***RMIS Viewprint Document Cover Sheet***

This document was retrieved from the Records Management Information System (RMIS). It is intended for information only and may not be the most recent or updated version.

Accession #: D4387017

Document #: RPP-20041

Title/Desc:
EXPECTED IMPACT OF HANFORD PROCESSING ORGANICS ON PLUTONIUM DURING WASTE SLUDGE RETRIEVAL

Pages: 20

MAR 1 8 2004

# ENGINEERING DATA TRANSMITTAL

1. EDT 820630

1A. Page 1 of

| | | |
|---|---|---|
| 2. To: (Receiving Organization)<br>Distribution | 3. From: (Originating Organization)<br>Analytical Process Development | 4. Related EDT No.:<br>NA<br>7. Purchase Order No.:<br>NA |
| 5. Proj./Prog./Dept./Div.:<br>Residual Hanford Tank Sludges | 6. Design Authority/Resp. Engr./Design Agent:<br>G. L. Troyer | 9. Equip./Component No.:<br>NA<br>10. System/Bldg./Facility:<br>NA |
| 8. Originator Remarks:<br>Expected Impact of Hanford Processing Organics on Plutonium During Tank Waste Sludge Retrieval | | 12. Major Assembly Dwg. No.:<br>NA<br>13. Permit/Permit Application No.:<br>NA |
| 11. Receiver Remarks: | 11A. Design Basis Document? ☐ Yes ☒ No<br>GLT per telecon 3/18/04 dmp | 14. Required Response Date:<br>NA |

15. DATA TRANSMITTED

| (A) Item No. | (B) Document/Drawing No. | (C) Sheet No. | (D) Rev. No. | (E) Title or Description of Data Transmitted | (F) Approval Designator | (G) Reason for Transmittal | (H) Originator Disposition | (I) Receiver Disposition |
|---|---|---|---|---|---|---|---|---|
| 1 | RPP-20041 | | 0 | Expected Impact of Hanford Processing Organics on Plutonium During Tank Waste Sludge Retrieval | NA | 1 | 1 | |

16. KEY

| Approval Designator (F) | Reason for Transmittal (G) | Disposition (H) & (I) |
|---|---|---|
| See TFC-ESHQ-Q-INSP-C-05 | 1. Approval 2. Review 3. Post-Review | 1. Approved 2. Approved w/comment 3. Reviewed no comment 4. Reviewed w/comment 5. Disapproved |

17. SIGNATURE/DISTRIBUTION

| (G) Reason | (H) Disp. | (J) Name | (K) Signature | (L) Date | (M) MSIN | (G) Reason | (H) Disp. | (J) Name | (K) Signature | (L) Date | (M) MSIN |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Design Auth. | | | | 4 | 1 | W. I. Winters | | | T6-07 |
| 1 | 1 | Resp. Engr.<br>G. L. Troyer | | 10-MAR-04 | T6-50 | | | | | | |
| 1 | 1 | Resp. Mgr.<br>C. M. Seidel | For C. Seidel | 3/10/04 | T6-14 | | | | | | |
| | | QA | | | | | | | | | |
| | | Safety | | | | | | | | | |
| | | Env. | | | | | | | | | |
| | | Design Agent | | | | | | | | | |

| | | |
|---|---|---|
| 18. For C. Seidel 3-10-04<br>Signature of EDT Originator Date | 19. DOE APPROVAL (if required)<br>Ctrl. No. | 20. 10-Mar-04<br>Design Auth./Resp. Engr./Resp. Mgr. Date |

BD-7400-172.2 (08/03)

# REPORT DISTRIBUTION COVERSHEET

| Author | Addressee | Correspondence No. |
|---|---|---|
| G. L. Troyer<br>373-1572 | Distribution | RPP-20041<br>Revision 0 |

Subject: EXPECTED IMPACT OF HANFORD PROCESSING ORGANICS ON PLUTONIUM DURING TANK WASTE SLUDGE RETRIEVAL

## DISTRIBUTION

| Approval | Date | Name | |
|---|---|---|---|
| | | CH2M HILL Hanford Group, Inc. | |
| | | K. D. Fowler | S5-08 |
| | | K. M. Hall | T6-12 |
| | | D. B. Hardy | T6-14 |
| | | B. R. Hill | T6-03 |
| | | L. L. Lockrem | T6-07 |
| | | D. L. Renberger | T6-03 |
| | | R. S. Robinson | S7-70 |
| | | C. M. Seidel | T6-14 |
| | | G. L. Troyer | T6-50 |
| | | W. I. Winters | T6-07 |
| | | APD LB/File | |
| | | Fluor Federal Services | |
| | | C. S. Eberle | A0-26 |
| | | A. F. Shattuck | A0-26 |
| | | H. Toffer | E6-41 |

# Expected Impact of Hanford Processing Organics on Plutonium During Tank Waste Sludge Retrieval

**G. L. Troyer, W. I. Winters**
CH2M HILL Hanford Group, Inc.
Richland, WA 99352
U.S. Department of Energy Contract DE-AC27-99RL14047

EDT/ECN: 820630 UC:
Cost Center: 7S110 Charge Code: 501916
B&R Code: Total Pages: 18

Key Words: organics, PUREX, REDOX, waste, plutonium, extraction, solvent, complexant, criticality, concentration

Abstract: This document evaluates the potential for extracting plutonium from Hanford waste tanks into residual organic solvents and how this process may have an impact on criticality specifications during the retrieval of wastes.

*TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name,* trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

Printed in the United States of America. To obtain copies of this document, contact: Document Control Services, P.O. Box 950, Mailstop H6-08, Richland WA 99352, Phone (509) 372-2420; Fax (509) 376-4989.

MAR 18 2004
DATE:
STA: 5
HANFORD RELEASE
ID: 12

3/18/04
Release Approval Date Release Stamp

**Approved For Public Release**

RPP-20041
Revision 0

# Expected Impact of Hanford Processing Organics on Plutonium During Tank Waste Sludge Retrieval

**G. L. Troyer**
**W. I. Winters**
CH2M HILL Hanford Group, Inc.

March 2004

CH2MHILL

Prepared for the U.S. Department of Energy
Office of River Protection

Contract No. DE-AC27-99RL14047

**Expected Impact of
Hanford Processing Organics on Plutonium
During Tank Waste Sludge Retrieval**

G. L. Troyer 10-Mar-04
G. L. Troyer, Scientist
Analytical Process Development

W. I. Winters 3/10/04
W. I. Winters, Scientist
Analytical Process Development

For Carey Seidel
C. M. Seidel, Manager 3/10/04
Analytical Process Development

## CONTENTS

1.0 INTRODUCTION ..... 1
2.0 PURPOSE ..... 1
3.0 SCOPE ..... 1
4.0 CASE DESCRIPTION ..... 1
5.0 RELEVANT CHEMISTRY ..... 2
5.1 Plutonium Aqueous Solubilities ..... 2
5.2 Solvent Extraction Factors ..... 4
5.2.1 Extractant Concentration ..... 5
5.2.2 Valence of the Metal ..... 6
5.2.3 Aqueous Acid Concentration or pH ..... 6
5.2.4 Aqueous Salting Agents and Complexing Agents ..... 7
5.2.5 Extractant Loading ..... 7
5.2.6 Engineering Effects ..... 7
5.3 Separation Process Plants ..... 7
5.3.1 Reduction and Oxidation (REDOX) Process ..... 8
5.3.2 Metal Recovery Process (U-Plant) ..... 8
5.3.3 Plutonium Finishing Plant (PFP) ..... 8
5.3.4 Plutonium-Uranium Extraction (PUREX) Process ..... 9
5.3.5 Fission Product Recovery (B-Plant) ..... 9
5.4 Summary of Relevant Chemistry ..... 10
6.0 RETRIEVAL EXPECTATIONS ..... 10
7.0 REFERENCES ..... 12

### Tables

Table 1. Expected Aqueous Concentrations at Limiting pH Values ..... 3
Table 2. Factors Influencing Mechanisms of Transuranic Separations In Caustic Hanford Waste ..... 10
Table 3. Estimated Potential Uptake of Plutonium in Organic During Sludge Retrieval ..... 11

### Figures

Figure 1. Plutonium Aqueous Chemistry State Phase Diagram. ..... 3
Figure 2. Effects of Valence State and Nitric Acid Concentration on Aqueous/Organic Distribution of Plutonium. ..... 5
Figure 3. Coordination Sphere for Pu(IV) in TBP ..... 6
Figure 4. Conceptual Tank Material Model with Organics. ..... 11

## Executive Summary

This document evaluates the potential for extracting plutonium from Hanford waste tanks into residual organic solvents and how this process may have an impact on criticality specifications during the retrieval of wastes. The two controlling factors for concentrating plutonium are the solubility of the plutonium in the wastes and the extraction efficiency of the potential organic extractants that may be found in these wastes.

Residual Hanford tank sludges contain plutonium in solid forms that are expected to be primarily insoluble Pu(IV) hydroxides. Evaluation of thermodynamic Pourbaix diagrams, documentation on solubility studies of various components in waste tank matrices, and actual analysis of plutonium in tank supernates all indicate that the solubility of Pu in the alkaline waste is on the order of $10^{-6}$ *M*.

Based on an upper limit plutonium solubility of $10^{-5}$ *M* in high pH and a conservative distribution coefficient for organic extractants of <0.01 (the $E_a^o$ for plutonium in 30% TBP at 0.07 *M* $HNO_3$), the estimated concentration for plutonium in the organic phase would be <1 x $10^{-7}$ *M*. This is well below the process control criteria. A significant increase in plutonium solubility or the $E_a^o$ would have to occur to raise this concentration to the 0.01 *M* concern level for organics. Measured tank chemical component values, expected operating conditions, and the characteristics of the expected chemistry and extraction mechanisms indicate that concentration of plutonium from Hanford tank residual sludges to associated process organic extractants is significantly below levels of concern.

## 1.0 INTRODUCTION

Certain Hanford waste tanks may contain various residual organic materials derived from nuclear fuels separations, particularly the chemical extractants used in the plutonium-uranium extraction (PUREX) (Westinghouse 1989, Sederburg 1994) process. Because they are less dense than water, the free organics may have formed surface layers where quantities are sufficient to become coalesced (Nguyen 2002). Other derived organics may be absorbed on solids or widely dispersed organics. As final tank retrieval operations proceed, these organic materials may become semi-homogenous mixes. Of concern is whether retrieval mixing may cause reestablishment of extractive conditions leading to undesirable concentration of species such as Pu, which may have an impact on nuclear criticality specifications.

## 2.0 PURPOSE

The purpose of this document is to identify and discuss relevant chemistries involved in retrieving residual Hanford tank waste sludges containing process organics and estimate the impact of these chemistries on Pu distribution during retrieval operations.

