

Determination of the Solubility of Np(IV)-(VI), Pu(III)-(VI), Am(III)-VI and Tc(IV), (V) Hydroxo Compounds in 0.5 - 14 M NaOH Solutions

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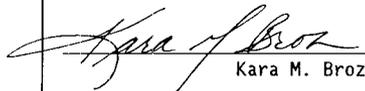
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Jim Hanson

Reply Separator

Subject: Re: Clearance for WHC-EP-0897
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Date: 9/17/96 6:51 AM

Thanks for your attention to this,

Cal

Cal,

It is on its way... snet to Kara Broz tonight...Plant Mail. Sorry, I have been swamped with the ten-year-plan and personnel issues,

JPH

Reply Separator

Subject: Clearance for WHC-EP-0897
Author: Calvin H Delegard at ^HANFORD03C
Date: 9/16/96 3:26 PM

Jim,

A couple weeks ago, I sent you a draft copy of the document WHC-EP-0897 for your review and clearance. The document concerns the solubility of the actinides and technetium compounds in alkaline solution -- the work was done by the Institute of Physical Chemistry in Russia. I want to issue the document before the contractor transition. Please advise me of the status of your clearance. I'd be glad to answer any questions.

Thanks,
Cal

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WHC-EP-0897 on Actinides and Technetium in Alkaline Media
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J. R. Jewett, Manager
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**DETERMINATION OF THE SOLUBILITY OF
Np(IV) - (VI), Pu(III) - (VI), Am(III) - (VI), AND Tc(IV), (V)
HYDROXO COMPOUNDS IN 0.5 - 14 M NaOH SOLUTIONS**

ABSTRACT

The solubilities of Am(III), Np(IV), Pu(IV), Tc(IV), Np(V), Pu(V), Am(V), and Tc(V) hydroxo compounds were studied in 0.5 to 14 M NaOH solutions at 25 ± 2 °C. The effects of fluoride, phosphate, carbonate, oxalate, and some other organic complexing agents on the solubilities of Np(IV), Pu(IV), and Tc(IV) hydroxides were investigated at 1.0 and 4.0 M NaOH. Some predictions were made on the dissolved (IV) and (V) species present in alkali solutions.

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EXECUTIVE SUMMARY

The solubilities of Am(III), Np(IV), Pu(IV), Tc(IV), Np(V), Pu(V), Am(V), and Tc(V) hydroxo compounds were studied in 0.5 to 14 M NaOH solutions at 25 ± 2 °C. The effects of fluoride, phosphate, carbonate, oxalate, and some other organic complexing agents on the solubilities of Np(IV), Pu(IV), and Tc(IV) hydroxides were investigated at 1.0 and 4.0 M NaOH. Predictions were made on the dissolved (IV) and (V) species present in alkali solutions.

The solubilities of $\text{NpO}_2 \cdot n\text{H}_2\text{O}$ and $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ were measured in 0.5 to 14 M NaOH in the presence of 0.1 M N_2H_4 under conditions designed to prevent their oxidation by atmospheric oxygen. The solubilities increase with increasing NaOH concentration from about 3×10^{-7} to 2.1×10^{-5} M for Np(IV) and from 1.4×10^{-8} to 9.8×10^{-6} M for Pu(IV). The formation of the anionic species, $\text{Np}(\text{OH})_5^-$ and $\text{Pu}(\text{OH})_6^{2-}$, in alkaline solution have been calculated from known values of the solubility products of $\text{Np}(\text{OH})_4$ and $\text{Pu}(\text{OH})_4$ and the experimental data. Spectrophotometric measurements to identify the $\text{Np}(\text{OH})_5^-$ and $\text{Pu}(\text{OH})_6^{2-}$ were unsuccessful because of low extinction coefficients. Complex-forming agents at concentrations from 0.05 to 0.5 M in 1 and 4 M NaOH with reductants yielded Np(IV) and Pu(IV) hydroxide solubilities increased 2 to 400-times from those observed in the absence of the agents.

The solubilities of Np(V), Pu(V), and Am(V) hydroxo compounds were found to be higher than those of the tetravalent actinide hydroxides and increase from $(0.5 \text{ to } 1.0) \times 10^{-4}$ M to 3.7×10^{-4} as NaOH concentration increases from 0.5 to 14 M. The composition of the

neptunium solid phase has been determined by X-ray diffractometry to be $\text{NpO}_2\text{OH}\cdot n\text{H}_2\text{O}$ under 0.5 M NaOH mother solution and $\text{Na}_2\text{NpO}_2(\text{OH})_3\cdot n\text{H}_2\text{O}$ under 5 M NaOH. The formation of $\text{Na}_3\text{NpO}_2(\text{OH})_4\cdot n\text{H}_2\text{O}$ is assumed at higher alkali concentration. The solution species NpO_2OH , $[\text{NpO}_2(\text{OH})_3]^{2-}$, and $[\text{NpO}_2(\text{OH})_4]^{3-}$ are presumed to exist in 0.5, 5, and 14 M NaOH solutions, respectively.

The solubilities of Pu(IV) hydroxo compounds in NaOH solutions in the presence of hydrazine are 3 to 30-times lower than those obtained by Delegard (1987) in the presence of air and by Karraker (1993) in evaporation of simulated NaOH waste solutions.

The solubilities of Np(IV) and Pu(IV) achieved in 0.5 to 14 M NaOH in 0.1 M N_2H_4 and the absence of applied external gamma radiation are below the transuranic waste (TRU) threshold of 100 nanocuries per gram solution. The solubility of Np(V) hydroxide compounds in 1 to 14 M NaOH are lower than the TRU threshold whereas the solubilities of the Pu(V) and Am(V) compounds are above the threshold.

The solubilities of the Tc(IV) and Tc(V) hydrated oxides in 0.02 M N_2H_4 and 1 M NaOH are comparable and about 3×10^{-5} M. The Tc(IV) hydrated oxide solubility increases about three-fold as NaOH concentration increases to 14 M whereas the Tc(V) hydrated oxide solubility decreases about two-fold. The technetium concentrations above Tc(IV) and Tc(V) hydrated oxides are established by the true solubilities of the solid phase, complex and colloid formation processes, oxidation by atmospheric oxygen or impurities to form Tc(VII), and solid phase aging and other surface processes.

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LIST OF TERMS

DOE

U.S. Department of Energy

DOE/EM

U.S. Department of Energy/Environmental Restoration and Waste Management

1.0 INTRODUCTION

Published data on the solubilities of Np, Pu, Am, and Tc hydroxo compounds in alkaline media (0.1 to 14 M NaOH) are less numerous than comparable data in neutral and acid media. Deeper knowledge of the solubilities of these compounds in alkaline media are required to support storage and processing operations for liquid and sludge radioactive nuclear wastes stored at the U.S. Department of Energy (DOE) Hanford and Savannah River Sites. A considerable part of these wastes, produced in plutonium production operations, are alkaline and accumulated in underground steel-lined tanks with volumes of hundreds of cubic meters. Processing and immobilization of alkaline radioactive wastes, specifically, their transformations to solid vitrified forms, are not performed in any country. Technologies for the necessary operations are in the development stage in the United States. Knowledge of the solubilities of the actinide and technetium hydroxo compounds is necessary for the development of vitrification processing technology of the alkaline radioactive wastes and for the fractionation of long-lived alpha-emitting transuranium elements and fission product technetium from the waste. This fractionation will decrease the amount of "long-lived" highly toxic wastes to be subjected to costly and long-term controlled storage.

The present program, arranged by representatives of the DOE, the Westinghouse Hanford Company, and the Institute of Physical Chemistry of the Russian Academy of Sciences, includes a study of the solubilities of tetra- and pentavalent Np, Pu, Am, and Tc hydroxo compounds in 0.5 to 14 M NaOH solutions. Also included are studies of the effects of a number of complex-forming and redox reagents present in the alkaline wastes on the solubilities of the radioactive solid compounds.

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2.0 LITERATURE DATA ON THE SOLUBILITIES OF Np Pu, Am, AND Tc HYDROXO COMPOUNDS IN ALKALINE SOLUTIONS

Data on the solubilities of Np, Pu, and Am hydroxo compounds in the III to VI oxidation states in alkaline media were first published in 1949 by the scientists of the Manhattan Project. These data have been confirmed, refined, and expanded by researchers from many countries. At present, only one review is available summarizing the solubility data for these compounds in alkaline media (Peretrukhin et al. 1995).

A brief survey of the solubility data for Np, Pu, and Am hydroxo compounds in 0.1 to 14 M NaOH solutions is presented.

2.1 TRIVALENT Np, Pu, AND Am HYDROXIDES

Trivalent actinide hydroxides have the composition $An(OH)_3 \cdot xH_2O$ and exhibit low solubilities in neutral and alkaline media. Neptunium and plutonium(III) hydroxides are unstable in alkaline media. Even in the absence of oxygen and other oxidants, they are oxidized to tetravalent hydroxides; $Np(OH)_3$ is oxidized rapidly, and $Pu(OH)_3$ is oxidized slowly (LaChappelle et al. 1949; Kraus and Dam 1949). Americium(III) hydroxide is thermodynamically stable in an alkaline medium. It is very slowly oxidized to $AmO_2 \cdot xH_2O$ with atmospheric oxygen and is rapidly oxidized by H_2O_2 and stronger oxidants (Penneman and Asprey 1955; and Penneman et al. 1961). According to the data of different authors, the solubility products of $Pu(OH)_3$ and $Am(OH)_3$ hydroxides are about 10^{-25} (Peretrukhin et al. 1995). The solubility of Pu(III) hydroxide in 5 M NH_4OH is 3.8×10^{-4} M (Cunningham 1954), and the solubility of Am(III) in 0.01 to 5 M NaOH is 1.6×10^{-6} M (Pazukhin and Kochergin 1989). The suggested chemical form of these alkali-dissolved hydroxides is a neutral $Am(OH)_3$ -type molecule, which is not amphoteric and does not form complexes with hydroxide.

2.2 TETRAVALENT Np, Pu, AND Am HYDROXIDES

Tetravalent "hydroxide" compounds are actually hydrous oxides and have the composition $An_2O \cdot xH_2O$. In alkaline media, the Np(IV) hydroxide is thermodynamically susceptible to oxidation by water. However, without oxidants, this reaction has a negligibly low rate (Peretrukhin et al. 1995). Plutonium(IV) and americium(IV) hydroxides are thermodynamically stable in aqueous alkaline media. According various data, the solubility products (K_{sp}) of $Np(OH)_4$ and $Pu(OH)_4$ range from 10^{-53} to 56) and $10^{-(62 \text{ to } 57)}$, respectively.

The solubility of $NpO_2 \cdot xH_2O$ in neutral media without complex-forming agents is about 10^{-8} M (LaChappelle et al. 1949). The solubility of $NpO_2 \cdot xH_2O$ in 0.8 M NaOH and 0.8 M Na_2SO_4 is 8.4×10^{-6} M (LaChappelle et al. 1949). Rai and Ryan (1985) showed that, under conditions excluding Np(IV) oxidation, the solubility of Np(IV) hydroxide in solutions

ranging from pH 6 to 14.2 is less than 10^{-3} M. The solubility also does not increase upon the addition of 0.01 M Na_2CO_3 . At NaOH concentration less than 0.8 M, no sign of Np(IV) hydroxide amphoterism, and the formation of Np(OH)_5 complexes, was found (Rai and Ryan 1985).

The solubility of the $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ and PuO_2 in water at pH 6 to 8 under conditions excluding oxidation was found to be 10^{-6} to 10^{-7} M (Nitsche 1991) and 10^{-7} to 10^{-9} M (Rai and Ryan 1982), respectively. Attempts to find literature data on the solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in NaOH solutions under conditions excluding oxidation were unsuccessful. The rate of oxidation of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ with atmospheric oxygen over 2 to 4 hours in 0.2 to 2 M NaOH is too slow to be measured reliably under specific conditions (Connick et al. 1949). The solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in 1 to 15 M NaOH solutions during long-term storage in the presence of atmospheric oxygen was studied (Delegard 1987). Under these conditions, the solubility was shown to increase with an increase in the alkali concentration (from about 10^{-8} M in 1 M NaOH to 10^{-3} M in 15 M NaOH). According to spectrophotometric data for the more concentrated solutions, the alkali-dissolved plutonium is mainly in the pentavalent state. The Pu(V) is explained by the oxidation of Pu(OH)_4 with oxygen and radiolysis products. The presence of carbonate and aluminate was found to increase the solubility of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ in NaOH solution.

2.3 Np(V) , Pu(V) , AND Am(V) HYDROXO COMPOUNDS

Compounds of composition AnO_2OH are formed upon precipitation of An(V) from acid solutions with a small excess of ammonia or alkali. At 0.1 to 0.5 M NaOH, $\text{NaNpO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ salts are formed; at higher NaOH concentrations, $\text{Na}_2\text{AnO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ salts are formed. Compounds of these types were obtained for Np(V) (Visyachscheva et al. 1984; and Cohen and Fried 1969), Pu(V) (Tananaev 1992), and Am(V) (Tananaev 1990a; and Tananaev 1991). The suggested forms of existence of these complexes in alkaline solutions are $[\text{AnO}_2(\text{OH})_2(\text{H}_2\text{O})_2]^-$ and $[\text{AnO}_2(\text{OH})_3(\text{H}_2\text{O})]^{2-}$, corresponding to the compositions found in solid phases, and, probably, $[\text{AnO}_2(\text{OH})_4]^{3-}$ (Peretrukhin et al. 1995; Delegard 1987; and Tananaev 1990b).

Data on the solubility of Np(V) in 1 M NaOH are varied: 6×10^{-4} M (Simakin et al. 1973), 1.2×10^{-4} M (Lierse et al. 1985), and 1.3×10^{-5} M (Neck et al. 1992). These differences are likely due to the metastability of the system and to the slow formation of colloids. No quantitative data on the solubilities of Pu(V) hydroxo compounds in alkaline solutions are published. However, the solubilities of these compounds were shown to increase, to $(3 \text{ to } 4) \times 10^{-3}$ M in 4 M NaOH, with increasing alkali concentration. This value remains constant for 2 to 3 hours but slowly decreases during storage (Bourges 1972; and Peretrukhin and Alekseeva 1974). The solubilities of Am(V) hydroxo compounds were determined to be 1.2×10^{-4} M in 0.46 M KOH and lower than 0.8×10^{-4} M in 5.3 M NaOH (Ivanov-Emin and Nisel'son 1960). In LiOH (Ermakov et al. 1977) or tetraalkylammonium hydroxide (Cohen and Fried 1969) solutions, the solubilities of pentavalent Np , Pu , and Am hydroxo

compounds are higher than those in analogous NaOH solutions by a factor of two to three. Exact data for these media are absent, however.

2.4 Np(VI), Pu(VI), AND Am(VI) HYDROXO COMPOUNDS

Upon precipitation with a small excess of alkali, hexavalent transuranium elements are likely to have the composition $AnO_3 \cdot xH_2O$. In weakly alkaline solutions, the solubility products of these compounds are comparable with those found for the uranium(VI) analogue; K_{sp} of 10^{-22} to 10^{-24} (Peretrukhin et al. 1995). Upon addition of a large excess of alkali, hexavalent Np, Pu, and Am display amphoteric behavior and form unidentified mixed compounds with hydroxide. The solubilities of Pu(VI) hydroxo compounds increase with increasing alkali concentration from 3.2×10^{-5} M in 1 M NaOH to 1×10^{-4} M in 10 M NaOH (Pérez-Bustamante 1965). The An(VI)-alkaline solution systems are metastable and show slow formation of the solid phase. Therefore, these systems may contain high Np(VI) and Am(VI) concentrations (up to 10^{-3} M), and still higher Pu(VI) concentrations, for some hours before formation of the solid phase. It is interesting to note in comparison that U(VI) hydroxo compounds (uranates and polyuranates) also give metastable solutions in sodium hydroxide media. Uranium(VI) concentrations in 1 M NaOH reach 10^{-3} M in the first 1 to 2 hours after precipitation under special conditions before slowly decreasing to 2×10^{-4} M (Abuzwida et al. 1991).

2.5 HEPTAVALENT Np, Pu, AND Am COMPOUNDS

Heptavalent Np and Pu solid-phase compounds of several types have been prepared: $MAnO_4 \cdot H_2O$, $M_3AnO_5 \cdot xH_2O$, and M_3AnO_6 where M is an alkali metal ion. Neptunium(VII) compounds and their alkaline solutions exhibit high stability and can be stored for months (Krot et al. 1977).

In alkaline solutions, plutonium(VII) is reduced by water. Plutonium(VII) solutions remain stable for several hours up to the point of noticeable accumulation of Pu(VI). Americium(VII) in alkaline solutions is reduced faster than Pu(VII). The solubilities of heptavalent Np and Pu in alkaline solutions are significantly higher than of hydroxides in the (III) to (VI) oxidation states. Thus, true 1 M NaOH solutions containing 5×10^{-2} M Np(VII) or Pu(VII), and 2 M LiOH solutions containing 0.2 M of Np(VII), can be obtained (Krot et al. 1977).

Studies of the solubilities of hexavalent and heptavalent Np, Pu, and Am are not included in the program of this work.

2.6 Tc(IV) AND Tc(V) HYDROXO COMPOUNDS

Pentavalent technetium in alkaline media is formed during the reduction of dissolved pertechnetate through a fast disproportionation of Tc(VI). Technetium(V) is stable in the absence of oxidants and reductants (Peretrukhin et al. 1995). However, no data are available on the separation of solid-phase Tc(V) hydroxo compounds from alkaline solutions, on their identification, or on their solubilities.

Solubility data for tetravalent technetium hydroxide, $\text{TcO}_2 \cdot n\text{H}_2\text{O}$, in neutral and weakly alkaline media have been summarized (Eriksen et al. 1992). At pH 7 to 10 and in the absence of complex-forming agents, the solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ is 10^{-9} to 10^{-8} M. Solubility increases an order of magnitude by increasing pH above 8.5. At pH 8 to 12 and in the presence of carbonate additives (up to 5 percent CO_2), the solubility of this hydroxide increases by 1 to 2 orders of magnitude (Eriksen et al. 1992; and Vikis et al. 1988). The suggested forms of existence of Tc(IV) at pH 8 to 11 are $\text{TcO}(\text{OH})_2$ and $[\text{TcO}(\text{OH})_3]^-$ hydroxo complexes; in the presence of carbonate ions, mixed hydroxocarbonate $[\text{Tc}(\text{OH})_3\text{CO}_3]^-$ -type complexes are formed (Eriksen et al. 1992). Data on the solubility of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ in 1 to 14 M NaOH are not available from the literature.

