



# Lawrence Berkeley Laboratory

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## EARTH SCIENCES DIVISION

Letter Report (T-418)

Progress Report on Solubility Measurements:  
October 1, 1987–September 30, 1988

H. Nitsche

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Letter Report (T-418): Progress Report on Solubility Measurements

*Heino Nitsche*

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Earth Sciences Division  
Lawrence Berkeley Laboratory  
1 Cyclotron Road  
Berkeley, California 94720

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This letter report describes the technical activities of the waste element solubility study during Fiscal Year 1988 (FY88, October 1, 1987 to September 30, 1988). It addresses the following topics:

1. Objective
2. Scope
3. Technical Progress
  - 3.1. Experimental Results
  - 3.2. Thermodynamic Data Review
4. References

Administrative activities during FY88 are not reported here.

#### 1. OBJECTIVE

This experimental waste element solubility study provides experimentally determined limits on radionuclide concentrations in groundwater from Yucca Mountain.

Furthermore, the results of this study are essential for

- (a) verifying the validity of radionuclide transport calculations, and for
- (b) providing the maximum concentrations for the radionuclide sorption tests (activity 8.3.1.3.4).

Solubility is the source term for radionuclide transport calculations. The solubility in this study is controlled by fewer variables than are used in the multiparameter transport model. Therefore, modeling must be capable of predicting the results of this waste element solubility study. Agreement between the experimental results and the modeling predictions will validate the geochemical module of the transport model.

The results of this waste element solubility study also provide the source terms for the radionuclide sorption tests on rocks and minerals present at Yucca Mountain. These source terms are

- (a) the solubility-limited concentrations and
- (b) the predominant solution species for each radionuclide.

The sorption study must be carried out under these conditions.

## 2. SCOPE

Meaningful solubility tests provide detailed knowledge of (a) the nature and the chemical composition of the solubility-controlling solid, (b) the concentration of the soluble phase, and (c) the species and their electric charge representing the soluble phase. The results depend on the conditions of the groundwater within the repository (chemical composition, pH, Eh, and temperature).

Detailed test and analyses to achieve these tasks are being developed. Solubility tests for nine radionuclides (neptunium, plutonium, americium, thorium, uranium, radium, nickel, tin, zirconium) are planned, but other waste elements may be included as more knowledge evolves. The tests are done in two different groundwaters (J-13 and UE-25p#1), three pH values (6, 7, and 8.5), and three temperatures (25°, 60°, and 90°C) to bracket expected conditions at the repository and along the flow paths to the environment. Tests are being developed to verify the effectiveness of separating the solid from the solution (filtration, centrifugation) because incomplete phase separation would lead to false solubility concentrations. Solution concentrations are determined by nuclear counting techniques ( $\alpha$ ,  $\beta$ -,  $\gamma$ -,  $L$  x-ray counting, and nuclear spectroscopy). Tests to determine the oxidation state and speciation of the soluble species are being developed (spectrophotometry, solvent extraction, and co-precipitation). The nature of the solubility-controlling solids is determined by (x-ray diffraction, chemical analyses, Fourier transform infrared spectroscopy, spectrophotometry, neutron activation

analysis). Overall, this study involves several thousand individual measurements.

These tests and analyses are controlled by the LANL-YMP Quality Assurance Program and test-specific Detailed Technical Procedures.

### 3. TECHNICAL PROGRESS

#### 3.1. EXPERIMENTAL RESULTS

We finished the solubility tests of  $^{237}\text{NpO}_2^+$ ,  $^{239}\text{Pu}^{4+}$ , and  $^{241}\text{Am}^{3+}/\text{Nd}^{3+}$  at  $90^\circ\text{C}$  and pH values of 6, 7, and 8.5 during FY 88.

We have already incorporated most of the results for neptunium and plutonium for this reporting period in our latest revision (January 1988) of Letter Report R707.

The americium-neodymium solubility tests in J-13 groundwater at  $90^\circ\text{C}$  were finished after a running time of 100 days. We substituted neodymium for americium to see whether indeed the formation of americium pseudocolloids caused the fluctuation in concentration with time, which we observed in the  $60^\circ\text{C}$  americium tests. The problems were discussed in detail in Letter Report R-707 (pages 57-62). Because of the similarity between the two elements, the results for neodymium also apply to americium. Neodymium and americium have nearly identical ionic radii (Shannon 1976) and valency and behave chemically almost the same. We spiked the stable isotope neodymium with Am-241 tracer. This reduced the  $\alpha$ -radiation level to about 10% of the level we used in the  $60^\circ\text{C}$  Am-243 solubility experiment. The Teflon container should withstand this lower  $\alpha$ -radiation level, thus avoiding pseudocolloid formation. Therefore, we should get steady-state concentrations from the neodymium solubility studies.

Figure 1 confirms our hypothesis. It shows the neodymium/americium concentrations as a function of equilibration time for the solubility solutions at pH 6, 7, and 8.5. Because of the unexpectedly low concentrations, the concentration determinations by  $\gamma$ -counting were very difficult, sometimes resulting in relatively large errors for the

concentrations. We calculated the following steady-state concentrations:

pH 6:  $(2 \pm 1) \times 10^{-9}$  M;

pH 7:  $(3 \pm 2) \times 10^{-10}$  M; and

pH 8.5:  $(3 \pm 2) \times 10^{-10}$  M.

