO_3, 0.5 M in H_2SO_4 and 0.02 M in $Na_2Cr_2O_7$. Then Zr^{4+}, as hold-back ion (1 mg/ml) and La^{3+} carrier (2 mg/ml) were added. 28 M HF, pretreated with a trace of $Na_2Cr_2O_7$ to oxidize possible reductants present, was added to precipitate the lanthanum fluoride from a solution 2 M in HF. The precipitate was digested for 10 min, centrifuged, and washed three times with a mixture of 1 M HNO_3 and 1 M HF until it was completely white. The precipitate was dissolved in 1 M HNO_3 (saturated with H_3BO_3) and counted for activity. The supernatant and the wash solutions were combined and assayed.

To check the capability of this method at trace concentrations, two Pu mixtures at the 10^{-4} M and 10^{-7} M levels were analyzed by the above-described methods in an Ar-atmosphere glove box. The concentrated mixture was prepared by dilution of partially electrolyzed PuO_2^{2+} stock with 1 M $HClO_4$ to yield a Pu concentration assayed as (7.54 $\pm$ 0.05) x 10^{-5} M (mixture 1). This mixture was also analyzed by absorption spectrophotometry. An aliquot at this solution was diluted with 1 M $HClO_4$ to give a total Pu concentration of (1.46 $\pm$ 0.01) x 10^{-7} M (mixture 2). Each extraction and coprecipitation was done in parallel for both concentrations to minimize possible changes of the solution composition with time. Results are given in Table 4.

The recovery for Pu^{4+} by TTA extraction at pH 0 agreed well for mixtures 1 and 2 with the results obtained by absorption spectroscopy on mixture 1. The Hexone extractions of mixtures 1 and 2 resulted in incomplete recovery of Pu^{4+} and PuO_2^{2+} in the organic phase. The speciation yielded only 80% for the material balance, and, even after correcting for the loss, the result was still too low. Some parts of the organic and aqueous phase appear to form an emulsion that is hard to separate and seems to adhere strongly to the walls of the extraction cone and may cause the loss in yield.

HDEHP extractions performed at pH 0 also extracted Pu^{4+} and PuO_2^{2+} and gave good agreement between mixtures 1 and 2. The material yield was quantitative, and the method seems to be superior to Hexone extraction. A value for PuO_2^{2+} was obtained by subtracting the Pu^{4+} (TTA, pH 0) from the sum of PuO_2^{2+} and Pu^{4+}. The HDEHP extraction at pH 1 agreed reasonably well for both mixtures and proved that no Pu^{3+} was present in either mixture.

Lanthanum fluoride precipitates Pu^{3+}, Pu^{4+}, and Pu(IV) colloid. Comparison of this value with the one for Pu^{4+} (TTA, pH 0) showed that neither Pu^{3+} nor colloidal plutonium was present. A value for PuO_2^{+} was derived by subtracting the calculated value for PuO_2^{2+} from the result for the LaF_3 supernatant.

This work has demonstrated the usefulness of some liquid-liquid extractants and a coprecipitation method for studying the distribution of oxidation states in solutions containing trace amounts of Pu. An analysis scheme using a combination of TTA at pH 0, HDEHP at pH 0 and 1, and LaF_3 coprecipitation will provide a reasonably complete understanding of the oxidation states present in the supernatant solutions used in plutonium solubility experiments.

Table 4.
Results in percent of oxidation state distribution determination on Pu oxidation state mixtures at 25±1 ° C, argon atmosphere. The superscripts a,b,c... refer to various solution fractions. The nomenclature b–a means solution b minus solution a, etc.

method	TTA,pH 0		HDEHP,pH 0		HDEHP,pH 1		Hexone		LaF_3		spectrum
mixture*	1	2	1	2	1	2	1	2	1	2	1
IV^a	70.9±0.3	74.0±1.4									73.5±4.0
III,V,VI,coll.	29.8±0.4	26.8±0.5									
IV,VI^b			93.5±0.4	89.7±1.4							
III,V,coll.			6.4±0.5	10.3±0.3							
VI^{b-a}			23.2±0.5	15.7±2.0							17.2±1.0
III,IV,VI^c					92.8±1.3	88.4±1.4					
$V,coll.^e$					7.7±0.4	11.6±0.3					
III^{c-b}					0±1.4	0±2					
IV,VI							66.7±0.4	69.8±1.4			
III,V,coll.							33.3±0.3	30 2±0.1			
III,IV,coll.									70.4±0.7	67.5±1.4	
V,VI^d									29.6±0.7	32.5±0.6	
$V^{d-(b-a)}$									6.4±0.3	16.8±2.1	9.3±9.3
$coll^{e-(d-(b-a))}$									1.3±1.0	0±2.1	0±5

Note: III,IV,V,VI = Pu oxidation states; coll = Pu(IV) colloid; * = mixture 1 (7.5×10^{-5} M) or mixture 2 (1.5×10^{-7} M).

5. RESULTS AND DISCUSSION

5.1 Neptunium

Figure 1 gives the results of the solubility measurements as a function of equilibration time at pH 6 for 25°C and 60°C; Figure 2 shows the results for pH 8.5 at 25°C and at 60°C.

In 0.01 M $NaClO_4$, and with 120 ppm total carbonate, steady-state values for the solution at pH 6 were calculated to be $(2.2 \pm 0.4) \times 10^{-3}$ M ($10^{-(2.66\pm0.08)}$ M) for 25°C using the last 10 data points and $(5 \pm 1) \times 10^{-3}$ M ($10^{-(2.31\pm0.09)}$ M) using the last 6 data points for 60°C. For pH 8.5 values of $(1.0 \pm 0.3) \times 10^{-4}$ M ($10^{-(4.02\pm0.13)}$ M) at 25°C (last 10 points) and $(1.6 \pm 0.3) \times 10^{-4}$ M ($10^{-(3.80\pm0.08)}$ M) at 60°C (last 6 points) were derived. The precipitates formed for each solution were:

a) pH 6, 25°C: brownish green, amorphous.

b) pH 6, 60°C: grayish white, crystalline.

c) pH 8.5, 25°C: brownish green, crystalline.

d) pH 8.5, 60°C: grayish white, crystalline.

The X-ray powder diffraction patterns from the crystalline materials are listed in Table 5. The precipitate formed in the solution at pH 6 and 25°C did not produce any pattern, and it may possibly be under the given conditions amorphous neptunium(V) hydroxide. No comparable X-ray data were found in the literature for the crystalline precipitates. The solid phase formed at pH 6 and 60°C (phase 1) is neither NpO_2 nor NpO_2OH, which is not known to exist in a crystalline form. The precipitates from the experiments at pH 6 and 8.5 at 60°C appear to be identical in their X-ray pattern, and it seems possible that the solubility-controlling solid phase exists in the form of a mixed sodium-neptunium carbonate or even as sodium-neptunium hydroxycarbonate. This hypothesis is supported by the fact that both precipitates dissolved in $HClO_4$ with the evolution of gas, which is very likely to be CO_2. The solid phases of both experiments at 25°C did not produce any visible gas bubbles when dissolved in acid.

Oxidation state distribution analysis for the neptunium supernatant solutions was performed by absorption spectrophotometry. Both solutions at pH 6 contained exclusively uncomplexed NpO_2^+.

The spectra for the pH 8.5 supernatants are shown in Figure 3 for 25°C and in Figure 4 for 60°C. Figures 5 and 6 depict an expanded view of the main absorption bands for 25°C and 60°C. The spectra show that the peak shifts from 980 nm. to 992 nm as the temperature changes from 25°C to 60°C. The spectrum for the solutions at the lower temperature (Fig. 5, spectrum (1)) shows a weak absorption line at 992 nm, next to the main absorption band at 980 nm. This feature is known to be due to carbonate complexation (NITSCHE 1985), and one can derive the amount of neptunium present as carbonate complex from the difference between the amounts of neptunium and free NpO_2^+ in solution. The spectrum indicates that approximately 39% of the NpO_2^+ (Fig. 5, spectrum (2)) is complexed by carbonate. At 60° nearly all the neptunium is present in solution as a carbonate complex (Fig. 6., spectrum (1)). Again, the complex(es) could be destroyed by acid addition to give uncomplexed NpO_2^+ (Fig. 6, spectrum (2)).