3.0 DETERMINATION OF THE SOLUBILITIES OF Np(IV) AND Pu(IV) HYDROXIDES

The purpose of this work was to study the solubilities of $\text{Np}(\text{OH})_4$ and $\text{Pu}(\text{OH})_4$ in alkaline solutions over a wide NaOH concentration range under conditions designed to exclude the oxidation of Np(IV) and Pu(IV) in the reaction media. In addition, the effects of a number of complex-forming reagents present in the Hanford alkaline wastes on the solubilities of Np(IV) and Pu(IV) hydroxides were studied.

3.1 EXPERIMENTAL PROCEDURES

The elements used in the experiments consisted primarily of the isotopes ^{237}Np and ^{239}Pu . The neptunium and plutonium were purified by precipitation as oxalates and by anion exchange (VP-1AP vinylpyridine resin of Russian manufacture was used).

The product nitric acid solutions of Np(IV) were evaporated with hydrochloric acid to dryness. The residue was dissolved in 4 M HCl and the neptunium adjusted to the tetravalent state with $\text{NH}_2\text{OH}\cdot\text{HCl}$. Then, Cs_2NpCl_6 was precipitated by addition of CsCl. The precipitate was filtered, washed with concentrated HCl and acetone, and dried in a desiccator. Stock solutions of Np(IV) were obtained as required by dissolving Cs_2NpCl_6 according to published procedures (Mefod'eva and Krot 1987). The amount of Cs_2NpCl_6 per experiment was 14.4 mg (0.02 mmol of neptunium).

Plutonium anion exchange eluate was adjusted to the (IV) state with H_2O_2 . Solutions of Pu(IV) hydroxide were prepared by adding Pu(IV) nitrate stock (0.02 mmol of Pu per experiment) to alkaline solutions with known NaOH concentrations.

All reagents were of chemical or special purity grade. The NaOH stock solutions were prepared at 16 and 1 M. The solubility of carbonate in concentrated alkali is about 0.01 M. The low carbonate solubility permitted storage of concentrated NaOH solutions in tightly closed plastic vessels for a comparatively long times without the formation of carbonate impurities in the working solution. The 1 M NaOH stock solution was prepared immediately before being required in the experiment. To exclude the introduction and presence of oxygen (an oxidant) in the stock acid and alkaline solutions, the solutions were deaerated by bubbling high-purity argon at room temperature. Reductants, up to 0.1 M $\text{Na}_2\text{S}_2\text{O}_4$ or hydrazine, also were introduced into the reaction volume as required. In accordance with published procedures (Mefod'eva et al. 1974), deaerated reaction solutions with Np(IV) hydroxide were covered with a layer of toluene to prevent oxidation by atmospheric oxygen.

The solid and liquid phases were mixed by bubbling argon at a flow rate of 0.7 to 1.0 mL per minute. Oxygen impurities in argon were removed using an absorbent (Voskresenskii 1973). The valent states of the actinides in solutions and solid samples were determined spectrophotometrically using a Shimadzu UV-3100 spectrophotometer (Japan).

Most radiometric analyses were conducted by the following procedure. A sample of the alkaline test solution was acidified with an aliquot of HNO_3 to about pH 3. To this solution, a solution of $\text{La}(\text{NO}_3)_3$ was added to give 2 mg La per mL concentration in the sample. Then, $\text{La}(\text{OH})_3$ was precipitated by addition of excess 1 M NaOH, the precipitate washed twice with a NH_4OH solution to pH 10, and the washed precipitate dissolved in 1 mL of 1 M HNO_3 . The acid solutions were dried; the alpha activities of the dried samples were measured with a solid scintillation detector using ^{237}Np and ^{239}Pu as standards. The lowest concentration of neptunium solution detectable with satisfactory accuracy using the lanthanum carrier procedure was about 10^{-6} M; for plutonium, the lowest detectable concentration was about 10^{-8} M.

Neptunium solution concentrations also were determined in selected more concentrated solution samples by gamma spectrometry. Neptunium concentrations at, or less than, 10^{-6} M were determined by alpha counting using a Beckman LS-6500LL liquid scintillation counter.

Literature data and studies in this laboratory show that in 0.5 to 14 M NaOH, Np(IV) is oxidized to the pentavalent state by dissolved oxygen. Taking this fact into account, the following procedure was used to study $\text{Np}(\text{OH})_4$ solubility in alkaline media. Two plastic vessels with bubbling apparatus and 20 mL volume were placed in the cell of a thermostat. Solution (10 mL) with identical and known NaOH and reductant concentrations was placed in each of these bubblers. The bubbling vessels were connected in series and a flow of argon (purified from oxygen) was passed through both vessels. The first vessel in the series served to saturate the Ar gas with the concentration of water vapor in equilibrium with the selected NaOH concentration. The saturation helped maintain constant alkali and reductant concentrations in the downstream bubbler vessel. As a further barrier to possible oxidation by atmospheric oxygen, 1 to 2 mL of toluene was added to the downstream bubbler to act as a floating cap on the test solutions.

Argon purging was conducted for about 15 to 20 minutes before the neptunium spike (a freshly prepared weakly alkaline solution of Np^{4+}) was injected by capillary into the downstream vessel. Upon introduction of the spike, a pinkish amorphous flocculent $\text{Np}(\text{OH})_4$ precipitate was observed.

After 3 hours' contact, the bubbling was stopped, and the mother liquor was separated from the precipitate while maintaining isolation from atmospheric oxygen with a layer of toluene. The mother liquor was thoroughly centrifuged and samples were taken. The Np valent states were determined spectrophotometrically and the Np solution concentrations determined.

Part of the solution for spectrophotometric study was acidified with 9.5 M HClO_4 so that the final H^+ solution concentration did not exceed 1 M. At 1 M acid, disproportionation of Np(V), a possible Np(IV) oxidation product, does not occur. The acidified sample was placed in a spectrophotometric cell (total volume 22 mL) with a 5 cm path length and the electron absorption spectrum was recorded.

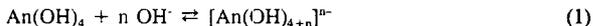
Neptunium(V) was not accumulated in supernatant solutions in detectable concentrations in the Np(IV) precipitation tests in 0.5 to 14 M NaOH and 0.1 M N₂H₅OH after 4 hours (Figure 3-1). However, spectrophotometric analysis of the solid phase, dissolved in 1 M HCl, always showed that 3 to 8 percent of the neptunium was pentavalent.

Because the Pu(OH)₄ precipitate in alkaline solutions containing 0.1 M N₂H₅OH is relatively stable to oxidation by atmospheric oxygen, the solubility test procedure was simplified and did not include special protection from air (the argon purge and toluene layer).

3.2 SOLUBILITIES OF Np(IV) AND Pu(IV) HYDROXIDES IN 0.5 TO 14 M NaOH

For Np(OH)₄, solution equilibrium is attained at 26 °C after about 150 minutes. Therefore, a contact time of 180 minutes was used in all experiments. For Pu(OH)₄, a different situation is observed. The metal concentration over the precipitate increases from the moment of the interaction between the alkaline solution and the Pu(IV) hydroxide, reaching a maximum after about 100 minutes, before decreasing (at about 180 minutes) and holding at a constant concentration (Figure 3-2). With further aging, the solution concentration again begins to increase. The increase continues for at least 72 hours with the aging of the precipitate, so that $C_{Pu} = C_0 t^{0.5}$; where C_{Pu} is the plutonium concentration at time, t , of contact of the hydroxide with the alkaline solution and C_0 is the initial plutonium concentration.

Table 3-1 and Figures 3-3 and 3-4 show the solubilities of Np(OH)₄ and Pu(OH)₄ in NaOH solutions. Neptunium and plutonium concentrations in the mother liquor increase with increasing NaOH concentration (Figures 3-3, 3-4, and 3-5). In analogy with published results (Sheka and Pevzner 1960), the following reaction appears to occur as alkali concentration increases:



This reaction results in the formation of a hydroxo complex. Formation of this complex can be described with a stability constant $K = \frac{[\text{An(OH)}_{4+n}]^{n-}}{[\text{An(OH)}_4][\text{OH}^-]^n}$. The solubility of the reaction product is higher than that of An(OH)₄. As a result, the neptunium and plutonium concentrations in the mother liquor increase with increasing NaOH concentration.

Figure 3-1. The Optical Absorption Spectrum of Saturated $\text{Np}(\text{OH})_4$ Solution After Acidification to 0.5 M HCl.

Spectrum recorded after 4 hours' contact in 4 M NaOH (5 cm path length; 26 °C).

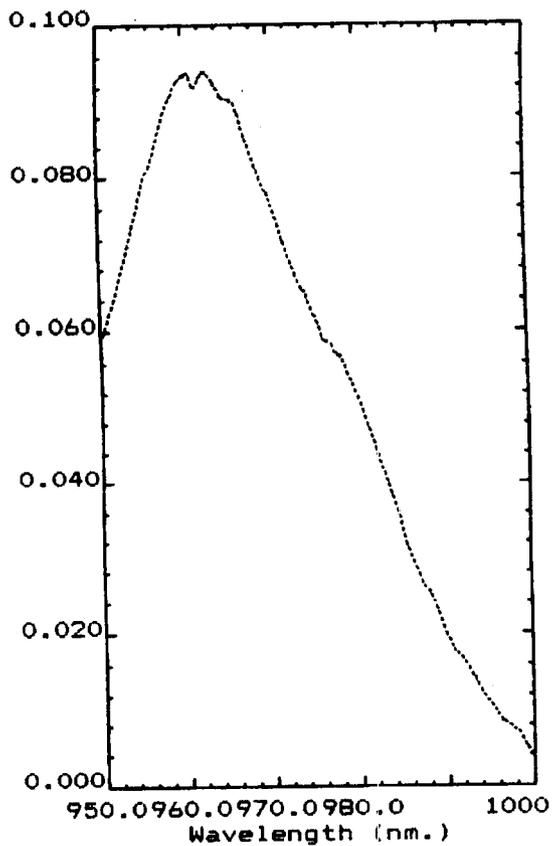


Figure 3-2. Change in Pu(IV) Concentration Above Pu(OH)₄ Solids as a Function of Time.

In 4 M NaOH at 28 °C.

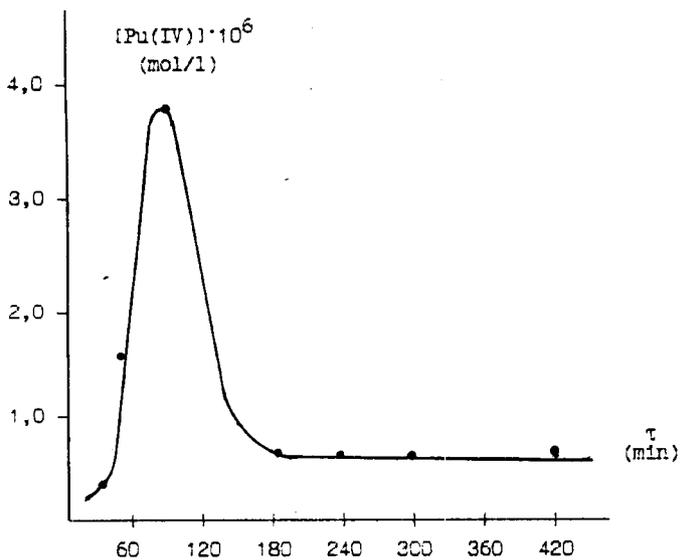


Table 3-1. Solubilities of $\text{Np}(\text{OH})_4$ and $\text{Pu}(\text{OH})_4$ in NaOH Solutions in the Presence of 0.1 M $\text{N}_2\text{H}_5\text{OH}$ ($T = 26 \pm 0.2$ °C).

No.	[NaOH], M	log [NaOH]	[Np(IV)], M	log [Np]	[Pu(IV)], M	log [Pu]
1	0.5	-0.30	3×10^{-7}	-6.52	1.4×10^{-8}	-7.82
2	1.0	0	5×10^{-7}	-6.30	6.7×10^{-8}	-7.18
3	2.0	0.30	1×10^{-6}	-6.00	2.3×10^{-7}	-6.64
4	4.0	0.60	4.6×10^{-6}	-5.33	5.8×10^{-7}	-6.24
5	6.0	0.79	1.0×10^{-5}	-4.96	2.5×10^{-6}	-5.71
6	8.0	0.90	1.3×10^{-5}	-4.89	3.4×10^{-6}	-5.47
7	9.9	1.00	1.8×10^{-5}	-4.74	5.0×10^{-6}	-5.30
8	14.1	1.15	2.1×10^{-5}	-4.69	9.8×10^{-6}	-5.01

Figure 3-3. Solubility of $\text{NpO}_2 \cdot n\text{H}_2\text{O}$ in Aqueous Solutions.

- 1 - In the presence of 0.1 M $\text{N}_2\text{H}_4\text{OH}$, present work;
- 2 - In the presence of 0.05 M $\text{Na}_2\text{S}_2\text{O}_4$ (Rai and Ryan 1985).

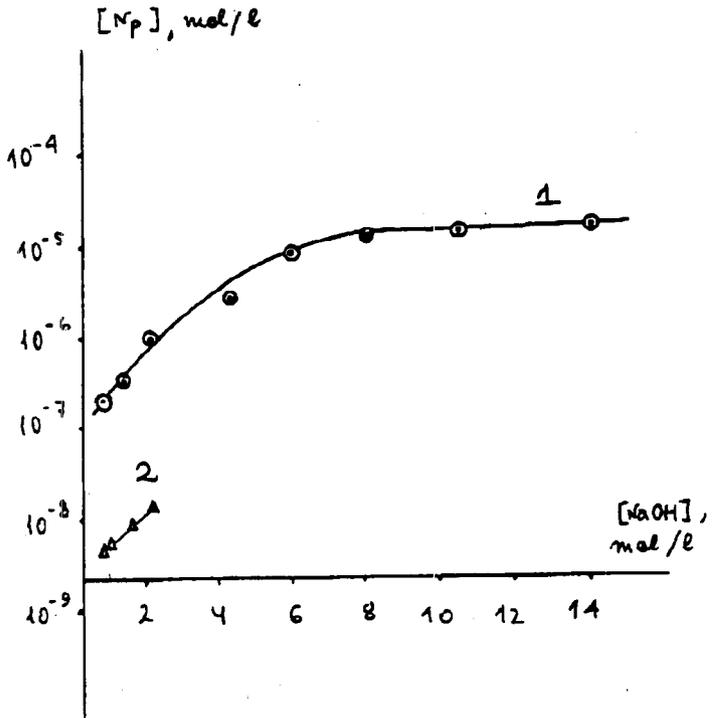


Figure 3-4. Solubility of $\text{PuO}_2 \cdot n\text{H}_2\text{O}$ in Aqueous Solutions.

- 1 - In NaOH solutions with 0.1 M $\text{N}_2\text{H}_5\text{OH}$, present work;
- 2 - In aerated NaOH solutions (Delegard 1987);
- 3 - In simulated waste (Karraker 1993).

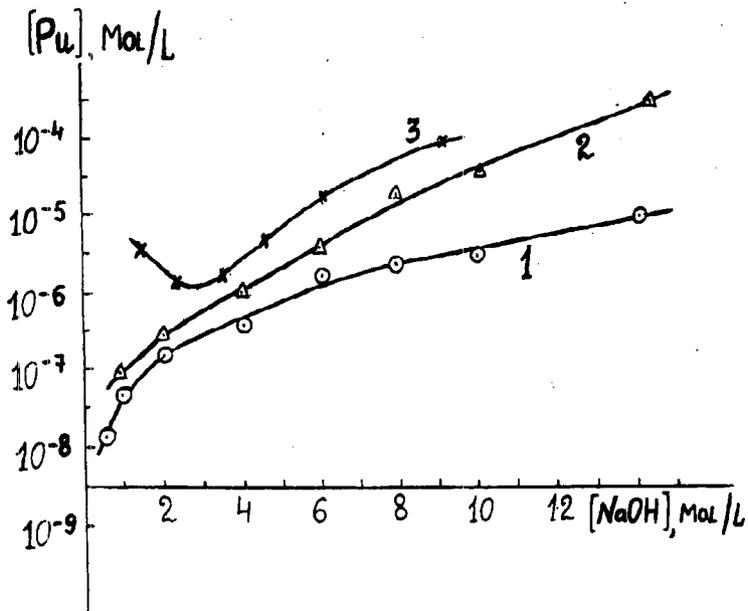
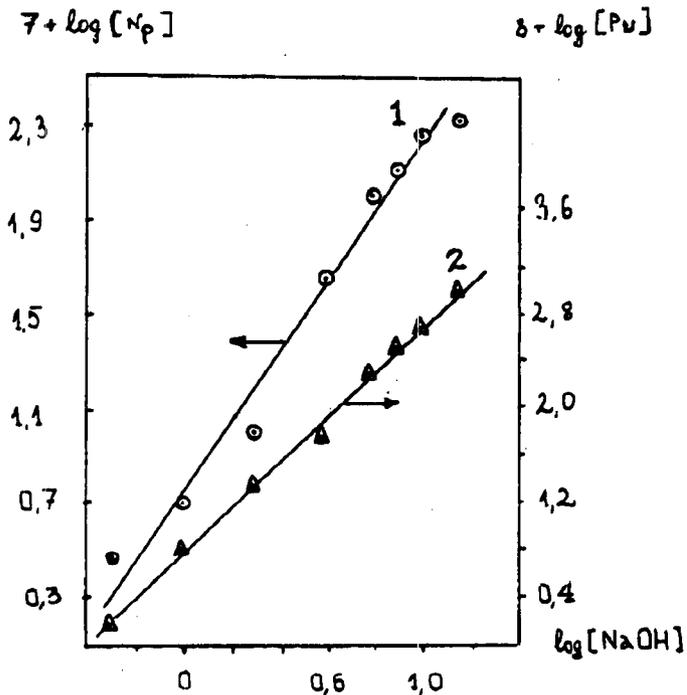


Figure 3-5. Actinide Concentrations Above Solid $\text{An}(\text{OH})_4$ as a Function of NaOH Concentration.

- 1 - $\text{Np}(\text{OH})_4$ in NaOH (26 °C);
- 2 - $\text{Pu}(\text{OH})_4$ in NaOH (26 °C).



The total solubility, S, of $\text{An}(\text{OH})_4$ in sodium hydroxide solution is the sum of the contributions of the neutral and charged species

$$S = [[\text{An}(\text{OH})_{4+n}]^{n-}] + [\text{An}(\text{OH})_4]. \quad (2)$$

The solubilities of $\text{An}(\text{IV})$ hydroxides in 1 to 14.1 M NaOH change from 10^{-7} to 10^{-5} M.