For each test one concentration was much higher than all the others (pH 7 at day 12 and pH 6 and 8.5 at day 26). We believe that this was caused by leaking filters. The filters are heated to near 90°C before they are used for the separation to ensure that they have the same temperature as the solution. This can sometimes cause cracking of the membrane. Unfortunately we cannot run the samples in duplicate because we would need a much larger volume for each test solution and the counting of each sample would be too time consuming. Each sample is counted already for up to 8 days to reach 30% precision.

The use of the stable americium homologue neodymium in these tests has shown that indeed the high  $\alpha$ -radiation field of the americium was responsible for the erratic concentration behavior in our solubility tests in J-13 groundwater at 60°C. Alpha radiation caused pitting in the test container, and the dislodged container particles served as nucleation centers for the americium to form pseudocolloids. We are looking for a more radiation-resistant container material; the results of some previous studies suggest the use of high-density linear polyethylene.

At the end of each test, we used x-ray powder diffraction to identify the solids formed. Like the J-13, 60°C americium solids, the precipitate at pH 6 was hexagonal Am-NdOHCO<sub>3</sub>, whereas the pH 7 and pH 8.5 solids were orthorhombic Am-NdOHCO<sub>3</sub> (Silva and Nitsche 1983). Reports on hexagonal AmOHCO<sub>3</sub> are unknown in the literature. We identified it on the basis of the match between its powder pattern and that of polymorphic NdOHCO<sub>3</sub>. The hexagonal structure of NdOHCO<sub>3</sub>

was solved with single-crystal x-ray diffraction (Christensen 1973). A comparison of this structure with that of the isolated americium solids formed at pH 6 at 60° and 90°C matched closely. This match identifies our americium precipitate as hexagonal  $\text{AmOHCO}_3$ . The hexagonal  $\text{AmOHCO}_3$  cell constants we determined are slightly smaller ( $a = 12.22$ ,  $c = 9.70$ ) than those of the neodymium analogue, which is consistent with their relative crystallographic radii. We have prepared a paper titled "First Evidence of Hexagonal  $\text{AmOHCO}_3$ ," which, after policy review, has been approved for publication.

We continued identifying our crystalline solids formed on the neptunium tests at 60° and 90°C. We have reviewed our x-ray powder diffraction data for the unknown solids from the neptunium experiments in J-13 water at 60° and 90°C. As a quick method of comparing the phases with published patterns of candidate neptunium compounds, we made a data base of intensities vs. 2 theta values. Representing these patterns as "stick diagrams" on transparencies allows us to identify a matching phase by merely overlaying the transparency on the unknown's pattern. We found that the 60°C, pH 8.5 precipitate contains  $\text{NaNpO}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  as the major phase. The remaining five solids we submitted to Los Alamos National Laboratory (LANL) for further identification by neutron activation analysis (NAA) to determine their elemental composition. Two of the five samples were analyzed. The results for both were inconclusive, because the samples were fused in quartz which interfered with the sodium analysis.

So far, we confirmed the presence of carbonate by FTIR spectroscopy. We are now looking for other possibilities to solve the elemental composition. We need to further characterize these solids, because they control the solubility. Eugene Standifer delivered a talk on the importance the solid's characterization at the Third Chemical Congress of North America held in Toronto, Canada, on June 5-10, 1988. The paper titled "Characterization of Transuranic Compounds from Solubility Experiments in a

Carbonate-Containing Groundwater," was written by E. M. Standifer, S. C. Lee, and H. Nitsche.

Solubility experiments for  $^{232}\text{NpO}_2^+$ ,  $^{239}\text{Pu}^{4+}$ , and  $^{241}\text{Am/Nd}$  in J-13 groundwater at  $25^\circ\text{C}$  and at pH values of 5.9, 7.0, and 8.5 were started. After approximately 50 days of running time, the neptunium test solutions are close to steady-state conditions as can be seen in Figs. 2, 3, and 4. The approximate solution concentrations at steady state are

pH 5.9:  $5 \times 10^{-3}$  M;

pH 7.0:  $1.5 \times 10^{-4}$  M; and

pH 8.5:  $5 \times 10^{-5}$  M.

The neptunium test for pH 7 shows very clearly the need to do solubility tests over long times until steady-state conditions are reached. The concentration decreased more than threefold from day 6 to day 48. We are currently determining the Eh, the speciation of the supernatant solutions, and the nature of the steady-state solids for the three neptunium test samples.

The americium/neodymium solutions have not yet reached steady-state conditions. The tests will continue until steady state is reached. Figures 5, 6, and 7 show the solution concentrations as a function of time for these tests.

The solubility tests for plutonium-239 have reached steady state as shown in Fig. 8. The approximate solution concentration are for

pH 5.9:  $1 \times 10^{-6}$  M;

pH 7.0:  $2 \times 10^{-7}$  M; and

pH 8.5:  $4 \times 10^{-7}$  M.

We are now investigating the oxidation state of the soluble plutonium and the properties of the steady-state solids.

All original data generated in these tests and analyses are located in designated storage areas at the Lawrence Berkeley Laboratory; a duplicate file is stored at LANL.

### 3.2. THERMODYNAMIC DATA REVIEW

On April 18 and 19, 1988, I participated in the "Workshop on the New Review of Neptunium and Plutonium Thermodynamics." The workshop was organized by Dr. Isabelle Poirot of the Organization for Economic Co-operation and Development Nuclear Energy Agency. The Nuclear Energy Agency (NEA) is located in Saclay near Paris (France). Dr. Hans Wanner, a Swiss national, shares the responsibilities for the Thermodynamic Data Bank with Dr. Poirot, a French national.

