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Decontamination of Alkaline Solutions from Technetium and Other Fission Products and from Some Actinides by Reductive Coprecipitation and Sorption on Metals

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**Decontamination of Alkaline Solutions from
Technetium and Other Fission Products
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Coprecipitation and Sorption on Metals**

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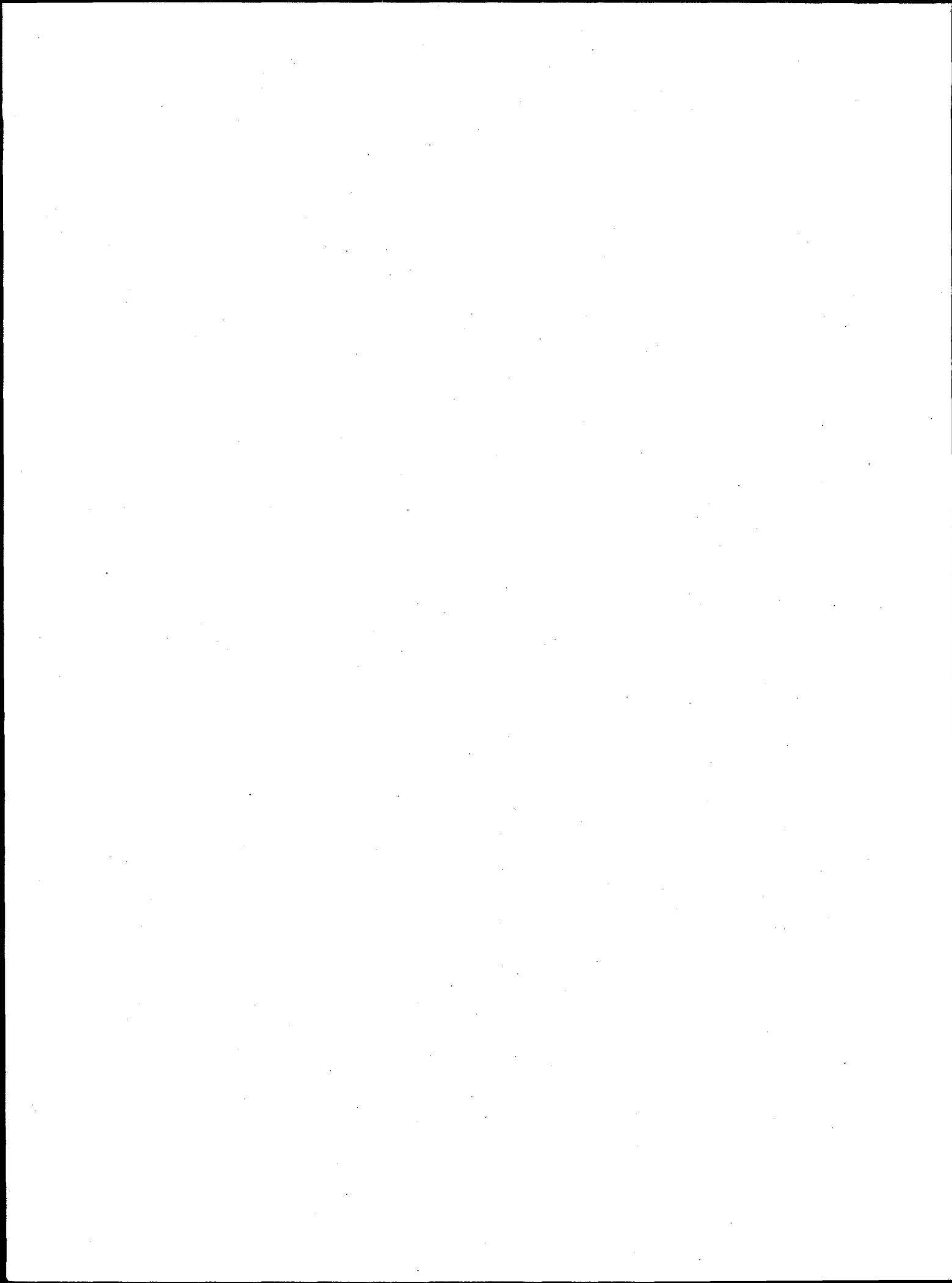
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Summary

Effective decontamination of alkaline solutions and Hanford Site tank waste simulants from technetium has been accomplished by reductive coprecipitation with iron(III) hydroxide. Addition of 1 M $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ to 0.5 to 4.0 M NaOH to a final concentration of 0.1 to 0.15 M coprecipitates more than 99% of the technetium from 0.5 to 1.0 M NaOH and 98 to 96% from 2.0 to 4.0 M NaOH. Similar results were obtained by reduction of Tc(VII) with 0.1 to 0.15 M hydrazine and subsequent addition of FeCl_3 to a final concentration of 0.15 M. Inclusion of four complex-forming agents [0.01 M phosphate, 0.1 M EDTA (ethylenediaminetetraacetate), 0.03 M citrate, and 0.1 M glycolate ($\text{HOCH}_2\text{CO}_2^-$)] to the alkaline solution decreases technetium coprecipitation with iron hydroxide to 85% under otherwise similar conditions. Inclusion of 0.04 M Na_2CrO_4 drastically decreases reductive coprecipitation of Tc(VII) in 0.5 to 4.0 M NaOH. Iron(II) salt, added to a 0.07 M excess over that of chromate, completely reduces chromate and provides greater than 99% coprecipitation of technetium with product iron(III) and chromium(III) hydroxides. Technetium(VII) reduction by hydrazine is slow in the presence of chromate in alkaline solution, and technetium coprecipitation is incomplete in these conditions. Decontamination of an alkaline Hanford Site tank waste simulant, containing 0.04 M chromate and eleven salts and complex-forming agents, by adding 1 M iron(II) salt solution was studied. Coprecipitation of 15 to 28% of the technetium and more than 99% of the plutonium occurred in the Fe/Cr(III) hydroxide precipitate produced by adding 0.05 to 0.10 M iron(II). Chromate reduction was incomplete. About 75% of the technetium was coprecipitated, and the chromate was completely reduced, after adding 0.2 M iron(II) salt.

Technetium(VII) capture from 0.5 to 4.0 M NaOH was insignificant or incomplete on coprecipitation carriers [$\text{Fe}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Mn}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, $\text{Co}(\text{OH})_3$] obtained by the Method of Appearing Reagents under conditions providing complete capture of Np(V) and Pu(VI). Under the same conditions, cesium-137 capture is insignificant and strontium-90 capture is incomplete with these metal hydroxide carriers. Sodium diuranate coprecipitation from 0.5 to 4 M NaOH removed about 15 to 60% of the technetium; sodium uranate coprecipitation removed 98 to 99% of the ^{90}Sr , and 1 to 12% of the ^{137}Cs .

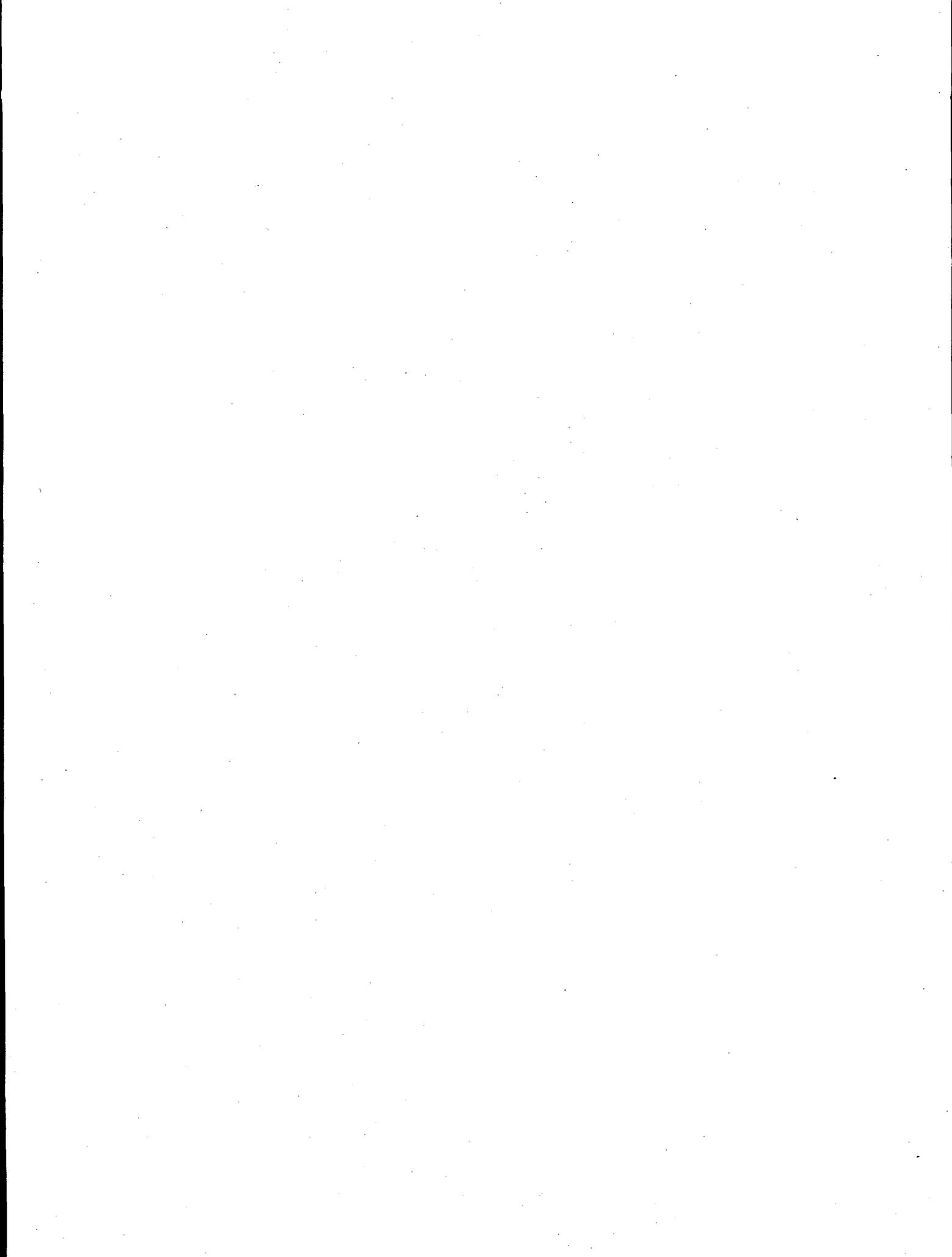
Reductive sorption of Tc(VII) on metals (Zn, Cr, Sn, and two Pb alloys) from 0.5 to 4 M NaOH and from alkaline waste simulant provided poor decontamination of these solutions. In contrast, greater than 98% of the plutonium(VI) was sorbed on chromium from 0.5 M NaOH at a surface area to volume ratio of 1.6 cm^{-1} .



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1.0 Introduction

Radiological and technological incentives exist to remove technetium from alkaline radioactive wastes. Reductive coprecipitation and sorption are two possible methods to achieve this separation.

Technetium-99 (2.13×10^5 year half-life) is a fission product that accumulates in significant amounts in irradiated nuclear fuel. For thermal neutron nuclear reactors, fuel with a typical 33,000 MWt-day/T burnup contains 1 kg technetium per ton of heavy metal. The beta activity of ^{99}Tc constitutes an insignificantly small part of the total activity of fission products at fuel discharge. However, after 300 years of decay, ^{99}Tc represents about half the total fission product beta activity (Choppin et al. 1995). The isolation of technetium from radioactive waste is being considered in treatment programs in a number of countries (France, England, Japan, Russia). As it is for the actinides, isolation of technetium as a separate fraction before waste vitrification may be economically reasonable for long-term storage.

According to estimates based on descriptions of Hanford Site tank waste (Delegard 1995), several tons of ^{99}Tc and, possibly, several hundred kilograms of ^{98}Tc are present from the bismuth phosphate, REDOX, and PUREX reprocessing of irradiated fuel at the Hanford Site. Isolation of technetium into a separate fraction avoids its possible reduction to metal during vitrification and eliminates its long-term hazard in the product glass waste form.