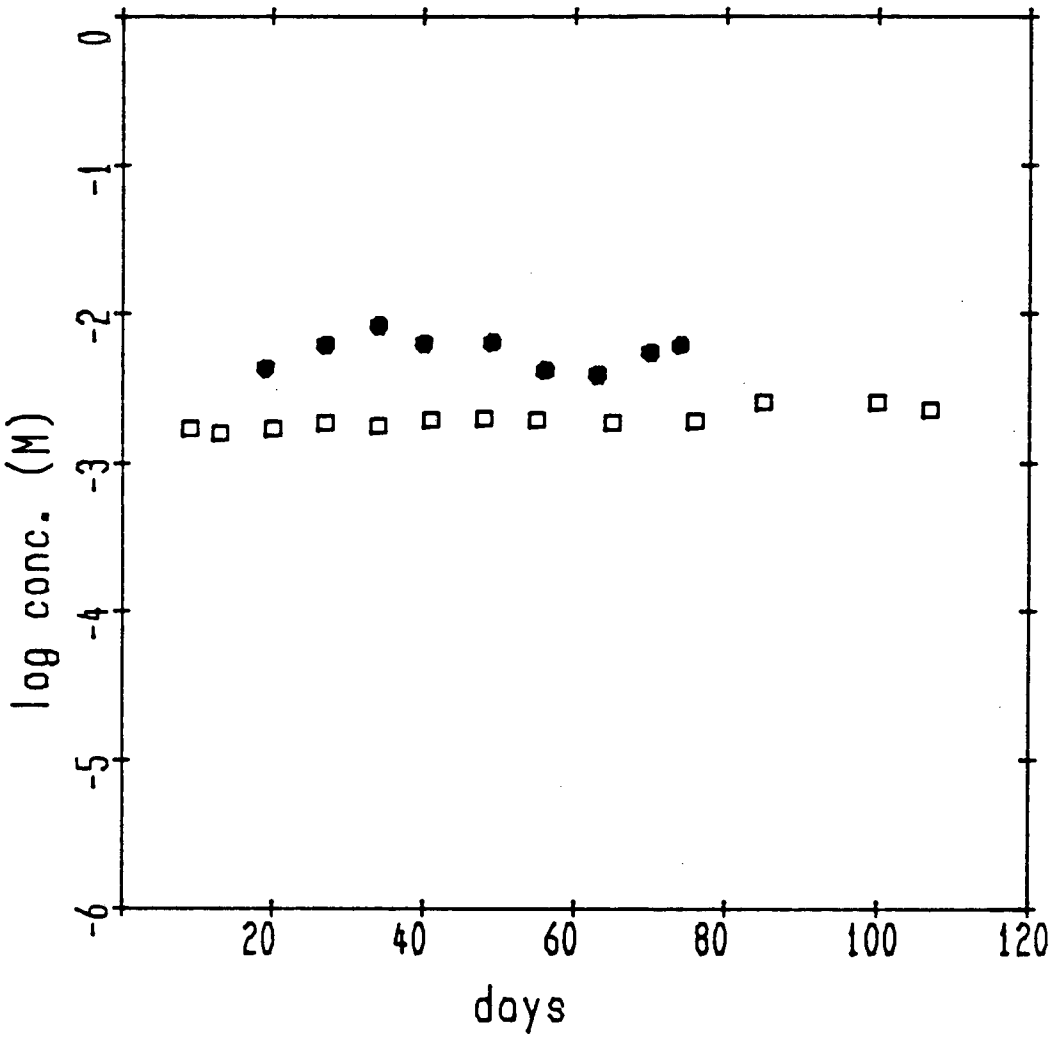

Figure 1. Solution concentrations of ^{237}Np in contact with precipitate obtained from supersaturation at pH 6.0 ± 0.1 in 0.01 M $NaClO_4$ and 120 ppm total carbonate concentration as a function of time. Open squares are for 25 ± 1°C; filled octagons are for 60 ± 1°C.

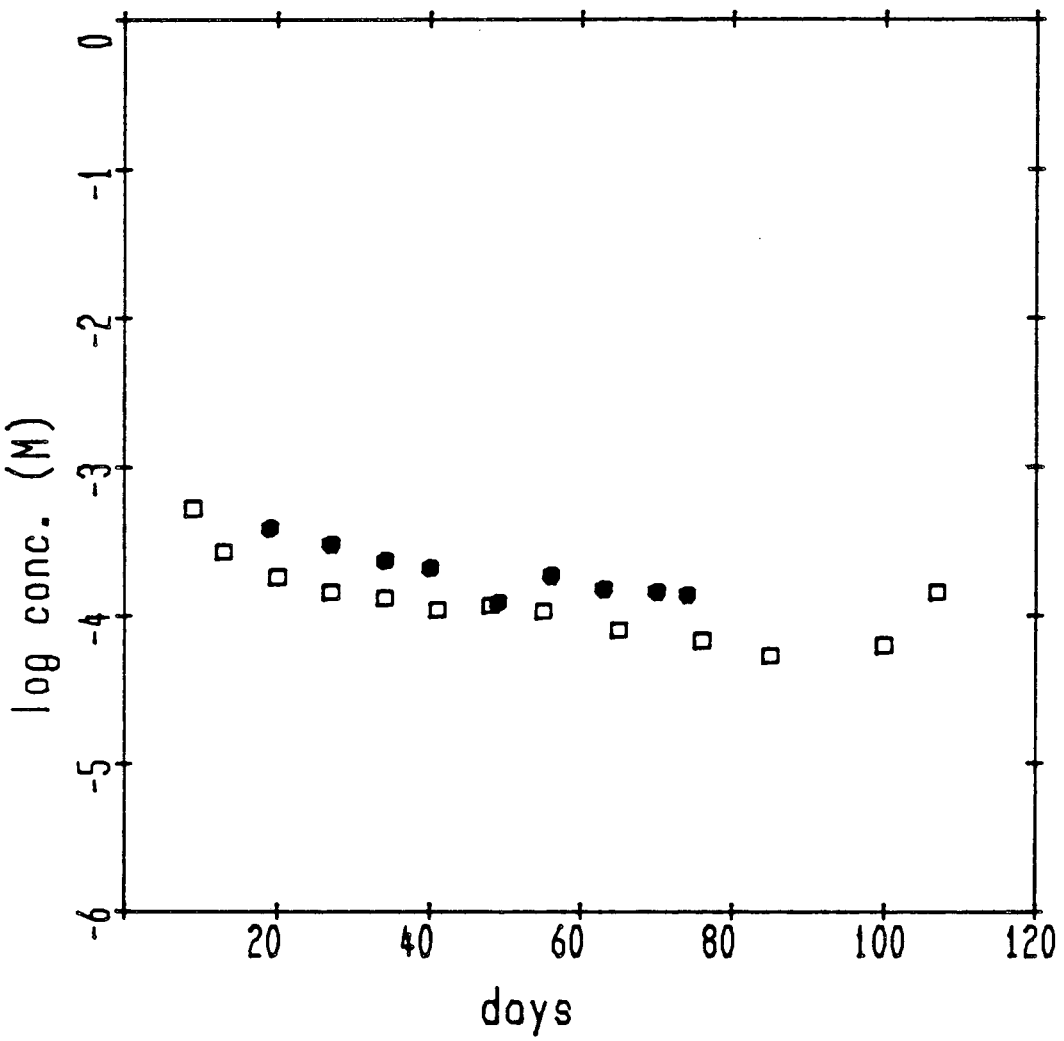

Figure 2. Solution concentrations of ^{237}Np in contact with precipitate obtained from supersaturation at pH 8.5 ± 0.1 in 0.01 M $NaClO_4$ and 120 ppm total carbonate concentration as a function of time. Open squares are for 25 ± 1°C; filled octagons are for 60 ± 1°C.

Table 5.
X-ray powder diffraction patterns of Np solid phases in 0.01 M $NaClO_4$, 120 ppm total carbonate, pH 6.0 at 60 ° C (phase 1), pH 8.5 at 25 ° C (phase 2a), and pH 8.5 at 60 ° C (phase 2b).

phase 1 d(A) I[a]	phase 2a d(A) I[a]	phase 2b d(A) I[a]
	9.94 s	
9.85 s		
	8.51 vs	8.47 vs
	6.92 s	6.86 vs
6.26 w		
4.94 m	4.91 m	4.90 s
	4.65 m	4.64 s
4.34 vs		4.33 m
4.23 m		4.24 m
3.99 s	4.00 m	3.99 m
	3.66 m	3.66 m
	3.45 m	3.45 m
3.23 s	3.23 s	3.22 s
3.07 m	3.05 w	3.05 w
	2.99 w	2.99 w
	2.92 m	2.92 m
	2.83 w	2.82 w
2.72 m		
2.63 w		
2.48 w		
2.41 w		
2.17 w		
2.11 w		
2.06 m		
1.98 w		
1.94 w		

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

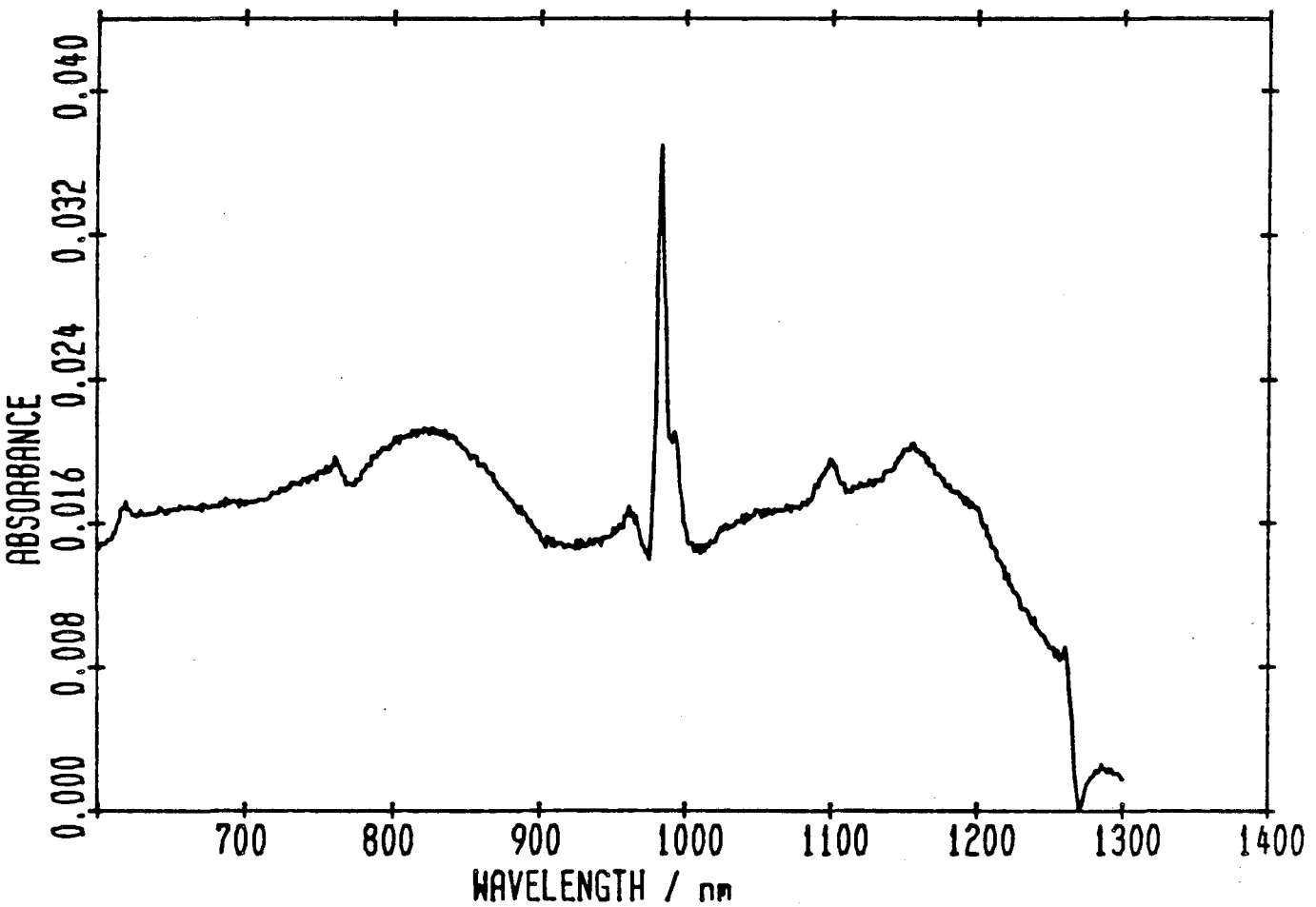

Figure 3. Absorption spectrum of ^{237}Np in 0.01 M $NaClO_4$ after reaching steady-state solubility conditions at 8.5 ± 0.1 and 25 ± 1°C; total carbonate concentration was 120 ppm.

