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Chemical Species of Plutonium in Hanford Radioactive Tank Waste

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CHEMICAL SPECIES OF PLUTONIUM IN HANFORD RADIOACTIVE TANK WASTE

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INTRODUCTION

Large quantities of radioactive wastes have been generated at the Hanford Site over its operating life. The wastes with the highest activities are stored underground in 177 large (mostly one million gallon volume) concrete tanks with steel liners. The wastes contain processing chemicals, cladding chemicals, fission products, and actinides that were neutralized to a basic pH before addition to the tanks to prevent corrosion of the steel liners. Because the mission of the Hanford Site was to provide plutonium for defense purposes, the amount of plutonium lost to the wastes was relatively small. The best estimate of the amount of plutonium lost to all the waste tanks is about 500 kg. Given uncertainties in the measurements, some estimates are as high as 1000 kg (Roetman et al. 1994). The wastes generally consist of (1) a sludge layer generated by precipitation of dissolved metals from aqueous wastes solutions during neutralization with sodium hydroxide, (2) a salt cake layer formed by crystallization of salts after evaporation of the supernate solution, and (3) an aqueous supernate solution that exists as a separate layer or as liquid contained in cavities between sludge or salt cake particles.

The identity of chemical species of plutonium in these wastes will allow a better understanding of the behavior of the plutonium during storage in tanks, retrieval of the wastes, and processing of the wastes. Plutonium chemistry in the wastes is important to criticality and environmental concerns, and in processing the wastes for final disposal.

Plutonium has been found to exist mainly in the sludge layers of the tanks along with other precipitated metal hydrous oxides. This is expected due to its low solubility in basic aqueous solutions. Tank supernate solutions do not contain high concentrations of plutonium even though some tanks contain high concentrations of complexing agents. The solutions also contain significant concentrations of hydroxide which competes with other potential complexants. The sodium nitrate and sodium phosphate salts that form most of the salt cake layers have little interaction with plutonium in the wastes and contain relatively small plutonium concentrations. For these reasons we will consider plutonium species in the sludges and supernate solutions only.

The low concentrations of plutonium in waste tank supernate solutions and in the solid sludges prevent identification of chemical species of plutonium by ordinary analytical techniques. Spectrophotometric measurements are not sensitive enough to identify plutonium oxidation states or complexes in these waste solutions. Identification of solid phases containing plutonium in sludge solids by x-ray diffraction or by microscopic techniques would be extremely difficult. Because of these technical problems, plutonium speciation was extrapolated from known behavior observed in laboratory studies of synthetic waste or of more chemically simple systems.

ORIGIN AND COMPOSITION OF WASTE

The Hanford Site was created by the United States' Manhattan Engineering District in 1943 to produce plutonium for nuclear weapons. Plutonium production operations on the Site ceased in 1990. Three separation (reprocessing) methods were used to produce pure plutonium product from irradiated uranium metal fuel. All relied on changes in plutonium oxidation state to achieve separation and decontamination, in nitric acid solution, from uranium, fission products, and other materials. The Bismuth Phosphate Process (1944-1956) was based on cyclic batchwise carrier precipitations with $BiPO_4$ and LaF_3. Separations were achieved because Pu(IV) is carried and Pu(VI) is not carried. Alternate precipitations with plutonium in the tetravalent and hexavalent states achieved a high degree of separation from uranium and fission products. The REDOX Process (1951-1967) used a continuous solvent extraction in methyl isobutyl ketone; Pu(VI) is extractable, Pu(III) is not. The PUREX Process (1956-1972, 1983-1990) used extraction in tributyl phosphate; Pu(IV) is extractable, Pu(III) is not.

Each process generated radioactive wastes containing spent process chemicals, dissolved fuel cladding (aluminum- or zirconium-based), fission products, uranium and plutonium process losses, and other transuranium elements (e.g., americium, neptunium). The wastes were neutralized to pH >8 and then discharged to storage in mild steel-lined reinforced concrete underground tanks. The Bismuth Phosphate Process did not recover uranium and this uranium-rich waste also was disposed to the waste tanks. The valuable uranium subsequently was reclaimed by tributyl phosphate solvent extraction in the Uranium Recovery Process (1952-1957).

The costs of tank storage drove each evolving process to optimize use of process chemicals. Wastes volumes of 64,000 liters/ton of uranium in the Bismuth Phosphate Process in 1945 were decreased to 1,300 liters/ton of uranium in the PUREX Process. Other methods were used to gain tank storage space. The isotopes $^{134,137}Cs$, $^{89,90}Sr$, and ^{60}Co were removed from dilute Bismuth Phosphate Process waste solutions by nickel ferrocyanide, calcium/strontium phosphate, and nickel sulfide coprecipitation, respectively (Waste Scavenging Process, 1954-1958). Discharge of the resulting decontaminated solution to the ground freed about 140 million liters, or 45% of the existing tank capacity.

Further decrease of waste volume was achieved through evaporation of water to concentrate liquors and form sodium nitrate and phosphate salt cakes. Practical limits in waste volume reduction, imposed by fission product isotope heat loading on the tanks, were addressed by removal of $^{134,137}Cs$ (ion exchange) and $^{89,90}Sr$ (solvent extraction) and their separate encapsulation (Waste Fractionation Process, 1967-1985). Organic chelating agents [ethylenediaminetetraacetate (EDTA), N-2-hydroxyethylethylenediaminetriacetate (HEDTA), citrate, glycolate) were used in this process to sequester iron and aid in waste dissolution. Additional volume reduction by vacuum evaporators created solutions as high as 13 M in sodium and crystallized sodium nitrate and other salts [$NaNO_2$, Na_2CO_3, $NaAl(OH)_4$]. Laboratory and equipment decontamination wastes, Plutonium Finishing Plant (PFP) plutonium scrap recovery wastes, ion exchange resins, and diatomaceous earth and portland cement liquid sorbents also have been added to some tanks.

About 330,000 metric tons of radioactive waste currently are stored in 177 underground tanks on the Site. The waste compositions are dominated by the facts that the plutonium separation processes were conducted in nitric acid and the wastes were made alkaline with sodium hydroxide prior to their disposal. Water and sodium nitrate thus constitute about 83 wt% of the tank waste; sodium nitrate-rich crystalline salt cake comprises about 42% of the waste volume. Water soluble sodium salts are found in liquors (about 33% of the waste volume) and water-insoluble compounds are found in liquor-saturated sludge (about 25 vol%). Plutonium primarily is found in the sludge with other metal hydrous oxides; lower plutonium concentrations are found in the liquors (Table 1).

Table 1. Composition of Hanford Site Tank Solutions and Sludges

	Concentration in Solutions (M) (Tank Number)					Concentration in Sludges (mole/dry kg) (Tank Number)			
Component	$BiPO_4$ Sludge Liquor (107-T)	Complexant Concentrate (102-AN)	Double Shell Slurry (101-AW)	Waste. Fract. (106-C)	Dilute Waste (108-AP)	$BiPO_4$ Sludge (107-T)	REDOX Sludge (104-S)	PUREX Sludge (101-AZ)	PFP Sludge (102-SY)
Al	0.0008	0.56	1.0	0.01	0.04	1.4	6.6	1.6	3.0
Bi	0.00008	NR*	<0.0006	0.005	NR	0.13	--	NR	NR
Ca	0.0001	0.01	0.0008	NR	NR	0.04	0.16	0.09	0.08
Cr	0.003	0.006	0.003	NR	NR	0.02	0.07	0.05	0.40
Fe	0.0004	0.0009	<0.0008	NR	<0.0001	1.2	0.05	2.7	0.26
Mn	0.000001	0.0007	0.0005	NR	NR	0.009	0.03	0.08	0.08
Na	2.3	10.4	10.0	4.0	0.76	12.9	8.0	6.0	9.7
Ni	0.0001	0.006	NR	NR	NR	0.01	0.001	0.12	0.06
Si	0.003	<0.0007	<0.005	0.05	NR	0.49	0.07	0.32	0.09
U	0.001	<0.0008	0.0009	0.002	NR	0.25	0.04	0.04	0.06
Zr	0.000009	NR	<0.0002	NR	NR	0.002	0.0006	0.59	NR
F^-	0.03	0.10	<0.04	0.009	0.03	1.4	0.01	0.20	0.06
NO_2^-	0.28	1.8	2.2	0.21	0.08	0.58	0.86	1.6	1.3
NO_3^-	1.4	3.6	3.5	1.1	0.24	2.7	0.47	1.3	3.5
PO_4^{3-}	0.06	0.05	0.02	0.04	0.003	2.7	0.005	0.01	0.28
SO_4^{2-}	0.11	0.14	0.01	0.05	0.005	0.24	0.04	0.31	0.67
CO_3^{2-}	0.15	1.1	0.21	0.75	0.14	0.56	0.11	0.77	0.92
OH^-	--	0.21	5.1	0.01	0.16	--	--	--	1.8
TOC	0.07	2.2	0.21	0.94	0.03	0.18	0.22	1.3	1.2
Pu	$<6.8x10^{-7}$	$3.5x10^{-7}$	$6.9x10^{-8}$	$1.3x10^{-5}$	$3.6x10^{-9}$	$1.8x10^{-5}$	$2.6x10^{-5}$	$4.8x10^{-4}$	$1.9x10^{-4}$
pH	10.2	13.2	--	10.3	13.2	11.4	12.9	13.6	--
Ref.	Valenzuela & Jensen (1994)	Jo et al. (1996)	Baldwin et al. (1995)	Castaing (1993)	Baldwin & Stephens (1996)	Valenzuela & Jensen (1994)	DiCenso et al. (1994)	Hodgson (1995)	Delegard (1995a)

* NR - not reported.

