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Investigation on the Coprecipitation of Transuranium Elements from Alkaline Solutions by the Method of Appearing Agents

Study of the Effects of Waste Components on Decontamination from Np(IV) and Pu(IV)

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September 1997

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

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Summary

The third stage of the study on the homogeneous coprecipitation of neptunium and plutonium from alkaline high-level radioactive waste solutions by the Method of Appearing Reagents has been completed. Alkaline radioactive wastes exist at the U.S. Department of Energy Hanford Site. The recent studies investigated the effects of neptunium chemical reductants, plutonium(IV) concentration, and the presence of bulk tank waste solution components on the decontamination from tetravalent neptunium and plutonium achieved by homogeneous coprecipitation.

Data on neptunium reduction to its tetravalent state in alkaline solution of different NaOH concentrations are given. Eleven reductants were tested to find those most suited to remove neptunium, through chemical reduction, from alkaline solution by homogeneous coprecipitation. Hydrazine, $VOSO_4$, and $Na_2S_2O_4$ were found to be the most effective reductants. The rates of reduction with these reductants were comparable with the kinetics of carrier formation. Solution decontamination factors of about 400 were attained for 10^{-6} $\underline{M}$ neptunium.

Coprecipitation of plutonium(IV) with carriers obtained as products of thermal hydrolysis, redox transformations, and catalytic decomposition of $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_5NO]^{2-}$, $Cr(NO_3)_3$, $KMnO_4$, and $Li_4UO_2(O_2)_3$ was studied and results are described. Under optimum conditions, a 100-fold decrease of plutonium concentration was possible with each of these reagents.

The influence of various waste components, at their nominal concentrations in Hanford Site tank waste solutions, on decontamination efficiency was estimated for all precipitation precursor reagents. Organic components had the most deleterious effects on the removal processes. In extreme cases, the presence of HEDTA and EDTA in test solutions completely prevented formation of cobalt and manganese hydroxide precipitates. Therefore, the decomposition of these organics is necessary if $Co(NH_3)_6Cl_3$ or $KMnO_4$ are to be used as precursors in genuine waste solutions.

The test results were interpreted to postulate the mechanisms of neptunium and plutonium capture by coprecipitation.

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1.0 Introduction

Over the past three years, the United States Department of Energy (DOE) has funded a research and development program at the Institute of Physical Chemistry of the Russian Academy of Sciences (IPC/RAS) to study actinide isolation from alkaline solutions for waste management purposes (Peretrukhin et al. 1995; Krot et al. 1996; Shilov et al. 1996a; and Peretrukhin et al. 1996). A large part of this research, including the present studies, relates to the development of treatment processes for high level radioactive alkaline wastes containing long-lived transuranium element (TRU) isotopes generated in the course of defense plutonium production at the Hanford Site.

In accordance with the agreement between the IPC/RAS and the DOE, studies on TRU removal from alkaline media by homogeneous coprecipitation with carriers, obtained by the Method of Appearing Reagents (MAR), was conducted in 1994-95 at the Laboratory of Transuranium Elements Chemistry of the IPC/RAS (Krot et al. 1996). A number of precipitating agents, which arise homogeneously throughout solution from decomposition of alkali-soluble precursor compounds, were tested. Based on these tests, the most promising carriers were selected for further investigation. Optimum conditions to obtain these carriers were defined and coprecipitations of Np(V,VI) and Pu(V,VI) with the selected carriers were studied at different NaOH concentrations. The research provided the first stage of work to create an effective technique for decontaminating waste solutions of long lived α-emitting radionuclides.

During these investigations, it was found that plutonium, introduced into solution as penta- or hexavalent species, coprecipitates well from 0.5 to 4.0 M NaOH solution with most of the studied carriers. It was supposed that this behavior was caused by the reduction of plutonium to the tetravalent state in the course of carrier formation. A few test experiments confirmed this supposition. To understand better the operative processes and to provide the most effective plutonium removal from alkaline waste solutions, it is necessary to study coprecipitation of Pu(IV) generated simultaneously with carrier formation in the system by chemical reduction and to study, as well, coprecipitation of Pu(IV) already present in solution before carrier formation. Because Pu(IV) hydrolysis is accompanied by polymerization, this factor also becomes important to determine its effects on the completeness of plutonium capture by carriers in alkaline media. Study of polymer aging is important because polymer properties change with aging and aged polymeric Pu(IV) likely is present in tank wastes. Because of these concerns, studies of Pu(IV) coprecipitation were performed.

The earlier studies showed that Np(V,VI) are poorly captured by most of the tested carriers. The poor capture likely is caused by the existence of stable anionic hydroxo neptunium complexes. In analogy with plutonium, transformation of neptunium to its tetravalent oxidation state should improve the efficiency of neptunium capture. Therefore, coprecipitation of Np(IV) with carriers generated by MAR is a promising area for study. In this work, the completeness of Np(IV) capture by hydroxide precipitates was compared for previously reduced Np(IV) and for Np(IV) generated simultaneously with the formation of carriers in solution.

The earlier studies on coprecipitation of actinides(V,VI) (Krot et al. 1996) concern alkaline solutions free of any additional components. However, nitrate, nitrite, aluminate, carbonate, sulfate, phosphate, fluoride, citrate, glycolate, EDTA, and HEDTA(a) are present in tank waste solutions (Delegard 1987a; Delegard 1995). These components may affect the decontamination efficiency of alkaline solutions from TRU. A significant task of the present research was to estimate the effects these waste components have on the efficiencies of TRU removal with the carriers formed by the MAR. Results of these experiments are reported.

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

2.0 Experimental Materials and Methods

Coprecipitation experiments for neptunium and plutonium were performed using ^{237}Np traced with ^{239}Np and ^{239}Pu traced with ^{238}Pu. Unless otherwise noted, all reagents were purchased from commercial sources and used as received without additional purification. Methods to prepare reagents not available from commercial sources were described in detail in the previous report (Krot et al. 1996). Experimental materials and methods are described.

2.1 TRU Isotopes

The bulk neptunium and plutonium materials used in the experiments were comprised of ^{237}Np and ^{239}Pu isotopes. The ^{243}Am isotope was used to generate the required ^{239}Np tracer.

Neptunium-237 solutions were prepared from neptunium dioxide starting compound by a standard procedure of dissolution and ion exchange purification. The product Np(V) was precipitated by ammonia solution and the solid Np(V) hydroxide was dissolved in a stoichiometric amount of nitric acid to obtain the stock ^{237}Np solution.

Plutonium solutions were prepared from a stock ^{239}Pu nitrate solution purified by anion exchange. Hydrogen peroxide was used to adjust plutonium to the tetravalent oxidation state; the nitric acid concentration in the stock solution was about 2 to 3 $\underline{M}$.

Concentrations of neptunium and plutonium solutions were determined by gravimetry or complexometry and their oxidation states were identified by spectrophotometry.

2.2 Radiotracers

Neptunium-239 and plutonium-238 have short half-lives and high specific activities. Use of these isotopes as radioactive tracers for neptunium and plutonium permits experimental results to be measured at lower neptunium and plutonium concentrations.

2.2.1 Neptunium-239

Americium-243 ($t_{½}$ 7370 years) rapidly reaches secular equilibrium with its 2.3 day half-life ^{239}Np daughter and was used to obtain ^{239}Np isotope. Ten milligrams of ^{243}Am in a dilute perchloric acid solution was aged one month to attain secular equilibrium. The americium concentration was 4×10^{-2} $\underline{M}$.

The in-grown ^{239}Np was oxidized to the hexavalent state by heating with concentrated nitric acid. The americium was separated from solution by precipitation of Am(III) oxalate under optimum conditions (Weigel and ter Meer 1967; Bagnall 1972; Matyukha and Karelin 1985): 0.1 $\underline{M}$ HNO_3 and 0.1 to

0.2 M $H_2C_2O_4$. Because Am(III) oxalate solubility depends on H^+ and oxalic acid concentrations, excess oxalic acid was used if HNO_3 concentrations were higher than 0.1 M. Complete precipitation of $Am_2(C_2O_4)_3 \cdot 10H_2O$ is reached at 0.1 to 0.3 M excess $H_2C_2O_4$ for 0.1 to 0.5 M H^+. The initial clotted precipitate became compact after 10 to 20 minutes of aging in the mother liquor. Heating on a water bath was used to accelerate the process. After one hour, the recrystallized americium oxalate precipitate was separated by centrifugation, dissolved (and oxalate destroyed) with nitric acid, and reserved for future generation of ^{239}Np.

The americium oxalate mother solution, containing the in-grown ^{239}Np, was heated with added nitric and perchloric acids to the formation of wet salts. This step decomposed oxalate and oxidized neptunium to its hexavalent state. The operation was repeated to guarantee complete oxalate decomposition. The product residue was dissolved in water to obtain the ^{239}Np tracer solution. The tracer was not examined for purity because the solubility of americium oxalate in the mother solution is known to be negligible.

The freshly prepared ^{239}Np tracer solution was used in the experiments within five days (two half-lives) of its separation. Tracer solution was added to the 1×10^{-7} M ^{237}Np experimental solution in adequate concentrations to provide an initial β-count rate of 2×10^5 counts/(min·mL). This concentration is sufficient to obtain reliable data above background counting rates even if the decontamination factor, DF, exceeds 10^3.

The ^{239}Np concentration was determined by direct measurement of β-activity of evaporated portions of solution deposited onto special stainless steel counting planchets. No additional operations to extract neptunium or to decrease salt concentration were done. Therefore, control measurements of counting efficiency as a function of NaOH concentration were conducted for each neptunium test series to account for beta self absorption.

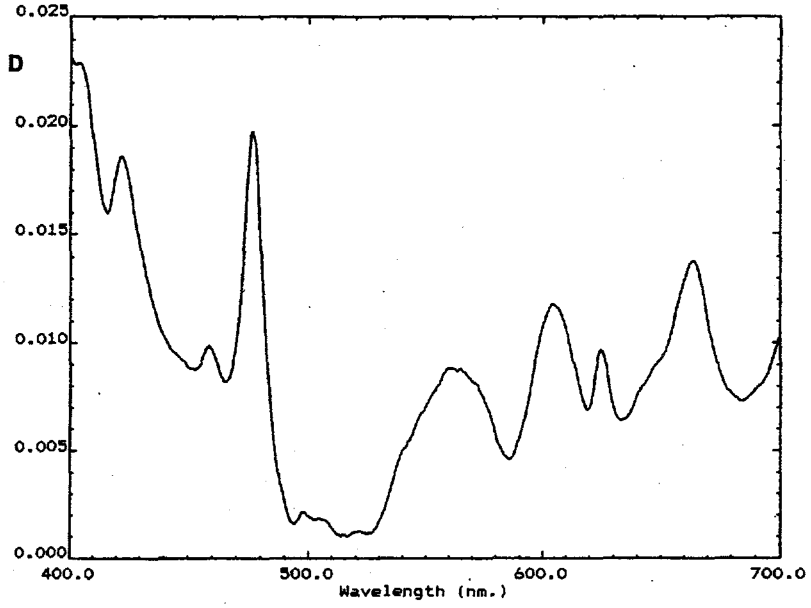
2.2.2 Plutonium-238

An isotopic mixture of ^{238}Pu and ^{239}Pu was used. Plutonium was cleansed of impurities by anion exchange and oxidized to the hexavalent state by fuming in perchloric acid. The absorbance of the product solution in a 1-cm cuvette at 830 nm was 0.491. Hence, Pu(VI) concentration was 9.32×10^{-4} M [$\varepsilon_{830} = 526$ L/(mole·cm)] and the total amount of Pu in 5 mL solution was 4.66×10^{-3} millimoles. Of this, 29% (or 0.323 mg) was ^{238}Pu according to certification data.

The solution was evaporated three times with concentrated HNO_3 to guarantee removal of perchloric acid. The wet residue was dissolved in 10 mL of 7.5 M HNO_3; hydrogen peroxide was added to give 20 to 30 g/L (about 1 to 1.5 M) concentration. The solution was heated to achieve complete decomposition of H_2O_2 and produce Pu(IV). The solution was transferred to a 50-mL volumetric flask and diluted to the mark with 1 M HNO_3. Thus, the final stock solution was 2.3 M HNO_3 and 0.93×10^{-4} M Pu(IV).

The optical absorption spectrum of the stock solution was measured in a 5-cm cuvette. The spectrum (Figure 2.1) closely matched published spectra of Pu(IV) in 2 M HNO_3 and indicated no contamination by Pu(VI) or Pu(III) (Katz et al. 1986).

Experimental solutions were prepared by diluting 0.05 mL of the initial solution with necessary amounts of aqueous alkaline test solution. The initial plutonium concentration was 4.6×10^{-7} M for all experiments. This concentration is lower than the solubility of plutonium(IV) hydroxide over a wide range of NaOH concentration (Peretrukhin et al. 1996; Delegard 1987a and 1987b).



[Pu] = 9.3×10^{-5} M; [HNO_3] = 2.3 M

Figure 2.1. Spectrum of Pu(IV) Stock Solution

2.3 TRU Removal Reagents

Reagents for TRU removal used in this study are listed in Table 2.1. These reagents were selected in the previous study and show high efficiency for TRU removal by coprecipitation (Krot et al. 1996). The carrier precipitation precursors were dissolved in water at appropriate concentrations prior to addition to alkaline test solutions. Initial solutions of lithium peroxouranate were obtained by the reaction of uranyl nitrate with hydrogen peroxide followed by addition of LiOH solution until complete dissolution of the uranyl peroxide salt was achieved. The concentrations of uranium and free excess alkali in the lithium peroxouranate solution were 0.2 M and 0.05 to 0.1 M, respectively.

Table 2.1. TRU Removal Reagents Used in the Study

No.	Precursor Reagent	Carrier Formation Conditions	Carrier
1	$Cr(NO)_3$	Thermal hydrolysis	$Cr(OH)_3 \cdot x\ H_2O$
2	$Co(NH_3)_6Cl_3$	Thermal hydrolysis	$Co(OH)_3 \cdot x\ H_2O$
3	$Na_2[Fe(CN)_5NO] \cdot 2H_2O$	Thermal hydrolysis	$Fe(OH)_3 \cdot x\ H_2O$
4	$Li_4UO_2(O_2)_3$	Catalytic decomposition in the presence of Cu^{2+}	$UO_3 \cdot x\ Na_2O \cdot yH_2O$
5	$KMnO_4$	Reduction to Mn(II), hydrolysis	$Mn(OH)_2 \cdot x\ H_2O$

2.4 TRU Removal Test Procedure

The TRU removal test procedure by MAR was similar to that described in the previous report (Krot et al. 1996). One difference lay in use of tracer solutions of ^{239}Np and ^{238}Pu to determine the removal efficiency of proposed carriers at 10^{-6} to 10^{-7} M TRU concentrations. Previous experiments used TRU concentrations around 10^{-4} M. Detailed descriptions of the experimental procedure for plutonium(IV) coprecipitation are presented.

The plutonium stock solution was about 10^{-4} M total Pu(IV) and contained about 3 x 10^{-5} M ^{238}Pu in 2.3 M HNO_3. Standard solutions of $[Co(NH_3)_6]^{3+}$, Cr^{3+}, $[Fe(CN)_5NO]^{2+}$, $KMnO_4$, and $Li_4UO_2(O_2)_3$ were prepared beforehand.

