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Investigation of the Behavior of Plutonium(V) in Alkaline Media

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Summary

The stability of the plutonium(V) oxidation state in alkaline media was studied with respect to the neighboring Pu(IV) and Pu(VI) oxidation states. Tests were conducted in 1 M or higher NaOH solutions in the presence and absence of other components of Hanford Site high-level tank waste.

Spectrophotometric techniques were found to be effective in studying the behavior of plutonium(V) in alkaline solution at plutonium concentrations above 10^{-3} M. To this end, plutonium(V) and plutonium(VI) solutions in NaOH were prepared and their spectra characterized.

In alkaline solutions with NaOH concentration below 8 M, plutonium(V) was found to be unstable to disproportionation occurring according to the reaction

$$2\ \mathrm{Pu(V)(aq)} \rightarrow \mathrm{Pu(VI)(aq)} + \mathrm{Pu(IV)(s)}$$

The disproportionation of Pu(V) is complicated by at least two simultaneous processes: 1) the sorption of a significant fraction of the Pu(V) onto the forming Pu(IV) hydrous oxide precipitate, and 2) partial reduction of Pu(VI) by water α-radiolysis products.

The extent of disproportionation increases with temperature and sharply falls with NaOH concentration. Plutonium(V) is stabilized in solutions simulating the composition of Hanford Site high-level waste with NaOH concentrations exceeding 4 M. This behavior can be ascribed to increasing plutonium(IV) hydrous oxide solubility caused by complex formation for the dissolved plutonium species.

In a complementary way, the extent of reproportionation of Pu(VI)(aq) and freshly precipitated Pu(IV) hydrous oxide increases sharply with increasing hydroxide concentration.

Disproportionation and reproportionation equilibrium constants were obtained for the range 4 to 8 M NaOH. Because of Pu(V) sorption on Pu(IV) solids and other factors, the constants do not have the expected reciprocal relationship. The formal potential of the Pu(V)/$PuO_2 \cdot xH_2O$ pair at 20°C in 1 M NaOH was estimated to be 0.4 ± 0.1 volts. The solubilities of Pu(V) and Pu(VI) compounds in NaOH solution were determined.

The plutonium(V) salt, $NH_4PuO_2CO_3$, was prepared. When stored as a separated solid compound, $NH_4PuO_2CO_3$ is relatively stable, decreasing in Pu(V) content several percent over 48 days. The stability of $NH_4PuO_2CO_3$ stored in NaOH solution is determined by the corresponding extent of Pu(V) disproportionation at that NaOH concentration.

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1.0 Introduction

The behavior of Pu(V) in acidic solution has been studied extensively. The stability of Pu(V) in acid is determined by the hydrogen ion concentration, the temperature, and other factors. In contrast, investigations of the behavior of Pu(V) in alkaline solution are scarce, and the data obtained by various authors are sometimes contradictory. For example, it has been hypothesized that Pu(V) should undergo disproportionation in strong alkali (Kraus 1956). However, only limited experimental verification of this supposition has been performed (Bourges 1972). Experiments also have revealed that by titrating acidic Pu(V) solutions with alkaline solution to high pH, the plutonyl(V) ions hydrolyze and the hydrolyzed ions, in turn, rapidly disproportionate (Kraus and Dam 1949; Hindman 1954).

The feasibility of Pu(V) disproportionation depends on the formal potentials of the adjacent Pu(V)/Pu(IV) and Pu(VI)/Pu(V) electrochemical pairs. Literature sources report various potentials for the first pair (Peretrukhin et al. 1995); the potential 0.44 V for Pu(V)/Pu(IV) in 4 M NaOH is most likely (Bourges 1972). The Pu(VI)/Pu(V) potential in 1 M NaOH is estimated to be 0.23 V (Bourges 1972). In 7.9 and 10.1 M NaOH, the Pu(VI)/Pu(V) potentials of 0.21 and 0.20 V, respectively, were obtained (Shilov 1976). Thus, disproportionation by the reaction

$$2\ \mathrm{Pu(V)} \rightarrow \mathrm{Pu(VI)} + 2\ \mathrm{Pu(IV)} \tag{1.1}$$

appears to be thermodynamically probable. The stability of Pu(V) in alkaline solutions in this process also should depend on the hydroxide concentration. In contrast, the formal potential of the Pu(V)/Pu(IV) pair has been measured polarographically to range from -0.61 V to -1.03 V as NaOH concentration increases from 0.1 to 14.1 M (Peretrukhin and Alekseeva 1974). These values differ greatly from other reported values. The disparity invites special consideration and is discussed in light of findings from the present investigations.

To date, explicit studies of Pu(V) disproportionation in alkali were reported only by way of the reproportionation reaction

$$\mathrm{Pu(VI)(aq)} + \mathrm{Pu(IV)(s)} \rightarrow 2\ \mathrm{Pu(V)(aq)} \tag{1.2}$$

(Bourges 1972). Nonetheless, the Pu(V) disproportionation process in alkali was mentioned in the literature as obvious and was invoked to interpret results obtained in studies of oxidation and reduction of plutonium in alkaline solution where, at hydroxide concentrations exceeding 8 M, it was assumed Pu(V) was stabilized in the form of hydroxide complexes (Shilov et al. 1996).

Studies of Pu(VI) stability in 1 to 15 M NaOH revealed that plutonium concentrations decreased with time (Delegard 1987). A corresponding solid phase increased with time while decreasing alkali concentration accelerated the plutonium precipitation rate. It is presumed that H_2O_2, formed in solution by radiolysis, reduced Pu(VI) to Pu(V) in these tests. The Pu(V) subsequently disproportionated. The more rapid decrease of plutonium concentration in dilute alkali likely is because of an increased Pu(V) disproportionation rate.

Plutonium(V) disproportionation has often been observed in previous tests conducted in this laboratory for alkaline Pu(V) solution having NaOH concentrations less than 6 M.

The objective of the present work was to study the stability of Pu(V) over a wide range of NaOH concentrations and to assess the rate and extent of the postulated disproportionation reaction.

To perform studies of Pu(V) stability in alkaline media, several fundamental investigations first were required. For example, systematic data on the absorption spectral of Pu(V), Pu(IV), and Pu(VI) in alkaline solution do not exist. Side reactions accompanying Pu(V) disproportionation have never been reported. Finally, practical techniques for preparing pure Pu(V) in alkaline media are unavailable in the literature. The supplementary investigations in these areas are of certain interest, and their findings are included in this report.

2.0 Instruments and Reagents

The isotopes ^{237}Np, ^{239}Np, and ^{239}Pu were used in the experiments. They were purified by anion exchange on a VP-1Ap vinylpyridine resin (of Russian manufacture) with subsequent oxalate precipitation by standard techniques.

Plutonium was stabilized in the tetravalent state with hydrogen peroxide and its concentration measured by complexometry. To prepare Pu(VI), concentrated $HClO_4$ was added to an aliquot of the initial Pu(IV) solution in nitric acid and boiled to the appearance of white vapor. The residual damp salts were dissolved in 0.01 $\underline{M}$ $HClO_4$. Spectrophotometric analysis showed the plutonium to be hexavalent.

The ^{237}Np(V) stock was prepared from standard ^{237}Np(V) nitrate solution purified by ion exchange. To produce neutral Np(V) solutions, Np(V) hydroxide was precipitated by adding ammonia solution, in the presence of nitrite, to the stock acid Np(V) solution. The resulting Np(V) hydroxide precipitate was then thoroughly washed with water to the point of peptization. Neutral solutions were obtained by dissolving the freshly precipitated and washed NpO_2OH in a stoichiometric amount of dilute HNO_3 solution followed by volumetric dilution of the dissolved solids with water.

The ^{239}Np stock was derived from ^{243}Am mother nuclide stored more than one month to achieve secular equilibrium with ^{239}Np. About 1 mL of weakly acidic 0.04 $\underline{M}$ (in metal) ^{243}Am solution was boiled down with concentrated HNO_3 to convert the ingrown neptunium to the hexavalent state. The HNO_3 concentration then was changed to 0.1 $\underline{M}$, and a 1 $\underline{M}$ $H_2C_2O_4$ solution was added in a small stoichiometric excess. A curdled Am(III) oxalate precipitate formed initially but thickened under the supernatant liquor. The residue was separated by centrifugation and the supernate fumed twice to dryness with $HClO_4$ to complete decomposition of the excess oxalate. The dried solution then was dissolved in 0.01 $\underline{M}$ $HClO_4$ and $NaNO_2$ added to convert neptunium to the pentavalent state. The solution thus obtained was used as a β-emitting tracer for ^{237}Np.

Standardized sodium hydroxide solutions (1 to 10 $\underline{M}$) were prepared as required just before the experiment. The initial 17.7 $\underline{M}$ NaOH stock solution was stored in a sealed plastic vessel. Virtually no contamination of this solution with carbonate was detected because sodium carbonate solubility in strong alkali is only 0.01 $\underline{M}$ (Rai and Ryan 1985). Pure and extra pure quality reagents were used in all experiments. Solutions were prepared from distilled water acidified to pH 4 and boiled to remove CO_2.

The neptunium and plutonium valences were measured with a Shimadzu model UV-3100 PC UV-Vis-NIR spectrophotometer (Japan). Radiometric measurements were performed on a PSO-2-4 radiometer (Russia) or Beckman LS6500 liquid scintillation counter (USA). Powder x-ray patterns of solid Pu(V) compounds were taken in a Guinier camera (100 mm, XDS-700 model, $CuK_{\alpha 1}$ radiation). A model U-5 thermostat (Germany) controlled solution temperatures to ±0.2°C. Liquid and solid phases were separated on a CLK-1 medical centrifuge (rotation velocity of 3000 rev/minute, separation factor 1750). Specific experimental techniques are described in order in the Results and Discussion section.

3.0 Results and Discussion

Methods of preparation and the properties of Pu(V) and Pu(VI) dissolved in alkaline solution were determined in preliminary experiments. Subsequent experiments were performed on the stability of Pu(V) as a function of solution composition and temperature. Results of these experiments and interpretation of their meaning are given in the following sections.

3.1 Electronic Absorption Spectra and Solubility of Pu(VI) in Alkaline Media

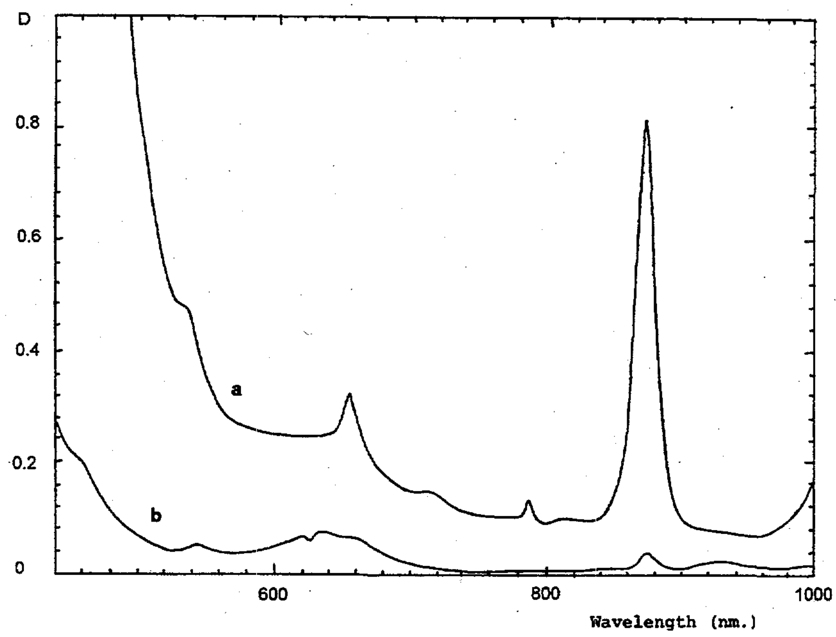
Though *f-f* electronic transitions in actinides are Laporte forbidden, actinide ions in acidic and neutral media often have intense absorption bands in the visible spectral range. The bands are allowed because asymmetric distortions in the ions' crystal fields relax the symmetry rules. The electronic absorption spectra (EAS) of An(V) and An(VI) in alkaline solutions, however, are expected to differ appreciably from those in acid because of changes in coordination. It has been observed that strong complexation and changes in the coordination geometry of actinide ions in alkaline media shift the original absorption bands found in acid toward the infrared (longer wavelength). The shifted peaks' extinction coefficients also are distinctly decreased. Despite the decreased absorbances, under the existing experimental conditions, spectrophotometry remains the only technique for direct identification of plutonium oxidation state in alkaline solution.

The solubility and stability of Pu(VI) in alkaline solution and the reproducibility of its absorption spectra were determined. Trial experiments demonstrated that at less than 2 $\underline{M}$ NaOH, and at greater than 5 x 10^{-4} $\underline{M}$ Pu(VI), yellow-brown solutions are produced whose spectra are unstable, changing with time and heating. Solutions with unstable spectra are produced both by addition of a weakly acidic Pu(VI) solution to alkali or by dissolving $PuO_3 \cdot H_2O$ (synthesis described by Bagnall and Laidler 1964) in alkali. The initial spectrum of such a solution is given in Figure 3.1.1 (a).

Aging a solution with NaOH concentration exceeding 1 $\underline{M}$ and Pu(VI) concentration less than 10^{-3} $\underline{M}$ for a few hours at 50°C causes the original yellow-brown solution to change to light green with a spectrum characteristic of Pu(VI) in alkali exceeding 2 $\underline{M}$ (Figure 3.1.1 [b]).