The sodium salt cakes have little interaction with plutonium and thus contain relatively small plutonium concentrations.

The broadly representative solution and sludge compositions shown in Table 1 reveal the waste heterogeneity, the pervasiveness of sodium nitrate (even in sludge), and the low plutonium concentrations. Crystalline phases identified in sludge include $BiPO_4$, $FePO_4$, goethite (α-FeOOH), gibbsite [γ-$Al(OH)_3$], boehmite (γ-AlOOH), cancrinite (nominally $NaAlSiO_4$), albite ($NaAlSi_3O_8$), $Na_2C_2O_4$, and $Na_7F(PO_4)_2 \cdot 19H_2O$ (a double salt of relatively low solubility). Sludges undoubtedly also contain amorphous iron, chromium, zirconium, and manganese hydrous oxides.

Plutonium concentrations in waste solutions range from about 10^{-9} to 10^{-5} M and from 10^{-6} to 10^{-4} moles per kilogram in sludge (Figure 1). Most of the plutonium in the waste tanks is concentrated in the sludge layers. Low concentrations in solution for all the tanks samples analyzed thus far indicate that there are no strong complexing agents in the tanks that greatly influence dissolution of plutonium under tank storage conditions. Tank C-106 has the highest plutonium concentration in solution (5×10^{-5} M), probably because of a low hydroxide concentration (10^{-5} M) and a high carbonate concentration (0.75 M). Both of these factors increase plutonium solubility and inhibit adsorption of plutonium on sludge solids, as will be discussed in the sections to follow. Concentrations of plutonium in the supernates would be expected to be much higher than those given in Figure 1 if the plutonium species were predominately (VI), as will be discussed later. Therefore, the oxidation state of plutonium in the wastes will be (IV) or (V).

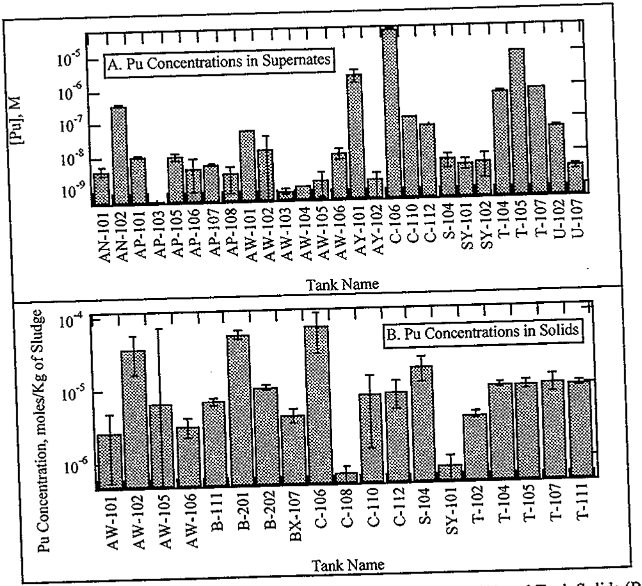

Figure 1. Plutonium Concentrations Measured in Tank Supernates (A) and Tank Solids (B).

PLUTONIUM SOLUTION CHEMISTRY IN ALKALINE MEDIA

The Hanford Site tank waste is alkaline (pH 8 to greater than 5 M NaOH). However, the chemistry of plutonium in alkaline media is considerably less investigated than that in acid. Published research on plutonium chemistry in alkaline media is reported primarily in (1) studies of Hanford Site tank waste, (2) related tank waste studies for the US Department of Energy's Savannah River Site, (3) studies of alkaline nuclear waste repository systems, and (4) investigations related to the discovery of heptavalent plutonium conducted at the Institute of Physical Chemistry (IPC) of the USSR Academy of Sciences. The chemistry of the transuranium elements and technetium in strongly alkaline media was recently reviewed by the IPC (Peretrukhin et al. 1995). However, the review does not contain the significant developments of the last few years. Following is a brief summary of the chemistry of Pu in alkaline solution as it applies to Hanford Site tank waste solution. The studies may be divided between those conducted for strongly concentrated ($\geq$ 0.5 M hydroxide) and moderately concentrated ($<$ 0.5 M hydroxide) alkaline media.

Plutonium in Strongly Alkaline Media

Earliest references to the chemistry of plutonium in strongly alkaline media are those of the Manhattan Project. Studies indicated that Pu(VI) and particularly (IV) form compounds of low solubility in aerated NaOH solution and do not readily interconvert between their tetra- and hexavalent oxidation states (Connick et al. 1949). Plutonium(III) hydroxide will reduce water in 1 M NaOH solution (Cunningham 1954) and thus should not be stable in tank waste. The solubility of Pu(VI) hydroxide in 5 M NaOH was reported to be about 5×10^{-4} M (Hindman 1954). In a later study, the increasing solubility of Pu(VI) hydroxide in potassium hydroxide solution (from about 10^{-5} to 10^{-4} M as potassium hydroxide concentration increased from 0.11 to 10 M) was attributed to formation of an anionic hydroxo complex (Pérez-Bustamante 1965). The discovery of heptavalent neptunium and plutonium, achieved by the oxidation of the respective hexavalent actinides by ozone in NaOH solution (Krot and Gel'man 1967), was followed by a program of experimental work at the IPC on the chemistry of this alkali-stabilized actinide oxidation state (Krot et al. 1977).

Plutonium Oxidation States in Solution. The oxidation-reduction potentials of Pu[(VII)-(VI); (VI)-(V); (VI)-(V); (IV)-(III)] in 0.1 to 14 M NaOH were studied by polarographic techniques (Peretrukhin and Alekseeva 1974). The results agreed with, and expanded on, slightly earlier findings (Bourges 1972 and 1973). Further investigations of the electrochemical and oxidation/reduction reaction behaviors of plutonium have since been conducted (Peretrukhin and Spitsyn 1983; Peretrukhin et al. 1994). The studies showed Pu(VII) can oxidize water to form oxygen in 0.1 to 15 M NaOH solution and Pu(III) can reduce water in 1 M NaOH solution (Peretrukhin and Spitsyn 1983) in agreement with earlier findings (Cunningham 1954). Thus, neither Pu(III) nor Pu(VII) should be stable in strongly alkaline waste. The Pu(VI)/(V) couple was found to be reversible (Peretrukhin and Alekseeva 1974; Bourges 1973). By implication, the respective Pu species should have similar structures while the Pu(V)/(IV) couple is irreversible (different structures).

All dissolved oxidation states are stable to disproportionation in NaOH solution as determined by electrochemical measurement (Peretrukhin and Spitsyn 1983; Peretrukhin et al. 1994). However, reproportionation of freshly precipitated Pu(IV) with Pu(VI) solution to form Pu(V) was found to be incomplete in 4 and 6 M NaOH. Based on these observations, the potential of the Pu(V)/Pu(IV)O_2•xH_2O couple was calculated to be 0.44 V at 4 M NaOH (Bourges 1972), about 1.3 V higher than observed in the Pu(V)/Pu(IV) solution couple. Plutonium(V) also was found to be unstable in three days' storage in 4 M NaOH but stable indefinitely in 12 M NaOH (Bourges 1973). In summary, though Pu(V) is seemingly stable toward disproportionation to form Pu(IV) and Pu(VI) solution species, Pu(V) apparently becomes *unstable* below 6 to 12 M NaOH, disproportionating to form Pu(IV) hydrous oxide and dissolved Pu(VI).

The formal potentials of the adjacent plutonium oxidation state couples and the plutonium oxidation state fields of stability in NaOH solution are presented in Figure 2. The nitrate/nitrite couple (Bratsch 1989), which may control the redox potential in nitrate/nitrite-laden tank waste solution, lies in the Pu(IV) hydrous oxide region of stability at 1 M NaOH; i.e., plutonium should be present as Pu(IV) hydrous oxide in tank waste but possibly present as Pu(V) in solution.