Experimental solutions were held in polyethylene tests tubes. At least 4 mL H_2O was added to each test tube. This was followed by 0.05 mL of 10^{-4} M Pu(IV) stock solution. The solution was stirred and a calculated amount of NaOH solution added to achieve the desired concentration. Precursor solutions and other reagents, if necessary, were added last. After that, the test tubes were kept under thermostatted conditions for 2 to 3 hours. Carrier formation conditions were those determined to be optimum in previous work (Krot et al. 1996). After coagulation, the product precipitate was separated by five-minutes' centrifugation and an aliquot of supernate solution was taken for analysis. This centrifugation and sampling procedure was repeated twice to assure completeness of separation. For plutonium, analysis of the residual activity of the mother solution was performed by liquid scintillation.

This procedure was conducted for 4 to 5 carrier concentrations at a fixed NaOH concentration. To determine the effects of NaOH concentration, 5 or 6 experiments also were performed with 0.5 to 8 M NaOH. Sets of experiments were performed separately for each carrier.

After the optimum precursor concentration was found for effective decontamination of solutions containing 10^{-6} to 10^{-7} M Pu(IV), tests to determine the influence of waste component ions on the removal effectiveness were performed at this precursor concentration. The experimental procedure was the same, except the necessary quantity of waste component was added to the alkaline solution before the carrier precursor was added.

2.5 Analytical Instrumentation and Measurement

Absorption spectrometry was used to identify radioelement oxidation states and, in some cases, determine their concentrations. Spectra were recorded using a UV-3101 spectrophotometer (Shimadzu Instruments, Inc., Japan). The β activity of ^{239}Np solutions was determined by a "Strahlungmessgerat - 20026" counter with solid plastic scintillator (RFT, former German Democratic Republic production). Analysis of α activity of supernate solutions was performed by the LS-6500 scintillation counter (Beckman Instruments, Inc., USA).

To determine the α activity concentration, 0.5 mL of alkaline coprecipitation mother solution were pipetted into a clean test tube and a known volume of 1 M HNO_3 added to give 0.2 to 0.5 M excess nitric acid. The volume of acidified sample was determined and 0.05 mL aliquots were taken for counting in 1 to 4 mL of liquid scintillator. Measurements of standard sample, prepared from plutonium alkaline solution with known plutonium concentration (0.05 μg/mL; about 2 x 10^{-7} M) were conducted simultaneously. Plutonium concentration calculations were made taking into account the dilution factors at neutralization, standard recoveries, and background counting corrections.

3.0 Results and Discussion

Results of the experiments on coprecipitation of Np(IV) and Pu(IV) by the Method of Appearing Reagents are described.

3.1 Coprecipitation of Neptunium(IV)

Experiments were begun with tests of neptunium coprecipitation. To achieve improved solution decontamination from neptunium, chemical reduction to the tetravalent oxidation state likely is required. Though some data on Np(V) reduction in alkaline solution exist (Shilov et al. 1996a), additional investigations on Np(V) reduction were thought to be useful. Therefore, experiments included tests of neptunium reduction to the tetravalent oxidation state.

3.1.1 Choice of Reductants

The difficulty of predicting the most effective reductant for neptunium(V) conversion to neptunium(IV) lies in the uncertainty in the Np(V)/Np(IV) electrochemical potential in alkaline solution (Shilov et al. 1996a). Therefore, a number of reagents, including those tested previously (Shilov et al. 1996a), were examined as reductants for neptunium(V) in alkalis to determine candidate reductants for coprecipitation removal tests. The tested reagents and experiment conditions are presented in Table 3.1.

From Table 3.1 it is shown that maximum neptunium reduction was achieved with sodium dithionite, vanadyl sulfate, hydrazine, and hydroxylamine. These reagents were chosen for more detailed examination. Hydroxylamine was excluded as undesirable because too high of a concentration is necessary to effect neptunium reduction. This result coincides with earlier findings where it was also shown that hydroxylamine is effective only at concentrations higher than 0.5 M (Shilov et al. 1996a). The reduction by sodium formate is investigated in detail in recent work (Shilov et al. 1997).

3.1.2 Kinetics and Completeness of Neptunium Reduction by Hydrazine

To understand the effect of hydrazine on neptunium removal, it is necessary to determine the kinetics and completeness of neptunium reduction under conditions determined as optimum for carrier formation by candidate MAR processes. Because neptunium(VI,V) reduction to Np(IV) requires a rearrangement of the species structure and is not accompanied by a disproportionation reaction [in contrast to plutonium(V)], reduction rates were not expected to be high. Therefore, it is especially important to ensure that neptunium reduction kinetics be similar or more rapid than the respective carrier formation kinetics. If reduction kinetics are slower than carrier precipitation, only sorption of the radionuclide on the freshly precipitated carrier can occur, not coprecipitation. This, obviously, will decrease removal efficiency.

Table 3.1. Reagents and Conditions Tested to Reduce Np(V) to Np(IV)

No.	Reductant	[Reductant], M	[NaOH], M	T, °C	Time, Hours	Initial [Np(V)], M	Np(IV) Produced, %
1	Sodium Dithionite, $Na_2S_2O_4$	0.1	2	60	2	2×10^{-4}	71
		0.1	4	60	2	2×10^{-4}	69
		0.1	2	20	24	2×10^{-4}	28
2	Sodium Thiosulfate, $Na_2S_2O_3$	1	2	20	24	2×10^{-4}	18
3	Sodium Sulfite, Na_2SO_3	1	2	20	24	2×10^{-4}	15
4	Zn (Metal)	--	2	60	3	1×10^{-4}	15
5	Chromium(II) Acetate, $Cr(CH_3COO)_2$	0.1	4	20	3	2×10^{-4}	10
6	Thiourea Dioxide, $(NH_2)_2CSO_2$	0.1	2	20	24	2×10^{-4}	27
		0.1	2	80	2	2×10^{-4}	31
7	Sodium Formate, HCOONa	1	2	60	3	2.5×10^{-4}	10
8	Vanadyl Sulfate, $VOSO_4$	0.003	2	80	2	2×10^{-4}	40
9	Vanadium(II) Sulfate, VSO_4	0.001	2	80	1	2×10^{-4}	11
10	Hydrazinium Nitrate, $N_2H_4 \cdot HNO_3$	0.1	2	80	3	2×10^{-4}	89
		0.2	2	80	2	2×10^{-4}	95
		0.5	2	80	2	2×10^{-4}	95
11	Hydroxylamine, $NH_2OH \cdot HCl$	0.1	2	90	4	2×10^{-4}	34
		0.5	2	90	2	2×10^{-4}	90

Data on neptunium(V) reduction by hydrazine in alkali as functions of reductant concentration, temperature, and NaOH concentration are given in Table 3.2.

Table 3.2. Kinetics of Neptunium Reduction by Hydrazine, $^{237}Np(V)_0 = (2 \text{ to } 4) \times 10^{-4}$ M

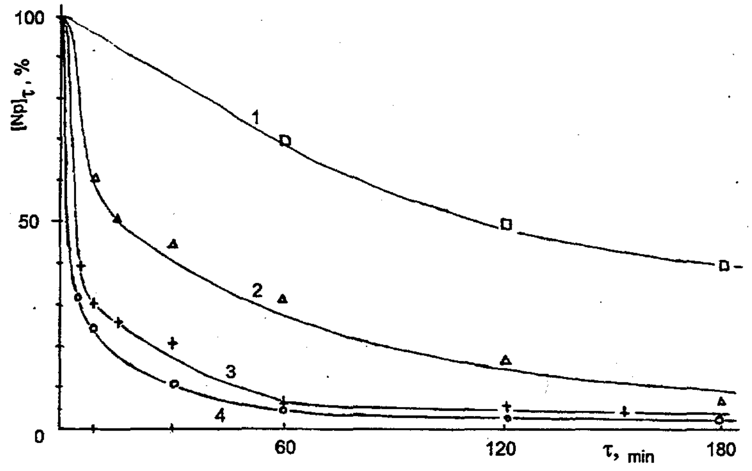
No.	[NaOH], M	T, °C	$[N_2H_4 \cdot HNO_3]$, M	Time, Minutes	[Np(V)], %
1	2	80	0.2	5	38
				10	30
				15	27
				30	20
				60	6
				120	5
2	2	60	0.2	10	40
				25	29
				50	21
				120	9
				180	5
3	2	40	0.2	10	49
				20	39
				40	30
				60	20
				120	11
				180	5
4	2	80	0.5	5	32
				10	26
				30	10
				60	5
				120	5
5	2	80	0.1	10	61
				15	51
				30	45
				60	32
				120	20
				180	11
				240	6

Table 3.2. (contd)

No.	[NaOH], M	T, °C	[$N_2H_4 \cdot HNO_3$], M	Time, Minutes	[Np(V)], %
6	4	80	0.2	15	64
				40	49
				120	32
				180	23
				240	16
				10 hours	13
7	6	80	0.2	15	77
				30	67
				60	61
				120	50
				180	41
				240	31
				10 hours	15
8	8	80	0.2	60	70
				120	60
				180	58
				240	55
				10 hours	45

These results are plotted in Figures 3.1, 3.2, and 3.3, where residual neptunium concentrations in the mother solution are plotted versus the time of reaction. It was found that at (2 to 4) x 10^{-4} M initial neptunium concentration (chosen in accordance with solubility data of Karraker [1994]), precipitates form in the course of neptunium reduction. Clearly, precipitation primarily is caused by the lower solubility of Np(IV) in alkali compared with Np(V) species. However, at initial Np(V) concentrations exceeding 2 x 10^{-4} M, precipitates form at elevated temperature even in the absence of reductant. Curve 1 of Figure 3.1, derived at 80°C, shows that hydrolysis at elevated temperature is not rapid and does not yield complete neptunium precipitation from solution. However, more than 50% of the neptunium precipitates in 3 to 5 hours.

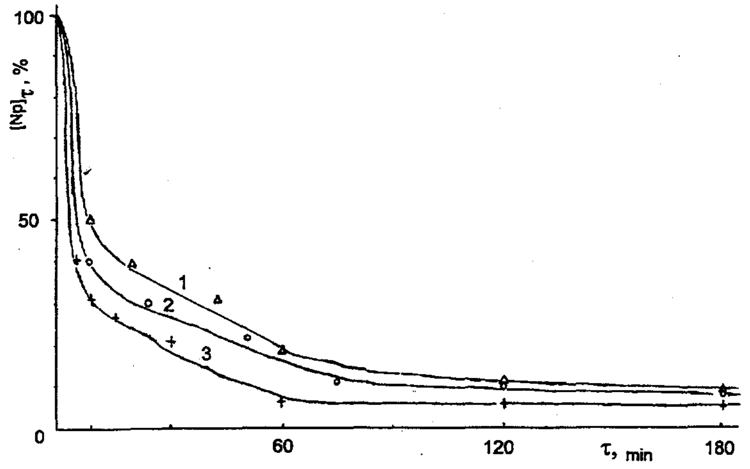
Introduction of hydrazine markedly increases neptunium separation from the solution to the precipitate fraction. The completeness of neptunium reduction at 80°C in 2 M NaOH is approximately the same for 0.1, 0.2, and 0.5 M N_2H_4 and exceeds 95%. The hydrazine concentration does, however,



2 $\underline{M}$ NaOH; 80°C; 2 x 10^{-4} $\underline{M}$ $Np(V)_0$
$[N_2H_4 \cdot HNO_3]$, $\underline{M}$

1 - 0	3 - 0.2
2 - 0.1	4 - 0.5

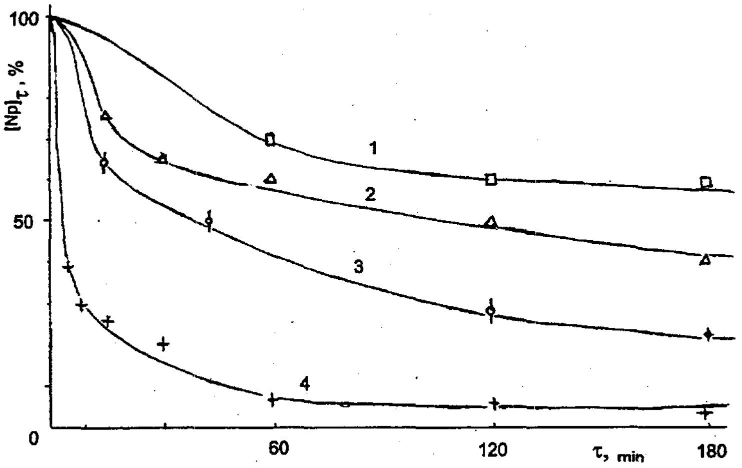
Figure 3.1. Kinetics of Np(V) Reductive Precipitation by Hydrazine as a Function of Hydrazine Concentration



2 $\underline{M}$ NaOH; 0.2 $\underline{M}$ $N_2H_4 \cdot HNO_3$; 2 x 10^{-4} $\underline{M}$ $Np(V)_0$
Temperature, °C

1 - 40
2 - 60
3 - 80

Figure 3.2. Kinetics of Np(V) Reductive Precipitation by Hydrazine as a Function of Temperature



0.2 $\underline{M}$ $N_2H_4 \cdot HNO_3$; 80°C
$[NaOH]/[Np(V)]_0$, $\underline{M}$

1 - 8/4.0 x 10^{-4}	3 - 4/2.5 x 10^{-4}
2 - 6/3.0 x 10^{-4}	4 - 2/2.0 x 10^{-4}

Figure 3.3. Kinetics of Np(V) Reductive Precipitation by Hydrazine as a Function of NaOH Concentration

markedly affect the kinetics of the process (curves 2 to 4, Figure 3.1). At 0.1 $\underline{M}$ hydrazine, only about 70% of the neptunium is reduced in 1 hour; in 0.2 and 0.5 $\underline{M}$ hydrazine, over 95% reduction occurs in the same time. Nevertheless, even 0.1 $\underline{M}$ hydrazine may be sufficient to effect neptunium removal by the Method of Appearing Reagents with $Cr(OH)_3 \cdot xH_2O$ as carrier, because, as shown by Krot and colleagues (1996), the formation kinetics of this carrier are similar to the kinetics of neptunium reduction by 0.1 $\underline{M}$ N_2H_4.

The temperature dependence of Np(V) reduction by hydrazine is shown in Figure 3.2. Tests were performed at 40, 60, and 80°C in 2 $\underline{M}$ NaOH using 0.2 $\underline{M}$ $N_2H_4 \cdot HNO_3$. The reaction rate increases with increasing temperature; heating the solution to 80°C achieves 95% neptunium reduction in one hour.

Additional decontamination may be caused by the capture of dissolved neptunium by the freshly precipitating $Np(OH)_4 \cdot xH_2O$. The precipitated solids act as a sorbent once a quantity of solids are formed. Capture of Np(V) by tetravalent neptunium hydroxide was noted in previous work (Shilov et al. 1996a).

The kinetics of Np(V) reduction in solutions of various NaOH concentration are given on Figure 3.3. From these data, it is clear that increasing alkali concentration strongly decreases the completeness of Np(V) reduction. Only 70, 50, and 30% of neptunium were reduced in 2 hours at 4, 6, and 8 M NaOH, respectively. Even 10 hours' heating did not produce complete reduction, leaving 13, 15, and 45% of the initial neptunium in solution (Table 3.2).

3.1.3 Coprecipitation of Np(IV) with $Cr(OH)_3$

The experiments described in the previous section had two major findings.

- With reduction of pentavalent neptunium in alkaline media, $Np(OH)_4$ forms. The $Np(OH)_4$ produces a solid phase which carries some of the Np(V). Though the amount of Np(IV) in the precipitate was not determined exactly, it was clearly demonstrated that neptunium reduction promotes neptunium removal from solution. By either mechanism, precipitation or capture, neptunium removal from solution is achieved.