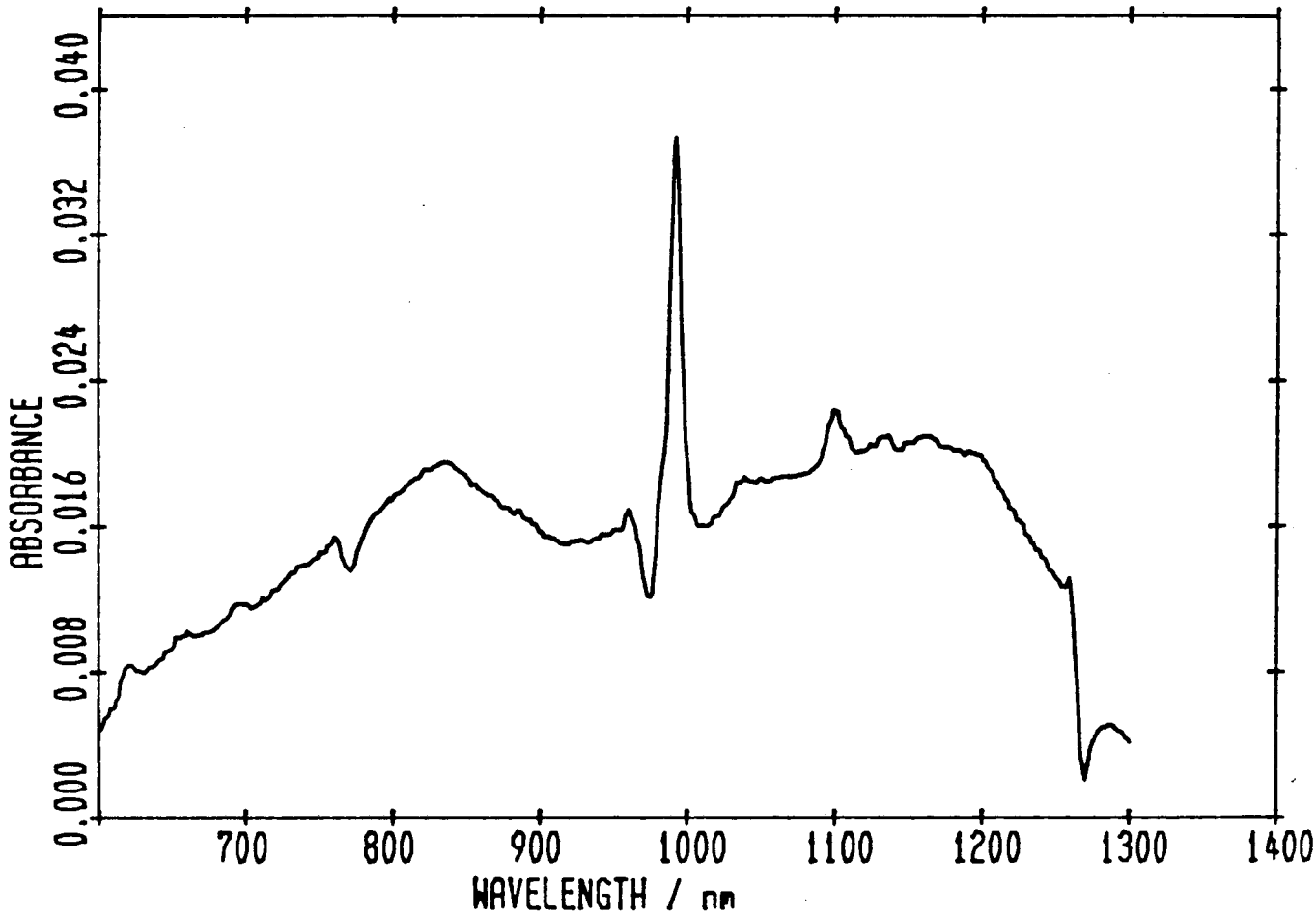

Figure 4. Absorption spectrum of ^{237}Np in 0.01 M $NaClO_4$ after reaching steady-state solubility conditions at 8.5 ± 0.1 and 60 ± 1°C; total carbonate concentration was 120 ppm.

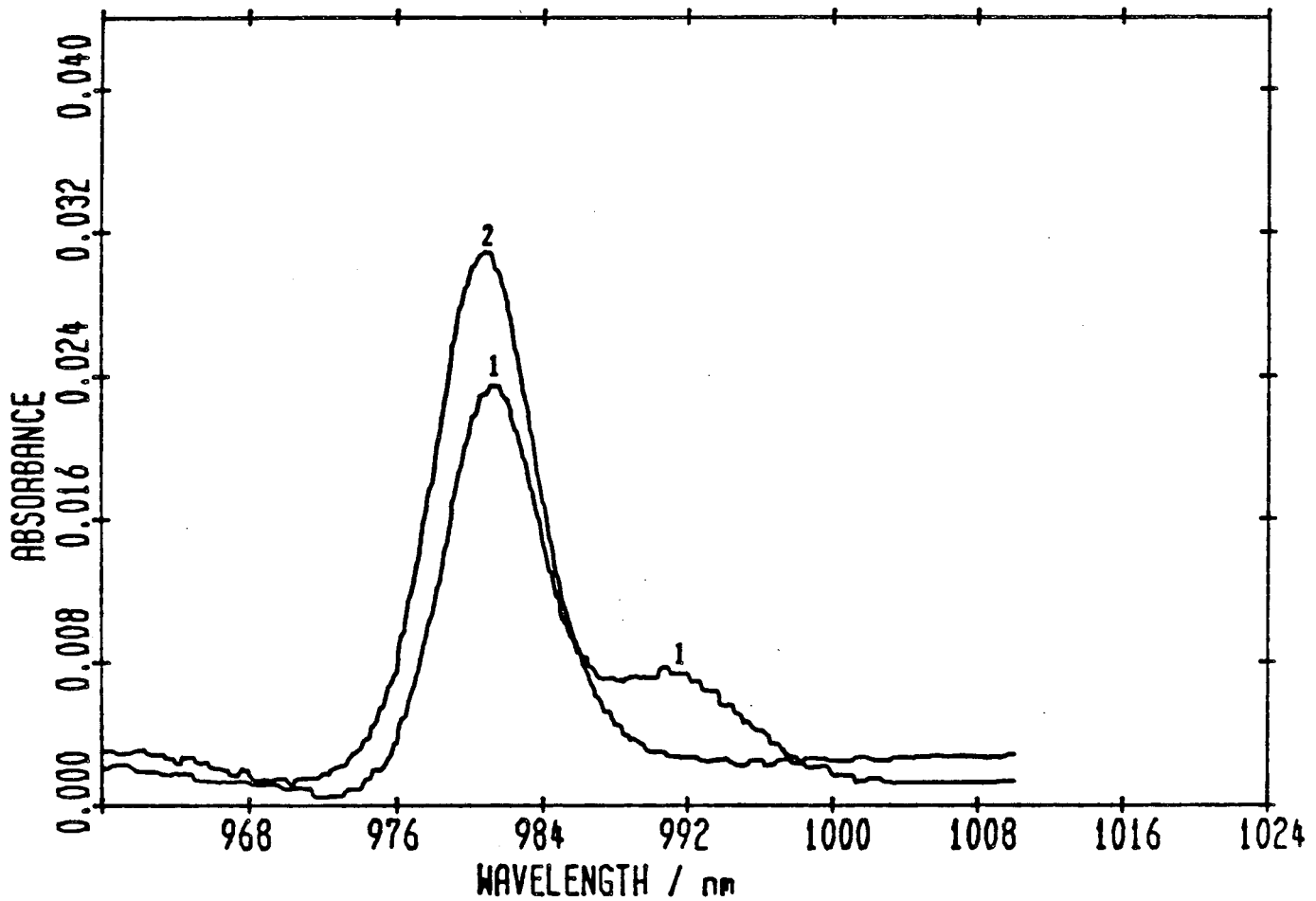

Figure 5. Absorption spectra of ^{237}Np: (1) in 0.01 M $NaClO_4$ at steady state, pH 8.5 ± 0.1, 25 ± 1°C; 120 ppm total carbonate; (2) solution (1) acidified with $HClO_4$.