The $\text{Np}(\text{OH})_4$ or $\text{Pu}(\text{OH})_4$ neutral species concentration in water, which can be calculated from the solubility product, SP, of $[\text{An}^{4+}][\text{OH}^-]^4$ (Penneman et al. 1961; and Nitsche 1991), is lower than the solubilities found in NaOH by a factor of about 10^4 . Consequently, the $\text{An}(\text{OH})_4$ concentration is negligible relative to the hydroxo complex concentration. With this simplification, and substitution of equation (1) and the stability constant of the complex (Sheka and Pevzner 1960), equation (2) transforms to the following equation:

$$\log S = n \log [\text{OH}^-] + \log (K[\text{An}(\text{OH})_4]). \quad (3)$$

The slope, n, is the number of hydroxide ions involved in the interaction between $\text{An}(\text{OH})_4$ and NaOH. For $\text{Np}(\text{OH})_4$, n is near 1 (Figure 3-5). The slope is consistent with the reaction, $\text{Np}(\text{OH})_4 + \text{OH}^- \rightleftharpoons \text{Np}(\text{OH})_5$, and is compatible with published observations on the synthesis of the compound $\text{NH}_4\text{Np}(\text{OH})_5$ (Cousson et al. 1986).

For the $\text{Pu}(\text{OH})_4$ reaction, the number of hydroxide ions, n, is 2 (Figure 3-5). Therefore, $\text{Pu}(\text{OH})_6^{2-}$ appears to be the form of $\text{Pu}(\text{IV})$ dissolved in alkaline solutions. In this connection, it is useful to note that compounds of the formula $\text{M}_3\text{Ln}(\text{OH})_6$ can be prepared in alkaline solutions from $\text{Ln}(\text{OH})_3$, where Ln is Yb or Lu (Ivanov-Emin and Nisel'son 1960).

The preceding calculations and interpretations must remain approximate, however, because the effects of ionic activities and varying solution ionic strength were neglected.

3.3 EFFECTS OF CARBONATE, PHOSPHATE, FLUORIDE, OXALATE, CITRATE, EDTA, AND GLYCOLATE COMPLEX-FORMING AGENTS ON THE SOLUBILITIES OF $\text{Np}(\text{IV})$ AND $\text{Pu}(\text{IV})$ HYDROXIDES IN ALKALIS

The preceding section described the dependence of the solubilities of neptunium(IV) and plutonium(IV) hydroxides on the NaOH solution concentration. The purpose was to estimate the actinides' concentrations in Hanford Site high-level alkaline waste solutions and to determine the ionic forms of these actinides. However, to obtain more complete information on these issues, it is necessary to study the solubilities of $\text{Np}(\text{OH})_4$ and $\text{Pu}(\text{OH})_4$ in the presence of complex-forming reagents also present in the wastes. The effects of carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), fluoride (F^-), glycolate ($\text{HOCH}_2\text{CO}_2^-$), citrate ($\text{C}_6\text{H}_5\text{O}_7^{3-}$), EDTA (ethylenediaminetetraacetate), and oxalate ($\text{C}_2\text{O}_4^{2-}$) on the solubilities of tetravalent Np and Pu hydroxides were investigated. The test conditions were designed to exclude the formation and accumulation of $\text{Np}(\text{V})$ and $\text{Pu}(\text{V})$ in solution.

The solubilities of $\text{Np}(\text{OH})_4$ and $\text{Pu}(\text{OH})_4$ in alkaline media in the presence of complex-forming reagents were studied using the procedure described in the previous section. The only difference concerned the determination of Pu and Np concentrations in the presence of salts of organic acids (citrate, glycolate, oxalate, or EDTA). To prepare supernatant solution samples for alpha radiometric analysis, the aliquots containing these agents were heated to 200 °C to decompose the organic components. The heating prevented formation of stable soluble actinide organic complexes during coprecipitation of the actinides with lanthanum hydroxide. As an additional step, the purified samples deposited on metal counting planchets were calcined at 400 to 450 °C. With this treatment, thin layers (less than 100 $\mu\text{g}/\text{cm}^2$) were obtained on the planchets and resulted in increased radiometric counting accuracy.

Solutions with NaOH concentrations of 1.0 and 4.0 M were used in the experiments. The NaOH concentrations generally represent the conditions under which Hanford high-level wastes are stored. The choice of the concentrations of the complex-forming reagents was determined by the same reasoning. The Np and Pu tetravalent states were stabilized by adding $\text{N}_2\text{H}_5\text{OH}$ or $\text{Na}_2\text{S}_2\text{O}_4$ reductants (up to 0.05 M) to the alkaline solutions.

Tables 3-2 and 3-3, and Figures 3-6 through 3-9, show the results of the experiments with complex-forming reagents and their effects on the $\text{Np}(\text{IV})$ and $\text{Pu}(\text{IV})$ solubilities in alkali.

The addition of complex-forming reagents to alkaline solutions generally increases the solubilities of $\text{Np}(\text{IV})$ and $\text{Pu}(\text{IV})$ hydroxides. As expected, the increase in the $\text{Pu}(\text{IV})$ hydroxide solubility in alkaline solutions in the presence of complex-forming reagents is much higher than that for $\text{Np}(\text{OH})_4$. The organic agents (EDTA, citrate, and glycolate) are the most effective of the tested materials in increasing solubility. The effect of complex-forming reagents on the solubilities of these actinides decreases with increasing alkali concentration.

3.4 COMPARISON OF RESULTS WITH LITERATURE DATA

Results of the current $\text{Np}(\text{IV})$ hydroxide solubility studies are compared with those of Rai and Ryan (1985) in Figure 3-3. The increasing solubility of $\text{Np}(\text{IV})$ hydroxide with increasing hydroxide concentration is evident in each of these studies conducted at 0.84 to 2.1 M NaOH (Rai and Ryan 1985) and 0.5 to 14 M NaOH. However, the solubility found by Rai and Ryan (1985) at about 1 M NaOH, 5.5×10^{-9} M, is much lower than the value found in the present study, 5.0×10^{-7} M. The difference can be explained by the lower content of soluble oxygen in the tests of Rai and Ryan (1985); experiments were performed with both an argon-filled glovebox and with strong antioxidants (0.05 M $\text{Na}_2\text{S}_2\text{O}_4$). Evidently, better purification from oxygen was obtained by Rai and Ryan (1985) than was obtained in the present study. Despite use of a hydrazine reductant, argon purging, and a floating toluene barrier to prevent oxidation to the more soluble $\text{Np}(\text{V})$ species in the $\text{Np}(\text{IV})$ hydroxide solubility tests (Section 1.1), $\text{Np}(\text{V})$ still was detected in the solid phase.

Table 3-2. The Effect of Complexing Agents on the Solubility of $\text{Np}(\text{OH})_4$ in Alkaline Media at 26 °C.

Agent Added	Concentrations of Agent, M	$\text{Np}(\text{OH})_4$ Solubility, M			Concentration Enhancement	
		1 M NaOH	4 M NaOH	[Np] Ratio in 4 M/1 M NaOH	in 1 M NaOH	in 4 M NaOH
None	--	5×10^{-7}	4.6×10^{-6}	9.2	--	--
Na_2CO_3 carbonate	0.05	1.3×10^{-5}	5.0×10^{-5}	3.8	26	11
	0.5	1.3×10^{-5}	5.7×10^{-5}	4.4	26	12
Na_2HPO_4 phosphate	0.01	6.5×10^{-5}	1.2×10^{-4}	1.8	130	26
	0.05	1.4×10^{-5}	1.1×10^{-4}	7.8	28	24
$\text{KF} \cdot 2\text{H}_2\text{O}$ fluoride	0.02	3.8×10^{-5}	1.0×10^{-4}	2.6	76	22
	0.1	1.4×10^{-5}	2.0×10^{-4}	14.3	28	43
HOCH_2CO_2 glycolate	0.1	1.4×10^{-4}	1.2×10^{-4}	0.9	280	26
	0.5	1.6×10^{-4}	3.2×10^{-4}	1.0	320	70
$\text{C}_6\text{H}_8\text{O}_7^{3-}$ citrate	0.03	1.5×10^{-4}	1.4×10^{-4}	1.0	300	30
	0.3	1.0×10^{-4}	2.7×10^{-4}	2.7	200	60
Na_2EDTA Trilon B	0.05	1.5×10^{-4}	1.4×10^{-4}	0.9	300	30
	0.2	2.1×10^{-4}	2.2×10^{-4}	1.0	420	48
$\text{H}_2\text{C}_2\text{O}_4$ oxalate	0.03	4.4×10^{-5}	1.5×10^{-4}	3.4	88	33
	0.075	8.1×10^{-5}	2.2×10^{-4}	2.7	160	28

Table 3-3. The Effect of Complexing Agents on the Solubility of $\text{Pu}(\text{OH})_4$ in Alkaline Media at 26 °C.

Agent Added	Concentrations of Agent, M	Pu(OH) ₄ Solubility, M			Concentration Enhancement	
		1 M NaOH	4 M NaOH	[Pu] Ratio in 4 M/1 M NaOH	in 1 M NaOH	in 4 M NaOH
None	--	6.7×10^{-8}	5.8×10^{-7}	8.6	--	--
Na ₂ CO ₃ carbonate	0.05	3.5×10^{-7}	9.6×10^{-7}	2.7	5.2	1.6
	0.5	1.1×10^{-6}	4.6×10^{-6}	4.2	16	7.9
Na ₂ HPO ₄ phosphate	0.01	3.8×10^{-7}	1.3×10^{-6}	3.4	5.7	2.2
	0.05	5.7×10^{-7}	3.1×10^{-6}	5.4	8.5	5.3
KF·2H ₂ O fluoride	0.02	2.7×10^{-7}	2.3×10^{-7}	0.9	4.0	0.4
	0.1	2.6×10^{-7}	3.2×10^{-7}	1.2	3.9	0.6
HOCH ₂ CO ₂ glycolate	0.1	1.8×10^{-6}	8.8×10^{-7}	0.5	27	1.5
	0.5	1.9×10^{-6}	1.2×10^{-6}	0.6	28	2.0
C ₆ H ₅ O ₇ ³⁻ citrate	0.03	1.8×10^{-6}	1.1×10^{-6}	0.6	27	1.9
	0.3	1.7×10^{-6}	1.1×10^{-6}	0.6	25	1.9
Na ₂ EDTA Trilon B	0.05	1.9×10^{-6}	2.0×10^{-7}	0.1	28	0.3
	0.2	1.7×10^{-6}	1.0×10^{-6}	0.6	25	1.7
H ₂ C ₂ O ₄ oxalate	0.03	4.2×10^{-7}	2.2×10^{-6}	5.2	6.2	3.8
	0.075	1.8×10^{-7}	1.2×10^{-6}	6.6	2.7	2.1

Figure 3-6. The Solubility of $\text{Np}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ in 1 M NaOH and 0.05 M $\text{Na}_2\text{S}_2\text{O}_4$ with Complexing Agents.

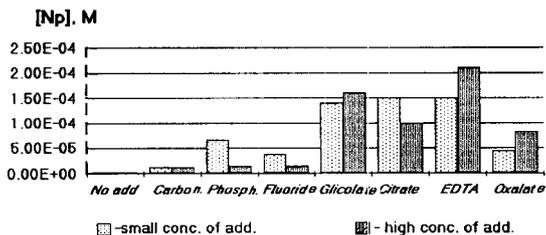


Figure 3-7. The Solubility of $\text{Np}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ in 4 M NaOH and 0.05 M $\text{Na}_2\text{S}_2\text{O}_4$ with Complexing Agents.

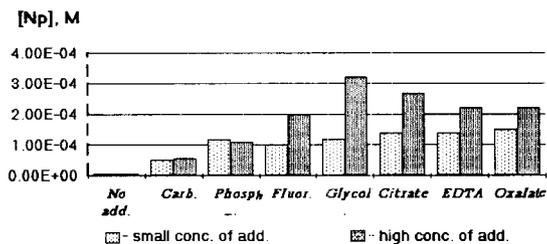


Figure 3-8. The Solubility of $\text{Pu}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ in 1 M NaOH and 0.04 M $\text{N}_2\text{H}_5\text{OH}$ with Complexing Agents.

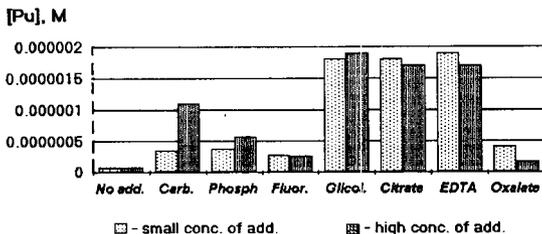
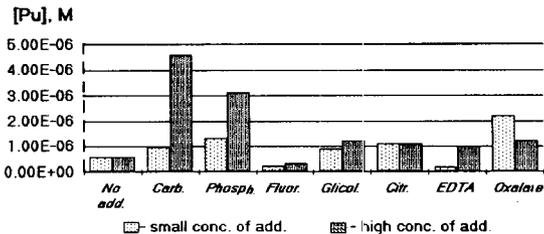


Figure 3-9. The Solubility of $\text{Pu}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ in 4 M NaOH and 0.04 M $\text{N}_2\text{H}_5\text{OH}$ with Complexing Agents.



Results of the present studies of Pu(IV) hydroxide solubility are compared with those of Delegard (1987) and Karraker (1993) in Figure 3-4. For a given NaOH concentration, the present values are 3- to 10-times lower than those of Delegard (1987) and 7- to 30-times lower than those of Karraker (1993). The higher solubilities reported in the literature can be explained also by oxidation. In this case, oxidation of Pu(IV) to Pu(V) or Pu(VI) occurs. Both Pu(V) and Pu(VI) form compounds whose solubilities are higher than those of Pu(IV). Neither Delegard (1987) nor Karraker (1993) excluded oxygen and both proposed that Pu(IV) oxidation occurred in their systems. In the present experiments, the effect of dissolved oxygen has been eliminated by use of hydrazine. The solubility of Pu(IV) hydroxide in the present study (6.7×10^{-8} M) is approaching, but still somewhat higher than, the solubility of Np(IV) hydroxide (5.5×10^{-9} M) reported by Rai and Ryan (1985).

4.0 DETERMINATION OF THE SOLUBILITIES OF An(V) HYDROXO COMPOUNDS IN 0.5 TO 14.0 M NaOH

4.1 EXPERIMENTAL PROCEDURES

The Np(V) salt $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ was prepared according to published procedures (Visyachscheva et al. 1984) by storing $\text{NpO}_2\text{OH} \cdot x\text{H}_2\text{O}$ in 5 M NaOH for eight days.

The precipitate was centrifuged, washed several times with a 50 percent aqueous ethanol solution followed by ethanol, and dried in a desiccator.

The Pu(V) salt $\text{Na}_2\text{PuO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ was obtained by chemically reducing a solution of Pu(VI) in 5.8 M NaOH. To coagulate the precipitate, the reaction mixture was warmed 10 minutes on a water bath. The reductant used, $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$, was selected based on the findings of Shilov and colleagues (1996). According to these data, at greater than 5 M NaOH, hydrazine hydrochloride does not reduce Pu(VI) to Pu(IV) even at high temperature.

To assure further that Pu(IV) would not form by reduction, the reductant was added at stoichiometric or lower quantities. The Pu valent states were determined spectrophotometrically. After the addition of the hydrazine, the color of the Pu(VI) solution rapidly changed from green to yellowish. The optical electron absorption spectrum of the solution (Figure 4-1) coincides with that of alkaline Pu(V) solution recorded previously (Delegard 1987; and Bourges 1972).

Heating the solution for about 10 minutes resulted in the formation of a mouse-gray $\text{Na}_2\text{PuO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ precipitate. The spectrum of the mother liquor (Figure 4-2) is similar to that of the stock solution. This indicates the presence of a small residual amount of Pu(VI) after the precipitation. The Pu(V) hydroxide was dissolved in $\sim 1 \text{ HClO}_4$. The spectrum of this solution shows absorption bands at 477 and 620 nm, assigned to the hydrated Pu^{4+} cation, and a peak at 831 nm, assigned to the plutonyl cation (Figure 4-3). These spectrophotometric data yield a calculated Pu(IV)/Pu(VI) concentration ratio close to unity. This shows that $\text{Na}_2\text{PuO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ does not contain any $\text{Pu}(\text{OH})_4$ or $\text{PuO}_2(\text{OH})_2$ impurities.

The salts of pentavalent americium were obtained by ozonizing a suspension of $\text{Am}(\text{OH})_3$ in 0.1 M NaOH and subsequently reducing Am(VI), formed after the ozonation, with a stoichiometric quantity of NaNO_2 . The identification of the compounds was carried out using X-ray diffraction analysis with a Guinier KhDS-70 camera (CuK_α radiation) on a Philips diffractometer (Germany).

Figure 4-1. The Optical Electron Spectrum of Plutonium(VI) and (V) in NaOH Solutions.

- 1 - Spectrum of 9.3×10^{-3} M Pu(VI) in 5.8 M NaOH after injection of $N_2H_4 \cdot 2HCl$ solution to 7.0×10^{-3} M final concentration;
- 2 - Spectrum of 8.8×10^{-4} M Pu(V) in 15 M NaOH solution (Delegard 1987).

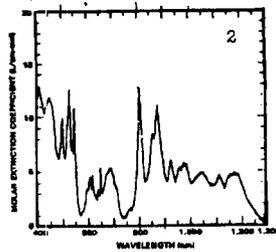
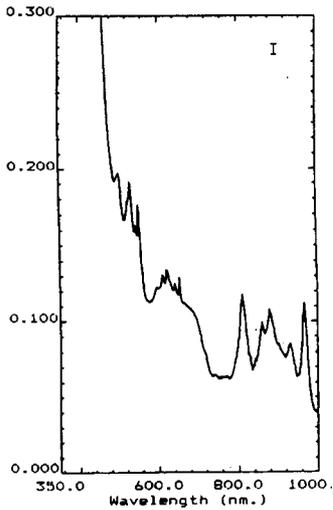


Figure 4-2. The Optical Electron Absorption Spectrum of Plutonium Solutions.

1 cm path length; 25 °C

- 1 - Spectrum of 9.0×10^{-3} M Pu(VI) in 5.8 M NaOH solution.
- 2 - Spectrum of mother liquor after precipitation of Pu(V) hydroxide in 5.8 M NaOH solution.

