PNNL-11901
UC-2030

Pacific Northwest National Laboratory

Operated by Battelle for the U.S. Department of Energy

Plutonium(IV) Precipitates Formed in Alkaline Media in the Presence of Various Anions

N. N. Krot
V. P. Shilov
A. B. Yusov
I. G. Tananaev
M. S. Grigoriev
A. Yu. Garnov
V. P. Perminov
L. N. Astafurova

September 1998

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

PNNL-11901

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

This document was printed on recycled paper.

PNNL-11901
UC-2030

Plutonium(IV) Precipitates Formed in Alkaline Media in the Presence of Various Anions

N.N. Krot
V.P. Shilov
A.B. Yusov
I.G. Tananaev
M.S. Grigoriev
A.Yu. Garnov
V.P. Perminov
L.N. Astafurova

September 1998

Prepared for
the U. S .Department of Energy
under Contract DE-AC06-76RLO 1830
and a Collaboration Agreement Made on May 20, 1997

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

This investigation was undertaken to obtain new data on the composition and properties of plutonium(IV) compounds formed under diverse conditions in strongly alkaline media in the presence of various anions. Such information is important to understand Pu(IV) behavior and the forms of its existence in the alkaline sludges of Hanford Site radioactive waste tanks. The knowledge then may be applied to assess plutonium disposition in the storage, retrieval, and treatment of Hanford Site tank wastes with respect to its criticality hazards and contribution to the transuranic waste inventory.

In all studied cases, Pu(IV) precipitates from 0.2 to 10 M NaOH solutions at 10 to 200°C to form nearly amorphous compounds of general composition $PuO_2 \cdot xH_2O$. Extended aging of the compounds does not produce well-crystallized phases. Aging was accelerated by coagulation at elevated temperatures, including hydrothermal conditions. The number of water molecules, x, associated with the PuO_2 solid depends strongly on the $PuO_2 \cdot xH_2O$ drying conditions but is not sensitive to the precipitation method (direct or reverse) or the coagulation time. For $PuO_2 \cdot xH_2O$ solids prepared at 10 to 60°C and dried at 20°C in desiccators over KOH pellets (1.7 torr H_2O vapor pressure) or over 25% H_2SO_4 (14.6 torr H_2O water vapor pressure), mean values of x are 1.6 and 2.8, respectively. The large difference in these values confirms the strongly hygroscopic properties of $PuO_2 \cdot xH_2O$. The x values decrease with increasing temperature. The composition of $PuO_2 \cdot xH_2O$ obtained at 180 to 200°C and dried over KOH has an average x of 0.60.

Thermogravimetric scans of various $PuO_2 \cdot xH_2O$ samples were similar regardless of compound preparation conditions. In all cases, the mass loss occurred monotonously, in one step, in the range 50 to 250°C. All differential thermal analyses showed mildly endothermic peaks at about 110°C. This confirmed that the water in $PuO_2 \cdot xH_2O$ does not have discrete states but has a continuous range of bonding energy.

Anhydrous PuO_2, produced by heating $PuO_2 \cdot xH_2O$, is strongly hygroscopic. The hygroscopicity remained even after prolonged heating at 500°C, disappearing only at 800°C. The minor influence of temperature on $PuO_2 \cdot xH_2O$ hygroscopicity can be explained by the rather high thermal stability of the primary crystallites. This supposition was confirmed by direct estimates of $PuO_2 \cdot xH_2O$ crystallite size by an X-ray powder diffraction method. It was found that $PuO_2 \cdot xH_2O$ crystallite size increases only from about 2.5 to 7 nm in the range 20 to 800°C.

Infrared (IR) spectra of $PuO_2 \cdot xH_2O$ solids prepared under different conditions closely resemble each other and show an intense band with maximum at 3400 cm^{-1}, three weak bands in the range 1700 to 1250 cm^{-1}, and an additional strong and generally split band between 600 and 350 cm^{-1}. The band at 3400 cm^{-1}, arising from valent water vibrations in the $PuO_2 \cdot xH_2O$ structure, is relatively wide and smooth and without shoulder. This observation confirms the assumption that water molecules have no discrete state in the compound structure. The bands with maxima at 1640 cm^{-1} and in the low frequency region can be attributed, respectively, to deformation vibrations of H_2O and valent vibrations of Pu-O bonds in PuO_2 crystallites.

Sedimentation of $PuO_2 \cdot xH_2O$ precipitates is usually complete in two to three hours. The settling rate decreases with increase in the solution phase density for the systems H_2O, 1 M NaOH, 3 M NaOH, and 3 M NaOH / 3 M $NaNO_3$. The influence of aging conditions on $PuO_2 \cdot xH_2O$ settling rate is weak and irregular. However, for compounds prepared under hydrothermal conditions at 160 to 200°C, settling rates in water and 1 M NaOH are considerably higher than the rates found for precipitates prepared at lower temperature. The specific volumes of settled $PuO_2 \cdot xH_2O$ are practically independent of the solution phase composition and density. However, the specific volumes decrease significantly with hydrothermal aging (180 to 200°C) to give specific volumes three times lower than those of precipitates aged at room temperature. Precipitate volumes after centrifugation are less sensitive to compound aging conditions and are about 5 mL/g Pu.

Plutonium concentrations in mother solutions centrifuged two minutes after $PuO_2 \cdot xH_2O$ precipitation are 100 to 1000 times higher than the compound's solubility under the same conditions. Plutonium concentration decreases with time but remains high even after one-day's coagulation. Precipitation of $PuO_2 \cdot xH_2O$ likely proceeds through colloid formation with the fine particles remaining suspended during centrifugation. Plutonium concentrations decrease about 100-fold by using ultrafiltration instead of centrifugation to separate phases.

Experiments showed that the compounds precipitated from 0.2 M NaOH at room temperature or from 1 M NaOH at 60°C in the presence of 2 M NO_2^-; 0.1 M $C_2O_4^{2-}$, $HOCH_2COO^-$, EDTA, HEDTA, or citrate; or 0.5 M CO_3^{2-} and SO_4^{2-} had, after careful water washing, the same composition and hygroscopic properties as the $PuO_2 \cdot xH_2O$ obtained by Pu(IV) nitrate precipitation from pure NaOH solutions. These anions did not significantly alter the rate or completeness of $PuO_2 \cdot xH_2O$ precipitation. Incorporation of NO_3^- in the $PuO_2 \cdot xH_2O$ was less than 0.03 mole percent, and sodium retention was less than 1 mole percent in precipitates formed by reaction of NaOH with acidic Pu(IV) nitrate solutions and washed five times with water.

Plutonium(IV) precipitation characteristics, however, were altered for alkaline solutions containing silicate or phosphate. In both cases, the color and volume of precipitates changed. The precipitates peptized considerably with water washing. Direct analyses of the Pu(IV) compounds precipitated from alkaline solution in the presence of 0.05 M SiO_3^{2-} at low NaOH concentrations showed that the compounds were more likely silicates than $PuO_2 \cdot xH_2O$. Significant amounts of silicate were detected even in products obtained from 7 M NaOH. Silicate also was found to interact with $PuO_2 \cdot xH_2O$ prepared separately under hydrothermal conditions. The alkali precipitation behavior of Pu(IV) is similar in the presence of phosphate and silicate. However, the degree of anion capture and the stability of compounds prepared at high NaOH concentration for phosphate are significantly lower than found for silicate.

Based on these results, it is reasonable to conclude that $PuO_2 \cdot xH_2O$ cannot be present in alkaline tank wastes containing significant silicate concentrations. Under such conditions, Pu(IV) should exist as various basic silicates according to the waste's composition. However, this conclusion may be complicated by the behavior of mixed hydroxides of Pu(IV) with Fe(III) or other waste components in the alkaline silicate media. This problem requires special investigation.

Acknowledgments

This work was performed at the Laboratory of Transuranium Element Chemistry of the Institute of Physical Chemistry, Russian Academy of Sciences (IPC/RAS), under an agreement between the US Department of Energy and IPC RAS. The work was supported by the US Department of Energy, Office of Science and Technology, under the Office of Environmental Management.

We are very thankful to Dr. Kurt Gerdes and Dr. Jerry Harness, Program Managers, Efficient Separation and Processing Crosscutting Program, for their active interest in our research. We also thank Dr. Jack Watson, Deputy Coordinator, for his useful advice and support. We are especially grateful to Mr. Cal Delegard for his unceasing attention to our work, valuable discussions of the experimental results, and great editorial help. We acknowledge, with thanks, the organizational efforts of Dr. Thomas Albert in contract implementation.

This page(s) is (are) intentionally left blank.

Contents

Figures

Tables

1.0 Introduction

The tendency of Pu(IV) to hydrolyze and form true solutions, colloid solutions, or insoluble precipitates has been known since the Manhattan Project (Seaborg and Katz 1954). Since then, specific studies have been performed to examine in detail the equilibria of Pu(IV) hydrolytic reactions in various media (Rabideau 1957; Rabideau and Kline 1960). Great attention also has been paid to the preparation, structure, and properties of Pu(IV) polymers or colloids (Ockenden and Welch 1956; Haire et al. 1971; Costanzo et al. 1973; Bell et al. 1973a and 1973b; Neu et al. 1997). These compounds found an important application in sol-gel technology for the preparation of nuclear fuel materials (see, for example, Louwrier 1968). A most important result of these works was the conclusion that Pu(IV) hydroxide, after some aging, consists of very small PuO_2 crystallites and should therefore be considered to be Pu(IV) hydrous oxide (Ockenden and Welch 1956; Haire et al. 1971). However, studies of the properties and behavior of solid Pu(IV) hydroxide in complex heterogeneous systems are rare.

The primary goal of our investigation was to obtain data on the composition and properties of Pu(IV) hydrous oxide or other compounds formed in alkaline media under different conditions. Such information is important to understand Pu(IV) behavior and the forms of its existence in the Hanford Site alkaline tank waste sludge. This knowledge then may be applied in assessing plutonium criticality hazards in the storage, retrieval, and treatment of Hanford Site tank wastes (Whyatt et al. 1996) as well as in understanding its contribution to the transuranic waste inventory (threshold at 100 nCi/g or about $5x10^{-6}$ M) of the separate solution and solid phases.

2.0 Experimental Materials and Methods

2.1 Reagents and Equipment

Most experiments were conducted using Pu(IV) nitrate solutions having known nitric acid concentrations. Plutonium solutions were prepared by following method: First, approximately 0.05 M plutonium nitrate in ~3 M HNO_3 was purified by the common anion exchange method. Hydrogen peroxide was added up to 0.05 M to this solution. The mixture was heated on a boiling water bath until the sharp change of solution color from blue to brown occurred, indicating complete H_2O_2 decomposition and transition of Pu(III) to Pu(IV). From this solution, $Pu(C_2O_4)_2{\cdot}6H_2O$ was precipitated by the slow addition of ~1 M oxalic acid to ~0.1 M excess with slight heating. After two hours of coagulation, the compound was separated from the mother solution by centrifugation and washed with a 1 M HNO_3/0.01 M $H_2C_2O_4$ solution. The $Pu(C_2O_4)_2{\cdot}6H_2O$ was dissolved in boiling concentrated HNO_3, and the product solution evaporated to a small volume. After cooling, the solution was diluted four-fold with 2 M HNO_3 and again treated with H_2O_2 to stabilize plutonium in the tetravalent state.

By this method, two Pu(IV) stock solutions were prepared having 0.233 and 0.206 M Pu, respectively. The free acid concentrations in the respective solutions were 3.10 and 4.35 M. The Pu(IV) state was verified by absorption spectrophotometry using a Shimadzu model UV-3100 PC UV-Vis-NIR spectrophotometer (Japan). Plutonium concentrations were determined by a gravimetric analysis. For this purpose, 0.1 mL aliquots of Pu(IV) stock solution were evaporated to dryness carefully (without boiling) in small platinum crucibles and the residues calcined at 800°C for about two hours to form PuO_2. The free HNO_3 concentrations in Pu(IV) solutions were determined by direct titration with 0.1 M NaOH using phenolphthalein as an indicator. It was assumed that four moles of sodium hydroxide were consumed to precipitate one mole of Pu(IV).

In some experiments, thorium was used to model Pu(IV) behavior in alkaline media. Initial 0.5 to 1 M thorium nitrate solutions were prepared by dissolving reagent-grade $Th(NO_3)_4{\cdot}5H_2O$ in 0.2 M HNO_3. Exact thorium solution concentrations were determined gravimetrically by precipitating thorium hydrous oxide with NH_4OH and calcining the precipitate to ThO_2. Working sodium hydroxide solutions, obtained by the dilution of 16.7 M chemical purity-grade NaOH, were stored in polyethylene bottles. Standard solutions of other reagents (such as $NaNO_2$, $NaNO_3$, Na_2SO_4, Na_3PO_4) were prepared by dissolving the corresponding salts in distilled water or by neutralizing the respective acids with NaOH.

Powder X-ray diffraction patterns of solid samples were measured by a 100-mm Guinier camera, model XDC-700, using $CuK_{\alpha 1}$-radiation (Philips PW 1140/90/96 generator, Holland) using Si as an internal standard. Infrared (IR) spectra were taken using a Specord-M80 instrument (Germany). Thermal analyses of compounds were performed with a Q-1500 D derivatograph (Hungary). Thermostats (U-2 model, Germany) were used to maintain constant solution temperature in the range 20 to 80°C within ±0.2°C. Separations of precipitates from supernatant liquids were performed using medical centrifuges (model CLK-1, Russia) operated at an acceleration of 1,750g. Weights of Pu(IV) compound samples were determined by a Sartorius (Germany) microbalance with a sensitivity pf 1 μg. The concentrations of plutonium solutions were measured by their specific α-activity using a LS-6500 scintillation counter (Beckman, USA). An automatic γ-counter (Tesla, Czech Republic) was used for ^{22}Na determination in solutions and compounds.