Alternatively, technetium may be transmuted into the stable precious metal ruthenium by irradiation in a strong neutron flux (Kozar and Peretrukhin 1996). Part of the expense for technetium isolation could therefore be recouped by its subsequent transmutation into stable ruthenium and by the sale of this precious metal. Ruthenium, isolated from ore, currently costs \$5 to \$10 per gram, depending on purity (Kozar and Peretrukhin 1996).

The present work is devoted to the study of technetium removal from simple NaOH solutions and from multicomponent solutions simulating Hanford Site alkaline wastes. Two methods were investigated: reductive coprecipitation with iron and other hydroxides and sorption of reduced technetium hydroxide on metals. Applying these techniques to the recovery of technetium from alkaline solutions has not been adequately studied compared with studies of solvent extraction and ion exchange removal of technetium from alkaline media. The latter methods are being investigated by U.S. researchers for their application to alkaline wastes kept in Hanford and Savannah River underground storage tanks (Schroeder et al. 1995; Bonnesen et al. 1996).

Removing technetium by coprecipitation on iron hydroxide was studied in this present work by the usual method of direct addition of iron(II, III) solution to the alkaline technetium-bearing solution. Under these conditions, the precipitate does not form throughout the whole solution volume but only in the volume where the solutions mix.

Tests of removal of ^{99}Tc , ^{137}Cs , and ^{90}Sr on carriers using homogeneous coprecipitation (the Method of Appearing Reagents) also were performed. In this technique, carrier precipitates evolve throughout the entire alkaline solution volume by slow decomposition of an alkali-soluble precursor solute. This technique was investigated for the decontamination of Hanford Site alkaline wastes of neptunium and plutonium in two recent studies (Krot et al. 1996; Bessonov et al. 1997). Sodium uranate and hydroxides of iron(III), manganese(II), chromium(III), and cobalt(II,III) were used as carriers under conditions previously shown to be successful for decontamination of alkaline solution from neptunium and plutonium. Carrier precipitation with sodium diuranate also was tested. Removal of both transuranium elements and technetium from alkaline waste solutions by formation of a single carrier-precipitate would be an attractive decontamination method.

Metals that are electroactive in alkaline solution (e.g., Zn, Cr, Sn) potentially can reduce Tc(VII), Np(V), and Pu(VI) to their respective tetravalent oxidation states and cause the adhesion of the product radioactive element hydroxides on the metal surface. However, the passivation of metals by formation of oxide films (e.g., the formation of $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ on chromium) can prevent the interaction of the active metal with the radioelements. In the case of chromium, transuranium elements and possibly technetium may be reduced and coprecipitated with chromium hydroxide. Few studies of the reductive sorption of Tc(VII), Np(V), and Pu(VI) from alkali appear in the technical literature. Therefore, this solution decontamination approach was also investigated.

Section 2.0 describes the literature review that was used to identify areas of potential research on decontamination of alkaline solution of technetium. Section 3.0 describes reductive coprecipitation of technetium by addition of an acidic iron solution. In Section 4.0, coprecipitation by the Method of Appearing Reagents is discussed. Reductive sorption of technetium is the subject of Section 5.0, and Section 6.0 contains discussion and comparison of results with the literature. Conclusions are in Section 7.0, while cited references can be found in Section 8.0.

2.0 Literature Review and Areas of Research

Information on the chemistry and removal of technetium from alkaline media are briefly reviewed in this section. Based on the review, potential areas of research on the decontamination of alkaline solution of technetium are then described.

2.1 Stability of Technetium Oxidation States in Alkaline Solution

The most stable technetium oxidation state in aqueous alkaline media, as well as in neutral and acidic media, is Tc(VII) which normally appears in the form of pertechnetate, TcO_4^- . Pertechnetates of alkaline metals and ammonium are highly soluble (tens of grams per liter) in water and aqueous alkaline solution. Hexavalent technetium, existing as TcO_4^{2-} , is unstable in alkaline solution and disproportionates in less than one second to form Tc(VII) and Tc(V). Pentavalent technetium is relatively stable in alkaline solution, forming colloidal suspensions and red to greyish-brown precipitates. Tetravalent technetium will precipitate in alkali to yield the hydrated oxide, $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. The hydroxides of Tc(IV) and Tc(V) are oxidized easily in alkali by hydrogen peroxide, atmospheric oxygen, and other oxidants (Lavrukhina and Pozdnyakov 1970; Spitsyn and Kuzina 1981; Peretruxhin et al. 1995; Shilov et al. 1996). One or more unidentified species of technetium have been recently shown to exist, in coexistence with pertechnetate, in alkaline Hanford Site tank waste. Such species may be Tc(IV) complexes with agents present in the wastes (Blanchard et al. 1997). Lower oxidation states of technetium, Tc(II) and even Tc(0), can be present in cathode deposits of TcO_2 obtained by electrolysis of alkaline Tc(VII) solutions (Lavrukhina and Pozdnyakov 1970; Love and Greendale 1960).

2.2 Methods for Technetium Isolation from Alkaline Media

Technical approaches for removing technetium from alkaline solution include ion exchange, solvent extraction, precipitation/coprecipitation, electrodeposition, and reductive deposition on active metals. These respective methods are described in the following sections.

2.2.1 Ion Exchange and Solvent Extraction

The most selective and studied method for Tc(VII) isolation from alkaline, acidic, and neutral solutions is anion exchange sorption. Ion exchange processes for technetium are undergoing vigorous investigation in a number of U.S. laboratories for application to high-level liquid alkaline waste treatment (Schroeder et al. 1995; Blanchard et al. 1997).

Solvent extraction also has been investigated. A number of solvent extraction agents are known to provide good recovery of technetium(VII) from alkaline solutions. Solvents include ketones and amines: acetone (the distribution coefficient, K_d , is 31), methylethylketone (K_d is 20), pyridine (K_d is

239), 2,4-dimethylpyridine (K_d is 1670), and 2-methyl-5-ethylpyridine (K_d is 930) (Spitsyn and Kuzina 1981). More recently, systematic research on crown ether extractants also has been performed (Bonnesen et al. 1996).

2.2.2 Precipitation and Coprecipitation

Methods of technetium precipitation and coprecipitation from alkaline solutions were originally described by those who discovered this artificial radioelement (Perrier and Segre 1937a). Technetium(VII) product was separated from molybdenum and ruthenium in alkaline media by coprecipitation with tetraphenylarsonium perchlorate or perchlorate (Perrier and Segre and 1937b). But these carriers are expensive. Perchlorate salts also can be explosive, especially during decomposition by calcination. Such salts therefore are not recommended for isolation of technetium from large volumes of radioactive waste.

Technetium(VII) can form nearly insoluble compounds in acidic or neutral media. Several such compounds are Tc_2S_7 , $(C_6H_5)_4PTcO_4$, $(C_4H_9)_4NTcO_4$, nitron pertechnetate ($C_{20}H_{17}N_4TcO_4$), and $TiTcO_4$. The solubility or stability of the bulky organic cations are low in alkaline solution; these compounds therefore are unsuitable for isolating technetium from alkaline media (Spitsyn and Kuzina 1981). Pertechnetate does not coprecipitate with iron or lanthanum hydroxide, but technetium can be coprecipitated from alkaline solutions with these metal hydroxide carriers after its reduction to the tetra- or pentavalent oxidation state.

The solubility of $TcO_2 \cdot nH_2O$ hydroxide in pH 7 to 10 solution in the absence of oxidants and complexing agents is 10^{-9} to $10^{-8}M$. The solubility increases significantly with increasing pH (Eriksen et al. 1992). In 1.0 to 3.6 M NaOH containing 0.02 M N_2H_4 and in the presence of air, the solubility of $TcO_2 \cdot nH_2O$ was found to be $(1.0 \text{ to } 1.2) \times 10^{-5}M$; the solubility of $Tc_2O_5 \cdot nH_2O$ under the same conditions is $6.1 \times 10^{-6} M$ (Peretrukhin et al. 1996). In 4 to 10 M NaOH, Tc(IV) reportedly forms $Tc(OH)_6^{2-}$ complexes; anionic complexes of undetermined composition exist for Tc(V) (Lavrukhina and Poadnyakov 1970; Colton et al. 1960).

The reduction of technetium from (VII) to (IV) by chemical reductants (e.g., N_2H_4 , NH_2OH , $Na_2S_2O_4$) proceeds with more difficulty in alkaline media than in acid. The process is slowed as Tc(V) hydroxide evolves, forming polymers and colloids (Peretrukhin et al. 1996). In most methods to concentrate technetium, its reduction to Tc(IV) is performed in acid media by adding an iron(II) or (III) salt solution; technetium is precipitated on iron or lanthanum hydroxide carriers by adding ammonia or alkali.

2.2.3 Electrodeposition

Electrodeposition of technetium from acid and alkaline aqueous solutions, as well as from nonaqueous solvents, is described by numerous researchers, beginning with the element's discoverers (Perrier and Segre 1937b; Lavrukhina and Pozdnyakov 1970; Peretrukhin et al. 1996). In acid and in the absence of oxidants, nitrate, and nitrite, the reduction of technetium to $TcO_2 \cdot nH_2O$ and further to

metal is possible (Spitsyn and Kuzina 1981; Eriksen et al. 1992). The reduction of Tc(VII) to Tc(IV) and the subsequent electrodeposition of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ occurs in alkaline solutions in the presence of nitrate and nitrite (Love and Greendale 1960). The researchers assert that technetium(VII) is reduced to metal from a 0.1 M NaOH and 1.0 M sodium citrate solution on a dropping mercury electrode at -1.55 V (measured versus the saturated calomel electrode).

The possibility of effective decontamination of nitrate-containing alkaline radwastes from technetium by cathodic precipitation of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ is described in reviews by Hobbs (1994) and Fletcher et al. (1991). The solubility of the electrodeposited $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ in anoxic 4.0 M NaOH is (5 to 7) $\times 10^{-7}$ M, about 50 times lower than the solubility obtained by chemical reduction of Tc(VII) or by hydrolysis of K_2TcCl_6 (Peretrukhin et al. 1996).

2.2.4 Reductive Technetium Sorption on Metals

Few references to the reduction of Tc(VII) to $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ and its sorption on an active metal are given in the technical literature. Decontamination of water solutions from technetium by its reductive sorption on metallic zinc and aluminum is described (Fletcher et al. 1991). Decontamination factors (DF) from technetium range from 3.3 to 18.6 for pH 1 to 2 solution using granulated or powdered zinc. With powdered aluminum and pH 13 to 14 solution, DFs ranged from 2.1 to 7.8. Researchers at the Tomsk radiochemical plant studied the recovery of technetium from weakly acidic first-cycle PUREX process raffinates using granulated zinc or iron (Volk et al. 1979). Recovery of more than 90% of the technetium on zinc and about 61% on iron were achieved while attaining a decontamination factor from fission products of about 30.

2.3 Areas of Research

No studies were found in the scientific literature on the reductive coprecipitation of Tc(VII) in NaOH solutions by the direct action of iron(II) salt or by a combination of another reductant and iron(III) salt. Because of this gap in chemical knowledge of a potentially promising technetium removal approach, studies were performed on reductive coprecipitation on iron hydroxide.

Neptunium(V) and plutonium(VI) have been shown to be coprecipitated from 0.5 to 4.0 M NaOH by manganese(II), cobalt(II), and chromium(III) hydroxides, and by sodium uranate. These carriers are generated homogeneously in alkaline solution by decomposition of soluble precursors by the Method of Appearing Reagents (MAR) (Krot et al. 1996). However, the behaviors of pertechnetate, cesium, and strontium during coprecipitation by the MAR are not described in the literature. Under sufficiently reducing conditions, Tc(VII) would be expected to convert to the (V) or (IV) oxidation state and be captured by MAR carriers. Coprecipitation of ^{137}Cs by metal hydroxides would not be expected to effect a separation of technetium from cesium. At least partial capture of strontium should occur on MAR carriers. Based on these considerations, coprecipitation of technetium, cesium, and strontium by the MAR was investigated. Sorption of technetium by reduction to Tc(IV) or (V) compounds on active metals in alkaline solution was also investigated.