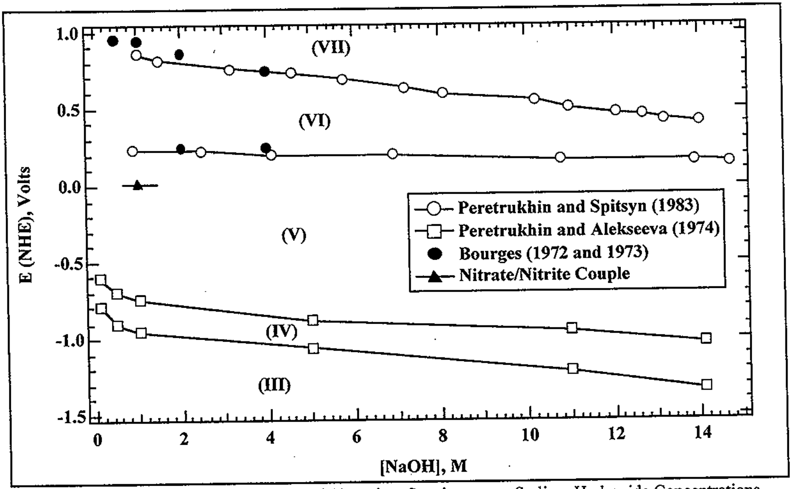

Figure 2. Formal Potentials of Dissolved Plutonium Species versus Sodium Hydroxide Concentrations.

Solubility of Plutonium Compounds. Studies were conducted at the Hanford Site to discover the effects of tank waste solution components (sodium hydroxide, nitrate, nitrite, aluminate, carbonate, phosphate, sulfate, fluoride, EDTA, HEDTA, citrate, and glycolate) on the solubilities of plutonium compounds precipitating in NaOH solution (Delegard and Gallagher 1983). Hydroxide, aluminate, and nitrate were found to increase plutonium compound solubility significantly while the organic agents (EDTA, HEDTA, citrate, and glycolate) had no discernible effect.

Subsequent solubility tests investigated the effects of varying sodium hydroxide, aluminate, nitrate, nitrite, and concentrations (Delegard 1985). The green colored plutonium solid phase formed when Pu(IV) nitrate solution was added to sodium hydroxide solution was identified by XRD to be poorly crystalline $PuO_2 \cdot xH_2O$. Brown solids were observed initially when Pu(VI) nitrate was added to NaOH solution. However, with months'-long aging, the solids became green $PuO_2 \cdot xH_2O$. The chemical reduction of Pu(VI) was attributed to α-radiolytic reactions (Peretrukhin et al. 1995).

The plutonium concentrations increased, then decreased, with time as the solid phase aged and increased sharply with increasing NaOH concentration. The observed solubilities were identical for tests begun by introduction of Pu(IV) nitrate and Pu(IV) hydrous oxide and the Pu(VI) data were trending to those of Pu(IV) (Figure 3). The measured potentials ranged roughly from +100 to -100 mV (Figure 2). The Pu(V) spectrum was observed at 15 M NaOH; Pu(V) also was found in 10 M NaOH. Direct identification of plutonium valence at lower hydroxide (and plutonium) concentrations was not possible because the spectra were too weak; however, indirect evidence for Pu(V) or (VI) was found at 5 M NaOH. These findings showed that Pu(IV) hydrous oxide dissolves in 10 to 15 M solution by being oxidized to form Pu(V) solution species. The plutonium hydrous oxide solubilities observed in aerated pure NaOH solution (Figure 3) increase about a factor of ten with each 2 to 3 M increase in hydroxide concentration.

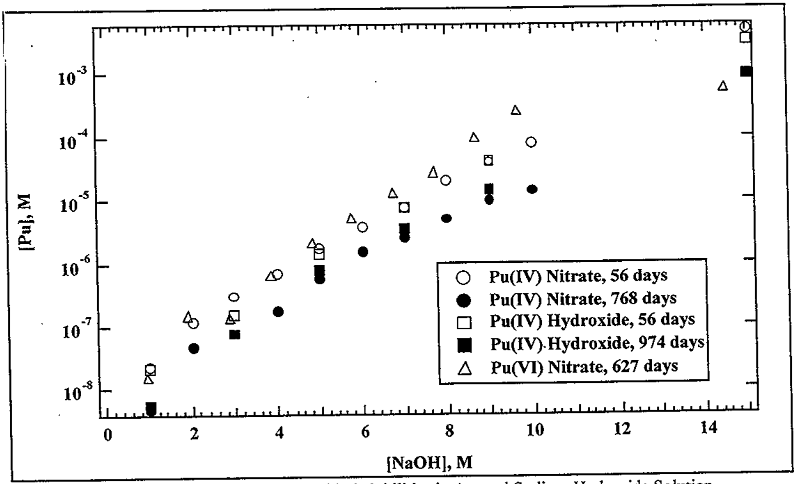

Figure 3. Plutonium Hydrous Oxide Solubilities in Aerated Sodium Hydroxide Solution.

Sodium nitrate and nitrite in NaOH solution were found to increase the plutonium solution concentration because of their contribution to the chemical activity of NaOH (Delegard 1985). However, in mixed (1 to 4 M) $NaNO_2$ and (4 to 7 M) NaOH solution, plutonium concentrations, and measured electrode potentials, were lower than found for pure NaOH solution of the same NaOH chemical activity. The logarithm of the ratio of the measured and expected plutonium concentration data in the NaOH/$NaNO_2$ experiments are proportional to the difference in the measured and expected electrode potentials (the plotted lines have a slope of one). These results support the one-electron oxidative dissolution of Pu(IV) hydrous oxide to form Pu(V) dissolved species (Delegard 1996). Aluminate and carbonate increased plutonium concentrations above that expected in pure NaOH solution of the same activity. Aluminate was postulated to form a 1:1 complex with Pu and carbonate a 2:1 complex.

Plutonium compound solubility in simulated highly alkaline radioactive waste solutions has been investigated at the Savannah River Site (Karraker 1993; Hobbs and Karraker 1996). Two types of tests were performed. Parametric tests identified and quantified the effects of waste components (sodium hydroxide, nitrate, nitrite, aluminate, carbonate, sulfate, and chloride), temperature (25°C and 60 °C), and time on plutonium compound solubility. Evaporation tests determined the influence of evaporative concentration of simulated waste solutions on plutonium compound solubility.

A simplified solubility equation based on hydroxide concentration was derived from the initial test data (unpublished Savannah River Site work), and selected Hanford Site studies for solutions containing sodium hydroxide, nitrate, nitrite, and other salts (Hobbs and Edwards 1993). The data and fit line estimate plutonium concentrations in salt-laden sodium hydroxide solution to be about 10 times higher than shown in Figure 3 for pure sodium hydroxide solutions. The additional salts, with their possible complexation of plutonium and influence on hydroxide chemical activity likely account for the higher observed plutonium concentrations.

The simulated waste evaporation tests also gave higher plutonium concentrations than found in pure NaOH solution for a given hydroxide concentration. The increase in plutonium concentration with NaOH concentration was not as pronounced as in pure NaOH solution. Plutonium concentration increased by about a factor of ten with each 3 to 4 M increase in NaOH concentration. The plutonium solid phase observed in the evaporation tests was $PuO_2 \cdot xH_2O$.

The effects of oxidation state and NaOH concentration are evident in the plutonium compound solubility results obtained in recent IPC research and earlier data (Figure 4). All tests were conducted at six hour to three day equilibration times. The short times diminished possible changes in oxidation state and decreased the effects of solid phase aging. Plutonium compound solubilities increased with increasing oxidation state and with hydroxide concentration.

The stability of Pu(IV) at lower hydroxide concentrations is shown by the similarity of the solubility data for Pu(IV) hydrous oxide in the presence of hydrazine reductant and in the presence of air. Only above 6 M NaOH did the added reductant affect Pu(IV) solubility, presumably by preventing Pu(IV) solids from oxidizing to form dissolved Pu(V) as observed in aerated 10 and 15 M NaOH solution. Disproportionation also was observed below 6 M NaOH in the Pu(V) solubility tests (Peretrukhin et al. 1996). Therefore, in pure NaOH solution, Pu(IV) solution species likely occur below 6 M NaOH while spectrophotometric data (Delegard 1985) indicate Pu(V) solution species are stable above 6 M NaOH.

Plutonium Complexation. The increasing plutonium hydrous oxide solubility with increasing NaOH concentration found for all Pu oxidation states is strong evidence of anionic hydroxide complexes [see Bourges 1973 for Pu(V), Pu(VI), and Pu(VII)]. Postulated hydroxide complexes vary with oxidation state and with hydroxide concentration but are all octahedrally coordinated by oxygen. Likely heptavalent complexes in alkaline solution are $[PuO_4(OH)_2]^{3-}$ (Krot et al. 1977) or $[PuO_5OH]^{4-}$ or

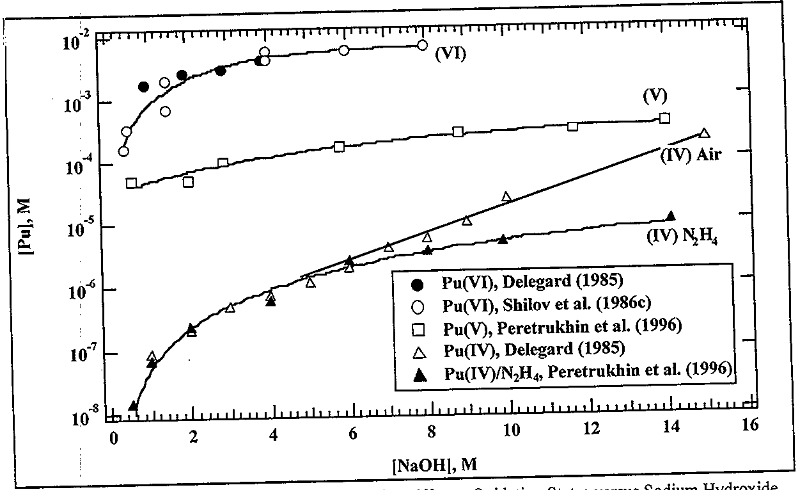

Figure 4. Plutonium Hydrous Oxide Solubilities for Different Oxidation States versus Sodium Hydroxide Concentrations.