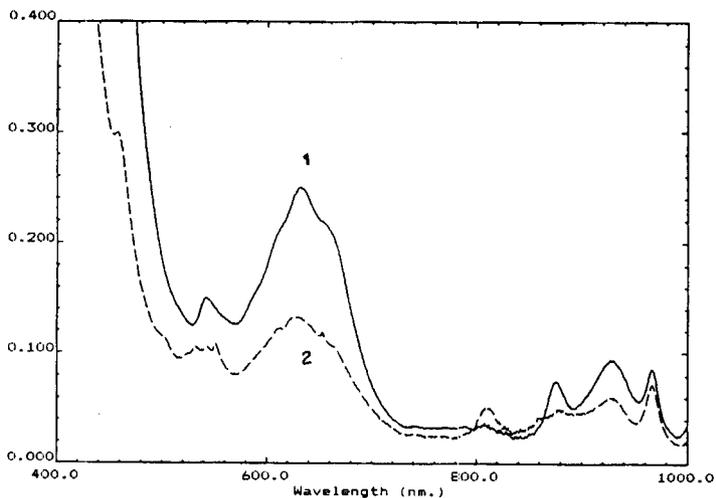
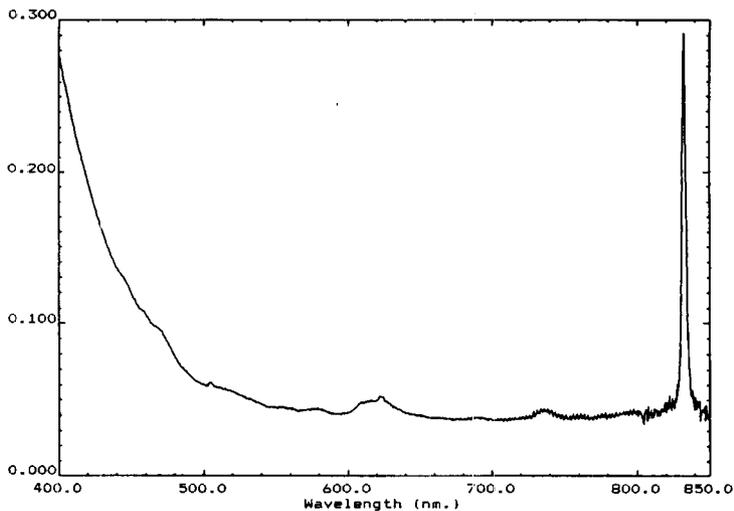


Figure 4-3. The Optical Electron Absorption Spectrum of Dissolved Plutonium Solids.

Solids prepared by reaction of 2.6×10^{-2} M Pu(VI) with 7.3×10^{-3} M $N_2H_4 \cdot 2HCl$; solids separated and dissolved in 1 M $HClO_4$.



Identical procedures were used to study the solubilities of the Np(V), Pu(V), and Am(V) hydroxo compounds. First, 0.04 mmol portions of the appropriate actinide hydroxo compound were placed in 7-mL plastic test tubes and alkaline solution of known concentration was added. The test tubes were tightly closed and shaken. After 72 hours' contact time, the precipitates and supernatant solutions were separated by centrifugation and the mother liquor analyzed for actinide concentration by radiometry.

To prepare the solutions for radiometric analysis, a sample of the mother solution was acidified with HNO₃ to about pH 3 and a solution of La(NO₃)₃ was added (to 2 mg La per mL). The La(OH)₃ hydroxide carrier was precipitated with an appropriate amount of 1 M NaOH, washed twice with NH₄OH solution to about pH 10, and dissolved with about 1 mL of 0.1 M HNO₃. The activity of the dried samples was measured with a scintillation α -counter using ²³⁷Np as a standard. The lowest concentration of neptunium solutions detectable by this method is about 10⁻⁶ M.

Because pentavalent actinides do not fully coprecipitate with La(OH)₃, a reductant was added to the acid solution prior to the precipitation and the solution heated on a water bath for 30 minutes. Neptunium solution concentrations also were determined by measuring low ²³⁷Np γ activities through the use of semiconductor γ -spectrometry. The semiconductor γ -spectrometer consisted of a DGDK-63V germanium-lithium detector, a PUG-1K preamplifier, a BUI-3K amplifier, and an AMA-03F pulse analyzer (all Russian production). To decrease the instrument background, the detector was covered with a shield consisting of 1 cm steel, 10 cm lead, and 16 cm polyethylene. The Np activity was determined from the 86.5 keV line (emission probability 12.6 percent). The lowest neptunium concentration that can be measured using this method is 30 Becquerel (about 1.2 μ g Np) per sample.

4.2 SOLUBILITY OF Np(V) HYDROXO COMPOUNDS IN ALKALINE SOLUTIONS

The solubility of Np(V) hydroxo compounds increased from about (1 to 6) $\times 10^{-4}$ M as alkali concentration increased from 0.5 to 17.5 M (Figures 4-4 and 4-5, Table 4-1).

Figure 4-4. Actinides Concentration Above An(V) Solids as a Function of NaOH Concentration.

- 1 - Np(V);
- 2 - Pu(V);
- 3 - Am(V);
- 4 - Np(V) in evaporated synthetic waste (Karraker 1994).

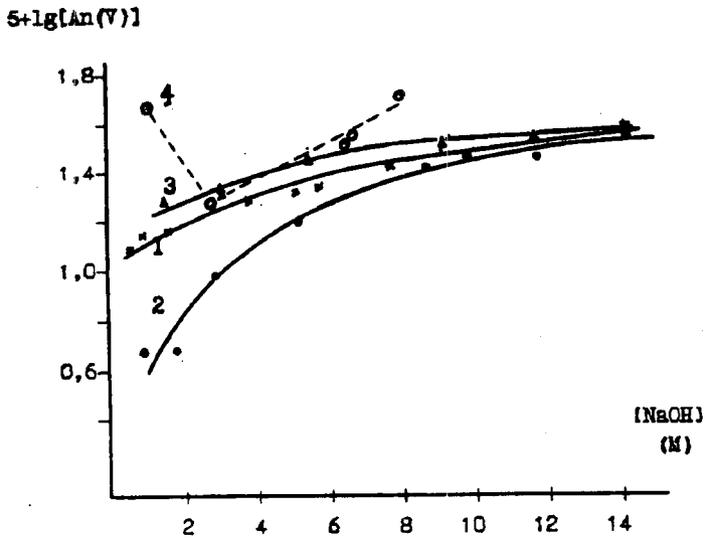


Figure 4-5. Np(V) Compound Solubility Versus NaOH Chemical Activity.

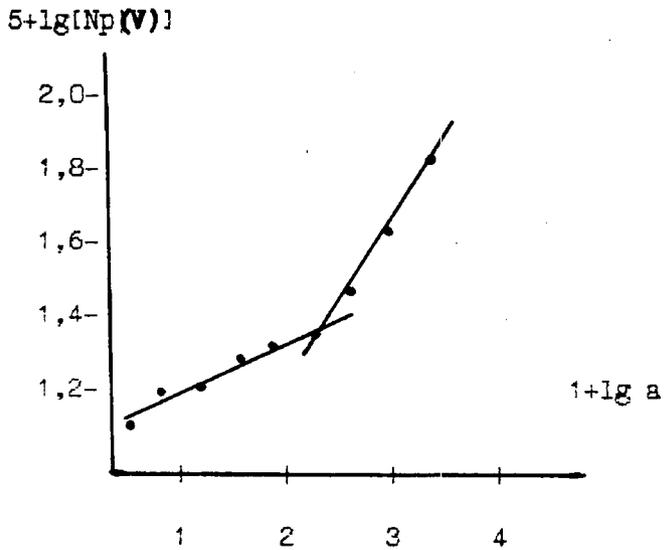


Table 4-1. Solubilities of Np(V) Hydroxo Compounds in NaOH Solutions.
(72 hours' contact time; 25 ± 2 °C)

Number	[NaOH], M	$\log a_{\text{NaOH}}$ *	[Np(V)], M	$\log [\text{Np(V)}]$
1	0.5	-0.50	1.3×10^{-4}	-3.89
2	1.1	-0.13	1.6×10^{-4}	-3.80
3	2.0	0.15	1.5×10^{-4}	-3.82
4	4.0	0.53	1.8×10^{-4}	-3.74
5	6.0	0.90	2.0×10^{-4}	-3.70
6	7.9	1.23	2.2×10^{-4}	-3.66
7	10.1	1.55	2.6×10^{-4}	-3.59
8	14.0	2.01	3.7×10^{-4}	-3.43
9	17.5	2.36	5.6×10^{-4}	-3.25

Note:

* a_{NaOH} is the chemical activity of NaOH.

Plots of either Np(V) concentration versus NaOH concentration or logarithm Np(V) concentration versus logarithm of NaOH chemical activity (a_{NaOH}) are non-monotonic. The logarithmic curve of the Np(V) hydroxo compounds' solubility versus a_{NaOH} (Figure 4-5) can be arbitrarily decomposed into two straight lines with different slopes. The two slopes indicate the occurrence of two processes dependent on NaOH concentration. This observation can be explained by the transformation of $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ to $\text{NaNpO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ at less than 6 M NaOH. An unidentified compound, whose solubility at high NaOH concentrations is greater than that of the initial hydroxide compound, also was observed.

The transformation of $\text{M}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ to $\text{MNpO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ (where M is an alkali metal) on contact with weakly alkaline solutions has been already described (Visyachscheva et al. 1984). At high alkali concentrations, $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ decomposes. This transformation is supported by X-ray powder diffraction evidence (Figures 4-6 and 4-7). Therefore, the increase in the solubility of $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ with increasing NaOH concentration may be related to changes in the structure of the initial hydroxide perhaps by change in the number of water molecules (x) in the crystal hydrate. Taking into account published findings (Sheka et al. 1960), further reaction appears to occur in the solid phase as alkali concentration increases:

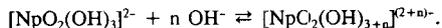


Figure 4-6. X-ray Powder Diffraction Diagrams of Np(V)-Hydroxide Compounds at Low NaOH Concentrations.

- 1 - $\text{NaNpO}_2(\text{OH})_2 \cdot x\text{H}_2\text{O}$ - (Visyachscheva et al. 1984);
- 2 - $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ after precipitation and storage in 5 M NaOH solution for 8 days.

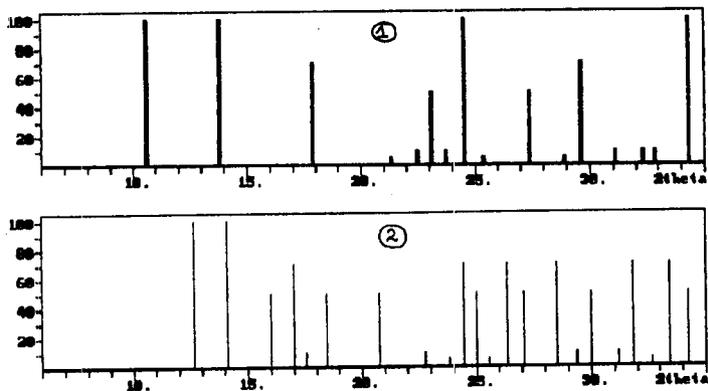
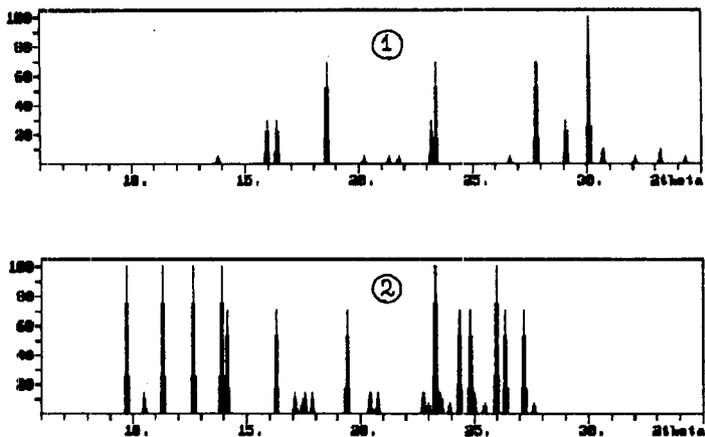


Figure 4-7. X-ray Powder Diffraction Diagrams of Np(V)-Hydroxide Compounds at High NaOH Concentrations.

- 1 - Compound from 14 days' storage of $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ in 14.0 M NaOH;
- 2 - Compound from 14 days' storage of $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ in 17.5 M NaOH.



This reaction forms a hydroxo complex with the stability constant

$$K = \frac{[[\text{NpO}_2(\text{OH})_{3+n}]^{(2+n)-}]}{([\text{NpO}_2(\text{OH})_3]^{2-}[\text{OH}^-]^n)} \quad (4)$$

The solubility of the salt of the product of this reaction is higher than that of $\text{Na}_2\text{NpO}_2(\text{OH})_3$ and leads to increased neptunium concentration with increased NaOH concentration.

The total solubility of the Np(V) salts in NaOH solution can be expressed:

$$S = [[\text{NpO}_2(\text{OH})_{3+n}]^{(2+n)-}] + [[\text{NpO}_2(\text{OH})_3]^{2-}] \quad (5)$$

The second term in the sum is small at high NaOH concentrations and can be neglected. Taking this into account, substituting from equation (4), and following the method described in the technical literature (Sheka and Pevzner 1960), equation (5) can be reconstructed to the equation of a straight line:

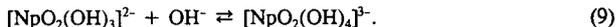
$$S = [[\text{NpO}_2(\text{OH})_{3+n}]^{(2+n)-}] = K \cdot [[\text{NpO}_2(\text{OH})_3]^{2-}] [\text{OH}^-]^n \quad (6)$$

$$\log S = n \log [\text{OH}^-] + \log (K \cdot [[\text{NpO}_2(\text{OH})_3]^{2-}]) \quad (7)$$

The slope, n , of this curve equals the number of OH^- ions involved in the interaction between $[\text{NpO}_2(\text{OH})_3]^{2-}$ and NaOH. As shown in Figure 4-5, n is close to 1. This suggests that in solutions with a high alkali concentration, the following reaction takes place:



or, in the ionic-molecular form,



The existence of the reaction described in (9) is corroborated by previous studies based on the electron absorption spectra of alkaline solutions of Np(V) (Tananaev 1990b) and the solid-phase interaction between $\text{Na}_2\text{NpO}_2(\text{OH})_3$ and NaOH (Tananaev 1991).

The solubilities observed for $\text{Na}_2\text{NpO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ are consistent with other reported data (Simakin et al. 1973).

4.3 SOLUBILITY OF Pu(V) HYDROXO COMPOUNDS IN ALKALINE SOLUTIONS

The solubilities obtained with $\text{Na}_2\text{PuO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ starting material are given in Table 4-2.

Table 4-2. Solubilities of Pu(V) Compounds in NaOH Solutions.
(starting compound $\text{Na}_2\text{PuO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$; 72 hours' contact time; 25 ± 2 °C)

Number	[NaOH], M	[Pu(V)], M
1	0.6	0.5×10^{-4}
2	2.0	0.5×10^{-4}
3	2.9	1.0×10^{-4}
4	5.8	1.6×10^{-4}
5	8.8	2.6×10^{-4}
6	11.7	2.8×10^{-4}
7	14.0	3.6×10^{-4}

Figure 4-4 shows that the solubilities of the plutonium compound(s) formed from $\text{Na}_2\text{PuO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ in less than 6 M NaOH are smaller than those of the neptunium compound. The plutonium concentration significantly increases with increasing NaOH concentration and approaches the Np(V) concentration under the specified conditions. The lower solubilities of the plutonium compound(s) compared with those of neptunium are not expected. This behavior may be explained, however, by plutonium disproportionation [to form Pu(IV)] and the instability of the $\text{Na}_2\text{PuO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ with time.

4.4 SOLUBILITY OF Am(V) AND Am(III) HYDROXO COMPOUNDS IN ALKALINE SOLUTIONS

During the 2 to 2.5-hour ozonation of 0.02 mmol $\text{Am}(\text{OH})_3$ in 0.01 M NaOH, the hydroxide precipitate dissolves to form a yellow-brown Am(VI) solution. Addition of NaNO_2 reductant stabilizes americium in the pentavalent state in the form of the salt of a hydroxo complex. The Am(V) salt crystallizes much faster than the neptunium and plutonium analogues. Crystalline precipitates can be obtained within three hours after precipitate coagulation. In addition, $\text{M}_2\text{AmO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ compounds (M is alkali metal) are formed even at about 0.5 M alkali (Tananaev 1990a). These findings indicate that the solubility of $\text{Na}_2\text{AmO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ at 1 to 2 M NaOH (Table 4-3) is higher than those of the analogous pentavalent neptunium and plutonium hydroxo compounds (Figure 4-4). Solubility data also are given for solids precipitated by addition of Am(III) solution to NaOH solution and for pre-formed and aged (by boiling) $\text{Am}(\text{OH})_3$ solids added to NaOH solution.

Table 4-3. Solubilities of Am(V) and Am(III) Compounds in NaOH Solutions. (starting materials $\text{Na}_2\text{AmO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$, Am(III) solution, and $\text{Am}(\text{OH})_3$; 72 hours' contact time; 25 ± 2 °C)

Number	[NaOH], M	[Am(V)], M	[Am(III)], M	
			Am(III) in NaOH mother solution	Am(OH) ₃ (s) aged by 3 hours' boiling
1	1.6	2.0×10^{-4}	--	--
2	2.9	2.2×10^{-4}	--	--
3	5.8	2.6×10^{-4}	--	--
4	8.8	2.7×10^{-4}	--	--
5	11.7	2.9×10^{-4}	--	--
6	1.0	--	6.9×10^{-6}	5.9×10^{-7}
7	5.0	--	6.0×10^{-6}	3.6×10^{-7}

According to these data, the solubility of the compound(s) formed from $\text{Na}_2\text{AmO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ is much higher than that of $\text{Am}(\text{OH})_3$, whether originating from Am(III) precipitation or from pre-formed $\text{Am}(\text{OH})_3$ solids. The solubilities of the Am(III) hydroxide hardly change with changing the NaOH concentration (1 to 5 M) and are close to the $(3 \text{ to } 4) \times 10^{-6}$ M solubilities reported elsewhere (Pazukhin and Kočergin 1989).

4.5 COMPARISON OF RESULTS WITH LITERATURE DATA

The solubility of Np(V) compounds in 0.5 to 14 M NaOH found in the present study are compared in Figure 4-4 with the concentrated simulated waste results of Karraker (1994). The solubility at 3 M NaOH reported by Karraker (1994) is 1.9×10^{-4} M, exceeding slightly the value 1.6×10^{-4} M found in the present studies. At 8 M NaOH, Karraker (1994) finds about 4.6×10^{-4} M Np; the present study finds about half that (2.3×10^{-4} M). Karraker (1994) proposes that partial air oxidation of Np(V) occurred during boiling and concentration of the simulated waste; in the present studies, introduction of atmospheric oxygen was diminished by nitrogen purging and capping of the test vessels.