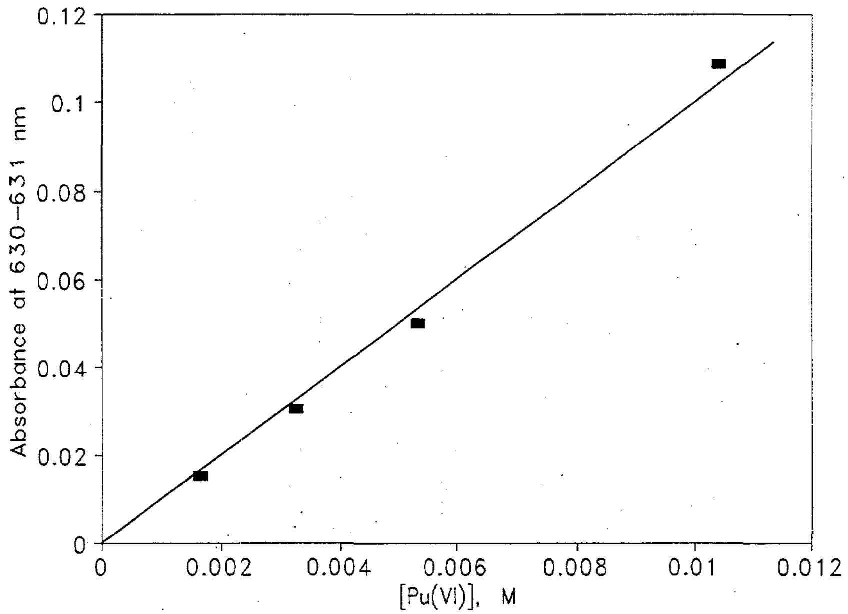
Over the range of 2 to 10 $\underline{M}$ NaOH, the EAS of Pu(VI) at 10^{-3} to 10^{-2} $\underline{M}$ remain invariable at room temperature for a few days and, at 95°C, for a few hours. The maximum of the absorption band at 631 nm can be used to determine Pu(VI) concentrations spectrophotometrically in solutions with NaOH concentrations exceeding 2 $\underline{M}$ (Figure 3.1.2).

The solubility of Pu(VI) was estimated in 2 to 10 $\underline{M}$ NaOH. To do this, $PuO_3 \cdot H_2O$ suspensions in solutions of selected NaOH concentration were stirred intensely for an hour in a cell maintained at 20 to 23°C. The temperature then was lowered to 15°C, and stirring continued for another hour. The suspensions then were centrifuged and the mother solution spectra measured.



a - [NaOH] < 2 M, b - [NaOH] > 2 M

Figure 3.1.1. Electronic Absorption Spectra of 5 x 10^{-3} M Pu(VI) at 20°C in NaOH Solution



(4 M NaOH; 20°C)

Figure 3.1.2. Absorbance of Alkaline Pu(VI) Solutions as a Function of Pu(VI) Concentration

The solubility of $PuO_3 \cdot H_2O$ at 15°C is about 10^{-2} M and practically invariant over the range 2 to 10 M NaOH (Table 3.1). The initial solid phase, $PuO_3 \cdot H_2O$, was confirmed by x-ray diffractometry; the equilibrium solid phase was not characterized. With increasing temperature, the Pu(VI) concentration increases significantly. Lower Pu(VI) solubility, 10^{-5} to 10^{-4} M Pu(VI) in 0.1 to 10 M KOH, respectively, is reported in Pérez-Bustamante (1965). The published results, however, are based on indirect methods.

Table 3.1.1. Solubility of $PuO_3 \cdot H_2O$ in 15°C NaOH Solution

[NaOH], M	[Pu(VI)], M
2	0.0111
3	0.0114
4	0.0118
8	0.0151
10	0.0169

3.2 Preparation of Alkaline Pu(V) Solutions

Alkaline plutonium(V) solutions were required for studies of Pu(V) stability. Methods to prepare alkaline Pu(V) solutions by chemical and electrochemical reduction of Pu(VI) and by dissolution of Pu(V) salts were investigated.

3.2.1 Preparation of Pu(V) by Reduction of Pu(VI)

Theoretically, to prepare alkaline solutions of Pu(V) by chemical reduction of Pu(VI), reducing agents with redox potential below 0.23 V can be used. However, other criteria such as rapid reduction kinetics and the absence of side reactions exist for selecting a suitable reducing agent.

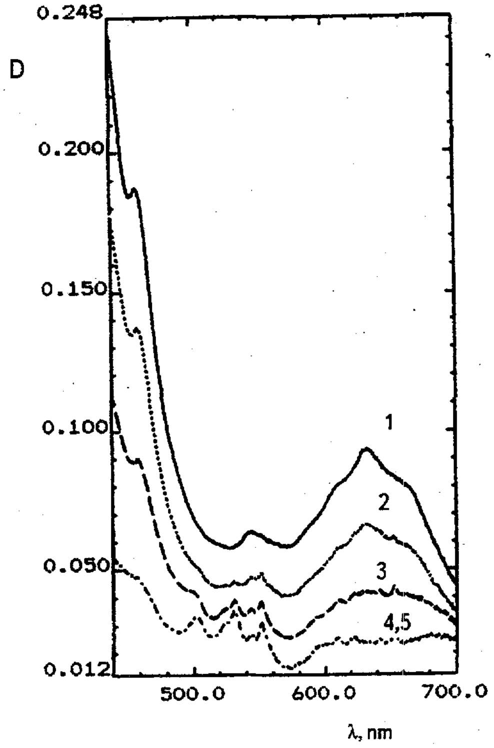
The reagents I^-, VO_2^{2-}, Sn^{2+}, N_2H_5OH, and H_2O_2 were tested for reduction of Pu(VI) to Pu(V). At room temperature, iodide does not react with Pu(VI) in 2 M NaOH even in the presence of CCl_4 (to remove product iodine). Both VO_2^{2-} and Sn^{2+} easily reduce Pu(VI) to Pu(V) at 2 and 4 M NaOH. If the Pu(VI) concentration exceeds 10^{-3} M, a fine white powder precipitate forms within a few minutes. Dilute alkaline solutions of VO_2^{2-} and Sn^{2+} are unstable, however, and are oxidized by atmospheric oxygen whenever their concentrations are below 5×10^{-3} M.

Rapid and complete room temperature reduction of Pu(VI) by H_2O_2 and N_2H_5OH has recently been reported (Shilov et al. 1997; Shilov and Budantseva 1997). The efficiencies of these reagents were tested by titration of alkaline Pu(VI) solution with the reducing agent at room temperature. Alkaline

Pu(VI) solutions were prepared containing 3 mmol Pu(VI). Initial experiments used LiOH solution because of the high actinide solubility in this medium. Experiments then were repeated in NaOH solution. Similar results were obtained for the two alkalis.

Aliquots of reducing agent dissolved in alkali of selected concentrations were added to similar alkaline Pu(VI) solutions; the EAS were recorded immediately upon complete mixing of the reagents. This process was repeated until a stoichiometric amount, with respect to the Pu(VI) → Pu(V) reduction, was reached. Results of the titration of Pu(VI) with N_2H_5OH in 5 M NaOH are given in Figure 3.2.1. No changes in the spectra were observed in the first ten minutes. With time, changes in the general pattern of the spectra of plutonium solution were observed as N_2H_5OH concentration increased to 0.4 mM. The solutions seemed almost colorless with a light pink tint. Then a grayish deposit appeared, forming not only with excess reducing agent but also in substoichiometric amounts. In the latter case, however, a few hours elapsed before the deposit formed.

When hydrogen peroxide was used as a reductant for Pu(VI) [at Pu(VI) concentrations exceeding 5×10^{-3} M], the solution color changed from green to dark gray. The gray color, stable for a few seconds, is apparently caused by formation of an unstable Pu(VI) peroxide complex. About 80% of the



1 - $[N_2H_5OH] = 0.0$ mM; [PuVI)] = 1.00 mM

2 - $[N_2H_5OH] = 0.1$ mM; [PuVI)] = 0.98 mM

3 - $[N_2H_5OH] = 0.2$ mM; [PuVI)] = 0.95 mM

4 - $[N_2H_5OH] = 0.4$ mM; [PuVI)] = 0.93 mM

5 - $[N_2H_5OH] = 0.8$ mM; [PuVI)] = 0.90 mM

(5 M NaOH; 22°C; 1-cm pathlength)

Figure 3.2.1. Electronic Absorption Spectra of Pu(VI) Solutions Reacted with Hydrazine

Pu(VI) was rapidly reduced. The remaining Pu(VI) reacted with H_2O_2 more slowly, however. Completion of the reaction (including initiation and formation of the deposit) required inconveniently long times.

Of the tested reducing agents, only hydrazine rapidly (during mixing) and completely converts Pu(VI) to Pu(V) at room temperature. The resulting Pu(V) solution was stable long enough for its absorption spectrum to be recorded (Figure 3.2.2).

Because the above reagents efficiently reduce Pu(VI) at 1 to 5 M NaOH, further Pu(V) reduction to Pu(IV) may also occur. Further reduction can not easily be verified because Pu(IV) forms only a hydrous oxide precipitate of limited solubility rather than stable or metastable solutions. Colloidal Pu(IV) particles, whose properties and behavior are very sensitive to the preparation procedure, storage, and other conditions, also can form. Even if Pu(V) solutions are prepared by reduction in NaOH solution exceeding 6 M, spectrophotometric measurements are difficult because light absorption by suspended Pu(IV) particles, which varies in time, is much higher than that of Pu(VI) and Pu(V) dissolved species.

Electrochemical reduction of Pu(VI) in alkaline solution also was investigated. Experiments were conducted in an H-shaped electrochemical cell with the anode and cathode compartments separated by porous filters filled with silica gel. The minimum working electrolyte volume was 1.5 mL, and the working area of the platinum electrode was 1.6 cm^2. Reduction of 10^{-3} M or higher Pu(VI) on a platinum electrode in 4 M or lower NaOH solution is strongly inhibited by deposition of green solids on the

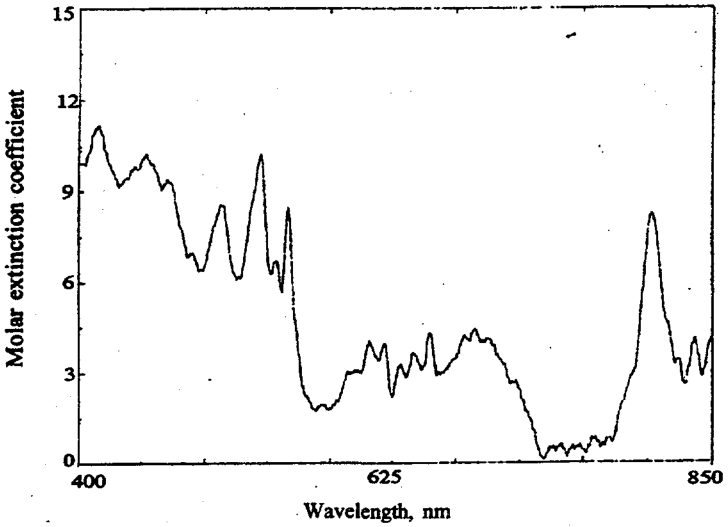


Figure 3.2.2. Visible/NIR Electronic Absorption Spectrum of 2 x 10^{-3} M Pu(V) in 8 M NaOH

platinum electrode surface. This deposit completely masks the electrode and the current virtually stops very soon after the beginning of electrolysis. The film deposit dissolves in strong heated nitric acid. In alkali, the film is destroyed by applying a voltage sufficient to oxidize water vigorously. The plutonium deposit then is oxidized to Pu(VII).

3.2.2 Preparation and Use of Pu(V) Salts and Their Stability in Air

The chemical and electrochemical experiments showed that preparation of alkaline Pu(V) solutions by Pu(VI) reduction gives inconsistent results and may introduce significant errors in subsequent measurements of Pu(V) disproportionation reaction parameters. Therefore, a fundamentally different approach, addition of a solid Pu(V) compound to the test solution, was chosen to prepare Pu(V) for disproportionation experiments. This technique eliminates uncertainty in the stoichiometry of the reduction of Pu(VI) and the possibility of further reduction to Pu(IV).

The Pu(V) compound selected for use in the disproportionation tests was crystalline $NH_4PuO_2CO_3$. This compound was synthesized by a technique published by Mefod'eva and Krot (1987). Because the actinide oxidation state in a crystalline matrix may change with time (Kazin and Tananaev 1989), tests were performed to determine the stability of the Pu(V) salt.

The purity of $NH_4PuO_2CO_3$ was first tested by dissolving a weighed portion of freshly prepared salt in 0.1 M HCl in a plastic test tube. The solution was centrifuged to separate it from possible solid admixtures. The solution absorption spectrum then was measured. The spectra exhibited intense absorbances at 569 and 831 nm that are characteristic of the hydrated PuO_2^+ and PuO_2^{2+} cations, respectively.

Several $NH_4PuO_2CO_3$ samples, each about 50 mg, were placed in plastic weighing bottles and stored both at room temperature in a desiccator and in a drying box at 85°C. Bottles were retrieved periodically, the salt dissolved, the spectra of the dissolved salt gathered, and the fractions of Pu(V) and Pu(VI) calculated.