3.0 Reductive Coprecipitation of Tc(VII) By Addition of Fe(II,III) Solution

Coprecipitation of technetium(IV) and other radionuclides that form low-solubility hydroxides often is achieved by mixing the acidic radionuclide solution with an acidic iron(II) or (III) salt solution. The blended solutions then are treated with alkali or ammonia to produce an iron hydroxide precipitate. Because the radionuclide and iron are intimately mixed and distributed homogeneously throughout the blended acid solutions, efficient capture of radionuclides by the precipitating iron hydroxide is accomplished. Decontamination factors observed for complexant-free technetium(IV) or actinide(III),(IV) solution by iron hydroxide coprecipitation from neutralized acid solutions usually range from 10^2 to 10^3 . Thus, more than 99% of the radionuclide reports to the solid phase.

However, when the solution to be decontaminated from radionuclides is alkaline and the iron salt solution is acidic, the iron and radionuclide are not intimately mixed in solution and encounter each other only when the iron hydroxide precipitate is forming. Less complete capture of technetium(IV) by iron hydroxide is attained by this method than can be achieved by alkaline neutralization of the acidic radionuclide/iron blend.

Studies of the completeness of reductive coprecipitation of Tc(VII) by addition of iron salt solution have been performed as functions of alkali and iron concentration, iron oxidation state [(II) or (III)], presence of hydrazine reductant, aeration, and deaeration by argon purging.

3.1 Experimental Procedure

Experiments were performed by the following procedure. First, an initial 5-mL solution of $(3 \text{ to } 5) \times 10^{-5} \text{ M}$ Tc(VII) and 0.5 to 4.0 M NaOH was placed in a centrifuge tube. For some experiments, reduction of Tc(VII) was achieved by adding hydrazine nitrate solution to a final concentration of 0.05 to 0.17 M and heating the solution 30 to 40 minutes at 70°C . The solutions were deaerated by purging them with argon for 10 to 15 minutes.

Coprecipitation was performed in the centrifuge tube containing the deaerated alkaline technetium solution by slow (dropwise) addition of freshly prepared and deaerated 1 M FeCl_3 or Mohr's salt $[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$. Solutions were stirred during coprecipitation using a mechanical stirrer rotating at 120 revolutions per minute (rpm). In a number of experiments, argon purging also was used to agitate the mixing solutions. After the iron salt addition was complete, the tube was closed tightly with a polyethylene stopper. The mixture was digested 30 to 60 minutes at 25 or 70°C to coagulate the precipitate. The solids then were separated by 10 minutes of centrifugation at 8000 rpm.

To determine the completeness of technetium partition to the precipitate, solution samples were taken from the solution before (0.1 mL) and after (0.2 mL) coprecipitation. The samples were acidified by addition of 0.1 to 0.2 mL of 4 M HNO_3 . Then, 7 mL of Beckman Ready Gel™ (Beckman

Instruments Inc., Fullerton CA) scintillation cocktail was added, and the β activity was measured on a Beckman LS-6500 liquid scintillation analyzer. The percentage of technetium reporting to the precipitate was calculated according to the following formula:

$$\text{Tc in Solids, \%} = 100\% \times [I_0 V_0 - I_f (V_0 + V_{Fe})] / I_0 V_0 \quad (3.1)$$

where I_0 and I_f are the specific radioactivities of the solution before and after the coprecipitation (in Bq/mL), V_0 is the volume of the alkaline technetium solution before coprecipitation (in mL), and V_{Fe} is the volume of the iron salt solution added to the technetium solution (in mL).

The DF from technetium was calculated as the ratio:

$$\text{DF} = I_0 V_0 / I_f (V_0 + V_{Fe}) \quad (3.2)$$

3.2 Reductive Coprecipitation of Tc(VII) by Hydrazine and FeCl₃

Initial studies examined the capture of technetium(VII) by iron(III) hydroxide obtained by the addition of iron trichloride to 3×10^{-5} M Tc(VII) in 0.5 to 4.0 M NaOH. It was found that Tc(VII) capture by Fe(III) hydroxide did not exceed 3% in the range 0.025 M to 0.15 M Fe(III). The captured Tc(VII) washed easily from the precipitate with 0.5 to 4.0 M NaOH. These results agree with reports that pertechnetate does not coprecipitate with Fe(III) hydroxide in the absence of reductants and is only partially captured by reversible sorption on the precipitate surface (Lavrukhina and Pozdnyakov 1970).

In the next set of experiments, the reductive coprecipitation of technetium by iron hydroxide was studied. The pertechnetate was reduced to Tc(IV) by hydrazine or vanadyl salt solution. The reduction of Tc(VII) to Tc(IV) was performed in 0.5 to 4.0 M NaOH by adding hydrazine nitrate to 0.17 M and heating the solution to 70°C for 40 minutes. One test with 0.014 M final concentration of vanadyl sulfate reductant was also performed. According to reported findings (Lavrukhina and Pozdnyakov 1970; Shilov et al. 1996; Shilov et al. 1997), these treatments completely transform Tc(VII) to the tetravalent state. Data on the completeness of technetium(IV) coprecipitation by iron(III) hydroxide are presented in Table 3.1.

The data show that technetium coprecipitation decreases with increasing NaOH concentration. More than 99% of the technetium coprecipitates (and the DF is greater than 100) from 0.5 or 1.0 M NaOH containing 0.1 M or more Fe(III). Increase in NaOH concentration lowers technetium capture to 98% in 2 M NaOH and to 96% in 4 M NaOH at 0.15 M Fe(III). Some of this decline may be explained by increasing formation of anionic complexes such as $[\text{Tc}(\text{OH})_6]^{2-}$ as NaOH concentration is raised (Colton et al. 1960).

The concentration of iron required to capture more than 99% of the technetium in 0.5 to 1.0 M NaOH was 0.10 to 0.15 M. This concentration is about a factor of 10 higher than that required to attain similar decontamination by alkaline coprecipitation of acidic blended Tc(IV) and Fe(III) solutions. The higher amount of carrier required for alkaline wastes obviously reflects the differences in the technetium

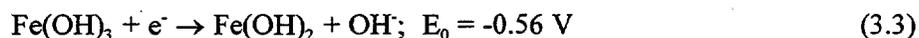
Table 3.1. Reductive Coprecipitation of Tc(VII) with Fe(III) Hydroxide from FeCl₃

[NaOH], M	[N ₂ H ₄], M	[FeCl ₃], M	T, °C	DF	Tc Capture, %
0.5	0.17	0.01	25	10.5	90.5
0.5	0.17	0.025	25	33.3	97.0
0.5	0.17	0.075	25	66.7	98.5
0.5	0.17	0.10	25	125	99.2
0.5	0.17	0.15	25	167	99.5
1.0	0.17	0.01	25	9.7	89.7
1.0	0.17	0.075	25	59	98.3
1.0	0.17	0.10	25	111	99.1
1.0	0.17	0.15	25	138	99.4
2.0	0.17	0.075	70	21.3	95.3
2.0	0.17	0.15	25	56.0	98.2
4.0	0.17	0.075	25	6.4	83.0
4.0	0.17	0.15	25	25	96.0
1.0	0.014 VOSO ₄	0.075	25	70	98.7

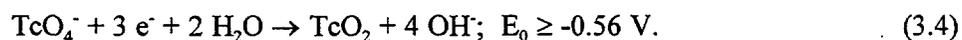
environment during precipitate formation. For acidic wastes blended with iron(III), technetium is intimately surrounded by precipitating iron(III) hydroxide during neutralization. For alkaline wastes, technetium arrives at the iron(III) hydroxide precipitate as it is being formed.

3.3 Reductive Coprecipitation of Tc(VII) by Iron(II) Salt

Divalent iron in alkaline solution is thermodynamically capable of reducing Tc(VII) to Tc(IV) or lower oxidation states. This conclusion follows from comparison of standard redox potentials in 1 M NaOH (Bard 1973) for the reaction



and for the reaction



The limiting value of the technetium potential (≥ -0.56 V) follows from experimental determination of Tc(VII) polarographic reduction halfwave potentials in 0.1 to 2 M NaOH obtained by various researchers and the still unknown overvoltage of this electrochemical reaction (Bard 1973).

It is known that green iron(II) hydroxide precipitate is rapidly oxidized in alkaline media by atmospheric oxygen to greyish-brown iron(III) hydroxide. The oxidation of iron(II) is thermodynamically capable of reducing pertechnetate and capturing the reduced technetium by coprecipitation. The coprecipitation of technetium with iron hydroxide was tested by adding freshly prepared 0.5 to 1.0 M Mohr's salt, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, to a solution of $(3 \text{ to } 5) \times 10^{-5}$ M Tc(VII) and 0.5 to 4 M NaOH under both oxic and anoxic conditions attained by argon bubbling. Tests also were conducted in the presence and absence of 0.17 M hydrazine reductant.

The results, presented in Table 3.2, show that coprecipitation of technetium from alkaline solution by Mohr's salt is more effective than by the joint action of hydrazine and iron trichloride. With oxic conditions, coprecipitation of more than 99% of the technetium was achieved in 0.5 to 1.0 M NaOH with 0.075 to 0.15 M Fe(II) both at room temperature and at 70°C. In 3 to 4 M NaOH, technetium coprecipitation under analogous conditions only reached 95 to 96%. Coprecipitation under anoxic conditions (argon purging) increased the capture of technetium by 1 to 2% at 0.025 M iron(II) but had insignificant effect at 0.075 to 0.15 M iron(II).

A significant difference in the behavior of coprecipitated technetium is observed under oxic and anoxic conditions during storage of the Fe(II,III) hydroxide precipitate in 1 to 4 M NaOH solution. In the absence of air, technetium remained in the precipitate for one week. With atmospheric oxygen present, technetium passed from the iron hydroxide precipitate into the supernatant solution at a rate of about 5% per day. No excess or holding reductant, such as hydrazine, was present in these tests.

3.4 Effect of Complexing Agents and Chromate on Reductive Coprecipitation of Tc(VII) by Iron(II) Salt

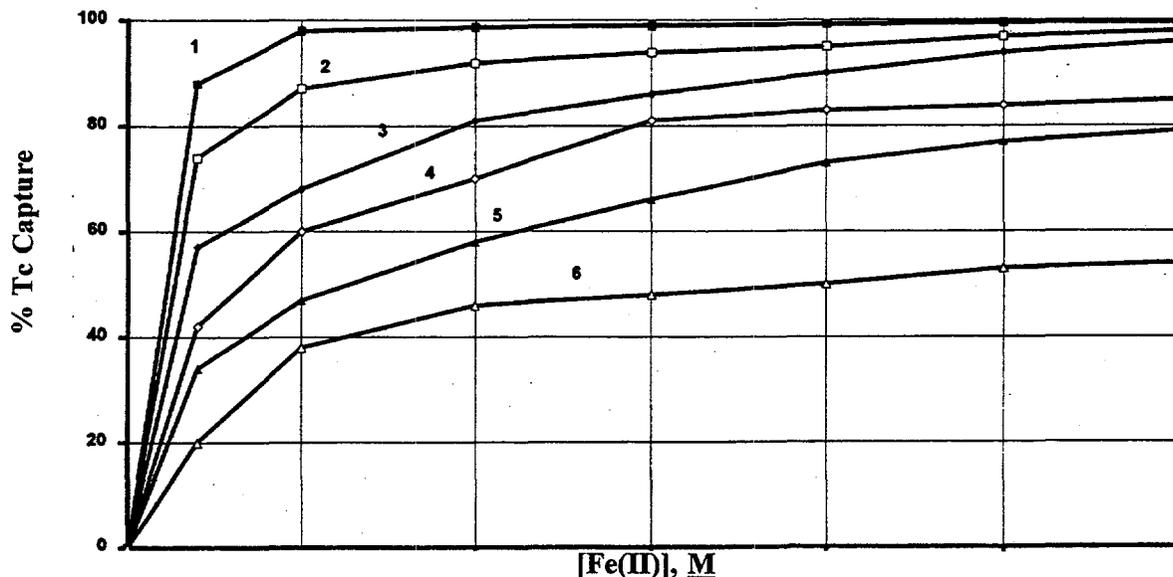
The effect of complexing agents commonly found in Hanford Site tank waste solution on technetium removal has been studied. Solutions containing 0.01 M phosphate, 0.1 M EDTA, 0.03 M citrate, and 0.1 M glycolate were prepared having NaOH concentrations ranging from 0.5 to 4 M. To these solutions, containing the indicated amounts of waste components, hydrazinium nitrate was added to attain a final 0.17 M concentration. The solutions were heated to 70°C for 30 to 40 minutes. Tests without hydrazine addition were run for comparison. A solution of Mohr's salt then was added, with stirring, to reach 0 to 0.15 M iron(II) concentration in the product slurry. The precipitates were settled and the supernatant solutions analyzed to determine decontamination from technetium. Results for the tests with the phosphate and organic complexants are given in Figure 3.1.