In summary, analysis and comparison of the present findings with those of the technical literature indicate that the solubilities of Np(IV), Pu(IV), and Np(V) hydroxo compounds can be increased by oxidation to higher, and more soluble, oxidation states.

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5.0 DETERMINATION OF Tc(IV) and Tc(V) HYDROXO COMPOUND SOLUBILITY IN 0.5 TO 15 M NaOH SOLUTIONS

5.1 EXPERIMENTAL PROCEDURES

The principal forms of existence of technetium in alkaline aqueous solutions in the presence of excess reductants are hydrated technetium(IV) and (V) oxides (Peretrukhin et al. 1995; and Spitsyn and Kuzina 1981). A priori, it can be suggested that the most suitable method for a study of the solubilities of the technetium oxides would be by liquid scintillation spectrometry measurements of the β activity concentrations of saturated solutions of these oxides. Because the Institute of Physical Chemistry laboratory did not have a liquid scintillation counter, the measurements of the soft β radiation of technetium-99 were conducted using a Tesla NZQ 605 dish $\alpha/\beta/\gamma$ automatic counter (Czechoslovakia origin). It is noted that accurate measurement of the soft β radiation of ^{99}Tc (maximum energy, E_{max} , is 300 keV; Spitsyn and Kuzina 1981) without correction for absorption by the associated alkali salt is impossible.

To correct for the β absorption, a number of reference solutions with known Tc and NaOH concentrations were prepared. Aliquots of the reference solutions (0.01 mL volume) were deposited on filtration paper targets placed on steel supports and also directly on steel targets for radioactivity measurements. All samples were dried in air for one day and radiometrically counted for β activity using the $\alpha/\beta/\gamma$ automated counter. The results with best reproducibility were obtained for samples deposited on the paper targets because the surface distribution of Tc and NaOH was the most uniform (Figure 5-1 and 5-2). Therefore, this method was adopted for determinations of technetium concentration.

The averaged relative absorption coefficients for all reference solutions studied are shown in Table 5-1. For comparison, Table 5-1 also shows analogous data for neutral aqueous solutions of KTcO_4 without macrocomponents. These coefficients were used to correct for β activity absorption by macrocomponents in the studied solutions.

Table 5-1. ^{99}Tc β -Activity Absorption Coefficients for 0.01 mL Solution Deposited on Paper Targets.

[NaOH], M	Concentration coefficients, $\text{M}(^{99}\text{Tc})/\text{count}$	Relative Coefficients
0	0.11×10^{-7}	1
0.41	1.10×10^{-7}	10
3.60	1.33×10^{-7}	12
7.12	1.65×10^{-7}	15
15.3	1.97×10^{-7}	17.7

Figure 5-1. Count Rate Versus ^{99}Tc Concentration for 0.01 mL Neutral Aqueous Solutions on Paper Targets.

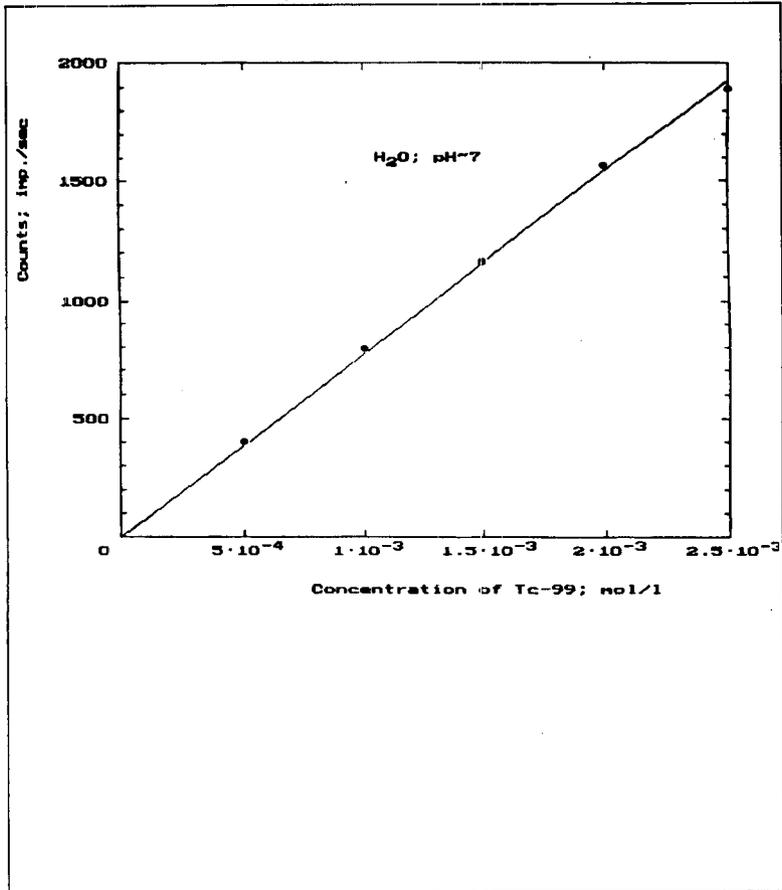
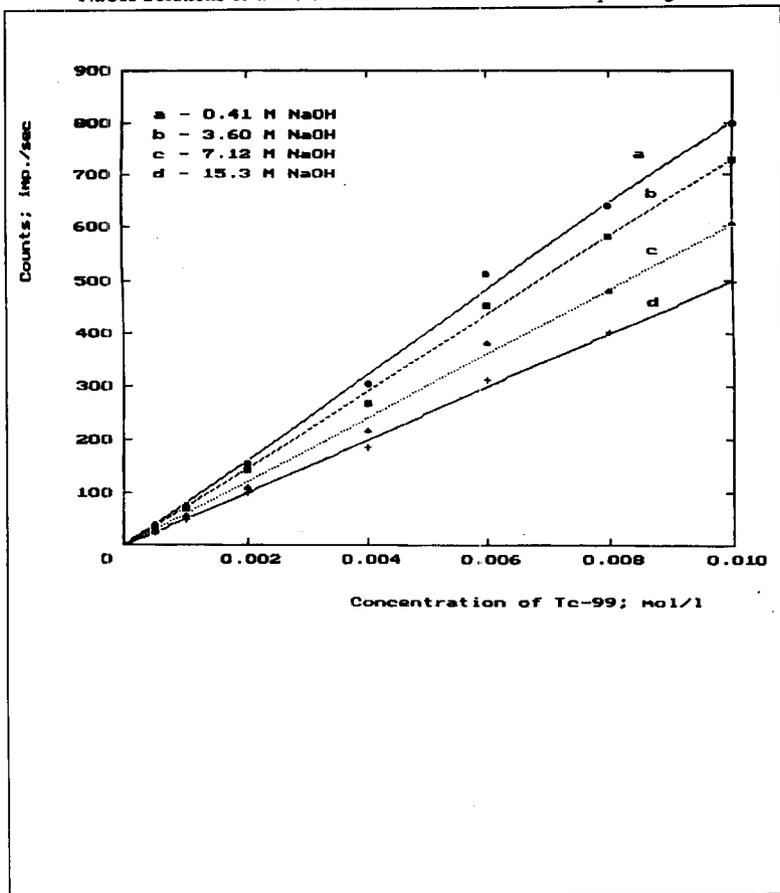


Figure 5-2. Count Rate Versus ^{99}Tc Concentration for 0.01 mL NaOH Solutions of Different NaOH Concentrations on Paper Targets.



Potassium pertechnetate, KTcO_4 , produced at the Mayak Production Association, Chelyabinsk, was purified by two recrystallizations from twice-distilled water and dried to constant weight in a desiccator at $110\text{ }^\circ\text{C}$. Reference and other technetium test solutions and initial compounds for synthesis of Tc(V) and Tc(IV) oxides were prepared using the purified KTcO_4 . The alkaline solutions were prepared using granulated chemically-pure NaOH from which carbonate impurities were first removed by washing away the outer layer with water. Other reagents were chemically pure and used as received. Measurements of solution concentrations were conducted using acid-base or redox titration according to standard procedures (Kolthoff and Sandell 1948; and Babko and Pilipenko 1974).

All manipulations with alkaline solutions were conducted in air. The polyethylene or polypropylene vessels used in the solubility tests were leached with concentrated alkaline solution for at least one week to remove alkali-soluble impurities. Test solutions sampled for analysis were clarified by centrifugation followed by filtration through polymer-fiber filters.

Reliable data on the forms of existence of technetium(V) and (IV) species in concentrated alkaline solutions, and their physicochemical properties, are inadequate in the open literature. Identification of the forms was performed using a variety of chemical and physicochemical methods: X-ray powder diffraction analysis, X-ray photoelectron and optical (ultraviolet, visible, and infrared) spectroscopies, static magnetic susceptibility measurements, paper electrophoresis, and chemical analysis. The experimental procedures and equipment are described elsewhere (Kryutchkov 1983; and Kryutchkov 1991). Only the most significant details of these studies are described here.

Hydrated technetium (IV) and (V) oxides were synthesized by the following two methods.

1. Compounds of the form M_2TcX_6 (where X is Cl^- or Br^- ; M is K^+ or NH_4^+) were prepared by the autoclave reduction of MTcO_4 with molecular hydrogen at 3 MPa initial pressure and $100\text{ }^\circ\text{C}$ in concentrated hydrohalide acid solutions following published procedures (Kryutchkov 1983). The product compounds were identified by the listed physicochemical methods and showed the absence of impurities. Table 5-2 lists the principal physicochemical properties of the synthesized compounds.
2. Technetium(IV) and (V) compounds were prepared by the reduction of MTcO_4 (where M is K^+ or NH_4^+) with concentrated hydrochloric acid. The M_2TcOCl_6 compounds were prepared at room temperature following published procedures (Kryutchkov 1983; and Spitsyn et al. 1971); the M_2TcCl_6 compounds were prepared by heating MTcO_4 acid solutions for about 3 hours at about $90\text{ }^\circ\text{C}$ and evaporation on a water bath according to published procedures (Spitsyn and Kuzina 1981; and Kryutchkov 1983). These compounds were also analyzed by physicochemical methods (Table 5-2). The products, M_2TcOCl_6 and M_2TcCl_6 , did not contain impurities. Technetium(IV) impurities in Tc(V) compounds (and the converse) were quantified by X-ray diffraction and spectrophotometric solution analyses. In all cases, the impurities accounted for less than 5 percent of the product.

Table 5-2. Physicochemical Properties of Technetium(V) and (IV) Compounds.

Compound	Principal X-ray Diffraction Lines; d, Å (relative intensity, %)	IR Spectra; Bands and Wavenumber, cm^{-1}	X-ray Photoelectron Spectrum; $\epsilon(3d_{5/2}, \text{eV})$	Magnetic Properties; $\mu_{\text{eff}}, \mu^{\text{B}}$ (number of unpaired electrons per molecule)
$\text{TcO}_2 \cdot n\text{H}_2\text{O}$	--	$\delta(\text{TcOH}) = 1120$; $\nu(\text{TcO}) = 905$; $\nu(\text{OH}) \cong 3200$	255.4 ± 0.2	$\sim 2.5 (\sim 2)$
TcO_2	3.336(100); 2.434(52); 1.747(16); 1.671(58)	--	$2.55.4 \pm 0.2$	$\sim 1.5 (\sim 1)$
$\text{Tc}_2\text{O}_7 \cdot n\text{H}_2\text{O}$	--	$\delta(\text{TcOH}) = 1130$; $\nu(\text{TcO}) = 900$; $\nu(\text{OH}) \cong 3200$	255.0 ± 0.2	T.I.P.* (0)
Tc_2O_7	7.828(100); 7.626(88); 3.815(32); 2.396(38)	--	255.6 ± 0.2	T.I.P.* (0)
K_2TcOCl_5	--	$\nu(\text{TcO}) = 1010$; $\delta(\text{OTcCl}) = 410$; $\nu(\text{TcCl}) = 335$; $\delta(\text{ClTcCl}) \cong 200$	257.6 ± 0.2	T.I.P.* (0)
K_2TcCl_6	5.670(100); 2.835(18); 2.455(62); 2.253(22)	$\nu(\text{TcCl}) = 333$; $\delta(\text{ClTcCl}) = 165$	257.0 ± 0.2	3.44(3)

Note:

*Temperature independent paramagnetism.

The halide and oxohalide technetium(V) and (IV) compounds obtained using methods 1 and 2 (about 1 g each) were placed on No. 4 glass filters and washed successively with 10, 5, and 2 mL of twice-distilled water. The "solution" passing through the filter changed to an intense brown color [these "solutions" were colloidal solutions of Tc(V) and (IV) hydroxides, respectively]. To peptize the colloidal solutions, 1 mL of 14 M NaOH was added dropwise until the formation of amorphous dark brown technetium hydroxide precipitates was

complete. The precipitates were allowed to settle for a day and then the supernatant solution was removed by decantation. Suspensions of the precipitates were divided into 5 to 7-mL portions, placed in polypropylene tubes, and centrifuged.

The mother liquors were then decanted and about 7 mL of water was added to the precipitates. The mixtures were vigorously shaken and then centrifuged again. Washings were repeated not less than 10 times, until the decanted water contained no chloride (verified qualitatively by reaction with AgNO_3) and the decant pH was about 7. After this thorough rinsing, part of the sample was separated from the mother liquor, dried in air, and then either dried at about 90 °C or calcined at 500 °C (for 3 hours) or 800 °C (for 1 hour) in an argon atmosphere. The other portions were left to stand in closed polypropylene tubes under twice-distilled water.

All technetium(IV) and (V) oxides obtained were identified using the above-described physicochemical methods. Table 5-2 shows the principal results of these investigations. These results show that the physicochemical properties of the synthesized compounds agree well with reported properties (Spitsyn and Kuzina 1981; Kryutchkov 1983; and Kryutchkov 1991). Before the use of the technetium oxides for studies of their solubilities and chemical reactions, small portions were placed in polypropylene tubes and 5 to 7 mL of twice-distilled water was added. The mixtures were vigorously shaken and then centrifuged. All these manipulations were repeated not less than five times to remove possible impurities of Tc(VII) that may appear during the storage of the samples.

Mathematical treatment of the experimental technetium compound solubility and reaction results was performed on an IBM PC 486 computer with the "Plotkin" program developed by V. M. Men'kin at the Institute of Physical Chemistry of the Russian Academy of Sciences.

5.2 RESULTS AND DISCUSSION

Results of the solubility studies of technetium(IV) and (V) oxides, both hydrated and dehydrated at 800 °C, versus the NaOH concentration are shown in Figures 5-3 and 5-4 and in Table 5-3. These figures display the averaged solubilities measured on the third day after the preparation of the systems in question. As shown below and in related studies (Shilov et al. 1996), in this period, all principal fast processes occur and relative equilibria [disturbed only by slow oxidation of the technetium(IV) and (V)] are established in most of these systems.

Most of the solutions are colorless. Almost all β activity can be extracted by acetone from these alkaline solutions. The only exceptions are the solutions with NH_2OH additives. These solutions change to a dark-brown color, decreasing in intensity with increasing alkalinity. During the extraction of these solutions with acetone, only part of β activity passes to the organic phase.

Figure 5-3. Technetium Concentration from Tc(IV) Solids in Aerated NaOH Solution After Three Days Contact.

- (a) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of $2.2 \times 10^{-2} \text{ M N}_2\text{H}_4$);
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of $4.0 \times 10^{-2} \text{ M Na}_2\text{SO}_3$);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of $4.1 \times 10^{-2} \text{ M NH}_2\text{OH}$);
- (e) TcO_2 ;
- (f) TcO_2 (in the presence of $2.2 \times 10^{-2} \text{ M N}_2\text{H}_4$).

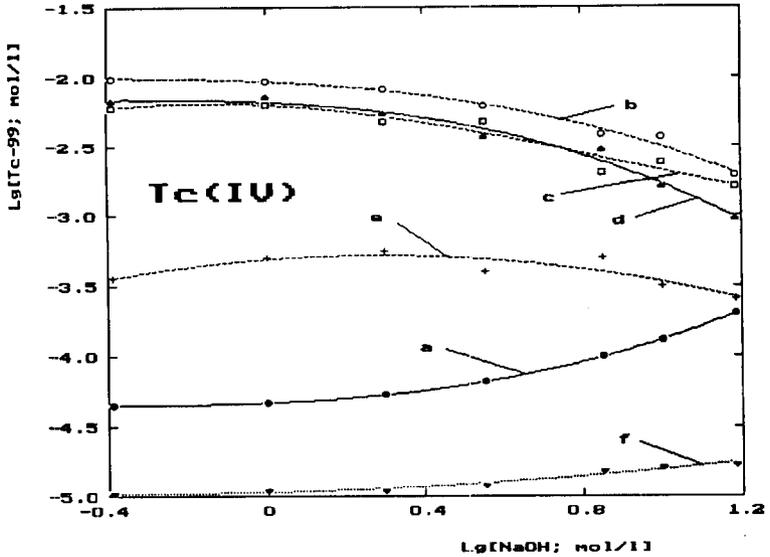


Figure 5-4. Technetium Concentration from Tc(V) Solids in Aerated NaOH Solution After Three Days Contact.

- (a) $Tc_2O_5 \cdot nH_2O$ (in the presence of 2.2×10^{-2} M N_2H_4);
- (b) $Tc_2O_5 \cdot nH_2O$;
- (c) $Tc_2O_5 \cdot nH_2O$ (in the presence of 4.0×10^{-2} M Na_2SO_3);
- (d) $Tc_2O_5 \cdot nH_2O$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (e) Tc_2O_5 ;
- (f) Tc_2O_5 (in the presence of 2.2×10^{-2} M N_2H_4).

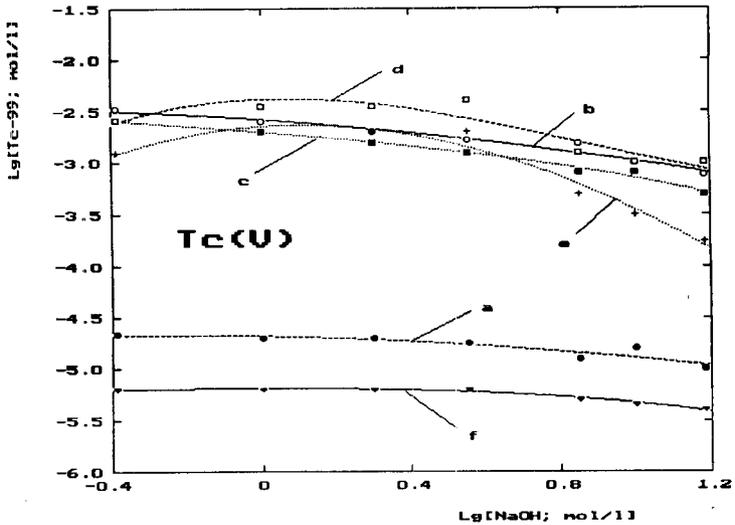


Table 5-3. Technetium Concentration from Tc(IV) and Tc(V) Solids in Aerated NaOH Solution with Various Reductants After Three Days' Contact.