The crystalline $NH_4PuO_2CO_3$ compound is quite stable. In general, the Pu(VI) content found in the starting compound after precipitating, washing, and dissolving ranged between 5 and 10%, the remainder being Pu(V). The normalized Pu(V) fraction in $NH_4PuO_2CO_3$, $Pu(V)_t/Pu(V)_i$, is defined as Q where $Pu(V)_t$ is the amount of Pu(V) at the time of measurement and $Pu(V)_i$ is the amount in the initial compound. The decrease in Q is 6 ± 1% after 48 days' storage at 12°C, about the same as observed at 85°C over 3 days. As shown in Figure 3.2.3, the Pu(V) fraction decreases linearly with time. This suggests that zero order increase of Pu(VI) fraction in $NH_4PuO_2CO_3$ occurs. Studies of the reaction mechanism are beyond the scope of this work. However, zero-order redox reactions often are observed in α-radiolysis reactions of actinide solutions.

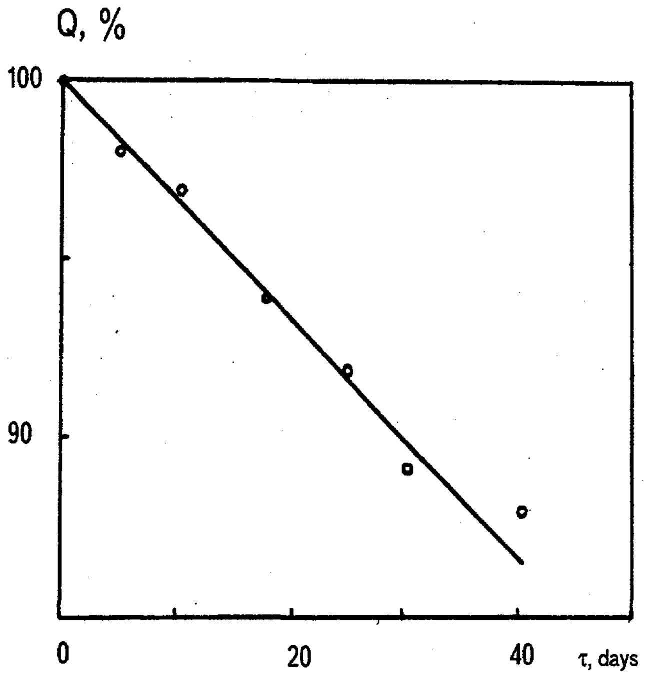


Figure 3.2.3. Pu(V) Content in Solid $NH_4PuO_2CO_3$ Stored in Air at 20°C as a Function of Time

3.2.3 Measurement of Pu(V) Solubility in Alkali

Alkaline Pu(V) solutions were prepared by dissolving crystalline $NH_4PuO_2CO_3$ in NaOH solutions of selected concentration. Addition of excess solid $NH_4PuO_2CO_3$ to NaOH solution thus served as a reservoir of Pu(V). The final Pu(V) concentration in a solution with no redox reactions provides a measure of the solubility of Pu(V) in NaOH solution. To estimate the Pu(V) solubility, a suspension of excess solid grayish-white $NH_4PuO_2CO_3$ was stirred thoroughly for 1.5 hours in a thermostatted cell held between 15 and 20°C. The solid phase became pink, and the centrifuge-clarified mother liquor was flesh-pink.

The Pu(V) concentration was measured by spectrophotometric titration with plutonium(VII) in 8 $\underline{M}$ NaOH. The Pu(VII) solutions were prepared by electrochemical oxidation of 10^{-2} $\underline{M}$ Pu(VI) in 3 $\underline{M}$ alkali. The NaOH concentration in the Pu(VII) stock was increased to 8 $\underline{M}$ by addition of concentrated alkali. The Pu(VII) concentration was determined by titration with a standard $K_4[Fe(CN)_6]$ solution.

Titration of aliquots of Pu(V) (at about 10^{-3} $\underline{M}$) in 8 $\underline{M}$ NaOH were performed with the standardized Pu(VII) solution in 8 $\underline{M}$ NaOH. The Pu(V) solubility found in 8 $\underline{M}$ NaOH is about (8 ± 3) x 10^{-3} $\underline{M}$. Further studies of Pu(V) solubility are described in Section 3.8.

3.3 Disproportionation of Pu(V) in Alkaline Solutions

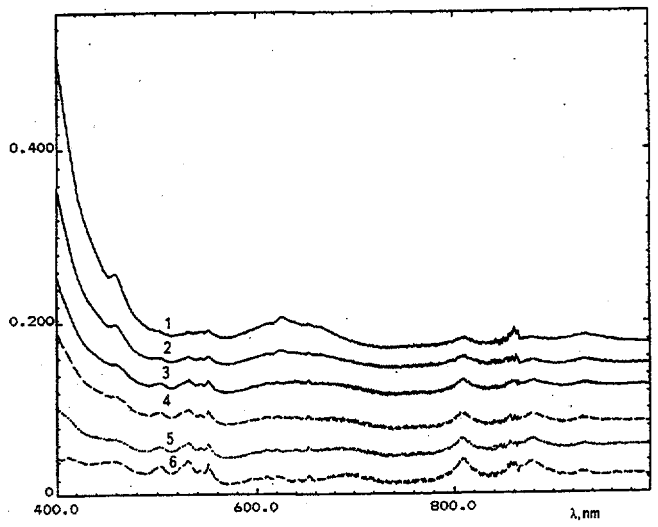
The approximate range of NaOH concentrations within which Pu(V) disproportionation occurs was determined by qualitative studies. Solid $NH_4PuO_2CO_3$ was added to alkaline solution and the slurry stirred vigorously. Within a few seconds, the gray precipitate converted to a flesh pink color. The deposit color then changed from pink to olive. The change from pink to olive occurred more rapidly as NaOH concentration decreased. However, no color change to olive was observed in solutions above 7.5 M NaOH; the solid phase remained bright pink for the duration of the experiment.

Following the scoping studies, quantitative experiments were performed. The initial quantitative tests were at room temperature to preclude temperature differences between equilibration and spectral measurements. For each test, about 0.027 mmol $NH_4PuO_2CO_3$ was prepared as a precipitate in a plastic vessel. The slightly grayish white sediment was washed once with 0.1 M NH_4HCO_3 solution and then with water. Then, 5 mL of alkali (to make 5.4×10^{-3} M total plutonium) at a known concentration was added and timing started for the experiment. Preliminary experiments revealed that precipitation and washing caused unavoidable losses of up to 15 wt.% of the $NH_4PuO_2CO_3$. Therefore, the total plutonium amount was measured upon completion of each experiment.

The suspensions were placed in a thermostat at a preset temperature and thoroughly stirred with a magnetic stirrer. At hourly intervals, stirring was stopped. The liquid phase was clarified by centrifugation and an EAS recorded in the range 1000 to 400 nm. The spectra showed a peak at 620 to 630 nm characteristic of Pu(VI) and peaks at 500 to 600 nm and 800 to 810 nm assigned to Pu(V). The spectra also contained absorption bands assigned to hydroxo complexes of Pu(V) and Pu(VI). The bands' intensities changed with NaOH concentration and times of contact between the precipitate and solution. After five hours' stirring at 12°C, the EAS pattern became stable. The initial Pu(V) and products of its disproportionation were assumed to be in equilibrium. At higher temperatures, more rapid approach to equilibrium was expected. Therefore, in subsequent tests at higher temperature, intermediate measurements of solution spectra were not performed and the Pu(VI) concentrations were determined five hours after beginning the experiment.

At lower temperature (-6°C), the solution was equilibrated with no stirring for 72 hours. No Pu(V) disproportionation studies were performed at temperatures above 40°C because of technical reasons. Figure 3.3.1 illustrates the EAS of equilibrated solutions as a function of NaOH concentration.

The Pu(V) and Pu(VI) concentrations in the supernatant were evaluated based on the measured molar extinction coefficients of Pu(V) and Pu(VI); ε^{V}_{531} of 10 L/(mol·cm) and ε^{VI}_{630} of 10 L/(mol·cm), respectively. The molar extinction coefficients were determined by spectrophotometric measurements and determinations of Pu(VI) and Pu(V) concentrations. The Pu(VI) concentration was determined by electrochemical oxidation to Pu(VII) and spectrophotometric titration with ferrocyanide. The Pu(V) concentration was determined by spectrophotometric titration with standardized Pu(VII). Cuvettes with 5-cm pathlength were used.



[NaOH], $\underline{M}$: 1 - 5.65, 2 - 6.10, 3 - 6.60, 4 - 7.00, 5 - 7.46, 6 - 8.02

Figure 3.3.1. Electronic Absorption Spectra of 40°C Equilibrated Pu(V) Solutions as a Function of NaOH Concentration

The total amount of plutonium(V) and (VI) present in solution was calculated based on the spectrophotometric measurements. The settled solid phase was dissolved in 0.2 $\underline{M}$ $HClO_4$ and the quantity of plutonium in the sediment determined. The total quantity of plutonium in the run is the sum of the solution and solid amounts. With the known initial Pu(V) quantity taken for the run and the equilibrium content of Pu(VI) in solution, the apparent equilibrium constant of the disproportionation reaction (K_d^{app}) can be calculated

$$2\ Pu(V) \rightleftarrows Pu(VI) + Pu(IV) \tag{3.1}$$

Strictly speaking, K_d^{app} is not a thermodynamic characteristic of equilibrium in the system studied. However, it specifies the ratio between various valence forms of plutonium participating in reaction (3.1)

$$K_d^{app} = ([Pu(IV)]\cdot[Pu(VI])/[Pu(V)]^2 \tag{3.2}$$

According to Reaction (3.1), the Pu(IV) equilibrium concentration ($[Pu(IV)_{equi.}]$) must equal the Pu(VI) equilibrium concentration ($[Pu(VI)_{equi.}]$). Therefore, Equation 3.2 may be transformed as follows:

$$K_d^{app} = [Pu(VI)_{equi.}]^2/([Pu(V)_{init.} - 2[Pu(VI)_{equi.}])^2 \quad (3.3)$$

where $[Pu(V)]_{init.}$ is the initial concentration of Pu(V) introduced in the reaction medium. In calculating K_d^{app}, an error associated with slow oxidation of Pu(V) to (VI) by atmospheric oxygen in the alkaline solution during the experiment is ignored. This effect is negligible; about 5% oxidation of Pu(V) occurs in 36 hours bubbling with pure oxygen at 25°C (Shilov et al. 1996).

Results of the disproportionation experiments are listed in Tables 3.3.1 and 3.3.2. These data indicate that K_d^{app} is dependent on temperature and NaOH concentration. Determination of K_d^{app} at

Table 3.3.1. Investigation of Pu(V) Disproportionation in 1 to 10 M NaOH Solutions; Material Balance at 40°C[(a)]

[NaOH], M	Initial Pu, mmoles	Equilibrium Pu in Solution, mmoles		Equilibrium Pu in Solids, mmoles
		Pu(VI)	Pu(V)	
1.00	0.0410	0.0200	not detected	0.0210
4.00	0.0380	0.0180	0.0008	0.0192
5.65	0.0213	0.0051	0.0015	0.0147
6.10	0.0202	0.0046	0.0021	0.0135
6.60	0.0206	0.0036	0.0028	0.0142
7.00	0.0203	0.0027	0.0036	0.0140
7.46	0.0202	0.0015	0.0046	0.0141
8.02	0.0208	0.0002	0.0072	0.0134
10.00	0.0210	not detected	0.0065	0.0145
(a) 3 mL total volume in all experiments.				

Table 3.3.2. Calculation of Equilibrium Constants of Pu(V) Disproportionation in 4 to 8 M NaOH Solutions at Different Temperatures

[NaOH], M	K_d^{app}				Amount of Pu(V) Decomposing, %			
	-6°C	12°C	20°C	40°C	-6°C	12°C	20°C	40°C
4.00	0.045	0.14	0.37	80	29.3	43.2	54.2	94.7
5.65	0.012	0.017	0.024	0.21	16.3	20.6	13.7	50.0
6.10	0.078	0.0091	0.015	0.17	15.1	15.9	19.1	47.8
6.60	0.0040	0.0057	0.0069	0.072	11.2	13.1	14.2	35.4
7.00	0.0002	--	0.0003	0.033	2.4	--	3.2	26.3
7.46	--	0.0001	0.0003	0.008	--	1.9	3.2	14.4
8.02	--	--	--	0.0001	--	--	--	1.9

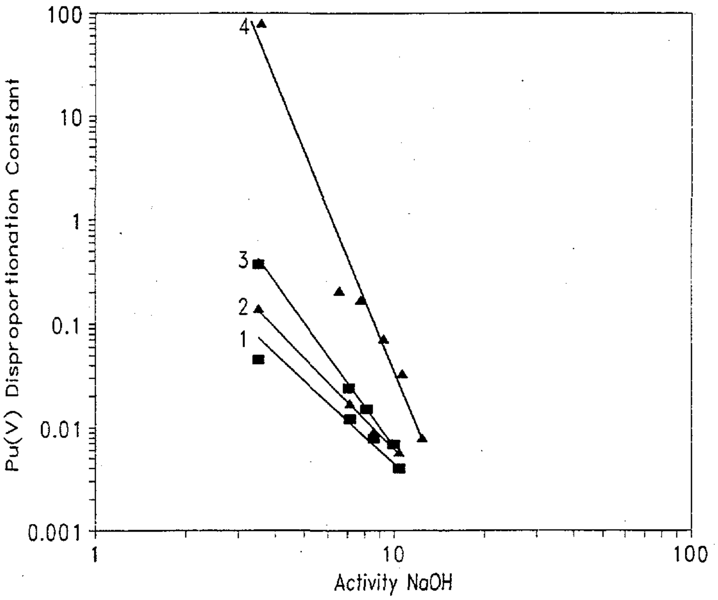
1 M NaOH was not possible because Pu(V) concentrations were too low to measure. Similarly, only approximate K_d^{app} values could be obtained at NaOH concentrations exceeding 8 M and at the lower temperatures where Pu(VI) concentrations were below detection. Plutonium(V) was observed to be stable at least one month in NaOH solutions exceeding 8 M.

