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**DBBP SOLVENT EXTRACTION RECOVERY
OF NEPTUNIUM AND PLUTONIUM
FROM PUREX 1WW SOLUTION**

FEBRUARY 1969

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DBBP SOLVENT EXTRACTION RECOVERY
OF NEPTUNIUM AND PLUTONIUM
FROM PUREX 1WW SOLUTION

By

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ABSTRACT

A batch solvent extraction process has been developed to recover neptunium and plutonium values from Hanford Purex process 1WW solution. Dibutylbutyl phosphonate (DBBP) diluted with a mixture of normal paraffin hydrocarbons is used as the extractant. The utility and feasibility of the DBBP extraction process have been fully demonstrated in laboratory scale tests with both synthetic and plant 1WW solutions. Plant scale tests of the process for possible eventual incorporation into the Hanford Purex process complex are recommended.

TABLE OF CONTENTS

LIST OF TABLES	.vii
INTRODUCTION	1
SUMMARY AND CONCLUSIONS	1
PROCESS CONCEPT	2
CHEMICAL FLOWSHEET	5
EXPERIMENTAL PROCEDURES	8
Materials	8
Synthetic 1WW Solutions	8
Extractant Components	10
Radioisotopes	10
Other Chemicals	11
Procedures	12
Distribution Ratio Measurements	12
Analyses	12
RESULTS AND DISCUSSION	12
Extraction Contact	13
Valence Adjustment Step	13
Extraction of Neptunium and Plutonium	15
Extraction of Contaminants	17
Scrub Contacts	19
HNO ₃ Scrub Contact	20
Oxalic Acid Scrub Contact	21
Strip Contact	23
Oxalic Acid Costrip of Neptunium and Plutonium	23
Stripping of Contaminants	24
Path of Acid in DBBP Process	25
Process Tests with Plant 1WW Solution	26
Extraction-Scrub-Strip Contacts	26
Effect of Solids in Plant 1WW Solution	29
Further Process Steps	32
Destruction of Oxalic Acid in Strip Solution	32
Disposition of Neptunium and Plutonium Product	33

Solvent Wash Step	34
Radiolytic Stability of DBBP Extractant	34
Compatibility of DBBP with Purex Process	38
ACKNOWLEDGEMENTS	43
REFERENCES	44

LIST OF TABLES

1	Composition of Synthetic 1WW Solutions	9
2	Radioisotopes Used in This Study	11
3	Adjustment of Neptunium Valence	14
4	DBBP Extraction of Neptunium and Plutonium from Synthetic 1WW Solutions	16
5	Successive DBBP Batch Extractions of Neptunium	17
6	Kinetics of Extraction of Plutonium	17
7	Extraction of Contaminants	18
8	Nitric Acid Scrub Data	20
9	Scrubbing of Zirconium with Nitric Acid Solutions	22
10	Oxalic Acid Scrub Data	23
11	Oxalic Acid Stripping of Neptunium and Plutonium	24
12	Stripping of Contaminants	25
13	Acid Distribution in DBBP Process	26
14	Extraction-Scrub-Strip Studies with Plant 1WW Solutions	28
15	Extraction-Scrub-Strip Studies - Fission Product Decontamination Factors	29
16	Extraction Contacts of Plant 1WW Solution with Irradiated Extractants	29
17	Retention of Neptunium and Plutonium on Solids in Synthetic 1WW Solutions	31
18	Sodium Carbonate Solvent Wash Data	35
19	Extraction of Neptunium and Plutonium by Irradiated Extractants	36
20	Conditions for Cyclic ^{60}Co Irradiation of 25% DBBP-NPH	37
21	Selected Properties of Cyclically Irradiated Extractant	37
22	Effects of Presence of DBBP in Purex Solvent - Kinetic Measurements	39
23	Effects of Presence of DBBP in Purex Solvent - Multiple Batch Contacts	40
24	Uranium Distribution Ratios for TBP-DBBP Solvents	42

DBBP SOLVENT EXTRACTION RECOVERY OF NEPTUNIUM AND PLUTONIUM FROM PUREX 1WW SOLUTION

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INTRODUCTION

Neutron irradiation of natural uranium in Hanford's nuclear reactors to produce ^{239}Pu also produces gram quantities of ^{237}Np . ^{237}Np is the starting material for production of ^{238}Pu , an isotopic power source recently used in several space vehicles.