2.2 Experimental Methods

2.2.1 Precipitation, Coagulation, and Isolation of Pu(IV) Compounds

Plutonium(IV) hydrous oxide samples were prepared by direct or reverse precipitation in polyethylene test tubes using amounts of NaOH or NH_4OH calculated to obtain a chosen excess of the precipitant. With direct precipitation, a calculated excess of NaOH or NH_4OH was added to a measured volume (usually 0.3-0.4 mL) of a Pu(IV) stock solution diluted three- to five-fold by water. With reverse precipitation, Pu(IV) stock solution aliquots were poured into polyethylene test tubes containing solution with known concentrations of NaOH or NH_4OH. In both cases, the resulting suspensions were stirred and kept for a controlled period of time at a chosen temperature in a thermostat or in a boiling water bath. The solid phases then were separated by centrifugation and washed four to five times with water. The pH of the last wash water was no higher than 8. Washed precipitates were collected in small crucibles, dried in a desiccator over KOH pellets, and converted into powders.

To prepare Pu(IV) hydrous oxide samples under hydrothermal conditions, NaOH or NH_4OH in an excess of about 0.2 M was added to 0.3 to 0.4 mL of Pu(IV) stock solution and the resulting mixture diluted to 5 to 7 mL with water. After stirring and coagulation at room temperature, the precipitate was separated from the mother solution by centrifugation and washed once with 5 mL of water. The precipitate then was suspended in 1 mL of standardized sodium or ammonium hydroxide and transferred into a Teflon test tube with a 6-mm outer diameter. The test tube was sealed in a glass ampoule and heated for several hours at a controlled temperature in the range 100 to 200°C. After cooling, the ampoule was opened, and the suspension was transferred to a centrifuge tube and treated as described for tests at lower temperatures.

Similar methods were used to prepare Pu(IV) compounds precipitated in the presence of various anions. Known amounts of the anion salts were introduced into aliquots of Pu(IV) stock solution (direct precipitation) or into NaOH solution (reverse precipitation) under conditions otherwise similar to those described for tests in the absence of additional anions.

2.2.2 Study of the Hygroscopic Properties and Composition of Pu(IV) Hydrous Oxide

To determine the hygroscopicity of Pu(IV) hydrous oxide, from 5 to 15 mg of $PuO_2 \cdot xH_2O$ were added to small platinum-plated cups (diameter ~12 mm, height ~3 mm, mass ~0.5 g), kept in a desiccator over KOH pellets for one to three days, the masses measured by obtaining weights for one to two minutes, and the results extrapolated to the time the cups were removed from the desiccator. The same procedure was performed after keeping the samples for one to three days in desiccators having 50% H_2SO_4 and 25% H_2SO_4. The water vapor pressures over KOH, 50% H_2SO_4, and 25% H_2SO_4 at 20°C, are 1.7, 6.9, and 14.6 torr, respectively, compared with 17.4 torr over water itself. By this method, it was possible to observe the water retention of materials in air with varied humidity. In some experiments, measurements were repeated two or three times to observe the reversibility of the hygroscopic properties of compounds under investigation. When hygroscopicity experiments were completed for a given sample, it was calcined at about 800°C for one to two hours to determine the weight of PuO_2 and calculate the amounts of water retained in products held in air at different humidities.

This method was tested by multiple analyses of the same batch of Pu(IV) hydrous oxide. As shown in Table 2.1, the error in determining the value of x in the composition of a single $PuO_2 \cdot xH_2O$ sample does not exceed ±0.1, or about 3% relative.

Table 2.1. Reproducibility of the Weight Analyses of a $PuO_2 \cdot xH_2O$ Sample

Mass of samples, mg		Molecular mass of $PuO_2 \cdot xH_2O$, M_m, g/mole			Hydration value, x		
Initial	Calcined	M_m	ΔM_m	$100\Delta M_m/M_m$	x	Δx	$100\Delta x/x$
5.400	4.586	319.1	+1.4	0.44	2.67	+0.08	3.1
8.670	7.409	317.1	-0.6	0.19	2.56	-0.03	1.2
2.809	2.407	316.3	-1.4	0.44	2.52	-0.07	2.7
45.768	38.979	318.2	+0.5	0.16	2.62	+0.03	1.2
Mean		317.7		0.31	2.59		2.1

2.2.3 Measurements of the IR Spectra of Pu(IV) Hydrous Oxide Compounds

To obtain an IR spectrum, the compound to be studied was first dried one to three days in a desiccator over KOH pellets. Then, 2 to 2.5 mg of the compound was mixed with 200 mg of special purity-grade NaCl or KBr and ground into powder for 10 to 20 minutes in an agate mortar. The mixture was converted into a transparent 2-cm diameter disk by pressing in a die about one minute with 190 kP/cm^2 pressure. The disk was set in a special holder and placed in the compartment of the IR spectrophotometer. The IR spectra were recorded in the range of 350 to 4000 cm^{-1} (NaCl matrix) or 250-4000 cm^{-1} (KBr matrix). Measurements at low wave numbers were performed using blank disks to compensate for IR absorption by the salt matrixes. The blank disks were prepared from pure NaCl or KBr by the same method.

2.2.4 Determination of the Sedimentation Rate and Specific Volumes of Pu(IV) Hydrous Oxide Samples

To determine sedimentation rate, 0.12 mmol of Pu(IV) was transformed into $PuO_2 \cdot xH_2O$ by direct or reverse precipitation and coagulated under controlled conditions, as described previously. The precipitate was separated from the mother solution by centrifugation and washed twice with 5 mL of water. The precipitate then was thoroughly mixed with 1.5 mL of water to obtain a uniform suspension that was quickly placed in a calibrated 6-mm inner-diameter glass tube. The precipitate's sedimentation rate was measured by visually observing its volume change over one to two hours. The solid phase then was centrifuged for five minutes, separated from the supernate, and mixed with 1.5 mL of 1 M NaOH. Measurements of the sedimentation rate of the resulting suspension were performed in the same way as in the tests with water. Sedimentation rates also were found in 3 M NaOH and 3 M NaOH / 3 M $NaNO_3$.

2.2.5 Study of the Rate and Completeness of Pu(IV) Hydrous Oxide Precipitation

To determine the rate and completeness of Pu(IV) hydrous oxide precipitation, a measured volume (usually 0.2 mL) of standard Pu(IV) solution was mixed with a known amount of NaOH to obtain $PuO_2 \cdot xH_2O$ by direct or reverse precipitation under controlled conditions, as described previously. After two minutes, the precipitate was centrifuged for one minute, and an aliquot of mother solution was taken for radiometric analysis. The precipitate then was suspended, kept for 10 minutes, and, after centrifugation, the supernate was sampled for analysis again. The tests also were repeated at 20 minutes and one day of contact time.

The same procedure was used to monitor the rate and completeness of Pu compound precipitation in the presence of various anions. The anions were added to the sodium hydroxide or Pu(IV) solution, respectively, before the reverse or direct precipitation.

3.0 Results and Discussion

3.1 Composition and Hygroscopic Properties of Pu(IV) Hydrous Oxides

3.1.1 Possible Formation of $Na_zPu(OH)_{4+z}$ or $PuO_{2-y}(NO_3)_{2y}{\cdot}xH_2O$ Compounds

It is known that tetravalent plutonium and neptunium are somewhat amphoteric, forming hydroxo complexes at high NaOH concentrations. Complexes of the form $An(OH)_5^-$ and $An(OH)_6^{2-}$ have been proposed (Peretrukhin et al. 1996). The compound $NH_4Np(OH)_5$ was prepared under hydrothermal conditions, and its structure was determined by single crystal x-ray diffractometry (Cousson 1986). Therefore, it is reasonable to suppose that, in strongly alkaline media, Pu(IV) can form solid compounds of composition $Na_zPu(OH)_{4+z}{\cdot}xH_2O$. To verify this supposition, Pu(IV) hydroxide samples were prepared using a 10 M NaOH solution isotopically labeled with ^{22}Na. The specific γ-activity of the solution was $5x10^4$ Bq $^{22}Na/mL$.

In these tests, 0.2 to 0.6 mL of 0.233 M Pu(IV) stock solution was mixed with 2 mL of 6- or 10-M ^{22}Na-labeled NaOH by direct or reverse addition; the precipitate was coagulated under controlled conditions in a polyethylene test tube. The precipitate then was separated and washed, in the first step, using 2 mL of water followed by 1 mL of ethanol; all subsequent washing steps were performed either with 2 mL of water or 2 mL of ethanol. The γ-activity of the precipitate was measured after each washing. The results were used to calculate the sodium content of the Pu(IV) compound. The precipitates' γ-activities without washing were about $8.5x10^3$ Bq. The background of the γ-counter was about 2 Bq.

The experimental results show that the Na^+ content in the precipitates after separation from the mother solution and the first washing step are 30 to 70 mol% (Table 3.1). These quantities accord with the amounts expected based on the volumes and dilution of the mother solution present interstitially in the solids. It is concluded that $Na_zPu(OH)_{4+z}{\cdot}xH_2O$ compounds are not formed by direct or reverse Pu(IV) precipitation from alkaline solutions with NaOH concentrations less than 9 M. This conclusion also is confirmed by measuring the x-ray diffraction pattern of moist Pu(IV) compound precipitated from 10 M NaOH and coagulated three hours at room temperature. The pattern only showed the very diffuse lines of PuO_2, similar to other $PuO_2{\cdot}xH_2O$ samples.

The data in Table 3.1 show also that complete removal of NaOH from $PuO_2{\cdot}xH_2O$ precipitates is achieved better by thorough water washing. Ethanol is less effective for this purpose. Perhaps the retention of NaOH by $PuO_2{\cdot}xH_2O$ is caused by its sorption on the precipitate surface. Based on these results, Pu(IV) precipitates prepared in subsequent tests were washed four to five times with water at liquid to solid ratios greater than 10.

Table 3.1. Sodium Contents in $PuO_2{\cdot}xH_2O$ Samples after Washing with Water or Ethanol

	Conditions of coagulation			Na content, mol%, after m washes				
Precipitation	[NaOH], M	T, °C	T, h	m=1	M=2	m=3	m=4	m=5
Reverse	9.1	25	3	47	19	5	~3	<1
	9.1	25	170	31	14	4	~2	<1
	6.5	25	3	63	48*	32*	--	--
	8.2	25	3	36	13	3	--	--
Direct	9.1	25	3	49	21	7	~2	<1
	9.1	80	8	53	22	8	~3	<1
	9.1	25	170	34	15	6	~2	<1
	9.1	25	3	35	16*	16*	15*	--
	9.1	25	170	45	17*	17*	16*	--
* Washed with ethanol.								

Limited information exists on the ability of Pu(IV) hydrous oxide to incorporate nitrate in alkaline precipitation (Kraus 1949). To obtain more definitive data, a number of $PuO_2{\cdot}xH_2O$ samples were prepared and analyzed for nitrate content. For the analysis, 5 to 20 mg of compound were dissolved, with slight heating, in 1 mL of concentrated sulfuric acid in the presence of 5 to 8 mg of salicylic acid. The resulting solutions then were treated to determine nitrate concentrations (Lur'e 1971). As shown in Table 3.2, the nitrate contents in $PuO_2{\cdot}xH_2O$ samples prepared under different conditions do not exceed 0.03 mol%. Such small concentrations cannot markedly affect $PuO_2{\cdot}xH_2O$ properties and were neglected in subsequent experiments.

Table 3.2. Content of NO_3^- in Some $PuO_2{\cdot}xH_2O$ Samples

Conditions of sample coagulation			$[NO_3^-]$,
[NaOH], M	T, °C	t, h	mol%
0.2	12	5	0.013
0.2	100	9	0.022
1.0	12	5	0.011
1.0	100	3	0.023
2.4	60	5	0.020

3.1.2 Composition and Hygroscopic Properties of $PuO_2{\cdot}xH_2O$

Most $PuO_2{\cdot}xH_2O$ solids were prepared using reverse (acid to alkali) precipitation with NaOH solutions. This technique avoided possible Pu(IV) disproportionation at the low acid concentrations that occur transitorily during NaOH addition to Pu(IV) solution. The probability of such reaction was appreciable because the plutonium stock solution concentrations were high. To decrease the probability of Pu(IV) disproportionation during $PuO_2{\cdot}xH_2O$ precipitation, the Pu(IV) stock solution aliquots were diluted three- to five-fold by water and quickly mixed, with intense stirring, with the chosen amount of NaOH solution.

As shown in Table 3.3, the $PuO_2 \cdot xH_2O$ compositions obtained under comparable drying conditions are independent of direct or reverse precipitation. The compositions likewise are not sensitive, at low temperatures, to the amount of excess NaOH or to the coagulation time. At higher aging temperatures, the compound hydration (x value for $PuO_2 \cdot xH_2O$) tends to decrease, especially at higher NaOH concentrations. This tendency is especially obvious for products obtained under hydrothermal conditions (Table 3.4). The compositions of the same samples, dried over 25% H_2SO_4 in a desiccator, are less sensitive to increasing temperature of aging.