I am one of the six appointed expert reviewers for the data review of the elements neptunium and plutonium, which are present in nuclear waste. A complete and reliable data base on their thermodynamic properties is of utmost importance to modeling efforts for the safety assessment of high-level waste repositories.

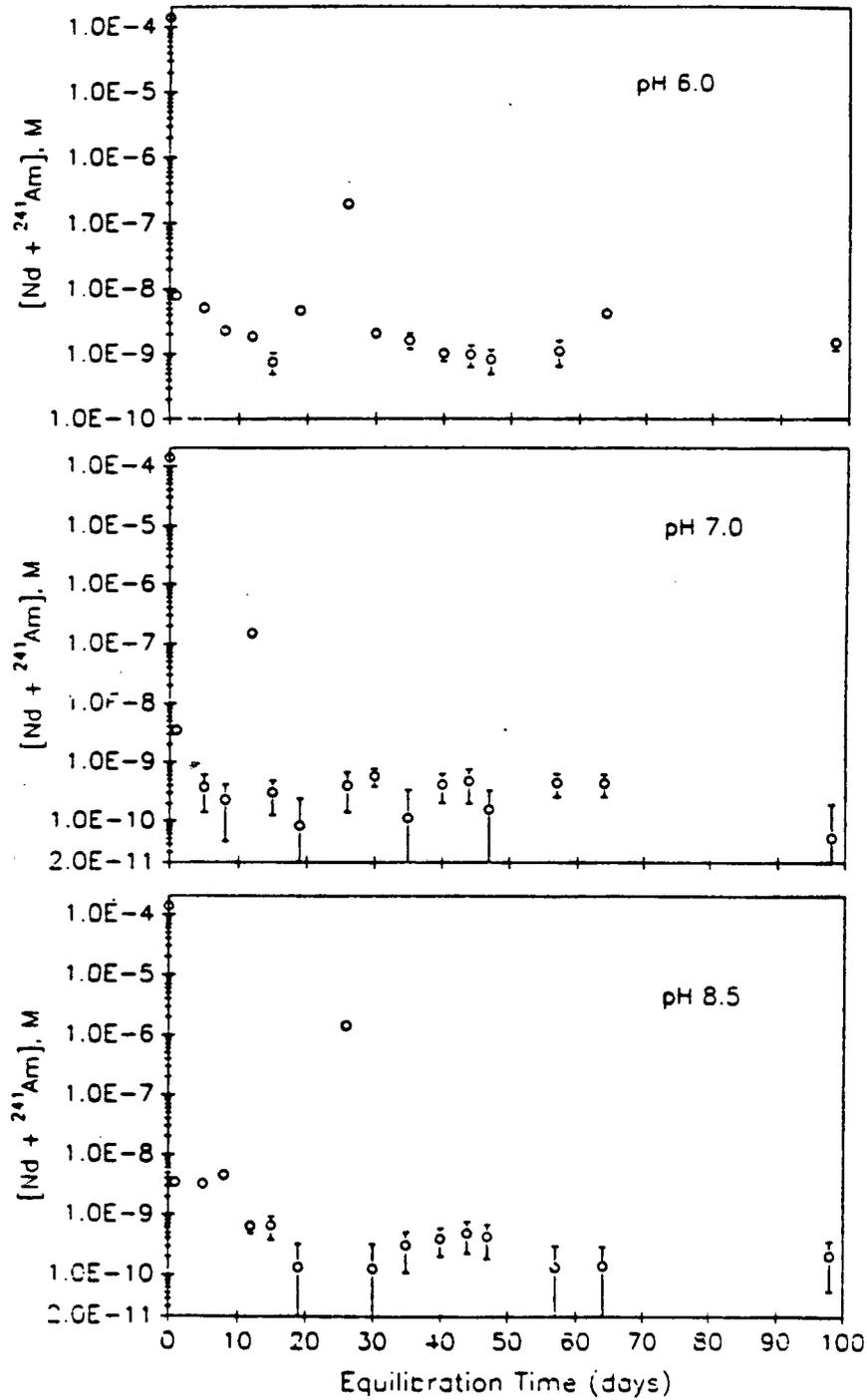
This data base will be different from the existing data bases because a group of experts will jointly decide on the availability and quality of published data. The review and the selection process will be documented as a part of the data base. This makes the data base superior to all other existing data compilations because the data selection process is transparent to the user. The primary purpose of this meeting was to establish the rules for the review and to assign the workload and the review time schedule to the individual reviewers. During FY 88, I started reviewing published data on the reduction potentials of uncomplexed neptunium and plutonium ions in aqueous solution.

#### 4. REFERENCES

Christensen 1973: A. N. Christensen, "Hydrothermal Preparation of Rare Earth Hydroxycarbonates. The Crystal Structure of  $\text{NdOHCO}_3$ ," *Acta Chem. Scand.* 27, 2973 (1973).

Shannon 1976: R. D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Cryst.* A32, 751 (1976).

Silva and Nitsche 1983: "Thermodynamic Properties of Chemical Species of Waste Radionuclides," Report NUREG/CP-0052, U.S. Nuclear Regulatory Commission (1983).



**Figure 1.** Solution concentrations as a function of equilibration time of neodymium/americiam-241 in contact with precipitate obtained from supersaturation in J-13 groundwater at  $90^\circ\text{C}$  and various pH values.