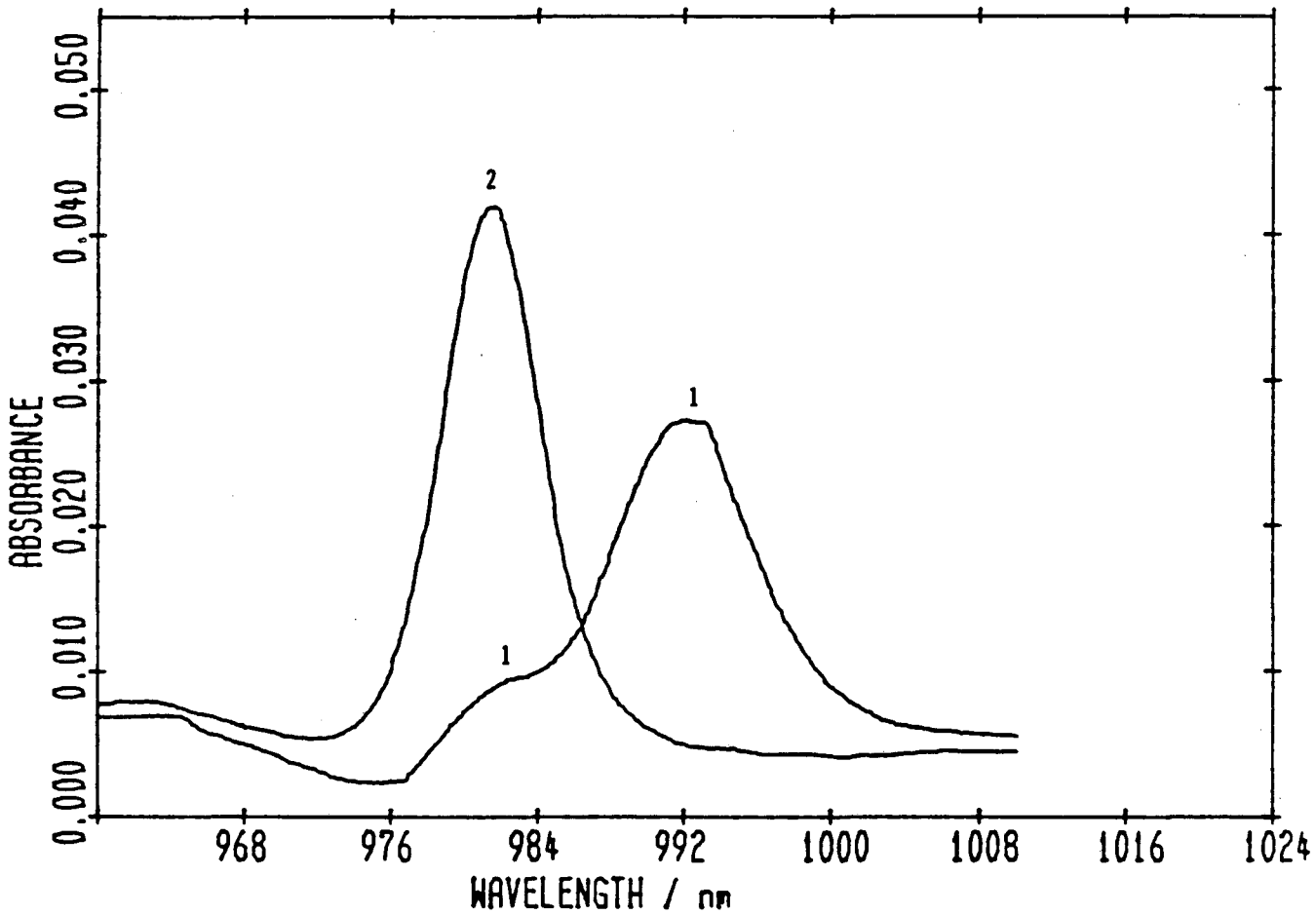

Figure 6. Absorption spectra of ^{237}Np: (1) in 0.01 M $NaClO_4$ at steady state, pH 8.5 ± 0.1 and 60 ± 1°C, 120 ppm total carbonate; (2) solution (1) acidified with $HClO_4$.

5.2 Plutonium

The results of the solubility measurements as a function of equilibration time are shown in Figure 7 for pH 6 and in Figure 8 for pH 8.5. In 0.01 M $NaClO_4$, and with 120 ppm total carbonate solutions, the following concentrations were determined at steady state:

a) pH 6, 25°C: $(2.1 \pm 0.8)\times10^{-8}$ M ($10^{-(7.72\pm0.18)}$ M) using the last 9 data points;

b) pH 6, 60°C: $(1.6 \pm 0.9)\times10^{-9}$ M ($10^{-(8.88\pm0.28)}$ M) using the last 6 data points;

c) pH 8.5 , 25°C: $(1.8 \pm 0.9)\times10^{-9}$ M ($10^{-(8.77\pm0.20)}$ M) using the last 6 data points;

d) pH 8.5 , 60°C: $(1.4 \pm 0.7)\times10^{-9}$ M ($10^{-(8.92\pm0.24)}$ M) using the last 5 data points.

The concentrations for the experiment at pH 8.5 and 25°C during the first 48 days can only be regarded as an upper limit, since the concentrations of these samples were below the detection limit of the counting assembly.

The precipitates formed in the four solutions had a dark greenish-brown appearance. When subjected to X-ray analysis, the solid phase from the pH 6, 25°C experiment produced a distinct powder pattern; the d-spacings are listed in Table 6. Because of the lack of reference data in the literature, the solid is unidentified. The precipitates formed at pH 6, 60°C and the one formed at pH 8.5, 60°C produced a series of identical broad and diffuse X-ray diffraction lines. When the patterns were visually compared with a pattern of PuO_2, similarities in the line locations were found. It is known that colloidal Pu(IV) produces an X-ray pattern with d-spacings identical to that of crystalline PuO_2, but the lines are broadened and diffuse (NEWTON, private communication). From this fact one can conclude that both solid phases at 60°C (pH 6 and 8.5) were present as Pu(IV) colloid or partially crystalline hydrous oxide. The precipitate formed in the solution at pH 8.5 and 25°C did not produce any pattern and remains unidentified. Acidification did not produce visible gas evolution with any of the four precipitates.

The supernatant solutions were analyzed by the coprecipitation/extraction method described in Section 4.3. The results are summarized in Table 7:

No oxidation state analysis was obtained for the solution at pH 8.5 and 25°C. At the time of this experiment no low-level counting facility was available with the capability to analyze extraction fractions accurately at levels as low as 10^{-10} M. This drawback was eliminated for the high-temperature experiments by improving the shielding of the low-energy γ counter. The relatively large uncertainties for pH 6 and 8.5 at 60°C are caused by errors due to the very low level counting and by error propagation due to the calculation of some oxidation states as the difference of results gathered by several extraction methods. At pH 6 the Pu was present at both temperatures as PuO_2^+ and PuO_2^{2+}, although it was initially added to the solution as Pu^{4+}. At pH 8.5 and 60°C some Pu remained in the +4 state, whereas the rest was oxidized to PuO_2^+.

5.3 Americium

The results of solubility measurements as a function of time for pH 6 (25°C, 60°C) and for pH 8.5 (25°C, 60°C) are shown in Figures 9 and 10. Steady-state values were calculated for pH 6 and 25°C to be $(3.1 \pm 0.3) \times 10^{-5}$ M ($10^{-(4.51\pm0.04)}$ M) from the last 8 data points and for pH 8.5 and 25°C to be $(2.0 \pm 1.9) \times 10^{-9}$ M ($10^{-(9.21\pm0.80)}$ M) from the last 11 points. No values were derived for the experiments at 60°C for either pH, since the solutions did not reach steady state within 69 days. The last sample for each

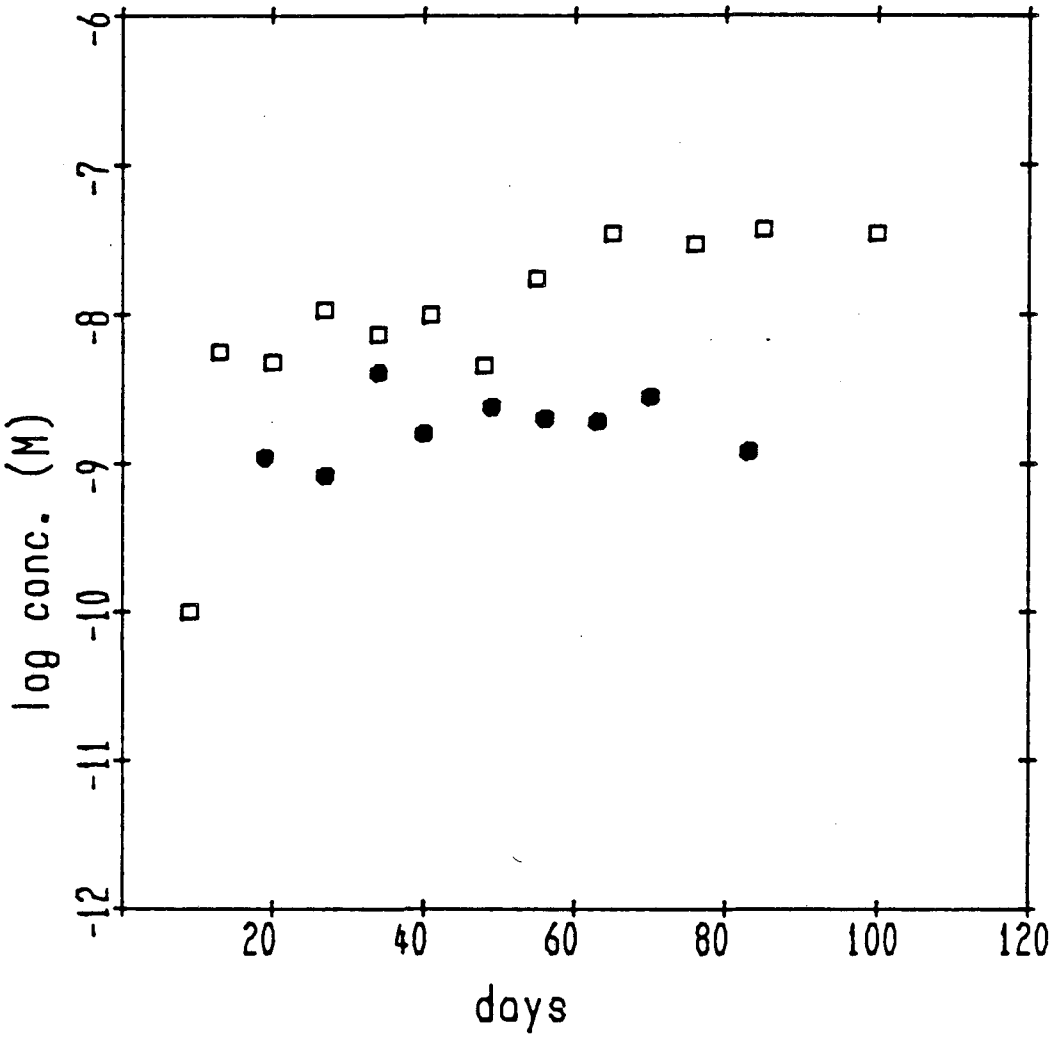

Figure 7. Solution concentrations of $^{238-242}Pu$ in contact with precipitate obtained from supersaturation at pH 6.0 ± 0.1 in 0.01 M $NaClO_4$ and 120 ppm total carbonate concentration as a function of time. Open squares are for 25 ± 1°C; filled octagons are for 60 ± 1°C.