Technology and equipment presently used in the Hanford Purex plant to recover and purify ^{237}Np have been described recently.^(1,2) Currently, only about 65 to 85% of the neptunium entering the Purex plant is recovered; the remaining 15 to 35% accumulates eventually in a highly-radioactive waste stream (1WW solution) and is not recovered.

This report describes a new batch solvent extraction process developed to recover neptunium from the 1WW solution. Small amounts of plutonium present in the waste are also extracted and recovered. This process uses dibutyl-butyl phosphonate (DBBP) diluted with NPH* as the extractant. Similar processes using either trilaurylamine (TLA) or bis-2(ethylhexyl)phosphoric acid (HDEHP) as the extractant have been described previously.^(3,4)

SUMMARY AND CONCLUSIONS

A batch DBBP solvent extraction process has been devised for recovery of neptunium (and also plutonium) values from Hanford Purex process 1WW solution. Laboratory tests of the

* NPH is the Hanford designation for a mixture of normal paraffin hydrocarbons, principally C_{10} through C_{14} , sold by the South Hampton Co., Houston, Texas.

process with both synthetic and plant 1WW solutions are described. Such tests have fully demonstrated the utility of the process, and its incorporation into the Hanford Purex complex merits further consideration.

In the recovery process, hydrazine is added to the 1WW solution to adjust both neptunium and plutonium to extractable valence states. Subsequent contact of the 1WW solution with a double volume portion of 25 vol% DBBP solvent extracts over 95% of the soluble fraction of both actinide elements. Approximately 27 to 40% of the $^{95}\text{ZrNb}$, 17 to 32% of the $^{106}\text{RuRh}$, and 12 to 46% of the $^{144}\text{CePr}$ activity in the 1WW solution (depending upon solvent irradiation history) report to the organic phase. These contaminants are largely removed by scrubbing the DBBP solution with small volumes of nitric and oxalic acid solutions. Finally, neptunium and plutonium are costripped into a 0.1M oxalic acid solution. After concentration and destruction of oxalate by reaction with nitric acid, this latter solution can be routed to the HA column to return the recovered neptunium and plutonium to the mainline Purex process. A detailed chemical flowsheet for this process is presented and discussed.

The DBBP extractant has excellent chemical and radiolytic stability when in contact with highly radioactive 1WW solution. Further, DBBP appears sufficiently compatible with the Purex process 30% tributyl phosphate (TBP) solvent to permit the use of both solvents in the same plant. On both counts DBBP is superior to either TLA or HDEHP and, thus, is the preferred solvent for a batch process for recovery of neptunium from Hanford Purex 1WW solution.

PROCESS CONCEPT

The scheme presently used in the Hanford Purex plant to recover ^{237}Np is shown in Figure 1 where the processing sequence envisioned with incorporation of a DBBP batch extraction process into the recovery complex is also shown.

FIGURE 1. *Integration of DBBP Process into Hanford Purex Neptunium Recovery Scheme*

In the current plant operation, after dissolution of fuel elements in HNO_3 , neptunium as Np(VI) is extracted into 30% TBP-NPH solvent along with uranium and plutonium in the HA column. [In normal operation about 15 to 35% of the neptunium and 0.1% of the plutonium are lost to the aqueous raffinate (HAW) from the HA column and are not subsequently recovered.] The pregnant solvent is scrubbed in the HS column to remove fission products. Plutonium is then partitioned into an aqueous phase in the 1BX column, and ferrous sulfamate is used to reduce the plutonium to the inextractable Pu(III) state. Neptunium and uranium are costripped from the solvent in the 1C column into a dilute HNO_3 aqueous stream. The 1C column product solution is concentrated, and uranium is reextracted in the 2D column. By control of the organic phase uranium concentration in this step, neptunium is forced into the 2D aqueous raffinate stream which is concentrated for backcycle to the HA column. Approximately one third of the backcycle stream is continuously processed through the 3A column where the neptunium is extracted into the organic phase. (Plutonium associated with the neptunium is forced into the 3AW stream, thence, to the backcycle stream for eventual recovery in the HA column.) The neptunium is stripped in the 3B column and returned to the 3A column. Neptunium is thus accumulated in the 3A-3B system and is periodically decontaminated and removed to a batch ion-exchange unit for final purification and loadout.

