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Purification of Alkaline Solutions and Wastes from Actinides and Technetium by Coprecipitation with Some Carriers Using the Method of Appearing Reagents: Final Report

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September 1998

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Prepared for the U.S. Department of Energy
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PNNL-11988

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**Purification of Alkaline Solutions and Wastes
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Summary

The coprecipitation of transuranium elements (TRU) and technetium from alkaline solutions and from simulants of Hanford Site tank wastes has been studied in reducing and oxidizing conditions on uranium(IV,VI) hydroxocompounds, tetraalkylammonium perrhenate and perchlorate, and on hydroxides of Fe(III), Co(III), Mn(II), and Cr(III) using the Method of Appearing Reagents (MAR). Coprecipitations in alkaline solution have been shown to give high decontamination factors (DF) at low content of carrier and in the presence of high salt concentrations.

Uranium(IV) hydroxide in concentrations higher than 3×10^{-3} M coprecipitates Pu and Cm in any oxidation state from 0.2 to 4 M NaOH with DFs of 110 to 1000 and Np and Tc with DFs of 51 to 176. Uranium(VI), introduced as a sodium uranate precipitate or the soluble peroxocomplex salt $\text{Na}_4\text{UO}_2(\text{O}_2)_3$, can be partially reduced in 0.2 to 2 M NaOH by hydrazine to $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ in the presence of $(1 \text{ to } 5) \times 10^{-5}$ M Tc(VII). The Tc(VII) is first reduced to Tc(IV). The product $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$, at 0.012 to 0.05 M uranium, coprecipitates Np, Pu, Cm, and Tc in any oxidation state with DFs greater than 100 from 0.2 to 1.5 M NaOH. Increasing alkali concentration to 4 M NaOH decreases the DFs slightly for TRU and drastically for Tc. Coprecipitation under the same conditions from simulated tank waste containing 3.2 M NaOH, 0.04 M CrO_4^{2-} and 11 complex-forming salts yields the following DFs: Np-12, Pu-27, Cm-35, Tc-3. The decrease of DFs in the waste simulant is associated with complex formation and with inhibition of Np and Tc coprecipitation by the Cr(III) hydroxide that is formed before Np(IV) and Tc(IV). Coprecipitated Tc may be effectively leached from $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ by oxidation of Tc(IV) to Tc(VII) by use of dilute H_2O_2 or by NaOH solution and air bubbling. Under these same conditions, more than 99% of the Pu is retained in the solid phase.

Technetium(VII) coprecipitates with $(5 \text{ to } 8) \times 10^{-4}$ M tetrabutylammonium (TBA) perrhenate in 0.01 to 0.02 M TBA hydroxide from 0.5 to 1.5 M NaOH to give DFs of 150 to 200. Coprecipitation with TBA perchlorate under similar conditions gives lower DFs than TBA perrhenate because the TBA perchlorate and TBA pertechnetate are not isomorphous.

Coprecipitations of Np and Pu with $\text{Co}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, and $\text{Mn}(\text{OH})_2$ obtained by the MAR from precursors in the range from pH 10.5 to 0.4 M NaOH give DFs from 80 to 400. The presence of EDTA and HEDTA disturbs the coprecipitation of Np and Pu with $\text{Fe}(\text{OH})_3$ or $\text{Co}(\text{OH})_3$. The negative effect of EDTA was eliminated by Ca^{2+} addition at a 1:1 molar ratio of Ca^{2+} :EDTA. The negative effect of HEDTA was eliminated by the addition of 0.11 M excess precursor $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ to increase the content of carrier $\text{Co}(\text{OH})_3$.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science and Technology, under the Office of Environmental Management. We thank Dr. Kurt D. Gerdes and Dr. Jerry Harness, Program Managers for Efficient Separations and Processing Crosscutting Program, for their active interest in our research and vigorous support of our program at the Institute of Physical Chemistry, Russian Academy of Sciences. We also thank Dr. Jack Watson, Deputy Coordinator, for his advice and support. The organizational skill of Dr. Thomas Albert in contract implementation is gratefully acknowledged. Finally we thank Mr. Cal Delegard for his encouraging attention to our work, useful discussion of the experimental results, and editorial help.

This work was a collaboration among a number of IPC/RAS scientists. Dr. V.I. Silin, postgraduate student A.V. Kareta, and technician Mrs. V.E. Trushina performed the studies of Tc, Np, Pu, and Cm coprecipitation on uranium hydroxocompounds (Section 3). Dr. A.G. Maslennikov investigated the electrochemical reduction of Tc(VII) and U(VI) by hydrazine. He also prepared the U(IV) stock solution used for the U(IV) hydrous oxide precipitate (Section 3). Dr. K.E. German and Ms E.V. Firsova, a graduate student, tested the coprecipitation of Tc with the tetraalkylammonium perrhenate and perchlorate salts (Section 4). Mr. A.V. Gelis, a research associate, and Professor V.P. Shilov performed the tests of transuranium element coprecipitation with (hydr)oxides of Fe, Co, Cr, and Mn by the MAR (Section 5). The work was directed by Professor V.F. Peretrukhin.

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1.0 Introduction

Vitrification and immobilization of alkaline radioactive wastes, stored in underground waste tanks at the Hanford Site and other U.S. plants, is a new task of radiochemical technology. Because of the complicated composition and the large volume of wastes, chemical treatment steps are required before vitrification. Such steps include concentrating the radionuclides to a small volume and decreasing the amount of nonradioactive components in the vitrified wastes. Purification of liquid alkaline wastes from actinides and long-lived fission products, including technetium, is part of preparing Hanford Site wastes for vitrification. Thus, researchers in U.S. laboratories have developed methods such as liquid-liquid extraction (Bonneson et al. 1996; Rogers et al. 1996; Bond et al. 1998), extraction and ion exchange chromatography, and sorption on inorganic materials (March et al. 1994a and 1994b; Schroeder et al. 1995) with the objective of removing radioelements from solution. The Institute of the Physical Chemistry of the Russian Academy of Sciences, under contract with the U.S. Department of Energy and coordinated by the Pacific Northwest National Laboratory, is investigating purification of alkaline wastes from actinides and technetium by coprecipitation methods on a series of carriers.

Industrial methods for plutonium separation from irradiated uranium fuel in the 1940s and 1950s were based on coprecipitations with the carriers BiPO_4 and LaF_3 (USA) and $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ (Russia). These processes left enormous quantities of alkaline wastes in the USA and acetic-nitric acid wastes in Russia. Plutonium separations subsequently made in both countries by the PUREX process left proportionately less nonradioactive salt in the radioactive wastes. Recent studies have shown that coprecipitation by the Method of Appearing Reagents (MAR) purifies alkaline waste solutions of transuranium elements and technetium with decontamination factors (DFs) of 100 to 1000 (Krot et al. 1996; Krot and Charushnikova 1997; Bessonov et al. 1997; Peretrukhin et al. 1997). In contrast to the BiPO_4 , LaF_3 , or $\text{NaUO}_2(\text{CH}_3\text{COO})_3$ coprecipitation methods for removing plutonium from nitric acid, coprecipitation of transuranic elements and technetium (IV,V) from NaOH solution on metal hydroxides or on uranate salts does not require salt removal. In addition, decontamination of alkaline solutions from transuranic elements requires introduction of only small concentrations (0.001 to 0.01 M) of metal hydroxide carrier (Krot et al. 1996).

The present work was undertaken to further develop coprecipitation techniques to purify alkaline solutions and simulated Hanford waste solutions by use of the carriers $\text{UO}_2 \cdot n\text{H}_2\text{O}$, $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$, sodium uranate, tetraalkylammonium salts, and transition metal hydroxides by the MAR and use of chemical reductants.

2.0 Coprecipitation Methods and Objectives of this Work

The bases for coprecipitation methods for decontaminating alkaline solution are reviewed in this section.

2.1 Coprecipitation Carriers for TRU and Technetium in Different Oxidation States in 0.1 to 4 M NaOH Solution

Sodium uranate salts are known to be effective carriers for Sr(II) and neptunium and plutonium in oxidation states IV, V, and VI. However, these salts interact weakly with Tc(VII) and Cs(I) (Krot et al. 1996; Bessonov et al. 1997; Peretrushin et al. 1997). Precipitation of 2.5×10^{-2} M sodium uranate in 0.1 to 4 M NaOH carries 15 to 60% of the ^{99}Tc , 1 to 12% of the ^{137}Cs , and 98% of the ^{90}Sr (Peretrushin et al. 1997).

Pertechnetate is efficiently coprecipitated with poorly soluble compounds formed by the precipitation of mono-charged anions such as ReO_4^- , ClO_4^- , IO_4^- , and BF_4^- with bulky mono-charged cations such as $[(\text{C}_6\text{H}_5)_4\text{As}]^+$ and $[(\text{C}_n\text{H}_{2n+1})_4\text{N}]^+$ ($n = 3$ to 7). These carriers are very selective for Tc(VII), achieving effective purification from the actinides and from fission products, including ruthenium. Perrhenate salts were shown to be the most effective isomorphous carriers for Tc(VII).

Unique properties of rhenium chemistry in alkaline media affect coprecipitation of technetium from alkali wastes. In dilute alkaline solution, Re(VII) exists as the tetrahedral oxoanion ReO_4^- . However, with increasing alkali concentration, some perrhenate converts to mesorhenate, ReO_5^{3-} (Majumdar et al. 1969, fig.1). Evidence for mesorhenate arises from the difference between the ultraviolet spectrum of rhenium(VII) in alkaline solution ($\epsilon_{260\text{ nm}} = 6400\text{ L/mol-cm}$, $\epsilon_{310\text{ nm}} = 1400\text{ L/mol-cm}$) and the well-known spectrum of perrhenate in neutral aqueous solution. Hexahedral coordination in mesorhenate $\text{ReO}_5(\text{H}_2\text{O})^{3-}$ or $\text{H}_2\text{ReO}_6^{3-}$ has been proposed (Sinjakova and Deme 1977). Differences in the shapes of the crystals precipitated from alkali from those precipitated at lower pH also have been noted.

The reaction to form mesorhenate is

Nevertheless, the fraction of perrhenate in up to 4 M NaOH apparently remains sufficient to provide high Tc(VII) coprecipitation efficiency.

Application of tetraalkylammonium hydroxide to Tc(VII) precipitation and coprecipitation is much more attractive for treatment of radioactive wastes because this salt converts to gas (CO_2 , H_2O , N_2) upon thermal treatment and thus does not increase the vitrified waste mass (Spitsyn and Kuzina 1981).

Tetravalent actinides and technetium are efficiently coprecipitated from NaOH solutions with hydroxides of several metals: Fe(II,III), Co(II,III), Mn(II,IV), Cr(III), La(III), and Th(IV) (Peretrushin et al. 1997; Lavrukhina and Pozdniakov 1966). However, these hydroxides are less effective for neptunium and plutonium(V,VI) in 0.1 to 4 M NaOH solutions and do not capture Tc(VII) at all (Peretrushin et al. 1997; Lavrukhina and Pozdniakov 1966; Spitsyn and Kuzina 1981). Thus, a carrier that can remove actinide(V,VI) and Tc(VII) simultaneously from alkaline solution is unknown and probably does not exist. However, the actinides and technetium can be removed from alkaline solution by coprecipitation with any of the listed hydroxides if the radioelements are first reduced to their tetravalent oxidation states.

No data were found regarding the coprecipitation of actinides and technetium from 0.5 to 4 M NaOH solutions with the carriers $\text{UO}_2 \cdot n\text{H}_2\text{O}$ and $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$. The latter compound is poorly investigated in alkaline media (Gmelin 1978; Cordfunke et al. 1968). However, its ability to coprecipitate plutonium and other actinides in different valent states from neutral solutions recently was predicted by comparison of its crystal structure to the mineral ianthinite [$\text{UO}_2 \cdot 5(\text{UO}_3) \cdot 10\text{H}_2\text{O}$] and the closeness of the ionic radii of U(IV, V, and VI) to those of the other actinides (Burns et al. 1997).

2.2 Different Techniques of Coprecipitation and Their Efficacy

Coprecipitation from alkaline media may be achieved in different ways for the same carrier. The various coprecipitation methods are compared according to their effectiveness in carrying radionuclides and the quantities of reagents (which ultimately contribute to the high activity waste fraction) required to achieve coprecipitation.

2.2.1 Direct Introduction of the Carrier into Solution

Direct introduction of the cation or anion necessary to form the precipitate into the solution to be purified is called direct strike coprecipitation. This classical method was used in early technologies to isolate plutonium from nitric acid solutions of irradiated fuel by coprecipitation with bismuth phosphate, lanthanum fluoride, and sodium uranyl triacetate. Direct strike coprecipitation from these nitric acid solutions required preliminary introduction of considerable amounts of hydrofluoric and phosphoric acids or sodium acetate. These necessary additions, however, produced large quantities of salts in the wastes (see first three reactions in Table 2.1).

More recently, direct coprecipitation of plutonium, neptunium, and technetium from alkaline media with iron(II,III) hydroxides was investigated at the Los Alamos National Laboratory (LANL) and at the Institute of Physical Chemistry of the Russian Academy of Sciences (IPC/RAS). Solutions of FeCl_2 and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ were added to 0.5 to 4 M NaOH solutions or to alkaline Hanford waste simulants containing Pu(IV,VI), Np(V,VI), and Tc(VII). Iron(II) apparently acts as a reducing agent and, especially when oxidized to form Fe(III) hydroxide, as a carrier for the actinides and technetium. In the LANL tests, purification of alkaline solutions and simulants from plutonium and neptunium becomes effective ($\text{DF} \geq 100$) when the concentration reached 0.15 to 0.2 M FeCl_2 or 8 to 12 g Fe(II)/L (Worl et al. 1995). To achieve decontamination factors (DFs) greater than 100 for Pu(IV,VI) and Tc(VII) in 0.5 to 2 M NaOH in the IPC/RAS tests required 0.075 M $\text{Fe}(\text{NH}_4)_2\text{SO}_4$ or 4 g Fe(II)/L. To purify 4 M NaOH required 8 g Fe(II)/L (Peretrukhin et al. 1997).