Despite the apparent five-hour equilibration time, the system will continue to change slowly but appreciably upon long-term storage. Plutonium(V) can be oxidized by atmospheric oxygen (Shilov et al. 1996). Solution radiolysis, sorption of Pu(V) and Pu(VI) ions on Pu(IV) hydrous oxide precipitates (Kraus and Dam 1949), dehydration of Pu(IV) hydrous oxide, and other processes are also possible. These changes all occur slowly and their effects were negligible for these short term experiments.

Table 3.3.3 summarizes the K_d^{app} calculation results and Figure 3.3.2 presents the dependence of K_d^{app} on the published chemical activities of NaOH (Handbook 1966). The negligible effects of

Table 3.3.3. Calculation of Pu(V) Disproportionation Constants at Different Temperatures and NaOH Concentrations

T, °C	[NaOH], M	a_{NaOH}	log a_{NaOH}	K_d^{app}	log K_d^{app}
-6	4.00	3.52	0.55	0.045	-1.35
	5.65	7.12	0.85	0.012	-1.92
	6.10	8.54	0.93	0.0078	-2.11
	6.60	10.43	1.02	0.0040	-2.40
	7.00	12.04	1.08	0.00020	-3.70
12	4.00	3.52	0.55	0.14	-0.85
	5.65	7.12	0.85	0.017	-1.77
	6.10	8.54	0.93	0.0091	-2.04
	6.60	10.43	1.02	0.0057	-2.24
	7.46	14.17	1.15	0.00010	-4.00
20	4.00	3.52	0.55	0.37	-0.43
	5.65	7.06	0.75	0.024	-1.62
	6.10	8.11	0.91	0.015	-1.82
	6.60	9.98	1.00	0.0069	-2.16
	7.00	11.76	1.07	0.00030	-3.52
	7.46	14.02	1.15	0.00030	-3.52
40	4.00	3.58	0.55	80	1.90
	5.65	6.55	0.82	0.21	-0.68
	6.10	7.75	0.89	0.17	-0.77
	6.60	9.24	0.97	0.072	-1.14
	7.00	10.64	1.03	0.033	-1.48
	7.46	12.46	1.10	0.008	-2.10
	8.02	15.48	1.19	0.0001	-4.00



1 - -6°C, 2 - 12°C, 3 - 20°C, 4 - 40°C

Figure 3.3.2. Plutonium(V) Disproportionation Constants as Functions of Temperature and NaOH Chemical Activity

dissolved plutonium on NaOH activity were ignored. The dependence, plotted in log-log coordinates, fits a straight line. A formal analytical relation for K_d^{app} as a function of the NaOH solution activity then may be derived:

$$K_d^{app} = K_d^0/(a_{NaOH})^x \tag{3.4}$$

Equation 3.4 was used to calculate constants K_d^0 and x with respect to temperature (Table 3.3.4). These coefficients are the equilibrium constants for disproportionation at unit NaOH solution activity

Table 3.3.4. Values of Constants K_d^0 and x Versus Temperature

T, °C	K_d^0	x
-6	2.2	2.8
12	4.6	2.8
20	37	3.6
40	3000	4.9

(about 1.5 M NaOH) and the number of OH^- groups entering into the reaction studied, respectively. The change of equilibrium constants and hydroxide dependencies with temperature may indicate a variable reaction mechanism.

3.4 Reproportionation of Pu(VI) and Pu(IV) in Alkaline Solution

Investigations of the reaction of Pu(VI) and Pu(IV) in alkaline solution have been performed in previous studies. The reproportionation constant for the reaction

$$\mathrm{Pu(VI)} + \mathrm{Pu(IV)} \rightleftarrows 2\ \mathrm{Pu(V)} \tag{3.5}$$

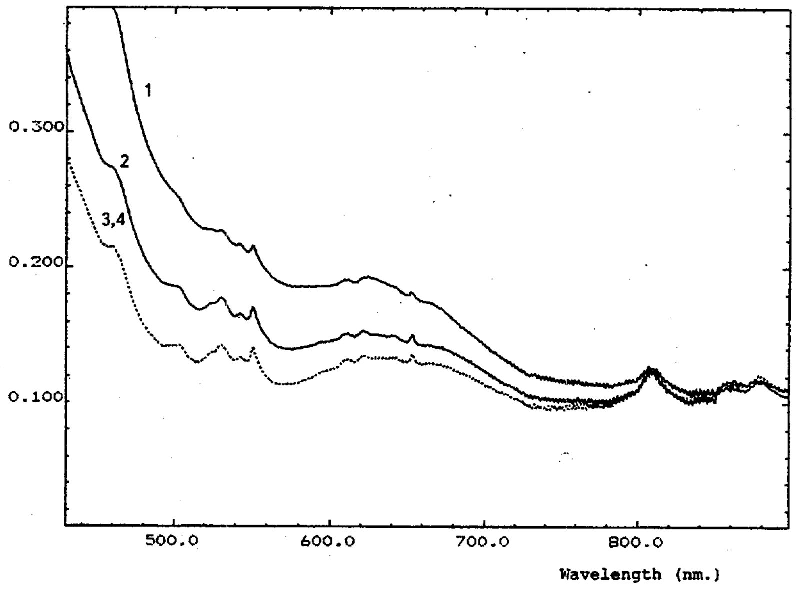
was found to be 2×10^{-5} in 4 M NaOH and 1.4×10^{-6} in 6 M NaOH (Bourges 1972).

To investigate Pu(VI) and Pu(IV) reproportionation in more detail, a known amount (about 0.0054 mmol) of freshly precipitated Pu(IV) hydrous oxide was washed with 8 M NaOH and placed in a plastic test tube. An alkaline Pu(VI) solution was then added in an amount of plutonium comparable to that of Pu(IV). The plutonium and NaOH concentrations were measured at the beginning of each experiment. The NaOH concentrations of the added Pu(VI) solutions were varied between 1 and 10 M. The absorption spectrum of the initial Pu(VI) solutions showed a broad absorption band with a maximum at 620 to 630 nm characteristic of the stable Pu(VI) species in alkali.

The solutions were thoroughly stirred and heated to 40°C. Optical spectra were recorded hourly. A significant drop in absorption at 600 to 700 nm was observed with time. This decrease was ascribed to reaction of Pu(VI) with Pu(IV). Generally within three hours from the beginning of experiment, solution spectral changes ceased. The initially greenish-olive Pu(IV) hydrous oxide sediment became brown. For solutions with higher NaOH concentration, the supernatant solution acquired a flesh pink color characteristic of Pu(V) hydroxy anions. The solution EAS showed the "trident" of absorption bands at 500 to 560 nm and a band at 809 nm characteristic of Pu(V) in alkaline solution (Figure 3.4.1).

Upon completion of the process (cessation of changes in the EAS), the difference between the initial and final Pu(VI) concentration was determined spectrophotometrically. Then contents of the entire test, both liquid and solid phase, were acidified and the overall plutonium concentration in the run determined to check the material balance. The measurement results are summarized in Table 3.4.1.

By use of the measured Pu(VI) concentration, the apparent equilibrium constants for the reproportionation reaction (3.5).



1 - 15 minutes, 2 - 30 minutes, 3 - 120 minutes, 4 - 180 minutes

Figure 3.4.1. Electronic Absorption Spectra of Pu(VI) and Pu(IV) Reproportionation at 8 M NaOH and 40°C as a Function of Time

Table 3.4.1. Reproportionation of Pu(VI) and Pu(IV) in NaOH Solution at 40°C. Plutonium Material Balance Before and After Experiment[(a)]

[NaOH], M	Initial Total Pu, mmoles	Initial Pu(VI), mmoles	Initial Pu(IV), mmoles	Final Pu(VI), mmoles
1.00	0.0124	0.0070	0.0054	0.0070
4.00	0.0126	0.0072	0.0054	0.0058
5.65	0.0120	0.0066	0.0054	0.0055
6.60	0.0097	0.0043	0.0054	0.0025
8.02	0.0101	0.0047	0.0054	0.0027
10.00	0.0121	0.0067	0.0054	0.0034
(a) 3 mL total volume in all experiments.				

may be calculated, through Equation 3.6, by Equation 3.7

$$K_r^{app} = [Pu(V)]/([Pu(VI)] \cdot [Pu(IV)]) \tag{3.6}$$

$$K_r^{app} = 4([Pu(VI)]_{init.} - [Pu(VI)]_{equi.})^2/([Pu(VI)]_{equi.} \cdot ([Pu(IV)]_{init.} - [Pu(VI)]_{init.} + [Pu(VI)]_{equi.} \tag{3.7}$$

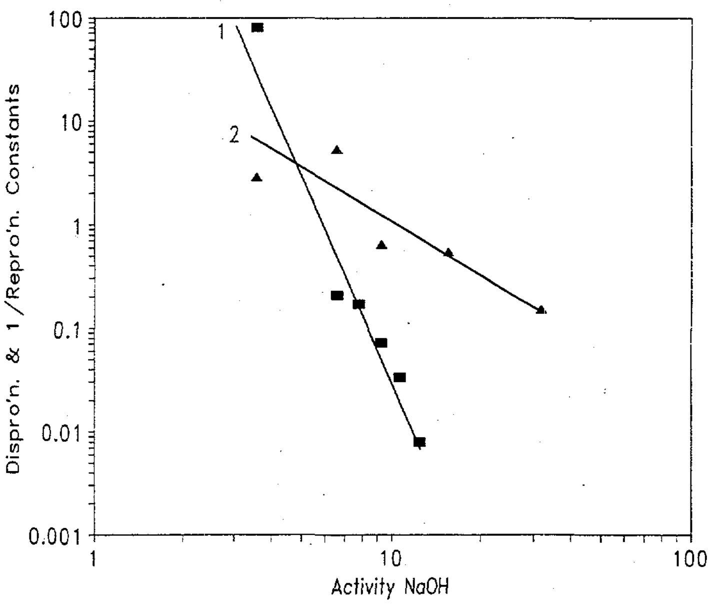
in terms of the indicated initial Pu(IV) and initial and equilibrium Pu(VI). Table 3.4.2 lists the apparent equilibrium constants for reproportionation and disproportionation as functions of NaOH concentration and chemical activity.

The disproportionation constants and the inverse reproportionation constants, plotted in log-log coordinates versus NaOH activity, give straight lines (Figure 3.4.2). Ideally, the equilibrium disproportionation constant (at a particular NaOH concentration and temperature) should be the mathematical reciprocal of the reproportionation constant. Though the experimental results of plutonium disproportionation and reproportionation in alkaline solutions are internally self consistent, the $1/K_r^{app}$ and K_d^{app} values differ appreciably.

This difference is a manifestation of complicated mechanisms in the heterogeneous processes involving Pu(IV) hydrous oxide, whose chemical properties depend not only on the conditions under which the reactions take place but also on the chemical nature of the species themselves. For example, in studying Pu(VI) and Pu(IV) reproportionation, it was found that no investigations of Pu(V) sorption on Pu(IV) hydrous oxide precipitate have been performed though evidence of such a mechanism was described in early research (Kraus and Dam 1949). Findings from the present research also demonstrate that the reactivity of Pu(IV) hydrous oxide depends on the manner of its preparation. Differences in Pu(IV) reactivity may partially explain the divergence between the present reproportionation equilibrium constants and the much lower values published by Bourges (1972). These issues are examined in Section 3.6.

Table 3.4.2. Equilibrium Constants of Pu(IV) and Pu(VI) Reproportionation and Pu(V) Disproportionation Versus NaOH Concentration at 40°C

[NaOH], M	K_r^{app}	$1/K_r^{app}$	K_d^{app}	log a_{NaOH}	$\log(1/K_r^{app})$
1.00	--	--	--	--	--
4.00	0.35	2.9	80	0.55	-0.46
5.65	0.19	5.3	0.21	0.82	-0.72
6.60	1.54	0.65	0.072	0.97	0.19
8.02	1.80	0.55	0.00010	1.19	0.26
10.00	6.41	0.15	--	1.50	0.82



1 - Disproportionation, 2 - Reciprocal Reproportionation

Figure 3.4.2. Disproportionation and Reciprocal Reproportionation Constants at 40°C as Functions of NaOH Chemical Activity

3.5 Determination of the Pu(V)/Pu(IV) Reduction Potential

The disproportionation and reproportionation data may be used to calculate the potential of the Pu(V)/Pu(IV) electrode pair. However, the apparent equilibrium constants K_d^{app} and K_r^{app} cannot formally be used to assess the thermodynamic characteristics of the disproportionation and reproportionation processes because they include terms for the Pu(IV) solid phase.