## 3.0 SCOPE

The scope of this document is limited to a literature review, summary of the chemistry and processes, and estimates of the potential uptake of Pu in residual process organics, such as tri-n-butyl phosphate (TBP), expected in Hanford waste tanks. Although this document discusses extractants other than TBP, to provide extended application reference, the examples focus on TBP systems and tank C-103. The results are limited to operational control values for Pu concentrations in target organics.

## 4.0 CASE DESCRIPTION

The reference bases for this study are the Hanford cascade waste tanks C-103 and C-105. These tanks are dish bottom design, single-shell tanks built in 1943 and 1944. They are 75 feet in diameter with an operating capacity of $2 \times 10^6$ L (530,000 gallons). These waste tanks were used during original B-plant operations to store metal wastes. Numerous transfers from and to contemporary tanks occurred. The primary additions to the tanks were metal waste, saltcake waste, B-Plant low-level waste, PUREX cladding waste, first-cycle decontamination waste , U recovery waste, decontamination waste, PUREX organic wash waste, thoria, PUREX low-level waste, PUREX high-level waste, PUREX sludge, hot semiworks, strontium sludge, in-tank ferrocyanide waste, and water (Agnew et al. 1995).

Based on these operations, primary received organic wastes contained tri-n-butyl phosphate (TBP), organic diluent, and other lesser components, both essential and degradation products. The predominant source of TBP in single-shell tanks was the PUREX process (Reddick 2004).

Tank 241-C-103 is believed at one time to have had a surface organic layer comprising less than 8000 L (2100 gallons) (Nguyen 1994) or a possible 1.9 cm (0.76 inch) surface layer. During saltwell pumping, the organic layer may have mixed with the solids in the tank, bringing it into close contact with the Pu-bearing bottom sludges.

The concern is for the projected final retrieval operation of residual solid wastes from organic bearing tanks. By sampling, these wastes are known to have measurable amounts of organic extractants with the primary concern for tank 241-C-103 being TBP. Because the tank was maintained at high pH and caustic content, most Pu and heavy metals are found precipitated into the tank bottom sludges. At issue is what can happen as the remaining materials are dissolved and stirred for sluicing. A possible scenario is that the agitation will allow residual Pu to be solubilized and extracted into the organics designed for that purpose. Under certain conditions, concentration of Pu into the organic might occur. Based on inventory estimates, aqueous solubilities of Pu, and Pu extraction efficiencies, Pu concentration in TBP can then be estimated for comparison to accepted concentration specification limits.

Some additional considerations are the upper limit criticality specification for Pu concentration in the organic and the retrieval process and sluicing medium. The first is to ensure that any $^{239}Pu$ concentration in the organics will not exceed 2.6 g/L or approximately 0.01 *M*. An example of the sluicing or working fluid for retrieval is use of supernate from tank AN-106.

This report identifies basic constraints leading to current consensus that there will be insufficient uptake of Pu to be of concern.

## 5.0 RELEVANT CHEMISTRY

The relevant chemistries in evaluating the potential of Pu exceeding control criteria are the solubility of Pu in the retrieval sluicing media and the extractability of the soluble Pu into the residual waste organic.

### 5.1 PLUTONIUM AQUEOUS SOLUBILITIES

Plutonium separations chemistry is dominated by treatments in various acid aqueous matrices. The PUREX process relies on varying concentrations of nitric acid, REDOX chemicals, and biphasic aqueous/organic retentions. The primary basis for this is the general solubility of metal ions in aqueous acids such as nitric acid ($HNO_3$) and the discovery that TBP works well as a metals extractant in this environment.

Plutonium solubilities are readily demonstrated by pH and electro-voltaic phase diagrams. The thermodynamic treatment of solid to aqueous relationship is shown from the reference (Pourbaix 1974) in Figure 1. In addition to general solubilities, the diagram shows that the most stable soluble form is Pu(IV). At pH found in the waste tanks (pH>10), most dissolved concentrations of Pu are expected to be on the order of micro molar ($10^{-6}$ *M*) scale or less. Figure 1 emphasizes that for Hanford waste storage tanks, the pH alone suppresses availability of Pu to dissolve into

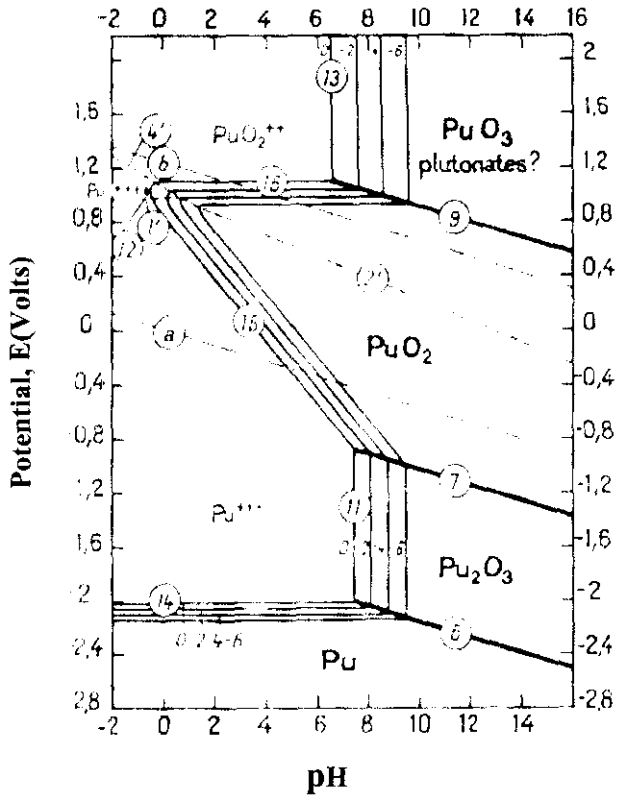


**Figure 1. Plutonium Aqueous Chemistry State Phase Diagram.**

Note: Bold labels indicate solid forms. (From Pourbaix 1974.)

the aqueous phase. This is substantiated by the Pu found in the supernates of tanks. For example, the pH in tank 241-C-103 supernate is ~10.4 and the Pu concentration is ~0.03 μCi/mL or 2.02 x $10^{-6}$ *M*. This makes the Pu generally unavailable for passing into the organic phase. For estimating Pu availability, a pH greater than or equal to 8.0 is assumed. This yields soluble aqueous concentrations as shown in Table 1, based on Pourbaix. The most stable form of Pu in solutions or solids is Pu(IV); an upper aqueous concentration bound of 1x$10^{-6}$ *M* can be assumed.