Purification of simulated alkaline waste solution (containing 3.2 M NaOH, 0.04 M Na_2CrO_4 and 11 organic and inorganic complexing salts) from Pu(IV,VI) and Tc(VII) is less effective by this technique. For plutonium, 99% removal can be reached if 8 g Fe(II)/L is used. Parasitic partial reduction of chromate to Cr(III) also occurs. To achieve only 76% Tc(VII) removal from the same simulant required 12 to 15 g Fe(II)/L while completely reduced chromate to Cr(III) (Peretrukhin et al. 1997).

Several reasons exist for the high Fe(II) chemical demand for the simulant waste solution. First, $\text{Fe}(\text{OH})_2$ precipitates rapidly but only at the interface of the FeCl_2 and NaOH solutions (Krot et al. 1996; Peretrukhin et al. 1997). Thus, much of the alkaline solution is not exposed to the reduced iron solution. Second, tetravalent plutonium and technetium can be sequestered by complexation with the inorganic or organic ligands present in simulant waste solutions (Bessonov et al. 1997). Finally, Fe(II) is consumed by reducing chromate, a component of many tank waste solutions, in an undesired side reaction.

Table 2.1. Decontamination Factors from Plutonium and Carrier/Salt Requirements for Direct Coprecipitation (DC) and the Method of Appearing Reagents (MAR)

Precipitation reaction	Type	Medium	DF	Content		Ref.
				Carrier	Salts	
$\text{La}^{3+} + \text{HF} \rightarrow \text{LaF}_3$	DC	1 M HNO_3	30-50	7×10^{-4} M (0.1 g/L)	1.5 M HF (63 g NaF/L)*	(a)
$\text{Bi}^{3+} + \text{PO}_4^{3-} \rightarrow \text{BiPO}_4$	DC	1 M HNO_3	30-50	8×10^{-3} M (2.5 g Bi^{3+} /L)	0.35 M H_3PO_4 (57 g Na_3PO_4 /L)*	(a)
$\text{UO}_2^{2+} + \text{CH}_3\text{COONa} \rightarrow \text{NaUO}_2(\text{CH}_3\text{COO})_3$	DC	(Na, H) acetate, NaNO_3	20-50	0.05-1 M UO_2^{2+}	5 M (Na, H) acetate (415 g Na acetate/L)	(b)
$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$ [with O_2]	DC	0.5 - 4 M NaOH	100	0.2 M (11 g/L) Fe^{2+}	--	(c)
$\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$ [with O_2]	DC	3.2 M NaOH	100	0.075 M (4 g/L) Fe^{2+}	--	(d)
$\text{FeO}_4^{2-} + \text{N}_2\text{H}_4 \rightarrow \text{Fe}(\text{OH})_3$ [60°C]	MAR	0.5 M NaOH 4 M NaOH	370 420	M (0.56 g/L) Fe	--	(e)
$[\text{Fe}(\text{CN})_5\text{NO}]^{2-} \rightarrow \text{Fe}(\text{OH})_3$ [80°C]	MAR	0.5 M NaOH 4 M NaOH	2,000 210	0.01 M (0.56 g/L) Fe	--	(e)
$[\text{UO}_2(\text{O}_3)]^{4-} \rightarrow \text{Na}_2\text{UO}_4$ [80°C with Cu(II)]	MAR	0.5 M NaOH 4 M NaOH	610 150	0.015 M (3.6 g/L) U	--	(e)

(a) Thompson and Seaborg 1956.
(b) Milyukova et al. 1967; p. 217.
(c) Worl et al. 1995.
(d) Peretruxhin et al. 1997.
(e) Krot et al. 1996.
* After neutralization.

2.2.2 Coprecipitation by the Method of Appearing Reagents

The MAR was elaborated at the IPC/RAS to purify alkaline radioactive waste solutions of transuranium elements (Krot et al. 1996; Krot and Charushnikova 1997; Bessonov et al. 1997). This technique produces the precipitant homogeneously throughout the alkaline solution by the decomposition of alkali-soluble precursor species. In contrast, direct introduction of the acidic precipitating agent [such as $\text{Fe}(\text{II})$ salt] into alkaline solution produces the precipitate only at the limited acid-alkali solution interface. As shown in Table 2.1, relatively low DFs and high quantities of precipitating agent are observed in the direct method.

Precursors used in coprecipitation by the MAR include alkali-soluble species such as FeO_4^{2-} and $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$. Both species can be decomposed in alkaline solution to form the precipitating carrier $\text{Fe}(\text{OH})_3$. Decomposition of FeO_4^{2-} is accomplished by chemical reduction, whereas hydrolysis decomposes $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$. The precipitating ion (Fe^{3+}) appears throughout the entire solution volume, precipitates as $\text{Fe}(\text{OH})_3$, and carries the hydrolyzable radionuclides from the alkaline solution.

Chemical reactions, reagent requirements, and decontamination factors of alkaline solutions from neptunium and plutonium for application of the MAR are given in Table 2.2 (Krot et al. 1996). Results of research performed at the IPC/RAS (Tables 2.1 and 2.2) show that for the same carrier in 0.5 to 4 M NaOH, DFs are higher and carrier requirements lower by the MAR than by direct coprecipitation.

Table 2.2. Decontamination of 0.5–4 M NaOH of Pu and Np by the MAR

Precipitation reaction	Type*	DF				[Carrier], M
		Pu (VI)		Np (V)		
		0.5 M NaOH	4 M NaOH	0.5 M NaOH	4 M NaOH	
$\text{MnO}_4^- + \text{H}_2\text{O}_2 \rightarrow \text{MnO}_2$	red.	70	4	20	4	0.01
$\text{MnO}_4^- + \text{NH}_2\text{OH} \rightarrow \text{Mn}(\text{OH})_2$	red.	430	200	52	3	0.01
$\text{FeO}_4^{2-} + \text{N}_2\text{H}_4 \rightarrow \text{Fe}(\text{OH})_3$	red.	370	420	35	5.5	0.01
$[\text{Fe}(\text{CN})_5\text{NO}]^{2-} + \text{N}_2\text{H}_4 \rightarrow \text{Fe}(\text{OH})_3, 80^\circ\text{C}$	hyd.	2,000	800	25	7	0.01
$[\text{UO}_2(\text{O}_2)_3]^{4-} \rightarrow \text{Na}_2\text{UO}_4, 60^\circ\text{C}$	ther. deco.	610	170	230	80	0.02 U(VI), 5×10^{-3} Cu(II)
$[\text{Co}(\text{NH}_3)_6]^{3+} \rightarrow \text{Co}(\text{OH})_3, 70^\circ\text{C}$	hyd.	600	1,500	3	12	0.024
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \rightarrow \text{Co}(\text{OH})_3, 70^\circ\text{C}$	hyd.	150	390	2	12	0.024
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{N}_2\text{H}_4 \rightarrow \text{Co}(\text{OH})_2, 60^\circ\text{C}$	red.	300	25	--	--	0.024
$\text{Cr}(\text{CH}_3\text{COO})_3 \rightarrow \text{Cr}(\text{OH})_3, 80^\circ\text{C}$	hyd.	260	300	300	2.7	0.01

* red. = reduction, hyd. = hydrolysis, ther. deco. = thermal decomposition with Cu(II) catalyst.

3.0 Separation of Tc and Actinides from Alkaline Solution by Reductive Coprecipitation with $\text{UO}_2 \cdot n\text{H}_2\text{O}$ and $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ Carriers

3.1 Experimental Materials and Analyses

The radionuclides ^{99}Tc , ^{237}Np , ^{238}Pu , ^{239}Pu , ^{241}Am , ^{244}Cm , and natural uranium were used in the experiments. Decontamination factors for alkaline solutions from the radionuclides were determined as the ratio of the solution concentrations before and after solid phase precipitation. The initial alkaline solutions were spiked with the radionuclides of interest to concentrations simulating those of genuine wastes and sufficient to permit determination of the DF. Duplicate 50 to 100 μL aliquots were taken to determine the initial concentrations. After solid phase precipitation (which normally carried more than 90% of the radionuclide), the precipitate was separated by centrifugation and a 200 to 300 μL aliquot of the supernatant solution taken. To analyze the Tc, Np, Pu, Am, and Cm isotopes, the solution aliquots were acidified with 100 μL of 1 to 4 M HNO_3 and placed into scintillation vials with 5 to 7 mL of Ready-Gel™ scintillation cocktail (Beckman, USA). Measurements of α and β activity solution concentrations were performed using a Beckman LS6500 liquid scintillation counter and its integral program to resolve the α and β peaks. Uranium concentrations were determined spectrophotometrically with arsenazo-III after having first been acidified with nitric acid (Riabchikov and Seniavin 1963). Uranium concentrations sometimes also were analyzed polarographically directly in the alkaline solutions by the limiting current of the $\text{U(VI)} + \text{e}^- \rightarrow \text{U(V)}$ wave (Abuzwida et al. 1991).

Uranium oxidation state(s) in its precipitates were determined by first dissolving the solid in 1 M HCl. A Shimadzu model UV-3100 PC UV-Vis-NIR spectrophotometer (Japan) was used to measure the optical spectra. The peak at 415 nm was used to quantify U(VI) and the peak at 648 nm was used for U(IV).

All reagents used in the experiments were analytically pure grade. The 0.5 to 4 M NaOH solutions were prepared with 16 M NaOH stock and distilled water. The solutions were kept in closed polyethylene vessels. Test solution carbonate concentrations were less than 0.01 M.

3.2 Coprecipitation of Pu(VI), Np(V), Am(III), and Tc(VII) from 0.5 to 4 M NaOH with $\text{UO}_2 \cdot n\text{H}_2\text{O}$

Uranium(IV) hydrous oxide was tested as a carrier for coprecipitating Pu, Np, Am, and Tc from alkaline solution. The results are reported in this section.

3.2.1 Experimental Technique

To obtain $\text{UO}_2 \cdot n\text{H}_2\text{O}$, a 5×10^{-2} M U(IV) solution in 0.2 M H_2SO_4 first was prepared by electrolysis of uranyl sulphate solution at a Hg cathode at -0.8 V. The cathode and anode compartments were separated by a cation exchange membrane. The electrolysis was continued until the solution became a dark red, characteristic of U(III), thus indicating the complete reduction of U(VI). The solution was placed in a stock solution vessel, agitated in the presence of air to reoxidize U(III) to U(IV), and kept closed in the dark. Aliquots of the U(IV) solution obtained in this way were added as required to alkaline solutions containing tracer quantities of Tc(VII), Np(V), Pu(VI), or Am(III) kept under agitation by argon bubbling. The product precipitate was kept at 20°C for 20 to 60 minutes and then centrifuged. Sampling to determine the specific radioactivity of the supernatant after $\text{UO}_2 \cdot n\text{H}_2\text{O}$ precipitation was performed at 20-minute intervals.

3.2.2 Experimental Results

The ability of U(IV) hydrous oxide to decontaminate 0.5 to 4 M NaOH from Pu(VI) is shown in Table 3.1. Alkaline solution DFs from plutonium were high ($DF > 100$) even with low concentrations (3×10^{-3} M) of U(IV) hydrous oxide precipitate. Increasing the U(IV) precipitate concentration to 5×10^{-2} M increased the DF of 0.5 M NaOH from Pu to 1,000 but the DFs decreased to ~ 300 when alkali concentration increased to 4 M NaOH.

Table 3.1. Coprecipitation of Tracer Quantities of Tc(IV), Np(V), Pu(IV), and Am(III) with $UO_2 \cdot nH_2O$ from Alkaline Solutions in Inert Atmosphere

[U(IV)], M	Decontamination factors											
	0.5 M NaOH				1.5 M NaOH				4.0 M NaOH			
	Tc(IV)	Np(V)	Pu(IV)	Am(III)	Tc(IV)	Np(V)	Pu(IV)	Am(III)	Tc(IV)	Np(V)	Pu(IV)	Am(III)
0.001	21	28	193	140	22	27	95	120	17	24	104	110
0.003	27	55	220	190	36	53	190	170	26	38	171	150
0.006	37	88	260	230	44	87	260	220	28	49	203	180
0.01	46	112	555	260	52	102	640	270	36	68	275	230
0.02	67	123	654	340	74	116	830	330	43	72	318	290
0.05	176	153	1130	430	153	135	940	410	51	84	370	330

Note: Coprecipitation by addition of 0.1 M $U(SO_4)_2$ in 0.2 M H_2SO_4 to spiked 0.5 to 4 M NaOH under argon bubbling and stirring.

Americium(III) also was captured efficiently by the U(IV) hydrous oxide precipitate, attaining DFs of 110 to 430 for 0.5 to 4 M NaOH at 1×10^{-3} to 5×10^{-5} M uranium. The DFs from Pu and Am were not affected by whether the tests were performed in argon or air atmosphere.

Neptunium(V) and Tc(VII) were trapped less completely than Pu(VI) in the $UO_2 \cdot nH_2O$. Decontamination factors observed by coprecipitating with 5×10^{-2} M U(IV) hydrous oxide under a bubbling argon inert atmosphere for two hours decreased from 176 to 51 for Tc and from 153 to 84 for Np as NaOH concentration increased from 0.5 to 4 M. The same tests conducted in the presence of air failed to achieve DFs of 100 for either Tc or Np. These observations suggest that the U(IV) hydrous oxide precipitate slowly reduces Tc(VII) and Np(V) to their respective (IV) oxidation states, while the reoxidation of the (IV)-valent Tc, Np, and U occurs in the presence of dissolved oxygen.

3.3 Coprecipitation of Tc(VII), Pu(VI), Np(V), and Cm(III) with Sodium Uranate under Reducing Conditions by Treatment with Hydrazine

Technetium(VII) and transuranic elements in higher oxidation states are known to be reduced by hydrazine to give poorly soluble hydrous oxides of the type $MO_2 \cdot nH_2O$ (Eriksen et al. 1992; Peretrukhin et al. 1996, 1997).

The technical literature show that hydrazine reacts slowly (reaction not noticeable over several hours) with the U(VI) present in alkali as the sodium uranate precipitate Na_2UO_4 or as the soluble peroxide complex salt $Na_4UO_2(O_2)_3$ (Krot et al. 1996; Gmelin 1978). With excess hydrazine and prolonged heating under an argon atmosphere, however, uranate is reduced in alkaline solution to give violet $U_3O_8 \cdot nH_2O$ and $UO_2 \cdot nH_2O$ (Gmelin 1978).