- For experiments attaining the highest extent of neptunium removal, the sensitivity limit of spectrophotometry was exceeded and the necessity of use of radiotracers (such as ^{239}Np) became evident. Application of ^{239}Np allows much more diluted neptunium alkaline solutions to be used and avoids $Np(OH)_4$ formation as a separate solid phase. In this way, the actual effectiveness of Np(IV) coprecipitation with carriers can be estimated without complications caused by Np(IV) hydroxide solubility.

Based of these findings, the subsequent experiments with Np(V) used decreased initial neptunium concentrations (1×10^{-6} to 1×10^{-7} M) and ^{239}Np was used as a radiotracer for analytical purposes. Chromium hydroxide, obtained by MAR, was used as a carrier. The decontamination factors (DF) were determined as the ratio of initial to final solution concentrations by β-counting of aliquots mounted by slow evaporation on special targets. By determination of DF values at intermediate times, information on decontamination kinetics was obtained. Because Np(V) and Np(VI) are known to coprecipitate very poorly with chromium hydroxide (Krot et al. 1996), it is reasonable to conclude that the kinetic data reflect also the rate of neptunium reduction to its tetravalent oxidation state.

Results of neptunium removal from alkaline solutions of various concentration using chromium acetate as a precursor and hydrazine as a reductant are presented in Table 3.3.

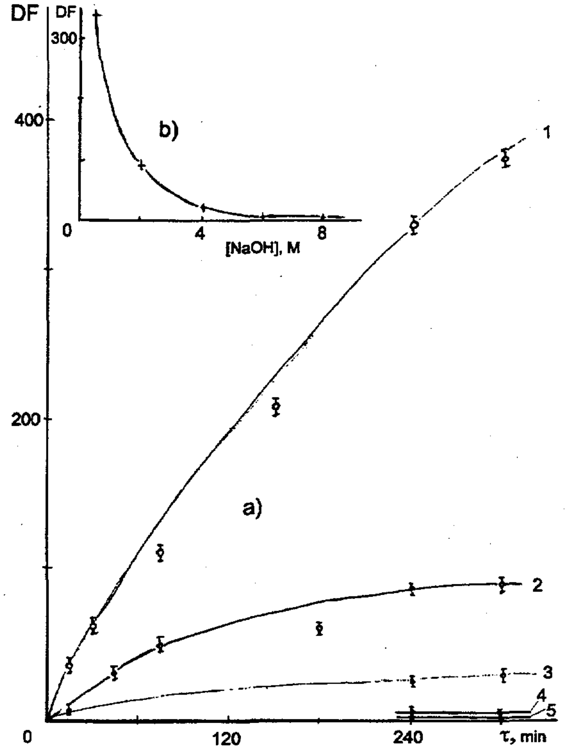
These data show that high-decontamination efficiency is possible for solutions with low NaOH concentration. Thus, DFs of greater than 300 were obtained in 0.5 M NaOH but already at 2 M NaOH, the DF decreased about three-fold. With further increase in NaOH concentration, the DFs dropped sharply (to 5 at 6 M NaOH). At 8 M NaOH, no decontamination occurred though some chromium hydroxide precipitate formed at 8 and 10 M NaOH. The kinetics of the neptunium coprecipitation process, illustrated in Figure 3.4, also show the dependence of DF on alkaline concentration under otherwise equal conditions.

Table 3.3. Coprecipitation of Neptunium with $Cr(OH)_3$ from Alkaline Solution Using $Cr(CH_3COO)_3$ Precursor and Hydrazine, $[Np(V)]_0 = 1 \times 10^{-6}$ M

No.	[NaOH], M	T, °C	[$Cr(CH_3COO)_3$], M	[$N_2H_4 \cdot HNO_3$], M	Time, Minutes	DF
1	0.5	80	0.02	0.2	15	34
					30	62
					75	110
					150	210
					240	330
					300	370
2	2	80	0.02	0.2	15	4
					45	30
					75	50
					180	60
					300	90
3	4	80	0.02	0.2	45	2
					105	8
					165	11
					240	19
					300	21
4	6	80	0.02	0.2	150	2
					210	3
					300	5
5	8	80	0.02	0.2	150	1
					210	1
					300	1

The next series of neptunium removal tests were conducted under similar conditions but with chromium nitrate rather than chromium acetate as precursor. The results are presented in Table 3.4.

By comparing the results in Tables 3.4 and 3.5, it is seen that $Cr(NO_3)_3$ removes neptunium from solution more rapidly and to a greater extent than does $Cr(CH_3COO)_3$. With two hours' heating at 80°C and 0.2 M $N_2H_4 \cdot HNO_3$, 0.02 M $Cr(NO_3)_3$ attained a DF of 440 in 1 M NaOH; with $Cr(CH_3COO)_3$ and at 0.5 M NaOH, the DF was only 200. Even with five hours' time, at lower NaOH concentrations,



1 x 10^{-6} M Np(V)$_0$; 0.2 M $N_2H_4 \cdot HNO_3$; 0.02 M $Cr(CH_3COO)_3$; 80°C

a. [NaOH], M

1 - 0.5
2 - 2.0
3 - 4.0
4 - 6.0
5 - 8.0

b. DF versus NaOH concentration at 4 hours

Figure 3.4. Kinetics of Neptunium Reductive Coprecipitation by Hydrazine with Cr(III) Hydroxide from $Cr(CH_3COO)_3$ as a Function of NaOH Concentration

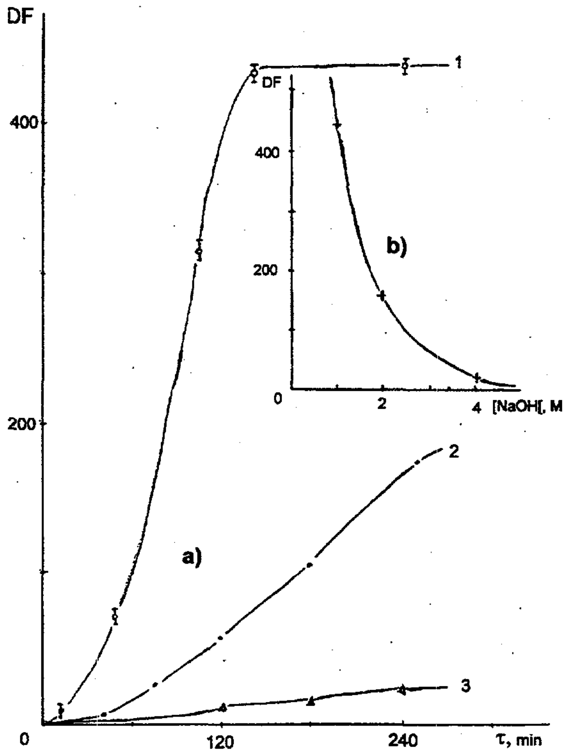
chromium acetate did not give DFs rivalling those obtained with chromium nitrate. For 2 and 4 M NaOH solutions, the DFs for the two precursors were comparable—100 and 20, respectively. The kinetics of neptunium removal from alkalis of different concentration and the dependence of DF on NaOH concentration are shown in Figure 3.5. The influence of precursor concentration and effect of temperature are shown in Figures 3.6 and 3.7, respectively.

Table 3.4. Coprecipitation of Neptunium with $Cr(OH)_3$ from Alkaline Solution Using $Cr(NO_3)_3$ Precursor and Hydrazine, $[Np(V)]_0 = 1 \times 10^{-6}$ M

No.	[NaOH], M	T, °C	$[Cr(NO_3)_3]$, M	$[N_2H_4 \cdot HNO_3]$, M	Time, Minutes	DF
1	1	80	0.01	0.2	15	9
					50	75
					105	315
					140	435
					240	440
2	1	80	0.05	0.2	15	160
					30	300
					50	430
					140	435
					180	440
3	2	80	0.01	0.2	40	4
					75	25
					120	60
					180	100
					240	175
4	4	80	0.01	0.2	50	1
					120	5
					180	15
					240	20
5	2	85	0.01	0.2	20	5
					60	20
					120	85
					180	145
					240	180
6	2	90	0.01	0.2	20	5
					50	15
					135	100
					180	180
					240	180

Table 3.5. Coprecipitation of Neptunium with $Cr(OH)_3$ from Alkaline Solution Using $Cr(NO_3)_3$ Precursor and Sodium Dithionite, $[Np(V)]_0 = 1 \times 10^{-6}$ M

No.	[NaOH], M	T, °C	$[Cr(NO_3)_3]$, M	$[Na_2S_2O_4]$, M	Time, Minutes	DF
1	1	80	0.01	0.025	25	73
					60	238
					90	330
					150	360
					195	370
					240	370
2	2	80	0.01	0.025	25	5.3
					60	16
					105	61
					140	89
					180	89
					240	90
3	4	80	0.01	0.025	25	5
					60	8
					105	10
					140	10.5
					180	11
					240	11
4	1	90	0.01	0.025	10	43
					30	92
					45	210
					60	320
					90	340
					150	370
					240	370
5	1	70	0.01	0.025	30	15.3
					60	46
					130	150
					180	260
					240	280



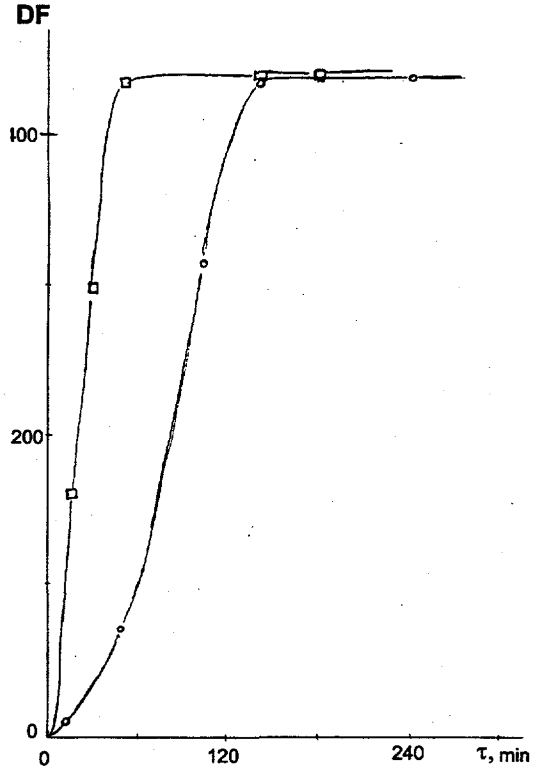
1 x 10^{-6} M Np(V)$_0$; 0.2 M $N_2H_4 \cdot HNO_3$; 0.02 M $Cr(NO_3)_3$; 80°C
a. [NaOH], M

1 - 1.0
2 - 2.0
3 - 4.0

b. DF versus NaOH concentration at 4 hours

Figure 3.5. Kinetics of Neptunium Reductive Coprecipitation by Hydrazine with Cr(III) Hydroxide from $Cr(NO_3)_3$ as a Function of NaOH Concentration

As shown in Figure 3.6, a five-fold increase of initial precursor concentration accelerates Np removal as a whole. Taking into account the anticipated vitrification of the separated solid high-level-waste fraction (should this technique be applied in practice), use of a higher chromium concentration may not be advisable given the low tolerance of the glass waste form for chromium. The influence of temperature on coprecipitation was studied in 2 M NaOH at 80, 85, and 90°C (Figure 3.7). It was found that temperature elevation increased the rate of neptunium removal by chromium hydroxide but did not increase the DF (which did not exceed 200).



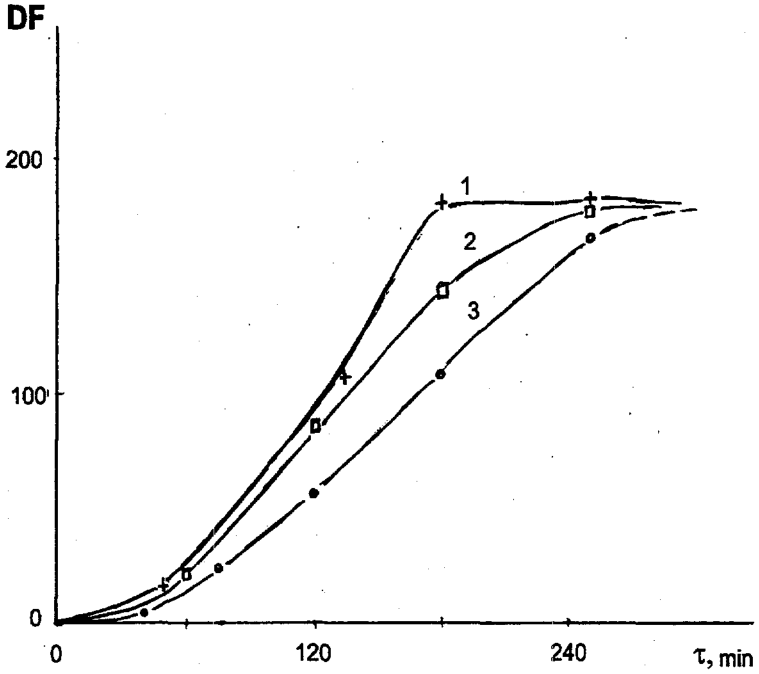
1×10^{-6} M $Np(V)_0$; 0.2 M $N_2H_4 \cdot HNO_3$; 1 M NaOH; 80°C
$[Cr(NO_3)_3]$, M

1 - 0.01
2 - 0.05

Figure 3.6. Kinetics of Neptunium Reductive Coprecipitation by Hydrazine with Cr(III) Hydroxide from $Cr(NO_3)_3$ as a Function of $Cr(NO_3)_3$ Concentration

Neptunium coprecipitation in combination with its reduction to the tetravalent oxidation state also was studied by use of sodium dithionite. The influence of alkali concentration and temperature on DFs again were determined. The experimental results are given in Table 3.5 and graphically presented in Figures 3.8 and 3.9.

Decontamination was effective (DF of 370) in 1 M NaOH. As found in previous experiments with hydrazine as reductant, increasing NaOH concentration decreases DF (90 and 10, respectively, in 2 and 4 M NaOH). Increasing temperature from 80 to 90°C accelerated neptunium reduction and carrier removal negligibly. Decreasing temperature ten degrees (from 80 to 70°C) lowered DFs markedly for a given reaction time. With four hours' heating at 70°C in 1 M NaOH initially containing 1×10^{-6} M Np(V), sodium dithionite, and chromium nitrate, the DF was only 285. The reaction does not appear to be complete even after four hours (curve 3, Figure 3.9).



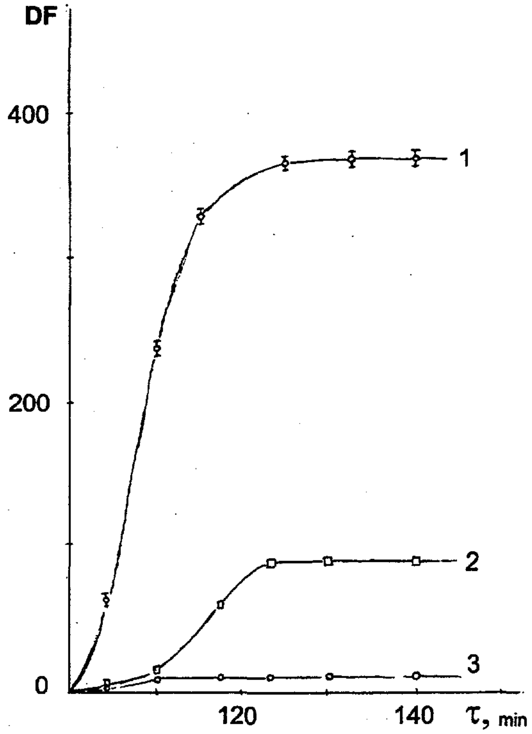
1 x 10^{-6} M Np(V)$_0$; 0.2 M $N_2H_4 \cdot HNO_3$; 0.01 M $Cr(NO_3)_3$; 2 M NaOH
Temperature, °C

1 - 90
2 - 85
3 - 80

Figure 3.7. Kinetics of Neptunium Reductive Coprecipitation by Hydrazine with Cr(III) Hydroxide from $Cr(NO_3)_3$ as a Function of Temperature

Vanadyl sulfate, with hydrazine nitrate and sodium dithionite, also was selected for more detailed examination. Data given in Table 3.6 and Figures 3.10 and 3.11 reflect the experimental results.