Table 3.3. Composition of $PuO_2 \cdot xH_2O$ Samples Prepared by NaOH Precipitation at 12 to 100°C

	Conditions of coagulation			x values after drying over		
Precipitation	[NaOH], M	T, °C	t, h	KOH	50% H_2SO_4	25% H_2SO_4
Reverse	0.2	12	0.2	1.51	2.28	2.63
	0.2	12	5	1.63	2.32	2.60
	1	12	5	1.47	2.19	2.74
	2.4	12	96	1.46	2.22	2.59
	15.4	12	160	1.63	2.41	2.63
	2.4	60	5	1.44	2.10	2.46
	1	100	1	1.55	2.15	2.69
	1	100	2	1.31	2.11	2.61
	1	100	9	1.56	2.18	2.52
	0.2	100	9	1.50	2.00	2.56
	3	100	9	1.17	1.72	2.33
	8.1	100	9	1.32	1.86	2.45
	15.4	100	9	1.28	1.98	2.47
Direct	0.2	12	0.2	1.57	2.16	2.70
	1	100	9	1.50	2.18	2.85
	1	60	5	1.62	2.25	2.96
	2	20	3	1.77	2.42	3.09
	0.2	20	3	1.61	2.18	3.16
	2	100	3	1.22	1.96	2.70
	8	100	3	1.37	1.88	2.86

The mean x values for $PuO_2 \cdot xH_2O$ precipitated at 10 to 60°C and dried over KOH pellets and over 25% H_2SO_4 are 1.56 and 2.76, respectively. The difference, Δx, (which is 1.20) reflects the hygroscopic properties of $PuO_2 \cdot xH_2O$. The $PuO_2 \cdot xH_2O$ products coagulated at 100°C but dried under the same conditions have mean x values of 1.38 and 2.72, respectively, and Δx is 1.34. For $PuO_2 \cdot xH_2O$ samples obtained under hydrothermal conditions at 180 to 200°C, the respective x values are 0.67 and 2.47, and Δx is 1.80. Thus, the number of water molecules in $PuO_2 \cdot xH_2O$ prepared under comparable conditions decreases with increasing temperature, but the hygroscopicities of the compounds increase slightly.

Table 3.4. Composition of $PuO_2{\cdot}xH_2O$ Samples Prepared under Hydrothermal Conditions

Conditions of coagulation			x values after drying		
[NaOH], M	T, °C	t, h	KOH	50% H_2SO_4	25% H_2SO_4
1	120	5	1.09	1.72	2.49
1	140	5	1.08	1.62	2.25
1	160	5	1.06	1.60	2.45
1	180	5	0.84	1.63	2.56
1	200	5	0.67	1.32	2.22
0.2	180	5	1.00	1.51	2.90
5	180	5	0.53	0.89	2.33
10	180	5	0.44	0.80	2.50
2	190	14	0.51	0.92	2.29

Experiments also were performed to study the composition and hygroscopic properties of $PuO_2{\cdot}xH_2O$ prepared at low OH^- concentrations. In these tests, the Pu(IV) precipitation was conducted with 0.2 to 0.3 M excess NH_4OH, and the precipitates were aged in the mother solutions. The $PuO_2{\cdot}xH_2O$ precipitates obtained with ammonium hydroxide were similar in composition and hygroscopic properties to those precipitated by NaOH (Table 3.5).

The loss and absorption of water by $PuO_2{\cdot}xH_2O$ with changing water vapor pressure are freely reversible. Tests showed that changes in $PuO_2{\cdot}xH_2O$ sample weights for materials kept, in turn, over three cycles of dehydration (dry KOH) and hydration (25% H_2SO_4) for one to three days were reproducible (Table 3.6).

Table 3.5. Composition of $PuO_2{\cdot}xH_2O$ Samples Prepared Using NH_4OH

Conditions of coagulation		x values after drying		
T, °C	t, h	KOH	50% H_2SO_4	25% H_2SO_4
25	0.1	1.79	2.33	2.58
25	5	1.42	2.49	2.88
60	5	1.17	2.58	2.81
100	5	1.10	2.03	2.66
100	12	1.27	2.41	2.52
120	3	1.17	1.89	2.38
140	3	0.98	1.71	2.44
155	3	0.51	1.07	1.59
180	3	0.66	1.34	2.18
180	9	0.54	1.25	2.32
200	3	0.49	1.19	2.02

Table 3.6. Reversibility of $PuO_2 \cdot xH_2O$ Hygroscopic Properties

Sample preparation conditions			Desiccant	Mass of sample in cycle number		
[NaOH], M	T, °C	t, h		1	2	3
0.2	100	9	KOH	17.505	17.455	17.452
			25% H_2SO_4	18.488	18.478	18.445
3	100	9	KOH	17.743	17.570	17.617
			25% H_2SO_4	19.042	19.020	19.001
1	25	3	KOH	14.376	14.392	14.348
			25% H_2SO_4	15.451	15.487	15.427
1	180	5	KOH	9.258	9.318	9.243
			25% H_2SO_4	10.067	10.086	10.049

The sensitivity to humidity is not unique to $PuO_2 \cdot xH_2O$. As seen in Table 3.7, the hygroscopic behavior of $ThO_2 \cdot xH_2O$ is very similar to that of $PuO_2 \cdot xH_2O$. Furthermore, semi-quantitative experiments showed that dried Np(IV) hydroxide also changes weight with change in air humidity. Because $NpO_2 \cdot xH_2O$ reacts quickly with atmospheric oxygen to form Np(V) compounds, however, its hygroscopic properties could not be studied in detail.

Table 3.7. Composition of $ThO_2 \cdot xH_2O$ Prepared by Direct Precipitation with NaOH or NH_4OH

	Conditions of coagulation			x values after drying		
Precipitant	[MOH], M	T, °C	t, h	KOH	50% H_2SO_4	25% H_2SO_4
NaOH	1	20	2	1.89	2.84	2.88
	1	20	120	1.80	2.94	2.99
	1	100	1	1.29	2.19	2.48
	1	100	9	1.26	2.23	2.68
	1	100	5	1.54	2.35	2.81
	1	120	5	1.19	2.12	2.30
	1	160	5	0.98	2.04	2.30
	1	200	5	0.57	1.19	2.21
	1	200	20	0.56	1.20	2.24
	3	100	5	1.25	2.18	2.54
	8	100	5	1.26	2.21	2.64
	15	100	5	1.18	2.18	2.67
NH_4OH	0.4	15	0.4	1.51	3.01	3.03
	0.4	25	5	1.83	2.63	2.76
	0.4	100	0.4	1.75	2.76	2.94
	0.4	100	12	1.92	3.17	3.28

3.1.3 Thermal Behavior of Pu(IV) Hydrous Oxide

From the data presented above it is evident that $PuO_2 \cdot xH_2O$ easily loses a part of its water even at room temperature. The dehydration of $PuO_2 \cdot xH_2O$ at elevated temperatures was studied by thermogravimetric and differential thermal techniques. The measurements were conducted with 25 to 50 mg $PuO_2 \cdot xH_2O$ previously dried in a desiccator over 50% H_2SO_4.

Thermogravimetric scans of the various $PuO_2 \cdot xH_2O$ samples were similar regardless of the preparation conditions. Selected scans are presented in Figure 3.1. In all cases, the mass loss occurred monotonously, in one step, over the range 50 to 300°C. All differential thermal analysis curves showed gentle endothermic peaks at about 110°C whose heights were proportional to the x values of the compounds being investigated. Based on these results, it was concluded that water in $PuO_2 \cdot xH_2O$ does not have discrete binding such as for a crystalline hydrate. Instead, a continuous range of bonding energy characterizes the associated water. This conclusion agrees well with the hygroscopic properties found for $PuO_2 \cdot xH_2O$ at room temperature.

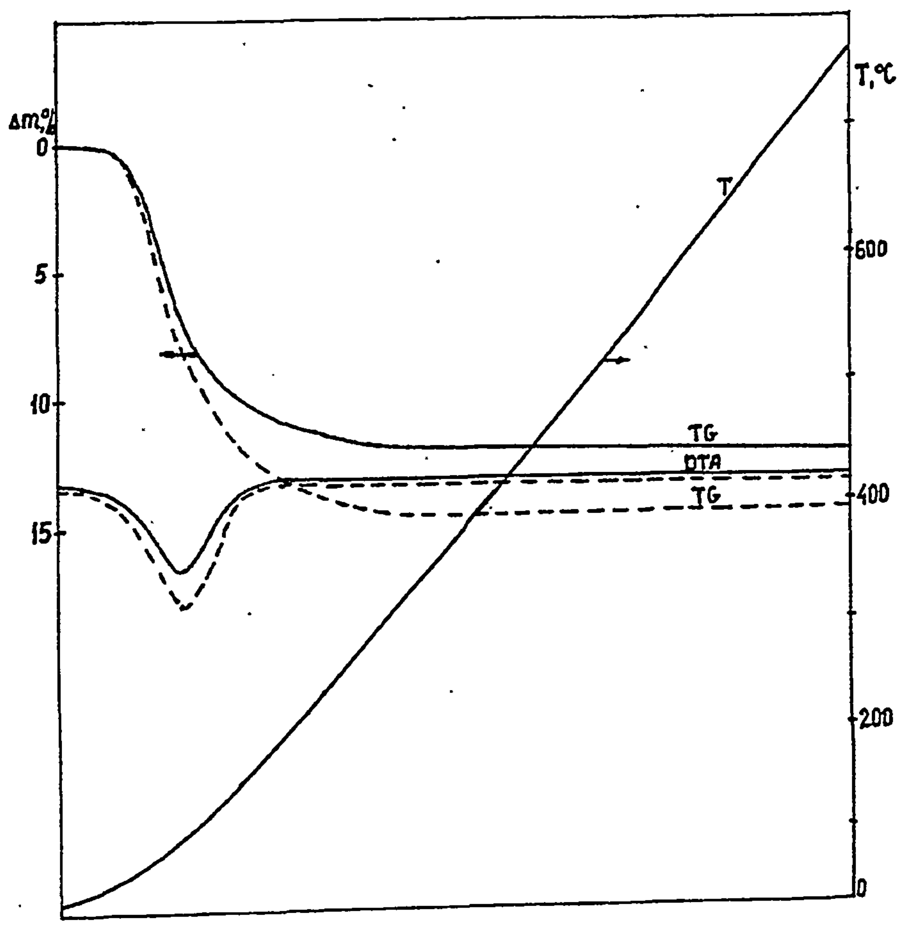

Figure 3.1. Thermal Analysis of $PuO_2 \cdot xH_2O$

______ $PuO_2 \cdot 2.1H_2O$
------ $PuO_2 \cdot 2.6H_2O$

The behavior of products obtained by isothermal heating of $PuO_2 \cdot xH_2O$ samples to elevated temperatures in air was studied. For this purpose ~12 mg of $PuO_2 \cdot xH_2O$, prepared by reverse precipitation from 1 M NaOH and subsequent coagulation for nine hours at 100°C, was heated stepwise at different temperatures for 1.5 hours. After each heating step, the product was stored one day in desiccators over dry KOH and then over 25% sulfuric acid and the weight measured. The temperature was maintained to ±3°C in the range 20 to 300°C and ±10°C above 300°C.

From data in Table 3.8 it is clear that the residual water content of $PuO_2 \cdot xH_2O$ decreases with increasing temperature. However, the ability of the heat-treated compounds to reabsorb water vapor under otherwise similar conditions is not affected by the drying temperature over the range 20 to 350°C. Remarkably, this ability is observed even at 520°C. Increasing the time of heating at constant temperature affects the hygroscopic properties of $PuO_2 \cdot xH_2O$ only to a very limited extent (Table 3.9).

Table 3.8. Hygroscopic Behavior of $PuO_2 \cdot xH_2O$ after Isothermal Heating for 1.5 Hours

Desiccant	x values for various heating temperatures, °C						
	20	165	195	295	350	520	800
KOH, x_1	1.50	1.23	0.97	0.74	0.37	0.04	0
25% H_2SO_4, x_2	2.85	2.48	2.20	2.08	1.67	0.66	0
Δx	1.35	1.25	1.23	1.34	1.30	0.62	0
Note: Product kept ~one day over desiccants; $\Delta x = x_2 - x_1$.							

Table 3.9. Hygroscopic Behavior of $PuO_2 \cdot xH_2O$ after Heating at 295°C for Various Times

Desiccant	x values for various times, h			
	1	2.5	5	7.5
KOH, x_1	0.75	0.73	0.66	0.60
25% H_2SO_4, x_2	2.03	2.14	1.97	1.91
Δx	1.28	1.41	1.31	1.31
Note: Product kept ~one day over desiccants; $\Delta x = x_2 - x_1$.				

The small influence of temperature on $PuO_2 \cdot xH_2O$ hygroscopicity can be explained by the high thermal stability of the primary crystallites. This supposition was confirmed by direct x-ray powder diffraction estimates of the crystallite sizes of $PuO_2 \cdot xH_2O$ samples heated to different temperatures. The estimates were based on data presented in Figures 3.2 and 3.3. The experiments were conducted using $PuO_2 \cdot xH_2O$ samples prepared by precipitation from 0.2, 1, and 10 M NaOH and coagulated three hours at 75°C. The samples (6±1 mg) then were heated for two hours to various temperatures and examined by x-ray powder diffractometry. The widths of the (111) diffraction line (Figure 3.2) were analyzed by densitometric measurements and by a computer scan method (Figure 3.3).