After appropriate blending with various other Purex process aqueous wastes the HAW solution is evaporated to yield a small volume of highly acid and highly radioactive waste solution (1WW solution). In the present plant operation, the 1WW solution is treated with sugar to destroy most of the nitrate and then neutralized with NaOH and routed to underground storage.

The DBBP extraction process outlined in Figure 1 is designed to recover neptunium and plutonium from the 1WW solution prior to the denitration step. This batch extraction process involves, firstly, addition of hydrazine to the 1WW solution to establish both plutonium and neptunium in the quadrivalent state. Both actinides are then coextracted into a DBBP-NPH solution. The resulting organic phase is scrubbed with small volumes of HNO_3 and oxalic acid solutions to remove most of the coextracted fission products. Finally, neptunium and plutonium are costripped into a large volume of 0.1M oxalic acid solution. Oxalate in the final strip solution is destroyed by reaction with HNO_3 (or, alternatively, HNO_3 and H_2O_2) to yield a suitable product solution for return of the recovered plutonium and neptunium to the mainline Purex process.

Improved overall plant recovery of neptunium with concomitant economic gain is certainly the foremost benefit that would accrue from incorporation of the DBBP extraction process into the Purex process complex. The DBBP process should also provide more flexibility in waste rework operations. Extensive rework operations have at times been necessary to recover product losses associated with operational difficulties and equipment failures.

CHEMICAL FLOWSHEET

A chemical flowsheet for the DBBP process is shown in Figure 2. Technical bases for the flowsheet are presented subsequently; however, certain key features are discussed here.

The DBBP process is designed to recover routinely 95% of the soluble neptunium values in plant 1WW solution. There is evidence, however, that from 8 to 20% of the neptunium in the 1WW solution is associated with the solids normally present in the waste solution. How much, if any, of this latter neptunium will extract into the DBBP phase has not been established. Loss of all the neptunium associated with the solids is naturally

FIGURE 2. DBBP Process Flowsheet

undesirable but not intolerable as a simple calculation shows. For example, suppose as much as 35% of the neptunium entering the Hanford Purex plant is lost to the 1WW stream. Also suppose that, of this amount, 20% is lost to the solids while 95% of that in solution is recovered by the DBBP process. Even under these conditions the overall plant neptunium recovery would be 92%.

Similar calculations can be made for recovery of plutonium from the 1WW solution. From 50 to 60% of the plutonium in the 1WW solution appears to be absorbed or otherwise associated with the solid material. If this material does not extract into DBBP, a point not yet established, only about half the plutonium in the 1WW solution will be recovered by the DBBP process. But, as noted earlier, in normal Purex process operation the plutonium loss to the 1WW stream is only about 0.1%. Furthermore, the economic value of the ^{239}Pu in the 1WW is considerably less than that of ^{237}Np . Under these circumstances, recovery of any of the plutonium from the 1WW stream can be regarded as an added economic benefit of the DBBP neptunium recovery scheme.

Equilibrium in each of the aqueous-organic contacts is attained in 3 to 5 min of emulsion-type mixing. The 60 min contact period specified in the flowsheet is an arbitrary choice believed to be representative of what might be used or required in plant scale equipment. Obviously, shorter contact times are desirable not only to decrease process time cycles but also to limit solvent radiolysis.

The flowsheet specifies that the DBBP extractant be carbonate-washed every sixth cycle, but this is also an arbitrary choice. Actual process operation may dictate more or less frequent solvent washing. Although not indicated in the flowsheet, it may also prove desirable, before the solvent wash step, to contact the DBBP phase a second time with 0.1M oxalic acid to remove residual neptunium and plutonium.