In contrast to $N_2H_4 \cdot HNO_3$ and $Na_2S_2O_4$, $VOSO_4$ was found to be a very effective reductant for neptunium not only in 0.5 to 1 M NaOH, but also in 2 M NaOH. The highest DFs in 0.5 to 2 M NaOH also were obtained with V(IV). Unfortunately, as observed in tests with other reductants, increasing NaOH concentration to 4 M sharply decreased DF. The dependence of DF on temperature for $VOSO_4$ is similar to that observed for $Na_2S_2O_4$ (compare Figures 3.11 and 3.9). However, the rate of neptunium reduction with sodium dithionite, and subsequently the rate of its carrier removal from solution, was markedly higher. With sodium dithionite, the reaction was complete in about 1.5 hours at 80 to 90°C; with $VOSO_4$, 3.5 hours were required at 80 to 90°C. At completion, the DF for V(IV) was about 450 versus 350 for dithionite.



1 x 10^{-6} M Np(V)$_0$; 0.025 M $Na_2S_2O_4$; 0.01 M $Cr(NO_3)_3$; 80°C
[NaOH], M

1 - 1.0
2 - 2.0
3 - 4.0

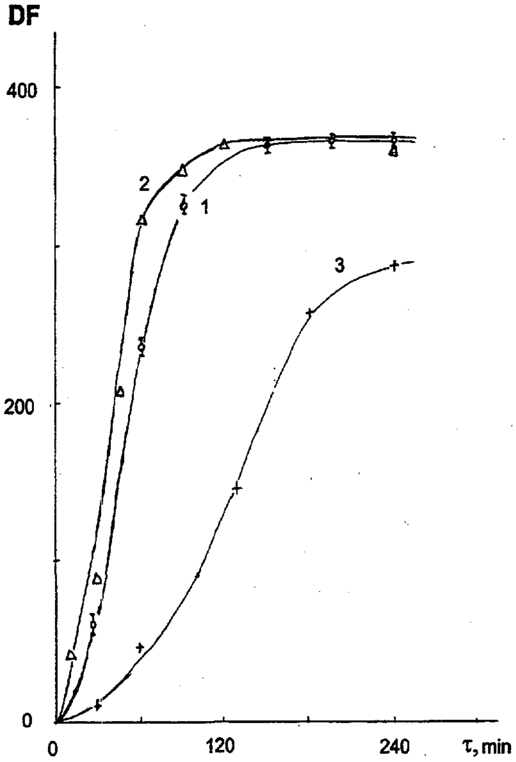
Figure 3.8. Kinetics of Neptunium Reductive Coprecipitation by Dithionite with Cr(III) Hydroxide from $Cr(NO_3)_3$ as a Function of NaoH Concentration

3.1.4 Conclusions

Tests of neptunium reduction to Np(IV) and its effect on coprecipitation produced the following conclusions.

- Effective removal of neptunium from alkaline solution is achieved by coprecipitation if neptunium is reduced to its tetravalent state.

- At least three reductants achieve neptunium reduction in the course of its coprecipitation with $Cr(OH)_3$ formed by the MAR from precursor $Cr(NO_3)_3$. Both $N_2H_4 \cdot HNO_3$ and $VOSO_4$ are effective in NaOH solutions up to 2 M and $Na_2S_2O_4$ up to 1 M NaOH.



1×10^{-6} M Np(V)$_0$; 0.025 M $Na_2S_2O_4$; 0.01 M $Cr(NO_3)_3$; 1 M NaOH
Temperature, °C

1 - 80
2 - 90
3 - 70

Figure 3.9. Kinetics of Neptunium Reductive Coprecipitation by Dithionite with Cr(III) Hydroxide from $Cr(NO_3)_3$ as a Function of Temperature

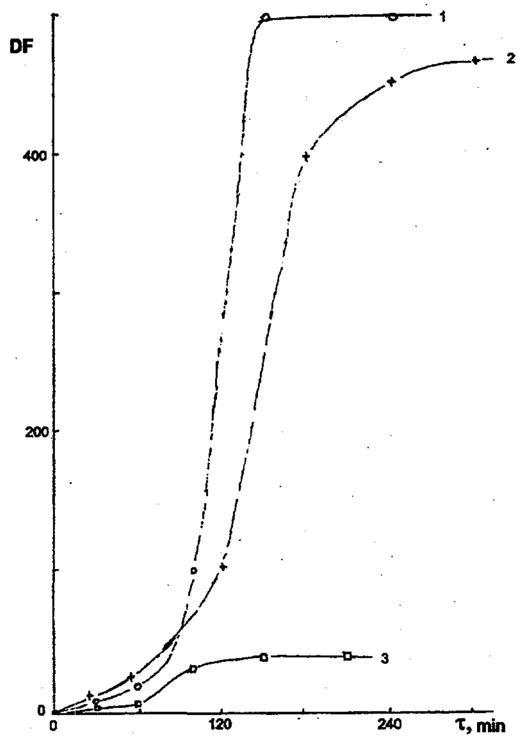
- At alkali concentrations 4 M and higher, decontamination efficiency is decreased significantly for all reductants. The three tested reductants show varying degrees of reduction completeness and DF but have similar trends.

3.2 Coprecipitation of Pu(IV)

It is well known that tetravalent neptunium and plutonium have analogous chemical behaviors. To perform work with these elements at low concentrations, ^{239}Np and ^{238}Pu tracers must be used. However, handling plutonium-238 (with its 88 year half-life, $t_{½}$) is considerably easier than the periodical renewal of stock neptunium tracer and necessary careful remeasurement of initial solution activity

Table 3.6. Coprecipitation of Neptunium with $Cr(OH)_3$ from Alkaline Solution Using $Cr(NO_3)_3$ Precursor and Vanadium(IV), $[Np(V)]_0 = 1 \times 10^{-6}$ M; $[Cr(NO_3)_3] = 0.01$ M

No.	[NaOH], M	T, °C	[$VOSO_4$], M	Time, Minutes	DF
1	1	80	0.01	25	13
				55	25
				120	104
				180	400
				240	450
				300	470
2	2	80	0.01	30	8
				60	18
				100	103
				150	500
				210	500
3	4	80	0.01	30	4
				60	6
				100	34
				150	50
				210	50
4	1	90	0.01	15	9
				45	27
				75	92
				120	320
				210	450
				300	460
5	1	70	0.01	30	6
				60	8
				120	14.5
				180	31
				270	300
				330	430



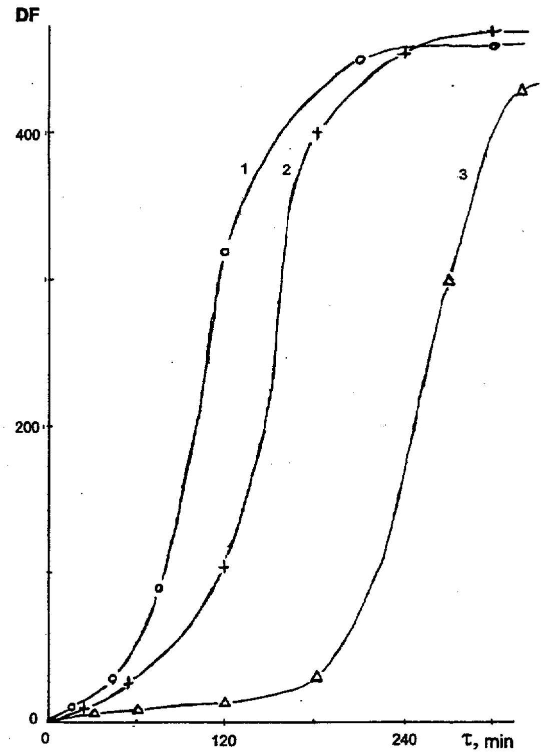
1 x 10^{-6} M Np(V)$_0$; 0.01 M VOSO4; 0.01 M Cr(NO$_3$)$_3$; 80°C
[NaOH], M

1 - 1.0
2 - 2.0
3 - 4.0

Figure 3.10. Kinetics of Neptunium Reductive Coprecipitation by Vanadyl with Cr(III) Hydroxide from Cr(NO$_3$)$_3$ as a Function of NaOH Concentration

required for ^{239}Np (t$_{½}$ of 2.3 days). Therefore, studies of the influence of tank waste composition on waste solution decontamination were only performed using ^{238}Pu-traced plutonium. It is expected that, in the presence of sufficiently strong reductants, neptunium(IV) behavior will parallel that of plutonium(IV).

Plutonium-238, as a high activity tracer, was used in the experiments for analytical reasons; i.e., to obtain trustworthy data on the residual activity of mother solutions after coprecipitation. The higher sensitivity obtained using ^{238}Pu permitted initial test solutions to contain 5 x 10^{-7} M total plutonium. If pure ^{239}Pu solutions were used, the residual activity of supernate solutions after coprecipitation would be insufficient to determine concentrations reliably.



1×10^{-6} M $Np(V)_0$; 0.01 M $VOSO_4$; 0.01 M $Cr(NO_3)_3$; 1 M NaOH
Temperature, °C

1 - 90
2 - 80
3 - 70

Figure 3.11. Kinetics of Neptunium Reductive Coprecipitation by Vanadyl with Cr(III) Hydroxide from $Cr(NO_3)_3$ as a Function of Temperature

The 5×10^{-7} M initial Pu(IV) concentration was chosen based on Pu(IV) hydroxide solubility in alkaline solutions (Peretrukhin et al. 1995; Peretrukhin et al. 1996; Karraker 1996). Tests were performed to assure that no plutonium hydroxide solid phase formed in alkali at the selected initial Pu(IV) concentrations. These experiments ensured that all further results could be attributed to coprecipitation and were not due to Pu(IV) thermal hydrolysis effects.

3.2.1 Removal of Pu(IV) from NaOH Solution on MAR Carriers

Tests of the coprecipitation of Pu(IV) by the MAR with different carriers were conducted in pure NaOH solutions. The optimum precursor concentrations and the influence of NaOH concentration on

DFs were determined. Hydrolysis conditions, times of precipitate coagulation and centrifugation, and other experimental parameters for each precursor were those recommended previously (Krot et al. 1996).

3.2.1.1 Coprecipitation with Cobalt(III) Hydroxide

As shown in Table 3.7, under conditions that guarantee hydrolytic decomposition of hexaamminecobalt(III), high DFs from Pu(IV) are observed over the range 0.5 to 6 M NaOH.

Clearly, decontamination increases with increasing of carrier concentration. However, approximately equal DFs were obtained for 0.012 to 0.05 M carrier; further experiments used 0.024 M $[Co(NH_3)_6]Cl_3$.

The coprecipitation of Pu(IV) with Co(III) hydroxide obtained by thermal hydrolysis of pentaammine cobalt(III) chloride occurs with somewhat lower efficiency (Table 3.8) than observed for the hexaammine precursor, although the effects of alkali and precursor concentrations are the same. Because similar results were observed previously for decontamination of alkaline solutions from Pu(V,VI) (Krot et al. 1996), the pentaammine precursor was not examined further but left as a candidate alternative reagent.

Table 3.7. Coprecipitation of Pu(IV) with Co(III) Hydroxide from $[Co(NH_3)_6]^{3+}$ Hydrolysis, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	$[Co(NH_3)_6Cl_3]$, M	DF
1	2.0	0.003	140
2	2.0	0.006	200
3	2.0	0.012	430
4	2.0	0.024	500
5	2.0	0.05	600
6	0.5	0.024	350
7	1.0	0.024	500
8	2.0	0.024	510
9	4.0	0.024	360
10	6.0	0.024	230
11	8.0	0.024	50

Table 3.8. Coprecipitation of Pu(IV) with Co(III) Hydroxide from $[Co(NH_3)_5Cl]^{2+}$ Hydrolysis, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 60°C; 2 hours

No.	[NaOH], M	$[[Co(NH_3)_5Cl]Cl_2]$, M	DF
1	2.0	0.003	70
2	2.0	0.006	90
3	2.0	0.012	150
4	2.0	0.024	280
5	2.0	0.05	600
6	0.5	0.024	130
7	1.0	0.024	120
8	2.0	0.024	210
9	4.0	0.024	130
10	6.0	0.024	70
11	8.8	0.024	20

3.2.1.2 Coprecipitation with Manganese Dioxide

Manganese dioxide may be generated in alkaline solution by the MAR using hydrogen peroxide, formate, or sulfite as reductants for permanganate. Studies of coprecipitation of penta- and hexavalent neptunium and plutonium with MnO_2 showed H_2O_2 to be the most effective reductant, active even without heating (Krot et al. 1996). However, hydrogen peroxide is not acceptable for tetravalent plutonium because of possible formation of Pu(IV) peroxo complexes. Therefore, Na_2SO_3 was used in the present work. Another reason to avoid use of H_2O_2 as a MnO_4^- reductant is the recently described alkaline oxidation of plutonium and neptunium to penta- and hexavalent species (Shilov et al. 1996b). Such oxidation is undesirable because freshly prepared MnO_2 is primarily a cation sorbent (Leontieva and Volkhin 1968) and Np,Pu(V,VI) are present in alkaline solutions as anionic hydroxo complexes (Tananaev 1989; Tananaev 1990). Data on Np,Pu(V,VI) coprecipitation with MnO_2 obtained by the MAR were presented in the previous report (Krot et al. 1996).

The extents of Pu(IV) removal as functions of precursor and alkali concentrations are shown in Table 3.9. Moderate increase of DF is observed with increasing carrier concentration but DF values were modest even at 0.05 M $KMnO_4$. The best removal efficiencies were observed only for 2 M or lower NaOH. Thus, practical application of MnO_2 as carrier for Np,Pu(IV) removal may be limited. On this basis, manganese dioxide was excluded from further consideration as a carrier precipitate.

Table 3.9. Coprecipitation of Pu(IV) with MnO_2 from MnO_4^- Reduction by Sulfite, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; $[Na_2SO_3] = 0.1$ M; 60°C; 2 hours

No.	[NaOH], M	$KMnO_4$, M	DF
1	2.0	0.003	8
2	2.0	0.006	16
3	2.0	0.012	50
4	2.0	0.024	40
5	2.0	0.05	40
6	0.5	0.024	25
7	1.0	0.024	50
8	2.0	0.024	40
9	4.0	0.024	3
10	6.0	0.024	2
11	8.0	0.024	1.4

3.2.1.3 Coprecipitation with Manganese(II) Hydroxide

Potassium permanganate precursor, with hydroxylamine reductant, were used to generate $Mn(OH)_2$ carrier. Optimum conditions for coprecipitation by the MAR required 0.1 M hydroxylamine (introduced as $NH_2OH \cdot HCl$) and two hours' reaction and coagulation time at 60°C (Krot et al. 1996). The present experiments with tetravalent plutonium were conducted under the same conditions. Experimental results are given in Table 3.10.

High DFs may be achieved in solutions with 1 M or less NaOH. In 2 to 4 M NaOH, DFs are markedly decreased and at higher NaOH concentrations, negligible decontamination was observed.