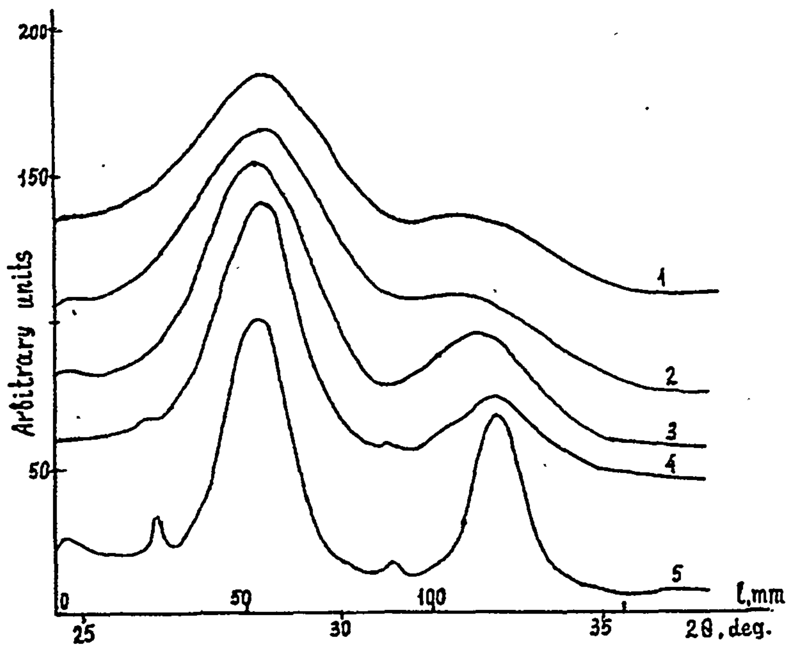

Figure 3.2. X-Ray Diffraction Patterns of $PuO_2 \cdot xH_2O$ and the Shape of the (111) Line as a Function of Heating Temperature (in °C):

1 - 75 2 - 200 3 - 300 4 - 400 5 - 800

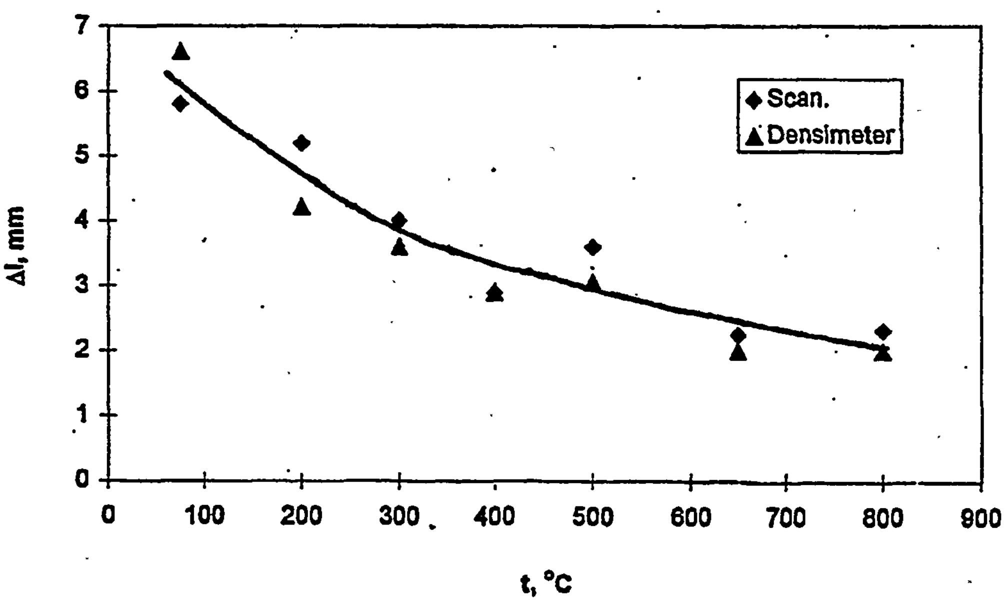

Figure 3.3. Half-Width of the (111) Diffraction Line of $PuO_2 \cdot xH_2O$ as a Function of Temperature

As shown in Figure 3.3, the half-width of the diffraction line smoothly decreases about three-fold as the heating temperature increases from 75 to 800°C. Nevertheless, the $PuO_2 \cdot xH_2O$ samples' diffraction line half-widths remain rather large even after two-hours' calcination at 800°C. Variations in the half-width as a function of heating time are insignificant (Figure 3.4). Similarly, variation of NaOH concentration had no distinct effect for any tested temperature.

The observed changes of the diffraction line half-width with temperature correspond to an increase in the $PuO_2 \cdot xH_2O$ crystallite size from about 2.5 to 7 nm. It is seen that the PuO_2 obtained by alkaline precipitation of $PuO_2 \cdot xH_2O$ followed by calcination at 800°C yields very small crystals; however, these crystals are not hygroscopic. It is likely that the hygroscopic properties of PuO_2 depend not only on the size of crystals but also on their regularity.

3.1.4 IR Spectra of $PuO_2 \cdot xH_2O$ Compounds

Infrared (IR) spectra were taken for the majority of $PuO_2 \cdot xH_2O$ samples prepared for the composition and hygroscopic property studies. Representative IR spectra are shown in Figure 3.5. The spectra closely resemble each other and show an intense band with a maximum at 3400 cm^{-1}, three weak bands in the interval 1700 to 1250 cm^{-1}, and an additional strong, and usually split, band between 600 and 350 cm^{-1}. The band at 3400 cm^{-1} undoubtedly arises from valent vibrations of water molecules in the $PuO_2 \cdot xH_2O$ structure. The band is relatively wide and smooth, without any shoulder. This fact confirms the previously mentioned assumption that there are no discrete states of water molecules in the structure of $PuO_2 \cdot xH_2O$.

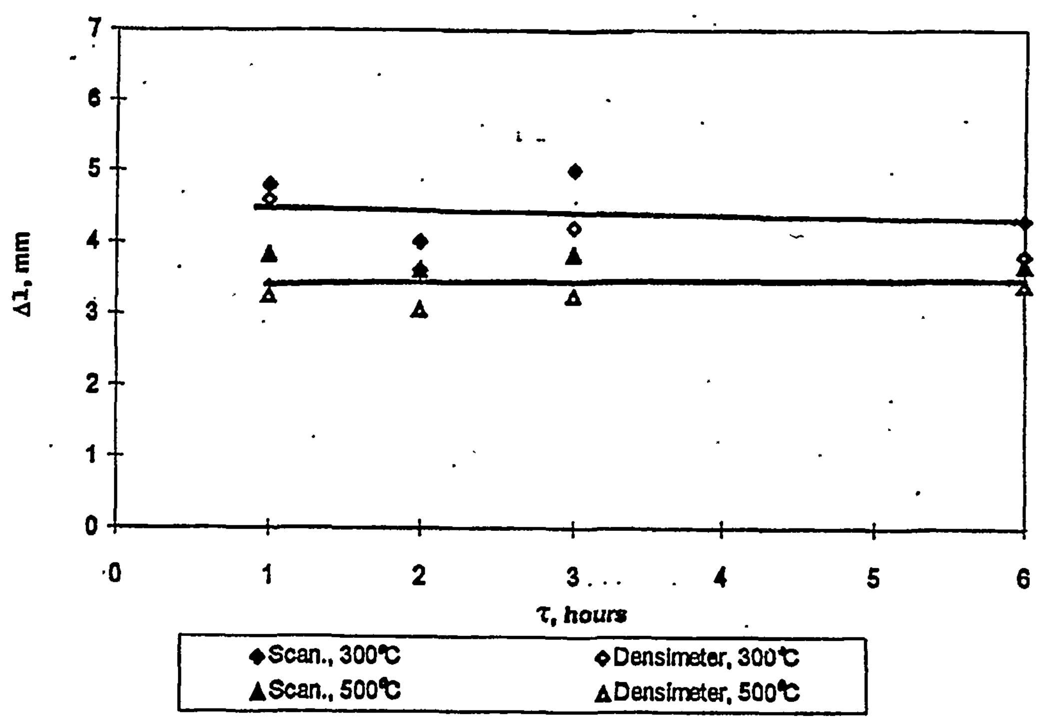

Figure 3.4. Half-Width of the (111) Diffraction Line of $PuO_2 \cdot xH_2O$ as a Function of Heating Time

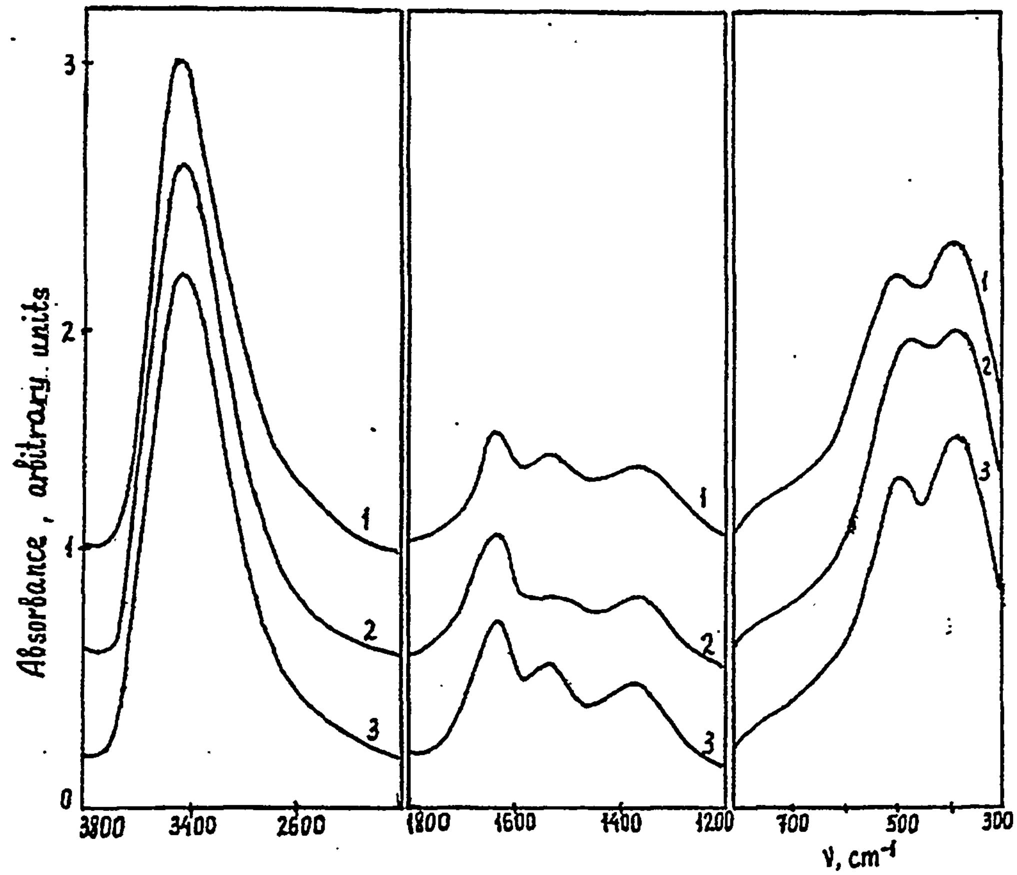

Figure 3.5. Infrared Absorption Spectra of $PuO_2 \cdot xH_2O$ Samples Aged under These Conditions:
1 - 0.2 M NaOH, 12°C, 1 hour
2 - 0.2 M NaOH, 200°C, 5 hours
3 - 8 M NaOH, 100°C, 9 hours

Of the three weak bands in the IR spectra of $PuO_2 \cdot xH_2O$, the one with maximum at 1630 cm^{-1} can be attributed to deformation vibrations of H_2O. Assignment of the other two bands is not clear. The bands' intensities vary from sample to sample and for some samples were not observed at all.

The band in the low frequency region perhaps can be attributed to valent vibrations of Pu-O bonds in the PuO_2 crystallites. The band's splitting into two components with maxima near 480 and 380 cm^{-1} may be explained by the existence two kinds of Pu-O bonds, such as at the inside (Pu-O-Pu) and at the surface (Pu-O) of the crystallites.

The IR spectra of $PuO_2 \cdot xH_2O$ and $ThO_2 \cdot xH_2O$ are similar (Figure 3.6). These spectra also closely resemble that of $NpO_2 \cdot xH_2O$ (Kharitonov 1973). The similarity of the IR spectra of all tetravalent actinide hydrous oxides confirms the similarity of their compositions and structures.

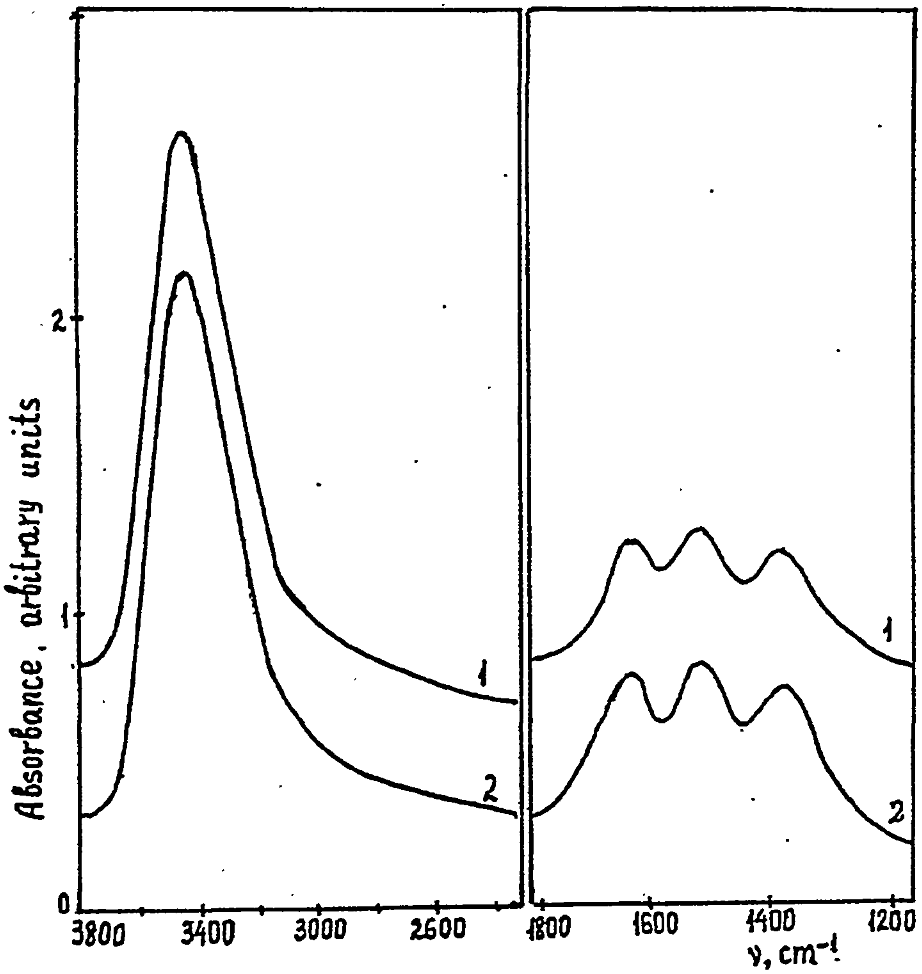

Figure 3.6. Infrared Absorption Spectra of $ThO_2{\cdot}xH_2O$ Samples Aged under These Conditions:
1 - 1 M NaOH, 20°C, 2 hours
2 - 8 M NaOH, 100°C, 5 hours

3.1.5 Sedimentation Rate and Specific Volume of $PuO_2{\cdot}xH_2O$

Data on the specific volumes of hydrous plutonium dioxide after aging under different conditions are of special interest in criticality safety determinations in the retrieval of alkaline waste tank sludge. The specific volumes have a more general significance as a physico-chemical characteristic of $PuO_2{\cdot}xH_2O$ compounds of different origin.