**Table 1. Expected Aqueous Concentrations at Limiting pH Values** (Pourbaix 1974).

| Oxidation State | Concentration at pH 8 (*M*) | Minimum pH at Conc. 1 x $10^{-6}$ (*M*) |
|---|---|---|
| Pu(III) | 2 x $10^{-2}$ | 9.5 |
| Pu(IV) | Solid, $PuO_2$ | 1.5 |
| Pu(VI) | 1 x $10^{-3}$ | 9.5 |

Additional studies (Delegard 1983) evaluated Pu solubility as a function of tank waste components. The Pu predicted solubility in mol/L was given by the following equation.

$$
\begin{aligned}
log(Pu) = & -5.6688 \\
& +0.1385 * log(NaNO_3) \\
& -0.1794 * log(NaOH) \\
& +0.1175 * log(NaAlO_2) \\
& +0.0125 * [log(NaNo_3)]^2 \\
& +2.0957 * [log(NaOH)]^2 \\
& +0.0090 * [log(NaAlO_2)]^2
\end{aligned}
$$

The response of this equation shows that while the Pu solubility increases at high concentrations of NaOH (4-5 *M*), it is limited to an upper value of $1 \times 10^{-5}$ mol/L and is reasonably comparable to the measured value noted above. This is also confirmed in other work (Peretrukin 1996).

The response equation does not include the common aqueous complexants, hydroxyethyl-ethylenediamine-triacetic acid (HEDTA, EDTA), and therefore shows no effect on solubility of Pu. A physical example of this is from tank AN-107, which has contained large quantities of HEDTA/EDTA. The measured Pu concentration is approximately $4 \times 10^{-6}$ *M*, comparable to other literature reference expectations.

## 5.2 SOLVENT EXTRACTION FACTORS

The extraction of metals into an organic extractant can take place by several different mechanisms (Marcus and Kertes 1969). Many variables can have an impact on the efficiency of these mechanisms. The distribution ratio or extraction coefficient, $E_a^o$, is the ratio of the concentration of the metal of interest in the organic phase to the concentration of the metal in the aqueous phase.

For TBP, this relationship may be defined (Cleveland 1979) as

$$E^o_{a[Pu(IV)]} = \frac{[Pu^{4+}_{(org.)}]}{[Pu^{4+}_{(aq.)}]} = K_1 [NO^-_{3(aq.)}]^4 [TBP_{(org.)}]^2$$

The larger the $E_a^o$, the more efficient the extraction will be for a given set of conditions. However, there may also be kinetic factors. Some of the factors that influence the $E_a^o$ are described in the following.

The basis for $E_a^o$ comes from equilibrium conditions for the various species of Pu as they partition between the aqueous and organic phases. The most probable equilibrium relationships for the three oxidation states and neutral Pu nitrate species are as follows:

$$
\begin{aligned}
Pu(NO_3)_3 + 3TBP &\rightleftharpoons Pu(NO_3)_3 \cdot 3TBP \\
Pu(NO_3)_4 + 2TBP &\rightleftharpoons Pu(NO_3)_4 \cdot 2TBP \\
Pu_2(NO_3)_2 + 2TBP &\rightleftharpoons Pu(NO_3)_2 \cdot 2TBP
\end{aligned}
$$

The neutral molecule equations are further defined for aqueous hydrolized systems. The corresponding equilibrium expression for the Pu(IV) valence is of the form

$$K_1 = \frac{[Pu(NO_3)_4 \cdot 2TBP_{(org.)}]}{[Pu^{4+}_{(aq.)}]\ [NO^{-}_{3(aq.)}]^4\ [TBP_{(org.)}]^2}$$

Therefore, the uptake of Pu into the organic from aqueous is driven by solubilities and the degree of hydrolysis for the Pu species. The variability of $E_a^o$ with pH (nitric acid concentration) is apparent from the relation shown in Figure 2. Because there is no readily available partitioning data for pH above 2 ($HNO_3$ <0.01 *M*), an upper bound on activity coefficient of 0.01 is assumed. This is considered a conservative estimate and is likely smaller.