3.2.1.4 Coprecipitation with Chromium(III) Hydroxide

In the present experiments, chromium(III) hydroxide precipitate was obtained from chromium(III) nitrate precursor. Previous data showed that chromium(III) hydroxide is best precipitated from Cr(III) salts in alkaline solutions using three hours' heating at about 80°C (Krot et al. 1996). In the course of studies on coprecipitation of neptunium(IV) in an earlier section of the present report, $Cr(NO_3)_3$ was shown to be kinetically preferable in comparison with chromium acetate used in prior studies as a precursor for Cr(III) hydroxide carrier formation. Therefore, three hours' thermal hydrolysis of $Cr(NO_3)_3$ in alkalis at 80°C was used in all tests on Pu(IV) removal by coprecipitation with Cr(III) hydroxide.

Table 3.10. Coprecipitation of Pu(IV) with $Mn(OH)_2$ from MnO_4^- Reduction by Sulfite, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; $[NH_2OH \cdot HCl] = 0.1$ M; 60°C; 2 hours

No.	[NaOH], M	$KMnO_4$, M	DF
1	2.0	0.003	10
2	2.0	0.006	20
3	2.0	0.012	30
4	2.0	0.024	50
5	2.0	0.05	60
6	0.5	0.024	220
7	1.0	0.024	230
8	2.0	0.024	50
9	4.0	0.024	60
10	6.0	0.024	16
11	8.0	0.024	3

The data in Table 3.11 show the DFs for Cr(III) hydroxide carrier and the dependence of DF on NaOH and precursor concentrations. Lower DFs, especially at high NaOH concentrations, occur in comparison with results obtained previously for Pu(VI) and (V) (Krot et al. 1996). The higher DFs observed in the previous tests likely indicate formation of a separate plutonium solid phase. The solubilities of penta- and hexavalent plutonium in alkali are substantially higher than the solubility of

Table 3.11. Coprecipitation of Pu(IV) with $Cr(OH)_3$ from $Cr(NO_3)_3$ Hydrolysis $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$Cr(NO_3)_3$, M	DF
1	2.0	0.003	31
2	2.0	0.006	56
3	2.0	0.012	68
4	2.0	0.024	75
5	2.0	0.05	21
6	0.5	0.024	375
7	1.0	0.024	200
8	2.0	0.024	110
9	4.0	0.024	20
10	6.0	0.024	3
11	8.8	0.024	1

tetravalent plutonium. The initial plutonium concentration in the previous experiments was 1×10^{-4} M. Reduction of a portion of the plutonium to the tetravalent oxidation state under test conditions likely contributed to the relatively high observed DF.

3.2.1.5 Coprecipitation with Iron(III) Hydroxide

Iron(III) hydroxide should be a promising reagent to remove TRU from tank waste solutions. Iron hydroxide coprecipitation is known to be a very effective technique for removal of heavy metals from slightly acid solutions. Application of Fe(III) hydroxide to alkaline Hanford site tank waste treatment was the subject of recent study (Worl et al. 1995). Neptunium and plutonium(V,VI) at 1×10^{-4} M initial concentrations also are removed from alkaline solution by this treatment (Krot et al. 1996). The effectiveness of iron precipitation to remove 5×10^{-7} M Pu(IV) was tested in the present experiments. At these lower concentrations, coprecipitation effects are measured under conditions precluding formation of a separate plutonium solid phase.

Preliminary tests showed the plutonium coprecipitation with Fe(III) hydroxide, obtained by hydrolytic decomposition of sodium nitroprusside precursor, proceeds as effectively as was observed using potassium ferrate precursor decomposed by chemical reduction. The dependence of DF on the carrier and alkali concentrations with $Na_2[Fe(CN)_5NO] \cdot 2H_2O$ precursor is given in Table 3.12. The general tendencies for iron precipitation were similar to those observed earlier. With higher carrier concentrations, higher DFs were observed. Effective plutonium removal was observed at 2×10^{-2} M nitroprusside. In the present tests, nitroprusside was effective, and the DF even increased somewhat, as NaOH concentration rose to 4 M (Table 3.12). Then, as usual, further increase in alkali concentration decreased solution decontamination.

Table 3.12. Coprecipitation of Pu(IV) with $Fe(OH)_3$ from Nitroprusside Thermal Hydrolysis, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[Na_2[Fe(CN)_5NO] \cdot 2H_2O]$, M	DF
1	2.0	0.003	4
2	2.0	0.006	23
3	2.0	0.012	100
4	2.0	0.024	218
5	2.0	0.05	250
6	0.5	0.024	152
7	1.0	0.024	221
8	2.0	0.024	283
9	4.0	0.024	270
10	6.0	0.024	18
11	8.0	0.024	3

3.2.2 Removal of Pu(IV) from Alkaline Waste Component Solutions by Co(III) Hydroxide

Experiments were conducted to determine the influence of various tank waste component anions on the efficiency of decontamination from trace Pu(IV) by MAR coprecipitating agents. In the initial tests, hexaamminecobalt(III) chloride was examined as precursor reagent for Co(III) hydroxide. This carrier, obtained by MAR, produced the highest overall DFs for Pu(VI), (V), and (IV), (and over the widest range of NaOH concentration) of any carrier studied.

The test series for Co(III) hydroxide, as well as all subsequent series, began with studies of the effects of inorganic waste component salts on the completeness of plutonium removal. Organic waste components, which possibly possess complexing properties, then were examined. Sodium salts were used throughout. The waste component anion concentrations were chosen according to published information on Hanford Site tank waste (Delegard 1987a; Delegard 1995; Worl et al. 1995) and were varied to zero to observe the component effects more clearly. The range of waste component concentration was extended somewhat for the organic complexing agents and carbonate.

3.2.2.1 Nitrate

According to prior studies, preparation of cobalt(III) hydroxide by the MAR is best accomplished if alkali concentration does not exceed 4 M (Krot et al. 1996). Therefore, a 1 to 4 M NaOH working interval for cobalt hydroxide precipitation was used to test Pu(IV) trace removal from alkaline waste solution. Two test series, at 1 and 4 M NaOH, were conducted for the entire $NaNO_3$ concentration range. In addition, the dependence of DF on NaOH concentration (from 0.5 to 4 M) at the highest investigated nitrate concentration (2 M) was also determined. A similar matrix of test conditions was used in all subsequent tests of the effects of waste components on solution decontamination.

The results given in Table 3.13 show nitrate to have little influence on decontamination if the coprecipitation occurs in 1 M NaOH. Even at 2 M $NaNO_3$, the DF is about 200. However, nitrate has a stronger effect in 4 M NaOH. As reflected by Pu(IV) DF, conditions for cobalt hydroxide coagulation in 4 M NaOH containing 0.5 to 2 M $NaNO_3$ are less favorable than at lower nitrate concentration. At constant 2 M $NaNO_3$, Pu(IV) DF decreases steadily as NaOH concentration increases from 0.5 to 4 M.

3.2.2.2 Nitrite

In 1 M NaOH, relatively low nitrite concentrations (0.1 to 0.25 M) give slight diminution of DF compared with pure NaOH solutions (Table 3.14). The Pu(IV) DFs are practically the same as are found in the presence of equal nitrate concentrations. However, increasing NO_2^- concentration to 0.5 M and higher exerts a stronger influence than found for nitrate; DFs are about two-fold lower than found for equal nitrate concentrations.

Table 3.13. Decontamination of NaOH/NO_3^- Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	$[[Co(NH_3)_6]^{3+}]$, M	$[NO_3^-]$, M	DF
1	1.0	0.02	2	200
2	1.0	0.02	1	200
3	1.0	0.02	0.5	300
4	1.0	0.02	0.25	300
5	1.0	0.02	0.1	400
6	1.0	0.02	0	500
7	4.0	0.02	2	40
8	4.0	0.02	1	70
9	4.0	0.02	0.5	100
10	4.0	0.02	0.25	110
11	4.0	0.02	0.1	150
12	4.0	0.02	0	350
13	0.5	0.02	2	215
14	2.0	0.02	2	100

In 4 M NaOH, the DF dependence on nitrate and nitrite concentrations practically coincide. The DFs are about 50 for both 2 M NO_3^- and NO_2^-.

Plutonium(IV) DF is not affected by varying NaOH concentration from 0.5 to 4 M at 2 M $NaNO_2$ and remains at about 70 throughout. This behavior contrasts with that shown in 2 M $NaNO_3$ where DFs decrease from 215 to 40 as NaOH concentration increases from 0.5 to 4 M.

3.2.2.3 Carbonate

The effect of carbonate was studied in the range 0.0 to 1.0 M (see Table 3.15). In both 1 and 4 M NaOH, monotonous decrease of cobalt(III) hydroxide efficiency was found with increasing carbonate concentration. Regardless of NaOH concentration, DFs did not exceed 100 if carbonate concentration was 1 M. Some tank wastes contain approximately 1 M Na_2CO_3.

3.2.2.4 Aluminate

Aluminate shows the most deleterious effects on decontamination efficiency of all tested inorganic waste components (Table 3.16). Plutonium coprecipitation with Co(III) hydroxide was successful only

Table 3.14. Decontamination of NaOH/NO_2^- Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	$[[Co(NH_3)_6]^{3+}]$, M	$[NO_2^-]$, M	DF
1	1.0	0.02	2	70
2	1.0	0.02	1	80
3	1.0	0.02	0.5	100
4	1.0	0.02	0.25	230
5	1.0	0.02	0.1	400
6	1.0	0.02	0	500
7	4.0	0.02	2	65
8	4.0	0.02	1	70
9	4.0	0.02	0.5	75
10	4.0	0.02	0.25	100
11	4.0	0.02	0.1	150
12	4.0	0.02	0	350
13	0.5	0.02	2	90
14	2.0	0.02	2	70

from solutions containing $Al(OH)_4^-$ concentrations not higher than 0.1 M. Even at that level, however, five- and three-fold decrease in DF occurs compared, respectively, with pure 1 and 4 M NaOH. At 0.25 M aluminate, DFs are close to those observed for 1 M carbonate. The DF dependences on NaOH concentration obtained at 1 M carbonate and 0.5 M aluminate are practically the same. One possible explanation of the profound effect of aluminate is that it has a structure $[Al(OH)_4^-]$ similar to that of Pu(IV) hydroxo aqueous species [e.g., $Pu(OH)_4$, $Pu(OH)_5^-$]. However, determining the mechanisms of the coprecipitation processes is outside the scope of the present research. This supposition may be considered more fully in subsequent work.

3.2.2.5 Sulfate, Phosphate, and Fluoride

No significant effect on DF was expected by the presence of SO_4^{2-}, PO_4^{3-}, and F^- because of their negligible anticipated concentrations in tank waste solution (Delegard 1987a). To verify this supposition, a control series of experiments was performed. The results presented in Table 3.17 confirm the initial suppositions.

Table 3.15. Decontamination of NaOH/CO_3^{2-} Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	$[[Co(NH_3)_6]^{3+}]$, M	$[CO_3^{2-}]$, M	DF
1	1.0	0.02	1	70
2	1.0	0.02	0.75	115
3	1.0	0.02	0.5	220
4	1.0	0.02	0.25	300
5	1.0	0.02	0.1	350
6	1.0	0.02	0	500
7	4.0	0.02	1	50
8	4.0	0.02	0.75	90
9	4.0	0.02	0.5	100
10	4.0	0.02	0.25	225
11	4.0	0.02	0.1	300
12	4.0	0.02	0	350
13	0.5	0.02	1	100
14	2.0	0.02	1	60

Table 3.16. Decontamination of NaOH/$Al(OH)_4^-$ Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	$[[Co(NH_3)_6]^{3+}]$, M	$[Al(OH)_4^-]$, M	DF
1	1.0	0.02	0.5	75
2	1.0	0.02	0.25	80
3	1.0	0.02	0.1	100
4	1.0	0.02	0.05	200
5	1.0	0.02	0.01	500
6	1.0	0.02	0	500
7	4.0	0.02	0.5	45
8	4.0	0.02	0.25	60
9	4.0	0.02	0.1	95
10	4.0	0.02	0.05	100
11	4.0	0.02	0.01	150
12	4.0	0.02	0	350
13	0.5	0.02	0.5	100
14	2.0	0.02	0.5	64

Table 3.17. Decontamination of NaOH/SO_4^{2-}, /PO_4^{3-}, and /F^- Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

Component	Concentration, M	[NaOH], M	$[[Co(NH_3)_6]^{3+}]$, M	DF
SO_4^{2-}	0.01	1.0	0.02	470
PO_4^{3-}	0.01	1.0	0.02	520
F^-	0.01	1.0	0.02	450
SO_4^{2-}	0.01	4.0	0.02	380
PO_4^{3-}	0.01	4.0	0.02	290
F^-	0.01	4.0	0.02	300

3.2.2.6 HEDTA and EDTA

The complexing agents and waste components, HEDTA and EDTA, were added to the test solutions as their tri- and tetrasodium salts, respectively. Substantial effects were observed in tests with HEDTA and EDTA (Tables 3.18 and 3.19).

Table 3.18. Decontamination of NaOH/HEDTA Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	$[[Co(NH_3)_6]^{3+}]$, M	[HEDTA], M	DF
1	1.0	0.02	0.2	--
2	1.0	0.02	0.1	--
3	1.0	0.02	0.05	--
4	1.0	0.02	0.025	7
5	1.0	0.02	0.01	45
6	1.0	0.02	0	500
7	4.0	0.02	0.2	--
8	4.0	0.02	0.1	--
9	4.0	0.02	0.05	--
10	4.0	0.02	0.025	--
11	4.0	0.02	0.01	10
12	4.0	0.02	0	400
13	0.5	0.02	0.2	--
14	2.0	0.02	0.2	--
15	6.0	0.02	0.2	--

Table 3.19. Decontamination of NaOH/EDTA Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	$[[Co(NH_3)_6]^{3+}]$, M	[EDTA], M	DF
1	1.0	0.02	0.2	--
2	1.0	0.02	0.1	--
3	1.0	0.02	0.05	1.5
4	1.0	0.02	0.025	2
5	1.0	0.02	0.01	100
6	1.0	0.02	0	500
7	4.0	0.02	0.2	--
8	4.0	0.02	0.1	--
9	4.0	0.02	0.05	12
10	4.0	0.02	0.025	70
11	4.0	0.02	0.01	75
12	4.0	0.02	0	400
13	0.5	0.02	0.2	--
14	2.0	0.02	0.2	--
15	6.0	0.02	0.2	--

The dashes in the DF columns of Tables 3.18 and 3.19 indicate that no precipitate formed under the stated conditions. In those experiments, the test solution remained absolutely transparent, only changing its color from orange to rose. It was evident that thermal decomposition of $[Co(NH_3)_6]^{3+}$ occurred, but cobalt remained in solution as stable soluble complexes of HEDTA or EDTA and did not form hydroxo complexes with subsequent precipitation of insoluble hydroxide compound. Hydrolysis did not occur even in 6 M NaOH in the presence of 0.2 M HEDTA or EDTA. Therefore, the presence of HEDTA and EDTA in waste solutions intended for TRU removal treatment by cobalt coprecipitation is not only undesirable but strictly unacceptable because their presence, even in concentrations as low as 0.025 M, prevents carrier formation. The deleterious effects of HEDTA and EDTA on the MAR make recent research on possible ways to decompose organic complexants in alkaline solution (Shilov et al. 1997) even more relevant.