Typical curves of $PuO_2{\cdot}xH_2O$ sedimentation are presented in Figure 3.7. The curves consist of an initial brief induction period followed by more rapid settling and end with lengthy gentle compaction. For compounds obtained by reverse precipitation, the sedimentation process is usually complete in two to three hours. The precipitate volume changes very slowly with additional time. However, some samples of $PuO_2{\cdot}xH_2O$ prepared by direct precipitation require longer times to complete their sedimentation.

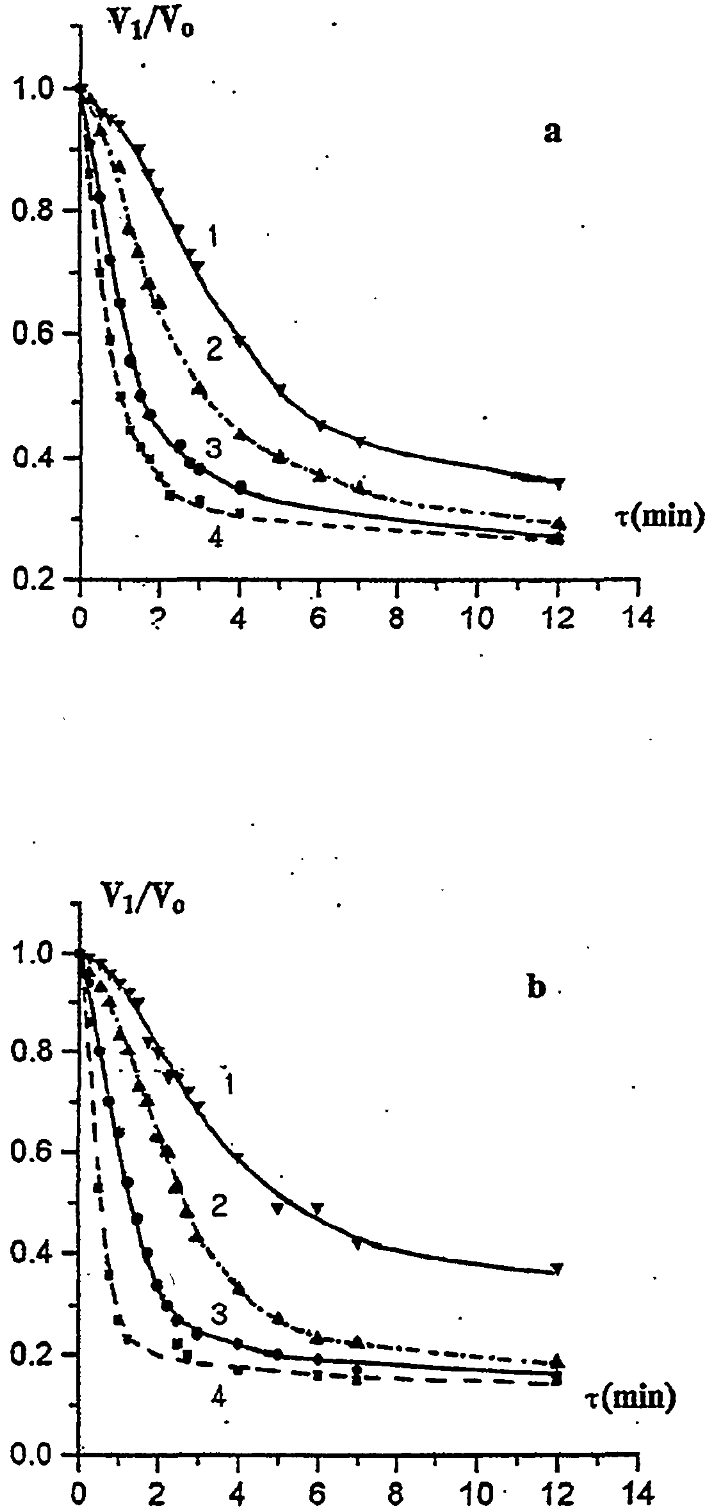

Figure 3.7. Sedimentation of $PuO_2{\cdot}xH_2O$ in
1 - 3 M NaOH / 3 M $NaNO_3$ 2 - 3 M NaOH 3 - 1 M NaOH 4 - H_2O at 20°C
$PuO_2{\cdot}xH_2O$ aging conditions: a) 1 M NaOH, 100°C, five hours; b) 1 M NaOH, 200°C, five hours

A semi-quantitative assessment of $PuO_2{\cdot}xH_2O$ sedimentation rate may be performed by calculating the time required to decrease the precipitate volume halfway between the initial and final volumes ($\tau_{1/2}$). As expected, for each sample, $\tau_{1/2}$ increases with increasing liquid phase density in the sequence H_2O < 1 M NaOH < 3 M NaOH < 3 M NaOH / 3 M $NaNO_3$ (Table 3.10). The influence of aging conditions on the sedimentation rate of $PuO_2{\cdot}xH_2O$ prepared by reverse precipitation is irregular and not well correlated. Only for compounds prepared under hydrothermal conditions at 160 to 200°C are the $\tau_{1/2}$ values in water and 1 M NaOH considerably lower than those found for precipitates prepared at lower temperatures.

Table 3.10. Sedimentation Rate of $PuO_2{\cdot}xH_2O$ Samples Prepared by Reverse Precipitation

Conditions of $PuO_2{\cdot}xH_2O$ aging			$\tau_{1/2}$ for different liquid media, minutes			
[NaOH], M	T, °C	t, h	H_2O	1 M NaOH	3 M NaOH	3 M NaOH / 3 M $NaNO_3$
0.2	22	5	1.4	1.5	1.6	3.8
0.2	60	5	1.8	1.5	3.8	8.2
0.2	100	5	1.4	1.5	2.7	4.8
1	100	5	0.65	1.1	2.0	3.4
3	100	5	1.5	1.4	2.7	4.4
8	100	5	1.0	1.3	2.2	2.9
1	120	5	0.65	1.1	2.7	5.5
1	160	5	0.50	1.0	1.6	4.5
1	200	5	0.45	1.2	2.3	4.2
0.2	180	5	0.60	1.2	2.1	5.8
8	180	5	0.65	1.3	2.5	5.5
3	180	1	1.1	1.3	3.5	--

The method of $PuO_2{\cdot}xH_2O$ preparation prior to aging has a large influence on the precipitate's sedimentation rate (Table 3.11). It is likely that in the transition from acid to alkaline media in the case of direct precipitation it is difficult, from experiment to experiment, to provide identical conditions for the creation of the incipient solid phase, thus giving poor reproducibility of precipitate sedimentation properties.

Table 3.11. Sedimentation Rate of $PuO_2{\cdot}xH_2O$ Samples Prepared by Direct Precipitation

Conditions of $PuO_2{\cdot}xH_2O$ aging			$\tau_{1/2}$ for different liquid media, minutes	
[NaOH], M	T, °C	t, h	H_2O	3 M NaOH
0.6	20	3	5.1	9.8
0.6	100	3	0.7	0.8
0.6	60	3	0.9	6.0
5.1	100	3	2.1	3.2
2.8	100	3	14	18
1.6	100	3	2.1	4.7
0.3	100	3	1	4.0

In contrast to sedimentation rate, the specific volume (V_1) of $PuO_2 \cdot xH_2O$ precipitates after two to three hours of sedimentation are practically independent of liquid phase composition and density (Tables 3.12 and 3.13). However, the specific volumes decrease significantly with $PuO_2 \cdot xH_2O$ aging. Samples coagulated under hydrothermal conditions at 180 to 200°C gave specific volumes after sedimentation about three-fold less than those of precipitates aged at room temperature. Precipitate volumes after centrifugation (V_2) are less sensitive to compound aging conditions. The average specific volumes are about 5 and 7 mL/g Pu for $PuO_2 \cdot xH_2O$ samples prepared by reverse and direct precipitation, respectively.

The observed change of $PuO_2 \cdot xH_2O$ specific volumes can be explained by changes in compound crystallinity and particle size. X-ray powder diffraction measurement show that the $PuO_2 \cdot xH_2O$ crystallite size for samples aged five hours at room and elevated temperatures increases from about 2.5 to about 4.5 nm. This phenomenon likely is accompanied by $PuO_2 \cdot xH_2O$ crystallite agglomeration with aging to form larger and denser particles.

Table 3.12. Specific Volumes of Reverse-Precipitated $PuO_2 \cdot xH_2O$ after Three Hours of Sedimentation (V_1) and after Centrifugation (V_2)

Conditions of $PuO_2 \cdot xH_2O$ aging			V_1 (V_2) for various media, mL/g Pu			
[NaOH], M	T, °C	t, h	H_2O	1 M NaOH	3 M NaOH	3 M NaOH / 3 M $NaNO_3$
0.2	22	0.4	23.9 (5.0)	16.9 (5.0)	14.0 (6.1)	12.6 (5.9)
0.2	22	5	19.4 (6.1)	16.6 (6.5)	17.6 (6.1)	16.6 (5.8)
1.3	22	3	15.9 (7.8)	--	16.6 (4.4)	--
0.2	60	5	21.1 (5.8)	18.0 (6.1)	17.6 (5.4)	15.9 (5.0)
1.3	60	3	16.3 (7.1)	--	22.7 (4.7)	--
0.2	100	5	19.5 (7.2)	16.5 (6.5)	15.0 (5.8)	16.5 (5.4)
1	100	5	15.0 (7.2)	16.5 (5.8)	16.5 (6.1)	15.9 (5.0)
1.3	100	3	14.6 (8.1)	--	17.6 (5.4)	--
3	100	5	16.1 (6.8)	16.1 (7.2)	14.0 (5.4)	12.2 (6.1)
8	100	5	15.9 (5.4)	15.0 (5.8)	12.6 (5.0)	12.2 (5.8)
1	120	5	11.9 (5.4)	12.9 (5.0)	11.9 (5.0)	12.2 (4.7)
1	140	5	8.2 (5.4)	8.6 (5.4)	7.9 (5.0)	7.9 (5.0)
1	160	5	10.1 (5.9)	9.3 (5.2)	9.3 (5.2)	10.8 (3.5)
1	180	5	7.7 (4.7)	8.4 (4.4)	7.4 (4.1)	7.4 (4.1)
1	200	5	7.7 (5.1)	7.7 (5.1)	7.4 (4.7)	7.4 (4.4)
0.2	180	5	8.8 (4.4)	8.5 (3.7)	8.8 (3.0)	9.1 (3.4)
3	180	5	8.4 (4.1)	8.4 (4.4)	8.1 (4.1)	7.40 (3.4)
8	180	5	8.8 (4.7)	9.5 (4.7)	9.5 (4.1)	9.5 (3.7)
3	180	1	10.5 (5.1)	11.5 (4.4)	1.5 (3.4)	-- (--)
3	180	10	5.0 (5.1)	5.7 (4.7)	5.4 (4.7)	5.4 (5.0)

Table 3.13. Specific Volumes of Direct-Precipitated $PuO_2 \cdot xH_2O$ after Three Hours of Sedimentation (V_1) and after Centrifugation (V_2)

Conditions of $PuO_2 \cdot xH_2O$ aging			V_1 (V_2) for various media, mL/g Pu	
[NaOH], M	T, °C	t, h	H_2O	3 M NaOH
0.6	20	3	17.0 (7.1)	10.2 (6.1)
0.6	100	3	21.3 (7.8)	16.2 (7.4)
0.6	60	3	19.4 (7.7)	16.1 (7.0)
5.1	100	3	18.3(6.6)	16.8(5.3)
2.8	100	3	22.0 (8.1)	19.6 (5.8)
1.6	100	3	20.0(7.0)	17.0(6.3)
0.3	100	3	25.4 (8.1)	23.7 (6.8)

3.1.6 Rate and Completeness of Pu(IV) Hydrous Oxide Precipitation

Study of the rate and completeness of $PuO_2 \cdot xH_2O$ precipitation under different conditions has practical interest. As shown in Table 3.14, the plutonium concentration in suspension decreases with increasing time. Plutonium concentrations remain high, however, even after one day of coagulation and settling. The high concentrations likely are the result of precipitation of $PuO_2 \cdot xH_2O$ through the formation of colloids and very fine particles. These particles remain in suspension even after centrifugation. The existence of fine particles is supported by the fact that plutonium concentrations in the centrifuged suspensions are widely scattered. Ultrafiltration (2-nm pore size filters) decreases plutonium concentrations in the mother solutions about a factor of 100 versus that found for settling (Table 3.15), giving additional evidence of fine particles. Plutonium concentrations in mother solutions over one-day aged $PuO_2 \cdot xH_2O$ are about a factor of 10 higher than those observed for similar centrifuged solutions. The centrifuged solutions, in turn, are about an order of magnitude higher in plutonium concentration than those observed in this and related published studies for the (ultrafiltered) solubility of the compounds in similar aerated NaOH solutions (Figure 3.8). The plutonium concentrations are not clearly affected by the volume of stock plutonium (V_{Pu}) used in the tests. The volume was varied to investigate the effects of possible Pu(IV) disproportionation in the reaction with NaOH solution.