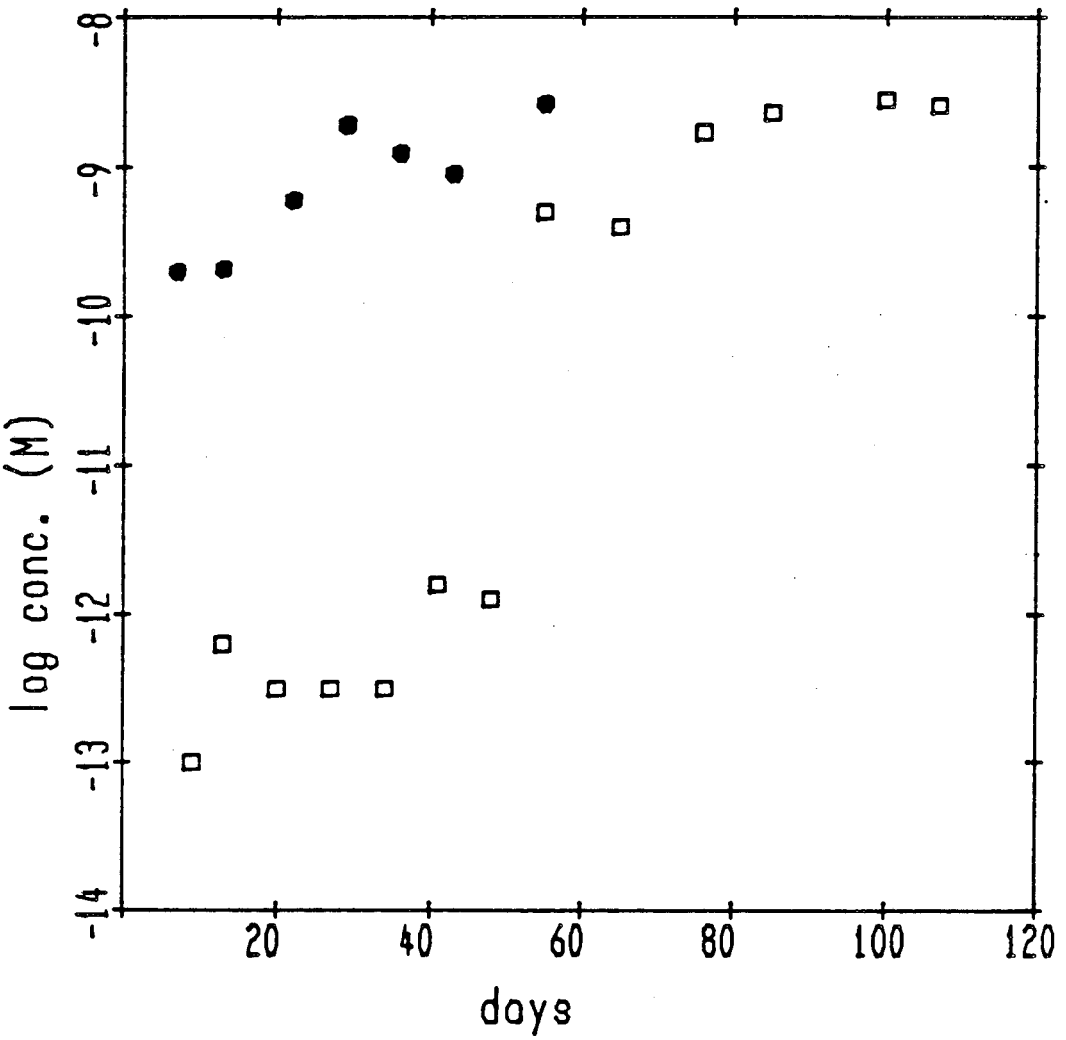

Figure 8. Solution concentrations of $^{238-242}Pu$ in contact with precipitate obtained from supersaturation at pH 8.5 ± 0.1 in 0.01 M $NaClO_4$ and 120 ppm total carbonate concentration as a function of time. Open squares are for 25 ± 1°C; filled octagons are for 60 ± 1°C.

Table 6.
X-ray powder diffraction pattern of Pu solid phase in 0.01 M $NaClO_4$, 120 ppm total carbonate, pH 6.0 at 25 ° C.

Pu solid phase	
d(A)	I[a]
7.61	w
3.83	w
3.61	w
2.81	vs
2.67	w
2.32	w
2.12	w
1.95	w

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

Table 7.
Results of oxidation state determination in plutonium solutions at steady state.

	pH 6, 25°C	pH 6, 60°C	pH 8.5, 60°C
Pu^{3+} + Pu(IV) colloid	0 ± 4%	9 ± 16%	0 ± 11%
Pu^{4+}	0 ± 3%	0 ± 13%	50 ± 8%
PuO_2^{+}	56 ± 5%	59 ± 21%	33 ± 20%
PuO_2^{2+}	44 ± 5%	30 ± 18%	0 ± 14%

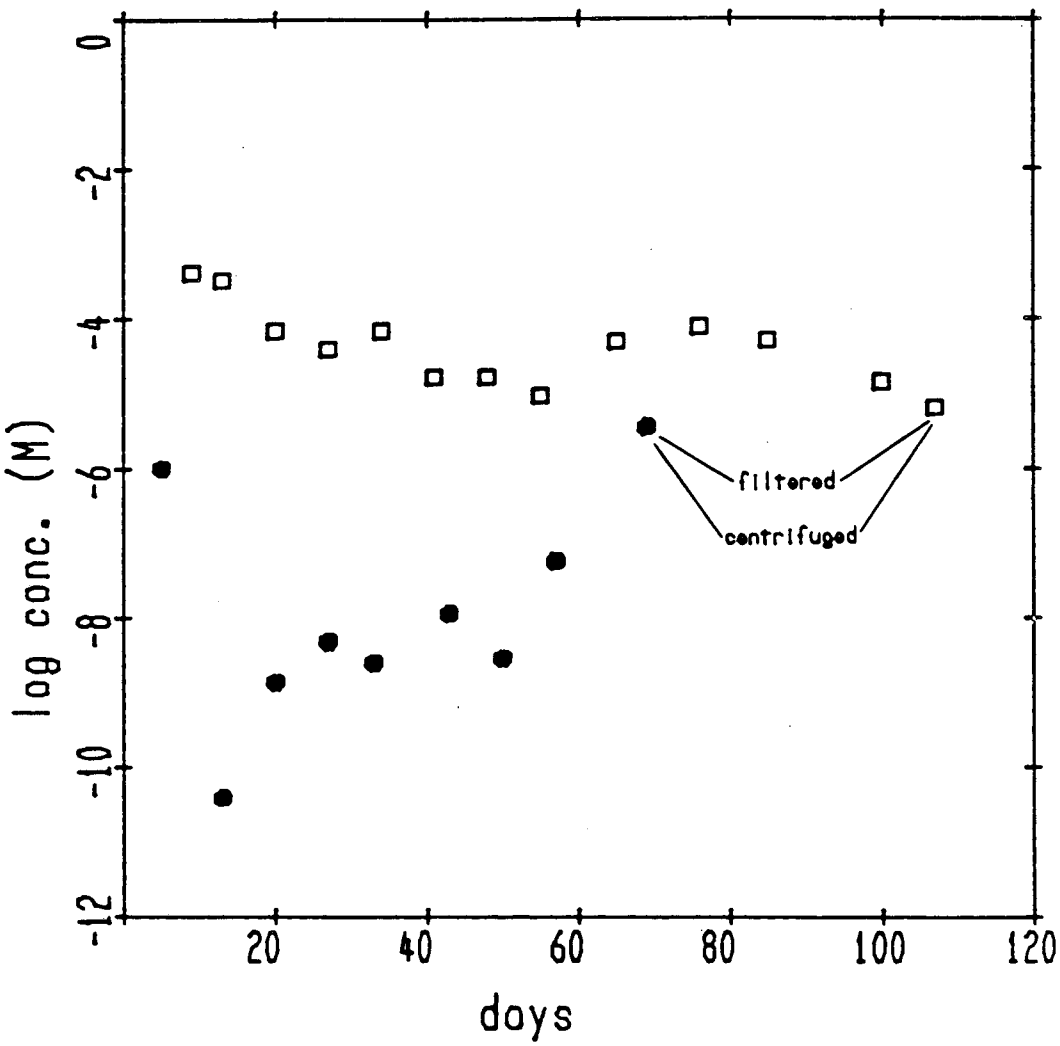

Figure 9. Solution concentrations of ^{243}Am in contact with precipitate obtained from supersaturation at pH 6.0 ± 0.1 in 0.01 M $NaClO_4$ and 120 ppm total carbonate concentration as a function of time. Open squares are for 25 ± 1°C; filled octagons are for 60 ± 1°C.