Treatment of neutral uranyl nitrate solution with hydrazinium nitrate in air slowly produces a violet precipitate, identified as hydrated oxide $U_3O_8 \cdot nH_2O$ ($n = 0.5$ or 1.5) or, according to later data,

$\text{UO}_{2.86} \cdot n\text{H}_2\text{O}$ (Cordfunke et al. 1968; Gmelin 1978). Uranium is present in both (VI) and (IV) oxidation states in the natural mineral ianthinite (Gmelin 1978). Based on the similarity of the ionic radii of uranium and transuranium elements in the same oxidation states, the possibility of actinide(VI,V,IV) incorporation into ianthinite's crystalline lattice recently was predicted (Burns et al. 1997).

Based on these observations, treatment of alkaline media with sodium uranate and hydrazine was tested in an effort to simultaneously coprecipitate technetium and actinides.

3.3.1 Reaction of Hydrazine with Sodium Uranate in Alkaline Media in the Presence of Technetium

The treatment of sodium uranate solutions and sludges in 0.5 to 4 M NaOH with 0.1 to 0.3 M $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$, and the effect of Tc(VII) on this reaction, were studied. The concentrations of U(VI) and Tc(VII) in alkaline solution were measured polarographically by use of a stationary mercury drop electrode. Spectrophotometry was found to be not as effective for U(VI) determination in alkaline solutions. Sample polarograms of U(VI) and Tc(VII) in 0.5 M NaOH are shown in Figure 3.1.

The dependences of the limiting currents for the reactions $\text{Tc(VII)} + 3\text{e}^- \rightarrow \text{Tc(IV)}$ and $\text{U(VI)} + \text{e}^- \rightarrow \text{U(V)}$ on the Tc(VII) and U(VI) concentrations in 0.5 M NaOH are given in Figure 3.2. These data show that the polarographic method can reliably determine Tc(VII) and U(VI) concentrations when they are present separately in alkaline solutions or sludges. If both are present simultaneously, their concentrations can be determined with sufficient accuracy by polarography only if the $[\text{Tc(VII)}]/[\text{U(VI)}]$ concentration ratio is higher than 0.1 (Figure 3.3.).

Figure 3.1. Test Polarography of U(VI) and Tc(VII) in 0.5 M NaOH
Stationary Hg Drop Electrode 0.5-Second Growing Time
(5-mV voltage step; 1-second step duration)

Figure 3.2. Calibration Curves for U(VI) and Tc(VII) Polarographic Reduction on a Stationary Mercury Drop Electrode in 0.5 M NaOH

Figure 3.3. Polarography of U(VI) – Tc(VII) Solutions in 0.5 M NaOH in the Presence and Absence of 0.01 M N₂H₄·HNO₃

The half-wave potentials of reductions $\text{Tc(VII)} + 3 e^- \rightarrow \text{Tc(IV)}$ and $\text{U(VI)} + e^- \rightarrow \text{U(V)}$ in 0.5 M NaOH are -0.69 V and -0.87 V versus the Ag/AgCl electrode. Thus Tc(VII) reduction to Tc(IV) occurs at a less negative potential than U(VI) reduction to U(V). The difference in half wave potentials of these irreversible electrochemical polarographic reactions is about 180 mV. Based on the electrode potential difference, Tc(IV) should be capable of reducing U(VI) at least partially to U(V). Uranium(V) is unstable toward disproportionation to U(IV) and U(VI).

The oxidation state of uranium in the solid phase was determined after its separation from alkaline solution by centrifugation, dissolution in 1 M HCl, and recording of the visible spectra. The concentrations of uranium(VI) and (IV) were determined from the optical absorbance at 415 and 648 nm, respectively. At these wavelengths, the absorbances of Tc(VII) and Tc(IV) are insignificant (Lavrukina and Pozdniakov 1966).

Reduction of U(VI) by 0.01 to 0.3 M hydrazine in the presence of air is not observed for 4×10^{-4} M Na_2UO_4 solutions or for suspensions containing up to 0.05 M Na_2UO_4 following two days of treatment at room temperature or during five hours of treatment at 70°C. Technetium(VII), however, at 1×10^{-5} to 2×10^{-4} M in 0.5 to 4 M NaOH, was reduced by 0.01 to 0.3 M $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ within five to ten minutes at room temperature in the presence of sodium uranate (Figure 3.4).

Further scoping experiments were performed on reactions of hydrazine with alkaline solutions and sludges containing sodium pertechnetate and uranate. In one set of tests, 0.1 M $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ was added to freshly prepared solutions of 2×10^{-4} M Tc(VII) and 2×10^{-4} M U(VI) in 0.5 and 2 M NaOH. Polarographic methods showed that complete reduction of technetium occurred within 10 to 15 minutes at room temperature to form brown-reddish Tc(IV) hydrous oxide or Tc(V) hydroxide precipitates. Uranium(VI) solution concentrations decreased 40 to 60% in the same tests. With 1×10^{-5} M initial

Figure 3.4. Decontamination Factors of NaOH Solutions from Technetium by Reductive Coprecipitation by Hydrazine on Na_2UO_4

Tc(VII) and 2×10^{-4} M uranate, addition of 0.2 M $\text{N}_2\text{H}_4 \cdot \text{HNO}_3$ chemically reduced Tc(VII) but without Tc(V) or (IV) precipitation. The U(VI) concentration remained unchanged over the first two to three hours at room temperature. However, 24 hours later, the U(VI) concentration was 4×10^{-5} M.

The results of hydrazine addition to alkaline pertechnetate and uranate solutions suggest that the first step is reduction of Tc(VII) by hydrazine to form $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. This is followed by

- adsorption and polymerization of uranate on the surface of the $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ precipitate
- chemical reaction of sodium uranate with $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ and hydrazine to partially reduce uranate to the less soluble $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ and $\text{UO}_2 \cdot n\text{H}_2\text{O}$.

Further studies were performed of the reaction of hydrazine with sodium uranate alkaline slurries both in the presence and absence of Tc(VII). In the first set of experiments, 0.1 to 0.3 M $\text{N}_2\text{H}_5\text{OH}$ was added to a solid sodium uranate suspension in 0.5 to 4 M NaOH. No apparent reaction was noted even one day later if the mixture was stored at 20°C or after 4 hours at 70°C . The situation changed markedly on adding $(1 \text{ to } 4) \times 10^{-5}$ M Tc(VII) to the alkaline uranate slurries with hydrazine. The yellow-orange color of sodium uranate changed slowly to grayish-green. This color change was easily detectable the day after addition at room temperature and 1 to 2 hours after addition if the temperature was 60°C or higher.

The grayish-green precipitates were centrifuged, dried in a flow of argon, and analyzed by x-ray powder diffraction using a Phillips ADP-10 diffractometer (CuK_α radiation with a graphite monochromator on the diffracted beam). The only crystalline phase detected was the sodium uranate starting material remaining unreduced by hydrazine. The absence in the reaction products of any crystalline form of reduced uranium produced by sodium uranate reaction with hydrazine may be expected based on literature data. Both $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ and $\text{UO}_2 \cdot n\text{H}_2\text{O}$ will precipitate from U(VI) solutions as amorphous solids (Gmelin 1978; Cordfunke et al. 1968). Crystallization requires prolonged (one week) treatment of the slurry at boiling temperatures in the absence of dissolved oxygen. It was also noted in the literature that the presence of oxidized uranium in the precipitate inhibits the conversion of $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ and $\text{UO}_2 \cdot n\text{H}_2\text{O}$ to their crystalline forms (Gmelin 1978; Cordfunke et al. 1968). Freshly precipitated Tc(IV) hydroxide also is amorphous (Spitsyn and Kuzina 1981) and would not be observed by x-ray diffraction.

Samples of the grayish-green precipitates obtained by reaction of hydrazine, Tc(VII), and sodium uranate in alkaline media were dissolved in 1 M HCl. The visible spectra of the resulting hydrochloric acid solutions, recorded by a Shimadzu 3100 PC UV-Vis-NIR spectrophotometer, are shown in Figure 3.5. The U(VI) and U(IV) distributions (determined by the absorbances at 415 nm and 648 nm, respectively) were found to be 80–90% U(VI) and 10–20% U(IV).

Under otherwise similar conditions, increasing the Tc(VII) concentration higher than 5×10^{-5} M did not increase the U(IV) fraction in the reaction products. The additional technetium likely converted to precipitated $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. Increase of hydrazine concentration from 0.2 to 0.4 M in tests with 5×10^{-2} M U(VI) as sodium uranate and 2×10^{-5} M Tc(VII) in 0.5 M NaOH increased the U(IV) fraction to 25%.

Figure 3.5. Absorption Spectra of HCl Solutions of Solids Produced by Hydrazine Reduction of Na_2UO_4 in the Absence (—) and Presence (---) of Tc

(—) 5 mL of 0.05 M U(VI) as Na_2UO_4 in 0.5 M NaOH containing 0.2 M N_2H_4 , aged three hours at ambient temperature, centrifuged, and the precipitate dissolved in 6 mL of 1.0 M HCl

(---) 5 mL of 0.05 M U(VI) as Na_2UO_4 in 0.5 M NaOH containing 0.2 M N_2H_4 and 5×10^{-5} M Tc(VII), aged three hours at ambient temperature, centrifuged, and the precipitate dissolved in 6 mL of 1.0 M HCl

The electrochemical and spectrophotometric data on the uranate/pertechnetate/hydrazine system in 0.5 to 2 M NaOH indicate that U(VI) reduction by hydrazine is accelerated by pertechnetate. The acceleration is thought to occur through Tc(IV) according to following mechanism:

The metathesis of yellow sodium uranate precipitate by hydrazine and technetium treatment to greyish-green product is described by the following reaction sequence:

The grayish-green precipitate obtained as a result of uranate and hydrazine reaction in the presence of technetium evidently is a mixture of three compounds - hydrated Na_2UO_4 , U_3O_8 , and UO_2 . Special new tests are necessary to determine the conditions required to reduce uranate quantitatively to $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ or

to $\text{UO}_2 \cdot n\text{H}_2\text{O}$ with hydrazine in alkaline solutions. In the present studies dealing with decontamination of alkaline wastes from actinides and technetium, it is important to note that sodium uranate and the indicated products of its reduction with hydrazine have individual qualities if applied as coprecipitation carriers. Sodium uranate is a good carrier for actinides(VI,V) but not for Tc(VII). Uranium(IV) hydrous oxide should be a good carrier for Np, Pu, and Tc in all oxidation states because it can reduce them to their poorly soluble (IV) oxidation states. The carrier $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ is not well studied, but according to theoretical predictions could incorporate actinides(VI,V,IV,III) in its crystalline lattice (Burns et al. 1997). No data were found on the ability of $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ to capture Tc(VII,V,IV).

3.3.2 Coprecipitation of Tc(VII) with Sodium Uranate in 0.5 to 4.0 NaOH Solutions in Reducing Conditions by Hydrazine

Incomplete coprecipitation of Tc(VII) with sodium uranate from NaOH solutions without reductant recently has been demonstrated (Peretrukhin et al. 1997). However, in the reducing conditions created by hydrazine, the oxidation states of both Tc(VII) and of uranium in sodium uranate change. Technetium, reduced by hydrazine to Tc(IV), forms the hydroxo compound $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. The solubility of Tc(IV) hydrous oxide in alkaline solution increases from 10^{-7} M in 0.01 M NaOH to 3×10^{-5} M in 4.0 M NaOH (Peretrukhin et al. 1996; Eriksen et al. 1992). As shown in Section 3.3.1, solid sodium uranate in alkaline suspension is partially reduced by hydrazine in the presence of technetium to form $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ or $\text{UO}_2 \cdot n\text{H}_2\text{O}$. The solubility of $\text{UO}_2 \cdot n\text{H}_2\text{O}$ in NaOH solution reportedly increases from 1.0×10^{-5} to 8.0×10^{-5} M with increase of alkali concentration from 0.5 to 4.0 M (Gmelin 1978; Peretrukhin et al. 1996). These concentrations are lower than those reported for sodium uranate solubility, about 5.0×10^{-4} M, under similar conditions (Peretrukhin et al. 1995). No data were found in the technical literature on the solubility of $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ in alkaline solution but the solubility should be lower than that of sodium uranate, provided nonoxidizing conditions are maintained.

Based on the identified reduction processes of pertechnetate and uranate taking place in alkali, it would be expected that the effectiveness of technetium coprecipitation in systems with solid sodium uranate would increase with hydrazine concentration. Coprecipitation in these systems was studied by first preparing alkaline suspensions of sodium uranate by the addition of NaOH solution to an aqueous solution of uranyl nitrate. The uranium concentration was varied from 5×10^{-4} to 5×10^{-2} M. No solid phase formation was observed in the absence of hydrazine at uranium concentrations less than 5×10^{-4} M. This finding agrees with previous studies of U(VI) solubility in 1 M NaOH (Peretrukhin et al. 1995). Technetium(VII) was introduced to the system as KTcO_4 solution in concentrations ranging from 1.0×10^{-5} to 1.0×10^{-4} M. Hydrazinium nitrate was added to the reaction mixture at concentrations from 0.1 to 0.3 M. The reaction temperature was maintained at 60 to 70°C and the suspension agitated by argon or air bubbling. Solution DFs from technetium were calculated as ratios of the solution β -activities before and after the experimental runs.

The DFs obtained under various experimental conditions are presented in Table 3.2 and Figure 3.4. In solutions containing from 0.5 to 1.5 M NaOH and more than 0.01 M U(VI), DFs exceeding 100 were observed, demonstrating the effective capture of Tc in the presence of hydrazine. DFs less than 100 were obtained for solutions containing less than 0.01 M U(VI). Increasing alkali concentration above 1.5 M also decreased solution decontamination from Tc.

The decontamination of alkaline solutions from technetium was found to be effective for NaOH concentrations less than 1.5 M and U(VI) concentrations greater than 0.01 M. The optimum hydrazine concentration was 0.2 to 0.3 M. The reaction is complete in three hours at 60°C or in 24 hours at a room temperature. Agitation of the suspension by atmospheric air decreased the DF 10 to 15 % compared with argon agitation.