$[PuO_6]^{5-}$ in greater than 10 M NaOH (Tananaev et al. 1992). The Pu(VI) complex $[PuO_2(OH)_4]^{2-}$ is proposed on spectrophotometric and electrochemical evidence above 1 M hydroxide (Tananaev 1989). Alkali metal salts $MPuO_2(OH)_2{\bullet}xH_2O$ and $M_2PuO_2(OH)_3{\bullet}xH_2O$ have been prepared (Tananaev 1992), the latter being the solid phase used in the Pu(V) compound solubility tests (Peretrukhin et al. 1996). Because of the existence of these compounds, and by electrochemical correlations, the Pu(V) dissolved species $[PuO_2H_2O(OH)_3]^{2-}$ and $[PuO_2(OH)_4]^{3-}$ have been proposed (Peretrukhin et al. 1995). The latter complex also was proposed on solubility and electrochemical bases (Delegard 1985). The Pu(V) and Pu(VI) complexes should have the same number of hydroxide ligands (i.e., four) since their electrode potential (Figure 2) is practically independent of NaOH concentration (Bourges 1973). The Pu(IV) hydroxide complex is less well established; $[Pu(OH)_6]^{2-}$ has been tentatively suggested on solubility data (Peretrukhin et al. 1996).

Thus, the plutonium hydrolysis products expected in pure NaOH solution are $[Pu(V)O_2(OH)_4]^{3-}$ above about 6 M and $[Pu(IV)(OH)_6]^{2-}$ below 6 M. The transition from Pu(IV) to (V) solution species likely occurs at lower NaOH concentration in tank wastes containing other dissolved salts which contribute to the hydroxide chemical activity.

A Pu(IV) carbonate complex, $[Pu(OH)_4(CO_3)_2]^{4-}$, has been postulated based on Pu(IV) hydrous oxide solubility in carbonate media at pH 12 and 13 (Yamaguchi et al. 1994). As shown in Figure 5, these data are consistent with solubilities observed at 0.25 to 1 M carbonate and 3 to 5 M hydroxide in controlled laboratory tests, and in high carbonate, Pu-saturated, Hanford Site tank wastes. Though spectrophotometric evidence for the Pu(IV) carbonate complex is inconclusive (Delegard 1995b), the solubility data show Pu(IV) carbonate complexation in tank waste to be likely.

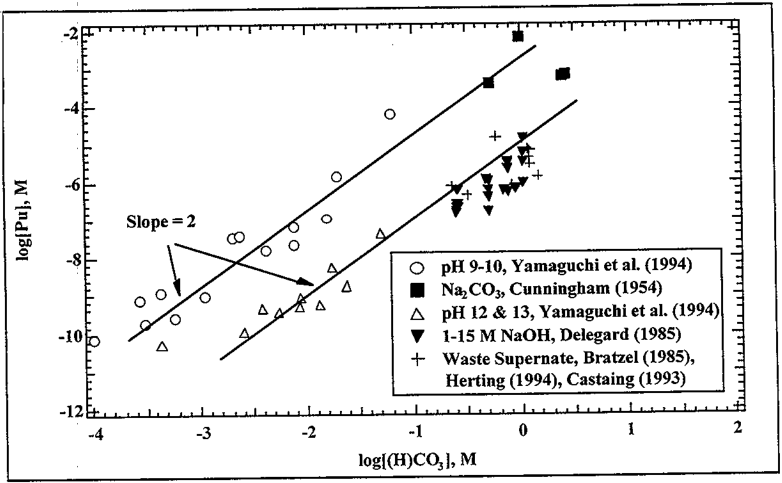

Figure 5. Enhancement of Plutonium Dissolution Due to Carbonate Complexation.

A 1:1 Pu(V):aluminate complex has been proposed based on Pu(IV) hydrous oxide solubility in 5 to 10 M NaOH and 0.3 to 2 M $NaAl(OH)_4$ (Delegard 1985). The oxidation state of the postulated complex, suggested by the observation of Pu(V) spectra in pure concentrated NaOH solution, was not confirmed. A red colored Pu(V) peroxide complex exists only in the cold at 1 M NaOH (Musikas 1971) but is increasingly stable at higher (12 to 16 M) NaOH concentration (Shilov et al. 1996b). However, peroxide itself is not stable in tank waste and the corresponding Pu(V) complexes are unlikely. Plutonium fluoride complexes in highly alkaline solution also are doubtful based on studies in the potassium hydroxide/fluoride aqueous system (Delegard 1987).

Oxidation/Reduction Reagents and Reactions. Oxidation/reduction reagents and reactions with freshly precipitated Pu(IV) hydrous oxide in strongly alkaline solution were recently reported (Shilov et al. 1996a). Oxidizing agents tested were air, oxygen, ozone, permanganate, persulfate, hypochlorite, hypobromite, ferricyanide, ferrate, and chromate; oxidation of Pu(V) with oxygen also was studied. Related studies for peroxide also have been published (Shilov et al. 1996b). All reagents except oxygen and chromate fully or partially oxidize Pu(IV) hydrous oxide (ozone, persulfate, and hypochlorite being the most effective). Oxygen can oxidize Pu(V) to Pu(VI). The rates and extents of oxidation increase with NaOH concentration and temperature. Nitrate and nitrate/nitrite in combination have no net effect on Pu oxidation state though nitrite by itself acts as a mild reducing agent by preventing oxidative dissolution to Pu(V) (Delegard 1985 and 1996). These data show that Pu(IV) hydrous oxide is not appreciably oxidized, beyond that observed in pure NaOH, by oxidizing agents present in the waste (mixed nitrite/nitrate, chromate, air).

Reducing agents in NaOH solution tested with Pu(V) and Pu(VI) were dithionite, sulfite, thiourea dioxide, hydrazine, and hydroxylamine. At lower hydroxide concentrations, reduction was complete for Pu(VI) or Pu(V) to Pu(IV) for all reductants listed except sulfite. Hydroquinone and ascorbate also reduce Pu(VI). Hydroxylamine is the most effective reductant. Lower hydroxide concentrations favor reduction. These data further sustain the finding that the higher oxidation states of plutonium are stabilized by increasing hydroxide concentrations. Tank wastes do not contain any of the named reducing agents. However, certain organic agents (formate, alcohols) present in tank wastes may act as reducing agents. Their effects are not known.

Radiation-Chemical Reactions. Radiolysis occurring the tank waste can influence oxidation state distribution by generating oxidants and reductants from water and by secondary reactions of the water radiolysis products with waste solutes. On average, the radioactive Hanford Site tank waste contains about one Curie (3.7×10^{10} Becquerel) of combined beta and gamma activity per liter (alpha activity is negligible). Most of the activity arises from decay of ^{90}Sr and ^{137}Cs. The radioactive decay energy deposits almost entirely in the waste to yield radiolytic dose rates up to 700 Rad/h (7 Gray/h or 60,000 Gray/y).

The behavior of Pu(VI) in aerated alkaline media under radiation-chemical conditions has been investigated (Pikaev et al. 1996). Samples were irradiated to absorbed doses up to 58,000 Gray. Radiation-chemical reduction occurred readily for 2×10^{-4} M Pu(VI) in 1.3 to 6.9 M NaOH to form Pu(IV) precipitates. Nitrate, nitrite, or EDTA did not significantly change this reaction. In contrast to Np(V), Pu(V) peroxide complexes were not observed in irradiated $NaOH/NaNO_3$ solution.

Other radiation-chemical studies of Pu(VI) stability (50,000 Gray dose in 2 to 6 M NaOH solution) also found reduction to Pu(IV) hydrous oxide (Karraker 1995). However, at higher (8 to 10 M) NaOH concentrations, reduction did not occur. Tests with 60,000 Gray irradiation in mixed $NaOH/NaNO_3/NaNO_2$ solutions were not markedly different from the tests with NaOH alone. The solubility of Pu(IV) hydrous oxide was measured in the presence and absence of gamma irradiation (Karraker 1994). For pure NaOH solutions, irradiation increased Pu concentration. With nitrate and nitrite present, irradiation had no distinct effect on plutonium hydrous oxide solubility.

Plutonium in Moderately Alkaline Media

Investigations of the chemistry of plutonium in moderately alkaline media have focused on environmental conditions (fresh and sea waters) and nuclear waste repository conditions (groundwaters and brines). However, few systematic studies have been performed under conditions simulating Hanford Site tank wastes.