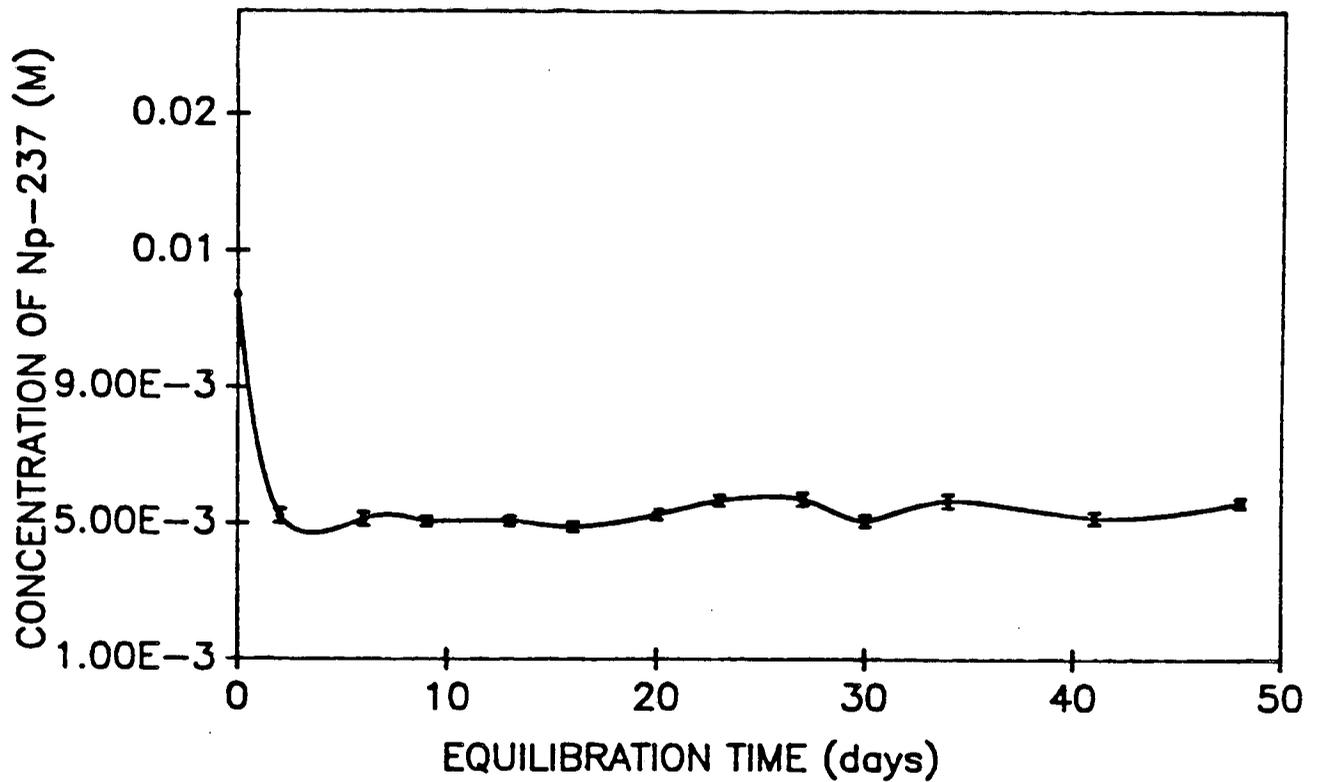
APPROACH OF J-13 WATER SOLUTION OF Np(V) AT  
pH 5.92 TO EQUILIBRIUM AT 25 DEGREES

Figure 2. Solution concentrations as a function of equilibration time for neptunium-237 in contact with precipitate obtained from supersaturation in J-13 groundwater at 25°C and pH 5.9. The neptunium was added initially (day 0) as  $\text{NpO}_2^+$ .