Table 3.2. Decontamination of NaOH Solution of Tc(VII), Np(V), Pu(VI), and Cm(III) by Three Hours' Reduction of Sodium Uranate by 0.3 M Hydrazine at 60°C

[NaOH], M	[Na ₂ UO ₄], M	DF*			
		Tc	Np	Pu	Cm
0.5	5x10 ⁻⁴	6.5	17	22	16
	5x10 ⁻³	84	92	160	112
	0.01	130	230	340	317
	0.03	166	--	--	--
	0.05	260	310	405	372
1.0	5x10 ⁻⁴	9.2	32	48	14
	5x10 ⁻³	53	83	165	98
	0.01	103	107	208	175
	0.03	122	140	221	234
	0.05	198	178	283	273
2.0	5x10 ⁻⁴	1.9	12	25	9
	5x10 ⁻³	6.1	67	82	61
	0.01	10.3	105	118	92
	0.03	16.7	132	184	178
	0.05	27.4	177	218	271
4.0	5x10 ⁻⁴	1.5	4	10	6
	5x10 ⁻³	1.9	21	37	45
	0.01	2.4	47	78	78
	0.03	4.8	84	105	114
	0.05	6.5	111	134	155
Note: All uranium initially present as Na ₂ UO ₄ . * 3x10 ⁻⁵ M Tc(VII) ₀ ; 3x10 ⁻⁵ M Np(V) ₀ ; 3x10 ⁻⁶ M Pu(VI) ₀ ; 6x10 ⁻⁹ M ²⁴⁴ Cm(III) ₀ .					

Thus, decontamination of alkaline sodium uranate suspensions of ⁹⁹Tc can be accomplished by hydrazine reduction and coprecipitation with U₃O₈·xH₂O. Without the reducing action of hydrazine, the DFs in alkaline sodium uranate suspensions hardly exceed 2. Introduction of hydrazine gives DFs from Tc greater than 100 in 0.2 to 1.5 M NaOH containing more than 0.01 M U(VI).

3.3.3 Coprecipitation of Np(V), Pu(VI), and Cm(III) with Sodium Uranate in 0.5 to 4.0 M NaOH in the Presence of Hydrazine with and without Tc(VII)

Sodium uranate in alkaline solution is reported to be an effective carrier for Np(V) and Pu(VI) (Krot et al. 1996). Complete capture of tri- and tetravalent actinides also has been demonstrated (Milyukova et al. 1967, p. 207). However, no information was found in the technical literature concerning the effect of hydrazine and Tc(VII) on the coprecipitation of Np(V), Pu(VI), and trivalent actinides with sodium uranate in alkaline solution.

The effects of hydrazine and Tc(VII) on the capture of actinides from alkaline suspensions of sodium uranate therefore were studied. From 0.1 to 0.2 mL of weakly acidic solution with known concentrations (α -activities) of ²³⁷Np(V), ²³⁹Pu(VI), or ²⁴⁴Cm(III) were added to 5 mL suspensions containing 5x10⁻⁴ to 5x10⁻² M sodium uranate and 0.2 to 0.3 M N₂H₄ in 0.5 to 4.0 M NaOH. A parallel similar series of experiments was conducted in which the suspensions also contained up to 3x10⁻⁵ M Tc(VII). The mixtures reacted three hours at 60°C. After reaction, the suspensions were centrifuged and the supernates'

radionuclide concentrations measured by liquid scintillation counting of the α - (actinide) and β - (technetium) activities. The DFs from each isotope were calculated as described previously.

The results, presented in Table 3.2, indicate high ($DF > 100$) capture of actinides was attained in the process performed with hydrazine but without Tc. Introduction of Tc(VII) caused the initial suspension precipitate to change color from yellow to green-gray, reflecting the reduction of sodium uranate to $U_3O_8 \cdot nH_2O$. The DF of sodium uranate suspensions from actinides obtained for tests with Tc(VII) were 30 to 80% greater than those achieved without Tc.

Thus hydrazine in 0.5 to 2.0 M NaOH suspensions of 5×10^{-4} to 5×10^{-2} M sodium uranate containing more than 1.0×10^{-5} M Tc(VII) decontaminates the solution of traces of Np, Pu, Cm, and Tc in any oxidation state. The decontamination from actinides and Tc is caused by the reductions of Tc, Pu, and Np to their (IV) oxidation states followed by capture of the reduced species with the $U_3O_8 \cdot nH_2O$ formed in this process.

3.3.4 Coprecipitation of Tc(VII), Np(V), Pu(VI), and Cm(III) from Alkaline Solutions Containing U(VI) Peroxide Complexes Reduced by Hydrazine

The coprecipitation of Np(V) and Pu(VI) by catalytic decomposition of the soluble $[UO_2(O_2)_3]^{4-}$ complex from alkaline solutions was developed by Krot and coworkers at the IPC/RAS (Krot et al. 1996). It was shown that in alkaline solution in the presence of a 10^{-3} M Cu(II) catalyst, the uranyl peroxo complex decomposes to form sodium uranate. This compound quantitatively captures Np(V) and Pu(VI) from alkaline solution, achieving DFs around 300. Subsequent experiments showed, however, that Tc(VII) is relatively unaffected by this precipitation, yielding DFs less than 3 (Peretrukhin et al. 1997).

Tests were performed to investigate the action of hydrazine in the coprecipitation of actinides and technetium from alkaline solution containing the U(VI) peroxo complex. In initial tests, it was found that addition of concentrated hydrazinium nitrate solution to 0.2 to 0.3 M concentration had no apparent effect on the U(VI) peroxo complex at room temperature even after 24 hours. Heating the solution to 70°C partially decomposed the peroxo complex in four hours. The observed phenomena prove that, in the absence of catalyst, the rate of reduction of the U(VI) peroxo complex with hydrazine in alkaline media is low.

Introduction of $(1.0 \text{ to } 5.0) \times 10^{-5}$ M Tc(VII) significantly accelerated the reduction of the U(VI) peroxo complex with hydrazine. After 0.5 hours' reaction at 60°C, a yellow precipitate, apparently sodium uranate, was observed. After 2.5 hours, the precipitate color had changed from yellow to green-gray indicating the reduction of sodium uranate to $U_3O_8 \cdot nH_2O$. The DFs obtained by this process for 0.5 to 1.0 M NaOH containing more than 0.01 M U(VI) were greater than 100 for technetium (Table 3.3). The actinides, present in the solution as Np(V), Pu(VI), and Cm(III), are also effectively captured under these conditions. Apparently, hydrazine reduces Np(V) and Pu(VI) to their (IV) oxidation states.

The DFs from Tc and the actinides shown in Tables 3.2 and 3.3 are similar despite the precipitant arising from differing uranium starting materials [i.e., sodium uranate and the U(VI) peroxo complex]. The similarity suggests that in both cases, the coprecipitation occurs with the same final precipitants (e.g., $U_3O_8 \cdot nH_2O$ or $UO_2 \cdot nH_2O$) and the solids will form provided that comparable precipitating temperatures and NaOH and hydrazine concentrations are maintained.

Table 3.3. Coprecipitation of Tc(VII), Np(V), Pu(VI), and Cm(III) by Decomposition of U(VI) Peroxide Complex from NaOH Solutions by Three Hours' Hydrazine Reduction at 60°C

[NaOH], M	[Na ₂ UO ₄], M	DF*			
		Tc	Np	Pu	Cm
0.5	5x10 ⁻⁴	12	14	18	13
	5x10 ⁻³	44	37	73	53
	0.01	107	103	134	118
	0.03	136	145	210	187
	0.05	173	237	335	285
1.0	5x10 ⁻⁴	10	24	25	11
	5x10 ⁻³	36	65	86	87
	0.01	92	87	127	124
	0.03	108	120	172	204
	0.05	147	137	187	248
2.0	5x10 ⁻⁴	1.8	8	16	7
	5x10 ⁻³	12	53	63	39
	0.01	37	86	94	76
	0.03	41	112	137	107
	0.05	45	121	152	236
4.0	5x10 ⁻⁴	1.4	3	7	9
	5x10 ⁻³	1.7	14	32	38
	0.01	2.1	42	64	61
	0.03	5.3	85	117	93
	0.05	7.2	104	223	134

* 3x10⁻⁵ M Tc(VII)₀; 3x10⁻⁵ M Np(V)₀; 3x10⁻⁶ M Pu(VI)₀; 6x10⁻⁹ M ²⁴⁴Cm(III)₀.

3.3.5 Coprecipitation of Tc(VII), Np(V), and Pu(VI) with Sodium Uranate from Simulated Alkaline Hanford Site Waste Solution by Reductive Action of Hydrazine

Alkaline radioactive waste solutions stored in Hanford Site tanks in the presence of sludges and salt-cake have compositions similar to that shown in Table 3.4. Sodium hydroxide and sodium nitrate, nitrite, and aluminate salts are the principal constituents of these solutions. Sodium chromate (0.04 M) and a number of inorganic (phosphate, carbonate, fluoride) and organic (EDTA, citrate, glycolate) anions capable of forming stable complexes with actinides and fission products also are found in the wastes as solid phase or solution components.

The decontamination by coprecipitation of the simulant solution with composition shown in Table 3.4 from Tc(VII), Np(V), Pu(VI), and Cm(III) has been studied. The coprecipitating agent was prepared by reducing sodium uranate with hydrazine. To prepare the sodium uranate solid phase, a volume of stock uranyl nitrate solution calculated to make 0.05 M U(VI) was introduced to the simulant solution. Weakly acidic solutions of ⁹⁹Tc(VII), and/or ²³⁷Np, ²³⁹Pu, ²⁴⁴Cm, and finally hydrazine were added to the freshly prepared U(VI) precipitate. The precipitate was agitated by nitrogen bubbling for three hours at 60°C. The precipitates were separated from solution by centrifugation, the radionuclide concentrations in the supernates measured by liquid scintillation, and the DFs calculated.

Table 3.4. Composition of Hanford Site Tank Waste Simulant Solution

Component	Concentration, M
NaOH	3.2
NaNO ₃	1.8
NaNO ₂	0.75
Na ₂ CO ₃	0.05
Na ₃ PO ₄	0.01
NaF	0.01
NaCl	0.05
Na ₂ SO ₄	0.01
Na ₂ CrO ₄	0.04
NaAl(OH) ₄	0.2
Na ₄ EDTA	0.1
Na glycolate	0.1
Na ₃ citrate	0.03

The results presented in Table 3.5 show that the DFs from Tc and the transuranium elements achieved in the simulant solution containing 0.04 M CrO₄²⁻ and 11 complex-forming anions were much lower than those obtained in pure 0.5 to 4 M NaOH solutions. The highest DFs were observed for ²⁴⁴Cm (DF of 35) and for ²³⁹Pu (27). However, even these values are from five to eight times less than those found for pure 2 to 4 M NaOH. Nevertheless, the single reductive coprecipitation step removes 96% of the ²³⁹Pu and 97% of the ²⁴⁴Cm from the simulant waste solution. The DFs for ²³⁷Np and ⁹⁹Tc obtained with the simulant solutions (12 and 3.4, respectively) were lower than those determined for ²³⁹Pu and ²⁴⁴Cm, removing about 90% of the Np and 70% of the Tc from the simulant solution. Progressive dilution of the simulant solution with water (at waste:water ratios of 1:1, 1:2, and 1:3) improves the decontamination, but DFs exceeding 100 only were obtained for ²³⁹Pu and ²⁴⁴Cm. The DFs achieved for ²³⁷Np and ⁹⁹Tc in the diluted simulants remain much less than 100 (Table 3.5).

The effects of four combined complex-forming agents (EDTA, citrate, glycolate, and phosphate) and separately of chromate on the efficiency of reductive precipitation of Tc(VII) with sodium uranate were studied. The four complex-forming anions were found to decrease the solution DF from Tc about 1.4- to 2.0-fold. Chromate's effect was more pronounced, decreasing the DF about 3-fold for 0.02 M CrO₄²⁻ (Table 3.6).

Table 3.5. Decontamination of Tank Waste Simulant Solutions from Tc(VII), Np(V), Pu(VI), and Cm(III) by Capture on Chemically Reduced Sodium Uranate

[NaOH], M	Waste:Water Ratio	DF*			
		Tc	Np	Pu	Cm
3.2	1:0	3.4	12	27	35
1.6	1:1	6.4	26	82	88
1.07	1:2	8.2	32	133	119
0.8	1:3	10.7	47	158	136

Note: Tank waste simulant solution composition presented in Table 4.3; 0.05 M U(VI)₀.
 * 3x10⁻⁵ M Tc(VII)₀; 3x10⁻⁵ M Np(V)₀; 3x10⁻⁶ M Pu(VI)₀; 6x10⁻⁹ M ²⁴⁴Cm(III)₀.

Table 3.6. Effect of Chromate Ions and Some Complex Forming Agents on Reductive Coprecipitation from Alkaline Solutions of Tc(VII) with 0.05 M Reduced Sodium Uranate

[NaOH], M	Complexants*	[CrO ₄ ²⁻], M	DF	Tc capture, %
0.5	0	0	236	99.6
0.5	Added	0	132	99.2
0.5	Added	0.02	53	98.2
1.0	0	0	188	99.5
1.0	Added	0	127	99.2
1.0	Added	0.02	48	97.1
1.5	0	0	144	99.3
1.5	Added	0	110	99.1
1.5	Added	0.02	31	96.7

Note: 2.6×10^{-5} M Tc(VII)₀; 0.22 M N₂H₄ reductant added.
 * 0.05 M EDTA; 0.015 M citrate; 0.05 M glycolate; 0.005 M Na₃PO₄.

As shown in Table 3.5, Np(V) and Tc(VII) have lower DFs than those of Pu(VI) and Cm(III). Reduction to Tc(IV), Np(IV), and Pu(IV) by hydrazine can occur in NaOH solution. However, Np(V) and Tc(VII) are not significantly removed from solution until all Cr(VI) is reduced to Cr(III) hydroxide. In the mean time, Pu(VI) is quickly reduced to Pu(IV) and captured, with Cm(III), by the uranium precipitate. It is also possible that Cr(III) hydroxide occupies the U₃O₈·nH₂O precipitate surface, inhibiting the capture of Np(IV) and Tc(IV).

3.3.6 Leaching of Tc, Np, Pu, and Cm from Reduced Sodium Uranate Precipitates Containing U₃O₈·nH₂O

Leaching of Tc, Np, Pu, and Cm from reduced sodium uranate containing U₃O₈·nH₂O in 0.5 to 2.0 M NaOH solutions has been studied in inert atmosphere (Ar bubbling) and in oxidative media created either by air bubbling or by H₂O₂ addition to the leaching solution.