Solubility of Plutonium Compounds and Hydrolysis. Studies of plutonium compound solubilities in aqueous solution were reviewed (Puigdomènech and Bruno 1991). In the absence of complexing ions (such as carbonate or phosphate), solubilities of the respective oxidation state solid phases are limited by hydrolysis. The solubility of $Pu(OH)_3$ was found to vary, near the detection limit, between about 10^{-9} and 10^{-10} M in the pH range of 8.5 to 13 (Felmy et al. 1989). Because additions of metallic iron powder and exclusion of air were necessary, existence of Pu(III) in tank waste is unlikely.

The plutonium concentration above Pu(IV) hydrous oxide decreases from 10^{-3} to 10^{-10} M as pH increases from 2 to 9; that is, about a factor of ten per pH unit (data summarized by Puigdomènech and Bruno 1991). From pH 9 to 13, an average Pu concentration of 7×10^{-11} M was observed in low carbonate (3×10^{-5} M) cement-equilibrated water (Ewart et al. 1992). These results are similar to data reported by Lierse (1985).

The plutonium concentration above a compound presumed to be PuO_2OH was 2.8×10^{-4} M at pH 8.3 (Gevantman and Kraus 1949). The plutonium concentrations above Pu(VI) hydroxide are near 10^{-8} M in the pH range 9 to 12.5 (Lierse 1985). Slightly increased solubility is shown at higher pH. This trend must curve sharply upward at yet higher pH to tie with Pu(VI) compound solubilities observed in NaOH solution (Figure 3).

Solubility of Plutonium Compounds and Carbonate Complexation. Plutonium concentrations increase dramatically in the presence of carbonate or, at lower pH, bicarbonate. Initial work in this field was performed under the Manhattan Project. For example, Pu(IV) hydroxide solubility in 0.53 to 2.7 M Na_2CO_3 at room temperature was found to range irregularly from 4×10^{-4} to 6.6×10^{-3} M Pu (versus about 10^{-10} M expected in the absence of carbonate). Plutonium(VI) carbonate was even more soluble, exceeding 0.3 M in 0.5 M Na_2CO_3 (Cunningham 1954).

Plutonium(III), reportedly unstable in carbonate media and rapidly air oxidized to Pu(IV) (Charyulu et al. 1991), should not exist in tank waste. Blue Pu(III) can, however, be produced by electrochemical reduction of Pu(IV) in bicarbonate solution (Wester and Sullivan 1983) and is stable in the absence of oxygen (Varlashkin et al. 1984).

Plutonium concentrations observed above $PuO_2{\bullet}xH_2O$ in bicarbonate solutions of pH 9.4 to 10.1 increase with the square of the total bicarbonate concentration (Yamaguchi et al. 1994). At low (10^{-4} M) total carbonate, Pu concentration is 7×10^{-11} M, identical to that observed by Ewart and colleagues (1992). At 0.1 M total carbonate and pH 10, about 2×10^{-5} M Pu was observed. Extrapolating to 1 M carbonate, about 2×10^{-3} M Pu should occur. This is similar to concentrations found by Manhattan Project researchers in molar Na_2CO_3 (Figure 5). Based on the solubility data, the 2:1 Pu(IV):carbonate complex $[Pu(OH)_2(CO_3)_2]^{2-}$ was postulated (Yamaguchi et al. 1994). Plutonium concentrations in carbonate-rich pH 10 waste solutions (Table 1) are substantially lower than predicted by these published data, however.

The solubility of PuO_2CO_3 as a function of total carbonate concentration has been determined and the complex $[PuO_2(CO_3)_3]^{4-}$ (an analogue of the well known uranyl triscarbonato complex) was proposed (Robouch and Vitorge 1987). At 10^{-2} M carbonate, about 10^{-3} M Pu was observed. About 0.2 M Pu(VI) was obtained in 1.0 M carbonate at pH 9.5 (Clark et al. 1993). These data indicate that under oxidizing bicarbonate conditions, and in the absence of sorption [which is known to be low for Pu(VI) carbonate complexes], plutonium should be completely dissolved in tank waste and not be found in the sludge phase. Because Pu is found primarily in the sludge phase, combined oxidizing and high bicarbonate conditions apparently do not exist in tank waste. However, if alkaline-side process to dissolve Pu from sludge is desired, oxidizing bicarbonate leaching conditions may be successful provided Pu is not deeply occluded in sludge particles.

Plutonium(V), unstable with respect to disproportionation to Pu(IV) and Pu(VI) in carbonate media from pH 9.3 to at least pH 11.4, becomes stable at pH 12.6 (Varlashkin et al. 1984). Nevertheless, Pu(V) carbonate complexes can be observed around pH 8 at low

(10^{-5} M) Pu(V) where disproportionation is less likely (Bennett et al. 1992). The formal oxidation potential for Pu(V)-Pu(VI) is about 0.35 V (versus NHE) in 2 M Na_2CO_3 at pH <13. The potential decreases to 0.31 V in 2 M Na_2CO_3 / 2 M NaOH (Varlashkin et al. 1984), about 10 mV higher than found in the absence of carbonate (Figure 2). Nitrite is an effective reducing agent and will maintain Pu(IV) in (bi)carbonate solution (Yamaguchi et al. 1994). The potential of the nitrate/nitrite couple is 0.017 V in 1 M OH^- (Bratsch 1989); at pH 10, the potential is 0.253 V. Therefore, if the Pu oxidation state is controlled by the abundant nitrate/nitrite, Pu(IV) carbonate should be stable in alkaline carbonate Hanford Site tank waste solution.

However, carbonate complexation of Pu(IV) yields to hydrolysis as pH increases. Thus, Pu(IV) dissolved in $NaHCO_3$ solution as a carbonate complex will hydrolyze and precipitate as the pH is raised above 11.4 (Varlashkin et al. 1984). As shown in Figure 5, the Pu(IV) complex formed at pH 12 and 13 is about 190-times less soluble than the complex observed at pH 9.4 to 10.1; the solid phase in both cases is Pu(IV) hydrous oxide (Yamaguchi et al. 1994).

Similarly, absorption spectra for Pu(VI) and Pu(V) carbonate complexes change markedly from pH 12.6 to molar NaOH in concentrated Na_2CO_3 solution, reflecting changes in the mixed hydroxide/carbonate complexes (Varlashkin et al. 1984). Spectra for both Pu(V) and (VI) tend to, but do not match, spectra observed in highly alkaline solution without carbonate. The technical literature on actinide carbonate complexation was reviewed recently (Clark et al. 1995). Because of the confounding influences of hydroxide and (bi)carbonate concentrations in the published research, the authors declined to identify specific Pu(IV) hydroxide/carbonate complexes.

PLUTONIUM SOLID PHASE CHEMISTRY IN ALKALINE MEDIA

Precipitation of Plutonium-Containing Solid Phases

Most of the high-level radioactive waste solutions generated from chemical operations at Hanford were acidic solutions containing metals dissolved in nitric acid. Small concentrations of dissolved plutonium (typically < 10^{-5} M Pu) that were not recovered in processing were also present in these waste solutions. Before sending the waste to underground tanks, the acid was neutralized with excess sodium hydroxide to prevent corrosion of the carbon steel tanks. Metals that were insoluble in basic solutions (including plutonium) were precipitated during neutralization. The hydrous oxides formed during neutralization are the major components of sludge in the tanks.

Precipitation of dissolved plutonium from waste solutions during neutralization of the waste could occur by (1) formation of a crystalline plutonium hydrous oxide phase, (2) formation of a non-crystalline, colloidal, hydrous oxide polymer, (3) formation of a crystalline solid solution phase where plutonium enters into the crystalline lattice of another hydrous oxide, or (4) by adsorption of plutonium species onto the surface of other hydrous hydroxides that are present in great excess in the waste solutions. The latter two processes are also considered to be coprecipitation mechanisms. Each of these potential precipitation mechanisms will be discussed below.

Concentrations of plutonium were very small compared to the other metals dissolved in the waste solutions from the various processing operations (Braun et al., 1994). For example, typical mole ratios of iron/plutonium and aluminum/plutonium were 12,000 and 28,000, respectively for bismuth phosphate waste; 1,400 and 132,000, respectively for REDOX waste; 63,000 and 1,400,000, respectively for PUREX aluminum clad wastes; 3,300 and 13,000, respectively for PUREX zirconium clad waste; and 100 and 7,400, respectively for plutonium finishing wastes (this does not include iron added to the waste as a criticality control). In addition to iron and aluminum, other dissolved metals such as uranium, zirconium, manganese, bismuth, chromium, nickel, tin, and others were present in the acid waste that were precipitated as hydrous oxides (see Table 1).

Formation of individual crystals of $PuO_2 \cdot xH_2O$ or hydrous plutonium oxide polymer was unlikely during neutralization because initial plutonium concentrations were thousands of times lower than the major metal ion concentrations in the waste solutions. To precipitate as a pure plutonium phase, either (1) there would have to be negligible interaction between dissolved plutonium and precipitated iron, aluminum and other hydrous oxides or (2) the plutonium would have to be precipitated before the iron and aluminum precipitates from waste solutions. There are many examples of strong adsorption of dissolved plutonium species onto hydrous oxide surfaces including aluminum and iron hydrous oxides. These sorption reactions are discussed in a later section and show that plutonium strongly bonds to precipitated hydrous oxide surfaces.