3.2.2.7 Citrate

Citrate is known to be a strong complexing agent for heavy elements in neutral and acidic media. The only information found in the technical literature on complex formation between TRU and citrate in alkaline media indicated citrate enhanced the solubility of Pu(IV) (Peretrukhin et al. 1996). However, it was difficult to predict plutonium behavior in coprecipitation processes with hydroxide carriers. Experimental data on the efficiency of Pu(IV) coprecipitation with Co(III) hydroxide as a function of citrate concentration are shown in Table 3.20.

It is seen that, in contrast to EDTA and HEDTA, low citrate concentrations have practically no effect on Pu(IV) removal by Co(III) hydroxide carrier. At citrate concentrations up to 0.03 M in 1 M NaOH, DFs of 400 to 500 are attained. Provided citrate concentrations do not exceed the nominal 0.03 M in alkaline Hanford high-level waste (Delegard 1987a), it is possible to neglect citrate's influence on decontamination efficiency. However, for 4 M NaOH solutions in the presence of 0.01 M or more citrate, the DF was about 100. The DF in 0.2 M citrate solution was not strongly dependent on NaOH concentration, decreasing from 200 to 100 as NaOH increased from 0.5 to 4 M.

Table 3.20. Decontamination of NaOH/Citrate Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	$[[Co(NH_3)_6]^{3+}]$, M	[Citrate], M	DF
1	1.0	0.02	0.2	150
2	1.0	0.02	0.1	220
3	1.0	0.02	0.06	350
4	1.0	0.02	0.03	400
5	1.0	0.02	0.01	400
6	1.0	0.02	0	500
7	4.0	0.02	0.2	100
8	4.0	0.02	0.1	100
9	4.0	0.02	0.06	110
10	4.0	0.02	0.03	100
11	4.0	0.02	0.01	150
12	4.0	0.02	0	370
13	0.5	0.02	0.2	200
14	2.0	0.02	0.2	150

3.2.2.8 Glycolate

The coprecipitation behavior of Pu(IV) in the presence of glycolate is very similar to that in the presence of citrate. Like citrate, glycolate does not prevent Co(III) hydroxide precipitation. The data in Table 3.21 show the dependence of decontamination on glycolate and NaOH concentrations.

Table 3.21. Decontamination of NaOH/Glycolate Solutions from Pu(IV) by Co(III) Hydroxide Coprecipitation, Pu(IV)]$_0$ = 5 x 10^{-7} M; 80°C; 2 hours

No.	[NaOH], M	[[Co(NH$_3$)$_6$]$^{3+}$], M	[CH$_2$OHCOO$^-$], M	DF
1	1.0	0.02	0.2	150
2	1.0	0.02	0.1	170
3	1.0	0.02	0.05	200
4	1.0	0.02	0.025	300
5	1.0	0.02	0.01	400
6	1.0	0.02	0	500
7	4.0	0.02	0.2	40
8	4.0	0.02	0.1	81
9	4.0	0.02	0.05	100
10	4.0	0.02	0.025	120
11	4.0	0.02	0.01	150
12	4.0	0.02	0	420
13	0.5	0.02	0.2	200
14	2.0	0.02	0.2	100

3.2.3 Removal of Pu(IV) from Alkaline Waste Component Solutions by Cr(III) Hydroxide

The same general experimental approach was used for Pu(IV) coprecipitation by chromium(III) hydroxide as was described for cobalt(III) hydroxide (see Section 3.2.2.). The optimum conditions for precipitation of $Cr(OH)_3$ (determined by Krot et al. 1996) were used for tests conducted in the presence of waste component anions: three hours' heating at 80°C of alkaline solution containing 0.01 M $Cr(NO_3)_3$ precipitate precursor.

3.2.3.1 Nitrate

The presence of nitrate in the hydrolytic decomposition of $Cr(NO_3)_3$ in 1 M NaOH decreased decontamination efficiency considerably (Table 3.22). Increasing salt concentration inevitably worsened coagulation conditions and simultaneously decreased the active sorption surface of the hydroxide precipitate. In an additional experiment (not listed in Table 3.22) on $Cr(NO_3)_3$ thermal hydrolysis in 0.2 M NaOH and 2 M $NaNO_3$, no Cr(III) hydroxide precipitate formed. With more concentrated alkali in the presence of NO_3^-, chromium hydroxide precipitation was observed. Nevertheless, nitrate is predicted to inhibit, to some extent, carrier formation from hydrolysis of $Cr(NO_3)_3$ precursor in the

Table 3.22. Decontamination of NaOH/NO_3^- Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	[$Cr(NO_3)_3$], M	[NO_3^-], M	DF
1	1.0	0.01	2	40
2	1.0	0.01	1	70
3	1.0	0.01	0.5	100
4	1.0	0.01	0.25	120
5	1.0	0.01	0.1	130
6	1.0	0.01	0	200
7	4.0	0.01	2	5
8	4.0	0.01	1	6
9	4.0	0.01	0.5	8
10	4.0	0.01	0.25	10
11	4.0	0.01	0.1	13
12	4.0	0.01	0	20
13	0.5	0.01	2	55
14	2.0	0.01	2	25

coprecipitation process. Nitrate also decreased Pu(IV) removal from strong alkaline solution even beyond the decrease observed because of the effect of increasing hydroxide. Thus DF decreased from 20 to 5 as nitrate concentration increased from 0 to 2 M in 4 M NaOH.

3.2.3.2 Nitrite

As was the case for nitrate, nitrite concentrations were varied from 0 to 2 M. The data presented in Table 3.23 show that nitrite had a small effect on DF in 1 M NaOH and, at lower nitrite concentrations, in 4 M NaOH. Plutonium(IV) capture from 4 M NaOH at 2 M $NaNO_2$, as in the case of nitrate, was very poor. Deactivation of the precipitate surface by nitrate or nitrite absorption and high solution viscosity may account for this decrease in DF.

3.2.3.3 Carbonate

Nominal (0.05 M) Na_2CO_3 concentrations indicated for Hanford Site tank wastes (Delegard 1987a) have no effect on Pu(IV) DF by Cr(III) hydroxide coprecipitation (Table 3.24). However, higher carbonate concentrations are known for tank wastes (Worl et al. 1995). Therefore the studied range of

Table 3.23. Decontamination of NaOH/NO_2^- Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	[$Cr(NO_3)_3$], M	[NO_2^-], M	DF
1	1.0	0.01	2	170
2	1.0	0.01	1	180
3	1.0	0.01	0.5	170
4	1.0	0.01	0.25	200
5	1.0	0.01	0.1	200
6	1.0	0.01	0	200
7	4.0	0.01	2	3
8	4.0	0.01	1	10
9	4.0	0.01	0.5	10
10	4.0	0.01	0.25	15
11	4.0	0.01	0.1	19
12	4.0	0.01	0	20
13	0.5	0.01	2	250
14	2.0	0.01	2	80

Table 3.24. Decontamination of NaOH/CO_3^{2-} Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	[$Cr(NO_3)_3$], M	[CO_3^{2-}], M	DF
1	1.0	0.01	1	60
2	1.0	0.01	0.75	100
3	1.0	0.01	0.5	170
4	1.0	0.01	0.25	180
5	1.0	0.01	0.1	180
6	1.0	0.01	0	200
7	4.0	0.01	1	6
8	4.0	0.01	0.75	10
9	4.0	0.01	0.5	15
10	4.0	0.01	0.25	23
11	4.0	0.01	0.1	28
12	4.0	0.01	0	20
13	0.5	0.01	1	80
14	2.0	0.01	1	27

carbonate concentrations was extended to 1 M. It was found that up to 0.5 M carbonate has no effect on Pu(IV) removal by chromium hydroxide from 1 and 4 M NaOH. However, for carbonate concentrations above 0.5 M, the DF is decreased considerably.

3.2.3.4 Aluminate

High aluminate concentrations are more deleterious for Cr(III) hydroxide coprecipitation than observed in the analogous Co(III) hydroxide process. Data of Table 3.25 show that Pu(IV) removal by coprecipitation with Cr(III) hydroxide becomes ineffective at 0.5 M aluminate, independent of NaOH concentration. These results most likely are caused by adsorption of $Al(OH)_4^-$ on the Cr(III) hydroxide surface and probable complexation of plutonium by aluminate (Delegard 1987a).

Table 3.25. Decontamination of $NaOH/Al(OH)_4^-$ Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[Cr(NO_3)_3]$, M	$[Al(OH)_4^-]$, M	DF
1	1.0	0.01	0.5	24
2	1.0	0.01	0.25	28
3	1.0	0.01	0.1	71
4	1.0	0.01	0.05	115
5	1.0	0.01	0.01	100
6	1.0	0.01	0	200
7	4.0	0.01	0.5	6
8	4.0	0.01	0.25	10
9	4.0	0.01	0.1	16
10	4.0	0.01	0.05	17
11	4.0	0.01	0.01	20
12	4.0	0.01	0	20
13	0.5	0.01	0.5	35
14	2.0	0.01	0.5	13

3.2.3.5 Sulfate, Phosphate, and Fluoride

Plutonium(IV) DFs are practically unaffected by the presence of low (0.01 M) concentrations of sulfate, phosphate, and fluoride (Table 3.26). It is clear that these anions at 0.01 M affect neither precipitate coagulation nor plutonium speciation in solutions where OH^- concentrations are so much higher.

Table 3.26. Decontamination of NaOH/SO_4^{2-}, /PO_4^{3-}, and /F^- Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[Pu(IV)]_0$ = 5 x 10^{-7} M; 80°C; 3 hours

Component	Concentration, M	[NaOH], M	$[Cr(NO_3)_3]$, M	DF
SO_4^{2-}	0.01	1	0.01	210
PO_4^{3-}	0.01	1	0.01	200
F^-	0.01	1	0.01	200
SO_4^{2-}	0.01	4	0.01	20
PO_4^{3-}	0.01	4	0.01	15
F^-	0.01	4	0.1	16

3.2.3.6 HEDTA and EDTA

In contrast with observations of $[Co(NH_3)_6]^{3+}$ hydrolysis in the presence of HEDTA or EDTA, strong complexants do not prevent carrier formation in the hydrolytic decomposition of chromium nitrate. Observed DFs are low for 4 M NaOH containing EDTA or HEDTA with EDTA having the greater deleterious effect. The effects of EDTA and HEDTA differ noticeably in 1 M NaOH (compare Tables 3.27 and 3.28). Whereas sharply decreased DFs are found in the presence of 0.01 M EDTA, DFs are unaffected at the same HEDTA concentration. Increasing HEDTA concentrations to 0.2 M gradually decrease the DF to about 100; DFs are 30 or lower in the range 0.01 to 0.2 M EDTA. Possible complex formation between tetravalent plutonium and EDTA, to produce a species having less affinity for sorption, may be responsible for the considerable decrease of DF in the presence of EDTA.

3.2.3.7 Citrate

The decontamination of alkaline solutions from Pu(IV) by coprecipitation with $Cr(OH)_3 \cdot xH_2O$ in the presence of citrate is effective (i.e., DF 100 or greater) in 1 M NaOH if the citrate concentration is not higher than 0.06 M. Steadily decreasing DFs were observed at higher citrate concentrations (Table 3.29). Again, in stronger NaOH, chromium(III) hydroxide is an ineffective carrier.

3.2.3.8 Glycolate

The influence of glycolate on Pu(IV) removal by chromium hydroxide coprecipitation is less than that of EDTA but similar to that found for HEDTA. The data in Table 3.30 show that the Pu(IV) removal from 1 M NaOH is satisfactory at all tested CH_2OHCOO^- (glycolate) concentrations. However, under the tested conditions with glycolate, cobalt(III) hydroxide shows DFs superior to those of Cr(III) hydroxide.

Table 3.27. Decontamination of NaOH/HEDTA Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[Cr(NO_3)_3]$, M	[HEDTA], M	DF
1	1.0	0.01	0.2	90
2	1.0	0.01	0.1	95
3	1.0	0.01	0.05	120
4	1.0	0.01	0.025	170
5	1.0	0.01	0.01	180
6	1.0	0.01	0	200
7	4.0	0.01	0.2	10
8	4.0	0.01	0.1	10
9	4.0	0.01	0.05	13
10	4.0	0.01	0.025	15
11	4.0	0.01	0.01	16
12	4.0	0.01	0	20
13	0.5	0.01	0.2	105
14	2.0	0.01	0.2	29

Table 3.28. Decontamination of NaOH/EDTA Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[Cr(NO_3)_3]$, M	[EDTA], M	DF
1	1.0	0.01	0.2	10
2	1.0	0.01	0.1	12
3	1.0	0.01	0.05	25
4	1.0	0.01	0.025	29
5	1.0	0.01	0.01	30
6	1.0	0.01	0	200
7	4.0	0.01	0.2	2
8	4.0	0.01	0.1	3
9	4.0	0.01	0.05	3
10	4.0	0.01	0.025	4
11	4.0	0.01	0.01	6
12	4.0	0.01	0	20
13	0.5	0.01	0.2	14
14	2.0	0.01	0.2	7

Table 3.29. Decontamination of NaOH/Citrate Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[\mathrm{Pu(IV)}]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[\mathrm{Cr(NO_3)_3}]$, M	[Citrate], M	DF
1	1.0	0.01	0.2	50
2	1.0	0.01	0.1	80
3	1.0	0.01	0.06	110
4	1.0	0.01	0.03	115
5	1.0	0.01	0.01	130
6	1.0	0.01	0	200
7	4.0	0.01	0.2	3
8	4.0	0.01	0.1	9
9	4.0	0.01	0.06	17
10	4.0	0.01	0.03	17
11	4.0	0.01	0.01	17
12	4.0	0.01	0	20
13	0.5	0.01	0.2	63
14	2.0	0.01	0.2	31

Table 3.30. Decontamination of NaOH/Glycolate Solutions from Pu(IV) by Cr(III) Hydroxide Coprecipitation, $[\mathrm{Pu(IV)}]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[\mathrm{Cr(NO_3)_3}]$, M	$[\mathrm{CH_2OHCOO^-}]$, M	DF
1	1.0	0.01	0.2	100
2	1.0	0.01	0.1	120
3	1.0	0.01	0.05	135
4	1.0	0.01	0.025	165
5	1.0	0.01	0.01	180
6	1.0	0.01	0	200
7	4.0	0.01	0.2	6
8	4.0	0.01	0.1	7
9	4.0	0.01	0.05	9
10	4.0	0.01	0.025	10
11	4.0	0.01	0.01	12
12	4.0	0.01	0	20
13	0.5	0.01	0.2	130
14	2.0	0.01	0.2	40

3.2.4 Removal of Pu(IV) from Alkaline Waste Component Solutions by Fe(III) Hydroxide

Iron(III) hydroxide was shown earlier to attain high DFs in pure NaOH solutions. Based on the results found for Co(III) and Cr(III) hydroxides, lower DFs were expected in the presence, and with increasing concentrations, of added salts. The effects of the selected individual waste components on coprecipitation by Fe(III) hydroxide were evaluated.

3.2.4.1 Nitrate

As shown in Table 3.31, the coprecipitation of Pu(IV) with Fe(III) hydroxide obtained from thermal hydrolysis of nitroprusside is practically unaffected by nitrate over the entire studied 0 to 2 M range. In fact, DFs in 4 M NaOH, though lower than for 1 M NaOH, still exceed 100 even in 2 M $NaNO_3$.

Table 3.31. Decontamination of NaOH/NO_3^- Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[[Fe(CN_5)NO]^{2-}]$, M	$[NO_3^-]$, M	DF
1	1.0	0.02	2	260
2	1.0	0.02	1	250
3	1.0	0.02	0.5	300
4	1.0	0.02	0.25	310
5	1.0	0.02	0.1	290
6	1.0	0.02	0	320
7	4.0	0.02	2	105
8	4.0	0.02	1	110
9	4.0	0.02	0.5	120
10	4.0	0.02	0.25	150
11	4.0	0.02	0.1	180
12	4.0	0.02	0	220
13	0.5	0.02	2	320
14	2.0	0.02	2	250
15	6.0	0.02	2	33
16	8.0	0.02	2	1.5

3.2.4.2 Nitrite

The Pu(IV) DFs as a function of nitrite concentration are given in Table 3.32. The results do not differ considerably from those obtained in the corresponding nitrate experiments.