The leach test results, presented in Table 3.7, show that radioelement leaching by 0.5 to 2.0 M NaOH under an inert atmosphere is insignificant, not exceeding 0.3% after two hours. In 4 M NaOH, the leaching increases and is about 1.6% for Tc and 0.7% for Pu. In the NaOH solutions not containing dissolved oxygen, the oxidation states of Tc and Pu do not change. Leaching of Tc and Pu from the precipitate may be caused by slow crystallization of the amorphous uranium hydrous oxides and

Table 3.7. Leaching of Tc and Pu from U₃O₈·nH₂O Precipitate by Two Hours of Air or Argon Bubbling at Ambient Temperature

[NaOH], M	Leaching, %			
	Ar bubbling		Air bubbling	
	Tc	Pu	Tc	Pu
0.5	0.14	0.11	18.7	0.21
1.0	0.18	0.12	20.7	0.24
2.0	0.41	0.28	25.9	0.43
4.0	1.6	0.8	27.8	1.2

Note: 10 g U (as U₃O₈·nH₂O)/L solution; 10 mL solution volume; 24 mL gas/min.

exsolution of the Tc and Pu. Two hours of air bubbling through the alkaline sludge sharply increases Tc leaching to 20 to 25%. Under the same conditions, Pu leaching is only 0.2 to 0.4% in 0.5 to 2 M NaOH.

Hydrogen peroxide treatment of $U_3O_8 \cdot nH_2O$ precipitates containing Tc and Pu effectively leaches Tc from the precipitate. About 75% of the Tc dissolved into 0.1 M H_2O_2 solution after 24 hours of unstirred room temperature contact and Pu leaching was about 0.5% (Table 3.8). The ratio of the precipitate mass to the solution volume was 10 g U (as U_3O_8)/L. Leaching by 0.3 M H_2O_2 under the same conditions with air bubbling dissolves about 99% of the Tc but less than 1% of the Pu. These data show that a Tc/Pu separation factor greater than 100 can be achieved by leaching with 0.1 M H_2O_2 .

The observed differences in the leaching behaviors of Tc and Pu in the reaction of the precipitate with atmospheric air or H_2O_2 is expected. Technetium(IV) is known to be easily oxidized to Tc(VII) both by atmospheric oxygen and by H_2O_2 (Shilov et al. 1996a). However, oxidation of Pu(IV) to its more soluble higher oxidation states by hydrogen peroxide or especially by oxygen in alkaline media is more difficult (Shilov et al. 1996b; Shilov et al. 1997a). Rapid leaching of Tc from the uranium hydroxo compound precipitate by alkaline solutions saturated with oxygen or containing H_2O_2 not only oxidizes Tc(IV) to Tc(VII), but also oxidatively metathesizes the $U_3O_8 \cdot nH_2O$ matrix to Na_2UO_4 . The slow Pu leaching may arise by simple oxidative dissolution of the carrier solid phase.

The results of the present study demonstrate the possibility of Tc and transuranium element recovery from alkaline solutions by their precipitation on reduced sodium uranate containing $U_3O_8 \cdot nH_2O$. The captured Tc, in turn, may be separated from Pu by selective leaching in alkaline solutions of H_2O_2 or by simple air bubbling.

Table 3.8. Tc and Pu Leaching from $U_3O_8 \cdot nH_2O$ Precipitates by NaOH/ H_2O_2 Solutions in Air Atmosphere at Ambient Temperature

Element	$U_3O_8 \cdot nH_2O$ precipitation from NaOH, M	Amount leached, %					
		0.5 M NaOH	2.0 M NaOH	4.0 M NaOH	0.2 M NaOH / 0.05 M H_2O_2		0.1 M H_2O_2
		1 day	1 day	1 day	2 hours stirring	1 day, no stirring	1 day, no stirring
Pu	0.5	0.35	0.75	7.4	0.5	4.2	0.2
	1.0	0.35	0.90	1.9	0.87	5.1	0.3
	2.0	0.09	0.85	1.3	0.9	4.85	0.8
	4.0	0.07	0.46	1.0	1.0	6.2	0.5
Tc	0.5	0.8	4.07	5.7	40.7	52.3	81.4
	1.0	0.8	5.67	5.9	29.1	41.1	65.7
	2.0	0.93	5.10	4.2	31.6	55.8	75.5
	4.0	1.05	10.7	8.1	41.6	69.1	74.5

4.0 Coprecipitation of Tc(VII) with Tetraalkylammonium Salts in Oxidizing Conditions

The Tc(VII) oxoanion, TcO_4^- or pertechnetate, is the usual form of technetium found in oxidizing aqueous solution. Carriers used to coprecipitate pertechnetate generally would be expected to be salts of large uncharged cations with large tetrahedral oxyanions. Other types of coprecipitating agents for pertechnetate also exist.

It has been shown that direct precipitation of pertechnetate takes place with tetrahexyl- and tetraheptylammonium cations (Masson et al. 1996). However, this method has some technical and chemical disadvantages because of the high solution viscosities and contamination of the precipitate with nitrate. Nitrate contamination also was noted in the precipitation of the tetraphenylarsonium salt (German 1989). Nitrate contamination is particularly undesirable because thermal decomposition of such organic salts would be highly exothermic.

For coprecipitation to be most effective, the cation selected itself should form a poorly soluble pertechnetate compound. Table 4.1 lists the solubilities of various Tc(VII) salts. Large uncharged organic cations such as $[(\text{C}_6\text{H}_5)_4\text{As}]^+$ and $[(\text{C}_n\text{H}_{2n+1})_4\text{N}]^+$ (where n is 3 to 7) form poorly soluble pertechnetate salts. Coprecipitation of TcO_4^- also is more efficient if analogous tetrahedral uncharged anions such as ReO_4^- , ClO_4^- , IO_4^- , or BF_4^- are used. The anions ReO_4^- and ClO_4^- are considered to be the most effective carriers for Tc(VII) separation (Lavrukhina and Pozdniakov 1966).

Table 4.1. Aqueous Solubilities of Technetium Salts

Pertechnetate cations	Solubility at 25°C, M	References*
Cesium	1.81×10^{-2}	a
	1.54×10^{-2}	b
	1.60×10^{-2}	c
Thallium	3.1×10^{-3}	a
	2.1×10^{-3} at 20°C	d
Tetrapropylammonium	7.8×10^{-3}	a
	$(8.7 \pm 0.2) \times 10^{-3}$	e
Tetrabutylammonium	$(4.3 \pm 0.2) \times 10^{-3}$	e
	4.2×10^{-3} at 20°C	f
Tetrapentylammonium	$(7.9 \pm 0.2) \times 10^{-4}$	e
Tetrahexylammonium	$(7.1 \pm 0.5) \times 10^{-5}$	e
Tetraheptylammonium	$(8.8 \pm 0.8) \times 10^{-6}$	e
Triphenylguanidinium	$(3.9 \pm 0.3) \times 10^{-3}$	f
Tetraphenylarsonium	$(4.0 \pm 0.2) \times 10^{-4}$	e
*References		
(a) Roberts 1971.		
(b) Keller and Kanellakopulos 1963.		
(c) Schmidt 1986.		
(d) Mikulaj et al. 1981.		
(e) Masson et al. 1996.		
(f) German 1989.		

Perchlorate (ClO_4^-), however, has some disadvantages. Its salts rarely are isostructural with the technetium analogues and the organic salts decompose exothermically (German 1989). In contrast, the perrhenate compounds decompose endothermically (Kuzina et al. 1987; German 1989). Under most chemical conditions, Re and Tc are stabilized as their tetrahedral oxoanions. Because perrhenate and pertechnetate have practically identical bond lengths, the respective salts usually are isomorphous (Mikulaj et al. 1981; German 1989). Their hydration energies and energies of crystal lattice formation also are similar. These compelling reasons justify selection of Re(VII) as the best nonisotopic carrier for Tc(VII) .

4.1 Research on the Coprecipitation of Tc(VII) with Tetraalkylammonium Perrhenate from 0.5 to 4 M NaOH Solution

Initial experiments examined the effect of component addition order on coprecipitation of technetium with tetrabutylammonium perrhenate. Results show the highest decontamination from technetium was obtained by first adding the entire quantity of tetrabutylammonium hydroxide to the contaminated solution and then adding the ammonium perrhenate (Table 4.2). Precipitations conducted in the reverse order or by simultaneous dropwise addition of the tetrabutylammonium hydroxide and ammonium perrhenate gave lower decontamination.

Table 4.2. Coprecipitation of Tc(VII) from 0.5 M NaOH by Tetrabutylammonium Perrhenate

Experimental conditions	Technetium remaining in solution, %	DF
1 st step: add 2.5 mL 0.2 M Bu_4NOH 2 nd step: add 2.5 mL 0.2 M NH_4ReO_4	0.71	140
1 st step: add 2.5 mL 0.2 M NH_4ReO_4 2 nd step: add 2.5 mL 0.2 M Bu_4NOH	11.1	9
Simultaneous addition of 2.5 mL 0.2 M Bu_4NOH and 2.5 mL of 0.2 M NH_4ReO_4	1.79	56
Note: 25 mL of 5×10^{-3} M Tc(VII)		

The influences of tetrabutylammonium hydroxide and ammonium perrhenate concentrations on decontamination of 1.0 and 1.5 M NaOH from Tc also were studied. From 0.10 to 0.15 g Re per liter ($[5.4 \text{ to } 8.1] \times 10^{-4}$ M) and 2.6 to 5.2 g Bu_4NOH per liter (0.01 to 0.02 M) were required to attain DFs of 150 to 200. The data for 1.5 M NaOH are shown in Table 4.3 and Figure 4.1; data for 1.0 M NaOH are shown in Table 4.4 and Figure 4.2.

The data in Tables 4.3 and 4.4 and Figures 4.1 and 4.2 show that to achieve high decontamination from Tc, the tetrabutylammonium hydroxide concentration must be at least 0.01 M (about 2.6 g/L). However, neither the alkali concentration nor the solution ionic strength (nitrate concentration) significantly affect decontamination efficiency.

Fractional dissolution studies were performed to investigate the incorporation of Tc(VII) in the bulk Bu_4NReO_4 precipitate. The precipitate formed in the experiment whose results are shown in Figure 4.2 was stored in contact with its mother solution for 10 days to allow complete recrystallization and agglomeration. The precipitate was centrifuged at 13,000 rpm and the solution decanted. Eight sequential leach contacts of the precipitate with distilled water then were performed. The leaching contacts involved 23 hours of stirring of the distilled water and precipitate mixture to allow the solution to become saturated in Bu_4NReO_4 . This was followed by centrifugation, decantation, aliquoting of the supernatant solution,

Table 4.3. Decontamination of 1.5 M NaOH from ^{99}Tc by Bu_4NReO_4

Coprecipitation conditions		DF with Bu_4NOH	
Volume 0.1 M NH_4ReO_4 , mL	Final $[\text{Re}]_{\text{total}}$, M*	0.02 M	0.01 M
0.25	2.5×10^{-4}	1.6	1.4
0.5	5.0×10^{-4}	2.4	1.9
1.0	5.3×10^{-4}	6.3	3.3
1.25	5.32×10^{-4}	10.1	4.2
2.0	5.36×10^{-4}	20	10
2.5	5.38×10^{-4}	31	14
3.0	5.41×10^{-4}	49	21
4.0	5.46×10^{-4}	88	31
5.0	5.51×10^{-4}	104	46
6.0	5.57×10^{-4}	160	62
7.0	5.62×10^{-4}	163	78
10	5.78×10^{-4}	165	104
15	6.04×10^{-4}	163	164

Note: 100 mL 1.5 M NaOH initially containing 5×10^{-4} M Tc.
 * $[\text{Re}]_{\text{total}} = [\text{Bu}_4\text{N}^+ \cdots \text{ReO}_4^-] + [\text{ReO}_4^-]$; where $\text{Bu}_4\text{N}^+ \cdots \text{ReO}_4^-$ is the ion pair calculated based on similar considerations for Tc (German et al. 1988).

Solution activity

Figure 4.1. Coprecipitation of Tc(VII) with Bu_4NReO_4 from 100 mL of 1.5 M NaOH 5×10^{-4} TcO_4^- Initial Concentration; 0.02 M Bu_4NOH ; 0.1 M NH_4ReO_4 Added Precipitating Agent

Table 4.4. Decontamination of 1.0 M NaOH from ^{99}Tc by Bu_4NReO_4

Volume 0.1 M NH_4ReO_4 , mL	DF with Bu_4NOH			
	0.02 M	0.015 M	0.01 M	0.005 M
0.2	1.5	1.4	1.3	1
0.25	1.6	1.5	1.4	1
0.4	2.1	1.9	1.6	1
0.5	2.4	2.2	1.9	1
0.6	2.9	2.5	2.1	1
0.8	4.1	3.3	2.6	1
1	6.3	4.7	3.2	1
1.25	10	8	4.2	1
2	20	15	9.2	1
2.5	31	22	13	1.03
3	49	35	21	1.07
4	87	60	31	2.1
5	104	75	46	2.8
6	207	110	62	3.5
7	208	168	78	4.2
8	205	175	89	4.8
10	209	180	103	6.2
15	210	179	163	7.8

Note: 100 mL 1.0 M NaOH initially containing 5×10^{-4} M Tc.

Figure 4.2. Coprecipitation of Tc(VII) with Bu_4NReO_4 from 1.0 M NaOH 5×10^{-4} TcO_4^- initial concentration; 0.005 to 0.02 M Bu_4NOH ; 0.1 M NH_4ReO_4 added precipitating agent

and radioactive counting to determine Tc concentration. It is recognized that some possible recrystallization and deagglomeration of the crystals could affect Tc distribution in the precipitates. Such effects were neglected in these tests, however.

Based on the solubility of Bu_4NReO_4 and the water volume used in each contact, and assuming uniformly sized crystals, the depth of solid removed with each leach contact was calculated. The amount of Tc found in solution was compared to the amount of bulk Bu_4NReO_4 salt dissolved to determine the radial distribution of Tc in the Bu_4NReO_4 precipitate. Higher distribution of Tc exists towards the center of the precipitate crystals (Table 4.5). This implies that most of the Tc is removed during the initial precipitation of the Bu_4NReO_4 salt.