The data of Figure 3.1 show that the presence of phosphate and the three organic complexing agents decreased technetium capture by iron hydroxide precipitate about 15%, i.e., from 99.5 to 85% in 1 M NaOH and from 96.5% to 80% in 4 M NaOH. A subsequent addition of Mohr's salt solution to the supernatants again only captured 80 to 85% of the remaining technetium. Thus the detrimental

Table 3.2. Reductive Coprecipitation of Tc(VII) with Fe(III) Hydroxide from Fe(II) in NaOH Solution in the Presence and Absence of Hydrazine

[NaOH], M	[Fe(II)], M	[N ₂ H ₄], M	Ar Bubbling	T, °C	DF	Tc Capture, %
0.5	0.025	--	No	70	17	94.1
0.5	0.025	--	Yes	70	25	96.0
0.5	0.025	0.17	No	70	26	96.2
0.5	0.025	0.17	Yes	70	31	96.5
0.5	0.05	0.17	No	70	52	98.1
0.5	0.075	0.17	No	70	111	99.1
0.5	0.15	0.17	No	70	250	99.6
0.5	0.15	0.17	No	25	200	99.5
1.0	0.025	--	No	25	18	94.5
1.0	0.025	--	Yes	25	24	95.8
1.0	0.025	0.17	No	25	23	95.6
1.0	0.05	0.17	No	25	45	97.8
1.0	0.075	0.17	No	25	91	98.9
1.0	0.1	0.17	No	25	166	99.4
1.0	0.15	0.17	No	25	250	99.6
1.0	0.15	0.17	Yes	25	330	99.7
2.0	0.025	0.17	No	25	7.4	87.1
2.0	0.05	0.17	No	25	12.5	92.2
2.0	0.075	0.17	No	25	17.5	94.3
2.0	0.15	0.17	No	25	91	98.9
2.0	0.15	0.17	Yes	25	100	99.0
4.0	0.025	0.17	Yes	25	2.7	63
4.0	0.075	0.17	Yes	25	7.1	86
4.0	0.15	0.17	Yes	25	19.2	95.8
4.0	0.15	0.17	No	25	18	95.7
4.0	0.15	0.17	No	70	25	96.0

$4.5 \times 10^{-5} \text{ M Tc(VII)}$; 70°C ; 30 minutes' reaction



- | | |
|----------------------------|---|
| 1 - 0.5 to 1 <u>M</u> NaOH | 4 - 1 <u>M</u> NaOH, 0.01 <u>M</u> PO ₄ ³⁻ , 0.1 <u>M</u> EDTA, 0.1 <u>M</u> glycolate, 0.03 <u>M</u> citrate |
| 2 - 2 <u>M</u> NaOH | 5 - 4 <u>M</u> NaOH, 0.01 <u>M</u> PO ₄ ³⁻ , 0.1 <u>M</u> EDTA, 0.1 <u>M</u> glycolate, 0.03 <u>M</u> citrate |
| 3 - 4 <u>M</u> NaOH | 6 - Simulant 3 (3.2 <u>M</u> NaOH, 0.04 <u>M</u> CrO ₄ ²⁻ , eleven other waste components) |

Figure 3.1. Reductive Coprecipitation of Technetium with Fe(OH)₃ from Fe(II)

effects of the added components do not disappear with repeated iron hydroxide coprecipitation. Technetium capture from 0.5 to 4.0 M NaOH solutions in the presence of four agents remains at 80 to 85%.

In separate experiments, the effect of 0.04 M chromate (CrO₄²⁻) on technetium capture by iron hydroxide was studied in 0.5 to 4 M NaOH. To ascertain the effect of chromate on the coprecipitation of technetium, initial tests with 1 and 4 M NaOH solution containing $3 \times 10^{-5} \text{ M Tc(VII)}$ and 0.04 M Cr(VI) were prepared. Hydrazinium nitrate was added to attain 0.17 M final concentration. The solutions were kept 1 hour at 70°C , and the chromium(III) hydroxide precipitate was separated by centrifugation. Technical literature (Krot et al. 1996) and our spectrophotometric measurements of chromate at its peak located at 371 nm show that chromate reduction by hydrazine proceeds slowly under these conditions, requiring many hours to reach completion.

Measurement of technetium capture by Cr(III) hydroxide precipitate formed from chromate reduction was performed according to the procedure described in Section 3.1. Technetium capture by Cr(III) hydroxide was incomplete, reaching only 17 and 8%, respectively, from 1 and 4 M NaOH (Table 3.3). The incomplete capture of technetium by chromium hydroxide under these conditions is the consequence of kinetically slow reduction of chromate to Cr(III) and the subsequent slow formation of the Cr(III) hydroxide solid phase. These kinetic observations coincide with prior research (Krot et al. 1996).

Table 3.3. Reductive Coprecipitation of Tc(VII) with Fe(III) and Cr(III) Hydroxide from Fe(II) in Alkaline 0.04 M Chromate Solution in the Presence and Absence of Hydrazine

[NaOH], M	[N ₂ H ₄], M	[(NH ₄) ₂ Fe(SO ₄) ₂], M	Tc Capture, %
1.0	0.17 (1 hour)	--	17
4.0	0.17 (1 hour)	--	8
0.5	--	0.075	42
0.5	--	0.1	64
0.5	--	0.15	99.6
1.0	--	0.075	99.2
1.0	--	0.15	99.7
3.0	--	0.075	94.4
3.0	--	0.15	96.6
1.0	0.17	0.05	96.4
1.0	0.17	0.075	99.5
1.0	0.17	0.15	99.6
4.0	0.17	0.05	94.1
4.0	0.17	0.075	96.6
4.0	0.17	0.15	96.8

More rapid and complete capture of technetium by hydroxide precipitates is achieved from alkaline chromate solutions by the combined action of hydrazine and iron(II) salt. A freshly prepared 1 M (NH₄)₂Fe(SO₄)₂ solution was slowly added with stirring to alkaline solutions of chromate and Tc(VII). The precipitate was separated by centrifugation and the amount of technetium capture by the precipitate determined from the radioactivities of the initial solution and the supernatant liquid. To study the combined action of hydrazine and Fe(II), hydrazinium nitrate was added to the alkaline solution of chromate and Tc(VII) to 0.17 M final concentration and the solution was kept for one hour at 70°C. To the product Cr(III) hydroxide precipitate slurry was added sufficient Fe(II) solution to make the final slurry 0.05 to 0.15 M in iron. The test tube was kept at room temperature for 30 minutes. Then the precipitate was separated by centrifugation, and the amount of technetium capture by the precipitate was determined.

As shown in Table 3.3, technetium capture by the mixed Fe(OH)₃/Cr(OH)₃ precipitate from 0.5 to 1.0 M NaOH was 99.5 to 99.7% for 0.15 M iron and 0.04 M chromium. Increasing the alkali concentration to 3 and 4 M NaOH, but at otherwise similar conditions, decreased technetium capture to 96 to 97%. Spectrophotometric measurements at 371 nm showed no chromate remaining in the 0.5 to 4.0 M NaOH supernatants

after the introduction of 0.17 M Mohr's salt. The data show that addition of divalent iron to 0.05 M excess with respect to chromate and pertechnetate gives fast and complete reduction to Cr(III) and Tc(IV). These components coprecipitate with Fe(III) hydroxide. The data also show that with the addition of hydrazine, similar decontamination results can be obtained with 0.05 to 0.075 M Fe(II).

3.5 Reductive Coprecipitation of Tc(VII) by Iron(II) Salt from Hanford Site Tank Waste Simulants

The reductive sorption of technetium was studied from waste simulant solutions containing NaOH, 3×10^{-5} M Tc(VII), 0.04 M Na₂CrO₄, and other inorganic and organic salt waste components. The simulant compositions given in Table 3.4 emulate the composition of Hanford Site tank waste solutions and were used in various tests described in this study.

Three approaches to coprecipitation were tested:

- hydrazine reduction of Tc(VII) and Cr(VI) followed by FeCl₃ addition to form Fe(OH)₃ and capture Tc(IV)
- addition of Mohr's salt to simultaneously reduce and coprecipitate Tc(IV) with Fe(OH)₃
- hydrazine reduction (for 1 hour at 70°C) followed by Mohr's salt addition.

Table 3.4. Composition of Hanford Site Tank Waste Simulant Solutions

Component	Concentration, M		
	Simulant 1	Simulant 2	Simulant 3
NaOH	2.0	3.5	3.2
NO ₃ ⁻	0.5	0.3	1.8
NO ₂ ⁻	0.2	0.2	0.75
CO ₃ ²⁻	0.05	0.025	0.05
PO ₄ ³⁻	--	0.005	0.01
F ⁻	--	0.005	0.01
Cl ⁻	--	0.02	0.05
SO ₄ ²⁻	--	0.005	0.01
CrO ₄ ²⁻	0.05	0.01	0.04
Al(OH) ₄ ⁻	--	0.2	0.2
Na ₂ EDTA	--	0.025	0.1
Na glycolate	--	0.025	0.1
Na ₃ citrate	--	0.015	0.03
N ₂ H ₄	--	0.04	--

The results, presented in Table 3.5, show that under all these conditions, a single coprecipitation of technetium from simulant 3 by the mixed $\text{Fe}(\text{OH})_3/\text{Cr}(\text{OH})_3$ precipitate was incomplete, removing only 15 to 76% of the technetium. The coprecipitation of plutonium from the same solution was also studied. Plutonium removal was much higher, achieving 98% or greater decontamination. The highest percentage of technetium capture (76%) was achieved by adding 1 M $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_2$ to the simulant to a final total iron(II) concentration of 0.2 M.

Measurement of chromate reduction by the action of Mohr's salt was performed by spectrophotometry at the 371 nm absorption maximum for chromate in a 0.1 mm-pathlength cuvette. With 0.15 M total added Fe(II), 68% of the initial 0.04 M chromate was reduced in aerated conditions. A further 0.1 M addition of iron(II) salt to the supernatant, followed by precipitation of Fe(III) hydroxide, resulted in about 75% capture of technetium by the precipitate and complete reduction of chromate. Increasing temperature to 80°C (from 20°C) and deaeration of the solution produced an insignificant change in technetium capture and chromate reduction by 0.15 M iron.

As shown by comparing results of the last two experiments in Table 3.5, using hydrazine followed by 0.15 M iron(II) salt achieves results comparable to use of 0.2 M Fe(II) alone. The prerduction by hydrazine decreases iron requirements (and precipitate amount) by 0.05 M.

Results from these tests indicate that effective decontamination of the simulated wastes from technetium is inhibited both by chromate and by other agents. Chromate, at 0.04 M, in a simulant waste solution is reduced to Cr(III) hydroxide by hydrazine slowly and incompletely under the test conditions (0.17 M N_2H_4 , 70°C). Iron(II) salt, present in 0.05 to 0.07 M excess, is more rapid and reduces chromate in about 30 minutes at 20 to 70°C. After the complete reduction of chromate, technetium capture by Fe(II,III) hydroxide from the waste simulant was 74 to 76%. This quantity is significantly lower than observed for

Table 3.5. Reductive Coprecipitation of 3×10^{-5} M Tc(VII) and 2×10^{-6} M Pu(VI) by Fe(II,III) and Cr(III) Hydroxides from Alkaline Waste Simulant 3 (3.2 M NaOH, 0.04 M Na_2CrO_4 , 11 other organic and inorganic components)

Reductant		Observations		
$[\text{N}_2\text{H}_4]$, <u>M</u>	$[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2]$, <u>M</u>	Cr(VI) Reduced, %	Tc Captured, %	Pu Captured, %
0.17 (1 hr, 70°C)	--	12	7	84
--	0.075 (0.5 hr, 25°C)	25	15	98-99
0.17 (1 hr, 25°C)	0.1	38	28	99
0.17 (1 hr, 70°C)	0.1	41	31	99
--	0.15 (0.5 hr, 25°C)	68	54	99
--	0.2 (0.5 hr, 25°C)	100	76	>99
0.17 (1 hr, 70°C)	0.15	100	74	>99

NaOH solutions in the absence of complexing agents (99 to 96% in 0.5 to 4 M NaOH, respectively). The inhibiting action of chromate disappears by chemical reduction; however, the inhibiting action of complexing agents remains after treating the simulant with hydrazine and iron(II) salt. Decontamination of the simulant from technetium by factors higher than 100 is possible without complexant destruction by performing three or four successive iron(II,III) hydroxide precipitations. Each precipitation removes about 75 to 80% of the technetium from the simulant solution. Further investigation of iron coprecipitation is necessary to decrease the iron(II) salt requirement.