To calculate the actual equilibrium constants, one should know the concentrations of all the valence forms of plutonium in solution. In this case, the Pu(IV) concentration is merely the solubility of Pu(IV) hydrous oxide (S) at the given temperature and alkali concentration. Data on Pu(IV) hydrous oxide solubility at 26°C are published (Peretrukhin et al. 1996). Unfortunately, the temperature dependence of solubility has not been studied. With the assumption that the heat of solution for Pu(IV) hydrous oxide is negligible compared to the heat of the reaction 2 Pu(V) → Pu(VI) + Pu(IV), thermodynamic equilibrium constants and the potential of the Pu(V)/Pu(IV) pair at 40°C can be calculated.

The formal equilibrium constant for disproportionation, K_f, was calculated by the equation

$$K_f = [\mathrm{Pu(VI)}]\cdot S/[\mathrm{Pu(V)}]^2 \qquad (3.8)$$

where [Pu(VI)] and [Pu(V)] are the Pu(VI) and Pu(V) concentrations determined from spectrophotometric measurements and S is the solubility of Pu(IV) hydroxide at 26°C (Peretrukhin et al. 1996).

The reaction free energy, G (= -RT $\ln K_f$), is related to the electrode potential

$$G = -RT \ln K_f = -nFE_f \tag{3.9}$$

where n is the reaction's electron change (one in this case), F is the Faraday constant, R is the gas constant, T the absolute temperature, and E_f the potential change (in volts). Thus,

$$E_f = 0.000198\ T \log K_f \tag{3.10}$$

The disproportionation reaction may be expressed as the sum of the respective oxidation and reduction half reactions for Pu(V)

$$\mathrm{Pu(V)} \rightarrow \mathrm{Pu(VI)} + e^-;\ E_{V/VI} \tag{3.11}$$

and

$$\mathrm{Pu(V)} + e^- \rightarrow \mathrm{Pu(IV)};\ E_{V/IV} \tag{3.12}$$

to give

$$2\ \mathrm{Pu(V)} \rightarrow \mathrm{Pu(IV)} + \mathrm{Pu(VI)};\ E_f = E_{V/VI} + E_{V/IV} \tag{3.13}$$

Because the $E_{VI/V}$ potential (which is the negative of $E_{V/VI}$) has been measured in previous research (Bourges 1972; Shilov 1976) and E_f can be determined by Equation (3.14), the $E_{V/IV}$ potential is E_f - $E_{V/VI}$ or $E_f + E_{VI/V}$. The calculated results for disproportionation and similarly computed reproportionation data are listed in Table 3.5.1.

The calculated Pu(V) reduction potentials, $E_{V/IV}$, given in Table 3.5.1, are lower than the $E_{VI/V}$ potentials and indicate that Pu(V) should not disproportionate in the range 4 to 8 M NaOH. This clearly contradicts the experimental observations at lower NaOH concentrations.

It may be that Pu(IV) hydrous oxide has a higher chemical activity under the experimental conditions in reactions with Pu(VI) and Pu(V). Also, the actual Pu(IV) concentration (which determines the equilibrium) may be much greater than the solubility of Pu(IV) hydrous oxide exhibited in pure alkaline

Table 3.5.1. Calculation of Thermodynamic Equilibrium Constants of Plutonium Disproportionation/ Reproportionation at 40°C and the Formal Potential of the Pu(V)/Pu(IV) Pair

From Disproportionation Data							
[NaOH], M	[Pu(VI)], M	[Pu(V)], M	[Pu(IV)][(a)] = S, M	K_f	E_f, V	$E_{VI/V}$,[(b)] V	$E_{V/IV}$, V
4.00	6.0×10^{-3}	2.7×10^{-4}	5.8×10^{-7}	4.77×10^{-2}	-0.082	0.22	0.14
6.60	1.2×10^{-3}	9.3×10^{-4}	2.8×10^{-6}	3.88×10^{-3}	-0.149	0.215	0.07
8.02	6.7×10^{-5}	2.4×10^{-3}	3.4×10^{-6}	3.95×10^{-5}	-0.273	0.21	-0.06
From Reproportionation Data							
[NaOH], M	[Pu(VI)], M	[Pu(V)], M	[Pu(IV)][(a)] = S, M	K_f	E_f, V	$E_{VI/V}$,[(b)] V	$E_{V/IV}$, V
4.00	1.9×10^{-3}	9.3×10^{-4}	5.8×10^{-7}	1.27×10^{-3}	-0.179	0.22	0.04
6.60	8.3×10^{-4}	1.2×10^{-3}	2.8×10^{-6}	1.61×10^{-3}	-0.173	0.215	0.04
8.02	9.0×10^{-4}	1.3×10^{-3}	3.4×10^{-6}	1.81×10^{-3}	-0.170	0.21	0.04
(a) Peretrukhin et al. 1996. (b) Bourges 1972; Shilov 1976.							

solutions. Therefore, the formal thermodynamic values, K_f, based on expected Pu(IV) solution concentration may not reflect the true reaction occurring in this system, which includes the participation of the various dissolved plutonium valence forms and a plutonium solid phase.

It is noted that at greater than 8 M NaOH, disproportionation does not occur and reproportionation goes almost to completion. Thus, at 8 M NaOH, the potential of the Pu(VI)/Pu(V) couple must be greater than that of the Pu(V)/Pu(IV) couple and K_f must be less than one. To account for the high chemical activity of Pu(IV) hydrous oxide, a plausible estimate of K_f is K_d^{app}, the apparent equilibrium constant for disproportionation. Thus, $E_{V/IV}$ may be estimated using K_d^{app} values (calculated in Section 3.3, presented in Table 3.3.3) in place of K_f. The $E_{V/IV}$ potential thus will reflect the half-reaction to form freshly precipitated Pu(IV) hydrous oxide

$$\mathrm{Pu(V)} + e^- \rightarrow \mathrm{PuO_2 \cdot xH_2O(s)} \tag{3.14}$$

rather than dissolved Pu(IV).

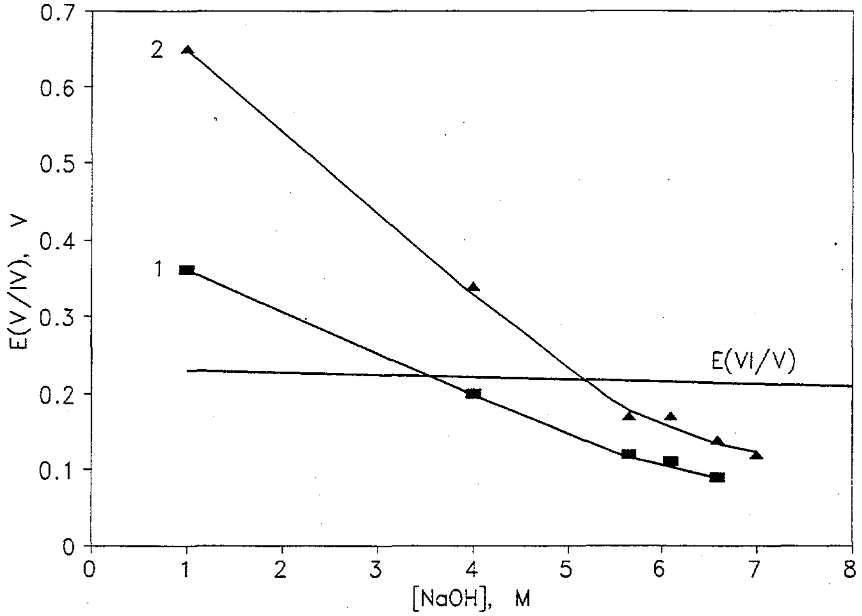
These data, summarized in Table 3.5.2, adequately describe the experimentally observed results. Figure 3.5.1, depicting the dependence of the electrode potentials on NaOH concentration show the Pu(V)/Pu(IV)O_2 potential becomes lower than the Pu(VI)/Pu(V) pair around 4 to 6 M NaOH.

The $E_{V/IV}$ results given in Table 3.5.2, derived from disproportionation experiments, strongly contrast with determinations of the same Pu(V)/Pu(IV) potential measured polarographically by a

Table 3.5.2. $E_{V/IV}$ as a Function of NaOH Concentration

T, °C	[NaOH], M	a_{NaOH}, m	$K_d^{app} = K_f$	E_f, V	$E_{VI/V}$,(a) V	$E_{V/IV}$, V
20	1.00	0.67	210(b)	0.135	0.23	0.36
	4.00	3.52	0.37	-0.025	0.22	0.20
	5.65	7.06	0.024	-0.094	0.215	0.12
	6.10	8.11	0.015	-0.106	0.215	0.11
	6.60	9.88	0.0069	-0.125	0.215	0.09
40	1.00	0.68	6.2 x 10^{6}(b)	0.421	0.23	0.65
	4.00	3.58	80	0.118	0.22	0.34
	5.65	6.55	0.21	-0.042	0.215	0.17
	6.10	7.75	0.17	-0.048	0.215	0.17
	6.60	9.24	0.072	-0.071	0.215	0.14
	7.00	10.64	0.033	-0.092	0.21	0.12

(a) Bourges 1972; Shilov 1976.
(b) Extrapolated values derived from Figure 3.3.2.



1 - 20°C, 2 - 40°C

Figure 3.5.1. Pu(V)/Pu(IV)O_2 Potential as a Function of NaOH Concentration

dropping mercury electrode (Peretrukhin and Alekseeva 1974). The polarographic potentials, ranging from -0.61 to -1.03 volts as NaOH concentration increased from 0.1 to 14.1 M, would preclude disproportionation at all NaOH concentrations.

The polarographic findings must be in error given the observed rapid disproportionation of Pu(V) occurring below 8 M NaOH. The polarographic study also contains some errors of technique and interpretation. Under conditions specified in the published study, reduction waves starting at potentials below -0.85 V were observed. The observed reduction wave showed a 100-mV slope, too steep to be a reversible process (59 mV). The effect of Pu(VI) concentration on polarographic waves also was not investigated. The authors stated that because of its low solubility, Pu(V) is partially removed from the "cathode reduction sphere." However, the present data show Pu(V) solubility to be several orders of magnitude higher than the concentrations used in the published study.

The polarographic study attributes the decrease in the wave amplitude with increasing NaOH concentration to diffusion of Pu(III) outward in the solution where it reacts with Pu(VI). Such diffusion would be plausible if the electrode were in a steady state. However, the dropping mercury electrode serves precisely to preclude the diffusion effects. The conclusion drawn in the polarographic study is that, if the observed reduction waves involve plutonium, Pu(V) starts being reduced at potentials near -1 V. However this potential likely is far below the actual value of the formal potential of the irreversible Pu((V)/Pu(IV) pair in alkali. This situation is similar to measurements of the potential of the H^+/H_2 pair in acid solution (E_f of 0.0 V). Actual measured potentials can be lower than -1.0 V in 0.1 to 1 M HCl or $HClO_4$ because of the irreversibility of the reaction and overpotential effects.

3.6 Trapping of Pu(V) and Np(V) from Alkaline Solution by Pu(IV) Hydrous Oxide

The results obtained in the disproportionation and reproportionation experiments indicate that a number of side processes occur. Thus, the multicomponent heterogeneous dis-/reproportionation system has a composition that varies with time in a complicated manner.

For a system initially containing only Pu(V) and NaOH, the following processes may theoretically occur:

disproportionation itself

$$2\ \mathrm{Pu(V)} \rightarrow \mathrm{Pu(IV)} + \mathrm{Pu(VI)} \tag{3.15}$$

reduction of Pu(VI) by water α-radiolysis products

$$\mathrm{Pu(VI)} \rightarrow \mathrm{Pu(V)} \tag{3.16}$$

reproportionation

$$Pu(IV) + Pu(VI) \rightarrow 2\ Pu(V) \tag{3.17}$$

and oxidation of Pu(V) by dissolved oxygen

$$2\ Pu(V) + O_2 \rightarrow 2\ Pu(VI) \tag{3.18}$$

In addition, precipitated Pu(IV) hydrous oxide can sorb dissolved plutonium in other valence forms. The quantity and further reactions of the trapped plutonium depend on the precipitation mechanism. It is quite likely that eventually, as the precipitate is aged, part of the trapped plutonium (V) and (VI) will migrate back to the solution and enter into reactions (3.15) to (3.18). Whether the trapped Pu(V) is capable of disproportionating in the solid phase is also unclear. Assuming that Pu(V) is coprecipitated with solid Pu(IV) hydrous oxide at a higher rate than is Pu(VI), the rate of Pu(V) removal from alkaline solutions by Pu(IV) hydrous oxide formed in the course of disproportionation can be determined.

The sorption of Pu(V) on Pu(IV) hydrous oxide was tested experimentally. Plutonium(IV) hydrous oxide was precipitated by adding 6 M NaOH to a solution of Pu(IV) in 2 M $(NH_4)_2CO_3$; the precipitate was washed with 6 M NaOH. Plutonium(V) in 6 M NaOH was prepared by dissolving $NH_4PuO_2CO_3$ in alkali; the Pu(V) concentration was measured spectrophotometrically. This solution of Pu(V) was introduced to the Pu(IV) precipitate and the reaction mixture stirred at 50°C. Periodically, an aliquot of suspension was centrifuged and the solution spectrum was recorded. The initial molar quantities of Pu(IV) solids and dissolved Pu(V) were approximately equal. The initial bright green Pu(IV) color changed to khaki 1 to 2 minutes after addition of alkaline Pu(V) solution. The only change in the spectrum of mother liquor reflected a greater than 50% decrease in Pu(V) concentration after about 5 minutes' stirring. No further change in the spectrum was observed with 2 hours' more stirring.