Table 4.5. Fractional Dissolution of Bu_4NReO_4 Precipitate Containing Tc

Layer	Radius (relative)	Re dissolved, %	Tc dissolved, %
1	0.989 - 0.999	3.13	2.0
2	0.978 - 0.989	3.13	1.9
3	0.967 - 0.978	3.13	1.9
4	0.956 - 0.967	3.13	2.0
5	0.945 - 0.956	3.13	2.1
6	0.825 - 0.945	28.1	21
7	0.654 - 0.825	28.1	29
8	0 - 0.654	28.1	39

4.2 Coprecipitation of Tc(VII) from 0.5 to 4 M NaOH with Tetrabutylammonium Perchlorate

The coprecipitation of Tc(VII) with Bu_4NClO_4 also was studied. The removal of Tc from alkaline solution by this agent was 50 times less effective (Table 4.6) than coprecipitation with the analogous perrhenate salt considered in Section 4.1. The poor relative perchlorate salt coprecipitation performance is expected based on the lack of isomorphism of the crystalline perchlorate and pertechnetate salts. This difference evidently arises from the considerable difference in Cl(VII) and Tc(VII) covalent radii and corresponding difference in ClO_4^- and TcO_4^- ionic radii (German 1989).

4.3 Summary of Test Results on Coprecipitation with Tetraalkylammonium Salts

Based on review of the technical literature concerning the chemical forms of Tc(VII) and structurally similar species [Re(VII) and Cl(VII)] in alkaline media, tetraalkylammonium salts were selected as promising precipitating agents. Such salts have low solubilities, may be recycled by specific procedures, and are converted to benign gases in vitrification.

Tetrabutylammonium perrhenate effectively removed Tc from 0.5 to 1.5 M NaOH solution, achieving DFs of 150 to 200 by use of 0.10 to 0.15 g Re and 2.6 to 5.2 g Bu_4NOH per liter of contaminated solution. Neither alkali concentration nor ionic strength significantly affected the decontamination efficiency. Decontamination by use of tetrabutylammonium perchlorate was 50 times less effective.

Table 4.6. Decontamination of 1.0 M NaOH from ^{99}Tc by Bu_4NClO_4

Volume 0.1 M NH_4ClO_4 , mL	DF with 0.01 M Bu_4NOH with	
	0.1 M NH_4ClO_4	0.1 M NH_4ReO_4
0.2	1	1.3
0.25	1	1.4
0.4	1	1.6
0.5	1	1.9
0.6	1	2.1
0.8	1	2.6
1	1	3.2
1.25	1	4.2
2	1	9.2
2.5	1	13
3	1	21
4	1	31
5	1	46
6	1.1	62
7	1.14	78
8	1.16	89
10	1.8	103
15	2.1	163

Coprecipitation of Tc(VII) with rhenium is efficient and technically feasible. Economic evaluations are required before its potential application to treat Hanford contaminated waste solutions. Coprecipitation of Tc(VII) with tetraalkylammonium perrhenate also may be useful in radiochemical analysis to concentrate Tc from dilute solution.

5.0 Removal of Transuranium Elements from Alkaline Solution and Hanford Waste Simulants by the Method of Appearing Reagents

In prior investigations, it was found that several carriers can efficiently remove long-lived transuranium (TRU) elements from 0.5 to 4.0 M NaOH solution by a homogeneous coprecipitation technique called the Method of Appearing Reagents (MAR) (Krot et al. 1996; Krot and Charushnikova 1997; Bessonov et al. 1997). The influences of Hanford tank waste components such as nitrate, nitrite, aluminate, carbonate, sulfate, phosphate, fluoride, citrate, glycolate, EDTA, and HEDTA on decontamination efficiency of alkaline solutions from TRU were investigated. The organic agents were found to significantly decrease decontamination efficiency at higher NaOH concentrations (Bessonov et al. 1997). To address this problem, investigations on wet chemical decomposition of organic complexants in alkaline media were conducted in prior studies (Shilov et al. 1997b).

The aim of the present research was to study TRU removal from less alkaline solutions by the MAR. The testing was performed for pH 9.3 to 0.4 M NaOH solutions both with and without the organic complexing agents; citrate, glycolate, EDTA, and HEDTA; and their decomposition products.

5.1 Experimental Materials and Methods

The experimental materials and methods used in tests of the application of the MAR with transition metal (hydr)oxide precipitates are described in the following subsections.

5.1.1 Radioisotopes

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 have been described in previous related studies (Krot et al. 1996). Experimental materials and methods to prepare TRU isotope solutions used in this study also were described earlier (Bessonov et al. 1997).

The bulk neptunium and plutonium used in the experiments were composed of ^{237}Np and ^{239}Pu isotopes. The ^{243}Am isotope was used to generate ^{239}Np tracer. Both ^{239}Np and ^{238}Pu have short half-lives and high specific activities. By use of these isotopes as radioactive tracers for Np and Pu, lower Np and Pu concentrations could be measured.

The ^{239}Np tracer solution was used in the experiments within five days (about two half-lives) of its separation from the ^{243}Am mother. The ^{239}Np tracer was added to the 1×10^{-7} M ^{237}Np experimental solution to provide an initial β -activity of 2×10^5 counts/(min·mL). This concentration is sufficient to obtain reliable data above background counting rates even with DFs of 1000.

An isotope mixture of ^{238}Pu and ^{239}Pu was used. The stock solution was 2.3 M HNO_3 containing 0.93×10^{-4} M Pu(IV). Chemically, 29% of the Pu was ^{238}Pu . Aliquots of Pu(IV) solution were prepared by diluting 0.22 mL of the stock Pu(IV) with 0.1 M HClO_4 ; the aliquots then were added to the alkaline test solutions. The initial Pu concentration was 1.38×10^{-7} M (including 4×10^{-8} M ^{238}Pu) for all experiments. This concentration is lower than the solubility of Pu(IV) hydrous oxide over a wide range of NaOH concentrations (Peretrukhin et al. 1996; Delegard 1987).

To prepare the Pu(VI) stock, 0.22 mL of the initial solution was diluted by mixing with 0.5 mL of concentrated HClO_4 . The mixture was slowly boiled to formation of damp salts and the residue dissolved

in 2.96 mL of 0.1 M HClO₄. The resulting 6.9×10^{-6} M Pu(VI) stock concentration was sufficiently low to avoid unwanted radiolytic Pu(VI) self-reduction over the duration of the experiment. The target initial Pu(VI) concentration in the alkaline media also was 1.38×10^{-7} M for all experiments.

5.1.2 Bulk Chemical Reagents

The coprecipitation precursor reagents and precipitation products used in this study are listed in Table 5.1. The formulas of metal hydroxides given in this table and subsequently in this section are only symbolic and may not describe the phases actually present in the precipitates. These precipitation reagents were selected based on their high efficiency for TRU removal, as described in previous studies (Krot et al. 1996; Bessonov et al. 1997). The carrier precipitation precursors were dissolved in water at appropriate concentrations prior to addition to alkaline solutions.

Table 5.1. TRU Removal Reagents Tested for Dilute Alkaline Solution

Precursor	Carrier formation conditions	Carrier
Cr(CH ₃ COO) ₃	Thermal hydrolysis	Cr(OH) ₃ ·xH ₂ O
Co(NH ₃) ₆ Cl ₃	Thermal hydrolysis	Co(OH) ₃ ·xH ₂ O
Na ₂ [Fe(CN) ₅ NO]	Thermal hydrolysis	Fe(OH) ₃ ·xH ₂ O
K ₂ FeO ₄	Reduction to Fe(III), hydrolysis	Fe(OH) ₃ ·xH ₂ O
KMnO ₄	Reduction to Mn(IV), hydrolysis	MnO ₂ ·xH ₂ O
KMnO ₄	Reduction to Mn(II), hydrolysis	Mn(OH) ₂ ·xH ₂ O

5.1.3 Coprecipitation Test Procedure

The TRU removal test procedure by the MAR used in the present tests was the same as described in previous reports (Krot et al. 1996; Bessonov et al. 1997). The experimental procedures used to prepare Pu(IV) and Pu(VI) are described in detail in these references.

Stock Co(NH₃)₆³⁺, Cr³⁺, Fe(CN)₅NO²⁺, and KMnO₄ solutions were prepared beforehand. For tests with FeO₄²⁻, K₂FeO₄ powder was added to the experimental solutions as needed because of the instability of K₂FeO₄ in solution. Experimental solutions were held in polyethylene test tubes. Calculated amounts of H₂O were added to each test tube. This was followed by 0.1 mL of Pu(IV) or Pu(VI) stock solutions. The solution was stirred and a calculated amount of NaOH or NH₄OH solution added to achieve the desired concentration. In each case the amount of NaOH added included the quantity required to form the metal hydroxide. Precipitation precursor solutions and other reagents, if necessary, were added last.

After the precursor addition, the test tubes were kept at thermostatted conditions for two to three hours. The carrier formation conditions used were those determined to be optimum in previous work (Krot et al. 1996; Bessonov et al. 1997). After coagulation, the product precipitate was separated by five minutes of centrifugation, and an aliquot of supernate solution was taken for analysis. This centrifugation and sampling procedure was repeated twice to ensure completeness of separation.

5.1.4 Analytical Measurements and Instrumentation

Absorption spectrometry was used to identify radioelement oxidation states and, in some cases, to determine their concentrations. Spectra were recorded using a model UV-3101 spectrophotometer (Shimadzu Instruments, Inc., Japan). To measure the pH of the ammonium solutions, a laboratory digital pH meter (Radelkis OP-211/1, Hungary) with glass electrode was used.

The β activities of ^{239}Np solutions and α activities of Pu solutions were determined by liquid scintillation using a model LS-6500 scintillation counter (Beckman Instruments, Inc., USA). To determine the activity concentration, 0.05 mL of the alkaline coprecipitation mother solution were pipeted for counting into 5 to 10 mL of liquid scintillation cocktail. Measurements of initial experimental solution concentrations (without coprecipitation) were conducted simultaneously for each experimental set. Plutonium and neptunium concentration calculations were made taking into account standard recoveries and background counting corrections.

5.2 Coprecipitation of Pu with Fe(III) Hydroxide Obtained by K_2FeO_4 Reduction

The first experiments tested selected carriers for Pu(IV) and (VI) removal from pure alkaline solutions at low NaOH concentrations. In prior tests, Fe(III) hydroxide was found to be a very effective reagent for TRU removal from 0.5 to 4 M NaOH in the presence of organic complexants (Bessonov et al. 1997). However, K_2FeO_4 was not tested as a Fe(III) hydroxide precursor for Pu coprecipitation from solution containing 0.5 M or lower NaOH. Sodium sulfite, as well as many other reductants, can be used to reduce K_2FeO_4 to Fe(III) hydroxide. Results from sulfite reduction are given in Table 5.2.

Table 5.2. Decontamination of NaOH and NH_4OH Solutions from Pu by Coprecipitation with $\text{Fe}(\text{OH})_3$ from 0.01 M K_2FeO_4 Reduction by 0.04 M Na_2SO_3

Solution	25°C, Three hours		50°C, Two hours	
	DF Pu(VI)	DF Pu(IV)	DF Pu(VI)	DF Pu(IV)
Ammonium buffer (0.1 M NH_4OH + 1 M NH_4Cl , pH 9.3)	25	60	30	30
0.2 M NH_4OH , pH 10.5	25	45	100	102
0.02 M NaOH	25	16	110	101
0.05 M NaOH	25	14	110	98
0.1 M NaOH	15	5	120	110
0.2 M NaOH	7.3	5	100	100
0.4 M NaOH	2.5	2.5	60	50
1.38×10^{-7} M Pu(VI)_0 and Pu(IV)_0				

Clearly, increasing temperature decreases the coagulation time and significantly increases DF. At 50°C, coprecipitation of both Pu(IV) and Pu(VI) with Fe(III) hydroxide occurs with high efficiency at pH 10.5 to 0.2 M NaOH. The independence with respect to oxidation state can be explained by the Na_2SO_3 reduction of Pu(VI) to Pu(V) during concurrent K_2FeO_4 reduction. Plutonium(V) is known to disproportionate in dilute alkali to form Pu(VI) and Pu(IV) (Shilov 1997c).

The Pu(IV) formed by the reduction is readily captured by Fe(III) hydroxide and the Pu(VI) produced by disproportionation is reduced by sulfite. With time, complete conversion of Pu(VI) to Pu(IV) occurs, and the product Pu(IV) is carried by the $\text{Fe}(\text{OH})_3$.

5.3 Coprecipitation of Pu with Fe(III) Hydroxide Obtained by $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ Hydrolysis

According to previous studies, the best conditions to coprecipitate TRU with Fe(III) hydroxide obtained from sodium nitroprusside are hydrolytic decomposition of 0.02 M $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ at 80°C (Krot et al. 1996). Later studies showed that nitroprusside is the most effective precursor for TRU capture from 1 to 4 M NaOH solutions containing organic complexants (Bessonov et al. 1997). Tests of nitroprusside precursor to produce $\text{Fe}(\text{OH})_3$ in solutions of pH 9.3 to 0.4 M NaOH were performed at the recommended 80°C and also at 70°C. Results are presented in Table 5.3.

Table 5.3. Decontamination of NaOH and NH_4OH Solutions from Pu by Coprecipitation with $\text{Fe}(\text{OH})_3$ from 0.02 M $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ Thermal Hydrolysis

Solution	70°C, Two hours	80°C, Three hours	
	DF Pu(IV)	DF Pu(IV)	DF Pu(VI)
Ammonium buffer (0.1 M NH_4OH + 1 M NH_4Cl , pH 9.3)	3	3	3
0.2 M NH_4OH , pH 10.5	12	9	15
0.02 M NaOH	20	53	100
0.05 M NaOH	41	150	126
0.1 M NaOH	72	209	97
0.2 M NaOH	68	539	150
0.4 M NaOH	66	425	330
Note: 1.38×10^{-7} M $\text{Pu}(\text{VI})_0$ and $\text{Pu}(\text{IV})_0$.			