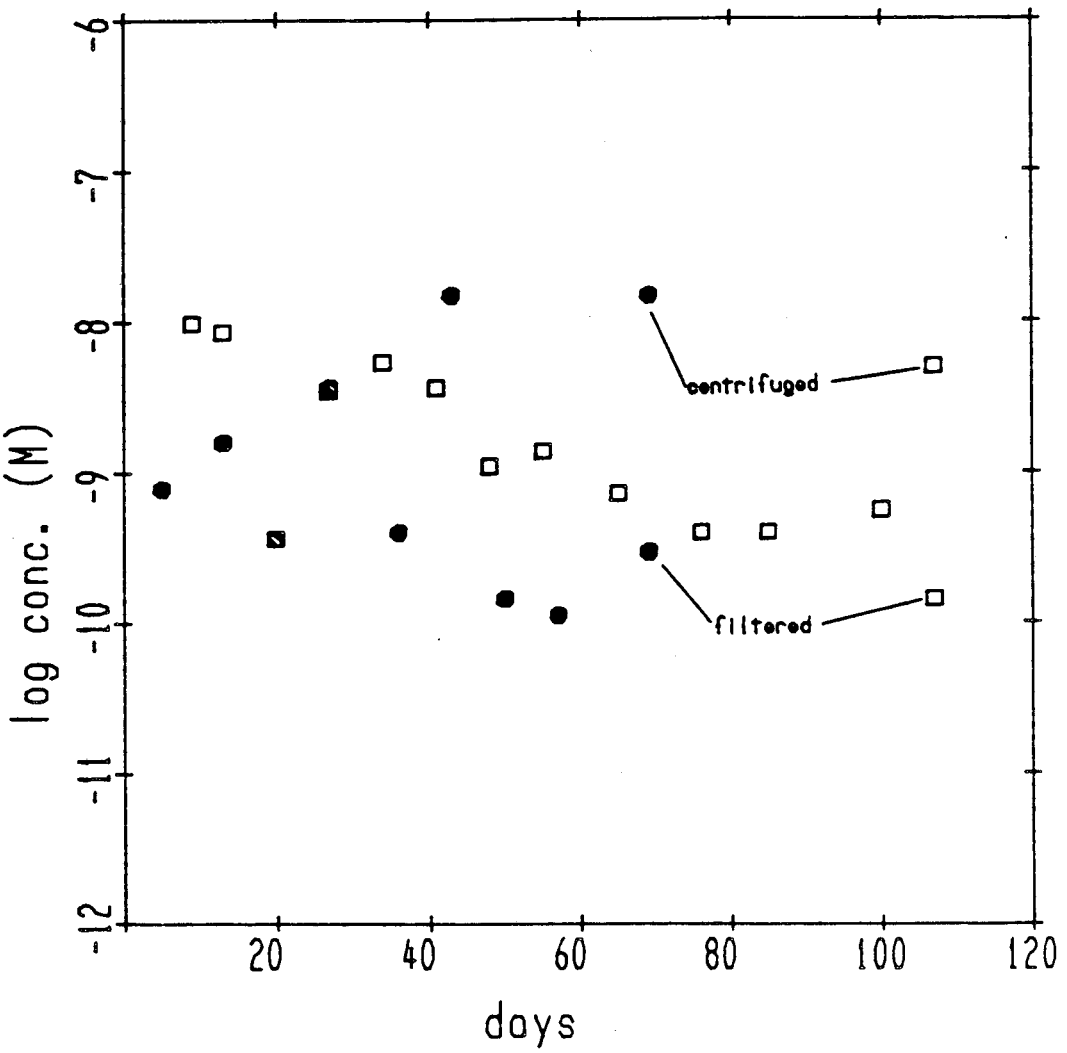

Figure 10. Solution concentrations of ^{243}Am in contact with precipitate obtained from supersaturation at pH 8.5 ± 0.1 in 0.01 M $NaClO_4$ and 120 ppm total carbonate concentration as a function of time. Open squares are for 25 ± 1°C; filled octagons are for 60 ± 1°C.

experiment (at day 107 for the 25°C solutions and at day 69 for the 60°C solutions) was separated from the solid phase in two ways: one part was filtered through the 4.1 nm Amicon filters as described in Section 3.3, whereas a second part was centrifuged at 12,000 rpm for 15 min. Centrifugation under these conditions provides gravitational settling of particles larger than 0.1 μm in size. The solution concentrations for the pH 6 experiments were determined to be equal for either separation method; the average particle size for these precipitates was larger than 0.1 μm. However, the pH 8.5 series showed differences when treated this way. The concentration increased from 1.4 x 10^{-10} M to 5.05 x 10^{-9} M for 25°C and from 3.0 x 10^{-10} M to 1.47 x 10^{-8} M for 60°C when the means of separation was changed from filtration to centrifugation. The results of these experiments are also included in Figures 9 and 10. As shown by the separation experiment, the dissolved material has a size smaller than 0.1 μm. Its presence in the solution may be the cause for the sporadic change in concentration with time in the pH 8.5, 60°C samples. Although the solid phase is separated from the supernatant solution with the Amicon centrifugal filters, colloids of very small particle size (<4.1 nm) may still be present in the solution before passing through the filter membrane. It is possible that some of this material is randomly sorbed onto the plastic walls of the membrane holder or onto the membrane itself, which would result in a random americium concentration in the filtrate. The nature of these species is not understood.

No oxidation state determination was performed on the supernatants, since there is no reason to believe that Am^{3+} could have been oxidized under the experimental Eh conditions. The reduction potential is estimated to be 1.27 V (ALLARD 1982, BERNKOPF 1984) at near-neutral pH values. The precipitates formed in all four solutions were light brown and crystalline. D-spacings and intensities of the X-ray powder diffraction patterns are listed in Table 8 for pH 6 (25°C, 60°C) and in Table 9 for pH 8.5 (25°C, 60°C). Independent of the solution pH (6 and 8.5), the solid formed at 60°C was $AmOHCO_3$. Though the solids remain unidentified for pH 6, 25°C and pH 8.5, 25°C, their crystal structures are identical, as indicated by the powder patterns.

Table 8.
Comparison of X-ray powder diffraction patterns of Am solid phases in 0.01 M $NaClO_4$, 120 ppm total carbonate, pH 6.0 at 25 °C (phase 1) and at 60 °C (phase 2) with patterns reported in the literature.

phase 1	phase 2	$AmOHCO_3$[c]	$Nd_2(CO_3)_3 \cdot 3H_2O$[c]	$Am(OH)_3$[d]
d(A) I[a]	d(A) I[a]	d(A) I[a]	d(A) I[a]	d(A) I[b]
8.43 s			7.56 m	
5.74 m			5.68 s	
				5.57 4
	5.50 w	5.51 w		
4.71 s				
			4.67 s	
	4.27 vs	4.28 s		
4.45 m				
4.21 m				
4.11 w				
3.96 m			3.93 s	
			3.83 w	
3.68 w	3.67 s	3.67 m		
			3.62 m	
	3.32 m	3.31 m		
3.23m				
				3.21 10
3.14 w				
				3.11 10
			3.09 s	
3.02 s			3.02 s	
		2.94 w	2.98 w	
	2.92 s	2.92 m		
			2.87 w	
2.81 w	2.82 w			
				2.78 1
			2.75 w	
2.69 w				
	2.64 w	2.64 w		
2.57 w			2.58 s	
	2.48 w	2.48 w		
				2.44 1
	2.40 w	2.40 w		
	2.32 m	2.33 m		
2.26 w			2.25 w	2.24 7
			2.17 w	
			2.08 w	2.10 3
	2.05 m	2.05 w		
				2.02 m
	1.98 w	1.98 w	1.98 w	
	1.92 w			
		1.89 w	1.87 m	1.86 7
	1.83 w	1.84 w	1.83 m	1.83 7
			1.78 m	1.77 1
			1.74 w	1.62 1
				1.61 1
			1.56 m	1.55 1
				1.43 1
				1.40 5
				1.32 2
				1.28 2
				1.21 1

(a) Relative intensities visually estimated: vs = very strong, s = strong, m = medium, w = weak.
(b) Relative intensities by diffractometer in percent.
(c) SILVA 1983.
(d) MILLIGAN 1968.

Table 9.
Comparison of X-ray powder diffraction patterns of Am solid phases in 0.01 M $NaClO_4$, 120 ppm total carbonate, pH 8.5 at 25 ° C (phase 1) and at 60 ° C (phase 2) with patterns reported in the literature.

phase 1	phase 2	$AmOHCO_3$[c]	$Nd_2(CO_3)_3 \cdot 3H_2O$[c]	$Am(OH)_3$[d]
d(A) I[a]	d(A) I[a]	d(A) I[a]	d(A) I[a]	d(A) I[b]
8.43 s				
			7.56 m	
5.77 w				
			5.68 s	
				5.57 4
	5.49 m	5.51 w		
4.74 m				
			4.67 s	
	4.29 vs	4.28 s		
4.44 w				
4.21 w				
4.10 w				
3.94 w			3.93 s	
			3.83 w	
3.67 w	3.68 s	3.67 m		
			3.62 m	
	3.31 m	3.31 m		
3.23 m				
				3.21 10
3.14 m				
				3.11 10
			3.09 s	
3.03 s			3.02 s	
		2.94 w	2.98 w	
	2.92 s	2.92 m		
			2.87 w	
2.81 w				
				2.78 1
			2.75 w	
2.69 w				
	2.64 w	2.64 w		
2.57 w			2.58 s	
	2.48 w	2.48 w		
2.42 w				2.44 1
	2.40 w	2.40 w		
	2.33 m	2.33 m		
2.27 w			2.25 w	2.24 7
			2.17 w	
			2.08 w	2.10 3
	2.06 m	2.05 w		
	1.99 m	1.98 w	1.98 w	
	1.93 w			
	1.89 w	1.88 w	1.87 m	1.86 7
	1.84 w	1.84 w	1.83 m	1.83 7
			1.78 m	1.77 1
			1.74 w	1.62 1
				1.61 1
			1.56 m	1.55 1
				1.43 1
				1.40 5
				1.32 2
				1.28 2
				1.21 1

(a) Relative intensities visually estimated: vs = very strong, s = strong, m = medium, w = weak.
(b) Relative intensities by diffractometer in percent.
(c) SILVA 1983.
(d) MILLIGAN 1968.

6. CONCLUSIONS

The objective of this study was to determine experimentally the temperature dependence of the solubilities and the distribution of oxidation states in solutions of neptunium, plutonium, and americium. For reasons of theoretical simplicity, only the influence of hydroxide and carbonate was considered by measuring the solubilities at steady state in noncomplexing perchlorate electrolyte at an overall carbonate concentration of 120 ppm. Solutions at pH 6 and 8.5 and temperatures of 25°C and 60°C were investigated. The results demonstrate the degree of importance of temperature change for solubility measurements, and they will assist the NRC in determining whether sufficient information is available on the solubilities of Np, Pu, and Am to predict their behavior accurately under repository conditions.