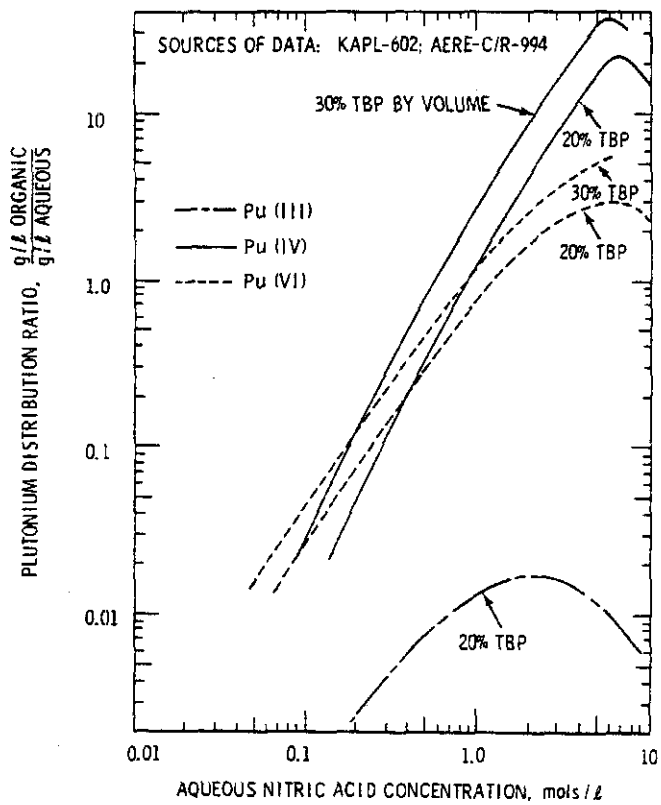


**Figure 2. Effects of Valence State and Nitric Acid Concentration on Aqueous/Organic Distribution of Plutonium.**

### 5.2.1 Extractant Concentration

Normally the $E_a^o$ will increase as the active extractant concentration increases. For waste tanks, it is possible that the extractant concentrations have increased compared to their original process levels because the more volatile diluent, normal paraffin hydrocarbon (NPH), has evaporated. This could have a tendency to increase the $E_a^o$ since the concentration of the reactive component such as TBP would increase. Further literature searches for actual results for Hanford tanks would be required to determine current inventories and relative concentrations for purposes of

estimating this impact. However, because the $E_a^o$ is already very small at high pH, the impact is not expected to be significant.

### 5.2.2 Valence of the Metal

The valence state of the metal ion can affect its $E_a^o$ as shown in Figure 2 (Westinghouse 1989). In general, Pu(III) does not extract well in the solvents described in Section 5.3. Pu(IV) and Pu(VI) will normally have higher $E_a^o$. In alkaline solutions, the limited soluble Pu species are normally plutonyl type anionic compounds such as $PuO_2(OH)_2^-$ or $PuO_2(OH)_3^-$ (Delegard et al. 1983). Even though referenceable $E_a^o$ data were not found for these anions, their extractability in alkaline solutions is expected to be low based on their anionic character and the solvent treatment processes described in Section 5.3.

The basis for this characteristic is twofold. The first involves the method of attachment of the metal ion to the extractant. In the nitric acid environment, Pu forms neutral nitrate species which fit readily into the stereochemistry of the TBP molecules. This relationship for Pu(IV) is shown in Figure 3. The second is that as the pH is raised, solvated Pu becomes plutonyl or negatively charged species. These species are generally not compatible with the coordination sites for TBP.

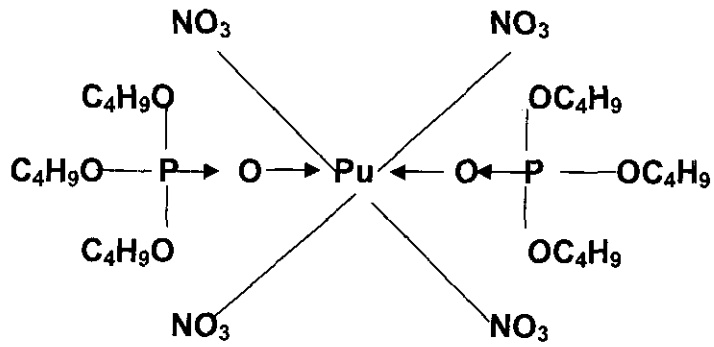


**Figure 3. Coordination Sphere for Pu(IV) in TBP.**
(Pu expresses a coordination sphere of six.)

### 5.2.3 Aqueous Acid Concentration or pH

For most of the solvents used in the processes described in Section 5.3 with the possible exception of hexone, the $E_a^o$ for Pu is better under higher (~1 *M*) acid conditions. At high pH or very low acid conditions, Pu will have the tendency to hydrolyze and form insoluble hydroxides ($Pu(OH)_4$) that are not extractable. The alkalinity of tank waste would support lower $E_a^o$ for Pu extraction.

### 5.2.4 Aqueous Salting Agents and Complexing Agents

The $E_a^o$ for Pu in acid solutions will increase by increasing the nitrate concentration for hexone and TBP systems (Schneider and Harmon 1959). Other ions such as sulfate, phosphate, oxalate, and fluoride will react with U(VI) and Pu(IV) to form stable complexes in the aqueous phase, significantly decreasing the $E_a^o$ of these metals in the extractant. Even though the waste tanks will contain a significant amount of nitrate, the lack of an acid condition should prevent nitrate from increasing the $E_a^o$ for the extractant. Conversely, the waste tanks also contain a fair amount of oxalate, fluoride, phosphate, and other organic complexants that should be even more effective complexing ions in the alkaline waste because they are not tied up with hydrogen ions as they are in acid systems. However if the pH is too high, these complexants will be competing with the hydroxyl ion for the metals. In either case the effect of these ions or hydroxyl ion would be to lower the $E_a^o$.

### 5.2.5 Extractant Loading

If the extractant becomes saturated with a metal, its $E_a^o$ for extracting metals is reduced because the effective concentration of the extractant or the quantity of available complexing sites is reduced. Tank waste will normally contain more U than Pu. If the volume of organic is very limited, it is possible that it could become saturated in one metal and reduce the $E_a^o$ for others. In the case of D2EHPA, it may become loaded with sodium ions under alkaline conditions and reduce the $E_a^o$ for other metals. Extractant loading is not expected to be much of a factor for extraction in alkaline tank wastes.