Table 3.14. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions; Phase Separation by Centrifugation

Precipitation conditions				[Pu] after coagulation, M			
Kind	V_{Pu}, mL	[NaOH], M	T, °C	2 min	15 min	40 min	1 day
Direct	0.1	0.2	20	7.5×10^{-6}	1.2×10^{-6}	1.0×10^{-6}	9.0×10^{-7}
		1		1.9×10^{-6}	1.1×10^{-6}	1.1×10^{-6}	9.0×10^{-7}
		4		7.5×10^{-5}	2.7×10^{-5}	--	1.7×10^{-6}
		8		1.7×10^{-5}	1.5×10^{-5}	--	6.5×10^{-6}
	0.05	1	20	2.1×10^{-5}	1.9×10^{-6}	--	1.2×10^{-6}
	0.1			1.3×10^{-5}	4.1×10^{-6}	--	1.1×10^{-6}
	0.2			1.4×10^{-5}	6.7×10^{-6}	--	8.7×10^{-6}
	0.6			2.4×10^{-5}	7.5×10^{-6}	--	9.5×10^{-7}
	0.2	1	40	2.3×10^{-5}	6.3×10^{-6}	--	1.1×10^{-6}
			60	4.3×10^{-5}	4.1×10^{-5}	--	8.7×10^{-7}
			80	3.4×10^{-5}	4.2×10^{-5}	--	8.4×10^{-7}
Reverse	0.2	0.2	20	1.0×10^{-5}	5.0×10^{-6}	4.3×10^{-6}	1.2×10^{-6}
		4	20	1.8×10^{-5}	2.7×10^{-6}	2.4×10^{-6}	2.0×10^{-6}
		0.2	60	3.3×10^{-6}	1.9×10^{-6}	1.2×10^{-6}	9.2×10^{-7}
		4	60	7.5×10^{-6}	3.4×10^{-6}	2.8×10^{-6}	2.4×10^{-6}
		0.2	100	1.8×10^{-6}	1.1×10^{-6}	--	7.2×10^{-7}
		4	100	5.1×10^{-6}	2.1×10^{-6}	--	1.8×10^{-6}
	0.1	0.2	100	1.2×10^{-5}	6.1×10^{-6}	3.3×10^{-6}	1.0×10^{-6}
		4	100	1.7×10^{-5}	2.3×10^{-6}	2.1×10^{-6}	1.9×10^{-6}
		0.2	20	2.3×10^{-5}	8.3×10^{-6}	--	9.2×10^{-7}
		4	20	3.5×10^{-5}	1.1×10^{-5}	--	1.4×10^{-6}
	0.05	1	60	2.8×10^{-5}	1.8×10^{-6}	--	9.5×10^{-7}
		1	60	3.9×10^{-5}	1.9×10^{-6}	--	7.5×10^{-7}
	0.1	1	60	2.7×10^{-5}	3.1×10^{-6}	--	1.1×10^{-6}
		1	60	4.7×10^{-5}	2.1×10^{-6}	--	9.7×10^{-7}
	0.2	1	60	3.4×10^{-5}	3.5×10^{-6}	--	8.9×10^{-7}
		1	60	4.4×10^{-5}	3.8×10^{-6}	--	1.3×10^{-6}

Table 3.15. Completeness of Pu(IV) Precipitation from Alkaline Solutions; Phase Separation by Ultrafiltration

Precipitation conditions			[Pu] before and after filtration, M			
			Aging 20 min		Aging 1 day	
Kind	[NaOH], M	T, °C	Before	After	Before	After
Direct	0.11	22	3.1×10^{-6}	1.2×10^{-8}	--	--
	0.20	22	9.7×10^{-6}	4.6×10^{-8}	2.4×10^{-6}	7.5×10^{-8}
	0.91	22	4.1×10^{-6}	3.9×10^{-8}	--	--
	2.0	22	1.3×10^{-5}	1.7×10^{-7}	4.0×10^{-6}	4.3×10^{-8}
	8.0	22	9.1×10^{-5}	1.7×10^{-6}	9.7×10^{-6}	4.1×10^{-6}

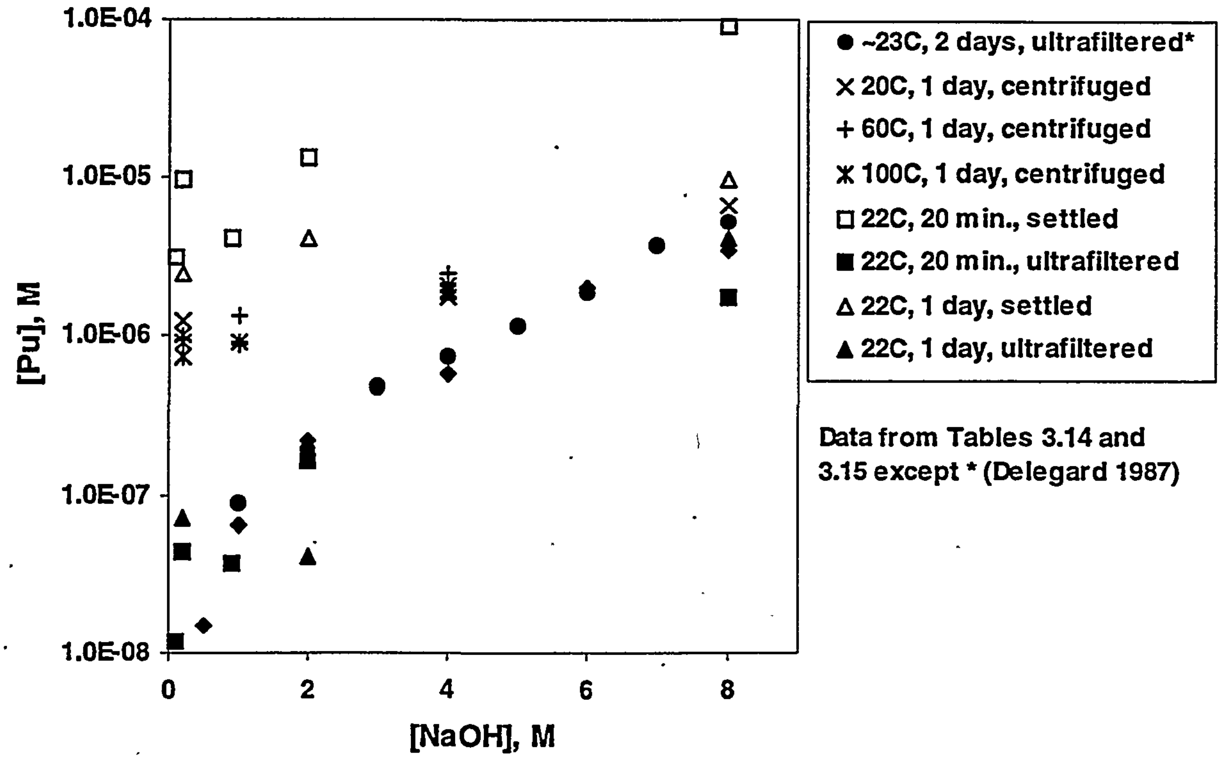

Figure 3.8. Gravity Settled, Centrifuged, and Ultrafiltered Plutonium Concentrations

3.2. Influence of Tank Waste Anions on $PuO_2 \cdot xH_2O$ Precipitation

3.2.1 The Influence of Nitrite, Oxalate, Sulfate, Carbonate, Citrate, Chromate, Ferrocyanide, Glycolate, EDTA, and HEDTA

Special investigations were performed to determine the influence of anions present in tank wastes on Pu(IV) precipitation by NaOH. In preliminary experiments, Pu(IV) was precipitated by the reverse method at 60°C from 1 M NaOH solutions containing different anions. The experiments showed that the plutonium compounds precipitated in the presence of 2 M NO_2^-; 0.5 M SO_4^{2-} or CO_3^{2-}; or 0.1 M $C_2O_4^{2-}$, EDTA,[(a)] HEDTA,[(b)] or citrate had, after careful water washing, the same composition and hygroscopic properties as the $PuO_2 \cdot xH_2O$ obtained by precipitating Pu(IV) from pure NaOH solutions. The IR spectra of the final products also exhibited no bands that could be attributed to absorption of the tested anions. However, remarkably distinct behavior was observed upon the precipitation of Pu(IV) in the presence of silicate and phosphate. The observations arising from tests with silicate and phosphate will be considered in detail separately.

(a) EDTA is ethylenediaminetetraacetate.
(b) HEDTA is *N*-2-hydroxyethylethylenediaminetriacetate.

Additional experiments on Pu(IV) precipitation were performed at room temperature from 0.2 M NaOH containing various anions. The product precipitates were coagulated three hours, carefully washed with water, and aged ~one hour in 5.5 M NaOH in a boiling water bath. The precipitates then were centrifuged and washed with water. The mother solutions and associated wash waters were analyzed for the corresponding anions. Nitrite was determined by a spectrophotometric method using sulfanylic acid and α-naphthylamine (Lur'e 1971). Concentrations of EDTA and HEDTA were determined by complexometric titration at pH ~2 with a standard 3×10^{-3} M $Th(NO_3)_4$ solution. Chromate concentrations were determined by direct measurement of light absorption at 372 nm. A spectrophotometric method also was used to measure $Fe(CN)_6^{4-}$ concentration. In this case, optical density was measured at 420 nm after persulfate oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$. Oxalate was measured by titration with $KMnO_4$ in ~1 M H_2SO_4. To confirm the absence of sulfate, the analyzed solution was neutralized with $HClO_4$ and mixed with $Ba(ClO_4)_2$. Carbonate was determined directly in the washed Pu(IV) precipitate by treating the precipitate with HNO_3 in a flow of Ar and capturing the evolved CO_2 in a $Ba(OH)_2$ solution.

As seen in Table 3.16, the coprecipitation of anions usually was below the sensitivity of the chosen analytic method. Exceptions occurred only for NO_2^- and CrO_4^{2-}. In both cases, however, the nitrite and chromate contents in the Pu(IV) precipitates were low and near their detection limits.

Table 3.16. Anion Content in $PuO_2{\cdot}xH_2O$ Precipitated from 0.2 M NaOH at 20°C in the Presence of Various Anions

Anion, A	[A] in NaOH solution, M	Mol% A in $PuO_2{\cdot}xH_2O$	Anion, A	[A] in NaOH solution, M	Mol% A in $PuO_2{\cdot}xH_2O$
NO_2^-	2	7	CrO_4^{2-}	0.2	2
EDTA	0.1	≤0.4	SO_4^{2-}	0.2	<0.01
HEDTA	0.1	<1	CO_3^{2-}	0.2	<0.1
$C_2O_4^{2-}$	0.1	<5	$Fe(CN)_6^{4-}$	0.2	<0.1

The listed anions did not significantly alter the rate or completeness of $PuO_2{\cdot}xH_2O$ precipitation (Tables 3.17 to 3.23). The expected increase of $PuO_2{\cdot}xH_2O$ solubility in the presence of carbonate and EDTA may have been obscured by the rather high concentration of fine plutonium hydrous oxide particles in the mother solutions after centrifugation.

Table 3.17. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of EDTA

Precipitation conditions				[Pu] after coagulation, M		
Kind	[EDTA], M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Direct	0.03	0.2	20	2.4×10^{-5}	1.6×10^{-5}	9.8×10^{-6}
		4	20	6.0×10^{-5}	2.7×10^{-5}	9.7×10^{-6}
		0.2	100	3.0×10^{-5}	8.9×10^{-6}	5.1×10^{-6}
		4	100	8.0×10^{-5}	1.9×10^{-5}	8.2×10^{-6}
Direct	0.1	0.2	20	2.7×10^{-5}	1.3×10^{-5}	9.4×10^{-6}
		4	20	6.4×10^{-5}	2.1×10^{-5}	1.1×10^{-5}
		0.2	100	4.1×10^{-5}	1.1×10^{-5}	6.2×10^{-6}
		4	100	6.1×10^{-5}	1.1×10^{-5}	8.6×10^{-6}

Table 3.18. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of HEDTA

Precipitation conditions				[Pu] after coagulation, M		
Kind	[HEDTA], M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Direct	0.03	0.2	20	2.3×10^{-5}	9.2×10^{-6}	1.4×10^{-6}
		4	20	6.7×10^{-5}	3.1×10^{-5}	1.2×10^{-5}
		0.2	100	2.7×10^{-5}	6.2×10^{-6}	2.7×10^{-6}
		4	100	4.3×10^{-5}	1.2×10^{-5}	7.4×10^{-6}
Direct	0.1	0.2	20	3.1×10^{-5}	1.4×10^{-5}	2.3×10^{-6}
		4	20	4.5×10^{-5}	2.3×10^{-5}	9.8×10^{-6}
		0.2	100	4.5×10^{-5}	8.3×10^{-6}	4.1×10^{-6}
		4	100	3.9×10^{-5}	1.4×10^{-5}	6.6×10^{-6}