The data show that nitroprusside thermal hydrolysis at 80°C gives DFs superior to those found at 70°C. Plutonium(VI) coprecipitates almost as well as Pu(IV). As in the coprecipitation tests with Fe(III) hydroxide from K_2FeO_4 , Pu(VI) reduction to Pu(V) may be occurring in the tests with nitroprusside. In this case, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ hydrolytic products may be the reductant(s). The resulting Pu(V) disproportionates to form Pu(VI) and Pu(IV) as previously described. Nitroprusside yields higher DFs at 0.05 to 0.4 M NaOH than does ferrate whereas ferrate gives higher DFs than nitroprusside at pH 9.3 and 10.5.

5.4 Coprecipitation of Pu with Manganese Dioxide Obtained by KMnO_4 Reduction

Previous tests showed manganese dioxide to be a satisfactory carrier only at low NaOH concentrations (Krot et al. 1996). For this reason, manganese dioxide was not investigated in subsequent tests in 1 to 4 M NaOH (Bessonov et al. 1997). Current tests at lower NaOH concentrations were performed to investigate manganese dioxide as a carrier.

The results in Table 5.4 show that sodium sulfite is a satisfactory reductant for permanganate but that peroxide is less satisfactory. The best conditions for coprecipitation are 50°C reaction with 0.04 M Na_2SO_3 and two hours of coagulation. At 50°C, the maximum DF is attained at 0.05 M NaOH.

Table 5.4. Decontamination of NaOH and NH₄OH Solutions from Pu by Coprecipitation with MnO₂ from 0.002 M MnO₄⁻ Reduction

Solution	25°C, one hour, 0.04 M SO ₃ ²⁻	50°C, two hours, 0.04 M SO ₃ ²⁻	25°C, one hour, 0.008 M H ₂ O ₂
	DF Pu(VI)	DF Pu(IV)	DF Pu(VI)
Ammonium buffer (0.1 M NH ₄ OH + 1 M NH ₄ Cl, pH 9.3)	35	40	40
0.2 M NH ₄ OH, pH 10.5	30	52	25
0.02 M NaOH	90	95	18
0.05 M NaOH, 0.01 M SO ₃ ²⁻	25	--	--
0.05 M NaOH, 0.02 M SO ₃ ²⁻	30	--	--
0.05 M NaOH	90	102	11
0.1 M NaOH	70	55	6
0.2 M NaOH	55	58	9
0.4 M NaOH	35	37	14

Note: 1.38×10^{-7} M Pu(VI)₀ and Pu(IV)₀.

The behavior of Pu(IV) deserves special consideration in this system. First, MnO₄⁻ likely oxidizes part of the Pu(IV) to Pu(VI) (Shilov et al. 1997a). Upon sodium sulfite addition, however, MnO₄⁻ is reduced to MnO₂. The excess Na₂SO₃ then converts part of the Pu(VI) to Pu(V). The Pu(V) disproportionates, producing Pu(VI) and Pu(IV), which readily coprecipitates with the MnO₂. The Pu(VI) from disproportionation is reduced to Pu(V) by sulfite, and the process continues until essentially all the plutonium reports as Pu(IV) to the MnO₂ precipitate.

5.5 Coprecipitation of Pu with Mn(II) Hydroxide Obtained by KMnO₄ Reduction

Potassium permanganate precursor was used to generate Mn(OH)₂ by reduction with hydroxylamine. Tests showed that optimum conditions for TRU coprecipitation are 3 hours of reaction of 0.004 M KMnO₄ with 0.06 M NH₂OH at 50°C. Full experimental results are given in Table 5.5.

Despite a three-fold excess of hydroxylamine, the precipitates contained some MnO₂ and hence had light brown or brownish colors. The proportion of MnO₂ depended on temperature, alkali concentration, and the solution stirring rate. Evidently, higher DFs were obtained if lower proportions of MnO₂ were present in the solid phase.

5.6 Coprecipitation of Pu with Cr(III) Hydroxide Obtained by Cr(CH₃COO)₃ Hydrolysis

The coprecipitation of plutonium in dilute alkaline media by Cr(OH)₃ produced by hydrolysis of Cr(III) acetate [Cr(CH₃COO)₃] was conducted according to the optimum conditions determined in prior tests (Krot et al. 1996). Results of Pu removal with Cr(OH)₃ are given in Table 5.6.

Because of the deleterious effects of organic compounds on decontamination efficiency of alkaline solutions from Pu with Cr(OH)₃ (Bessonov et al. 1997) and the relatively low DFs found in the present tests, Cr(III) hydroxide is judged to be a poor carrier for decontaminating dilute alkaline solutions of Pu.

Table 5.5. Decontamination of NaOH and NH₄OH Solutions from Pu by Coprecipitation with Mn(OH)₂ from KMnO₄ Reduction by NH₂OH

Solution	25°C, three hours, 0.002 M KMnO ₄ , 0.004 M NH ₂ OH	50°C, three hours, 0.004 M KMnO ₄ , 0.06 M NH ₂ OH	
	DF Pu(VI)	DF Pu(VI)	DF Pu(IV)
Ammonium buffer (0.1 M NH ₄ OH + 1 M NH ₄ Cl, pH 9.3)	2.5	1.3	3
0.2 M NH ₄ OH, pH 10.5	25	40	70
0.02 M NaOH	40	100	170
0.05 M NaOH	40	100	160
0.1 M NaOH	70	120	250
0.1 M NaOH, 0.004 M KMnO ₄	80	--	--
0.1 M NaOH, 0.008 M KMnO ₄ , 0.06 M NH ₂ OH	115	--	--
0.2 M NaOH	55	150	150
0.4 M NaOH	32	125	130

Note: 1.38×10^{-7} M Pu(VI)₀ and Pu(IV)₀.

Table 5.6. Decontamination of NaOH and NH₄OH Solutions from Pu by Coprecipitation with Cr(OH)₃ from 0.01 M Cr(CH₃COO)₃ Thermal Hydrolysis

Solution	80°C, five hours	
	DF Pu(IV)	DF Pu(VI)
Ammonium buffer (0.1 M NH ₄ OH + 1 M NH ₄ Cl, pH 9.3)	7.6	1.8
0.2 M NH ₄ OH, pH 10.5	26	6
0.02 M NaOH	32	16
0.05 M NaOH	51	17
0.1 M NaOH	76	60
0.2 M NaOH	118	50
0.4 M NaOH	162	55

Note: 1.38×10^{-7} M Pu(VI)₀ and Pu(IV)₀.

5.7 Coprecipitation of Pu with Co(III) Hydroxide Obtained by Co(NH₃)₆Cl₃ Hydrolysis

According to previous work, hexaamminecobalt(III) chloride [Co(NH₃)₆Cl₃] is an effective precursor to obtain Co(III) hydroxide carrier for TRU removal from alkaline solution by the Method of Appearing Reagents (Krot et al. 1996; Bessonov et al. 1997). Results from tests with less alkaline solutions (Table 5.7) confirm the earlier data.

Table 5.7. Decontamination of NaOH and NH₄OH Solutions from Pu by Coprecipitation with Co(OH)₃ from 0.02 M Co(NH₃)₆Cl₃ Thermal Hydrolysis

Solution	80°C, three hours	
	DF Pu(IV)	DF Pu(VI)
Ammonium buffer (0.1 M NH ₄ OH + 1 M NH ₄ Cl, pH 9.3)	1, no ppt	1, no ppt
0.2 M NH ₄ OH, pH 10.5	370	11
0.02 M NaOH	350	63
0.05 M NaOH	400	110
0.1 M NaOH	500	100
0.2 M NaOH	200	49
0.4 M NaOH	350	101
Note: 1.38×10^{-7} M Pu(VI) ₀ and Pu(IV) ₀ .		

No carrier precipitated in the pH 9.3 tests. The low hydroxide concentration, high ammonium ion concentrations, and inhibiting effect of 1 M NH₄Cl on [Co(NH₃)₆]³⁺ hydrolysis likely contributed to keeping the Co(III) dissolved. Though some reduction of Pu(VI) by NH₃ also may have occurred, DFs still were higher for Pu(IV) than for Pu(VI).

5.8 Removal of Pu(IV) from Alkaline Solutions of Waste Components

In previous studies, it was found that citrate, glycolate and especially EDTA and HEDTA seriously degrade the decontamination of alkaline solutions from TRU by the MAR (Bessonov et al. 1997). Of the various precursors and carriers tested, Fe(III) hydroxide obtained by nitroprusside hydrolysis produced the highest DFs from 0.5 to 4 M NaOH solutions containing organic complexing agents. Based on these earlier findings, tests were performed to determine the performance of nitroprusside precursor and Fe(III) hydroxide carrier in decontaminating organic-bearing dilute alkaline solutions of Pu(IV). Test results are given in Table 5.8.

The influences of glycolate and citrate on DF from Pu(IV) decrease with increasing NaOH concentration but the DFs from EDTA solutions remain unchanged. Precipitates did not form in the presence of 0.1 M Na₃HEDTA. Based on findings described in sections 5.5 and 5.7 of this report, Mn(II) and Co(III) hydroxides could be considered as candidate carriers. Scoping tests showed, however, that neither Mn(II) nor Co(III) formed hydroxide precipitates in 0.1 or 0.3 M NaOH solutions containing 0.1 M Na₃HEDTA or 0.1 M Na₄EDTA.

Table 5.8. Decontamination of Dilute NaOH Solution Containing Organic Complexing Agents from Pu by Coprecipitation with Fe(OH)₃ from 0.02 M [Fe(CN)₅NO]²⁻ Thermal Hydrolysis

Complexant, 0.1 M	80°C, three hours	
	0.1 M NaOH	0.3 M NaOH
	DF Pu(IV)	DF Pu(IV)
Na ₄ EDTA	7.6	8
Na ₃ HEDTA	1, no ppt	1, no ppt
Na glycolate	32	42
Na ₃ citrate	42	93
Note: 1.38×10^{-7} M Pu(IV) ₀ .		

Subsequent experiments were directed towards decomposing HEDTA and EDTA to decrease their deleterious effects on decontamination efficiency. Wet oxidation methods to decompose organic complexing agents in alkaline media, developed and described in earlier studies, showed persulfate to be most effective (Shilov et al. 1997b). Therefore, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was tested to destroy organic complexants present in dilute alkaline solutions.

The initial concentrations of $\text{Na}_2\text{S}_2\text{O}_8$ and Na_4EDTA in the alkaline test solutions were 0.5 M and 0.05 M, respectively. After treatment, the EDTA concentrations were found to be 8 to 10% of the initial values. The treated solutions then were treated with nitroprusside to produce $\text{Fe}(\text{OH})_3$ and the DFs from Pu(IV) were measured. The DFs of the persulfate-treated solutions containing residual EDTA and EDTA decomposition products increased with increasing alkali concentration (Table 5.9). However, the DFs found for the persulfate-treated solutions are comparable with, or even lower, than the DFs found for solutions not treated by persulfate.

Tests also were performed on persulfate-treated 0.1 to 1 M NaOH solutions containing EDTA or HEDTA by coprecipitation with Cr(III) and Co(III) hydroxide. The test results, presented in Table 5.10, are compared with findings of similar tests without persulfate treatment. The results show the DFs for most conditions increased by the persulfate treatment. Similar tests showed Mn(II) did not form any hydroxide precipitate in the presence of persulfate-decomposed EDTA or HEDTA in 0.1 to 1 M NaOH.

To increase the completeness of EDTA decomposition by persulfate, Ag^+ was added to an alkaline solution containing EDTA and $\text{S}_2\text{O}_8^{2-}$. Silver(I) is known to be an effective catalyst for EDTA decomposition by $\text{Na}_2\text{S}_2\text{O}_8$ in alkaline solution (Shilov et al. 1997b). Results showed, however, that the Ag(I) addition did not improve Pu(IV) coprecipitation for any tested carrier.

An alternative method to diminish the influence of complexing agents is to sequester (mask) them with an added metal ion. Such additions would introduce less salt to the waste than wet oxidation techniques (e.g., persulfate). The added metal ion must form a relatively soluble hydroxide as well as stable complexes with the targeted complexing agents. Calcium(II) was considered based on these factors.

Table 5.9. Decontamination of NaOH Solutions from Pu(IV) by Coprecipitation with $\text{Fe}(\text{OH})_3$ from 0.02 M $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ Thermal Hydrolysis and in the Presence and Absence of EDTA/ $\text{Na}_2\text{S}_2\text{O}_8$ Decomposition Products

[NaOH], M	80°C, three hours	
	DF with $\text{S}_2\text{O}_8^{2-}$	DF without $\text{S}_2\text{O}_8^{2-}$
0.1	2.1	7.6
0.3	32	8
0.73	49	--
1	--	220*
1.73	86.5	--
3.9	80	--
4	--	130*
Notes: $[\text{Na}_4\text{EDTA}]_0$ 0.05 M 1.38×10^{-7} M $[\text{Pu}(\text{IV})]_0$ * 5×10^{-7} M $[\text{Pu}(\text{IV})]_0$; Bessonov et al. 1997.		

Table 5.10. Decontamination of Complexant-Bearing NaOH Solutions from Pu(IV) by Coprecipitation with Cr(OH)₃ from 0.01 M Cr(CH₃COO)₃ and Co(OH)₃ from 0.02 M [Co(NH₃)₆]³⁺ Thermal Hydrolyses with and without Persulfate Treatment

Complexant, 0.05 M	[NaOH], M	Cr(OH) ₃ , 80°C, three hours		Co(OH) ₃ , 80°C, three hours	
		DF with S ₂ O ₈ ²⁻	DF without S ₂ O ₈ ²⁻	DF with S ₂ O ₈ ²⁻	DF without S ₂ O ₈ ²⁻
EDTA	0.1	23	--	21	--
	0.5	36	--	6.6	--
	0.73	65	--	8.6	--
	1.0	--	25*	--	1.5*
HEDTA	0.15	35	--	4.2	--
	0.4	8.2	--	2.0	--
	0.89	7.5	--	3.5	--
	1.0	--	120*	--	no ppt*

Note: 1.38×10^{-7} M [Pu(IV)]₀.
 * 5×10^{-7} M [Pu(IV)]₀; Bessonov et al. 1997.

Results of decontaminating alkaline EDTA- and HEDTA-bearing solutions of Pu(IV) with Fe(III) hydroxide from nitroprusside precursor in the presence Ca²⁺ are given in Table 5.11. The results are compared with results found for similar tests in the absence of Ca²⁺. The Ca²⁺ addition distinctly improved DFs for both EDTA- and HEDTA-bearing solutions.