### 5.2.6 Engineering Effects

The efficiency of extraction will also depend on engineering factors such as how well the organic is dispersed in the aqueous phase and how well the phases separate. If there is poor contact between the organic and aqueous phases, the efficiency of extraction will be poor. Other factors such as temperature and organic to aqueous ratios can affect the efficiency of the extraction. If the solvents are not separable but are associated with solid particles, the contact efficiency with the aqueous should be poor.

## 5.3 SEPARATION PROCESS PLANTS

The organic extractants potentially found in Hanford high-level waste tanks are derived from five major processes, which used solvent extraction technology to process nuclear spent fuel, purify products, and to treat wastes. All of these processes were designed to extract the desired components from acid solutions into organic solvents. Because the solvents were primarily designed for acid extractions, there are limited references to the use of these organics under the alkaline conditions that are found currently in high-level waste tanks. However, alkaline conditions were normally used in all these processes for solvent treatment to remove solvent impurities (Westinghouse 1989), undesirable fission products, or residual products (U, Pu)

(Westinghouse 1989). Descriptions of these processes and the solvents used in the extractions are described in Sections 5.3.1 through 5.3.5.

### 5.3.1 Reduction and Oxidation (REDOX) Process

The REDOX process used hexone (methyl isobutyl ketone) directly to extract Pu and U from low concentrations of $HNO_3$ with aluminum nitrate as a salting agent. In some cases sufficient aluminum nitrate was added to make the feed solutions actually acid deficient (Hanford Works 1951). Sodium carbonate (2%) and dilute caustic (Hanford Works 1951) were used to remove residual Pu, U, and fission products from the used solvent. Because of volatility (116 °C boiling point), it is highly unlikely that significant quantities of hexone remain in the tank waste. Even if hexone is present, the extractability of Pu and U are expected to be low in the alkaline wastes based on the washing process used to clean the solvent.

### 5.3.2 Metal Recovery Process (U-Plant)

This process was used in the 1950s to recover U not recovered from the waste tanks in the bismuth phosphate process for Pu production. The process (Jones 1993) used tributyl phosphate (12.5%TBP) diluted in a kerosene-type solvent to extract U from bismuth phosphate waste that had been acidified with $HNO_3$ to 2-6 *M*. This was the first production use of TBP and as the process matured, the TBP concentration was increased to greater than 15% (Reddick 2004). Ferrous sulfamate and sulfamic acid were used to keep the residual Pu in the Pu(III) valence state so that it would not extract. The TBP extractant was used in three additional processes described below.

### 5.3.3 Plutonium Finishing Plant (PFP)

The PFP was used to purify Pu and recover Pu scrap from metal processing. The processes at PFP (Recuplex and Plutonium Recovery Facility, PRF) used TBP (20%) dissolved in carbon tetrachloride (CCl4) to extract Pu from 2.5 *M* $HNO_3$ (Jones 1993). The used solvent was washed with 0.495M $Na_2CO_3$ to remove the TBP degradation product, dibutyl phosphate (DBP), and residual Pu. PFP also used dibutyl butyl phosphonate (25%DBBP/CCl4) to extract and recover $^{241}Am$ from $HNO_3$. Both Am and Pu were stripped from the DBBP with low molarity (0.05 *M*) $HNO_3$. In an evaluation of using DBBP as an extractant for Pu (Kingsley et al. 1961), $Na_2CO_3$ (5%, 0.47 *M*) was found to be an effective stripping reagent for removing Pu from DBBP. Distribution coefficients, $E_a^o$, for the first stage ranged between 0.004 and 0.028 and less than 1% Pu remained in the organic after one contact. Both low nitric acid and low sodium carbonate solutions can be used to remove Pu from the DBBP. Therefore like TBP, the high pH or alkaline conditions do not support extraction into the residual DBBP in wastes.

### 5.3.4 Plutonium-Uranium Extraction (PUREX) Process

PUREX was the largest production process at Hanford using TBP to separate U and Pu from spent nuclear fuel. The majority of PUREX operations used 30% TBP (Reddick 2004; reduced to 25% TBP in last few years of operation) in normal paraffin hydrocarbon (NPH) as the extractant for Pu and U. NPH is a mixture of aliphatic hydrocarbons with carbon chains from $C_{10}$ to $C_{15}$. The extraction of U and Pu was done under varying strong (0.5-3.0 *M*) $HNO_3$ acid concentrations. Low concentration (0.1 *M*) $HNO_3$ was used to strip the U from the TBP/NPH and a reducing agent, ferrous sulfamate in $HNO_3$, was used to strip the Pu. Multiple cycles of the extraction process were used to purify the products. TBP will slowly hydrolyze in $HNO_3$ or NaOH to form dibutyl phosphate (DBP) and mono butyl phosphate (MBP). Under acid conditions DBP can form strong complexes with U, Pu and some fission products and have large distribution coefficients ($E_a^0$) between the organic and aqueous phases. MBP is relatively insoluble in either phase under acid conditions and can form emulsions or interfacial scum (Westinghouse 1989).