Table 3.19. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of $C_2O_4^{2-}$

Precipitation conditions				[Pu] after coagulation, M		
Kind	$[C_2O_4^{2-}]$, M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Direct	0.02	0.2	20	2.0×10^{-5}	5.9×10^{-6}	8.7×10^{-7}
		4	20	2.9×10^{-5}	7.4×10^{-6}	9.1×10^{-7}
		0.2	100	3.8×10^{-6}	2.4×10^{-6}	9.9×10^{-7}
		4	100	6.3×10^{-6}	3.4×10^{-6}	1.3×10^{-6}
Direct	0.05	0.2	20	3.4×10^{-5}	9.3×10^{-6}	8.2×10^{-7}
		4	20	4.6×10^{-5}	7.1×10^{-6}	9.7×10^{-7}
		0.2	100	6.8×10^{-6}	1.7×10^{-6}	1.2×10^{-6}
		4	100	7.9×10^{-6}	6.7×10^{-6}	1.5×10^{-6}

Table 3.20. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of NO_2^-

Precipitation conditions				[Pu] after coagulation, M		
Kind	$[NO_2^-]$, M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Reverse	0.1	0.2	20	$8.3x10^{-6}$	$8.9x10^{-6}$	$8.2x10^{-7}$
		4	20	$2.6x10^{-5}$	$6.4x10^{-6}$	$1.1x10^{-6}$
		0.2	100	$2.7x10^{-6}$	$1.5x10^{-6}$	$7.9x10^{-7}$
		4	100	$4.1x10^{-6}$	$2.0x10^{-6}$	$7.9x10^{-7}$
	0.5	0.2	20	$4.3x10^{-5}$	$7.4x10^{-6}$	$6.2x10^{-7}$
		4	20	$2.6x10^{-5}$	$8.2x10^{-6}$	$8.1x10^{-7}$
		0.2	100	$3.4x10^{-6}$	$2.2x10^{-6}$	$1.1x10^{-6}$
		4	100	$4.9x10^{-6}$	$3.1x10^{-6}$	$1.2x10^{-6}$

Table 3.21. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of $HOCH_2CO_2^-$

Precipitation conditions				[Pu] after coagulation, M		
Kind	$[HOCH_2CO_2^-]$, M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Reverse	0.2	0.2	20	$8.3x10^{-5}$	$8.9x10^{-6}$	$4.4x10^{-6}$
		4	20	$9.6x10^{-5}$	$6.4x10^{-5}$	$1.1x10^{-5}$
		0.2	100	$2.7x10^{-5}$	$1.5x10^{-5}$	$3.9x10^{-6}$
		4	100	$4.9x10^{-5}$	$1.7x10^{-5}$	$9.4x10^{-6}$
	0.5	0.2	20	$4.3x10^{-5}$	$7.4x10^{-6}$	$4.2x10^{-6}$
		4	20	$2.6x10^{-5}$	$1.2x10^{-5}$	$8.3x10^{-6}$
		0.2	100	$3.9x10^{-5}$	$7.4x10^{-6}$	$3.1x10^{-6}$
		4	100	$5.7x10^{-5}$	$8.8x10^{-6}$	$9.2x10^{-6}$

Table 3.22. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of Citrate

Precipitation conditions				[Pu] after coagulation, M		
Kind	[Citrate], M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Reverse	0.01	0.2	20	$8.3x10^{-5}$	$1.9x10^{-5}$	$2.2x10^{-6}$
		4	20	$9.6x10^{-5}$	$2.4x10^{-5}$	$5.1x10^{-6}$
		0.2	100	$8.7x10^{-5}$	$1.5x10^{-5}$	$1.9x10^{-6}$
		4	100	$7.3x10^{-5}$	$1.3x10^{-5}$	$4.4x10^{-6}$
	0.05	0.2	20	$4.3x10^{-5}$	$6.4x10^{-6}$	$2.1x10^{-6}$
		4	20	$3.7x10^{-5}$	$2.2x10^{-5}$	$7.1x10^{-6}$
		0.2	100	$4.5x10^{-5}$	$2.3x10^{-6}$	$1.1x10^{-5}$
		4	100	$2.9x10^{-5}$	$9.1x10^{-6}$	$6.2x10^{-6}$

Table 3.23. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of CO_3^{2-}

Precipitation conditions				[Pu] after coagulation, M		
Kind	$[CO_3^{2-}]$, M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Reverse	0.1	0.2	20	4.3×10^{-5}	9.9×10^{-6}	3.2×10^{-6}
		4	20	5.6×10^{-5}	1.4×10^{-5}	8.1×10^{-6}
		0.2	100	2.3×10^{-5}	8.8×10^{-6}	4.3×10^{-6}
		4	100	4.5×10^{-5}	9.5×10^{-6}	8.4×10^{-6}
	0.2	0.2	20	5.2×10^{-5}	2.0×10^{-5}	3.4×10^{-6}
		4	20	6.1×10^{-5}	8.4×10^{-6}	7.3×10^{-6}
		0.2	100	3.1×10^{-5}	1.9×10^{-5}	4.7×10^{-6}
		4	100	5.3×10^{-5}	9.7×10^{-6}	6.8×10^{-6}
	0.4	0.2	20	5.1×10^{-5}	1.4×10^{-5}	2.8×10^{-6}
		4	20	7.4×10^{-5}	9.2×10^{-6}	6.2×10^{-6}
		0.2	100	3.9×10^{-5}	1.1×10^{-5}	3.1×10^{-6}
		4	100	4.9×10^{-5}	1.3×10^{-5}	9.3×10^{-6}
	1.0	0.2	20	6.4×10^{-5}	2.2×10^{-5}	4.1×10^{-6}
		4	20	6.9×10^{-5}	1.3×10^{-5}	9.1×10^{-6}
		0.2	100	4.3×10^{-5}	1.2×10^{-5}	5.2×10^{-6}
		4	100	3.8×10^{-5}	1.2×10^{-5}	1.2×10^{-5}

3.2.2 The Influence of Silicate and Phosphate

In contrast to the situations observed for anions considered in the previous section, Pu(IV) precipitation characteristics were remarkably altered for alkaline solutions containing silicate or phosphate. For both silicate and phosphate, the color of the precipitates was greenish-gray rather than the green observed in the presence (or absence) of the other anions. An increase in the specific volumes of the precipitates also was evident. Water washing of the precipitates produced significant peptization. These results prompted further study of Pu(IV) precipitation in the presence of silicate and phosphate.

The IR spectra of products obtained by Pu(IV) alkali precipitation in the presence of silicate show a very intense absorption band with maximum at 1000 cm^{-1} and two shoulders (Figure 3.8). This band is attributed to valent vibrations of silicate. A shoulder also is observed on a strong absorption band attributed to the valent vibration of water. These unique IR spectral features indicate that large amounts of silicate are present in the products being examined. This conclusion was confirmed by direct analyses of Pu(IV) compounds precipitated from alkaline solutions in the presence of silicate. The data in Table 3.24 show that the compounds precipitated and coagulated at low NaOH concentration behave more like Pu(IV) silicates than Pu(IV) hydrous oxides. Significant amounts of silicate were detected even in the products obtained from precipitation from 7 M NaOH. In addition, silicate was found to interact with $PuO_2 \cdot xH_2O$ prepared separately under hydrothermal conditions. The interaction of silicate and

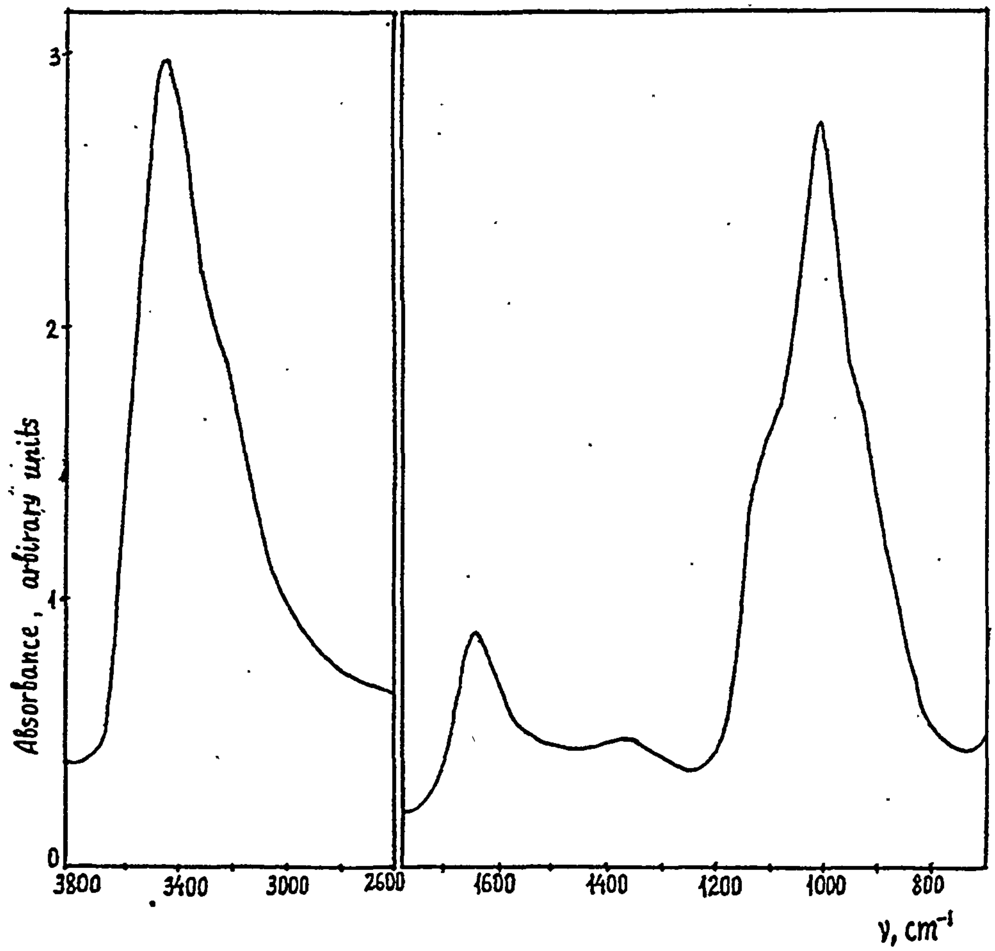

Figure 3.9. Infrared Absorption Spectrum of $PuO_2 \cdot 0.88SiO_2 \cdot xH_2O$

Table 3.24. Composition of $PuO_2 \cdot ySiO_2 \cdot xH_2O$ Compounds Obtained by Pu(IV) Precipitation from Alkaline Solutions in the Presence of Silicate at 20°C

Conditions of precipitation			Conditions of coagulation			y
Type	[NaOH], M	$[SiO_3^{2-}]$, M	[NaOH], M	T, °C	t, h	
Direct	0.2	0.05	0.2	20	3	1.36
	0.2	0.05	0.2	100	3	1.38
Reverse	1	0.05	1	20	3	0.88
	0.2	0.05	0.2	20	5	1.78
	1	0.05	1	60	3	1.60
	7	0.05	7	100	3	0.30
	1	0.05	1	100	2	0.50(a)
	1	0.05	1	100	2	0.82(b)

(a) Interaction of 1 M NaOH / 0.05M Na_2SiO_3 with $PuO_2 \cdot xH_2O$ samples obtained under hydrothermal conditions at 120°C.
(b) Interaction of 1 M NaOH / 0.05M Na_2SiO_3 with $PuO_2 \cdot xH_2O$ samples obtained under hydrothermal conditions at140°C.

solid phase $PuO_2 \cdot xH_2O$ forms compounds of composition similar to those products precipitated directly from the respective alkaline silicate solutions. X-ray powder diffraction patterns of these products have practically no lines of PuO_2 crystallites.

Based on these results, it is concluded that $PuO_2 \cdot xH_2O$ cannot be present in alkaline tank wastes containing significant silicate concentrations. Under such conditions, Pu(IV) should exist as various basic silicates according to the waste composition. However, this conclusion requires additional study and may be complicated by the behavior of mixed hydroxides of Pu(IV) and Fe(III) or other elements in alkaline silicate media. This problem, too, requires special investigation.

The precipitation behavior of Pu(IV) in alkali is similar in the presence of phosphate and silicate. However, the degree of anion capture and the stability of the product compounds at high NaOH concentration for phosphate are significantly lower than for silicate (Table 3.25). Infrared spectra of basic Pu(IV) phosphates have a characteristic strong and complex band with maximum at 1020 cm^{-1} (Figure 3.9).

The completeness of Pu(IV) precipitation from silicate- and phosphate-bearing alkaline solutions is somewhat lower than from similar pure NaOH media (Tables 3.26 and 3.27). Part of the reason may be that the precipitate peptizes upon washing with water or dilute electrolytes.

