Inorganica Chimica Acta, 127 (1987) 121–128

Effects of Temperature on the Solubility and Speciation of Selected Actinides in Near-neutral Solution

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(Received July 2, 1986; revised September 22, 1986)

Abstract

The solubility and speciation predictions for actinide waste elements, needed to meet the requirements for licensing a high-level radioactive waste disposal, 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. 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. A summary of the results is given in Table I. 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 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

TABLE I. 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

pH	Log steady-state concentration (M)		Oxidation state in supernatant solution		Solid phase	
	25 °C	60 °C	25 °C	60 °C	25 °C	60 °C
Np						
6	−(2.66 ± 0.08)	−(2.31 ± 0.09)	V = 100%	V = 100%	amorphous	crystalline unidentified
8.5	−(4.02 ± 0.13)	−(3.80 ± 0.08)	V = 100%	V = 100%	crystalline unidentified	crystalline unidentified
Pu						
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 $PuO_2 \cdot xH_2O$
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						
6	−(4.51 ± 0.04)	did not reach steady state after 69 days	III = 100%	III = 100%	crystalline[a] unidentified	$AmOHCO_3$
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.

0020-1693/87/$3.50

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.

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) [1, 2].

Although the likelihood of waste form failure is significantly reduced by the use of multiple barriers, the migration of contaminated groundwater must be 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 [3].

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 [4], 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 [5–12].

The objective of this study is to experimentally determine trends of 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 [3, 13]. 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.

Experimental

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 standard radioanalytical methods were used for nuclide identification and concentration determination. Results of radioactive counting are given within a 95.5% confidence interval ($\pm 2\sigma_R$).

The preparation and the adjustment of oxidation states for the actinide stock solutions have been described elsewhere [14]. The $^{232}NpO_2^+$ stock was $(1.17 \pm 0.03) \times 10^{-1}$ M; $^{238-242}Pu^{4+}$ stock was $(2.54 \pm 0.07) \times 10^{-1}$ M and had a specific activity of 2.07×10^6 dpm/μg. The ^{243}Am stock was $(1.69 \pm 0.02) \times 10^{-2}$ M.

All solutions were prepared with deionized, 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 [12]. 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 solution's 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.

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. Details for this computer system have been described previously [15].

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 ℃ [16]. Nominal pH values for the buffers at 60 ℃ were calculated from their temperature coefficients (phosphate, $dpH/dt = -0.0028$ unit ℃; borax, $dpH/dt = -0.008$ unit ℃).

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 ℃ or 60 ± 1 ℃. 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 [3]. 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 ℃ or 60 ± 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 [14, 17, 18].

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 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 Kα radiation filtered through Ni was used. The oxidation states in the supernatant solution at steady state was determined for Np by absorption-spectrophotometry and for Pu by an extraction/coprecipitation method [14].

Results and Discussion

Neptunium

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 ($10^{-(2.66 \pm 0.08)}$ M) for 25 °C using the last 10 data points and $(5 \pm 1) \times 10^{-3}$ M ($10^{-(2.31 \pm 0.09)}$ 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 ($10^{-(4.02 \pm 0.13)}$ M) at 25 °C (last 10 points) and $(1.6 \pm 0.3) \times 10^{-4}$ M ($10^{-(3.80 \pm 0.08)}$ 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 precipitate formed in the solution at pH 6 and 25 °C did not produce any X-ray powder diffraction 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 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 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 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 [15], 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^+ is complexed by carbonate. At 60 °C nearly all the neptunium is present in solution as a carbonate complex. Again, the complex(es) could be destroyed by acid addition to give uncomplexed NpO_2^+.

Plutonium

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: $(2.1 \pm 0.8) \times 10^{-8}$ M ($10^{-(7.72 \pm 0.18)}$ M) using the last 9 data points;
(b) pH 6, 60 °C: $(1.6 \pm 0.9) \times 10^{-9}$ M ($10^{-(8.88 \pm 0.28)}$ M) using the last 6 data points;
(c) $(1.8 \pm 0.9) \times 10^{-9}$ M ($10^{-(8.77 \pm 0.20)}$ M) using the last 6 data points;
(d) pH 8.5, 60 °C: $(1.4 \pm 0.7) \times 10^{-9}$ M ($10^{-(8.92 \pm 0.24)}$ M) using the last 5 data points.

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. 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 [19]. 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 elsewhere [14]. The results are summarized in Table II.

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-

TABLE II. 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%

energy γ counter. The relatively large uncertainties for pH 6 and 8.5 at 60 ℃ 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 ℃ some Pu remained in the +4 state, whereas the rest was oxidized to PuO_2^+.

Americium

Steady-state values were calculated for pH 6 and 25 ℃ to be $(3.1 \pm 0.3) \times 10^{-5}$ M ($10^{-(4.51 \pm 0.04)}$ M) from the last 8 data points and for pH 8.5 and 25 ℃ to be $(2.0 \pm 1.9) \times 10^{-9}$ M ($10^{-(9.21 \pm 0.80)}$ M) from the last 11 points. No values were derived for the experiments at 60 ℃ for either pH, since the solutions did not reach steady state within 69 days. The last sample for each experiment (at day 107 for the 25 ℃ solutions and at day 69 for the 60 ℃ solutions) was separated from the solid phase in two ways: one part was filtered through the 4.1 nm Amicon filters as described previously, 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 1.4×10^{-10} M to 5.05×10^{-9} M for 25 ℃ and from 3.0×10^{-10} M to 1.47×10^{-8} M for 60 ℃ when the means of separation was changed from filtration to centrifugation. 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 ℃ 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 eV [13, 18] at near-neutral pH values. The precipitates formed in all four solutions were light brown and crystalline. Though the solids remain unidentified for pH 6, 25 ℃ and pH 8.5, 25 ℃, their crystal structures are identical.