A prediction of which metal ions precipitated first during neutralization also shows that pure $PuO_2 \cdot xH_2O$ or hydrous polymer were not likely formed in the waste from dissolved plutonium. In a nitric acid solution containing plutonium(IV) as the only dissolved hydrolyzable metal ion, neutralization with sodium hydroxide, as required for waste solutions sent to the tanks, would produce plutonium polymer along with plutonium hydroxide. However, because of the low solubility of iron and aluminum hydroxides and their much higher initial concentrations in the waste solution, these compounds will precipitate first as the waste is neutralized and plutonium will be coprecipitated with them. A comparison of equilibrium solubilities of amorphous $PuO_2 \cdot xH_2O$ (Rai et al. 1980), amorphous $Fe(OH)_3$ (Lindsay 1979), and crystalline $Al(OH)_3$ (gibbsite) (Lindsay 1979) are given for a range of pH values in Table 2. Assuming no significant precipitation rate differences these data show that iron will precipitate before any plutonium can precipitate as plutonium hydrous oxide during the waste neutralization process.

Table 2. Comparison of Plutonium, Iron, and Aluminum Hydroxide Solubilities.

	Log of Solubilities (M)		
pH	$PuO_2 \cdot xH_2O$, Amorphous	$Fe(OH)_3$, Amorphous	$Al(OH)_3$, Crystalline
3	-3.6	-5.5	-1
4	-4.4	-7.1	-3
5	-5.3	-8.0	-6
6	-6.0	-9.2	-7
7	-6.8	-10.0	-7
8	-7.6	-10.3	-7
9	-8.4	-10.0	-6

Amorphous iron is much less soluble than amorphous plutonium hydroxide. Since the wastes contain thousands of times more iron and aluminum than plutonium, a pure plutonium phase (plutonium hydroxide or polymer) will not likely be formed, but the plutonium will be coprecipitated on the iron and aluminum hydroxide that are precipitated first.

The rate of iron hydroxide precipitation during waste neutralization was rapid compared to the rate of plutonium hydroxide precipitation (or plutonium hydroxide polymer formation). As long as the initial molar ratio of $[OH^-]/[Fe^{3+}]$ is greater than three, amorphous $Fe(OH)_3$ will precipitate immediately (Yariv and Cross 1979). During neutralization of the acidic wastes, this ratio greatly exceeded three. Toth et al. (1981) have shown that the rate of plutonium hydroxide polymer formation is slow at the plutonium concentrations known to exist in the acidic wastes. The rate of polymer formation decreases with decreasing plutonium concentration. For example, only about 30% of the plutonium in a 0.05 M plutonium solution was polymerized after one hour at an acid concentration of 0.092 M. Because the plutonium concentration in the waste is about 10,000 times less than 0.05 M, polymer formation would be expected to be much slower.

Typical concentrations of plutonium in the acid wastes range from 10^{-5} to 10^{-6} M. At these low plutonium concentrations, incipient polymerization of plutonium hydroxide requires a relatively high pH. Also, polymerization is not instantaneous, but requires an induction period before the polymer is formed (Toth et al. 1981). Although polymer formation is unlikely, any polymer that is formed has a strong affinity to adhere to other particles suspended in solution or on nearby surfaces (Dran et al. 1994).

Some plutonium existed as solids in the waste before neutralization. These were in the form of oxides or other insoluble precipitates (fluorides, phosphates, etc.). Small amounts of solid plutonium oxide were added to the tanks, mainly from the Plutonium Finishing Plant. These are oxides that were not dissolved during plutonium scrap processing and ended up in the acid waste as suspended solids. These solids were disposed of in a single waste tank, SY-102.

Hobbs (1995) has shown that plutonium was effectively coprecipitated with iron and uranium hydroxides from simulated acidic PUREX waste solutions by making the solutions 0.6 M in sodium hydroxide. The concentrations of plutonium in the resulting supernate solutions were more than a factor of 100 lower than blank solutions that contained only plutonium nitrate before neutralization. The precipitated plutonium was therefore either adsorbed on the precipitated hydroxides or was incorporated into a crystalline phase of these compounds. Since x-ray diffraction measurements of the dried precipitates show that they were mostly amorphous, adsorption seems more likely. Also, plutonium is not likely to be incorporated into an iron compound crystalline structure because of the great difference in ionic radii of Fe(III) and Pu(IV). This is discussed further below.

Herting (1995) has studied coprecipitation of plutonium from actual waste tank supernate solutions using iron hydroxide. The initial concentration of plutonium in these supernate solutions was 0.037 µCi/mL. First, sodium hydroxide solution was added to samples of supernate solution from Tank 107-AN to make the solutions 1.5 M and 3.0 M in free hydroxide. This addition removed about 22 - 27 % of the plutonium from solution, but addition of 0.3 M ferric nitrate solution removed an additional 46 - 57 % of the initial plutonium by coprecipitation with ferric hydroxide. These results show that coprecipitation of plutonium with iron hydroxide occurs under actual tank waste conditions.

Coprecipitation of plutonium with iron and zirconium hydroxides has been used as a separation technique in analytical methods for measurement of plutonium concentrations and identification of plutonium oxidation states in solution. These methods depend on the preferential adsorption of plutonium on the hydrous oxide surfaces generated when base is added to the acidic solutions. Plutonium and other actinide elements were separated from other Hanford tank waste components by coprecipitation with iron hydroxides (Maiti and Kaye 1992). Separation of plutonium from platinum solutions was successfully accomplished by coprecipitation of plutonium with ferric hydroxide (Johnson and Fowler

1967). Plutonium was removed from basic solutions using ferric hydroxide generated by adding sodium ferrate (Na_4FeO_5) to the solutions (Stupin and Ozernoi 1994). The ferrate was slowly reduced by water and the resulting ferric hydroxide precipitate adsorbed the dissolved plutonium. The pH ranges where Pu(III), Pu(IV), and Pu(VI) coprecipitate with iron and zirconium hydroxides was determined by Novikov and Starovoit (1969). They found that Pu(IV) coprecipitated at the lowest pH range, followed by Pu(III) and Pu(VI) as the pH was increased. Separation of the different oxidation states by this method was explained by the relative tendencies of these species to hydrolyze.

The vast majority of liquids added to the tanks were aqueous solutions of soluble nitrates resulting from neutralization of nitric acid waste streams. The concentrations of plutonium in these aqueous solutions are very low due to the strong sorption reactions of dissolved plutonium with precipitated metal hydrous oxide surfaces. Also, the solubility of plutonium hydrous oxide is very small. Maximum expected concentrations of dissolved plutonium, based on solubility studies, is about 10^{-10} to 10^{-2} M, depending on the hydroxide and carbonate concentrations in solution (see Figure 5). The concentration of plutonium in tank 241-C-106 supernate solution was determined by measurement to be $5x10^{-5}$ M (see Figure 1). This value is lower than expected for the solubility of $PuO_2{\cdot}xH_2O$ because of the high carbonate and relatively low hydroxide concentrations in the supernate solutions, as discussed in more detail later. This lower concentration is likely due to plutonium sorption on sludge solids. The dissolved plutonium species are probably anionic hydroxide and carbonate complexes of Pu(V) and Pu(IV), respectively.

Sorption of plutonium on the large surface areas of the solid metal hydrous oxides precipitated during neutralization is the most important coprecipitation mechanism. The hydrous oxides of iron and aluminum, in particular, develop large, amorphous surfaces as they are formed that attract heavy metal ions (Laitinen, 1960). The sorption capacity (in terms of available sorption sites) for iron hydrous oxide gel has been estimated to be about 500 μmoles/mmole Fe (Kinniburgh and Jackson, 1981). This capacity greatly exceeds the molar ratios of Pu/Fe in the waste tank sludges which range from about 0.016 to 10 μmoles/mmole Fe.

Coprecipitation as Solid Solutions

Coprecipitation of plutonium as a micro component in the crystalline lattice of solid crystalline phases precipitated during waste neutralization would require that (1) the substituted macro ion must have about the same ionic radius as plutonium and (2) the crystal lattices of the micro and macro components must be isomorphous or isodimorphous (can form a common crystalline lattice structure). Since the initial precipitates of the macro ions were amorphous solids (iron, aluminum, bismuth, and zirconium hydroxides, mostly), according to Baes and Mesmer (1976), solid solutions were not possible. Partial crystallization will slowly occur during years of storage of the wastes that could result in solid solution formation. This is not important for most of the wastes containing mostly iron and aluminum solids because of the large difference in ionic radii and charge for Pu(IV) and Fe(III) or Al(III). Shannon and Prewitt (1969) give values of crystal ionic radii of 1.10 Å for octacoordinate Pu(IV), 0.74 Å for hexacoordinate Fe(III), and 0.67 Å for hexacoordinate aluminum. Obviously, it would be unlikely for the large plutonium ion to substitute for iron or aluminum in the same crystalline lattice.