The properties of these impurities were undesirable and were removed by a solvent treatment system. The process used two separate solvent treatment systems, one for the high level and Pu cycles and a separate system for the final U cycle. An alkaline permanganate wash of the TBP/NPH was used to remove the degradation components. The alkaline $Na_2CO_3$ (0.24 *M*) formed sodium salts with the DBP and MBP making them more soluble in the aqueous phase than the organic. The permanganate precipitated under the alkaline conditions and the manganese dioxide ($MnO_2$) formed helped remove many of the fission products contaminating the TBP/NPH. Because Hanford tank wastes are all alkaline, the contributions of DBP and MBP to any separable organic phase should be minimal because of their higher aqueous solubility at high PHS. The alkaline tank conditions should also limit the extraction of any soluble Pu present in the wastes into residual TBP.

### 5.3.5 Fission Product Recovery (B-Plant)

The B-Plant fission product recovery process used a mixture of di(2-ethylhexyl) phosphoric acid (0.3 *M* D2EHPA or HDEHP) and (0.2 *M*)TBP in NPH solvent to extract and separate $^{90}Sr$ and fission product rare earths from PUREX acidified waste streams. D2EHPA was also investigated as an extractant (Buckingham 1967) for Pu and Np but was never routinely used. The Pu(IV) and Np(IV) were extracted from about a 1M $HNO_3$ solution and stripped from the organic with 0.1 *M* oxalic acid. The solvent treatment for this flow sheet used 1 *M* $Na_2CO_3$ with 0.1 *M* citrate or tartrate to prevent precipitation of U and other metals. This was essentially the same solvent clean-up used for the fission product recovery process. The $Na_2CO_3$ wash converts the D2EHPA to its sodium form NaD2EHP. This salt is sparingly soluble in aqueous solutions that contain sodium ions. If TBP is not present, a third phase of this sodium salt may form between the aqueous and NPH layers (Buckingham 1967). Data indicate that the decontamination factor for analytes were expected to behave similar to Pu(IV) such as Ce(IV) and Zr(IV) is around 30. Therefore the tank waste conditions are not expected to be favorable for extraction of Pu in any residual D2EHPA/TBP that is present.

## 5.4 SUMMARY OF RELEVANT CHEMISTRY

The above discussions cross a number of chemical and physical aspects of the relationship between Hanford organic extractants and Pu interaction. These are summarized in Table 2. In general, most aspects indicate a reluctance of Pu to become reconcentrated into the organics of the waste tanks. Where they exist, the positive concentrators are minor or significantly outweighed by Pu solubility conditions that do not allow interaction with the organic layer. Lowered $E_a^o$ in the high pH wastes significantly suppresses concentration of Pu into organic components.

**Table 2. Factors Influencing Mechanisms of Transuranic Separations In Caustic Hanford Waste**

| Factor | Pu Aqueous Solubility | Pu Extractability |
|---|---|---|
| Aqueous, high pH | Low ($Pu(OH)_4$) | Low $E_a^o$ (<.01) |
| Extractant concentration | NA | Increases $E_a^o$ |
| Oxidation state | Pu[IV]<Pu[III]<Pu[VI] | Pu[III]<<Pu[VI]<Pu[IV] |
| Engineering effect | Poor mixing, less solubility | Poor mixing, lower $E_a^o$ |
| Salt effect | Unknown | Increases $E_a^o$ |
| Extractant loading | NA | Lowers $E_a^o$ |
| Carbonate | NA | Cleans up TBP extractant, lowers $E_a^o$ (caustic) |
| Complexants ($NO_3^-$,$CO_3^{2-}$,Org, $F^-$) | Increases | Lowers $E_a^o$ |
| REDOX process, hexone | NA | Evaporated |
| PFP process, DBBP | NA | Poor |
| B-Plant process, D2EHPA | NA | Poor |

## 6.0 RETRIEVAL EXPECTATIONS

The primary effectors for concentrating Pu into Hanford tank waste organics are Pu solubility and organic/aqueous partitioning coefficients. Alkalinity of the wastes minimizes both Pu solubility in the aqueous phase and extractability of Pu into the organic phase. Therefore, expected performance with regard to Pu uptake from retrieval sluicing can be estimated as boundary conditions from the available data.

Assuming pH is above 8 and that sluicing uses similar high caustic diluents, an upper estimate of concentration and inventory can be made. The conceptual model is shown in Figure 4. The parameters and estimated resulting concentrations and inventory are shown in Table 3. Of

particular note is that the organic Pu inventory estimates assume an upper bound 100% TBP without consideration of decomposition of TBP due to caustic and radiolytic environment.

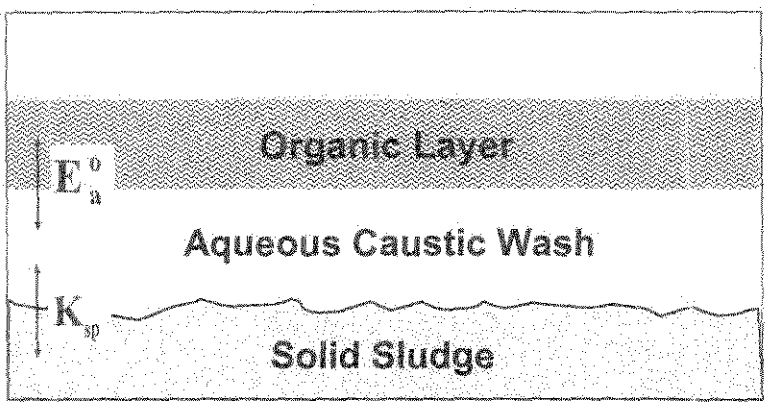


**Figure 4. Conceptual Tank Material Model with Organics.**

**Note:** Plutonium in sludge must first be dissolved ($K_{sp}$) into aqueous caustic wash before it can be transferred into associated organic extractants ($E_a^0$).