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 non-complexing perchlorate electrolyte at an overall carbonate concentration of 120 ppm. Solutions at pH 6 and 8.5 and temperatures of 25 ℃ and 60 ℃ 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 ℃ to 60 ℃.

(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 ℃ was present as carbonate complex, whereas at 60 ℃ nearly all Np was complexed.

(d) The neptunium solids formed were crystalline, with the exception of the one for pH 6, 25 ℃. Their chemical composition could not be identified. The two precipitates formed at 60 ℃ appeared to contain carbonate, but the ones at 25 ℃ 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 ℃ to 60 ℃. At pH 8.5 no significant change in concentration with temperature occurred at steady state.

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

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

Recently Silva [22] 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 ℃, 60 ℃, 100 ℃, and 150 ℃. 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 ℃ and from the average values of the heat capacity changes for the reactions between 25 ℃ and the higher temperature [5–12]. 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 Figs. 1 through 3.

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 ℃ is defined [23] as:

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

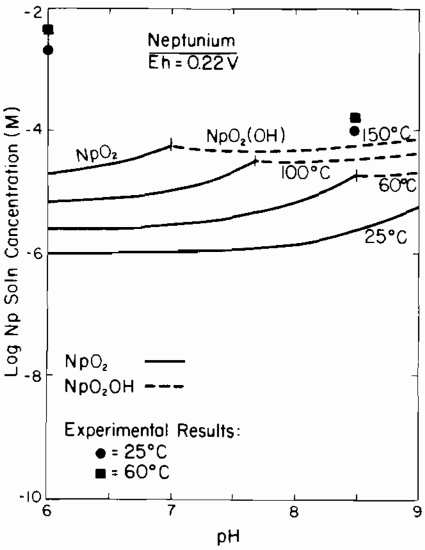

Fig. 1. Sums of the calculated concentrations of Np (all species, curves are labeled with controlling solid phase) for 0.01 M ionic strength, *Eh* = 0.22 V, and total fixed carbonate (all species) concentration of 120 ppm as a function of pH and temperature (from ref. 22, with permission of the author). Also included are experimentally determined data points from this study.

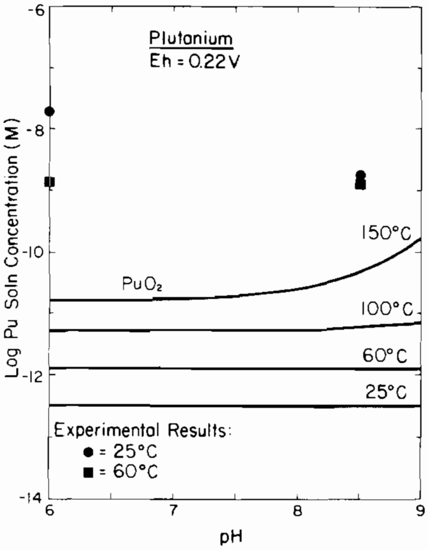

Fig. 2. Sums of the calculated concentrations of Pu (all species, curves are labeled with controlling solid phase) for 0.01 M ionic strength, *Eh* = 0.22 V, and total fixed carbonate (all species) concentration of 120 ppm as a function of pH and temperature (from ref. 22, with permission of the author). Also included are experimentally determined data points from this study.

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 [13] 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:

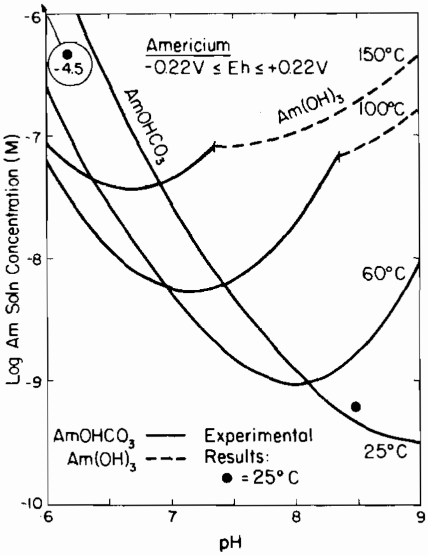

Fig. 3. Sums of the calculated concentrations of Am (all species, curves are labeled with controlling solid phase) for 0.01 M ionic strength, *Eh* = 0.22 V, and total fixed carbonate (all species) concentration of 120 ppm as a function of pH and temperature (from ref. 22, with permission of the author). Also included are experimentally determined data points from this study.

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

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 Figs. 1 to 3 are the experimental results for pH 6 and 8.5 at 25 °C and 60 °C. For neptunium (Fig. 1) the experimental solubilities are substantially larger (~3 orders of magnitude for pH 6 and ~15 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. 2) 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. 3) 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.

Supplementary Material

Figures depicting the results of the solubility measurements as a function of equilibration time, listings of X-ray powder diffraction patterns from the solid phases, and absorption spectra of the ^{237}Np-supernatant solutions at steady-state are available as supplementary material.

Acknowledgements

Thanks are due to R. C. Gatti for his excellent assistance with the experimental work and to L. Williams for typing the manuscript.

The author is indebted for the use of ^{243}Am to the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, through the transplutonium element production facilities at the Oak Ridge National Laboratory.

This work was supported by the U.S. Nuclear Regulatory Commission through NRC FIN No. B 3040 under U.S. Department of Energy Contract DE-AC03-76SF00098.

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