Table 3.25. Composition of $PuO_2 \cdot yP_2O_5 \cdot xH_2O$ Compounds Obtained by Pu(IV) Precipitation from Alkaline Solutions in the Presence of Phosphate at 20°C

Conditions of precipitation			Conditions of coagulation			y
Type	[NaOH], M	$[PO_4^{3-}]$, M	[NaOH], M	T, °C	t, h	
Direct	0.2	0.05	0.2	20	4 d	0.15
	0.2	0.05	0.2	100	3	0.15
	0.5	0.04	0.5	100	3	0.12
	1	0.04	1	100	3	0.08
	3.6	0.04	3.6	100	3	0.03
	12	0.04	12	100	3	0.01
Reverse	1	0.04	1	20	3	0.10
	1	0.04	1	60	3	0.09
	1	0.05	1	100	3	0.11
	2	0.04	2	100	3	0.07
	0.2	0.05	0.2	20	3	0.14
	0.2	0.05	0.2	60	3	0.15
	0.2	0.05	0.2	100	3	0.12
	0.2	0.05	0.2	100	3	0.14

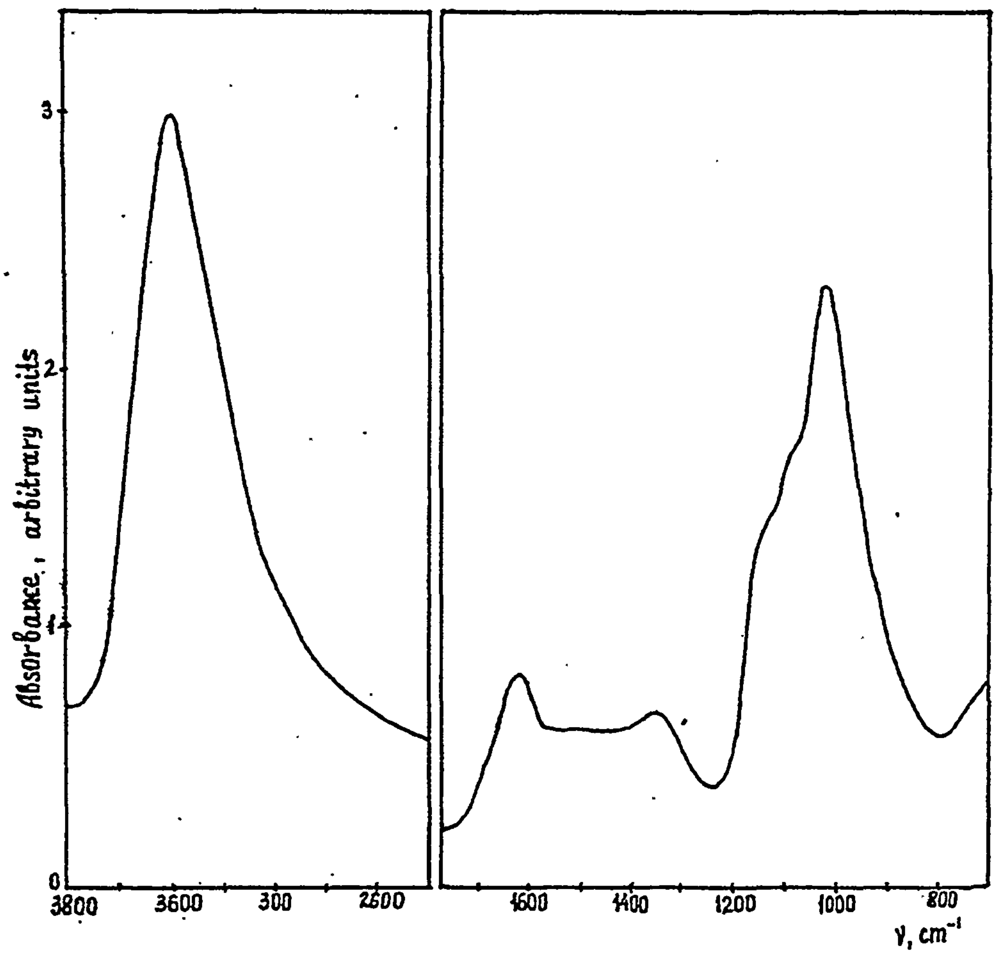

Figure 3.10. Infrared Absorption Spectrum of $PuO_2 \cdot 0.15\ P_2O_5 \cdot xH_2O$

Table 3.26. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of SiO_3^{2-}

Precipitation conditions				[Pu] after coagulation, M		
Kind	$[SiO_3^{2-}]$, M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Reverse	0.02	0.2	20	1.3×10^{-5}	6.0×10^{-6}	3.5×10^{-6}
		4	20	1.1×10^{-4}	3.0×10^{-5}	2.0×10^{-5}
		0.2	100	1.7×10^{-5}	1.3×10^{-5}	1.3×10^{-5}
		4	100	2.0×10^{-5}	1.9×10^{-5}	1.8×10^{-5}
	0.1	0.2	20	1.7×10^{-5}	8.2×10^{-6}	5.0×10^{-6}
		4	20	8.0×10^{-5}	4.2×10^{-5}	2.7×10^{-5}
		0.2	100	2.0×10^{-5}	1.8×10^{-5}	1.4×10^{-5}
		4	100	2.9×10^{-5}	2.7×10^{-5}	2.0×10^{-5}

Table 3.27. Rate and Completeness of Pu(IV) Precipitation from Alkaline Solutions in the Presence of PO_4^{3-}

Precipitation conditions				[Pu] after coagulation, M		
Kind	$[PO_4^{3-}]$, M	[NaOH], M	T, °C	2 minutes	15 minutes	1 day
Reverse	0.03	0.2	20	$1.1x10^{-5}$	$4.9x10^{-6}$	$2.0x10^{-6}$
		4	20	$7.3x10^{-5}$	$2.1x10^{-5}$	$1.4x10^{-5}$
		0.2	100	$2.5x10^{-6}$	$2.5x10^{-6}$	$2.4x10^{-6}$
		4	100	$3.2x10^{-5}$	$1.8x10^{-5}$	$1.0x10^{-5}$
	0.1	0.2	20	$1.4x10^{-5}$	$7.2x10^{-6}$	$2.1x10^{-6}$
		4	20	$4.1x10^{-5}$	$2.7x10^{-5}$	$2.0x10^{-5}$
		0.2	100	$9.9x10^{-6}$	$8.0x10^{-6}$	$7.3x10^{-6}$
		4	100	$4.0x10^{-5}$	$3.1x10^{-5}$	$2.3x10^{-5}$

4.0 Conclusions

Several general conclusions can be drawn concerning the composition and properties of Pu(IV) hydrous oxide compounds precipitated from alkaline solutions of different compositions. First, $PuO_2 \cdot xH_2O$ is relatively stable and does not readily transform to well-crystallized plutonium dioxide with long-term aging. The Pu(IV) hydrous oxide consists of very small PuO_2 crystallites and retains water with continuous range of bonding energy. Part of the water is easily lost, but this process is reversible. The composition and properties of $PuO_2 \cdot xH_2O$ are not strongly altered by long-term aging, as modeled by heating the compound under hydrothermal conditions.

The stability of semi-amorphous $PuO_2 \cdot xH_2O$ to transformation into crystalline dioxide upon aging is a very important and favorable property for criticality safety in the retrieval and treatment of alkaline tank waste. This is because crystalline PuO_2 has high density and an apparent low tendency to agglomerate with amorphous hydroxide compounds present in alkaline tank waste. Therefore, crystalline PuO_2 could more easily concentrate during tank waste treatment operations than the semi-amorphous $PuO_2 \cdot xH_2O$.

Precipitation of $PuO_2 \cdot xH_2O$ from alkaline media produces a solid phase and very fine particles that remain in suspension in the supernatant solution. Because of the fine particles, plutonium concentrations found in centrifuged mother solutions over $PuO_2 \cdot xH_2O$ are about two to three orders of magnitude higher than the observed solubility of this compound. The ready suspension of $PuO_2 \cdot xH_2O$ should be taken into account in choosing methods for the separation and purification of alkaline liquid tank wastes from plutonium.

The specific volumes of $PuO_2 \cdot xH_2O$ precipitates after two to three hours of sedimentation are practically independent of the liquid phase composition and are about 20 mL/g Pu for slightly aged samples. The specific volumes decrease with $PuO_2 \cdot xH_2O$ aging and become about 7 mL/g Pu for samples coagulated five hours under 180 to 200°C hydrothermal conditions. Thus, plutonium concentration in the retrieved sediments of alkaline tank wastes cannot exceed 150 g/L. The actual plutonium concentration should be significantly lower because of agglomeration of $PuO_2 \cdot xH_2O$ with other components of tank sludge or by formation of Pu(IV) mixed hydroxides with different elements.

Plutonium(IV) hydrous oxide does not interact with sodium ion, nitrate, nitrite, sulfate, carbonate, oxalate, citrate, EDTA, or HEDTA to form separate compounds. However, Pu(IV) hydrous oxide can react in alkaline media with silicate and, to a lesser extent, with phosphate. Thus, the Pu(IV) compounds precipitated from alkaline solution in the presence of 0.05 M SiO_3^{2-} at low NaOH concentrations more likely are silicates than $PuO_2 \cdot xH_2O$. Significant amounts of silicate even are incorporated into products obtained in 7 M NaOH. Plutonium(IV) hydrous oxide prepared separately under hydrothermal conditions retains its ability to form silicate-containing products. Because of the strong observed interaction of Pu(IV) with silicate, it is reasonable to conclude that $PuO_2 \cdot xH_2O$ cannot be present in alkaline tank wastes containing significant silicate concentrations. Under such conditions, Pu(IV) should exist as various basic silicates. The Pu(IV) basic silicates, in contrast to $PuO_2 \cdot xH_2O$, also are readily peptized.

However, this conclusion may be complicated by the unknown behavior of mixed hydroxides of Pu(IV) with other elements present in alkaline silicate media. Resolution of this question requires special investigation.

In conclusion, it is noted that the problem of criticality safety arising from treatment of wastes containing plutonium or enriched uranium also may be addressed by using neutron poisons. In this approach, borate may be added to the alkaline wastes' solution phase. It is well known that most of the volume of any sludge or hydroxide precipitate is comprised of a solution phase. Borates have high solubility in NaOH solutions. Therefore, it is reasonable to suppose that added borate will be uniformly distributed throughout the sludge and precipitate volume. Calculations show (Whyatt et al. 1996) that in the presence of 1 g boron/L, the threshold plutonium concentration posing a criticality hazard increases about four-fold. With this in mind, it would desirable to consider in detail the state and behavior of borate in complex heterogeneous systems modeling the Hanford Site tank wastes of different origins.

5.0 References

Bell JT, DA Costanzo, and RE Biggers. 1973a. "Plutonium Polymerization - II. Kinetics of the Plutonium(IV) Polymerization." *Journal of Inorganic and Nuclear Chemistry,* 35(2):623-628.

Bell JT, CF Coleman, DA Costanzo, and RE Biggers. 1973b. "Plutonium Polymerization - III. The Nitrate Precipitation of Pu(IV) Polymer." *Journal of Inorganic and Nuclear Chemistry,* 35(2):629-632.

Costanzo DA, RE Biggers, and JT Bell. 1973. "Plutonium Polymerization - 1. A Spectrophotometric Study of the Polymerization of Plutonium(IV)." *Journal of Inorganic and Nuclear Chemistry,* 35(2):609-622.

Cousson A, H Abazli, F Nectoux, J Jove, M Pages, and M Gasperin. 1986. "Hydroxides of Neptunium(IV): Crystal Structure of Ammonium Neptunium Hydroxide $(NH_4)Np(OH)_5$ and Moessbauer Resonance Study of $Np(OH)_4$." *Journal of Less-Common Metals* 121:405-414.

Delegard CH. 1987. "Solubility of $PuO_2{\cdot}xH_2O$ in Alkaline Hanford High-Level Waste Solution." *Radiochimica Acta,* 41(1):11-21. Also published as RHO-RE-SA-75 P, Rockwell Hanford Company, Richland, Washington (1985).

Haire RG, MH Lloyd, ML Beasley, and WO Milligan. 1971. "Aging of Hydrous Plutonium Dioxide." *Journal of Electron Microscopy,* 20(1):8-16.

Kharitonov YY and AI Moskvin. 1973. "Investigation of the IR Spectra of Some Neptunium Compounds. I. Hydroxide, Nitrates, and Sulfates." *Radiokhimiya,* 15(20):181-185. Published in English in *Soviet Radiochemistry.*

Kraus K. 1949. "Hydrolytic Behavior of Plutonium(IV). Analysis of Hydroxide Precipitates from Plutonium(IV) Solutions" Paper 4.17 in *The Transuranium Elements,* GT Seaborg, JJ Katz, and WM Manning, eds. National Nuclear Energy Series, Div. IV, Vol. 14B, Part I, pp. 519-527. McGraw-Hill Book Co., New York.

Louwrier KP, C Ronchi, T Steemers, and E Zamorani. 1968. "Sol-Gel Process for Plutonium Oxide at the European Institute for Transuranium Elements." *Proceedings of Sol-Gel Processes for Ceramic Nuclear Fuel,* p. 97-106. International Atomic Energy Agency, Vienna.

Lur'e YY, ed. 1971. *Unified Methods of Analysis of Water,* p. 376. Khimiya Publishing, Moscow (in Russian).

Neu MP, RK Schulze, SD Conradson, JD Farr, and RG Haire. 1997. "Polymeric Plutonium(IV) Hydroxide: Formation, Prevalence, and Structural and Physical Characteristics." *Plutonium Futures - The Science; Topical Conference on Plutonium and Actinides.* Santa Fe, New Mexico.

Ockenden DW and GA Welch. 1956. "The Preparation and Properties of Some Plutonium Compounds. V. Colloidal Quadrivalent Plutonium." *Journal of the Chemical Society,* (9):3358-3363.

Peretrukhin VF, SV Kryutchkov, VI Silin, and IG Tananaev. 1996. *Determination of the Solubility of Np(IV)-(VI), Pu(III)-(VI), Am(III)-(VI) and Tc(IV,V) Hydroxo Compounds in 0.5-14 M NaOH Solutions*. WHC-EP-0897, Westinghouse Hanford Company, Richland, Washington.

Rabideau SW. 1957. "The Hydrolysis of Plutonium(IV)." *Journal of the American Chemical Society*, 79(14):3675-3677.

Rabideau SW and RJ Kline. 1960. "A Spectrophotometric Study of the Hydrolysis of Plutonium(IV)." *Journal of Physical Chemistry*, 64(5):680-682.

Seaborg GT and JJ Katz, eds. 1954. *The Actinide Elements*. McGraw-Hill, New York.

Whyatt GA, RJ Serne, SV Mattigod, Y Onishi, MR Powell, JH Westsik Jr, LM Liljegren, GR Golcar, KP Recknagle, PM Doctor, VG Zhirnov, and J Dixon. 1996. *Potential for Criticality in Hanford Tanks Resulting from Retrieval of Tank Waste*. PNNL-11304, Pacific Northwest National Laboratory, Richland, Washington.