**Table 3. Estimated Potential Uptake of Plutonium in Organic During Sludge Retrieval.**

| Solid to Aqueous Dissolution | | Aqueous to Organic Transfer Estimates | | |
|---|---|---|---|---|
| **Species** | **Aqueous Concentration (@pH, *M*)** | **Partition Coefficient, $E_a^0$** | **Pu in Organic Concentration (*M*)** | **Pu in Organic Inventory, 7500 L** |
| Based on Thermodynamics (Pourbaix, 1974; Westinghouse, 1989) | | | | |
| $Pu^{3+}$ | @8+, $<1 \times 10^{-2}$ | <.0001 | $<1 \times 10^{-6}$ | <1.8 g |
| $Pu^{4+}$ | @6+, $<1 \times 10^{-6}$ | <.01 | $<1 \times 10^{-8}$ | <.018 g |
| $Pu^{6+}$ | @8+, $<1 \times 10^{-3}$ | <.01 | $<1 \times 10^{-5}$ | <18 g |
| Based on estimates from High Caustic Media (Peretrukin 1996; Westinghouse 1989) | | | | |
| $Pu^{4+}$ | @12+, $<1 \times 10^{-7}$ | <.01 | $<1 \times 10^{-9}$ | <.0018 g |

It must be noted that measurements in high caustic show that the solubility of Pu increases from $1 \times 10^{-7}$ to $1 \times 10^{-4}$ *M* as caustic increases from 1 to 10 *M* respectively (Peretrukin 1996; see also Delegard 1983 and Section 5.1). However, this effect is of minor concern because hydroxide concentrations as high as 10 *M* are not expected and the solubilities are so low that the amount of Pu extracted is still small.

While they appear to be more soluble, the presence of $Pu^{3+}$ and $Pu^{6+}$ is limited by oxidation state stability. This is shown in Figure 1 in which $Pu^{4+}$ predominates the more neutral region of the thermodynamic chart.

As a further point of reference related to solubility, tanks AN-106 and AN-107 contain significant quantities of organics. The measured concentrations of Pu in the aqueous calculate to be 2 x $10^{-6}$ *M* and 4 x $10^{-6}$ *M* respectively and are in agreement with thermodynmics (Pourbaix 1974) and other referenced studies. Thus, using an upper bound of 1 x $10^{-5}$ *M* is practically valid.

In summary, the characteristics of the expected chemistry and extraction mechanisms indicate that concentration of Pu from Hanford tank residual sludges to associated process organic extractants is significantly below levels of concern.

## 7.0 REFERENCES

Agnew, S. F., R. A. Corbin, T. B. Duran, K. A. Jurgensen, T. P. Ortiz, and B. L. Young; September 1995; *Waste Status and Transaction Record Summary for the Northeast Quadrant*; WHC-SD-WM-TI-615, Rev. 1; Los Alamos National Laboratory, Los Alamos, New Mexico.

Buckingham, J. S., August 31, 1967, *Waste Management Technical Manual*, ISO-100 Volumes 1 and 2, Richland Washington.

Cleveland, J. M., 1979, *The Chemistry of Plutonium*, American Nuclear Society, LaGrange Park, Illinois.

Delegard, C. H., and S. A. Gallagher, October 1983, *Effects of Hanford High Level Waste Components on the Solubility of Cobalt, Strontium, Neptunium, Plutonium and Americium*, RHO-RE-ST-3-P, Richland Washington.

Hanford Works, July 10, 1951, *REDOX Technical Manual*, HW-18700, Volumes 1 and 2, Hanford Atomic Products Operation, Richland Washington.

Jones, T. E., September 1993, *Hanford Technical Exchange Program, Process Chemistry at Hanford (Genesis of Hanford Wastes)*, PNL-SA-23121 S, Richland Washington.

Kingsley, R. S., and H. W. Crocker, June 15, 1961, *Studies of Dibutyl Butyl Phosphonate as an Extractant for Plutonium from the Recuplex Waste Stream*, HW-69910, Richland Washington.

Marcus, Y. and A. S. Kertes, 1969, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley Interscience, New York, New York.

Nguyen, D. M., .September 2002, *Tank Characterization Report for Single-Shell Tank 241-C-203*, HNF-SD-WM-ER-558, Rev. 1, CH2M HILL Hanford Group, Inc., Richland, Washington.

Peretrukin, V. F., S. V. Kryutchkov, V. I. Silin, and I. G. Tananaev, September 1996, *Determination of the Solubility of Np(IV)-(VI), Pu(III)-(VI), Am(III)-(VI) and Tc(IV), (V) Hydroxo Compounds in ).5-14 M NaOH Solutions*, WHC-EP-0987, Westinghouse Hanford Co., Richland, Washington.

Pourbaix, M., 1974, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd ed., National Association of Corrosion Engineers, Houston Texas.

Reddick, G. W., Jr., 2004, "Reject: Tank C-103: TBP Case Study.Doc" (e-mail to G. L. Troyer, February 26), CH2M HILL Hanford Group, Inc., Richland, Washington.

Schneider, R. A., and K. M. Harmon, July 1, 1959, *Hanford Analytical Technical Manual*, Analytical Solvent Extraction, HW-53368, Richland Washington.

Sederburg, J. P., and J. A. Reddick, December 1994, *TBP and Diluent Mass Balances in the PUREX Plant at Hanford 1955-1991*, WHC-MR-0483, Rev 0, Westinghouse Hanford Company.

Westinghouse, 1989, *PUREX Technical Manual*, WHC-SP-0479, Volumes 1 and 2, Westinghouse Hanford Co., Richland Washington.