Curve of Figures 5-3 and 5-4	Reductant	TcO ₂ (nH ₂ O) [Tc], M		Tc ₂ O ₇ (nH ₂ O) [Tc], M	
		1.0 M NaOH	3.6 M NaOH	1.0 M NaOH	3.6 M NaOH
a	2.2×10^{-2} M N ₂ H ₄	4.5×10^{-5}	6.4×10^{-5}	1.9×10^{-5}	1.8×10^{-5}
b	None	8.8×10^{-3}	6.0×10^{-3}	2.5×10^{-3}	1.6×10^{-3}
c	4.0×10^{-2} M Na ₂ SO ₃	6.0×10^{-3}	4.4×10^{-3}	1.9×10^{-3}	1.3×10^{-3}
d	4.1×10^{-2} M NH ₂ OH	6.8×10^{-3}	3.5×10^{-3}	3.4×10^{-3}	4.1×10^{-3}
e	None	4.6×10^{-4} *	3.8×10^{-4} *	2.5×10^{-3} *	1.9×10^{-3} *
f	2.2×10^{-2} M N ₂ H ₄	1.0×10^{-5} *	1.2×10^{-5} *	6.1×10^{-6} *	6.1×10^{-6} *

Note:

*Calced solids.

The solutions can be decolorized by addition of solid alkali or by rapid freezing to liquid nitrogen temperature followed by settling. A corollary decrease in β activity also occurs. The preceding observations indicate that the browning of these solutions is related to the formation of colloidal, rather than true, solutions of reduced technetium.

It is noted that the products obtained by use of various reductants in alkaline Tc(VII) solutions behave in an analogous manner. Of the possible dissolved technetium species, only Tc(VII) ions are colorless and extracted with acetone (Spitsyn and Kuzina 1981). Therefore, most of the β activity in alkaline solutions in pseudoequilibrium with solid reduced technetium oxide and hydroxide phases is due to Tc(VII). The only exceptions are solutions with added N₂H₄. For solutions with N₂H₄, oxidation to technetium(VII) by atmospheric oxygen and the formation of colloids do not take place. Thus, for solutions with hydrazine, almost all β activity will be due to the true solubility of the oxides. This conclusion is also supported by the observed very slow change with time in the solubilities of these oxides in hydrazine-containing solutions (shown below) and in related studies (Shilov et al. 1996).

The data presented in Figures 5-3 and 5-4 demonstrate the following facts:

1. Other conditions being equal, the solubilities of technetium(IV) and (V) oxides and hydroxides are of the same order of magnitude.

2. Other conditions being equal, the solubilities of the dehydrated oxides are lower than those of the hydrated oxides by 1 to 2 orders of magnitude. This indicates that the state of the surface of the solids and their crystallinity play important roles in the dissolution. Note that a similar effect also takes place in the case of transuranium element oxides and hydroxides (Peretrukhin et al. 1995).
3. The total solubilities of technetium(IV) and (V) hydroxides measured in air are little affected by the addition of SO_3^{2-} or NH_2OH reductants. However, N_2H_4 additives exhibit stronger reducing properties in alkaline media. In this case, the solubilities of technetium(IV) and (V) oxides and hydroxides are significantly lower (by 1 to 2.5 orders of magnitude, depending on other conditions). Again, this is related to the suppression of oxidation processes in hydrazine-containing solutions. Thus, the solubilities measured under these conditions characterize the true solubilities of the Tc(IV) and (V) oxides and hydroxides. The solubilities measured in the presence of hydrazine are not complicated by oxidation and colloid-formation processes.
4. The total solubilities of Tc(IV) and (V) hydroxides and oxides, measured in air, as a rule, decrease with increasing NaOH concentration. This is likely due to a decrease in the oxygen solubility in aqueous solutions with increasing alkali concentration. This decreases the rate of Tc(IV) and (V) hydroxides' oxidation by dissolved oxygen.
5. The solubilities of Tc(IV) oxides and hydroxides in the presence of N_2H_4 increase with increasing NaOH concentration. The increase indicates that Tc(IV) hydroxo complexes form.
6. Plots of the solubilities of technetium(V) hydroxide in the presence of NH_2OH and technetium(V) oxide without reducing additives versus the alkali concentration pass through a maximum near 3 M NaOH. This might be the total result of changes in the true solubility of Tc(V) oxide or hydroxide, the solubility of oxygen in the alkaline solution, and in the rate constant for the oxidation of the solid phases with atmospheric oxygen (Shilov et al. 1996).

To explain the listed observations, changes in the solubilities of technetium oxides and hydroxides with time were studied. Results of the kinetic studies are shown in Figures 5-5 through 5-12. In these figures, all curves have similar kinetic characteristics.

First, it is noted that the starting technetium concentration must be 0. Therefore, all the kinetic curves can be divided into two linear regions consistent with relatively fast initial dissolution and slower subsequent processes, respectively (in Figures 5-5 through 5-12, only slow regions in the form of straight lines are shown). The first region normally ends within 1 to 3 days, whereas the second one lasts for 10 to 30 days and, in some cases, for more than 30 days. Note that for solutions with hydrazine additives, the second region resembles kinetic curves for equilibrium processes. The observations are not at variance with the hypothesis that the solubilities of these oxides in hydrazine-containing media are determined by their true solubilities and are not accompanied by secondary processes. In the cases

Figure 5-5. Technetium Concentration from Tc(IV) Solids Versus Time in Aerated 0.5 M NaOH.

- (a) TcO_2 ;
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4).

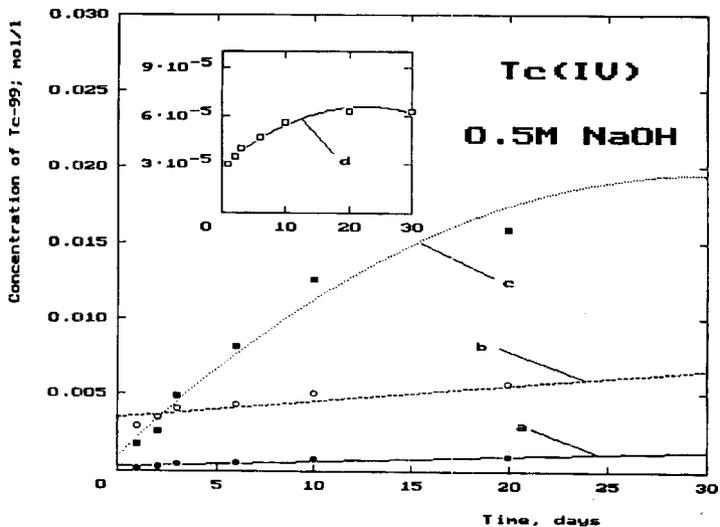


Figure 5-6. Technetium Concentration from Tc(IV) Solids Versus Time in Aerated 4.0 M NaOH.

- (a) TcO_2 ;
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4).

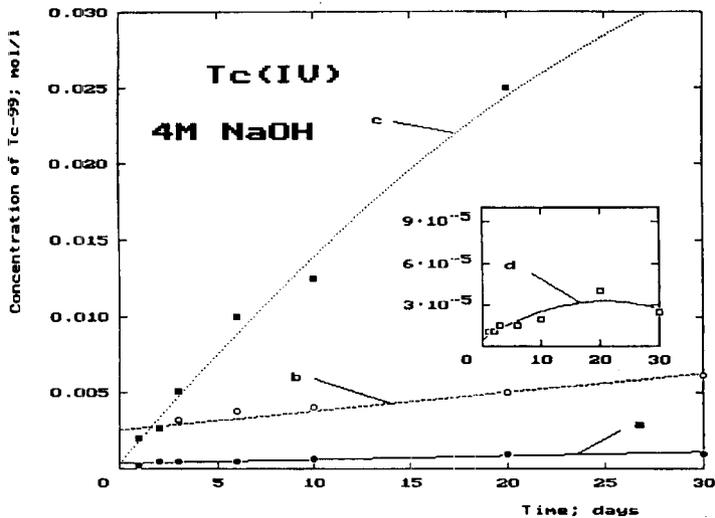


Figure 5-7. Technetium Concentration from Tc(IV) Solids Versus Time in Aerated 8.0 M NaOH.

- (a) TcO_2 ;
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4).

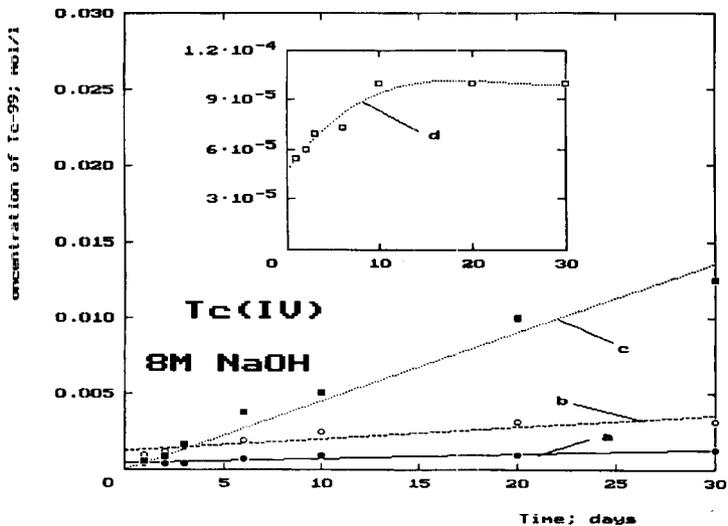


Figure 5-8. Technetium Concentration from Tc(IV) Solids Versus Time in Aerated 15.0 M NaOH.

- (a) TcO_2 ;
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4).

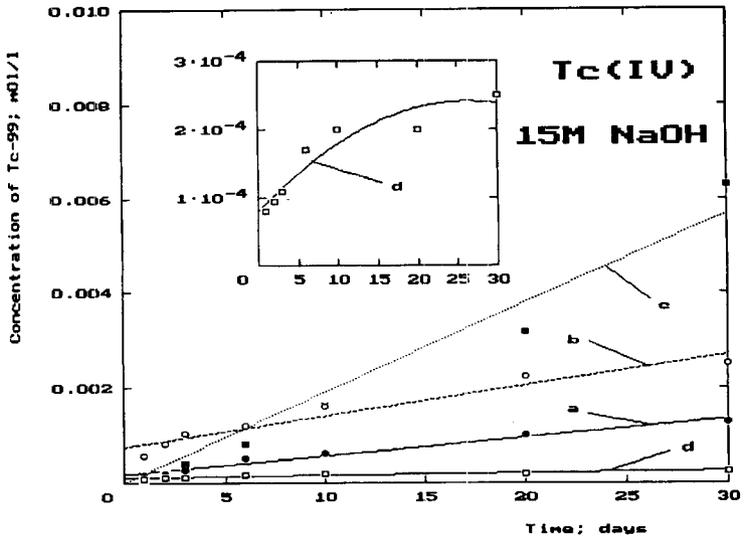


Figure 5-9. Technetium Concentration from Tc(V) Solids Versus Time in Aerated 0.5 M NaOH.

- (a) TcO_2 ;
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4).

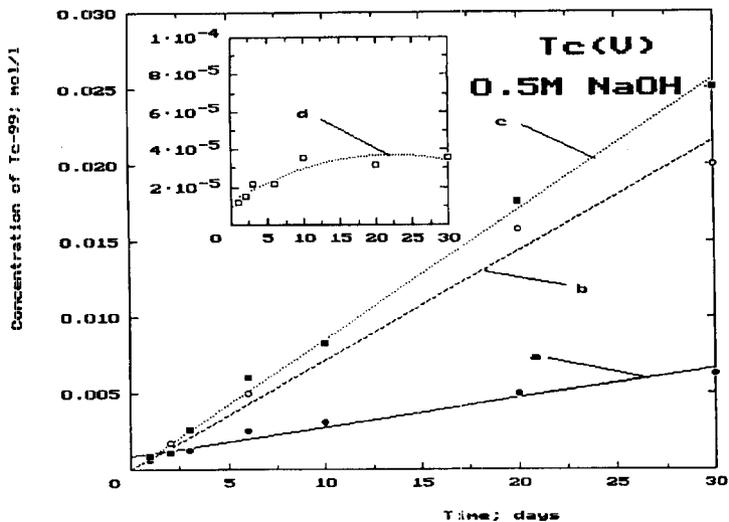


Figure 5-10. Technetium Concentration from Tc(V) Solids Versus Time in Aerated 4.0 M NaOH.

- (a) TcO_2 ;
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4).

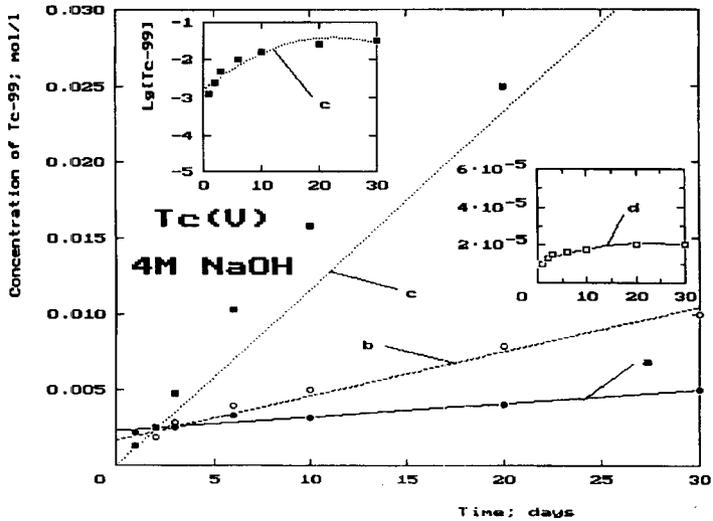


Figure 5-11. Technetium Concentration from Tc(V) Solids Versus Time in Aerated 8.0 M NaOH.

- (a) TcO_2 ;
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4).

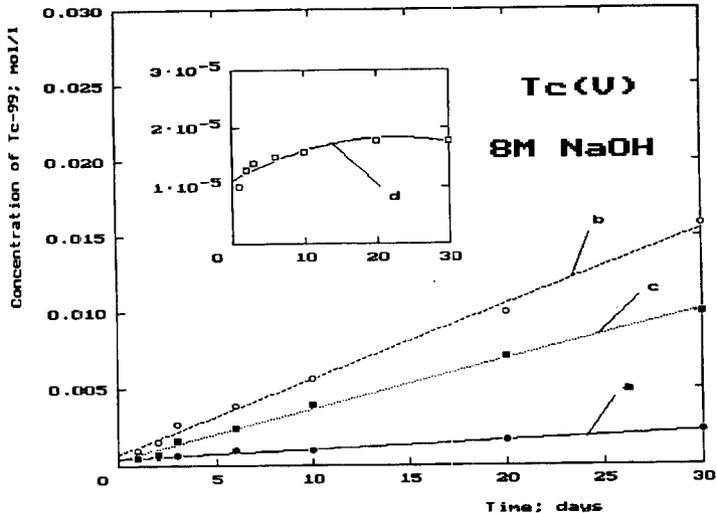
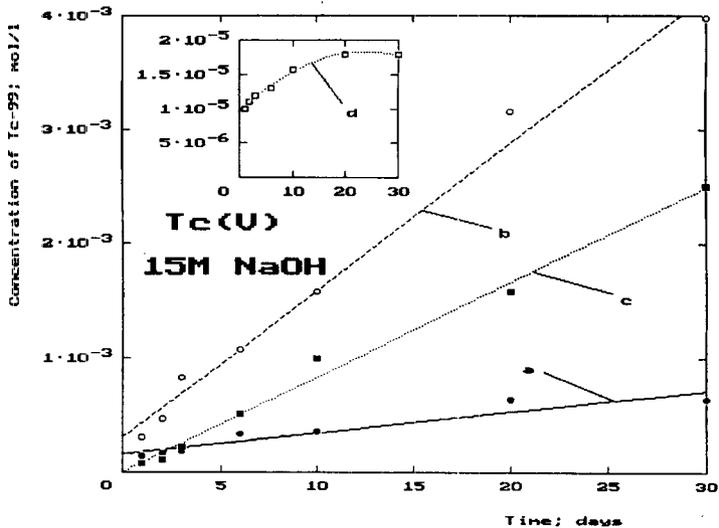


Figure 5-12. Technetium Concentration from Tc(V) Solids Versus Time in Aerated 15.0 M NaOH.

- (a) TcO_2 ;
- (b) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (c) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 4.1×10^{-2} M NH_2OH);
- (d) $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4).



without hydrazine, the second regions are virtually linear; i.e., the processes occurring in this region obey a zero-order kinetics in terms of technetium concentration.

The evidence suggest that the rapid initial regions on the kinetic curves are due to heterogeneous processes leading to technetium compound dissolution. Rates of heterogeneous dissolution processes are often determined by the crystallinity of the solid phase, the state of its surface, the presence of active centers on the surface (relative to a given process), and the concentration of these centers. In general, each specific process and solid phase can be expected to have its own rate of technetium dissolution. As previously mentioned, for most cases, the dissolution will be consistent with a heterogeneous oxidation to Tc(VII). For solutions with added NH_2OH , dissolution will be consistent with a heterogeneous dissolution and oxidation and formation of colloidal solutions. For solutions with added N_2H_4 , this process will be consistent with a true heterogeneous dissolution, not complicated by colloid formation and oxidation processes, and limited by diffusion from the solid to solution phase. In general, the duration of the rapid dissolution step and the amount of technetium dissolved will depend on the concentration of active centers in the solid (relative to a specific process) and the "activity" of these centers.

As the active centers are spent, the solid phase begins the second, slower kinetics stage. The rate of the secondary oxidation processes (colloid-formation) will be significantly higher. The total rate of technetium appearance in solution will be limited by the heterogeneous primary dissolution processes and will not depend on the technetium concentration. This behavior is observed as shown in Figures 5-5 through 5-12.

The conclusions drawn from the data presented in Figures 5-5 through 5-12 are confirmed by recent related studies (Shilov et al. 1996) which show the kinetic curves of technetium oxide and hydroxide dissolution in the presence of oxidants and complex-forming agents. The reported studies showed that Tc(IV) and Tc(V) oxides and hydroxides slowly dissolve as pertechnetate in aerated solutions. The dissolution occurs in both the presence or absence of other oxidants or reductants (except hydrazine) as well as in the presence or absence of complex-forming ions. The technetium can be preserved in the solid phase only by use of at least 2×10^{-2} M added hydrazine. Therefore, a study of the effect of various reductants on Tc(VII) in alkaline solutions is of particular interest.