4.0 Coprecipitation of ^{99}Tc , ^{137}Cs , and ^{90}Sr by the Method of Appearing Reagents

Effective decontamination of alkaline solutions from neptunium and plutonium by homogeneous coprecipitation with carriers formed from soluble precursors by reduction, hydrolysis, or decomposition has been described in recent research (Krot et al. 1997; Bessonov et al. 1997). This technique is called the Method of Appearing Reagents, or MAR. Because the behaviors of Tc, Cs, and Sr under conditions described for MAR have not been investigated, experiments were performed in this area. Test results are reported and discussed in this section. Tests of nonhomogeneous coprecipitation also were conducted using uranyl nitrate to form sodium diuranate carrier.

4.1 Experimental Procedure

In a typical experiment, 5 mL of 0.5 to 4.0 M NaOH containing $(0.3 \text{ to } 7) \times 10^{-4}$ M TcO_4^- was added to a thermostatted centrifuge tube, and a 0.1 mL sample was withdrawn for analysis. Then a calculated amount of soluble precursor reagent was added to this solution. The mixture was held at the proper temperature for the time known through previous studies to be necessary to form and coagulate the precipitate (Krot et al. 1996).

The solution with precipitate then was cooled to room temperature and centrifuged at 8000 rpm for 10 minutes to separate the precipitate from the supernatant liquid. A 0.2-mL aliquot of the supernatant was taken for technetium concentration analysis. Centrifugation continued for 10 minutes more. A sample again was withdrawn for analysis to confirm the completeness of precipitation. The solution samples were acidified by nitric acid (0.1 to 0.2 mL of 1 to 4 M HNO_3) and 5 to 7 mL of Ready Gel (Beckman) scintillation cocktail were added. The ^{99}Tc β activity was measured radiometrically using a Beckman LS-6500 liquid scintillation counter.

Similar tests were performed for solutions spiked with ^{137}Cs or with ^{90}Sr . The concentrations of ^{137}Cs in solution before and after coprecipitation with metal hydroxide were measured on a high-resolution gamma spectrometer of Russian production (AMA-OZF) with a Ge-Li detector using the 662-keV line. The β activity of ^{90}Sr was determined as the difference between the combined activity of $^{90}\text{Sr} + ^{90}\text{Y}$ (daughter) and the β activity of the more energetic ^{90}Y . The ^{90}Y was measured by interposing a 0.6-mm Al foil between the sample and detector. The foil absorbed all the β radiation of ^{90}Sr and about 50% of the ^{90}Y β radiation. A 7-mm anthracene-plastic detector was used for β measurement of ^{90}Sr and ^{90}Y .

4.2 Coprecipitation of Technetium by the Method of Appearing Reagents

Experimental verifications of technetium coprecipitation from 0.5 to 4.0 M NaOH by hydroxides of Co(III) and (II), Fe(III), Cr(III), and Mn(II) were performed. These carriers were prepared by hydrolysis or reductive decomposition of soluble precursors under conditions previously found to

provide optimum solution decontamination from plutonium and neptunium (Krot et al. 1996). Tests also were performed using sodium diuranate prepared by alkaline hydrolysis of uranyl nitrate added to the alkaline test solutions.

4.2.1 Cobalt(II,III) Hydroxide

The coprecipitation of technetium with cobalt hydroxide, formed by the hydrolysis of hexaammine, $[\text{Co}(\text{NH}_3)_6]^{3+}$, or pentaammine, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, complexes in 1.0 to 4.0 M NaOH, was conducted in the presence and absence of hydrazine reductant. The precipitate that formed generally was Co(III) hydroxide. However, with hydrazine present, pentaammine cobalt is reduced prior to hydrolysis and forms the hydroxide $\text{Co}(\text{OH})_2$ (Krot et al. 1996).

As shown in Tables 4.1 and 4.2, technetium(VII) coprecipitates poorly with Co(III) and (II) hydroxides. Under analogous conditions, plutonium (DF up to 1000) and neptunium (DF up to 100) are removed very well (Krot et al. 1996). At best, only slight decontamination of alkaline solution from technetium (DF of 1.3) is observed in 4.0 M NaOH containing 0.1 M hydrazine.

Table 4.1. Coprecipitation of Tc(VII) from NaOH Solution by Co(III) Hydroxide Produced by Hydrolysis of $[\text{Co}(\text{NH}_3)_6]^{3+}$

[NaOH], M	$[[\text{Co}(\text{NH}_3)_6]^{3+}]$, M	[Tc(VII)], M	$[\text{N}_2\text{H}_4]$, M	T, °C	t, Hours	DF
1.0	0.025	6.4×10^{-4}	0.1	60	2	1.08
4.0	0.025	5.0×10^{-4}	0.1	70	2	1.33
4.0	0.025	5.0×10^{-4}	--	70	2	1.04

Table 4.2. Coprecipitation of Tc(VII) from NaOH Solution by Co(II) Hydroxide with Hydrazine and Co(III) Hydroxide Without Hydrazine Produced by Hydrolysis of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

[NaOH], M	$[[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}]$, M	[Tc(VII)], M	$[\text{N}_2\text{H}_4]$, M	T, °C	t, Hours	DF
4.0	0.024	5.0×10^{-4}	--	70	2	1.08
4.0	0.024	5.0×10^{-4}	0.1	70	2	1.12
0.5	0.024	3.6×10^{-4}	--	70	2	1.04
0.5	0.024	6.4×10^{-4}	0.1	60	2	1.05

4.2.2 Iron(III) Hydroxide

The coprecipitation of technetium with iron(III) hydroxide formed in alkaline solution by hydrolytic decomposition of 0.03 M nitroprusside ($[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$) was conducted in 0.5 to 4 M NaOH both in the presence and absence of hydrazine. Data presented in Table 4.3 show results of these experiments. The highest solution DF achieved, 7.2, occurred from 4 M NaOH containing 0.1 M hydrazine and digested at 80°C for three hours. Solution DFs increased with increasing NaOH concentration.

Table 4.3. Coprecipitation of Tc(VII) from NaOH Solution by Fe(III) Hydroxide Produced by Hydrolysis of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ With and Without Hydrazine

[NaOH], M	$[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, M	[Tc(VII)], M	$[\text{N}_2\text{H}_4]$, M	T, °C	t, Hours	DF
0.5	0.03	7.5×10^{-4}	0.1	80	3	1.4
1.0	0.03	7.5×10^{-4}	0.1	80	3	3.0
4.0	0.03	1.4×10^{-3}	0.1	60	2	5.6
4.0	0.01	1.4×10^{-3}	0.1	60	2	2.0
0.5	0.03	6.8×10^{-4}	--	80	3	1.3
1.0	0.03	6.8×10^{-4}	--	80	3	3.2
4.0	0.03	6.5×10^{-4}	0.1	80	3	7.2

4.2.3 Chromium(III) Hydroxide

The coprecipitation of technetium with chromium(III) hydroxide produced by alkaline hydrolysis of chromium acetate, $\text{Cr}(\text{CH}_3\text{COO})_3$, was performed in 1.0 M NaOH with 0.005 M and 0.01 M carrier. The mixture was kept at 80°C for 5 hours. A DF of 1.1 was attained for 0.01 M chromium acetate and no decontamination (DF of 1) for 0.005 M carrier. In contrast to plutonium and neptunium, technetium coprecipitates poorly with chromium hydroxide produced without added reductant from $\text{Cr}(\text{CH}_3\text{COO})_3$ hydrolysis.

4.2.4 Manganese(II) Hydroxide

Coprecipitation of technetium with manganese(II) hydroxide, produced in alkaline solution by reduction of MnO_4^- with excess hydroxylamine, was tested in 1 M and 4 M NaOH solutions. As the data in Table 4.4 show, technetium is partially coprecipitated by Mn(II) hydroxide from 1 and 4 M NaOH. Tests also were performed with tank waste simulants. Simulant 1 (whose composition is described in Table 3.4) contains no organic components; Simulant 3 contains organic and inorganic components. As indicated in Table 4.4, the presence of these components decreased the modest DFs further.

Table 4.4. Coprecipitation of Tc(VII) from NaOH and Simulated Waste Solution by Mn(II) Hydroxide Produced by Reduction of Permanganate by Hydroxylamine

[NaOH], M	[MnO ₄ ⁻], M	[Tc(VII)], M	T, °C	t, Hours	DF
1	0.02	6.8 x 10 ⁻⁴	50	3	1.9
4	0.02	6.8 x 10 ⁻⁴	50	3	2.9
2 (Sim. 1)	0.02	5.8 x 10 ⁻⁴	50	3	1.8
3.2 (Sim. 3)	0.02	1.8 x 10 ⁻⁴	50	3	1.3

4.2.5 Sodium Diuranate

Coprecipitation of technetium with sodium diuranate from alkaline solutions was performed by adding uranyl nitrate, UO₂(NO₃)₂, to the alkaline solution. In some tests, technetium was initially present in the alkaline solution, and uranyl nitrate was added. In other tests, technetium was initially present in the uranyl nitrate solution added to the alkaline solution. To eliminate interference with ⁹⁹Tc β measurements, the uranyl nitrate stock first was decontaminated of ²³⁴Th and other B-emitting decay products by extraction in diethyl ether (15 mL) and washing with a small amount (0.5 mL) of water. The coprecipitation experiments were performed by introducing sufficient uranyl nitrate to make the final slurry concentration 0.02 M. Tests with NaOH solution, Simulant 1, or Simulant 3 (Table 3.4) were performed. The results of the experiments using technetium-spiked uranyl nitrate are presented in Table 4.5.

As shown in Table 4.5, coprecipitation of Tc(VII) with sodium diuranate is low in pure NaOH solutions without reductant. In alkaline solutions simulating Hanford Site wastes, DFs also are low. With 0.1 M hydrazine reductant, the DF increased slightly to 2.4 and 1.8, respectively, in 1.0 and 4.0 M NaOH.

Table 4.5. Coprecipitation of Tc(VII) from NaOH and Simulated Waste Solutions by Sodium Diuranate Produced by Hydrolysis of Technetium-Spiked Uranyl Nitrate

[NaOH], M	[UO ₂ (NO ₃) ₂], M	[Tc(VII)], M	[N ₂ H ₄], M	T, °C	t, Hours	DF
0.5	0.024	3.5 x 10 ⁻⁵	--	80	1	1.17
1.0	0.024	4.0 x 10 ⁻⁵	0.1	60	3	2.4
2.0	0.024	3.5 x 10 ⁻⁵	--	80	1	1.34
4.0	0.024	4.0 x 10 ⁻⁵	0.1	60	3	1.8
2 (Sim. 1)	0.024	3.0 x 10 ⁻⁵	0.075	60	3	2.3
3.2 (Sim. 3)	0.024	3.0 x 10 ⁻⁵	0.075	60	3	1.3

4.3 Coprecipitation of Cesium by the Method of Appearing Reagents

The distribution of ^{137}Cs has been studied between alkaline solutions and metal hydroxide precipitates [$\text{Co}(\text{OH})_2$, $\text{Co}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, $\text{Mn}(\text{OH})_2$, and $\text{Cr}(\text{OH})_3$] produced homogeneously throughout the solution volume by decomposition of soluble precursors (the MAR). Conditions under which the precipitates formed, determined by Krot et al. (1996), gave moderate decontamination from neptunium and generally excellent decontamination from plutonium. As shown in the previous section, partial coprecipitation of technetium can be attained if the reductant hydrazine is used.