APPROACH OF J-13 WATER SOLUTION OF Np(V) AT  
pH 7 TO EQUILIBRIUM AT 25 DEGREES

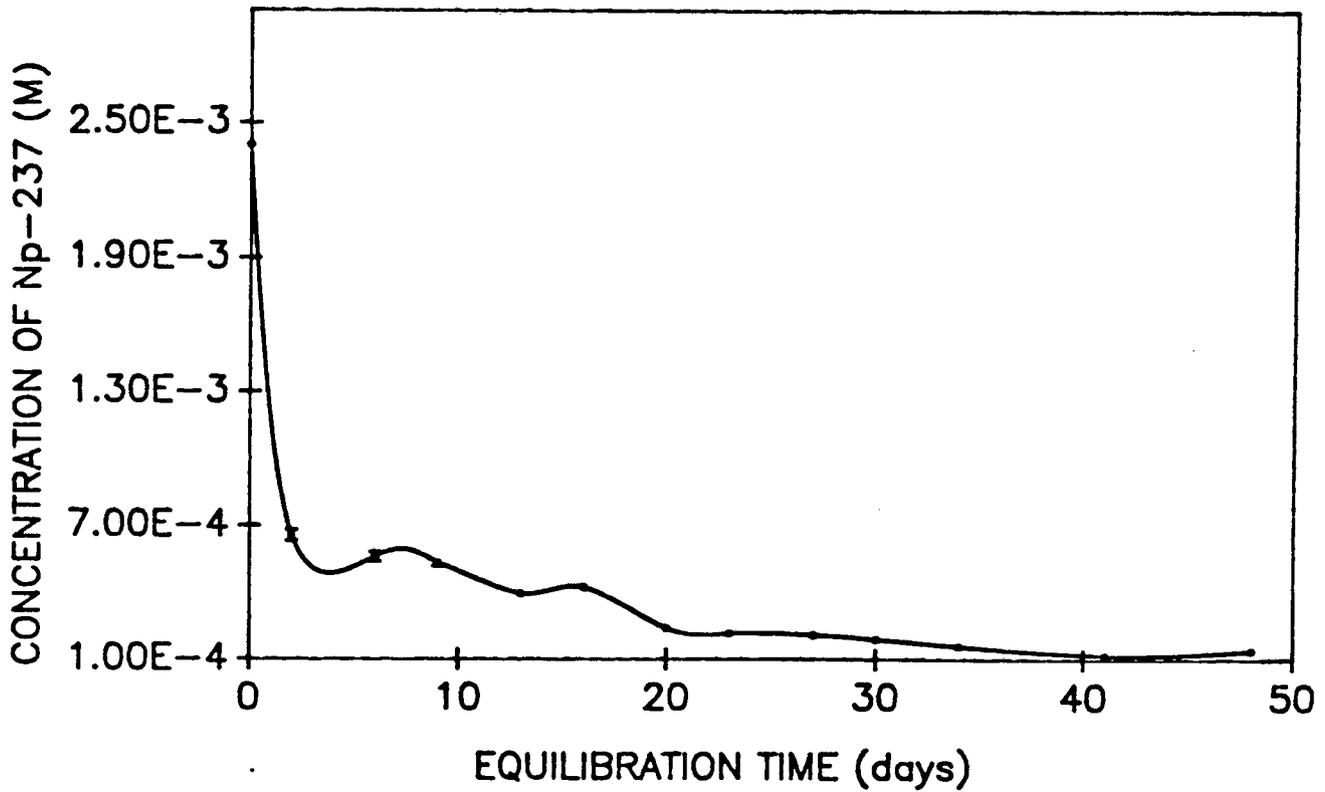


Figure 3. Solution concentrations as a function of equilibration time for neptunium-237 in contact with precipitate obtained from supersaturation in J-13 groundwater at 25°C and pH 7.0. The neptunium was added initially (day 0) as  $\text{NpO}_2^+$ .

APPROACH OF J-13 WATER SOLUTION OF Np(V) AT  
pH 8.5 TO EQUILIBRIUM AT 25 DEGREES

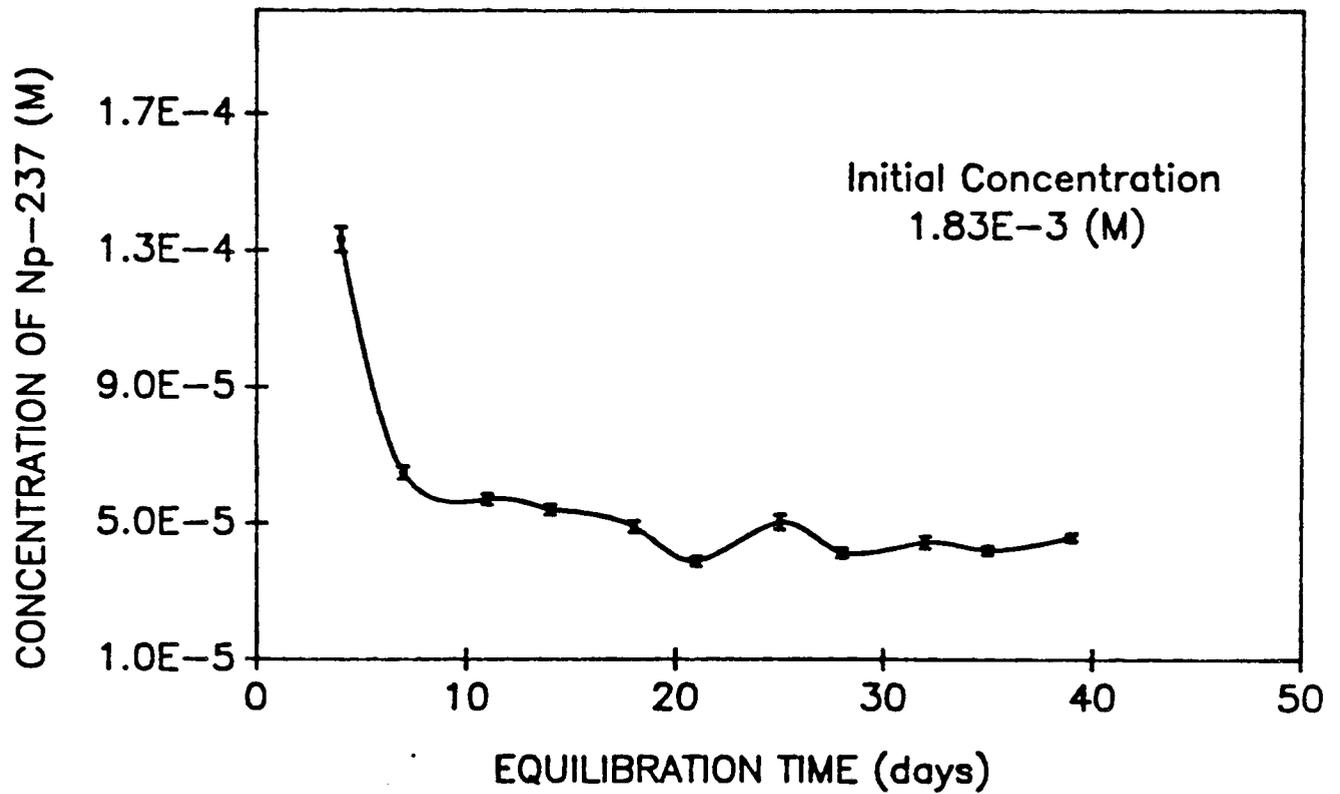


Figure 4. Solution concentrations as a function of equilibration time for neptunium-237 in contact with precipitate obtained from supersaturation in J-13 groundwater at 25°C and pH 8.5. The neptunium was added initially (day 0) as  $\text{NpO}_2^+$ .