The following conclusions can be drawn from the experimental results.

1. Neptunium:

a) The solubility of NpO_2^+ was slightly enhanced at pH 6 and 8.5 when the temperature increased from 25°C to 60°C.

b) Regardless of the temperature in both pH 6 solutions, the soluble neptunium at steady state was uncomplexed NpO_2^+. The oxidation state did not change from the initial conditions.

c) At pH 8.5 the complexing of carbonate increased with temperature. Approximately 40 % of the soluble neptunium at 25°C was present as carbonate complex, whereas at 60°C nearly all Np was complexed.

d) The neptunium solids formed were crystalline, with the exception of the one for pH 6, 25°C. Their chemical composition could not be identified. The two precipitates formed at 60°C appeared to contain carbonate, but the ones at 25°C did not.

2. Plutonium:

a) At pH 6 the solubility of plutonium, initially added to the solution as Pu^{4+}, decreased by one order of magnitude as the temperature changed from 25°C to 60°C. At pH 8.5 no significant change in concentration with temperature occured at steady state.

b) At pH 6 the soluble plutonium at steady state was present as PuO_2^+ and PuO_2^{2+}. At 25°C the PuO_2^+: PuO_2^{2+} ratio was approximately 1:1, and it increased to 2:1 at 60°C.

c) At pH 8.5 and 60°C half of the initial Pu^{4+} remained in the +4 state. The other half was oxidized to PuO_2^+. It appears that the lower oxidation state becomes stabilized with increasing temperature.

d) The precipitates from the 25°C series remained unidentified; they were crystalline at pH 6 and amorphous at pH 8.5. The high-temperature solids formed at both pH values were Pu(IV) colloid or partially crystalline hydrous oxide ($PuO_2 \cdot xH_2O$).

3. Americium:

a) No conclusion about the temperature dependence of the americium solubility could be drawn, since no steady-state values for 60°C at either pH value were obtained within 69 days. At pH 6 the concentration increased steadily with time; at pH 8.5 the concentration increased and decreased with time seemingly at random by up to 1.5 orders of magnitude. The americium solutions at pH 8.5 contained dissolved solids, which may be the cause for the sporadic change in concentration with time.

b) At 60°C $AmOHCO_3$ was the stable solid phase for the solutions at pH 6 and pH 8.5. At 25°C the solid phases were identical and crystalline for both pH's, but they remained unidentified.

Recently SILVA (SILVA 1984) has published modeling calculations on the solubilities of U, Np, Pu, and Am utilizing the computer code MINEQL. As input, data bases were generated that contained the various solubility product, hydrolysis, carbonate complexation, and redox constants for the four actinides for 25°C, 60°C, 100°C, and 150°C. The equilibrium constants for a reaction at a given temperature were approximated from known or estimated values of the entropy changes for the reactions at 25°C and from the average values of the heat capacity changes for the reactions between 25°C and the higher temperature (CRISS 1964A and 1964B, HELGESON 1969, BAES 1976 and 1981, LEMIRE 1980, TURNER 1981, PHILLIPS 1985). The stable solid phases and solution species formed were calculated as a function of pH (6 to 9) and Eh (–0.22, 0.0, + 0.22 V) for an ionic strength of 0.01 M and a total fixed carbonate concentration of 120 ppm (all species). The results of the calculations for Np, Pu, and Am at an Eh value of 0.22 V are shown in Figures 11 through 13.

The parameters for this experimental determination of the solubilities for Np, Pu, and Am were chosen to match as closely as possible those used in SILVA's calculations. The carbonate concentrations and the ionic strength of the solutions are identical; the pH's 6 and 8.5 lie within his pH range of 6 to 9. The Eh in the experiment is determined by the average oxygen pressure of 100 ppm in the inert-atmosphere glove box. The Eh at 25°C is defined (STUMM 1980) as:

$$\mathrm{Eh} = 1.23 + \frac{0.059}{4}\log p_{O_2} - 0.059\ \mathrm{pH}.$$

At the experimental oxygen level, the solution at pH 6 and pH 8.5 would have Eh values of 0.82 V and 0.67 V, respectively. However, experiments have shown (RAI 1982, ALLARD 1982) that the use of an operational Eh, which accounts for the "irreversible oxygen potential," seems to describe the conditions more realistically. It is defined as:

$$\mathrm{Eh} \sim (0.8\text{–}0.7) + \frac{0.059}{4}\log p_{O_2} - 0.059\ \mathrm{pH}.$$

Using this equation, Eh values of 0.39–0.29 V and 0.24–0.14 V are calculated for pH 6 and pH 8.5, respectively. For this reason SILVA's calculations for an Eh of 0.22 V seem to simulate the experimental conditions the closest. However, it is emphasized that no primary Eh control was maintained during the experiment. The electron potential of the solutions is controlled primarily by the potentials of the actinide complexes and compounds present. The experiment has shown that many of the complexes and compounds formed are unknown, and as a consequence their reduction potentials are also unknown. From this argument it seems questionable that an Eh value of +0.22 V describes the experimental solution with sufficient accuracy.

Also included in Figures 11 to 13 are the experimental results for pH 6 and 8.5 at 25°C and 60°C. For neptunium (Fig. 11) the experimental solubilities are substantially

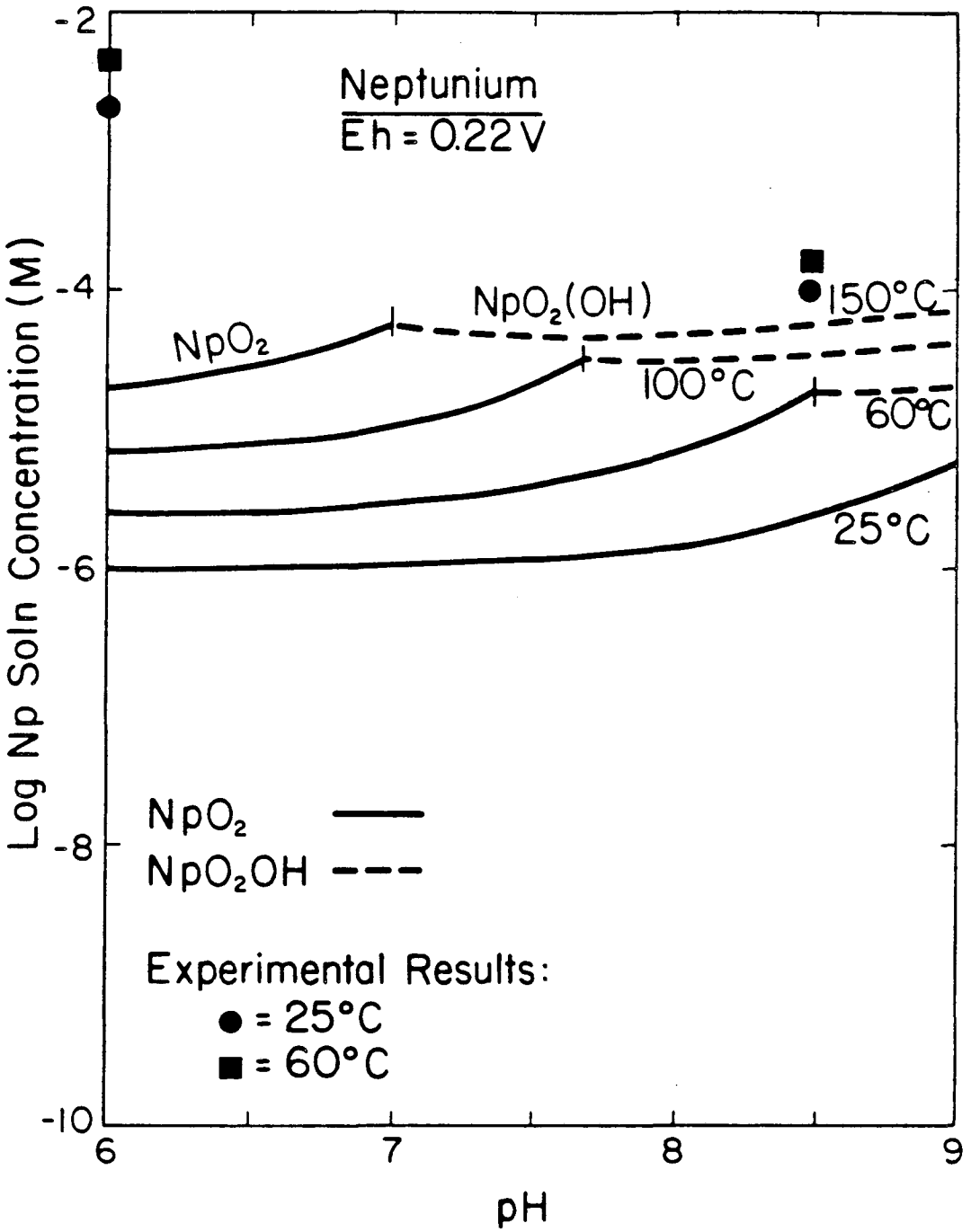

Figure 11. Sums of the calculated concentrations of Np (all species, curves are labeled with controlling solid phase) for 0.01 M ionic strength, Eh = 0.22 V, and total fixed carbonate (all species) concentration of 120 ppm as a function of pH and temperature (from SILVA 1984, with permission of the author). Also included are experimentally determined data points from this study.