It was found, however, that the transition metal hydroxide precipitates captured only 1 to 3% of the ^{137}Cs present in alkaline solution. Furthermore, the captured cesium washed easily from the precipitate when treated with fresh 0.1 M NaOH. After three 5-mL washings, the precipitates contained less than 0.1% of the ^{137}Cs present in the initial solution. These tests show that neptunium and plutonium, which, under optimum conditions, can be captured almost completely by the hydroxide precipitates, can be decontaminated from cesium by a factor of approximately 10^3 after three washings of the carrier precipitate.

Tests also were performed by adding alkali-soluble uranyl peroxide precursor to the alkaline test solutions. The ^{137}Cs capture found on the product sodium uranate carrier precipitate in 0.5 to 1 M NaOH was around 10% (Table 4.6).

Cesium coprecipitated with sodium uranate is not removed when the precipitate is washed with 0.1 M NaOH. After three 0.5-mL washings, the precipitate obtained in 0.5 and 1.0 M NaOH contained 1 to 4% of the total cesium present in the initial solution. Therefore, Np(V) and Pu(VI), which coprecipitate well with sodium uranate from 0.5 to 1.0 M NaOH, will be decontaminated from ^{137}Cs only by a factor of 25 to 100.

Table 4.6. Coprecipitation of Cesium from NaOH Solutions by Sodium Diuranate Produced by Decomposition of Uranyl Peroxide at 50°C

[NaOH], M	Cs Captured, %	DF
0.5	13.0	1.15
1.0	9.3	1.09
2.0	4.0	1.04
4.0	1.0	1.01

4.4 Coprecipitation of Strontium by the Method of Appearing Reagents

In contrast to cesium, strontium coprecipitates to some extent with all the studied carriers except Mn(OH)_2 from 0.5 to 4 M NaOH. The DFs for this element range from 10 to 150 under optimum conditions for Co(OH)_2 , Co(OH)_3 , Fe(OH)_3 , MnO_2 , Cr(OH)_3 , and Na_2UO_4 . Maximum DFs are observed for Na_2UO_4 . The experimental procedure to produce the precipitates was similar to that described in previous sections and was based on the studies of Krot et al. (1996). The coprecipitation test data are presented in Table 4.7.

As in the case of cesium, it was necessary to determine how strongly strontium is retained on the precipitates, and if it is possible to remove it by washing with dilute NaOH. Multiple leaching of ^{90}Sr -loaded carriers with 0.1 M NaOH was performed to ascertain the strength of retention. Leaching results are given in Table 4.8.

As shown by the data, strontium is not readily leached from most precipitates and possibly forms mixed hydroxide compounds of variable composition with the d-metals and uranium. Of the precipitates tested, MnO_2 is the least effective in retaining ^{90}Sr and Na_2UO_4 the most effective.

Leaching of strontium from the carrier precipitate becomes possible if EDTA is part of the washing solution. By use of EDTA, a significant part of the precipitate itself also is dissolved. Results of leaching of strontium-loaded Co(OH)_3 and Fe(OH)_3 by 0.05 M NaOH and 0.05 M EDTA are shown in Table 4.9.

Table 4.7. Coprecipitation of Strontium with Various Carriers

Carrier	Concentration, <u>M</u>	T, °C	[NaOH], <u>M</u>	DF
Co(OH) ₃ ^(a)	0.05	40	1.0	9
Co(OH) ₃ ^(a)	0.01	70	0.5	25
Co(OH) ₃ ^(a)	0.05	80	1.0	23
Co(OH) ₃ ^(a)	0.05	80	1.0	12
Co(OH) ₃ ^(b)	0.01	70	0.5	94
Co(OH) ₃ ^(b)	0.02	40	1.0	23
Co(OH) ₂ ^(b)	0.01	70	0.5	17
Fe(OH) ₃ ^(c)	0.01	40	1.0	23
Fe(OH) ₃ ^(c)	0.01	80	1.0	23
Fe(OH) ₃ ^(d)	0.01	70	0.5	10
Fe(OH) ₃ ^(d)	0.02	80	1.0	16
MnO ₂	0.01	50	0.5	25
MnO ₂	0.01	50	1.0	10
MnO ₂	0.01	50	2.0	4
MnO ₂	0.01	50	4.0	3
Mn(OH) ₂	0.01	50	0.5	2
Mn(OH) ₂	0.01	50	1.0	2
Mn(OH) ₂	0.01	50	2.0	2
Mn(OH) ₂	0.01	50	4.0	~1.5
Na ₂ UO ₄	0.002	60	3.0	160
Na ₂ UO ₄	0.005	60	3.0	130
Na ₂ UO ₄	0.01	60	3.0	90
Na ₂ UO ₄	0.01	60	0.5	150
Na ₂ UO ₄	0.01	60	1.0	140
Na ₂ UO ₄	0.01	60	2.0	70
Na ₂ UO ₄	0.01	60	8.0	20
Cr(OH) ₃	0.01	80	0.5	17
Cr(OH) ₃	0.01	80	1.0	14
Cr(OH) ₃	0.01	80	2.0	12
Cr(OH) ₃	0.01	80	4.0	11
(a) Co(NH ₃) ₆ Cl ₃ precursor				
(b) Co(NH ₃) ₅ Cl ₃ precursor				
(c) Na ₂ FeO ₄ precursor				
(d) Na ₂ Fe(CN) ₅ NO precursor				

Table 4.8. Leaching of ^{90}Sr from Precipitates Obtained by the Method of Appearing Reagents with 0.1 M NaOH

Carrier	Precipitation [NaOH], M	Leach T, °C	^{90}Sr Leached, % of Amount Initially in Solids				Residual ^{90}Sr , %
			1	2	3	4	
$\text{Co}(\text{OH})_3$	0.5	80	0.5	3.9	3.1	2.8	82.0
$\text{Co}(\text{OH})_3$	1.0	80	0.3	1.4	0.5	0.5	96.7
$\text{Fe}(\text{OH})_3$	0.5	80	0.7	0.5	0.8	0.7	97.3
$\text{Fe}(\text{OH})_3$	1.0	80	0.5	0.7	1.0	1.5	96.3
$\text{Mn}(\text{OH})_2$	0.5	50	4.1	1.7	1.1	1.0	91.5
$\text{Mn}(\text{OH})_2$	1.0	50	5.3	1.7	1.8	1.5	89.7
MnO_2	0.5	50	60.0	10.6	2.9	2.5	24.0
MnO_2	1.0	50	47.9	6.5	6.3	5.8	33.4
Na_2UO_4	0.5	60	1.0	0.6	0.2	0.2	98.0
Na_2UO_4	1.0	60	0.4	0.1	0.1	0.2	99.2

Table 4.9. Leaching of ^{90}Sr from Precipitates Obtained by the Method of Appearing Reagents with 0.05 M NaOH and 0.05 M EDTA

Carrier	Precipitation [NaOH], M	Leach T, °C	^{90}Sr Leached, % of Amount Initially in Solids				Residual ^{90}Sr , %
			1	2	3	4	
$\text{Co}(\text{OH})_3$	0.5	80	54.0	45.0	0.5	0.2	0.3
$\text{Co}(\text{OH})_3$	1.0	80	99.0	0.5	0.2	0.2	0.1
$\text{Fe}(\text{OH})_3$	0.5	80	77.0	22.0	0.5	0.2	0.3
$\text{Fe}(\text{OH})_3$	1.0	80	77.0	22.0	0.4	0.5	0.1

5.0 Reductive Sorption of Tc(VII), Np(V), and Pu(VI) from Alkaline Solutions by Active Metals

To be effective in reductive sorption of technetium, a metal must have an alkaline solution redox potential sufficient to reduce Tc(VII), pertechnetate, to the relatively insoluble $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. The potential of the Tc(VII)/Tc(IV) O_2 pair is about -0.6 V with respect to the normal hydrogen electrode, NHE (Peretrukhin et al. 1995; Bard 1973). A second requirement is that the metal cannot passivate in alkaline solution; that is, there must be no formation of an oxide film, insoluble in alkali, that would break contact of the solution with the metal. Based on these criteria, Pb, Sn, Sb, and Zn metals were chosen to study sorption of technetium. Associated sorption of neptunium and plutonium from alkaline solutions, by reduction and creation of their respective AnO_2 films, also was studied. Finally, sorption on Cr, which is covered by film of $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, was studied. The solubility of this film in alkali increases with increasing alkali concentration. The redox potentials of these metals are presented in Table 5.1. Sorption on the alloys Pb-1.5%Sb and Sn(63.5%)-Pb(34%)-Sb(2.5%) also was studied.

Table 5.1. Redox Potentials, in 1 M NaOH, of Metals Chosen for Tc(VII) Reductive Sorption (Bard 1973)

Couple	Potential, vs NHE, in Volts				
	Zn	Cr	Sn	Sb	Pb
$\text{Me}^{3+,2+}/\text{Me}^0$	-1.2	-(1.2 to 1.48)	-0.91	-0.59	-0.58
$\text{Me}^{4+}/\text{Me}^{2+}$	--	--	-0.93	--	--

5.1 Experimental Procedure

The metals were used in the form of granules, 3 to 3.5 mm in radius, and washed with acetone, 0.5 M HCl, and water before exposure to the test solutions. The reductive sorption was studied in static conditions by shaking 5 mL of alkaline solution containing $(1 \text{ to } 4) \times 10^{-5}$ M Tc(VII), Np(V), or Pu(VI) with five metal granules. The geometric surface area thus was 5.6 to 7.7 cm^2 , and the surface area to volume ratio was about 1.3 cm^{-1} . Sorption also was studied in dynamic conditions by passing alkaline solution of radionuclide through a column 150 mm high and 10 mm inner diameter filled with metal granules.

Sorption was studied from 0.5 to 4 M NaOH as well as from solutions similar in composition to Hanford Site liquid wastes (see Table 3.4). Sorption on metals was studied both in oxic conditions (i.e., in the presence of atmospheric oxygen dissolved in alkaline solutions) and in anoxic conditions (dissolved oxygen removed by purging with argon for 10 to 15 minutes). After contact with metal granules, the solution was centrifuged for 10 minutes at 8000 rpm and two parallel samples taken

(0.2 mL each). These samples were acidified with 0.2 mL of 4 M HNO₃. Then 7 mL of Ready Gel cocktail (Beckman) was added, and α or β activities were measured on a Beckman LS-6500 liquid scintillation counter. For measurements of the radioactivity of ²³⁷Np solutions, which contain daughter ²³³Pa, the narrow peak corresponding to α radiation of ²³⁷Np was stripped from the total spectrum using a program installed in the instrument. The residual contribution of the daughter protactinium to the ²³⁷Np peak was negligible and did not change the DFs.

5.2 Results and Discussion

Reductive sorption on active metals was tested for technetium, neptunium, and plutonium. Results for each element are discussed in the following sections.

5.2.1 Reductive Sorption of Technetium

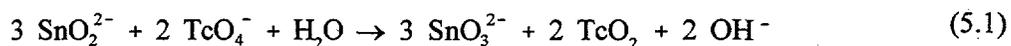
The DF of alkaline solutions and tank waste simulants from technetium by sorption on zinc, chromium, tin, and two lead alloys are presented in Table 5.2. The DFs for 0.5 to 3.5 M NaOH solutions from technetium obtained by sorption on metal granules with 2.5 hours of contact range from 1.07 to 5.7.

Dynamic experiments were performed by passing alkaline solution or simulant through the 150-mm high by 10-mm diameter column filled with metal granules at 6 to 7 mL per hour. The DFs on different metals ranged from 2.1 to 8.9 (Table 5.2). The highest DFs, 5.7 in static conditions and 8.9 in dynamic conditions, were obtained by sorption on zinc from 3.5 M NaOH.