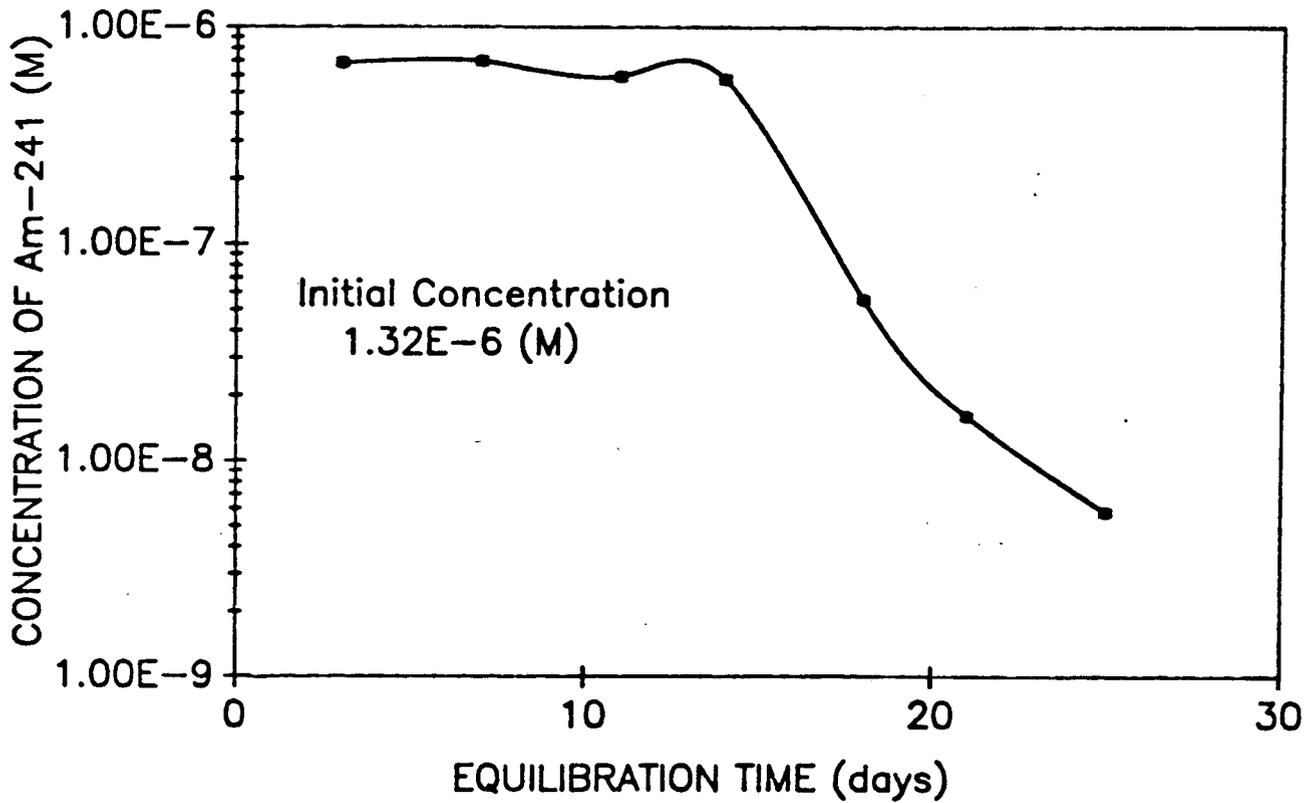
APPROACH OF J-13 WATER SOLUTION OF Am(III) AT  
pH 5.92 TO EQUILIBRIUM AT 25 DEGREES

Figure 5. Solution concentrations as a function of equilibration time for neodymium/ameridium-241 in contact with precipitate obtained from supersaturation in J-13 groundwater at 25°C and pH 5.9. The neodymium/ameridium was added initially (day 0) as  $\text{Nd}^{3+}/\text{Am}^{3+}$ .