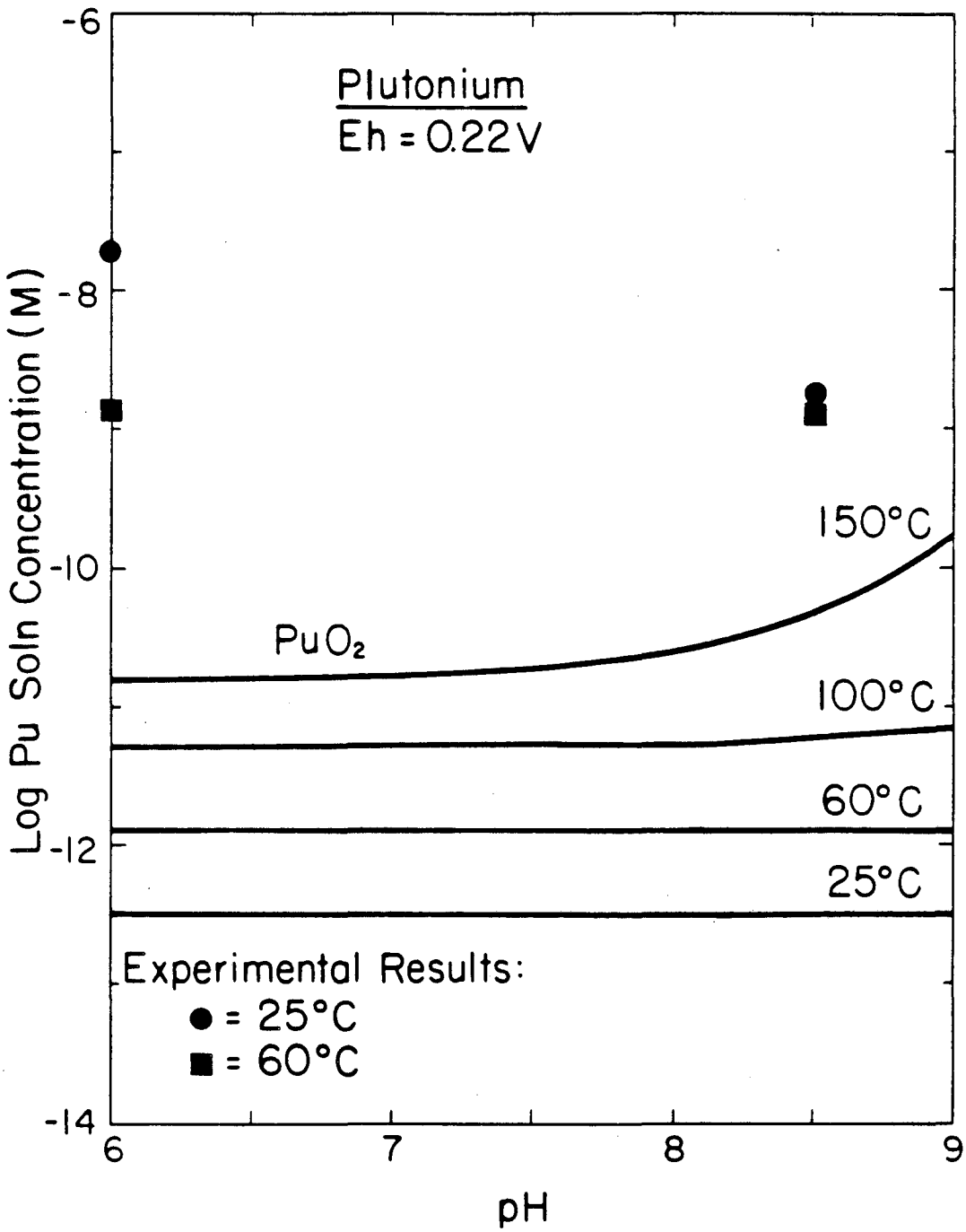

Figure 12. Sums of the calculated concentrations of Pu (all species, curves are labeled with controlling solid phase) for 0.01 M ionic strength, Eh = 0.22 V, and total fixed carbonate (all species) concentration of 120 ppm as a function of pH and temperature (from SILVA 1984, with permission of the author). Also included are experimentally determined data points from this study.

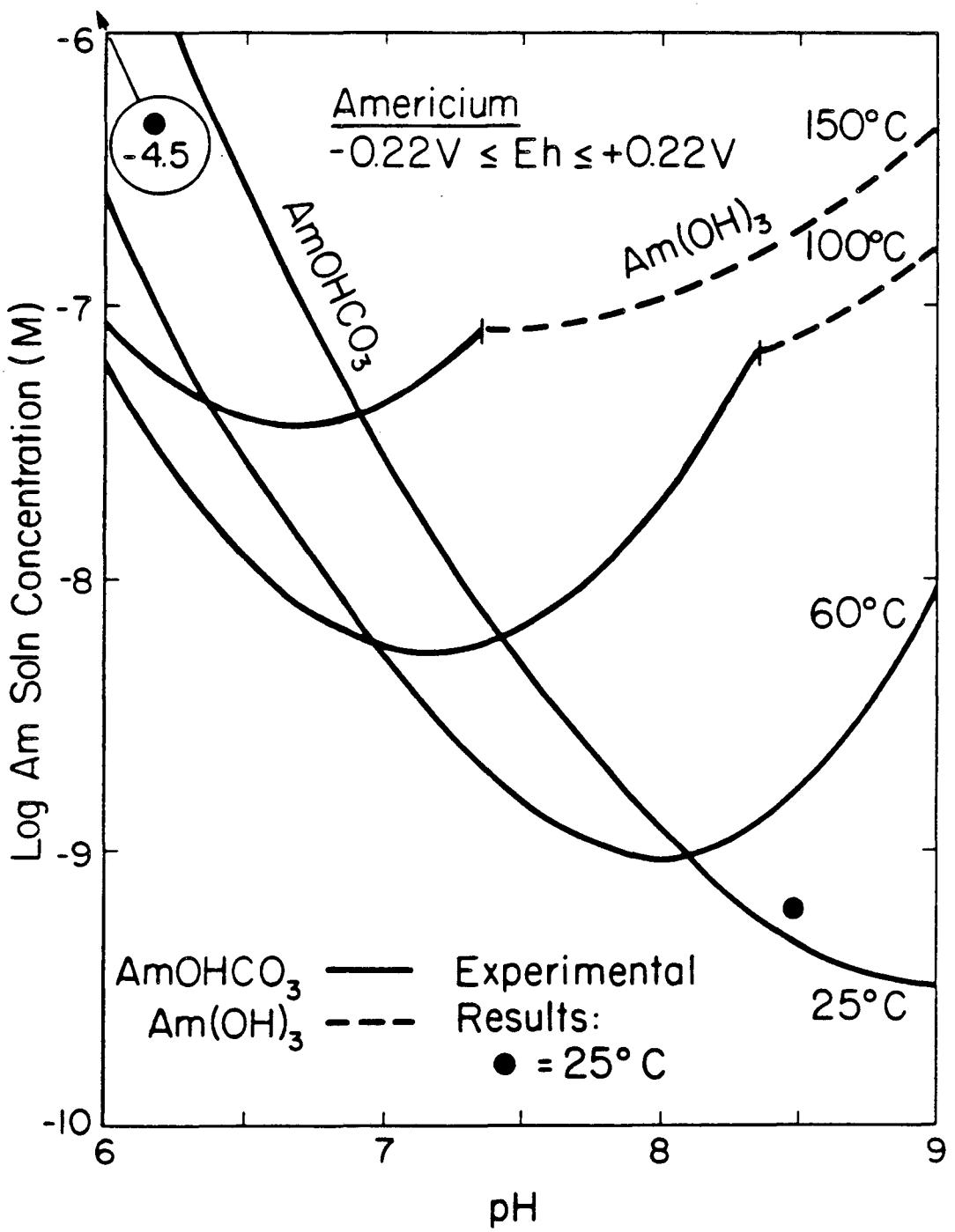

Figure 13. Sums of the calculated concentrations of Am (all species, curves are labeled with controlling solid phase) for 0.01 M ionic strength, Eh = 0.22 V, and total fixed carbonate (all species) concentration of 120 ppm as a function of pH and temperature (from SILVA 1984, with permission of the author). Also included are experimentally determined data points from this study.

larger (~ 3 orders of magnitude for pH 6 and ~ 1.5 orders of magnitude for pH 8.5) than the calculated values. The model predicted NpO_2 as solid phase, whereas the precipitates from the experiment were not NpO_2 but nevertheless remained unidentified. At both pH's and 60°C the solids contained carbonate, but the 25°C solids were carbonate free. For plutonium (Fig. 12) the discrepancy between the theoretical calculations and the experimental results are even more significant: At pH 6 the experimental solubility values were about 3–4 orders of magnitude larger and at pH 8.5 approximately 3 orders of magnitude larger than the calculated values. At 25°C and both pH's the solids remained unidentified. At 60°C the solids formed at both pH values were Pu(IV) colloid or partially crystalline hydrous oxide ($PuO_2 \cdot xH_2O$), which is different from the modeling predictions based on crystalline PuO_2. For americium (Fig. 13) the theoretical calculations appear to agree rather well with the experimental findings; at 25°C the model predicted the solubility to be close to the experimental values, although the solid formed in the experiment is not $AmOHCO_3$, as was assumed for the calculation. At 60°C no steady-state solubility values were obtained from the experiment, but the solid phase formed was $AmOHCO_3$, as was predicted by the model.

This comparison of experimentally determined values with solubility predictions gained from modeling calculations done under similar conditions demonstrates very clearly the shortcomings of attempts to predict solubility by calculations alone. The experimental reality appears to be far more complicated and interconnected than the description provided by an often limited or even incorrect set of thermodynamic equations serving as input for the model. Many solid phases and solution species formed in the experiment are still unknown, and therefore no equation set describing the thermodynamic properties is available for input in the data base.

The results of this work show the need to study radionuclide solubility experimentally in groundwaters from a prospective HLW repository site to predict accurately the maximum tolerable concentrations of radioactive materials that might migrate from the storage location to the accessible environment. Furthermore, solubility studies must be made at elevated temperatures in order to approximate repository conditions. Efforts should be made to increase the data base on thermodynamic solutions to improve the results of geochemical modeling. An increased effort to acquire experimental data and to improve the quality of theoretical knowledge should lead to an agreement between modeling predictions and experimental solution data. When consistent results can be obtained by these two approaches, a high degree of confidence can be placed in the data on radionuclide solubility and speciation that are required to license a nuclear waste repository.

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