Table 5.2. Reductive Sorption of $(3 \text{ to } 9) \times 10^{-5}$ M Tc(VII) by Metals from Alkaline Solutions and Waste Simulants at 70°C

Solution	Decontamination Factor for Static (Sta) and Dynamic (Dyn) Conditions									
	Zn		Cr		Sn		Pb + 1.5%Sb		Sn-63.5% Pb-34% Sb-2.5%	
	Sta	Dyn	Sta	Dyn	Sta	Dyn	Sta	Dyn	Sta	Dyn
0.5 M NaOH	1.4	1.9	1.07	1.15	1.15	2.8	1.2	2.9	1.5	4.3
1.0 M NaOH	1.46	3.6	1.09	1.23	1.23	3.9	1.3	3.5	1.9	5.4
2.0 M NaOH	3.9	4.7	1.3	1.4	1.27	4.1	1.4	3.8	1.8	5.3
3.5 M NaOH	5.7	8.9	1.03	1.11	1.4	4.6	1.8	5.1	1.8	3.5
Simulant 1	6.0	5.8	1.23	1.32	1.21	3.5	1.8	6.0	1.7	5.1
Simulant 2	--	--	1.03	1.05	1.1	1.2	1.6	3.7	1.4	1.8
Simulant 3	1.7	2.3	1.01	1.03	1.03	1.1	1.5	3.2	1.2	1.5

By comparison, technetium sorbed from pH 1 to 2 solution on granulated zinc gives a DF of 3.3; on powdered zinc, the DF is 18.6 (Fletcher et al. 1991). Other researchers obtained DFs from PUREX raffinates of about 10 on granulated zinc (Volk et al. 1979). As would be expected from the electrode potential data (Table 5.1), tin, lead, and their alloys prove to be less effective than zinc. Somewhat unexpected is that DFs obtained on tin are lower than on alloys of lead and antimony. The tin couples are over 0.3 volts lower than those of either lead or antimony and would be expected on a purely thermodynamic basis to show better technetium reduction:



The DFs from technetium increase as hydroxide concentrations increase from 0.5 to 3.5 M NaOH. For the waste simulants, which contained 0.04 M CrO_4^{2-} , complexing agents, and other waste components, the DFs on all tested metals are lower than for pure alkalis. Two hours' contact of chromate-bearing simulants with metals changed solution color from yellow to green; with longer contact, precipitation of dark-green sediments is observed. The solids apparently are chromium(III) or antimony(III) hydroxides and, in dilute alkalis, also zinc, lead, or tin hydroxides.

Attempts were made to improve the alkaline solution and simulant waste decontamination from technetium by sorption on the metals at 60 to 70°C temperature and under anoxic conditions obtained by argon purging. Increasing temperature from 20°C to 60 or 70°C increased DFs about 20 to 30%. Removal of dissolved oxygen gave no significant effect.

Repeated passing of technetium-bearing test solutions through the metal granule column or contacting the solution with fresh metal granules give DFs for each stage about 10 to 20% lower than indicated in Table 5.2. It is noted that enhanced decontamination can be obtained by passing the solution through the zinc column two or three times. With this multiple treatment, the solution is decontaminated of technetium to a concentration of (5 to 7) $\times 10^{-7}$ M. This concentration is lower than the solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ obtained by chemical methods and is close to the solubility of technetium dioxide electro-deposited from 4 M NaOH solutions (Peretrukhin et al. 1996).

Removal of technetium sorbed on metal granules was performed with 5% hydrogen peroxide solution. Thirty minutes of shaking 5 mL 5% H_2O_2 solution with five granules of chromium desorbed about 90% of the technetium. Shaking with a fresh portion of hydrogen peroxide gave combined technetium recovery from the surface of 98 to 99%. About 96 to 98% of the technetium deposited as TcO_2 on a column of metal granules can be desorbed by two column volumes of 5% hydrogen peroxide.

The DFs for alkaline solution and simulants from technetium obtained in the present work by sorption on Zn, Sn, Pb alloys, and on Cr are not high enough to recommend this method for use in laboratory practice or for the decontamination of industrial alkaline wastes. To attain more complete recovery of technetium by sorption on the studied metals, it is necessary to increase the ratio of the metal surface to the volume of alkaline solution or to filter the solution through a longer column. However, under such conditions, dissolution of zinc, tin, lead, and antimony by the alkaline solution can be significant and introduce unacceptable components into the wastes to be vitrified.

5.2.2 Reductive Sorption of Neptunium(V) and Plutonium(VI)

Sorption of neptunium and plutonium on the studied metals yielded DFs ranging from 11 to 67 for 0.5 to 1.0 M NaOH. The reductive sorption of Np(V) and Pu(VI) becomes less effective when concentration increases to 4 M NaOH (DF from 1.1 to 9.2) and for Simulant 3 (Table 3.4) containing 3.2 M NaOH, 0.04 M Na₂CrO₄, and other waste components (DF from 1.8 to 4.3). Complete results are given in Table 5.3.

Table 5.3. Reductive Sorption of Np(V) and Pu(VI) from Alkaline Solutions on Metals and Alloys Under Static Conditions

(0.1 to 7.0) x 10⁻⁶ M Np(V) and Pu(VI)
Surface area/volume = 1.3 cm⁻¹

Metal or Alloy	Solution	DF			
		Np(V)		Pu(VI)	
		20°C	60°C	20°C	60°C
Cr	0.5 <u>M</u> NaOH	12	19	53	67
	1.0 <u>M</u> NaOH	15	22	34	40
	2.0 <u>M</u> NaOH	--	7.2	11	14
	4.0 <u>M</u> NaOH	3.2	3.7	3.7	4.3
	Simulant 3	2.1	2.0	3.5	2.8
	50% diluted Simulant 3	--	8.0	8.5	4.3
Zn	1.0 <u>M</u> NaOH	47	64	32	37
	4.0 <u>M</u> NaOH	2.3	2.5	8.4	9.2
	Simulant 3	1.8	1.9	3.8	3.7
Sn	1.0 <u>M</u> NaOH	35	42	15	18
	4.0 <u>M</u> NaOH	2.0	2.2	4.3	6.4
	Simulant 3	2.5	2.7	1.4	1.5
Pb - Sb	1 <u>M</u> NaOH	13	18	21	27
	4 <u>M</u> NaOH	1.1	1.7	4.2	1.7
Sn - Pb - Sb	1 <u>M</u> NaOH	22	24	11	16
	4 <u>M</u> NaOH	2.7	2.5	4.0	2.1
	Simulant 3	1.9	2.2	3.9	3.5

As shown in Table 5.3, plutonium is sorbed better than neptunium on all studied metals. The rate of plutonium sorption from alkaline solutions also is significantly higher than that of neptunium. Figure 5.1 shows the rate of plutonium sorption. Decontamination factors exceeding 10 are reached for Pu(VI) after 1 to 2 hours; for Np(V) in analogous conditions, 10 to 20 hours are required to exceed a DF of 10. This observation is consistent with literature reports which indicate that reduction of Pu(VI) to Pu(IV) in alkaline solution proceeds more readily and under milder conditions than reduction of Np(V) to Np(IV) (Shilov et al. 1996).

High DFs from neptunium (12 to 22) and especially from plutonium (34 to 67) were obtained by sorption on chromium granules in 0.5 to 1.0 M NaOH. Passing deaerated 1.5×10^{-5} M Pu in 1 M NaOH twice through a 150-mm long column filled with chromium granules decreased plutonium concentration over a factor of 100 to 1.2×10^{-7} M (Figure 5.2). A third passing of this solution through the column decreased plutonium concentration insignificantly. More than two hours of subsequent contact of the filtrate with a fresh portion of chromium granules decreased plutonium concentration from 1.1×10^{-7} M to 8.7×10^{-8} M. This concentration is near the solubility of $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ in 1 M NaOH (Peretrukhin et al. 1996). Thus, decontamination of 0.5 to 1 M NaOH from Pu(VI) by contact with metallic chromium granules becomes constant at about 1.2×10^{-7} M Pu. Further decrease of plutonium concentration by sorption on chromium granules is marginal.

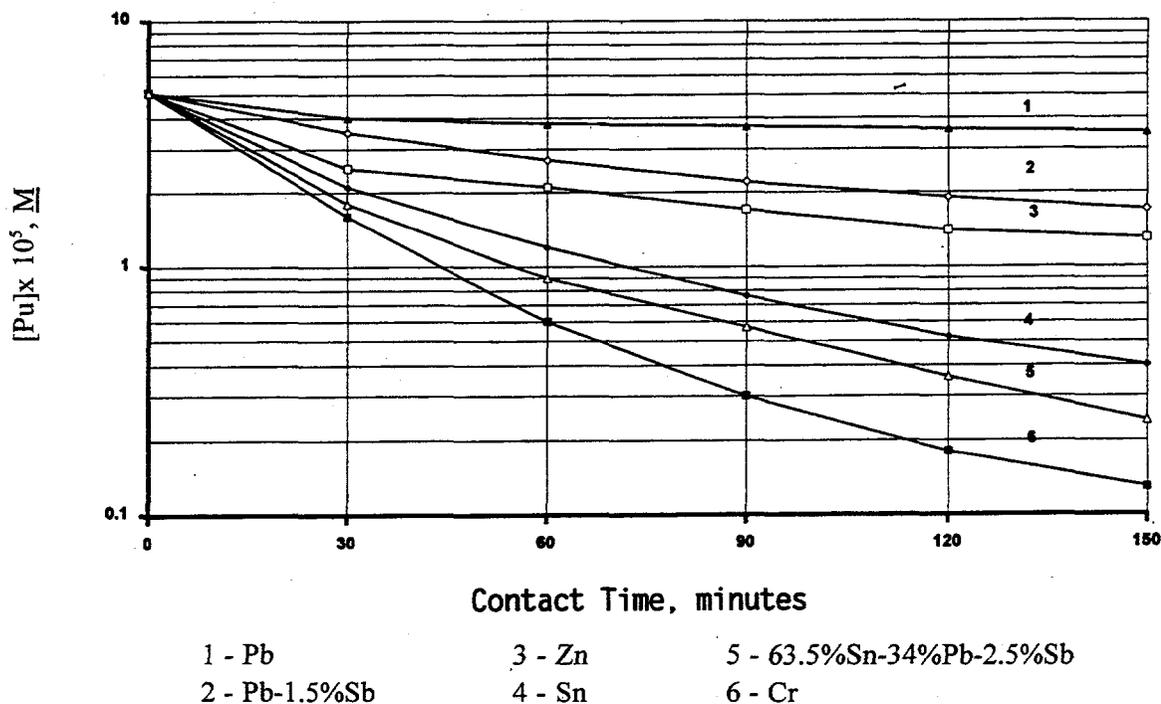


Figure 5.1. Reductive Sorption of Pu(VI) on Metals from 1 M NaOH at 60°C

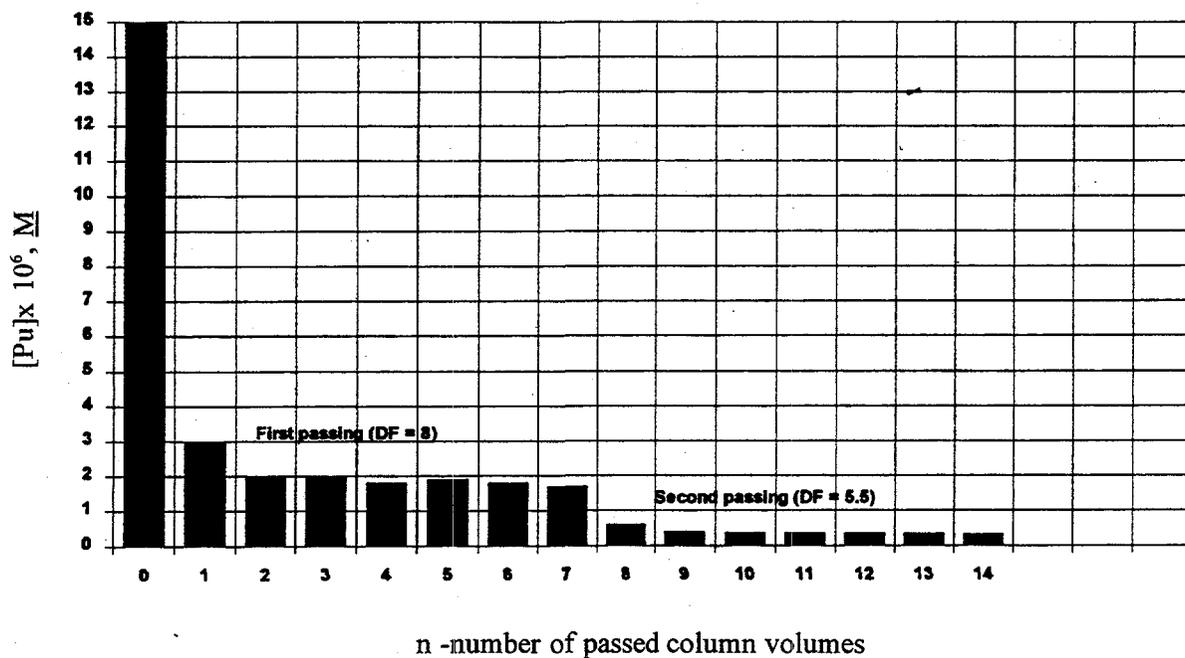


Figure 5.2. Reductive Sorption of Pu(VI) on Chromium Granules in a Column from Four-Fold Diluted Simulant 3 at 60°C

The removal of neptunium and plutonium sorbed on chromium and other metal granules was studied. The ratio of geometric surface area to the solution volume was 1.6 cm^{-1} and 30 minutes of time was spent for each contact. Nitric and hydrochloric acids at 1 and 2 M concentration, respectively, effectively remove sorbed Pu (Figure 5.3). However, a 5% hydrogen peroxide solution has little effect on plutonium sorbed on metals; its action on neptunium is incomplete, removing only 27% after two contacts and 30 minutes.