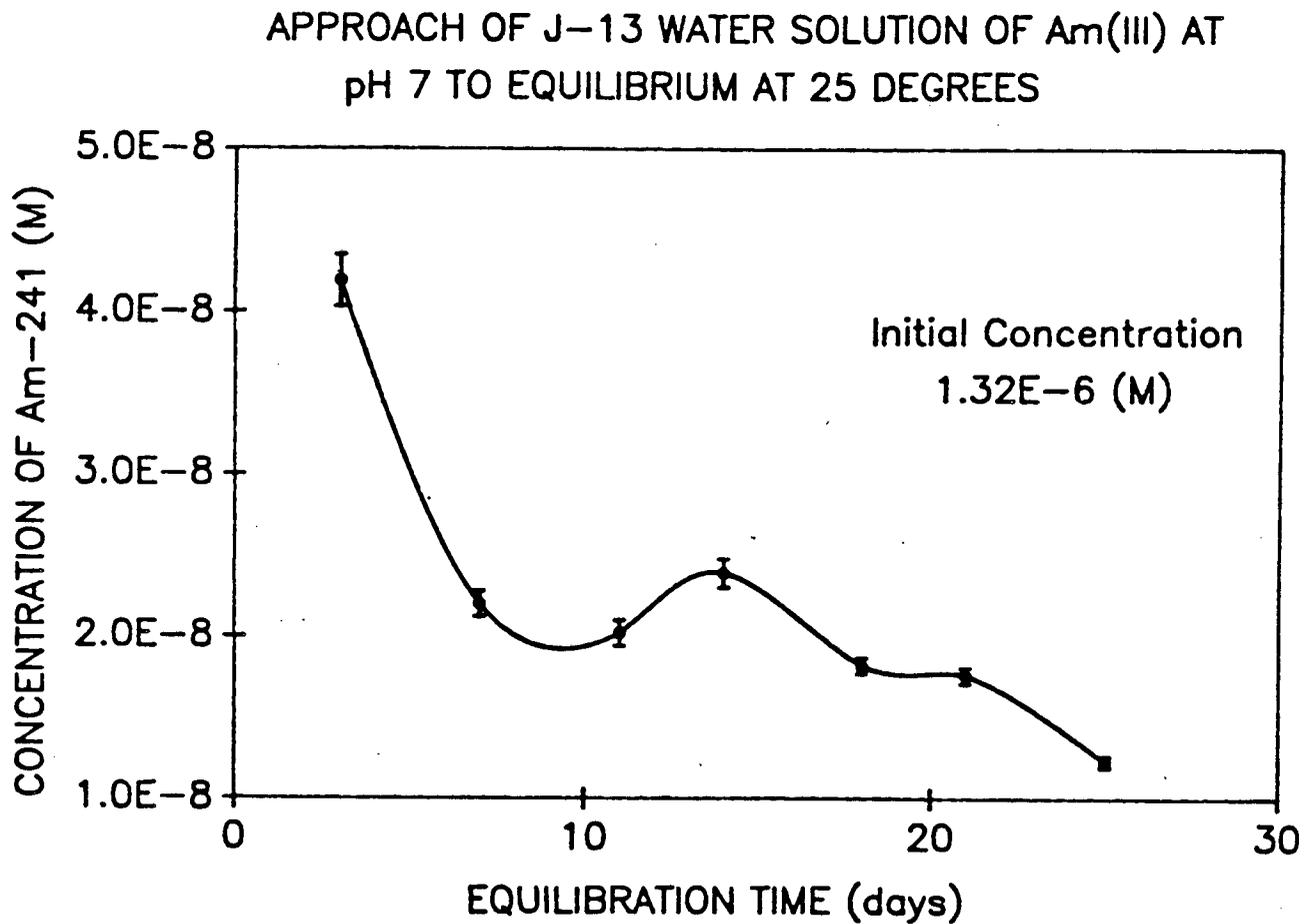


Figure 6. Solution concentrations as a function of equilibration time for neodymium/ameridium-241 in contact with precipitate obtained from supersaturation in J-13 groundwater at 25°C and pH 7.0. The neodymium/ameridium was added initially (day 0) as  $\text{Nd}^{3+}/\text{Am}^{3+}$ .