To investigate sorption of pentavalent actinides onto Pu(IV) hydrous oxide, further tests were performed with neptunium(V) as a chemical analogue to plutonium(V). Experiments were conducted with a model system involving ^{237}Np(V) with a ^{239}Np tracer to imitate Pu(V). The ^{239}Np tracer permitted lower concentrations to be used and precluded precipitation of a separate neptunium solid phase.

Experiments were conducted by mixing selected amounts of a Pu(VI) solution of a known concentration, NaOH, and the mixed ^{239}Np tracer with ^{237}Np carrier. The dependence of the ^{239}Np β counting rate on NaOH concentration (because of solute absorption on planchet mounts) was determined in preliminary experiments. In addition, the activity of the ^{239}Np solution was measured daily prior to experiments; corrections for decay were required and incorporated in the measurements.

Initial solutions, 10 mL in volume, were poured into polyethylene test tubes, heated for 15 minutes at a selected temperature in a thermostat, and then an amount of hydroxylamine necessary for Pu(VI) reduction was added to the continuously stirred solution. Neptunium(V) is not reduced under these conditions (Shilov et al. 1996). At selected intervals, the test tubes were cooled, centrifuged, and 0.1 mL of the clarified solution was sampled for further analysis. The test tubes were returned to the thermostat for continued reaction with stirring.

The amount of neptunium sorbed at a given reaction time was estimated by the ratio of β activity of a solution sample taken after reaction and the activity of the initial solution. Temperature, NaOH concentration, and Np(V)/Pu(VI) concentration ratios in the original solution were varied. Table 3.6.1 lists the quantitative characteristics of Np(V) sorption on precipitated Pu(IV) hydrous oxide for experiments with equal initial Np(V) and Pu(VI) concentrations.

Selected results are displayed in Table 3.6.2 and Figure 3.6.1 as partition coefficients, K_c. The partition coefficients vary as a function of the NaOH concentration and are defined

$$K_c = [Np(V)_c]/[Np(V)_s] \tag{3.19}$$

where $[Np(V)_c]$ and $[Np(V)_s]$ are the neptunium concentrations in the residue and solution, respectively. The partition coefficient diminishes as the NaOH concentration increases. One reason for this decrease is decrease in the velocity of particle motion as NaOH concentration and solution viscosity increases. Because the mass of sorbent varies with time, measurements of K_c are recorded at specified times.

Table 3.6.1. Dependence of Np(V) Sorption by Pu(IV) Precipitates on Time, Temperature, and NaOH Concentration, [Np(V)] = [Pu(VI)] = 2 x 10^{-5} M

		Np(V) Remaining in Solution, %						
T, °C	[NaOH], M	2 Min.	5 Min.	10 Min.	20 Min.	30 Min.	60 Min.	120 Min.
40	2	100	100	97	91	86	78	70
	4	100	100	100	96	88	84	77
	6	100	100	100	97	91	89	84
	8	100	100	100	98	96	91	88
60	2	97	94	90	83	76	60	54
	4	98	96	92	87	82	67	57
	6	100	98	94	90	85	72	60
	8	100	100	97	93	90	78	66
80	2	96	93	89	83	76	60	47
	4	98	96	92	87	82	66	53
	6	100	98	94	90	85	71	60
	8	100	100	97	93	90	78	66

Table 3.6.2. Np(V) Partition Coefficient Between Solution and Precipitating Pu(IV) Hydrous Oxide at 60°C, 120 Minutes, as a Function of NaOH Concentration

[NaOH], M	[Np_s], Solution, M	[Np_c], in Solids, M	K_c	log K_c
2	1.15×10^{-5}	9.28×10^{-6}	0.807	-0.093
4	1.09×10^{-5}	8.44×10^{-6}	0.774	-0.111
6	1.21×10^{-5}	8.10×10^{-6}	0.669	-0.175
8	1.32×10^{-5}	6.96×10^{-6}	0.527	-0.278

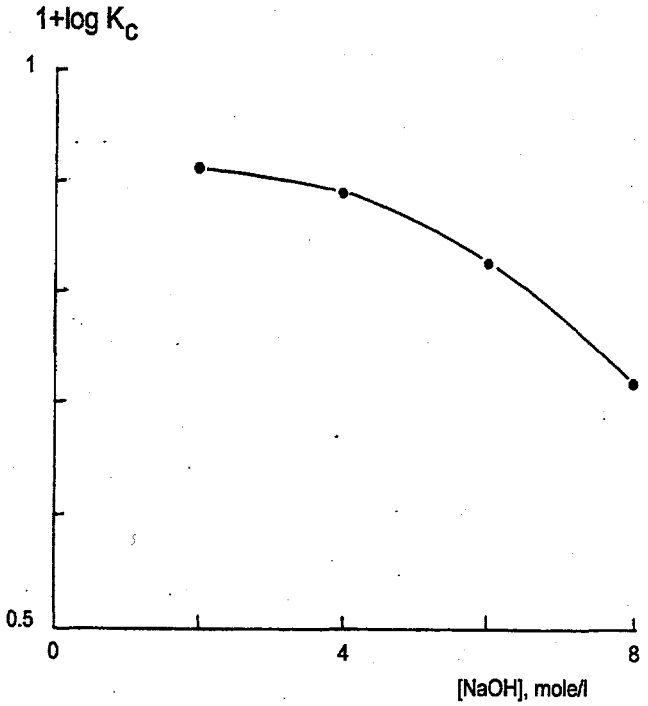


Figure 3.6.1. Neptunium(V) Partition Coefficient on Pu(IV) Hydrous Oxide as a Function of NaOH Concentration

The amount of constituent trapped in a system of coprecipitating components can be characterized satisfactorily provided the constituent is present in microscopic concentration and the other in macroscopic concentrations. In this case, however, the microscopic concentrations of both components are similar. Therefore, for some experiments, the plutonium solution concentrations were measured to gain additional information.

The experimental results indicate that precipitating Pu(IV) hydrous oxide entrains a significant amount of Np(V). Formation of a mixed neptunium-plutonium compound is unlikely, although the possibility of isomorphic coprecipitation in amorphous systems has been considered (Lavrukhina 1957). The mechanism of trapping may be the following. First, as Pu(V) is reduced, the amount in solution decreases while the amount of solid phase Pu(IV) increases. Because the system is not stirred, and Pu(VI) is reduced at a slow rate (Shilov et al. 1996), the solid phase is formed as thin Pu(IV) hydrous oxide layers. Neptunium(V) is sorbed on each fresh layer. Then the next Pu(IV) layer is produced and the process is repeated. As is well known, chemisorbed species only reach monolayer thickness. The chemisorption rate increases with temperature, as corroborated by these experiments.

Neptunium(V) partition between the solution and the solid Pu(IV) hydrous oxide phase by the proposed layer-by-layer mechanism must obey the Doerner-Hoskins adsorption law (Mikheev 1976) described by the formula:

$$\log[(x_0 - x)/x_0] = P \log[(y_0 - y)/y_0] \tag{3.20}$$

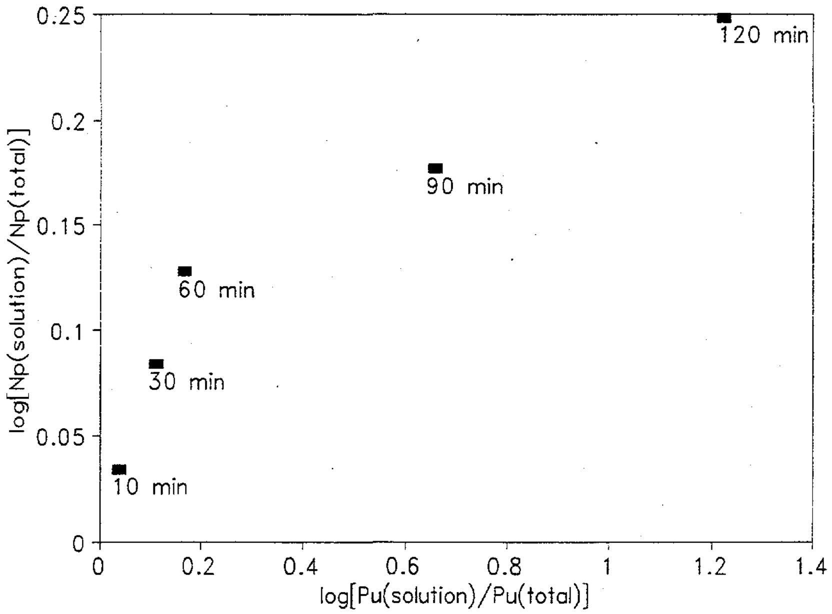
where x and x_0 are the amounts of Np(V) in the precipitate and in the whole system, respectively, and y and y_0 are the comparable figures for plutonium. The differences, x_0-x and y_0-y, represent the amounts of neptunium and plutonium in solution. The parameter P is a function of many variables. In this case there is no necessity to discuss their meaning. The Doerner-Hoskins terms for neptunium and plutonium are given in Table 3.6.3. It has been shown (Gordon 1955; Cohen and Gordon 1960) that Equation 3.21 is applicable to homogeneous coprecipitation (i.e., the method of appearing reagents, Krot et al. 1996).

Table 3.6.3. Np(V) Coprecipitation Characteristics with Pu(IV) Hydrous Oxide, (40°C, 4 M NaOH, 2 x 10^{-5} M Np(V), [Np(V)]:[Pu(VI)] = 1:1)

Time, Min.	[Np], M	[Pu], M	log[(Np$_0$-Np)/ Np$_0$]	log[(Pu$_0$-Pu)/ Pu$_0$]	P
10	1.85 x 10^{-5}	1.83 x 10^{-5}	-0.034	-0.039	0.88
30	1.65 x 10^{-5}	1.55 x 10^{-5}	-0.084	-0.111	0.75
60	1.49 x 10^{-5}	1.36 x 10^{-5}	-0.129	-0.167	0.76
90	1.33 x 10^{-5}	0.44 x 10^{-5}	-0.177	-0.658	0.27
120	1.13 x 10^{-5}	0.12 x 10^{-5}	-0.248	-1.222	0.20

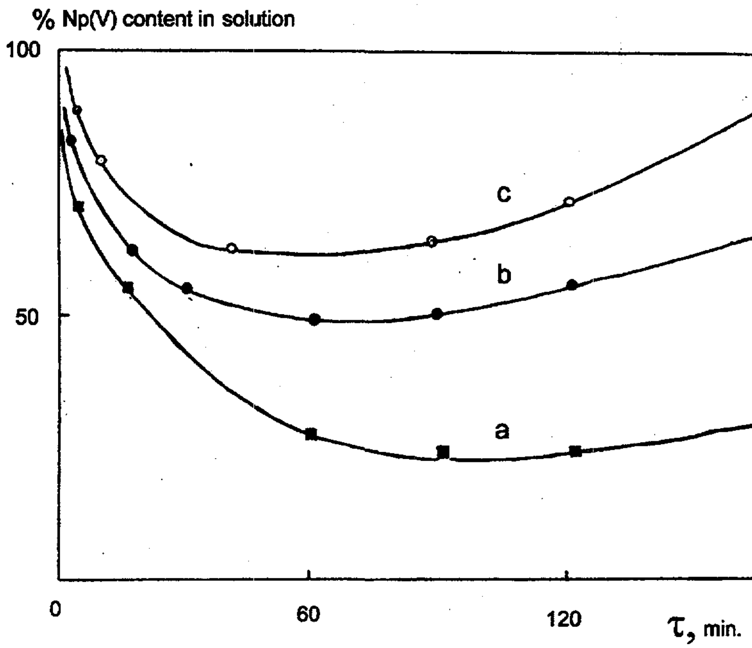
The trapping process is satisfactorily depicted by a straight line at exposure times below about 60 minutes, consistent with the surface adsorption mechanism (Figure 3.6.2). The affinity of the Np(V) for Pu(IV) solids is so high that the concentration of sorbed Np(V) becomes evenly distributed over the Pu(IV) solids surface. Under certain conditions, purely physical Np(V) trapping may also occur. Indeed, at initial [Np(V)]:[Pu(VI)] ratios exceeding unity, the amount of coprecipitated Np(V) shows a minimum with time. After additional contact time, the Np(V) content in the solution increases, perhaps because the solid phase becomes more ordered and Np(V) is excluded (Figure 3.6.3).

These results suggest that quantitative studies of Pu(V) disproportionation can be significantly complicated by adsorption of Pu(V) on the Pu(IV) hydrous oxide precipitate. However, if the experimental time does not exceed about 30 minutes, the expected error in the plutonium material balance is limited to about 20%.



(4 M NaOH; 40°C)

Figure 3.6.2. Coprecipitation Isotherm for Np(V) with Pu(IV) Hydrous Oxide



a - Np(V):Pu(VI) = 1:1, b - Np(V):Pu(VI) = 1:10, c - Np(V):Pu(VI) = 1:20

Figure 3.6.3. Neptunium(V) Capture on Precipitating Pu(IV) Hydrous Oxide as Functions of Time and Np(V):Pu(VI) Ratio

3.7 Pu(V) Behavior in Model Salt Solutions

The behavior of solid Pu(V) carbonate in alkaline solutions of complex composition was studied. The tested solutions contained a number of components characteristic of Hanford Site tank waste (Delegard 1987). The compositions of the model waste mixtures are summarized in Table 3.7.1.