Toward this end, experiments to study the effects of $(1 \text{ to } 5) \times 10^2$ M N_2H_4 , NH_2OH , Na_2SO_3 , or $\text{Na}_2\text{S}_2\text{O}_4$ on 5×10^{-3} M KTcO_4 in 0.5 to 15 M NaOH were conducted. Of the four reductants employed, only hydrazine rapidly (about 15 minutes) and completely (to greater than 90 percent) reduced pertechnetate. Instantaneously, upon mixing, a pink solution with an optical absorption maximum, λ_{max} , near 500 nm is formed (molar extinction coefficient, ϵ , is $200 \text{ M}^{-1}\text{cm}^{-1}$). This solution gradually changes to a brown colloidal suspension having no characteristic absorption maxima over the entire measured spectral region. The conversion to the brown colloid requires one hour to several days.

The resulting brown solutions are very stable. They can be in equilibrium with the solid phase hydroxide from several hours to several months. The rate of colloid peptization can be increased by fast freezing or heating the suspensions, or by adding considerable quantities of foreign inert electrolytes.

Pertechnetate is not reduced by sulfite under the described conditions. In the case of NH_4OH and $\text{Na}_2\text{S}_2\text{O}_4$, an intermediate variant is observed. Only 10 to 40 percent reduction to pink complexes occurs within 1 to 4 hours; these complexes gradually (1 to 10 days) change to brown colloidal suspensions. For NH_4OH , the absorption maxima of the pink complex are near 430 and 540 nm.

The reduced products were identified by the following physicochemical observations.

1. Paper electrophoresis of the brown colloidal suspensions and pink true solutions showed that at least 95 percent of all dissolved technetium was present as neutral species. Electrophoresis conditions were 0.5 to 8 M NaOH, 0.02 M N_2H_4 , 30 cm paper length, 100 to 200 V working voltage, and 0.5 to 2 hours' time. Analogous results also were obtained for brown colloidal solutions formed upon the hydrolysis of Tc(IV) and Tc(V) halide complexes in an alkaline medium.
2. Addition of excess concentrated hydrochloric acid and several drops of a concentrated ammonium rhodanide (ammonium thiocyanate, NH_4SCN) solution to either the brown colloidal suspensions or the pink true solutions first forms a pink solution with an absorption maximum, λ_{max} , near 500 nm. The pink solutions gradually become dark yellow with λ_{max} near 400 nm. Analogous results were obtained by reacting hydrochloric acid and ammonium rhodanide with the hydrolysis products of Tc(V) halide complexes. However, reaction of the hydrolysis products of technetium(IV) halide complexes under similar conditions immediately yields dark-yellow solutions with λ_{max} near 400 nm; these solutions are gradually oxidized in air to pink solutions with λ_{max} 500 nm. The observed changes of color and optical spectra were related to redox transformations of the complexes $[\text{Tc}(\text{NCS})_6]^{2-}$ (λ_{max} is 500 nm) and $[\text{Tc}(\text{NCS})_6]^-$ (λ_{max} is 400 nm) in air (Spitsyn and Kuzina 1981; and Schwochau 1983). According to other published data, this is related to the transformation of a pair of analogous Tc(IV)/(III) rhodanide complexes (Trop et al. 1980).
3. Rapid cooling of the brown colloidal solutions of reduced technetium complexes, followed by their freezing, leads to the formation of small black particles of amorphous precipitate. Repeated washing of this precipitate with water (up to pH neutrality of the washing water), followed by drying and calcination at 800 °C in an argon atmosphere for 1 hour, yields a black powder. An X-ray diffraction analysis of this powder showed it to be identical with Tc_2O_7 obtained by the hydrolysis of Tc(V) halide complexes or upon radiolysis of alkaline KTcO_4 solutions (Pikaev et al. 1996). Cerimetric titration of similar technetium hydrated oxide identified the (V) oxidation state (Kryutchkov 1983). Several years' storage of Tc(V) and Tc(IV) hydroxides in air in the absence of moisture gives no visible changes in their chemical compositions

(Kryutchkov 1983; and Kryutchkov 1991). On the other hand, when allowed to stand in aerated humid conditions, these hydroxides are gradually oxidized to Tc(VII). Reduction of these hydroxides is not observed in aerated conditions in the presence of water even in the presence of about 0.1 M hydrazine. The principal physicochemical properties of Tc(V) and Tc(IV) hydroxides are given in Table 5-2.

The results indicate that both the pink true solutions and the brown colloidal suspensions of reduced technetium are neutral Tc(V) complexes. The decrease in the true solubilities of Tc(V) hydroxides with increasing NaOH concentration is difficult to explain (Figure 5-4). On the other hand, the solubilities of Tc(IV) hydroxides increase with increasing NaOH concentration. The increasing solubility may indicate a partial formation of anionic Tc(IV) hydroxo complexes (Figure 5-3).

The results obtained in this work and in related studies (Shilov et al. 1996) indicate that oxidation of Tc(IV) and Tc(V) hydroxides by atmospheric oxygen can be suppressed by hydrazine. Therefore, all dissolved technetium found in hydrazine-bearing alkaline solutions containing Tc(IV) or Tc(V) hydroxides results from the true solubilities of these solid phases.

The effects of various complex-forming ions on the true solubilities of these hydroxides in hydrazine-bearing alkaline solution was investigated. Figures 5-13 and 5-14, and Table 5-4, show the results obtained from this study. In general, complex-forming ions increase the solubilities of Tc(IV) hydroxides. In the presence of oxalate, phosphate and fluoride, the solubility increases from about 5×10^{-5} to about 2×10^{-3} M. The increase is related to the formation of more soluble technetium(IV) complexes. For some complex-forming ions (citrate, phosphate, and fluoride), a complicated dependence of the solubility on the concentration of complex-forming ions is observed. This behavior likely is because of the formation of mixed hydroxo complexes with these ligands and the related competition between formation of simple hydroxo and mixed complexes. Related studies, which show that complex formation of Tc(IV) and (V) in alkaline solution can either increase or decrease the rates of the redox reactions (Shilov et al. 1996), also may reflect the competition between formation of the simple hydroxo and mixed hydroxo-ligand complexes.

Figure 5-13. The Solubility of $TcO_2 \cdot nH_2O$ in 1 M NaOH and 0.05 M N_2H_4 with Complexing Agents.

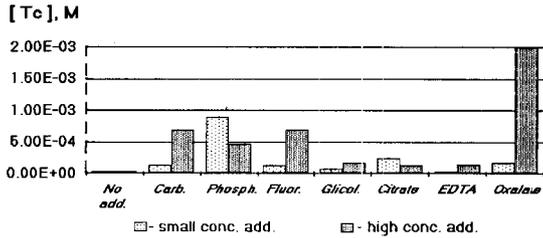


Figure 5-14. The Solubility of $TcO_2 \cdot nH_2O$ in 4 M NaOH and 0.05 M N_2H_4 with Complexing Agents.

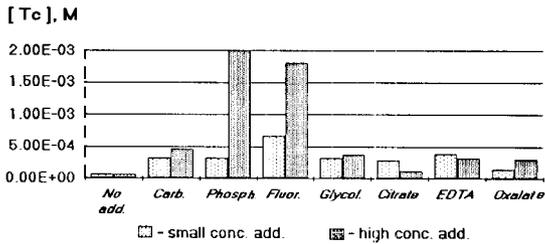


Table 5-4. The Effect of Complexing Agents on the Solubility of $TcO_2 \cdot nH_2O$ in Alkaline Media.

Agent Added	Concentrations of Agent, M	$TcO_2 \cdot nH_2O$ Solubility, M			Concentration Enhancement	
		1 M NaOH	4 M NaOH	[Tc] Ratio in 4 M/1 M NaOH	in 1 M NaOH	in 4 M NaOH
None	--	4.0×10^{-5}	6.3×10^{-5}	1.6	--	--
Na_2CO_3 carbonate	0.5	7.0×10^{-4}	4.5×10^{-4}	0.6	18	7
	0.05	1.3×10^{-4}	3.2×10^{-4}	2.5	3	5
$C_6H_8O_7^{3-}$ citrate	0.3	1.3×10^{-4}	1.2×10^{-4}	1	3	2
	0.03	2.5×10^{-4}	2.9×10^{-4}	1.2	6	5
$HOCH_2CO_2^-$ glycolate	0.5	1.7×10^{-4}	3.7×10^{-4}	2.2	4	6
	0.1	8.0×10^{-5}	3.1×10^{-4}	3.9	2	5
Na_2EDTA Trilon B	0.2	1.4×10^{-4}	3.2×10^{-4}	2.3	4	5
	0.05	4.0×10^{-5}	3.9×10^{-4}	10	1	6
Na_2HPO_4 phosphate	0.1	4.7×10^{-4}	2.0×10^{-3}	4.2	12	32
	0.01	8.9×10^{-4}	3.1×10^{-4}	0.3	22	5
$H_2C_2O_4$ oxalate	0.075	2.0×10^{-3}	3.0×10^{-4}	0.2	50	5
	0.03	1.7×10^{-4}	1.8×10^{-3}	11	4	28
$KF \cdot 2H_2O$ fluoride	0.1	7.0×10^{-4}	1.8×10^{-3}	2.6	18	28
	0.02	1.3×10^{-4}	6.6×10^{-4}	5	3	10

Figures 5-15 and 5-16 and Table 5-5 show the results of the solubility studies of Tc(IV) and Tc(V) oxides and hydroxides previously stored dry in air for various times. Clearly, aging significantly affects the solubilities of the compounds. Aging has an analogous but even stronger effect on the kinetics of oxidation by atmospheric oxygen (Shilov et al. 1996). The decreased solubility and oxidation rate are likely to be related to the heterogeneous character of all reactions considered. Thus, the aging can change the specific surface of the compounds and the concentration of sites which are active with respect to any specific reaction. This decreased activity therefore should change the rates of both reversible and irreversible reactions.

Figure 5-15. Technetium Concentration from Aged Tc(IV) Solids in Aerated NaOH Solution After Three Days' Contact.

- (a) 1-day aged $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4);
- (b) 4-month aged $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (in the presence of 2.2×10^{-2} M N_2H_4);
- (c) 1-day aged TcO_2 (in the presence of 2.2×10^{-2} M N_2H_4);
- (d) 4-month aged TcO_2 (in the presence of 2.2×10^{-2} M N_2H_4);
- (e) 1-day aged $\text{TcO}_2 \cdot n\text{H}_2\text{O}$;
- (f) 4-month aged $\text{TcO}_2 \cdot n\text{H}_2\text{O}$.

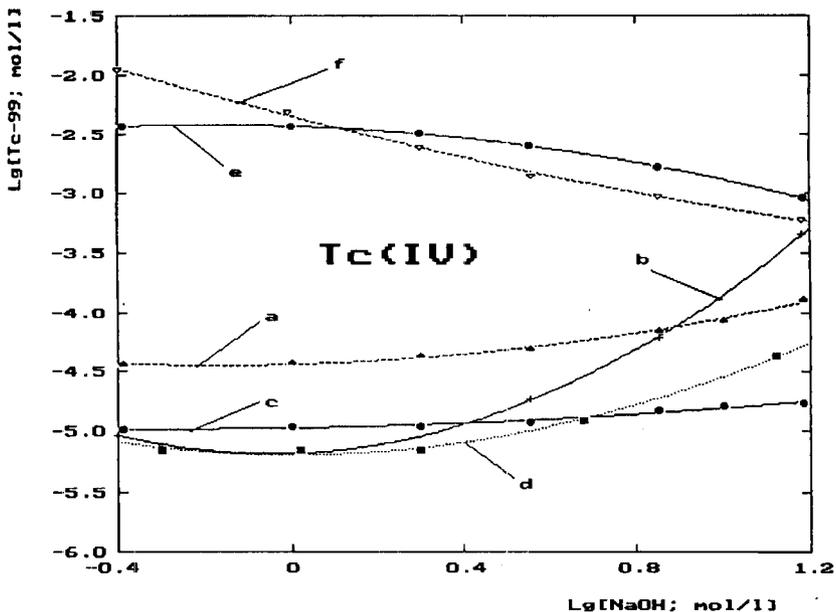


Figure 5-16. Technetium Concentration from Aged Tc(V) Solids in Aerated NaOH Solution After Three Days' Contact.

- (a) 1-day aged $Tc_2O_5 \cdot nH_2O$ (in the presence of 2.2×10^{-2} M N_2H_4);
- (b) 4-month aged $Tc_2O_5 \cdot nH_2O$ (in the presence of 2.2×10^{-2} M N_2H_4);
- (c) 1-day aged Tc_2O_5 (in the presence of 2.2×10^{-2} M N_2H_4);
- (d) 4-month aged Tc_2O_5 (in the presence of 2.2×10^{-2} M N_2H_4);
- (e) 1-day aged $Tc_2O_5 \cdot nH_2O$;
- (f) 4-month aged $Tc_2O_5 \cdot nH_2O$.

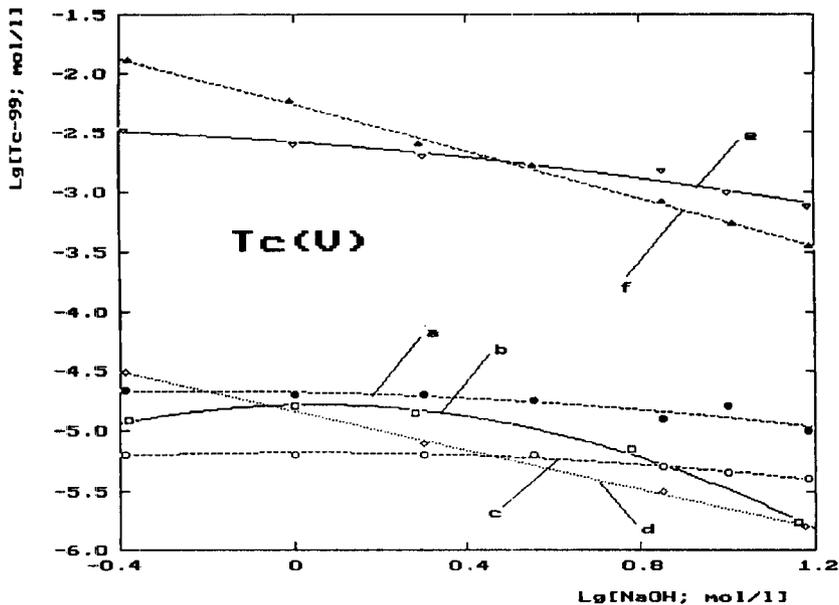


Table 5-5. Technetium Concentration from Aged Tc(IV) and Tc(V) Solids in Aerated NaOH Solution with or without Hydrazine After Three Days' Contact.

Curve of Figures 5-15 and 5-16	[N ₂ H ₄], M and (Aging Time)	TcO ₂ ·(nH ₂ O) [Tc], M		Tc ₂ O ₅ ·(nH ₂ O) [Tc], M	
		1.0 M NaOH	3.6 M NaOH	1.0 M NaOH	3.6 M NaOH
a	2.2×10 ⁻² M N ₂ H ₄ (1 day)	3.6×10 ⁻⁵	5.0×10 ⁻⁵	2.2×10 ⁻⁵	1.8×10 ⁻⁵
b	2.2×10 ⁻² M N ₂ H ₄ (4 months)	6.6×10 ⁻⁶	1.0×10 ⁻⁵	1.6×10 ⁻⁵	1.0×10 ⁻⁵
c	2.2×10 ⁻² M N ₂ H ₄ (1 day)	1.0×10 ⁻⁵ *	1.1×10 ⁻⁵	6.1×10 ⁻⁶ *	6.4×10 ⁻⁶ *
d	2.2×10 ⁻² M N ₂ H ₄ (4 months)	6.6×10 ⁻⁶ *	1.0×10 ⁻⁵	1.6×10 ⁻⁵ *	6.4×10 ⁻⁶ *
e	None (1 day)	3.7×10 ⁻³	2.5×10 ⁻³	2.5×10 ⁻³	1.6×10 ⁻³
f	None (4 months)	4.8×10 ⁻³	1.4×10 ⁻³	5.4×10 ⁻³	1.6×10 ⁻³

* calcined solids

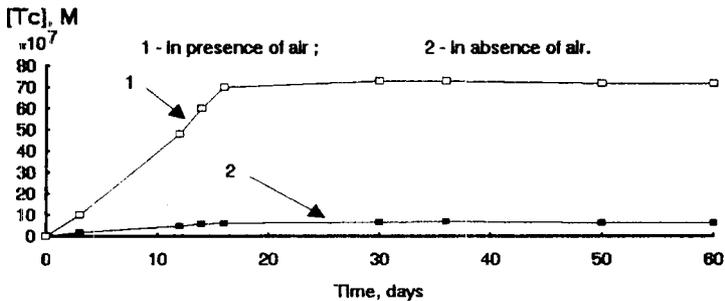
5.3 SOLUBILITY OF ELECTRODEPOSITED TcO₂·nH₂O

The solubility of electrodeposited TcO₂·nH₂O in alkaline media was investigated. The technetium hydroxide was prepared by electrolysis of 4.0 M NaOH, 5.0×10⁻³ M KTCO₄, and 4.0×10⁻² M Na₂CO₃ in a cylindrical-shaped Teflon vessel. A 2.5-cm² diameter stainless steel disk served as cathode and a 1-cm² platinum plate served as anode. The cathode potential for reduction of Tc(VII) was -1.5 V versus the saturated hydrogen electrode; cathode current density was 50 to 70 mA/cm². Temperature was not controlled. Argon was bubbled through the electrolyte during electrolysis. Hydrogen bubbles appeared on the cathode surface and fine black grains covered the metallic disk. After 60 to 80 minutes of electrolysis, the thickness of the deposited TcO₂·nH₂O layer was about 0.2 mg/cm². The deposit adhered well to the metallic cathode base.

The solubility of the electrodeposited TcO₂·nH₂O was investigated under aerated and oxygen-free conditions. Disks with TcO₂·H₂O electrodeposits were immersed into two similar plastic vessels containing 50 mL of 4 M NaOH. One vessel was tightly closed and stored in a dry box under argon. The second vessel was left open in contact with air. Solution samples were taken periodically from both vessels. Data on solubility of electrodeposited TcO₂·nH₂O as function of time are shown in Figure 5-17.

The solubility of the electrodeposited $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ differed strongly under the two conditions and is about ten times higher in the aerated condition. In addition, the solubilities of the electrodeposited Tc(IV) hydroxide under both aerated and oxygen-free conditions are less than that of Tc(IV) hydroxide prepared by chemical methods. The lower solubilities perhaps can be explained by decreased hydration of the electrodeposited materials occurring because of the stronger reducing conditions imposed during electrolysis.