The hydrolysis of metal ions has been studied extensively (Baes and Mesmer, 1976). It has been shown that as these hydrolysis reactions occur, there is a tendency for the ions to aggregate through hydroxyl bridging, forming dimers, trimers, or extensive polymeric networks which can reach colloid dimensions. These polymers can then condense with the loss of water to form oxygen-bridged polymeric species (Thiyagarajan et al., 1990). The polymers can contain more than one metal hydroxide (hydroxides of other metal ions present in the initial solution mixtures) bonded to the polymer. For example, if uranium is present during plutonium or thorium hydroxide polymerization, the uranium is bonded through hydroxyl bridges to the polymer (Toth et al., 1981; and Toth et al., 1984). This type of bonding is similar to that proposed for surface complexation models of sorption of hydrolyzable metal ions on oxide surfaces (Schindler, 1981; and Davis et al., 1978). Surface complexation models have been successfully used to predict sorption of uranyl ions onto amorphous iron hydrous oxide, goethite, and hematite solids (Hsi and Langmuir, 1985). Structures of uranyl complexes at the surface of clay minerals have been identified by Chisholm-Brause et al. (1994). These studies indicate that the trace levels of plutonium present during neutralization of acidic wastes will be bonded to other hydrous oxides that are present in much greater abundance in the sludge waste.

Sorption/Desorption Reactions

Most plutonium in the high-level waste tanks exists as a dilute solid mixture with coprecipitated hydrous oxides in sludge layers. The plutonium is strongly sorbed onto the surfaces of these hydrous oxides. Sorption has been shown to be an important mechanism in the removal and fixation of plutonium from aqueous solution by a wide variety of metal hydrous oxides, including those that are present in tank sludges. These hydrous oxides include both pure phases and minerals that contain a mixture of phases. Plutonium sorption on goethite and hematite from basic solutions containing high dissolved salt was very strong (170 to 1,400 mL/g) according to work reported by Ticknor (1993). Sorption of Pu(IV) from solutions containing high concentrations of carbonate onto alumina, silica gel, and hydrous titanium oxide was also very strong (Pius et al., 1995). Carbonate lowered the sorption distribution coefficient for these adsorbents, but even at 0.5 M carbonate the coefficients were 60 mL/g, 1,300 mL/g, and 15,000 mL/g, respectively for alumina, silica gel, and hydrous titanium oxide. In bicarbonate solutions the distribution coefficient for Pu(IV) sorption on alumina was lowered to about 30 mL/g at 0.5 M bicarbonate (Charyulu et al., 1991). This is likely due to a lower pH in bicarbonate solutions which favors a carbonate complex over a hydroxide complex. Sanchez et al. (1985) measured sorption of Pu(IV) and Pu(V) on goethite over a range of pH values and carbonate concentrations. They found that Pu(V) was reduced to Pu(IV) and that the Pu(IV) was strongly sorbed above a pH of about 6. High carbonate concentrations decreased sorption at a pH of 8.6. At 1 M $NaHCO_3$, plutonium sorption was completely inhibited. Carbonate concentrations at or above 1 M and pH values at or below 8.6 in a tank supernate solution will be very rare at Hanford. The solubility of sodium carbonate limits the carbonate concentrations in sodium nitrate-saturated supernates to less than about 0.3 M (Barney 1976).

Barney et al. (1992) measured adsorption of plutonium from wastewater solutions onto commercial aluminum adsorbents over a pH range of 5.5 to 9.0. Plutonium adsorption Kd values increased from about 10 mL/g at a pH of 5.5 to about 50,000 mL/g at a pH of 9.0. The slopes of Kd versus pH curves were close to one, which indicates that one hydrogen ion is released to the solution for each plutonium ion that is adsorbed on the alumina surface. This behavior is typical of adsorption reactions of multivalent hydrolyzable metal ions with oxide surfaces. Plutonium precipitation was not significant in these tests since changing the initial concentration of plutonium from about 10^{-9} to 10^{-10} M did not affect the

Kd values. Also, the initial plutonium concentrations were below the measured solubility limits of plutonium hydroxide.

Delegard et al. (1984) performed screening tests to identify waste components that could significantly affect sorption of plutonium from simulated tank supernate on three shallow sediments typical of the Hanford site. They found that sorption was decreased by the chelating agents, 0.05 M EDTA and 0.1 M HEDTA, but not by carbonate at 0.05 M. Sorption of Pu(IV) on a Hanford shallow sediment from a synthetic groundwater containing 0.003 M carbonate ranged from about 5,000 mL/g to 30,000 mL/g (Barney 1992). Pu(VI) sorption, however, was almost insignificant.

Partial crystallization of the fresh, amorphous iron and aluminum hydrous oxide precipitates occurs as these precipitates age in the tanks. This has been shown recently by Hobbs (1995) who precipitated insoluble metal hydrous oxides from synthetic acidic Purex waste solutions containing plutonium by adding a sodium hydroxide solution. After standing for two months, the precipitated solids (mainly iron, aluminum, uranium, and nickel hydrous oxides) were analyzed by X-ray diffraction. Most of the solids were amorphous, but crystalline goethite (α-FeOOH), gibbsite ($Al_2O_3 \cdot 3H_2O$), bayerite ($Al_2O_3 \cdot 3H_2O$), and sodium diuranite ($Na_2U_2O_7$) were also found. This crystallization did not affect the concentration of plutonium dissolved in the supernate over a 59-day period. The plutonium concentrations were more than 100 times lower than the solubility of pure $PuO_2 \cdot xH_2O$ when iron or uranium were present in the original solutions, showing that plutonium was effectively coprecipitated with iron and aluminum hydrous oxides.

The effects of iron hydrous oxide crystallinity on sorption of metal ions was studied by Tochiyama et al., 1994. They measured Np(V) sorption on α-FeOOH that was prepared by adding a $Fe(NO_3)_3$ solution to 1 M NaOH. The crystallinity was increased by heating the α-FeOOH to 130°C and 300°C. At 300°C, the diffraction pattern was similar to hematite (α-Fe_2O_3). Sorption distribution coefficients were lowered from about 10^4 cm^3/g Fe to 10^3 cm^3/g Fe at a pH of 7 by the 300°C heat treatment and were essentially unchanged by the 130°C treatment. The lower Np sorption may also be due to a lower surface area after heating, but this was not measured. The sorption capacity of the hydrous oxides for plutonium sorption probably decreases somewhat with aging, but the initial capacity is so large that the effect of crystallization is likely to be small.

Isotopic exchange studies with metal ions adsorbed on alumina gel show that some metal ions are steadily incorporated into the bulk structure as the gel is aged. For example, the percent of zinc adsorbed onto alumina gel that is isotopically exchangeable decreases steadily until at 400 hours only 10 % of the sorbed zinc was exchangeable (Kinniburgh and Jackson 1981). A shift to lower pH values in the sorption - pH curves for Ni, Cu, Zn, and Cd sorption on alumina gel as it ages also is evidence for incorporation of these metal ions into the gel structures. Plutonium ions initially adsorbed onto the iron and aluminum gels formed during neutralization of the acid waste solutions will also likely be incorporated into the aging gel structure. This incorporation could account for the observed irreversibility of plutonium sorption on these materials discussed below.

Any chemical mechanism for concentrating the plutonium in a waste tank would require transport of plutonium from the solid phase to the aqueous liquid phase and then to a small volume solid phase. Sorbed plutonium must be desorbed into the aqueous phase of the waste mixture. Plutonium sorption on hydrous oxides is known to be mostly irreversible (DOE 1988; and Alberts and Orlandini 1981) unless the solution composition in contact with the plutonium is dramatically altered. This would require (1) the addition of organic or inorganic plutonium complexants, (2) a change in the redox potential of the solution by adding oxidants or reductants, or (3) acidification of the solution.

The desorption of heavy metals and other chemical species adsorbed onto oxides has been found to be incomplete, suggesting that the sorption reaction is not completely reversible. This is consistent with the behavior of "specifically adsorbed" cations/anions or cations/anions that are chemisorbed to oxide surfaces (Hingston 1981). This observation has been made for a wide range of metal ions (including plutonium), anions, and organic compounds. Barney (1984) observed incomplete reversibility for sorption of uranium, neptunium, technetium, selenium, and radium sorption on a sandstone-claystone under oxidizing and reducing conditions. Payne et al. (1994) also found that a portion of uranium sorbed onto iron oxides to be irreversibly incorporated within the mineral structure. Ho and Doern (1985) found that most of the uranyl species sorbed onto hematite was irreversibly retained on the solid during desorption experiments. This was attributed to multiple bonding sites on the hematite that vary in binding strength. Ticknor et al. (1986) found that sorption of cesium, cerium, and americium on rock surfaces (granite, gabbro, syenite, and anorthosite) was essentially irreversible. Mishra and Tiwary (1995) found that sorption of strontium from aqueous solution on hydrous magnesium oxide was essentially irreversible even when the temperature was increased and the pH lowered. They explain these observations by postulating that the strontium is bonded to the hydrous oxide surface by chemisorption reactions. Sorption of cerium and thorium oxide colloids or pseudocolloids on mineral surfaces (vitreous silica, mica, hematite or goethite) was also found to be partially irreversible (Dran et al. 1994). Irreversible sorption has also been observed for other metal ions including nickel and cobalt (Di Toro et al. 1986), zinc (Elrashidi and O'Connor 1982), and molybdenum (Karmian and Cox 1978); for anions including iodine (Bors 1992), fluoride (Peek and Volk 1985), and borate (Elrashidi and O'Connor 1982); and for organics including 2,4,5,2',4',5'-hexachlorobiphenyl (Di Toro and Horzempa 1982), 2,4,5-trichlorophenoxyacetic acid (Koskinen et al. 1979), bromacil and diquat (Corwin and Farmer 1984). and phenolic compounds (Isaacson and Frink 1984). Irreversible sorption of plutonium on the sludge particles in Hanford waste tanks will help prevent the separation of plutonium from the neutron absorbers in the sludge.