Experiments were performed by adding 4 mL of the model waste brine (Table 3.7.1), containing either 2 or 4 M NaOH, to freshly precipitated $NH_4PuO_2CO_3$ solids. The solids had been washed and slightly dried in air. The resulting suspension (about 3.5×10^{-3} M in total Pu) was placed in a cell maintained at a constant temperature and equipped with a magnetic stirrer. At selected contact times, the cell contents were transferred to a centrifuge test tube, rapidly cooled, centrifuged, and the solution absorption spectrum recorded.

At 50°C and 4 M NaOH, the solid Pu(V) carbonate salt dissolved completely in 5 to 7 minutes, producing a flesh pink transparent solution whose spectrum showed Pu(V) absorption bands. The solution was heated further and the spectra were recorded after one and three hours. No changes in the spectra

Table 3.7.1. Composition of the Model Waste Salt Solution

Waste Component	Concentration, M
$NaNO_3$	2
$NaNO_2$	2
$NaAl(OH)_4$	0.5
Na_2CO_3	0.05
Na_2SO_4	0.01
NaF	0.01
Na_3HEDTA	0.1
Na_4EDTA	0.03
Na_3 Citrate	0.03
Na Glycolate	0.1
Na Acetate	0.1
NaOH	1.9 - 7.9

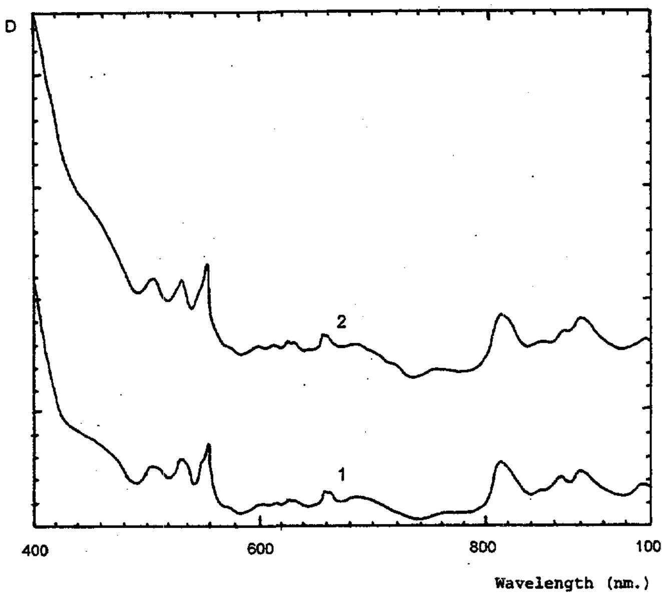
were detected. Subsequent storage of the solution for 24 hours at room temperature also did not change the EAS (Figure 3.7.1). Under otherwise similar conditions, the behavior of Pu(V) carbonate salt in pure 4 M NaOH was studied. Within 30 seconds' contact, the carbonate solids became olive colored and the solution green. The EAS of this solution was that of Pu(VI) (Figure 3.7.2).

The Pu(V) carbonate salt also dissolved easily in the 2 M NaOH model waste salt solution. However, heating the solution at 50°C for one hour produced an olive residue. The mother liquor spectrum exhibited a band with maximum at 870 nm indicating Pu(VI). The intensity of this band decreased slightly as the suspension was heated further.

Plutonium solubility is enhanced in the model waste mixture. Presumably, complexation and shift of the disproportionation reaction,

$$2\ \mathrm{Pu(V)} \rightleftarrows \mathrm{Pu(IV)} + \mathrm{Pu(VI)} \tag{3.21}$$

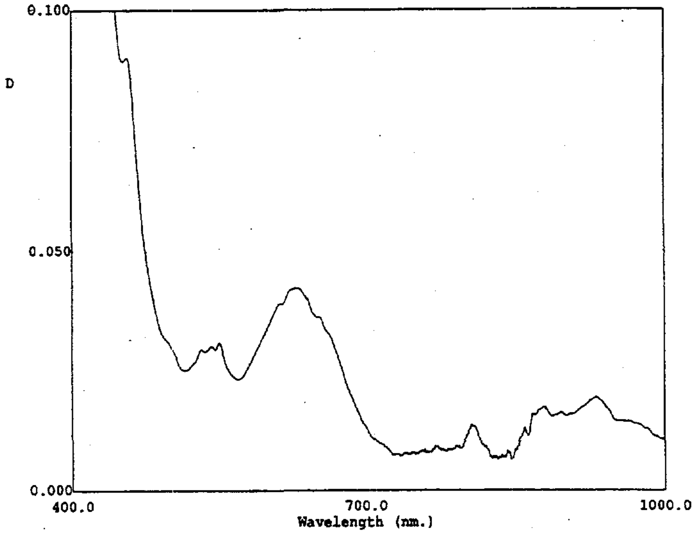
to the left occurs in the presence of the additional salts.



(4 M NaOH; 50°C)

1 - 3 hours, 2 - 24 hours

Figure 3.7.1. Electronic Absorption Spectra of $NH_4PuO_2CO_3$ Dissolved in Model Hanford Site Waste Solution as a Function of Time



(50°C)

Figure 3.7.2. Electronic Absorption Spectrum of $NH_4PuO_2CO_3$ Dissolved in 4 M NaOH

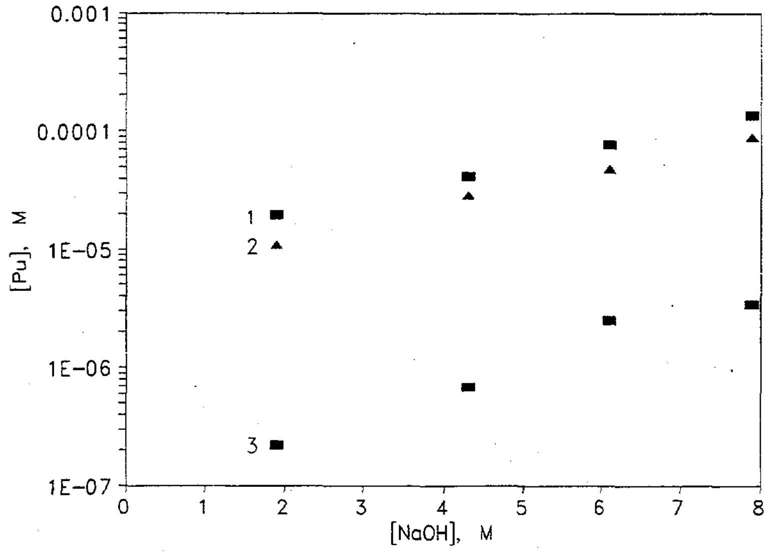
Experiments were conducted to assess Pu(IV) hydrous oxide solubility in model salt solutions containing various NaOH concentrations. Freshly precipitated Pu(IV) solids and Pu(IV) solids aged for 1.5 months under a pure NaOH solution of the appropriate concentration were prepared for these tests. The respective Pu(IV) solids were covered with 3 mL of model waste solution and stirred at a thermostatted 50°C temperature. Based on previous data (Peretrukhin et al. 1996), it was assumed that a steady Pu(IV) supernatant concentration would be attained in three hours. Therefore, after three hours, the cell contents were cooled, centrifuged, and the solution concentrations determined. Supernate portions were taken, acidified to 0.5 M HNO_3, and counted by liquid scintillation. Results are given in Table 3.7.2.

In all cases, the plutonium concentration increases with increasing NaOH concentration. The solubility of aged Pu(IV) hydrous oxide is slightly lower than that of the freshly precipitated material (Figure 3.7.3). This aging effect agrees with earlier findings in alkaline media (Delegard 1987) as well as results under more acidic conditions (Rai and Ryan 1982). The data listed in Table 3.7.2 show the solubility of Pu(IV) hydrous oxide in the simulant waste solution to be at least an order of magnitude higher than in pure NaOH of the same NaOH concentration but containing hydrazine reductant to prevent Pu(IV) oxidation (Peretrukhin et al. 1996). The higher solubility is explained by the enhanced stability of Pu(V) under aerated and complexing conditions as observed in this work and in earlier studies (Delegard 1987).

Table 3.7.2. Plutonium Concentration Over Fresh and Aged Pu(IV) Solids Held at 50°C for 3 Hours in Simulant Waste Brine

	Fresh Pu(IV) Solids		Aged Pu(IV) Solids		Pu(IV) Solids at 26°C in Pure NaOH Solution(a)
[NaOH], M	[Pu], M	log [Pu]	[Pu], M	log [Pu]	[Pu], M
1.9	1.95×10^{-5}	-4.71	1.10×10^{-5}	-4.95	2.2×10^{-7}
4.3	4.19×10^{-5}	-4.37	2.89×10^{-5}	-4.54	6.9×10^{-7}
6.1	7.71×10^{-5}	-4.11	4.82×10^{-5}	-4.32	2.5×10^{-6}
7.9	13.3×10^{-5}	-3.87	8.92×10^{-5}	-4.05	3.4×10^{-6}

(a) Solution also contained 0.1 M N_2H_4 reductant (Peretrukhin et al. 1996).



1 - Freshly Prepared Pu(IV) Hydrous Oxide in Model Waste,
2 - Pu(IV) Hydrous Oxide, Aged 45 Days in NaOH Solution, in Model Waste,
3 - Freshly Prepared Pu(IV) Hydrous Oxide in Pure NaOH Solution

Figure 3.7.3. Solubility of Pu(IV) Hydrous Oxide in Model Hanford Site Waste and Pure NaOH Solution as Functions of Solids Aging and NaOH Concentration

The stabilities of Pu(VI) in NaOH solutions of each of the model brine components and in the full model brine itself were determined. Plutonium(VI) was reduced at an appreciable rate (a few percent per hour in 50°C 4 M NaOH) only in the presence of HEDTA. Other components, with NaOH, had no strong effect on Pu(VI) stability. Interestingly, a further addition of $NaNO_2$ (to 2 M) accelerated reduction in the HEDTA solution. With the additional $NaNO_2$, Pu(VI) was almost completely reduced to Pu(V) within 1.5 to 3 hours. Plutonium(VI) in the full model brine also was reduced within 3 hours.

3.8 Solubility of Hydroxide Compounds of Pu(V) in NaOH Solutions

Experiments showed that addition of NaOH solutions to solid $NH_4PuO_2CO_3$ causes recrystallization of the starting salt within a few minutes. A hydroxide compound of Pu(V) is formed, accompanied a change in the sediment color from grayish-white to pink. No reflections characteristic of the initial compound are detected in the X-ray diffraction patterns of the product formed by reaction between the double Pu(V) carbonate salt and the alkaline solutions. Electronic absorption spectra of saturated solutions of the product Pu(V) hydroxide compounds show Pu(V) hydroxy anion absorption bands.

The solubility of the Pu(V) hydroxide compound $Na_2PuO_2(OH)_3 \cdot xH_2O$ reportedly increased from 5×10^{-5} to 3.6×10^{-4} M as NaOH concentration increased from 0.6 to 14 M (Peretrukhin et al. 1996). These values differ from solubilities of analogous Np(V) and Am(V) salts at NaOH concentrations below about 6 M but were comparable at higher NaOH concentrations.

In the light of experimental data obtained in the present work, knowledge of the stability of Pu(V) in alkaline solution alters appreciably. Thus it appears that the material alleged to be $Na_2PuO_2(OH)_3 \cdot xH_2O$ in the earlier solubility study (Peretrukhin et al. 1996) was at least a mixture of Pu(IV) hydrous oxide and sorbed Pu(V). In the earlier work, X-ray diffraction was used to identify $Na_2PuO_2(OH)_3 \cdot xH_2O$ as the solid phase. This compound was prepared at 6 M NaOH with the assumption that Pu(V) was stable at this concentration.

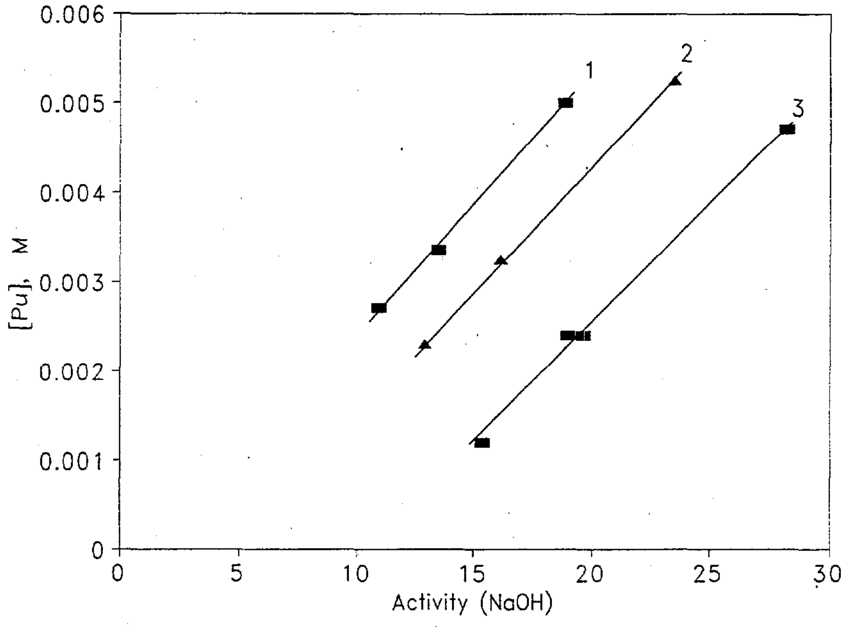
In fact, at 6 M NaOH, 50 to 60% Pu(V) disproportionation occurs. The starting material thus contained a mixture of Pu valence states and caused mistaken assignment of the observed absorption bands in the electronic spectra solely to Pu(V) (Peretrukhin et al. 1996). The present data confirm the earlier measured spectrum of Pu(V) though the extinction coefficients are somewhat lower than the 10 to 15 L/(mol·cm) reported for prominent peaks (500, 530, 550, 810, and 875 nm) in 15 M NaOH (Delegard 1987).