Calcium ion, however, does not form stable complexes with either citrate or glycolate in alkaline solution (Sillen et al. 1964). Therefore, the presence of Ca²⁺ in citrate- or glycolate-bearing solutions was found not to improve the DFs attained by Fe(III) hydroxide precipitation.

Coprecipitation of Pu(IV) with Co(III) hydroxide from alkaline solutions containing organic complexants also was tested in the presence and absence of Ca²⁺. Table 5.12 displays these results and results of prior similar tests without added Ca²⁺ (Bessonov et al. 1997).

Table 5.11. Decontamination of NaOH Solutions from Pu(IV) by Coprecipitation with Fe(OH)₃ from 0.02 M [Fe(CN)₅NO]²⁻ Thermal Hydrolysis in the Presence and Absence of 0.1 M CaCl₂

Solution	80°C, three hours			
	0.1 M EDTA		0.1 M HEDTA	
	DF with 0.1 M Ca ²⁺	DF without 0.1 M Ca ²⁺	DF with 0.1 M Ca ²⁺	DF without 0.1 M Ca ²⁺
Ammonium buffer (0.1 M NH ₄ OH + 1 M NH ₄ Cl, pH 9.3)	2	--	2	--
0.2 M NH ₄ OH, pH 10.5	10	--	4	--
0.02 M NaOH	104	--	8	--
0.05 M NaOH	138	--	16	--
0.1 M NaOH	152	7.6	89	1.0
0.2 M NaOH	141	--	55	--
0.3 M NaOH	--	8	--	7.6
0.4 M NaOH	115	--	42	--

Table 5.12. Decontamination of NaOH Solutions Containing Complexants from Pu(IV) by Coprecipitation with Co(OH)₃ from [Co(NH₃)₆]³⁺ Thermal Hydrolysis

Solution	80°C, two hours			
	0.1 M EDTA, 0.02 M Co ³⁺ , 0.1 M Ca ²⁺	0.1 M HEDTA, 0.13 M Co ³⁺ , 0 M Ca ²⁺	0.1 M citrate, 0.02 M Co ³⁺ , 0 M Ca ²⁺	0.1 M glycolate, 0.02 M Co ³⁺ , 0 M Ca ²⁺
	DF	DF	DF	DF
Ammonium buffer (0.1 M NH ₄ OH + 1 M NH ₄ Cl, pH 9.3)	1	1	1	1
0.2 M NH ₄ OH, pH 10.5	9	1.2	1	11
0.02 M NaOH	20	5.8	2	23.6
0.05 M NaOH	133	59	13	52.5
0.1 M NaOH	126	69	78	105
0.2 M NaOH	--	160	--	--
0.2 M NaOH	--	95	--	--
0.2 M NaOH	160	170	118	101
0.4 M NaOH	130	167	128	102
1.0 M NaOH; 0.02M Co ³⁺ ; 0 M Ca ²⁺ ; 5x10 ⁻⁷ M Pu(IV) ₀ (Bessonov et al. 1997)	no ppt	no ppt	220	170

The data show that 0.1 M Ca(II) does not displace Co(III) from its apparent EDTA complex in pH 9.3 solution. However, Ca(II) becomes increasingly effective as alkalinity increases. Without added Ca(II), however, Co(OH)₃ does not form from 0.02 M [Co(NH₃)₆]³⁺ hydrolysis even at 1 M NaOH if 0.1 M EDTA is present.

In tests with 0.1 M HEDTA, 0.13 M added [Co(NH₃)₆]³⁺ was used. The amount of Co(III) added thus was sufficient for Co(III) to act as its own masking agent for HEDTA and to form the Co(OH)₃ precipitate. This approach yielded results similar to those found with 0.1 M added Ca(II). Without Ca(II) and Co(III) concentrations in excess of 0.1 M HEDTA, no precipitate formed even at 1 M NaOH. Citrate and glycolate have less influence on Co(OH)₃ precipitation than do EDTA or HEDTA (Bessonov et al. 1997) but, as shown in the present tests, their influences are still sufficient to give DFs of 1 at pH 9.3.

5.9 Removal of Np from Alkaline Solutions of Waste Components

Previous studies show that Np(V) is difficult to coprecipitate from alkaline solutions with most carriers by the MAR (Krot et al. 1996; Bessonov et al. 1997). Decontamination improves substantially, however, if the neptunium is first reduced to the (IV) oxidation state. Vanadyl(IV) sulfate was found to be one of the more effective Np(V) reductants (Shilov et al. 1997b).

Coprecipitation of Np(V) with Co(III) hydroxide was tested because of its high effectiveness as a carrier. The concentration of the mixed ²³⁷Np/²³⁹Np spike was 1x10⁻⁷ M in all tests. Preliminary experiments showed that V(IV) rapidly reduces Co(III) to Co(II). As a result of this reaction, Np(IV) is not formed under optimum Co(III) and V(IV) concentrations for coprecipitation (0.02 and 0.01 M, respectively). To obtain Np(IV) and reach high DFs, the [Co(NH₃)₆]³⁺ must be added 25 to 30 minutes after the initiation of the Np(V) reduction by vanadyl(IV) sulfate in alkaline solution. Data on the coprecipitation of Np(IV) with Co(OH)₃ after 30 minutes Np(V) reduction time by VOSO₄ are presented in Table 5.13.

Table 5.13. Decontamination of NaOH Solutions from Np(V) by Reduction with 0.1 M VO₂SO₄ and Coprecipitation with Co(OH)₃ and Co(OH)₂ from 0.02 M [Co(NH₃)₆]³⁺ Thermal Hydrolysis

Solution	80°C, two hours
	DF
Ammonium buffer (0.1 M NH ₄ OH + 1 M NH ₄ Cl, pH 9.3)	20
0.2 M NH ₄ OH, pH 10.5	23
0.02 M NaOH	80
0.05 M NaOH	160
0.1 M NaOH	400
0.2 M NaOH	370
0.4 M NaOH	250

Cobalt(II) and Co(III) hydroxides were observed in each test's precipitate because the V(IV) excess remaining after the 30-minute reduction of Np(V) to Np(IV) converted part of the Co(III) to Co(II). At pH 9.3, only Co(II) hydroxide was observed in the sediment. Neptunium removal by Co(OH)₃ coprecipitation was tested for alkaline solution containing organic complexing agents. In the tests, V(IV) was used to reduce Np(V) to Np(IV) and [Co(NH₃)₆]³⁺ used as the precursor. The reductant was added 30 minutes before adding the precursor. For results see Table 5.14.

The relatively poor decontamination of alkaline solutions containing Np(V), VOSO₄, Ca²⁺, Na₄EDTA, and Co(NH₃)₆Cl₃ (compared with that of the similar plutonium system without vanadyl shown in Table 5.12) may be explained by the formation of a very stable VOEDTA²⁻ complex. The rate of reaction between V(IV) and Np(V) apparently is significantly decreased by the formation of this complex, limiting Np(IV) conversion and its carrying by the Co(OH)₃ precipitate. Alternative Np(V) reductants such as sodium dithionite or N₂H₄·HNO₃ (Bessonov et al. 1997) may provide better solution DFs from Np(V) by Co(OH)₃ coprecipitation.

Table 5.14. Decontamination of NaOH Solutions Containing Complexants from Np(V) by Reduction with 0.1 M VO₂SO₄ and Coprecipitation with Co(OH)₃ and Co(OH)₂ from [Co(NH₃)₆]³⁺ Thermal Hydrolysis

Solution	80°C, 3.5 hours			
	0.1 M EDTA, 0.02 M Co ³⁺ , 0.1 M Ca ²⁺	0.1 M HEDTA, 0.13 M Co ³⁺ , 0 M Ca ²⁺	0.1 M citrate, 0.02 M Co ³⁺ , 0 M Ca ²⁺	0.1 M glycolate, 0.02 M Co ³⁺ , 0 M Ca ²⁺
	DF	DF	DF	DF
Ammonium buffer (0.1 M NH ₄ OH + 1 M NH ₄ Cl, pH 9.3)	4	12	13	20
0.2 M NH ₄ OH, pH 10.5	4.4	19	17	26
0.02 M NaOH	4.1	160	78	125
0.05 M NaOH	5.0	270	109	160
0.1 M NaOH	3.9	90	117	130
0.2 M NaOH	4.2	75	150	153
0.4 M NaOH	4.9	80	134	147
1.0 M NaOH; 0.02M Co ³⁺ ; 0 M Ca ²⁺ ; 5x10 ⁻⁷ M Pu(IV) ₀ (Bessonov et al. 1997)	no ppt	no ppt	220	170

6.0 Conclusions

Plutonium(IV) and Am(III) are quantitatively coprecipitated from 0.5 to 4.0 M NaOH by 3×10^{-3} to 5×10^{-2} M UO_2 to give DFs ranging from 110 to more than 1,000. This method is less effective for decontamination from Np and Tc, however, giving DFs of 84 to 153 for Np and 51 to 176 for Tc at 5×10^{-2} M UO_2 . An equimolar mixture of U(VI) and U(IV) hydroxides improves the DFs by 10 to 20% over those observed for UO_2 . The improvement may be related to formation of $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$, which is an excellent host for carrying actinides in all oxidation states.

The slow reduction of U(VI) by N_2H_4 occurring with solid Na_2UO_4 or with the soluble peroxide complex $\text{Na}_4\text{UO}_2(\text{O}_2)_3$ in dilute NaOH is accelerated by Tc(VII). The reaction product, a suspension of $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$, is formed from 0.2 to 2.0 M NaOH containing 5.0×10^{-3} to 5.0×10^{-2} M U(VI), $(1.0 \text{ to } 5.0) \times 10^{-5}$ M Tc(VII), and 0.2 to 0.3 M N_2H_4 . The product $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ coprecipitates Cm(III) with DFs of 61 to 372, Np(V) with DFs of 67 to 310, Pu(VI) with DFs of 82 to 405, and Tc(VII) with DFs of 8 to 260. The Tc, Np, and Pu first are reduced to their respective (IV) oxidation states.

The action of 0.2 to 0.3 M hydrazine on alkaline slurries of Na_2UO_4 in simulated Hanford Site waste solutions containing 3.2 M NaOH, chromate, and 11 other inorganic and organic complex-forming ions, also captures Tc and the TRU elements. However the DFs [35 for Cm(III), 12 for Np(V), 27 for Pu(VI), and 3.4 for Tc(VII)] are lower than observed in pure NaOH solutions. The decreased DFs are associated with the complex formation of TRU and Tc(IV) and inhibition of their coprecipitation by parasitic Cr(III) hydroxide precipitation.

Leaching of Pu and Tc from $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ precipitating agent by argon bubbling through 0.2 to 1.0 M NaOH does not exceed 0.1 to 0.3% after five hours at ambient temperature. Increasing the NaOH concentration to 4.0 M increases leaching to 0.7% for Pu and 1.4% for Tc. Agitation of the $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ precipitate in 1 M NaOH with air for five hours sharply increases Tc leaching to 80% but only slightly increases Pu leaching to 0.3%. A 0.1 to 0.3 M H_2O_2 solution quantitatively leaches Tc from the precipitate but retains more than 99% of the Pu in the solid phase. The ready leaching of Tc under oxidizing conditions occurs because Tc(IV) oxidizes to soluble Tc(VII) with simultaneous oxidation of the $\text{U}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ precipitate to sodium uranate salt. The Pu is stable towards oxidation under these conditions and is retained in the solid sodium uranate.

Tetraalkylammonium salts were identified as potential coprecipitation carriers for Tc(VII) because they can be recycled as well as transformed to benign gases in vitrification. Technetium removal from 0.5 to 1.5 M NaOH by coprecipitation with tetraalkylammonium perrhenate achieves DFs of 150 to 200. Reagent requirements are 0.10 to 0.15 g Re and 2.6 to 5.2 g Bu_4NOH per liter solution. The order of reagent addition to the contaminated solution (first Bu_4NOH then NH_4ReO_4) is important. The reverse order gives poor decontamination. Neither NaOH concentration nor the ionic strength affects the decontamination efficiency. Technetium coprecipitation with tetrabutylammonium perchlorate is 50 times less effective than perrhenate because the pertechnetate and perchlorate salts are not isomorphous.

Capture of Np and Pu by coprecipitation with $\text{Co}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, MnO_2 , and $\text{Mn}(\text{OH})_2$ from $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, K_2FeO_4 , $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, $\text{Cr}(\text{CH}_3\text{COO})_3$, and KMnO_4 precursors has been studied by the MAR. Coprecipitation of Np and Pu from pH 10.5 to 0.4 M NaOH is semiquantitative with DFs of 80 to 400.

Decontamination of pH 10.5 to 0.4 M NaOH from Pu by MAR coprecipitation in the presence of reductants such as NH_2OH or NH_3 does not depend on whether the initial oxidation state of Pu is (IV) or (VI). Plutonium(VI) either is reduced to Pu(V) by the reducing agents introduced to the system or formed

by the precursors' hydrolysis. Plutonium(V), in turn, disproportionates to form Pu(VI) and Pu(IV). With subsequent reduction of the formed Pu(VI), eventually all Pu is stabilized in the (IV) oxidation state.

Coprecipitation of Pu from dilute alkaline solution with $\text{Fe}(\text{OH})_3$ in the presence of EDTA is inhibited by the formation of stable Fe(III)-EDTA complexes. The effect of EDTA is diminished by the addition of Ca^{2+} as a masking agent provided that the Ca^{2+} :EDTA ratio is at least 1:1. The DFs from Pu of the Ca^{2+} -treated solutions range from 10 to 150.

Coprecipitation of Pu from dilute alkaline solution with $\text{Co}(\text{OH})_3$ is diminished in the presence of HEDTA because of formation of stable Co(III)-HEDTA complexes. The effect of complex formation is eliminated by the introduction of 0.11 M excess $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ (0.13 M total). In this case, Co(III) acts as its own masking agent, enabling the precipitation of the Co(III) hydroxide carrier sufficient to provide quantitative coprecipitation of Pu.

To attain quantitative capture of Np with Co(III) hydroxide from alkaline solutions, reduction of Np(V) to Np(IV) is required. Vanadyl(IV) is known to be an effective Np(V) reductant. In the presence of EDTA, however, VO^{2+} is found to be ineffective because of its complexation by EDTA. In this case, sodium dithionite or NH_2OH may be better alternative reductants.

7.0 References

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