However, in the nitrite experiments, an important peculiarity of nitroprusside hydrolysis was discovered. With nitrite present, the $[Fe(CN)_5NO]^{2-}$ hydrolysis reaction is decelerated. In 2 M nitrite and 4 M NaOH, the induction period described previously (Krot et al. 1996) extends to more than two hours. During this period, no precipitate forms. Deceleration of carrier formation was also noted at lower nitrite concentrations. Based on these observations, the time allowed for hydrolysis was extended to four hours. Despite the extended time, the hydrolytic decomposition processes were still not complete, especially in solutions with high nitrite and alkali concentrations. This was revealed by the residual intense yellow solution color showing nitroprusside remained even after four hours' heating. In the absence of nitrite, all solutions become colorless in 1.5 to 2 hours corresponding to the decomposition of $[Fe(CN)_5NO]^{2-}$ (Krot et al. 1996).

Table 3.32. Decontamination of $NaOH/NO_2^-$ Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 4 hours

No.	[NaOH], M	$[[Fe(CN)_5NO]^{2-}]$, M	$[NO_2^-]$, M	DF
1	1.0	0.02	2	200
2	1.0	0.02	1	300
3	1.0	0.02	0.5	340
4	1.0	0.02	0.25	300
5	1.0	0.02	0.1	300
6	1.0	0.02	0	320
7	4.0	0.02	2	90
8	4.0	0.02	1	130
9	4.0	0.02	0.5	150
10	4.0	0.02	0.25	150
11	4.0	0.02	0.1	130
12	4.0	0.02	0	220
13	0.5	0.02	2	320
14	2.0	0.02	2	260
15	6.0	0.02	2	30
16	8.0	0.02	2	1.5

A possible explanation of this effect may be that additional nitrite shifts the equilibrium

$$[\mathrm{Fe(CN)_5NO}]^{2-} + 2\ \mathrm{OH}^- \rightleftarrows [\mathrm{Fe(CN)_5NO_2}]^{4-} + \mathrm{H_2O} \tag{3.1}$$

to the right and thus slows hydrolysis of the pentacyanonitrosyl complex (Baraldo et al. 1994).

3.2.4.3 Carbonate

The coprecipitation behavior of plutonium depends to a considerable extent on its ionic form in solution. Plutonium(IV) likely is present in strongly alkaline media as $\mathrm{Pu(OH)}_{n+4}^{n-}$ anions. It would be expected that as the anions' negative charge increases, its ability to sorb on hydroxide precipitates decreases. The anionic charge would increase with increasing alkali concentration and further hydroxide coordination. Such reasons may explain the decreasing DF observed with increasing alkali concentration. This is true not only for carbonate tests, but for all other waste component tests as well.

Anionic complexes also may form through carbonate ligation and thus influence plutonium coprecipitation behavior. The thermodynamic stability constants of Pu(IV) carbonate and hydroxo complexes are similar. Thus, OH^- ligand groups may be partially replaced by $\mathrm{CO_3}^{2-}$ and further decrease coprecipitation DFs. In the experiments with Fe(III) hydroxide, DFs decreased sharply as $\mathrm{CO_3}^{2-}$ reached and exceeded 0.5 M in 4 M NaOH (Table 3.33). In 1 M NaOH solution, carbonate had no noticeable influence on DF over the range 0 to 1 M $\mathrm{Na_2CO_3}$.

3.2.4.4 Aluminate

Diminished decontamination efficiency was observed with aluminate concentration as low as 0.05 M in 1 and 4 M NaOH. The DF dropped from over 200 to 90 and 30, respectively, upon increasing $\mathrm{Al(OH)_4}^-$ concentration to 0.5 M in these solutions (Table 3.34).

3.2.4.5 Sulfate, Phosphate, and Fluoride

Control tests on minor inorganic anions were also conducted for iron(III) hydroxide precipitation. In results similar to cobalt(III) and chromium(III), 0.01 M $\mathrm{SO_4}^{2-}$, $\mathrm{PO_4}^{3-}$, and F^- had no measurable effect on Pu(IV) removal from 1 and 4 M NaOH (Table 3.35).

3.2.4.6 Organic Components

The tested organic components exerted comparable effects on decontamination efficiency under the same experimental conditions. Somewhat lower DFs for glycolate, compared with other complexants, were obtained in 1 M NaOH. In 4 M NaOH, the largest decrease in DF was found with citrate. Plutonium was removed satisfactorily in the presence of up to 0.01 M citrate; with higher citrate concentrations, a sharp decrease in DF was observed.

Table 3.33. Decontamination of NaOH/CO_3^{2-} Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[[Fe(CN)_5NO]^{2-}]$, M	$[CO_3^{2-}]$, M	DF
1	1.0	0.02	1	270
2	1.0	0.02	0.75	290
3	1.0	0.02	0.5	270
4	1.0	0.02	0.25	290
5	1.0	0.02	0.1	260
6	1.0	0.02	0	320
7	4.0	0.02	1	20
8	4.0	0.02	0.75	30
9	4.0	0.02	0.5	30
10	4.0	0.02	0.25	150
11	4.0	0.02	0.1	140
12	4.0	0.02	0	220
13	0.5	0.02	1	310
14	2.0	0.02	1	120
15	6	0.02	1	14

The results and conditions of the experiments with the organic complexants and Fe(III) hydroxide are given in Tables 3.36 to 3.39. In contrast to what was observed for hydrolytic decomposition of hexaamminecobalt in the presence of high concentrations of EDTA and HEDTA, under no conditions was Fe(III) hydroxide carrier formation prevented.

3.2.5 Removal of Pu(IV) from Alkaline Waste Component Solutions by Mn(II) Hydroxide

The Mn(II) hydroxide precipitate was prepared by chemically reducing 0.02 M $KMnO_4$ to $Mn(OH)_2$ with 0.1 M NH_2OH. The precipitate was allowed to coagulate for three hours at 50°C. In previous studies (Krot et al. 1996), the plutonium concentration was 1×10^{-4} M; i.e., higher than the solubility of Pu(IV). In the present experiments, 5×10^{-7} M Pu was used. Results obtained in prior work and in the present experiments are compared in Table 3.40.

The data illustrate that in the previous studies, where Pu concentrations were higher than Pu(IV) hydroxide solubility, coprecipitation of Pu with Mn(II) hydroxide was accompanied by the formation of Pu(IV) hydroxide solid phase. The decreasing DF with increasing alkali concentration reflects the increasing $Mn(OH)_2$ solubility in alkali.

Table 3.34. Decontamination of NaOH/Al(OH)$_4^-$ Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, [Pu(IV)]$_0$ = 5 x 10^{-7} M; 80°C; 3 hours

No.	[NaOH], M	[[Fe(CN)$_5$NO]$^{2-}$], M	[Al(OH)$_4^-$], M	DF
1	1.0	0.02	0.5	90
2	1.0	0.02	0.25	150
3	1.0	0.02	0.1	190
4	1.0	0.02	0.05	170
5	1.0	0.02	0.01	200
6	1.0	0.02	0	320
7	4.0	0.02	0.5	35
8	4.0	0.02	0.25	90
9	4.0	0.02	0.1	80
10	4.0	0.02	0.05	110
11	4.0	0.02	0.01	150
12	4.0	0.02	0	220
13	0.5	0.02	0.5	180
14	2.0	0.02	0.5	70
15	6.0	0.02	0.5	30
16	8.0	0.02	0.5	3

Table 3.35. Decontamination of NaOH/SO$_4^{2-}$, /PO$_4^{3-}$, and /F$^-$ Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, [Pu(IV)]$_0$ = 5 x 10^{-7} M; 80°C; 3 hours

Component	Concentration, M	[NaOH], M	[[Fe(CN)$_5$NO]$^{2-}$], M	DF
SO$_4^{2-}$	0.01	1	0.02	340
PO$_4^{3-}$	0.01	1	0.02	310
F$^-$	0.01	1	0.02	300
SO$_4^{2-}$	0.01	4	0.02	200
PO$_4^{3-}$	0.01	4	0.02	170
F$^-$	0.01	4	0.02	150

Table 3.36. Decontamination of NaOH/HEDTA Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[[Fe(CN)_5NO]^{2-}]$, M	[HEDTA], M	DF
1	1.0	0.02	0.2	200
2	1.0	0.02	0.1	260
3	1.0	0.02	0.05	200
4	1.0	0.02	0.025	240
5	1.0	0.02	0.01	240
6	1.0	0.02	0	320
7	4.0	0.02	0.2	80
8	4.0	0.02	0.1	110
9	4.0	0.02	0.05	100
10	4.0	0.02	0.025	110
11	4.0	0.02	0.01	110
12	4.0	0.02	0	220
13	0.5	0.02	0.2	10
14	2.0	0.02	0.2	90

Table 3.37. Decontamination of NaOH/EDTA Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[[Fe(CN)_5NO]^{2-}]$, M	[EDTA], M	DF
1	1.0	0.02	0.2	240
2	1.0	0.02	0.1	190
3	1.0	0.02	0.05	220
4	1.0	0.02	0.025	210
5	1.0	0.02	0.01	250
6	1.0	0.02	0	320
7	4.0	0.02	0.2	100
8	4.0	0.02	0.1	90
9	4.0	0.02	0.05	130
10	4.0	0.02	0.025	110
11	4.0	0.02	0.01	110
12	4.0	0.02	0	220
13	0.5	0.02	0.2	240
14	2.0	0.02	0.2	250

Table 3.38. Decontamination of NaOH/Citrate Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[[Fe(CN)_5NO]^{2-}]$, M	[Citrate], M	DF
1	1.0	0.02	0.2	210
2	1.0	0.02	0.1	200
3	1.0	0.02	0.06	230
4	1.0	0.02	0.03	250
5	1.0	0.02	0.01	260
6	1.0	0.02	0	320
7	4.0	0.02	0.2	25
8	4.0	0.02	0.1	30
9	4.0	0.02	0.06	20
10	4.0	0.02	0.03	20
11	4.0	0.02	0.01	110
12	4.0	0.02	0	220
13	0.5	0.02	0.2	150
14	2.0	0.02	0.2	80

Table 3.39. Decontamination of NaOH/Glycolate Solutions from Pu(IV) by Fe(III) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 80°C; 3 hours

No.	[NaOH], M	$[[Fe(CN)_5NO]^{2-}]$, M	$[CH_2OHCOO^-]$, M	DF
1	1.0	0.02	0.2	170
2	1.0	0.02	0.1	170
3	1.0	0.02	0.05	150
4	1.0	0.02	0.025	180
5	1.0	0.02	0.01	230
6	1.0	0.02	0	320
7	4.0	0.02	0.2	50
8	4.0	0.02	0.1	70
9	4.0	0.02	0.05	80
10	4.0	0.02	0.025	90
11	4.0	0.02	0.01	80
12	4.0	0.02	0	220
13	0.5	0.02	0.2	170
14	2.0	0.02	0.2	180

Table 3.40. Decontamination of NaOH Solutions from Pu(IV) by Mn(II) Hydroxide Coprecipitation, 50°C; 3 hours

No.	[NaOH], M	[$KMnO_4$], M	DF, $[Pu]_0 = 1 \times 10^{-4}$ M[a]	DF, $[Pu]_0 = 5 \times 10^{-7}$ M
1	0.5	0.01	430	--
2	1.0	0.01	260	--
3	2.0	0.01	250	--
4	4.0	0.01	200	--
5	0.5	0.02	--	217
6	1.0	0.02	--	225
7	2.0	0.02	--	51
8	4.0	0.02	400	30

(a) Krot et al. 1996.

The effects of noncomplexing singly charged inorganic anions on DF was found to be small. The concentration range studied was based on a prior report on Hanford Site tank waste (Delegard 1987a). Carbonate was the only inorganic ion having a significant effect on coprecipitation of Pu with $Mn(OH)_2$. Carbonate formed $MnCO_3$ precipitate and complexed Pu(IV). Data illustrating the dependence of DF on CO_3^{2-} concentration at various NaOH concentrations are presented in Table 3.41.

Decontamination of alkaline solutions from Pu with Mn(II) hydroxide is possible in relatively dilute alkali at or below 0.05 M CO_3^{2-}.

Organic complex-forming agents (EDTA, HEDTA, citrate) seriously inhibit Pu coprecipitation with $Mn(OH)_2$. These agents sharply decreased DF (20 to 30 or less in 0.5 to 4 M NaOH) because of the extremely high solubility of $Mn(OH)_2$ in solutions with complexant concentrations exceeding 0.01 M.

3.2.6 Removal of Pu(IV) from Alkaline Waste Component Solutions by Sodium Uranate

Sodium uranate may be homogeneously precipitated in alkaline solution by catalytic decomposition of the soluble uranyl peroxide complex precursor. The optimum decomposition conditions are by use of 5×10^{-3} M Cu(II) catalyst with three hours' heating at 60° C. Results of coprecipitation of Pu(V,VI) with sodium uranates were presented in prior work (Krot et al. 1996). However, 5×10^{-5} M Pu(V,VI) was used in the previous tests. It recently has been found that Pu(V) is produced by the reaction of Pu(VI) with hydrogen peroxide in alkaline media free of additional complex forming agents and salt components (Shilov et al. 1996b).

In the present experiments, Pu was initially in the (IV) oxidation state. The recently published studies also showed that Pu(IV) is oxidized to Pu(V) by hydrogen peroxide in alkaline media (Shilov et al. 1996b). Therefore, in both the present and previous sodium uranate coprecipitation tests (Krot

Table 3.41. Decontamination of NaOH/CO_3^{2-} Solutions from Pu(IV) by Mn(II) Hydroxide Coprecipitation, $[Pu(IV)]_0 = 5 \times 10^{-7}$ M; 0.02 M $KMnO_4$; 0.1 M NH_2OH; 50°C; 3 hours

No.	[NaOH], M	[Na_2CO_3], M	DF
1	0.5	0	217
2	0.5	0.5	22
3	1.0	0	225
4	1.0	0.01	180
5	1.0	0.05	147
6	1.0	0.25	38
7	1.0	0.5	23
8	2.0	0	51
9	2.0	0.5	10
10	4.0	0	30
11	4.0	0.01	22
12	4.0	0.05	14
13	4.0	0.25	11
14	4.0	0.5	7

et al. 1996), Pu existed as Pu(V). Because the solubility of Pu(V) hydroxo compounds in alkaline solution is about 10^{-5} M to 10^{-4} M (Peretrukhin et al. 1996), the present tests were run at 5×10^{-7} M to preclude the formation of a separate Pu(V) solid phase. The solution decontamination data obtained in the previous experiments (Krot et al. 1996) are compared with present experimental results in Table 3.42.

Table 3.42. Decontamination of NaOH Solutions from Pu(IV) by Sodium Uranate Coprecipitation 0.01 M $[UO_2(O_2)_3]^{4-}$; 5×10^{-3} M Cu(II); 60°C; 3 hours

No.	[NaOH], M	DF at $[Pu]_0 = 5 \times 10^{-5}$ M[(a)]	DF at $[Pu]_0 = 5 \times 10^{-7}$ M
1	0.5	590	200
2	1.0	360	153
3	2.0	320	145
4	4.0	150	102
(a) Krot et al. 1996.			