Figure 5-17. The Solubility of Electrodeposited $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ in 4 M NaOH as Function of Time.



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6.0 CONCLUSIONS

1. The solubility of tetravalent neptunium hydroxide in NaOH solutions in the range 4.0 to 14 M NaOH has been studied. Determination of the solubilities was conducted under conditions decreasing the possibility of Np oxidation to higher valent forms. For this purpose, a reductant (generally 0.1 M hydrazine) was introduced into the reaction volume. It was shown that increasing alkali concentration results in the proportional increase in $\text{Np}(\text{OH})_4$ solubility. Thus, in 4 M NaOH, the Np concentration in solution over the $\text{Np}(\text{IV})$ precipitate is about 5×10^{-6} M; at 14 M NaOH, the concentration is about 2×10^{-5} M. These observations may be explained by the formation of anionic complexes of the form $\text{Np}(\text{OH})_5^-$. The yield of these complexes increases with increasing alkali concentration.
2. The solubility of tetravalent plutonium hydroxide in NaOH solutions in the range 0.5 to 14 M NaOH was determined. Hydrazine, at up to 0.5 M concentration, was added to the tests solutions to eliminate $\text{Pu}(\text{IV})$ oxidation. The solubilities of the freshly-prepared $\text{Pu}(\text{IV})$ hydroxide, aged for 240 minutes at 26 °C, have been estimated. At 0.5 M NaOH, the Pu concentration over the precipitate is about 1×10^{-8} M; at 14 M NaOH concentration, it is 9×10^{-6} M. The solubility of $\text{Pu}(\text{OH})_4$ increases with the square of alkali concentration. The increase in $\text{Pu}(\text{IV})$ solubility with increasing alkali concentration may be explained by the formation of anionic complexes of the form $\text{Pu}(\text{OH})_5^-$ and $\text{Pu}(\text{OH})_6^{2-}$.
3. The solubilities of tetravalent Np and Pu hydroxides in the presence of complexing agents (carbonate, fluoride, phosphate, and salts of some organic acids) have been studied in 1 and 4 M NaOH. Actinide concentrations increase 2 to 400 times in the presence of complexing agents at fixed alkali concentrations.
4. The solubilities of pentavalent neptunium, plutonium, and americium hydroxide compounds, having the common starting composition $\text{Na}_2\text{AnO}_2(\text{OH})_3 \cdot x\text{H}_2\text{O}$ (where An is Np, Pu, and Am) in NaOH solutions have been determined. As NaOH concentration increases from 0.5 to 14.1 M, the solubilities of the compounds increase from about 1×10^{-4} M to 4×10^{-4} M. For the plutonium compound at NaOH concentrations less than 5 M, the solubility is lower. The decreased solubility apparently is because of disproportionation of $\text{Pu}(\text{V})$.
5. The solubilities of $\text{Tc}(\text{IV})$ and $\text{Tc}(\text{V})$ oxides and hydroxides are established by the following factors: (a) the true solubilities of the solid phase without change in the technetium oxidation state in solution; (b) complex-formation processes in solution; (c) colloid formation processes; (d) oxidation by atmospheric oxygen or impurities to form $\text{Tc}(\text{VII})$; (e) solid phase aging or other surface processes.

6. In aerated solutions, the attainment of solubility equilibrium for Tc(IV) and Tc(V) oxides and hydroxides in 0.5 to 15 M NaOH is possible only in the presence of 0.02 to 0.05 M hydrazine. The true solubilities of Tc(V) and (IV) oxides and hydroxides, in the absence of complex-forming agents, vary from about 5×10^{-6} to 5×10^{-4} M depending on aging, colloid formation, and surface conditions.
7. Complex-forming agents generally increase the true solubilities of Tc(IV) hydroxides. For oxalate, phosphate and fluoride, the solubility ranges from about 5×10^{-5} to 2×10^{-3} M and is related to the formation of more soluble Tc(IV) complexes. For some complex-forming agents (citrate, phosphate, and fluoride), a complicated dependence of the solubility on the concentration of complex-forming agents is observed. This behavior likely is because of the formation of mixed hydroxo complexes with these ligands and the associated competition for the formations of simple hydroxo and mixed complexes.
8. Pertechnetate (at 0.001 M) is quantitatively reduced to Tc(V) by 0.02 to 0.05 M hydrazine in less than 1 hour. At first, pink true solution of Tc(V) are formed. These solutions then change to brown colloidal suspensions, which later change to a mixture of colloids in equilibrium with the solid-phase hydroxide. The suspensions remain stable for a period of several hours to several days. Peptization of the colloidal suspensions can be significantly accelerated and conducted with quantitative yield by a fast freezing or heating of the solutions, or by adding considerable quantities of foreign inert electrolytes. Technetium(V) hydroxo complexes in the form of pink true solutions and brown colloidal suspensions are neutral-charge particles or molecules.
9. Hydroxylamine and sulfite of the same concentrations do not preserve Tc(V) and Tc(IV) oxides and hydroxides in aerated alkaline solutions and can not compete with oxidation by atmospheric oxygen. With these reductants, nearly complete oxidation of Tc(V) and Tc(IV) hydroxides requires several weeks to several months (depending on other conditions). Sulfite does not reduce pertechnetate in alkaline solution, whereas NH_2OH and $\text{Na}_2\text{S}_2\text{O}_4$ (at 0.05 M) slowly and partially (10 to 40%) reduce 0.005 to 0.05 M pertechnetate to pink solutions of Tc(V) hydroxo complexes.
10. Aging of Tc(IV) and Tc(V) hydroxides and oxides can increase or decrease their true and total solubilities about two-fold (depending on NaOH concentration and other conditions).
11. To form Tc(IV) and (V) precipitates and to retain them in the solid phase in the presence of atmospheric oxygen, at least 0.02 M hydrazine is required.
12. Electrodeposited Tc(IV) hydroxide has much lower solubility than chemically prepared $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ in aerated 1 to 4 M NaOH.

7.0. ACKNOWLEDGEMENTS

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8.0. REFERENCES

- Abuzwida, M. A., A. G. Maslennikov, and V. F. Peretrukhin, 1991, "Voltamperometric Determination of Uranium and Plutonium in Alkaline Solutions," *Journal of Radioanalytical and Nuclear Chemistry*, 147(1), 41-50.
- Babko, A. K., and A. T. Pilipenko, 1974, *Fotometricheskiy analiz. Metodi opredeleniya nemetallov*, Khimiya, Moscow, USSR (in Russian).
- Bourges, J., 1972, "Preparation et Identification du Plutonium a l'Etat d'Oxydation-V en Milieu Basique," *Radiochemical and Radioanalytical Letters*, 12(2-3), pp. 111-119 (in French).
- Cohen D., and S. Fried, 1969, "Some Observation on the Chemistry of Neptunium in Basic Solution," *Inorganic and Nuclear Chemistry Letters*, 5(8), pp. 653-663.
- Connick, R. E., W. H. McVey, and G. E. Sheline, 1949, "Note on the Stability of Pu(IV) in Alkaline Solution." In: *The Transuranium Elements*, G. T. Seaborg, J. J. Katz, and W. M. Manning, Eds., National Nuclear Energy Series, Div. IV, vol. 14B, part I, p. 335, McGraw-Hill Book Company, New York, New York, USA.
- Cousson A., H. Abazli, F. Nectoux, J. Jove, M. Pages, and M. Gasperin, 1986, "Hydroxides of Neptunium(IV): Crystal Structure of Ammonium Neptunium Hydroxide (NH₄Np(OH)₅) and Moessbauer Resonance Study of Np(OH)₄," *Journal of Less-Common Metals*, 121, pp. 405-414 (in French).
- Cunningham, B. B., 1954, "Preparation and Properties of Pu Compounds." In: *The Actinide Elements*, G. T. Seaborg and J. J. Katz, Eds., National Nuclear Energy Series, Div. IV, vol. 14A, Chapter 10, p. 308, McGraw-Hill Book Company, New York, New York, USA.
- Delegard, C. H., 1987, "Solubility of PuO₂·xH₂O in Alkaline Hanford High-Level Waste Solution," *Radiochimica Acta*, 41(1), pp. 11-21. Also published, 1985, as RHO-RE-SA-75 P, Rockwell Hanford Company, Richland, Washington, USA.
- Eriksen, T. E., P. Ndalamba, J. Bruno, and M. Caceci, 1992, "The Solubility of Technetium Dioxide Hydrate (TcO₂·nH₂O) in Neutral to Alkaline Solutions Under Constant pCO₂," *Radiochimica Acta*, 58/59, pp. 67-70.
- Ermakov, V. S., V. F. Peretrukhin, and N. N. Krot, 1977, "Redox Potentials of the Couples Np(VI)-Np(V) and Pu(VI)-(V) in LiOH Solutions," *Radiokhimiya* 19(2), 253 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.

-
-
- Ivanov-Emin, B. N. and L. A. Nisel'son, 1960, "Amphoteric Properties of Ytterbium and Lutetium Hydroxides," *Zhurnal Neorganicheskoi Khimii*, 5(9), pp. 1921-1923 (in Russian). Journal available in English translation as *Russian Journal of Inorganic Chemistry (English Translation)*.
- Karraker, D. G., 1993, *Solubility of Plutonium in Waste Evaporation*, WSRC-TR-93-578, Rev. 0, Westinghouse Savannah River Company, Aiken, South Carolina, USA.
- Karraker, D. G., 1994, *Solubility of Neptunium in Alkaline High Level Waste*, WSRC-TR-0526, Rev. 1, Westinghouse Savannah River Company, Aiken, South Carolina, USA.
- Kolthoff, N. M., and E. B. Sandell, 1948, *Kolichestvennii analiz*, Goskhimizdat, Moscow, USSR (in Russian). Available in English as *Textbook of Qualitative Inorganic Analysis*, revised edition, MacMillan Company, New York, New York, USA (1943).
- Kraus, K. A., and J. R. Dam, 1949, "Hydrolytic Behaviour of Pu(III). Acid Base Titration of Pu(III)." In: *The Transuranium Elements*, G. T. Seaborg, J. J. Katz, and W. M. Manning, Eds., National Nuclear Energy Series, Div. IV, vol. 14B, part I, pp. 466-477, McGraw-Hill Book Company, New York, New York, USA.
- Krot, N. N., A. D. Gel'man, M. P. Mefod'eva, V. P. Shilov, V. F. Peretruxhin, and V. I. Spitsyn, 1977, *Semivalentnoe Sostoyanie Neptuniya, Plutoniya, Ameritsiya*, Nauka, Moscow, USSR. Available in English as "Heptavalent States of Neptunium, Plutonium, and Americium," UCRL-Trans-11798, Lawrence Livermore National Laboratory, Livermore, California, USA.
- Kryutchkov, S. V., 1991, *Khimiya klasternih soedinenii tekhnetsiya*, Second Doctoral Thesis, Institute of Physical Chemistry of the Russian Academy of Sciences, Moscow, USSR (in Russian).
- Kryutchkov, S. V., 1983, *Issledovanie physicohimicheskikh svoistv soedineniy tekhnetsiya*, Doctoral Thesis, Institute of Physical Chemistry of the USSR Academy of Sciences, Moscow, USSR (in Russian).
- LaChappelle, T. J., L. B. Magnusson, and J. C. Hindman, 1949, "Chemistry of Neptunium. First Preparation and Solubilities of Some Neptunium Compounds in Aqueous Solutions." In: *Transuranium Elements*, National Nuclear Energy Series, G. T. Seaborg, J. J. Katz, and W. M. Manning, Eds., Div. IV, vol. 14B, part II, pp. 1097-1110, McGraw-Hill Book Company, New York, New York, USA.
- Lierse Ch., W. Treiber, and J. I. Kim, 1985, "Hydrolysis Reactions of Neptunium(V)," *Radiochimica Acta*, 38(1), pp. 27-28.
-
-

-
-
- Mefod'eva, M. P., and N. N. Krot, 1987, *Compounds of Transuranium Elements*, Nauka, Moscow, USSR, p. 130 (in Russian).
- Mefod'eva, M. P., N. N. Krot, T. V. Afonas'eva, and A. D. Gel'man, 1974, "Hydrolysis of Neptunium(III)," *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, (10), pp. 2370-2372 (in Russian). Available in English translation as *Bulletin of the Academy of Science USSR, Division of Chemical Science (English Translation)*.
- Neck V., J. I. Kim, and B. Kannelakopoulos, 1992, "Solubility and Hydrolysis Behavior of Neptunium(V)," *Radiochimica Acta* 56(1), pp. 25-31.
- Nitsche, H., 1991, "Solubility Studies of Transuranium Elements for Nuclear Waste Disposal: Principles and Overview," *Radiochimica Acta*, 52/53, Part I, pp. 3-8.
- Pazukhin, É. M., and S. M. Kochergin, 1989, "Stability Constants of Hydrolyzed Forms of Americium(III) and Solubility Product of Its Hydroxide," *Radiokhimiya*, 31(4), pp. 72-78 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.
- Penneman, R. A., and L. B. Asprey, 1955, "A Review of Am and Cm Chemistry," *Proceedings of the 1st International Conference on Peaceful Use of Atomic Energy*, vol. 7, p. 355, Geneva, Switzerland.
- Penneman, R. A., J. S. Coleman, and T. S. Keenan, 1961, "Alkaline Oxidation of Americium - Preparation and Reactions of Americium(IV) Hydroxide," *Journal of Inorganic and Nuclear Chemistry*, 17(1 and 2), pp. 138-145.
- Peretrukhin, V. F. and D. P. Alekseeva, 1974, "Polarographic Properties of Higher Oxidation States of Plutonium in Aqueous Alkaline Solutions," *Radiokhimiya*, 16(6), pp. 843-849 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.
- Peretrukhin, V. F., V. P. Shilov, and A. K. Pikaev, 1995, *Alkaline Chemistry of Transuranium Elements and Technetium and Treatment of Alkaline Radioactive Wastes*, WHC-EP-0817, pp. 2-18, Westinghouse Hanford Company, Richland, Washington, USA.
- Pérez-Bustamante, J. A., 1965, "Solubility Product of Tetravalent Plutonium Hydroxide and Study of the Amphoteric Character of Hexavalent Plutonium Hydroxide," *Radiochimica Acta*, 4(2), pp. 67-71.
- Pikaev, A. K., A. V. Gogolev, S. V. Kryutchkov, V. P. Shilov, V. N. Chulkov, L. I. Belyaeva, and L. N. Astafurova, 1996, *Radiolysis of Actinides and Technetium in Alkaline Media*, WHC-EP-0901, Westinghouse Hanford Company, Richland, Washington, USA.
-
-

-
-
- Rai, D. and J. L. Ryan, 1985, "Neptunium(IV) Hydrous Oxide Solubility under Reducing and Carbonate Conditions," *Inorganic Chemistry*, 24(3), pp. 247-251.
- Rai, D. and J. L. Ryan, 1982, "Crystallinity and Solubility of Pu(IV) Oxide and Hydrous Oxide in Aged Aqueous Suspensions," *Radiochimica Acta*, 30, pp. 213-216.
- Schwochau, K., 1983, "The Present Status of Technetium Chemistry," *Radiochimica Acta*, 32(1-3), p. 139.
- Sheka, I. A. and Ts. V. Pevzner, 1960, "Solubility of Zirconium and Hafnium Hydroxides in Sodium Hydroxide Solutions," *Zhurnal Neorganicheskoi Khimii*, 5(10), pp. 2311-2314 (in Russian). Journal available in English translation as *Russian Journal of Inorganic Chemistry (English Translation)*.
- Shilov, V. P., N. N. Krot, S. V. Kryutchkov, A. Yusov, N. Budantseva, A. Garnov, V. Perminov, and L. Astafurova, 1996, *Investigation of Some Redox Reactions of Neptunium, Plutonium, Americium, and Technetium in Alkaline Media*, WHC-EP-0886, Westinghouse Hanford Company, Richland, Washington, USA.
- Simakin, G. A., I. V. Matyashchuk, and N. A. Vladimirova, 1973, "Neptunium(VI) - Neptunium(V) Pair Potential in Sodium Hydroxide Solutions," *Radiokhimiya*, 15(1), pp. 98-100 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.
- Spitsyn, V. I., M. I. Glinkina, and A. F. Kuzina, 1971, "Chemistry of Technetium(V)," *Doklady Akademii Nauk SSSR*, 200(6), p. 1372 (in Russian). Journal available in English translation as *Doklady Chemistry (English Translation)* or *Doklady Physical Chemistry (English Translation)*.
- Spitsyn, V. I., and A. F. Kuzina, 1981, *Tekhnetsiy*, Nauka, Moscow, USSR (in Russian).
- Tananaev, I. G., 1992, "Hydroxide Compounds of Pu(V)," *Radiokhimiya*, 34(2), pp. 1-4 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.
- Tananaev, I. G., 1991, "Production and Investigation of Properties of Hydroxide Compounds of Pentavalent Neptunium and Americium," *Radiokhimiya*, 33, no. 3, pp. 24-31 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.
- Tananaev, I. G., 1990a, "Some Hydroxide Compounds of Pentavalent Americium," *Radiokhimiya*, 32, no. 4, pp. 4-6 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.
- Tananaev, I. G., 1990b, "Forms of Pentavalent Neptunium and Americium in Aqueous Alkaline Media," *Radiokhimiya*, 32, no. 5, pp. 53-57 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.
-
-

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- Trop, H. S., A. Davison, A. G. Jones, M. A. Davis, D. J. Szalda, and S. Lippard, 1980, "Synthesis and Physical Properties of Hexakis(isothiocyanato)technetate(III) and -(IV) Complexes. Structure of the $[\text{Tc}(\text{NCS})_6]^{3-}$ Ion," *Inorganic Chemistry*, 19(5), p. 1105.
- Vikis, A. C., F. Garisto, and R. J. Lemire, 1988, *Proceedings of the International Symposium on Uranium and Electricity*, Saskatoon, Saskatchewan, Canada.
- Visyachscheva, G. I., Yu. F. Volkov, G. A. Simakin, and I. I. Kapshukov, 1984, "Some Hydroxides of Pentavalent Neptunium," *Radiokhimiya*, 26(2), pp. 171-176 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.
- Voskresenskii, P. I., 1973, *Technology of Laboratory Work*, Khimiya, Moscow, USSR, p. 482 (in Russian).
- Zubarev, V. G., and N. N. Krot, 1982, "Separation of Americium(V) Oxalate Compounds from Solution," *Radiokhimiya*, 24(3), pp. 319-321 (in Russian). Journal available in English translation as *Soviet Radiochemistry*.

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