This is illustrated in Figure 6 which shows the relationships between sorption, desorption, and solubility of plutonium in the tanks. The heavy line is the sorption isotherm which shows that as more plutonium is sorbed on the solid phase, plutonium concentrations in solution increase until the solubility limit for $PuO_2•xH_2O$ is reached. The desorption isotherms are nearly flat because of the partial irreversibility of the sorption reaction. The position of the desorption isotherm depends on the concentration of plutonium in the solid.

CONCLUSIONS

Sodium nitrate rich alkaline wastes exist as crystalline salt cakes, high ionic strength solutions, and water-insoluble sludges in underground radioactive storage tanks on the Hanford Site. Plutonium concentrations are negligible in salt cake but range from 10^{-9} to 10^{-5} M in solution and from 10^{-6} to 10^{-4} moles per kilogram in sludge. Because of the significance of Pu in nuclear criticality safety and as a transuranic element with special long term storage requirements, understanding the chemical behavior of plutonium in these materials is important in current waste storage operations and in planning and designing future waste partitioning and processing operations.

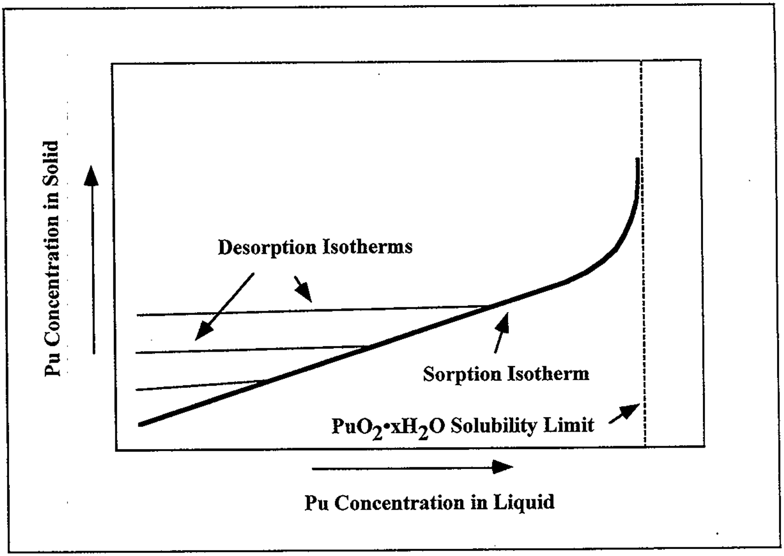

Figure 6. Model Sorption and Desorption Isotherms for Plutonium Sorption on Metal Hydrous Oxides.

The low chemical concentrations of Pu in the waste, and the wastes' complexity, make direct identification of plutonium dissolved species and solid phases impossible. Therefore, studies must be conducted with model systems and the results extrapolated to real wastes. In model systems, having solely Pu-bearing solid phases, marked stability of Pu(IV) hydrous oxide solid phase is found. Plutonium(IV) hydrous oxide ultimately forms following introduction of Pu(III), Pu(IV), Pu(V), and Pu(VI) to sodium hydroxide solution and thus Pu(IV) is the expected solid phase oxidation state in tank waste. Only in the presence of strong oxidants or reductants do plutonium solid phases containing other oxidation states form. Mixed nitrate/nitrite, and radiolysis products, are ubiquitous in tank waste and should stabilize Pu(IV) in the solid phase.

Based on studies with model systems, the chemistry of plutonium in alkaline Hanford Site tank waste solution (pH 8 to about 4 M sodium hydroxide) is expected to be controlled by the wastes' alkalinity and by the presence of key waste constituents:

- Oxidation/reduction. Plutonium oxidation state distribution in waste solutions with molar sodium hydroxide concentrations are not strongly affected by possible oxidants found in tank waste (mixed nitrate/nitrite, chromate, atmospheric oxygen). However, oxidizing chemicals added to achieve future waste processing goals (organic destruction, sludge dissolution) can oxidize plutonium from the solid and increase its solution concentration. Plutonium exists in the waste solutions at Pu(VI) or Pu(V) or a mixture of both oxidation states.

- Hydrolysis. At low carbonate concentrations (less than about 0.1 M) and in sodium hydroxide solutions between about 1 and 6 M, plutonium will hydrolyze to form hydroxide-complexed Pu(IV) species such as $[Pu(OH)_6]^{2-}$. At lower sodium hydroxide concentrations, less hydrolyzed Pu(IV) dissolved species will form. In sodium hydroxide solutions greater than 6 M (lower in the presence of added salts which can increase hydroxide chemical activity), oxidation and hydrolysis will occur to form hydroxide-complexed Pu(V) species such as $[PuO_2(OH)_4]^{3-}$.

- Pu(IV) carbonate complexes. Carbonate complexation significantly enhances solubility. In solutions with pH 12 to 5 M NaOH, 1 M carbonate dissolves about 10^{-5} M Pu by formation of carbonate complexes such as $[Pu(OH)_4(CO_3)_2]^{4-}$. Increased solubility because of high carbonate concentrations apparently occurs in many Hanford Site tank waste solutions. At pH 9 to 10, 1 M (bi)carbonate can dissolve as much as $2x10^{-3}$ M plutonium to form carbonate complexes such as $[Pu(OH)_4(CO_3)_2]^{4-}$.

The trace-level concentrations of dissolved plutonium present in acidic waste solutions from the Hanford Site processing plants were coprecipitated with the voluminous hydrous oxides (of aluminum, iron, chromium, zirconium and others) which were also present in the acid waste during neutralization of the waste with sodium hydroxide. The coprecipitation mechanism was adsorption of plutonium on the large surfaces of the hydrous oxides as they were precipitating from solution. These hydrous oxide surfaces had a great excess capacity for adsorption of plutonium from the neutralized solutions. It is unlikely that significant amounts of hydrous plutonium oxide, plutonium hydrous oxide polymer, or solid solutions of plutonium in crystalline hydroxides were formed during neutralization because of the low concentrations of plutonium present and the known extensive adsorption reactions of plutonium on the hydrous oxides.

As these hydrous oxide precipitates aged in the basic solution environment of the underground tanks, the plutonium was incorporated into the bulk structure of the sludge solids. Condensation of the initially-formed hydroxyl bridges between metal ions yielded oxygen bridges that are stronger and hold the plutonium in the sludge structure more tightly. Isotope exchange experiments with other hyrolyzable metal ions adsorbed onto oxide surfaces show that the fraction of the adsorbed metal ion that is exchangeable decreases over time. This explains the difficulty experienced in extracting plutonium from the sludge solids even with strong acids and oxidizing agents. Also, the partially irreversible adsorption of plutonium on oxide surfaces can be explained by this mechanism. Once adsorbed onto an oxide surface, plutonium is not readily desorbed from that surface.

Not all of the plutonium in the wastes was dissolved before neutralization of the acid wastes. Plutonium-containing solids were also present in some wastes before neutralization. These solids included plutonium oxide that remained undissolved and suspended in processing solutions, mainly from the Plutonium Finishing Plant. Plutonium solids such as plutonium fluoride and plutonium dibutyl phosphate from chemical processing would likely be converted to the hydrous oxide, $PuO_2 \cdot xH_2O$ upon neutralization. Because of its stability in the wastes environment, it is likely to be unchanged with aging.

Numerous areas of research remain on the chemistry of plutonium in alkaline tank waste media. The primary fields are in the distribution and behavior of plutonium in sludge components. Tests to determine the affinity of plutonium for various sludges phases and elements (e.g. iron and aluminum hydrous oxides, aluminosilicates, etc.) must be performed with model systems as functions of solution compositions (pH, carbonate, redox agents), solid phases, and time. Sedimentation or other classification tests with real wastes also should be performed to determine the association of plutonium with particular phases or elements. Leaching tests of genuine waste sludges should be performed to determine if oxidation, complexation, or both can be successful in stripping plutonium from sludge components as an aid in sludge decontamination and as a possible mode of plutonium redistribution in tank waste.

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