In general, increasing NaOH concentration decreased DF because of the increasing solubility of sodium uranate. On the other hand, increasing solution viscosity with concentration can affect diffusion processes. The viscosity of alkaline solutions up to 2 M NaOH do not differ significantly from the viscosity of pure water. Decreased reaction rates caused by diffusion can be expected in higher than 3.5 to 4.0 M NaOH and in concentrated salt solutions.

Because the solubility of Pu(V) increases with NaOH concentration (Peretrukhin et al. 1996), formation of a Pu(V) hydroxo compound solid phase becomes less probable in more concentrated NaOH solutions. Based on the data compared in Table 3.42, it appears that at 5×10^{-5} M Pu and higher, coprecipitation of Pu(V) with sodium uranates can be accompanied by the formation of a separate Pu(V) hydroxo compound solid phase.

The effects of different inorganic salts and complex forming agents on coprecipitation of Pu with sodium uranate carrier also were surveyed. The magnitudes of concentrations of these addition components were based on a nominal Hanford site tank waste solution composition (Delegard 1987a). The effect of each component was studied separately. Results of the studies of salt effects are presented in Table 3.43.

Table 3.43. Decontamination of NaOH/Salt Solutions from Pu(IV) by Sodium Uranate Coprecipitation, $[Pu]_0 = 5 \times 10^{-7}$ M; 0.01 M $[UO_2(O_2)_3]^{4-}$; 5×10^{-3} M Cu(II); 60°C; 3 hours

No.	[NaOH], M	Salt	[Salt], M	DF, with Salt	DF, Without Salt[(a)]
1	0.5	$NaNO_3$	2	172	200
2	1.0	$NaNO_3$	2	133	153
3	2.0	$NaNO_3$	2	107	145
4	4.0	$NaNO_3$	2	89	102
5	0.5	$NaNO_2$	2	165	200
6	1.0	$NaNO_2$	2	130	153
7	2.0	$NaNO_2$	2	105	145
8	4.0	$NaNO_2$	2	86	102
9	0.5	$NaAl(OH)_4$	0.5	189	200
10	1.0	$NaAl(OH)_4$	0.5	176	153
11	2.0	$NaAl(OH)_4$	0.5	164	145
12	4.0	$NaAl(OH)_4$	0.5	100	102
13	0.5	Na_2CO_3	0.5	17	200
14	1.0	Na_2CO_3	0.5	24	153
15	2.0	Na_2CO_3	0.5	25	145
16	4.0	Na_2CO_3	0.5	23	102

(a) Krot et al. 1996.

As shown in Table 3.43, high concentrations of singly charged anion salts (nitrate, nitrite, and aluminate) do not significantly change the observed DF compared with the saltless system. The data illustrate that increasing ionic strength, by itself, does not strongly affect the coprecipitation process. However, further addition of non complex-forming salts to the point that viscosity significantly increases would decrease microcomponent diffusion coefficients and affect coprecipitation. Genuine tank wastes, saturated in many sodium salts, likely are in this high viscosity regime.

In contrast, carbonate affects the process strongly because of its ability to form complexes. The stability constants for actinide hydroxo and carbonate complexes are known to be comparable. Addition of high concentrations of carbonate increases uranate salt solubility and decreases DF. Table 3.44 illustrates the dependence of DF on CO_3^{2-} concentration.

It is seen that DF is unaffected by varying carbonate concentration at less than 0.1 M carbonate. At higher carbonate concentrations, DFs are decreased. Thus, solutions may require removal of CO_3^{2-} to achieve satisfactory DF at the present ratio of uranate carrier to carbonate. One possible methods to remove carbonate may be precipitation with Ba^{2+} to form $BaCO_3$.

The effects of organic agents on decontamination by sodium uranate also were studied. The data, obtained at nominal waste concentrations (Delegard 1987a), are presented in Table 3.45.

The data given in Table 3.45 show that at these high complexant concentrations, EDTA, HEDTA, and citrate significantly decrease DF. Glycolate has a relatively minor effect. To determine the threshold effect of the studied complex forming agents, further experiments were conducted. Table 3.46 illustrates the dependence of DF on complexant concentration.

These results show that to obtain satisfactory decontamination using 0.01 M $[UO_2(O_2)_3]^{4-}$, the complexant concentrations should not exceed 0.015 M to 0.025 M. Though these higher concentrations are comparable to the carrier precursor concentration, sodium uranate precipitation is still possible because the stability constant of the uranate hydroxo complex is greater than that of the respective uranyl organic complex. However, decreased uranate precipitation was observed in the studied systems at organic complexant concentrations higher than the indicated range.

Table 3.44. Decontamination of $NaOH/CO_3^{2-}$ Solutions from Pu(IV) by Sodium Uranate Coprecipitation, $[Pu]_0 = 5 \times 10^{-7}$ M; 0.01 M $[UO_2(O_2)_3]^{4-}$; 5×10^{-3} M Cu(II); 60°C; 3 hours

No.	$[Na_2CO_3]$, M	DF in 1 M NaOH	DF in 4 M NaOH
1	0.01	180	91
2	0.10	107	78
3	0.25	52	46
4	0.50	24	25

Table 3.45. Decontamination of NaOH/Organic Complexant Solutions from Pu(IV) by Sodium Uranate Coprecipitation, $[Pu]_0 = 5 \times 10^{-7}$ M; 0.01 M $[UO_2(O_2)_3]^{4-}$; 5×10^{-3} M Cu(II); 60°C; 3 hours

No.	[NaOH], M	Complexant	[Complexant], M	DF, with Complexant	DF, Without Complexant
1	0.5	Na glycolate	0.1	150	200
2	1.0	Na glycolate	0.1	103	153
3	2.0	Na glycolate	0.1	81	145
4	4.0	Na glycolate	0.1	80	102
5	0.5	Na_3HEDTA	0.1	3	200
6	1.0	Na_3HEDTA	0.1	4	153
7	2.0	Na_3HEDTA	0.1	4	145
8	4.0	Na_3HEDTA	0.1	5	102
9	0.5	Na_4EDTA	0.05	8	200
10	1.0	Na_4EDTA	0.05	9	153
11	2.0	Na_4EDTA	0.05	9	145
12	4.0	Na_4EDTA	0.05	14	102
13	0.5	Na_3citrate	0.05	9	200
14	1.0	Na_3citrate	0.05	9	153
15	2.0	Na_3citrate	0.05	12	145
16	4.0	Na_3citrate	0.05	10	102

3.2.7 Removal of Aged Pu(IV) from NaOH Solution

It is known that Pu(IV) forms polymer aggregates even at 10^{-8} M Pu(IV) in alkaline solution (Grebenshchikova and Davydov 1961). The properties of freshly prepared and aged polymers may differ considerably, depending on various factors.

The "aging" effect on coprecipitation of Pu(IV) was studied for cobalt(III) and chromium(III) hydroxide carriers. In these tests, the initial Pu(IV) concentration was 5×10^{-7} M and the aging was varied from 1 to 30 days. The aged Pu(IV) hydroxide was prepared by adding Pu(IV) nitrate stock solution to argon-purged NaOH solutions of selected concentration (0.5, 1, 2, 4, and 8 M). The samples were tightly capped and stored at 18 to 23°C. In the absence of carriers, the solution radioactivity concentration remained constant over the duration of the experiment. This observation means that plutonium forms a rather stable solution. Therefore it is possible to neglect processes such as formation of a Pu(IV) hydroxide solid phase and adsorption of plutonium on the vessel walls.

As shown in Tables 3.47 and 3.48, the time of aging had no significant effect on DF; in particular, no decrease in decontamination efficiency was observed for the tested carriers. However, the duration of the experiments (30 days maximum) cannot be compared with the storage time of genuine waste at the Hanford Site.

Table 3.46. Decontamination of NaOH/Organic Complexant Solutions from Pu(IV) by Sodium Uranate Coprecipitation; Effect of Concentration, $[Pu]_0 = 5 \times 10^{-7}$ M; 0.01 M $[UO_2(O_2)_3]^{4-}$; 5×10^{-3} M Cu(II); 60°C; 3 hours

No.	Complexant	[Complexant], M	DF in 1 M NaOH	DF in 4 M NaOH
1	Na_3HEDTA	0.006	201	106
2	Na_3HEDTA	0.0125	178	102
3	Na_3HEDTA	0.025	15	96
4	Na_3HEDTA	0.05	8	60
5	Na_3HEDTA	0.10	3	10
6	Na_4EDTA	0.006	211	109
7	Na_4EDTA	0.0125	163	103
8	Na_4EDTA	0.025	96	82
9	Na_4EDTA	0.05	10	14
10	Na_3Citrate	0.004	180	115
11	Na_3Citrate	0.0075	172	106
12	Na_3Citrate	0.015	104	80
13	Na_3Citrate	0.03	32	20
14	Na_3Citrate	0.05	9	10

Table 3.47. Decontamination of NaOH Solutions from Aged Pu(IV) by Cobalt(III) Hydroxide Coprecipitation, $[Pu]_0 = 5 \times 10^{-7}$ M; 80°C; 2 hours

No.	[NaOH], M	DF after Aging			
		1 day	3 days	15 days	30 days
1	0.5	300	250	260	260
2	1	300	250	240	240
3	2	200	120	150	100
4	4	50	24	26	25
5	8	6	8	17	15

Table 3.48. Decontamination of NaOH Solutions from Aged Pu(IV) by Chromium(III) Hydroxide Coprecipitation, $[Pu]_0 = 5 \times 10^{-7}$ $\underline{M}$; 80°C; 3 hours

No.	[NaOH], M	DF after Aging			
		1 day	3 days	15 days	30 days
1	0.5	150	120	125	125
2	1	100	100	70	70
3	2	50	50	35	30
4	4	10	9	5	5
5	8	1	1	1	1

4.0 Summary and Conclusions

The present study is a continuation of a research project whose goal is to create an effective technique for decontaminating radioactive high activity waste solutions of long lived and extremely dangerous α-emitting radionuclides. The project began in 1995 and included consideration of coprecipitation. Based on these early enquiries, an experimental program was proposed to evaluate homogeneous coprecipitation by the Method of Appearing Reagents (MAR) as a means to remove transuranium elements (neptunium and plutonium) from alkaline Hanford Site tank waste solutions.

Candidate carriers and carrier precursors for the coprecipitation of transuranium elements from alkaline solutions were proposed and studied in the initial experimental program. Sodium uranate, manganese dioxide, and the hydroxides of cobalt, chromium, iron, and manganese were tested as prospective carriers and selected for further examination based on preliminary information on their behaviors in alkaline media. Besides the ready availability of soluble precursor compounds for all these carriers, the completeness of their separation from solution, their chemical behaviors in alkali, and their precipitation kinetics data were obtained.

Results in the second stage of research showed high decontamination of alkaline solution could be obtained from neptunium and plutonium introduced in their penta- and hexavalent oxidation states. It was noted that the decontamination from plutonium usually was significantly higher than from neptunium. The corresponding redox reactions of these actinides occurring under precipitate-forming conditions likely account for this difference. Thus, the low decontamination from neptunium was suspected to be caused by its stabilization in the pentavalent state whereas plutonium precipitated with carriers, completely or partially, as its tetravalent form.

To confirm these suppositions, a series of tests was conducted. First, investigations of neptunium reduction to its tetravalent state in alkaline media were performed. Then, capture of the reduced neptunium by carriers formed by the MAR was examined. The experiments on neptunium removal showed, as expected, that transformation of neptunium to Np(IV) significantly increases decontamination efficiency.

It was found that decontamination is most effective if the rate of carrier formation equals, or is somewhat slower than, the kinetics of neptunium reduction, $Np(V,VI) \rightarrow Np(IV)$. A number of reductants were tested. Hydrazine, vanadyl sulfate, and sodium dithionite were found to be the most effective reductants. These reductants also meet the kinetics requirements. The three reductants showed varying success when used with candidate MAR carriers.

Plutonium reduction to the tetravalent state under coprecipitation conditions was confirmed. Therefore, further detailed investigations of Pu(IV) coprecipitation were performed. The Pu(IV) results may be extended to Np(IV) because of the known similarity of their chemical properties.

In conducting tests with Pu(IV), initial plutonium concentrations were decreased to 5 x 10^{-7} M. This concentration is near or below the solubility of Pu(IV), depending on the alkali concentration being investigated. Separate experiments were performed to confirm that plutonium(IV) hydroxide did not precipitate under the studied conditions.

It was shown that all the proposed carrier precursors are effective for plutonium coprecipitation under conditions similar to those determined in earlier tests (Krot et al. 1996). At optimum conditions, coprecipitation with hydroxides of cobalt(III), manganese(II), chromium(III), and iron(III) achieved decontamination factors from plutonium(IV) of 200 or higher. Manganese(IV) oxide precipitation gave lower decontamination.

However, as alkali concentration increased, decontamination efficiency decreased. This result is partially explained by formation of anionic plutonium(IV) complexes. The complexes presumably have the form $Pu(OH)_{4+n}^{n-}$. If so, increasing alkali concentration should increase hydroxide coordination to give increasing negative charge and corresponding decrease in absorption by hydroxide precipitates.

Besides actinide oxidation state, various inorganic and organic components present in genuine Hanford Site tank waste solution were shown to influence the effectiveness of coprecipitation processes. Such effects may be caused by changes in the chemical behavior of transuranium elements because of complex formation with waste components. The waste solution components also can alter the hydrolysis and coagulation conditions for precipitating carriers. Thus, changes in the physical-chemical properties of the aqueous phase (e.g., viscosity; ionic strength) by addition of any waste component may affect the efficiency of TRU removal.

Because the goal of the present work was limited to identification and definition of coprecipitation processes to decrease TRU concentration in high activity tank waste solution, determination of the exact contribution each of these factors (e.g., complexation, viscosity) to removal efficiency was too complicated and extensive a problem to be considered in detail. Instead, the sum of the physical and chemical effects were measured by the effectiveness of TRU(IV) transfer into solid phase; i.e., as the decontamination factor, DF.

Experimental DFs from Pu(IV) were measured to identify the effects of 12 waste components separately and over selected concentration ranges. Five carriers were tested. They were obtained by the MAR from their respective precursors by thermal hydrolysis, chemical reduction, or catalytic decomposition. Though DFs generally decreased with increasing component concentration, the decontamination efficiency often remained high and DFs exceeding 100 were obtained.

The overall moderate decrease in coprecipitation in the presence of inorganic waste anions may present indirect evidence of simple ionic competition in an adsorption mechanism on hydroxide carriers. Results obtained with sodium uranate show that isomorphic cocrystallization of plutonium with uranium also may take place.

Organic complexants in alkaline solutions have a profound effect on many precipitation processes. In sufficient concentration, the presence of HEDTA or EDTA in alkaline solution prevented carrier formation with $[Co(NH_3)_6]^{3+}$ as precursor. The same effect was observed for manganese(II). These organic complexants also significantly decreased plutonium coprecipitation with chromium(III) hydroxide and sodium uranate. Only sodium nitroprusside, as iron(III) hydroxide precursor, resisted the influence of complexants. Neither HEDTA nor EDTA prevented precipitate formation from nitroprusside; high DFs from plutonium also were obtained. Generally, however, the organic waste components had deleterious effects on DF. Their decomposition before TRU removal from waste solutions by the MAR may be necessary.

Based on results obtained in the prior studies (Krot et al. 1996) and on the present findings, it is possible to outline further directions for this research program. Tests using compositions simulating actual Hanford Site tank waste solution should be performed. Because of the unique properties of the five tested precursors, the best agent likely will vary according to waste stream composition. Therefore, further laboratory and pilot testing with simulant and actual tank waste solutions must be performed.

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