The solubility of the plutonium(V) hydroxide compound produced by recrystallization of $NH_4PuO_2CO_3$ was measured over a narrow and high NaOH concentration range (7.5 to 10 M) to avoid disproportionation at lower NaOH concentrations. The solubility of the product Pu(V) hydroxide compound increases with NaOH concentration, and, under the conditions of these particular experiments, the Pu(V) is slowly oxidized to Pu(VI). These data are consistent with earlier results (Tananaev and Mironov 1991).

The relatively high solubility of the Pu(V) hydroxide compound (Figure 3.8.1), compared with Np(V) and Am(V) compounds precipitated in strong NaOH solution, may indicate that, at high alkali concentrations, Pu(V) forms $M_3AnO_2(OH)_4$ with a much greater yield than do Np(V) and Am(V) by the reaction

$$Na_2PuO_2(OH)_3 + NaOH \rightarrow Na_3PuO_2(OH)_4 \tag{3.22}$$

The high solubility of the product may be due to its peculiar structure. In analogy with An(VII) salts (containing discrete $[AnO_4(OH)_2]^{3-}$ ions [Tomilin et al. 1981]), the $M_3PuO_2(OH)_4$ structure may be island-like. That is, the crystalline compounds do not have An-O-An bonding. Compounds of this type generally have relatively high solubility.



1 - 50°C, 2 - 30°C, 3 - 12°C

Figure 3.8.1. Solubility of Pu(V) Salts as a Function of Temperature and NaOH Chemical Activity

3.9 Long-Term Stability of Crystalline Pu(V) Compounds Stored in Alkaline Solution

The behavior of solid ammonium Pu(V) carbonate stored under NaOH solutions of various concentrations was studied. The storage time at room temperature with no stirring was 60 days.

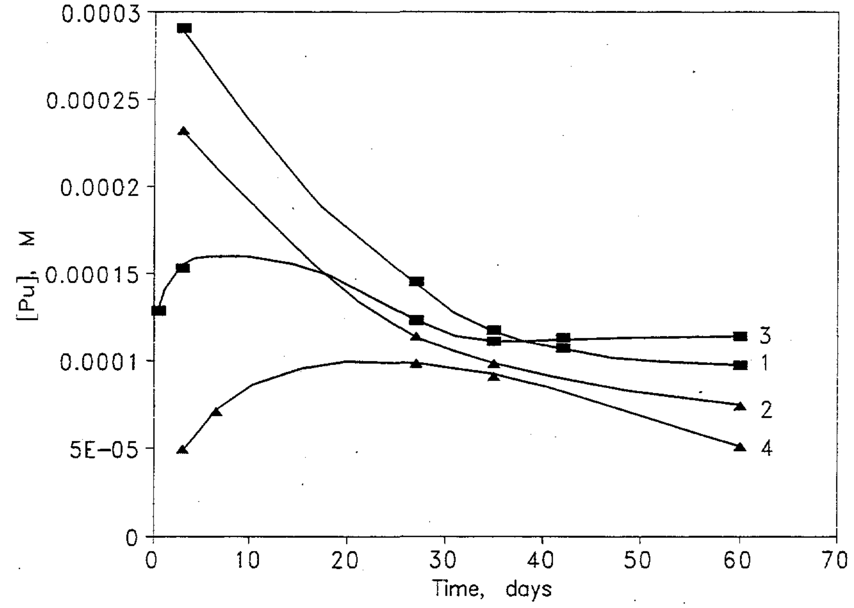
Equal amounts of the salt $NH_4PuO_2CO_3 \cdot xH_2O$ were synthesized in four stoppered polyethylene test tubes. The solids were washed with a 0.01 M $(NH_4)_2CO_3$ and separated by centrifugation, and 5 mL of NaOH solution (1, 2, 4, and 6 M) were added to give 5×10^{-3} M total Pu. Experiment timing began from the time of NaOH addition. At selected times, the suspensions were centrifuged, the supernatant solutions poured into plastic 1-cm path length spectrophotometer cells, and the absorption spectra recorded. The solutions were returned to the test tubes and left for the next storage period. Because poorly wetted plastic cuvettes were used, solution losses in these manipulations were small.

It was supposed that as $NH_4PuO_2CO_3 \cdot xH_2O$ dissolved Pu(V) would disproportionate and Pu(VI) concentration increase in the alkaline supernatant. In these unstirred experiments, the slow reaction step could have been plutonium diffusion toward the solid/liquid interface. Because the primary purpose was merely to study the qualitative characteristics of the slow process, the Pu(VI) concentration increase was monitored by measuring the increase in the optical absorption at 350 to 370 nm (rather than at 630 nm where the extinction coefficient is very low).

The behavior of solid $NH_4PuO_2CO_3 \cdot xH_2O$ changed dramatically with NaOH concentration. When in contact with 1 M NaOH, the solids immediately acquired a characteristic olive color, and the supernatant liquid became greenish. In 2 and 4 M NaOH, a similar effect was observed in 2 and 18 hours, respectively. The optical density of the solutions at 350 nm rose; the EAS also showed weak Pu(V) spectral features in the initial stages.

In 6 M NaOH, the residue retained its original color for a few hours and then became pink; the pink color changed to olive in six days. The solution remained virtually colorless.

Curves illustrating changes in Pu(VI) solution concentration with time are given in Figure 3.9.1. It is likely that various processes proceed simultaneously for solid $NH_4PuO_2CO_3 \cdot xH_2O$ stored in NaOH solution. First, Pu(V) dissolves in alkali, its solubility increasing with NaOH concentration. Concurrently, Pu(V) disproportionates to a decreasing extent with increasing NaOH concentration. Some part of the Pu(V) is entrained or adsorbed by the precipitating Pu(IV) hydrous oxide formed by the reaction. In addition, Pu(IV) contaminates the surface of the $NH_4PuO_2CO_3 \cdot xH_2O$ solids and likely slows its further dissolution.

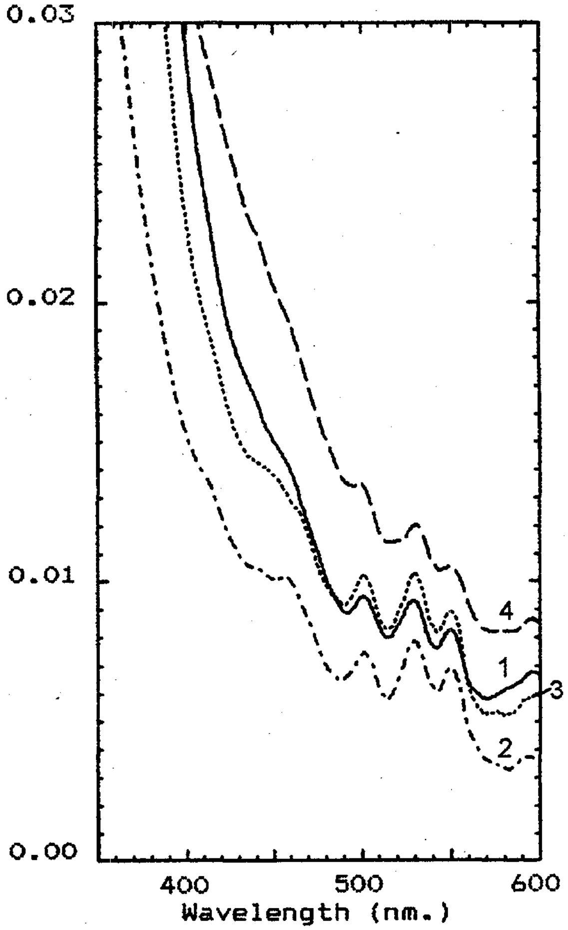


1 - 1 M NaOH, 2 - 2 M NaOH, 3 - 4 M NaOH, 4 - 6 M NaOH

Figure 3.9.1. Plutonium(VI) Solution Concentration from Disproportionation of Pu(V) as a Function of NaOH Concentration and Time

Opposite effects in dissolution processes and disproportionation of dissolved Pu(V) may explain the observed curve maxima. Decrease of Pu(VI) concentration with time can be attributed both to trapping by the precipitating Pu(IV) hydrous oxide and to radiation-induced chemical reduction of Pu(VI). After 60 days, weak Pu(V) absorption bands were only detected in the EAS of 6 M NaOH (Figure 3.9.2).

Therefore, solid Pu(V) compounds held in alkaline solution undergo several processes concurrently. In such systems, particularly at NaOH concentrations less than 4 M, plutonium may be present in multiple valence forms.



1 - 3 days, 2 - 6 days, 3 - 27 days, 4 - 60 days

Figure 3.9.2. Electronic Absorption Spectra of 6 M NaOH Solution of $NH_4PuO_2CO_3$ as Functions of Time

4.0 Conclusions

The behavior of Pu(V) in alkaline solution was studied over a wide range of NaOH concentrations. Experiments were conducted both in pure NaOH solution and in solutions simulating the compositions of Hanford Site high-level tank waste.

1. Extensive development of experimental techniques was required to study Pu(V). The studies provided some new data on the properties of Pu(VI), Pu(V), and Pu(IV) in alkaline media. The stability of alkaline Pu(VI) solutions under various conditions was assessed. The Pu(VI) species does not change when solution is heated to 95°C for a few hours in 2 to 8 M NaOH and (1 to 10) x 10^{-3} M Pu(VI). An absorption band with a maximum at 630 nm and molar extinction coefficient of 10 L/(mol·cm) can be used to identify Pu(VI). The solubility of Pu(VI) at 2 to 10 M NaOH is nearly constant and about 10^{-2} M at 15°C. The spectrum of Pu(V) in 8 M NaOH was measured. The extinction coefficient of Pu(V), determined by spectrophotometric measurement and titration with alkaline Pu(VII), is 8 L/(mol·cm) at 531 and 809 nm. The solubility of Pu(V) increases with increasing NaOH concentration and is (8 ± 3) x 10^{-3} M at 20°C in 8 M NaOH.

   Methods for preparing alkaline Pu(V) solutions by reduction of Pu(VI) were explored. Among the reducing agents tested were I^-, VO_2^{2-}, Sn^{2+}, N_2H_5OH, and H_2O_2. The efficiency and kinetic characteristics of Pu(VI) reduction by these reagents were assessed. The preparation of alkaline Pu(V) solutions by electrochemical reduction also was investigated. It was found that alkaline Pu(V) solutions prepared by reduction of Pu(VI) give inconsistent results and introduce significant uncertainties in studying Pu(V) disproportionation. Therefore, Pu(V) solutions were prepared by dissolving crystalline $NH_4PuO_2CO_3$ salt in selected alkaline solutions. This salt is relatively stable when stored in air, losing 6% of its Pu(V) content after 48 days' storage at room temperature.

2. Disproportionation of Pu(V) to form dissolved Pu(VI) and Pu(IV) precipitates can be observed at NaOH concentrations up to 8 M. The rate of disproportionation increases with temperature and decreases with increasing hydroxide concentration. Experimental data were obtained at 4 to 8 M NaOH and -6 to 40°C. The disproportionation equilibrium constant at 20°C decreases from 0.37 to 3 x 10^{-4} as NaOH concentration increases from 4 to 7 M.

   The reproportionation reaction of dissolved Pu(VI) with freshly precipitated Pu(IV) hydrous oxide to form dissolved Pu(V) was studied in the range 1 to 10 M NaOH and at 40°C. The reciprocal of the reproportionation equilibrium constant was significantly different from the disproportionation equilibrium constant at the same NaOH concentration. Based on the disproportionation reaction equilibria and known Pu(VI)/Pu(V) potential, the potential of the Pu(V)/$PuO_2 \cdot xH_2O$ pair was estimated to be 0.4 ± 0.1 V at 1 M NaOH.

Based on tests with Np(V), the solid Pu(IV) hydrous oxide formed by disproportionation can adsorb up to 50% of the Pu(V).

Experiments thus have demonstrated that Pu(V) is unstable in NaOH solution below 8 M. The disproportionation is accompanied by a number of processes: partial reduction of the Pu(VI) formed by the products of water α radiolysis, sorption and trapping of Pu(V) by Pu(IV) hydrous oxide, aging of the Pu(IV) solids, and return of part of the sorbed Pu(V) to solution. These processes stabilize various plutonium valence forms in strong alkali.

3. The investigations permit elucidation of the basic features of Pu(V) behavior in strongly alkaline media. A complex interaction between the Pu(VI), Pu(V), and Pu(IV) valence forms, strongly affected by solution composition and temperature, exists under these conditions. Based on these studies, the valence behaviors and interactions of plutonium in alkaline solutions can be predicted.

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