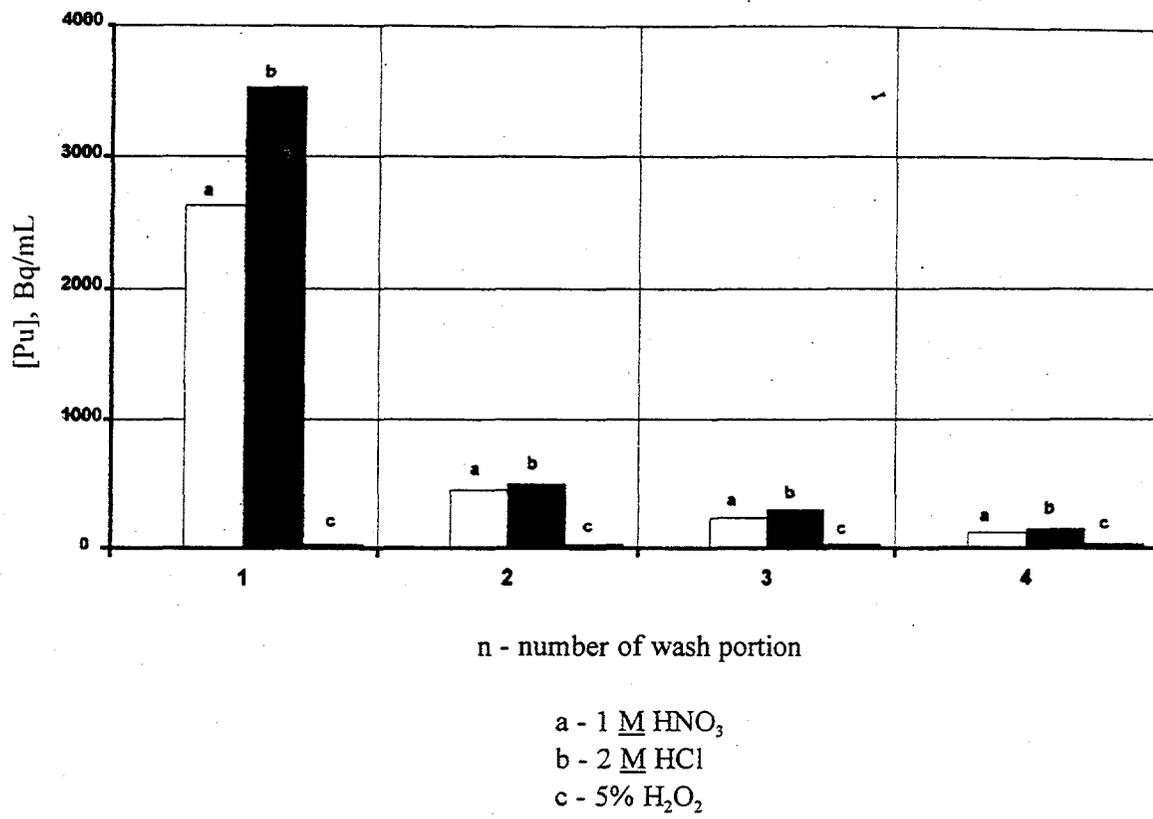


Figure 5.3. Removal of Sorbed Plutonium from Chromium

6.0 Discussion and Comparison of Results with Literature Data

No information was found in the technical literature on the decontamination of alkaline solution from technetium by coprecipitation on iron hydroxide by the hydrolysis of iron(II) or (III) salt. Therefore, comparisons were made between results from the present study and recent results on coprecipitation of Np(IV,V) from alkaline solutions and tank waste simulants by iron(II) and (III) salts (Worl et al. 1995) and with the results on the precipitation of neptunium and plutonium from alkaline solution by Method of Appearing Reagents (Krot et al. 1996).

Neptunium coprecipitates to 99.7% completion by the action of 0.15 M FeCl₂ on alkaline simulant containing 3.5 M NaOH, 0.64 M CO₃²⁻, 0.03 M PO₄³⁻, and 0.1 M SO₄⁻ but no organic components (Worl et al. 1995). It was shown in Section 2.0 that more than 99% of the plutonium and about 75% of the technetium coprecipitates by the action of 0.2 M iron(II) salt on simulant waste containing 3.2 M NaOH, 0.04 M Na₂CrO₄, and 11 other components including 0.1 M EDTA, 0.1 M glycolate, and 0.03 M citrate. The iron(II) salt required in the present experiments was higher than used in previous work probably because the chromate in the simulant used in the present studies consumed iron(II) in its reduction to Cr(III).

In other experiments, however, almost complete absence of Np, Pu, and Am coprecipitation was observed for two-fold and four-fold dilutions of "complexant concentrate" waste simulants containing 0.3 M gluconate (HOCH₂[CH(OH)]₄CO₂⁻), 0.23 M iminodiacetate [HN(CH₂CO₂)₂²⁻], 0.007 M NTA [N(CH₂CO₂)₃³⁻], 0.038 M HEDTA (*N*-2-hydroxyethylethylenediaminetriacetate), 0.064 M citrate, and 0.003 M EDTA (Worl et al. 1995). Final Fe(II) and Fe(III) precipitant additions reached 0.15 M. The simulant also contained molybdate, silicate, and zirconyl salts. The decrease of radioelement coprecipitation caused by increasing concentrations of complexing agents is well known. For example, it was used in the bismuth phosphate process for recovering plutonium from irradiated nuclear fuel (Katz and Seaborg 1957).

The complete cessation of actinide coprecipitation by iron(II,III) added directly to alkaline wastes containing high, but realistic, concentrations of organic complexing agents is discouraging. Better decontamination of complexant-bearing solutions from Np and Pu was observed recently by homogeneous coprecipitation achieved through the MAR (Bessonov et al. 1997). However, the poor coprecipitation of technetium (VII) with iron(III) and other hydroxides observed in the present tests by the MAR, even in the presence of hydrazine, indicates that sufficiently reducing conditions have not been attained. Coprecipitation of actinides and technetium from alkaline waste media requires further investigation if it is to be successful.

Sorption of Tc, Np, and Pu from alkaline solutions on granulated metals (Zn, Sn, Pb, alloys of Pb, and Cr) gave decontamination factors close to those observed for low acidic and alkaline solutions (Fletcher et al. 1991; Volk et al. 1979). The low DFs obtained, however, show that technetium sorption on metals is not as attractive as electrodeposition for decontamination of alkaline solutions (Hobbs 1994; Fletcher et al. 1991). Sorption of Pu(VI) from alkaline solutions on granulated chromium is effective (DF of 67 from 0.5 M NaOH) and may be an interesting approach to decontamination of alkaline waste.

7.0 Conclusions

Decontamination of 0.5 to 4.0 M NaOH from Tc(VII) can be performed by reductive coprecipitation with iron hydroxide by the direct action of iron(II) salt or the combined action of hydrazine and iron(III) salt. Technetium capture by the precipitate reaches about 99.7% from 0.5 to 1.0 M NaOH and about 96% from 2 to 4 M NaOH for 0.1 to 0.15 M iron(II) salt or for 0.1 M hydrazine and 0.1 to 0.15 M iron(III) salt.

Technetium capture from 0.5 to 4.0 M NaOH by iron(III) hydroxide precipitate generated from 0.15 M addition of Fe(II) decreases from around 98% to about 80% in the presence of complexing agents found in tank waste (e.g., phosphate, aluminate, EDTA, citrate, and glycolate at 0.03 to 0.1 M each).

Addition of 0.04 M sodium chromate to 0.5 to 4.0 M NaOH drastically decreases the reductive coprecipitation of Tc(VII) because iron(II) salt is consumed in the reduction of chromate. Iron(II) salt added to 0.07 M excess with respect to chromate reduces chromate completely and rapidly (in 0.5 hour). Coprecipitation of about 99.7% of the technetium in 0.5 to 1.0 M NaOH, and about 97% in 2 to 4 M NaOH, is observed. Use of hydrazine and iron(III) salt instead of iron(II) gives slow and incomplete reduction of chromate and lower technetium coprecipitation.

The reductive coprecipitation of Tc(VII) and Pu(VI) by Fe(II) from alkaline simulant waste containing 3.5 M NaOH, 0.04 M Na₂CrO₄, and 11 other components is lower than observed for pure NaOH solution. Coprecipitation of plutonium is 98 to 99% and that of technetium only 8 to 30% for 0.05 to 0.1 M Fe(II); chromate reduction also is incomplete. Technetium coprecipitation reaches 70 to 75% by adding 0.2 M Fe(II) and complete chromate reduction is observed. Subsequent additional treatment of supernates with Fe(II) also give 70 to 75% technetium coprecipitation possibly because of Tc(IV) complexation by ligands present in the supernatant.

In contrast to plutonium and neptunium, Tc(VII) capture from 0.5 to 4.0 M NaOH is insignificant or incomplete on Fe(OH)₃, Cr(OH)₃, Mn(OH)₂, Co(OH)₃, and Co(OH)₂ carriers generated homogeneously from soluble precursors by the MAR. Technetium capture by coprecipitation with Na₂U₂O₇ prepared by addition of uranyl nitrate also is low (15 to 60%). Under the same conditions for the transition metal carriers, the ¹³⁷Cs capture is insignificant, and ⁹⁰Sr capture is moderate. Sodium uranate, generated by decomposition of soluble uranyl peroxide, gives the best performance from 0.5 to 4 M NaOH, capturing about 98 to 99% of the ⁹⁰Sr and 1 to 12% of the ¹³⁷Cs.

Contact of (3 to 5) x 10⁻⁵ M Tc(VII) alkaline solutions with granules of Zn, Cr, Sn, and Pb alloys cause incomplete reductive sorption of TcO₂·nH₂O on the metal surface. The DFs of 0.5 to 4.0 M NaOH solutions from technetium are 1.1 to 1.8 for a surface area to solution volume ratio of 1.3 cm⁻¹. Reductive sorption of Pu(VI) and Np(V) on these metals, especially for chromium, is more effective than observed for Tc(VII). Plutonium sorption exceeds 98% (DF 67) from 0.5 M NaOH.

Of the techniques investigated in this study, reductive coprecipitation by the action of Fe(II) is judged to be the most promising for technetium removal from alkaline solution. This technique also coprecipitates plutonium and chromium, as Cr(III) hydroxide, and does not require preliminary destruction of organic complexing agents if their concentrations are lower than about 0.05 M. Further studies are necessary to decrease Fe(II) consumption and thus the mass of waste destined for vitrification. Coprecipitation with sodium uranate gives good decontamination of chromate-bearing solutions from Np(V), Pu(VI), and Sr. Further studies to improve Tc capture under non reducing conditions may be fruitful.

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