APPROACH OF J-13 WATER SOLUTION OF Am(III) AT  
pH 8.5 TO EQUILIBRIUM AT 25 DEGREES

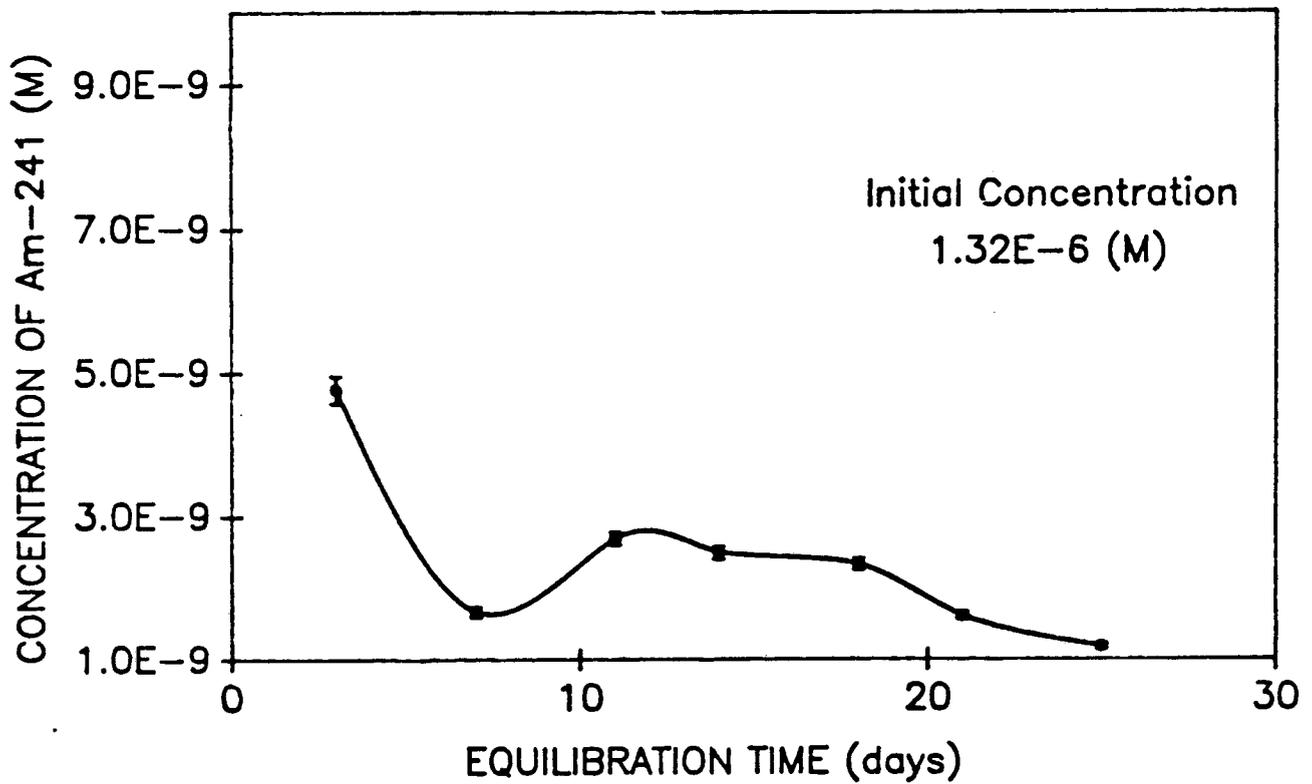


Figure 7. Solution concentrations as a function of equilibration time for neodymium/ameridium-241 in contact with precipitate obtained from supersaturation in J-13 groundwater at 25°C and pH 8.5. The neodymium/ameridium was added initially (day 0) as  $\text{Nd}^{3+}/\text{Am}^{3+}$ .

Approach of J-13 Water Solutions of Pu  
to Equilibrium at 25 Degrees

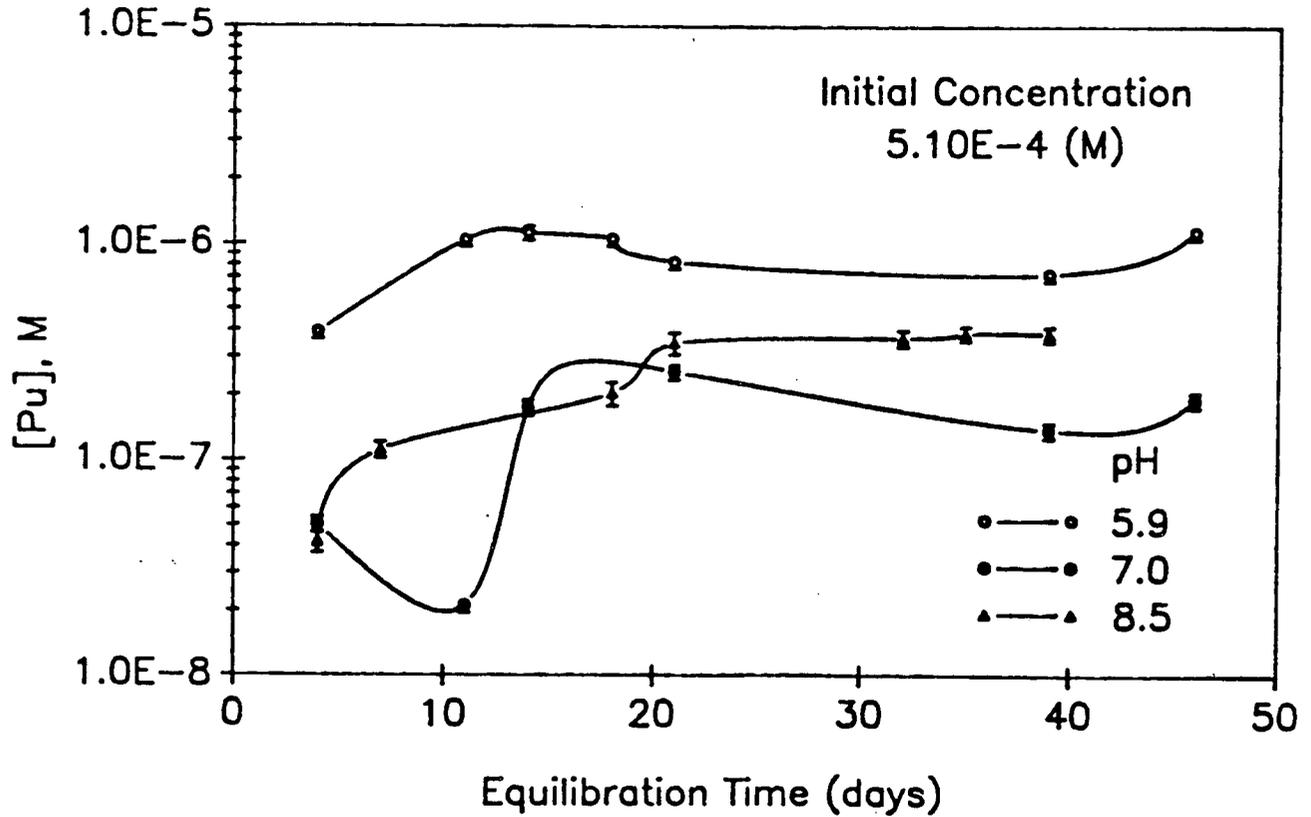


Figure 8. Solution concentrations as a function of equilibration time for plutonium-239 in contact with precipitate obtained from supersaturation in J-13 groundwater at 25°C, at various pH values; pH 5.9 (open circles), pH 7.0 (filled circles), pH 8.5 (triangles). The plutonium was added initially (day 0) as Pu<sup>4+</sup>.

LAWRENCE BERKELEY LABORATORY  
TECHNICAL INFORMATION DEPARTMENT  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720