The small volume of spent oxalic acid scrub solution produced in the DBBP process contains 80 to 90% of the ^{95}Zr in the 1WW solution. Similarly, the spent HNO_3 scrub contains only 15 to 20% of the $^{106}\text{RuRh}$ and $^{144}\text{CePr}$ in the 1WW. It is believed the latter material can be recycled to the 1WW concentrator without serious consequences to performance of the DBBP process. However, since such recycle of the oxalic acid scrub material is not feasible, a special disposal scheme is required. A suitable scheme might be the addition of the spent scrub to the raffinate from the DBBP extraction contact before this material is denitrated. It is worth mentioning that the oxalic acid scrub provides an excellent concentrate source for recovery of ^{95}Zr if a need for substantial amounts of this radioisotope should arise.

Finally, the percentages of $^{95}\text{ZrNb}$, $^{106}\text{RuRh}$, and $^{144}\text{CePr}$ shown reporting to the DBBP phase in the extraction contact are based on values expected for unirradiated extractant. Small changes in distribution of these fission products will occur as the result of solvent radiolysis, but the flowsheet shown is flexible enough to accommodate these small fluctuations easily.

EXPERIMENTAL PROCEDURES

MATERIALS

Synthetic 1WW Solutions

The composition of the synthetic 1WW solutions used in this study are listed in Table 1. The bulk of the experimental work was conducted with 1WW-1 solution; its composition approximates that of 1WW solution currently produced in the Hanford Purex plant. The other solutions listed were prepared to investigate the effects of changed acidity (1WW-2 and 1WW-3), of eliminating sulfate (1WW-4), and of eliminating both iron and sulfate (1WW-5). Such changes from present day 1WW composition might result from various Purex process modifications.

TABLE 1. Composition of Synthetic 1WW Solutions

Component	Concentration, M				
	Solution No. (a)				
	1WW-1	1WW-2	1WW-3	1WW-4	1WW-5
HNO ₃	4.68	3.68	5.68	6.48	6.48
H ₂ SO ₄	0.79	(b)	(b)	0.0	0.0
NaNO ₃	0.68	(b)	(b)	(b)	(b)
Fe(NO ₃) ₃	0.35	(b)	(b)	(b)	0.0
Al(NO ₃) ₃	0.125	(b)	(b)	(b)	(b)
Cr(NO ₃) ₃	0.025	(b)	(b)	(b)	(b)
H ₃ PO ₄	0.015	(b)	(b)	(b)	(b)
Ni(NO ₃) ₂	0.015	(b)	(b)	(b)	(b)
La(NO ₃) ₃	0.0048	(b)	(b)	(b)	(b)
Zr(SO ₄) ₂	0.0032	(b)	(b)	(b)	(b)
HF	0.0030	(b)	(b)	(b)	(b)
Ce(NO ₃) ₃	0.0025	(b)	(b)	(b)	(b)
CsCl	0.0022	(b)	(b)	(b)	(b)
RuCl ₃	0.0017	(b)	(b)	(b)	(b)
UO ₂ (NO ₃) ₂	0.00034	(b)	(b)	(b)	(b)
Plutonium	10 ⁻⁶ to 10 ⁻⁵	(b)	(b)	(b)	(b)
Neptunium	10 ⁻⁶ to 10 ⁻⁵	(b)	(b)	(b)	(b)

(a) For identification purposes only.

(b) Same as 1WW-1 solution.

The synthetic 1WW solutions were prepared by mixing appropriate amounts of stock solutions of the listed chemicals. For convenience only, zirconium and ruthenium were added to the 1WW solutions as Zr(SO₄)₂ and RuCl₃; the exact species of zirconium and ruthenium in plant 1WW solutions are not known.

Each of the synthetic 1WW solutions was free of solids when initially prepared. However, small amounts of solids--presumably, sulfates and phosphates--slowly precipitated as the

solutions stood at room temperature. Plant 1WW solutions also contain solids; consequences of these solids to the DBBP extraction process are discussed subsequently.

Finally, as discussed more fully later, plant 1WW solution is believed to contain plutonium(IV) and neptunium, at least partly as neptunium(V). Accordingly, about one to two days before use in extraction contacts, the synthetic 1WW solutions were adjusted to 10^{-6} to 10^{-5} M plutonium and/or neptunium by appropriate addition of $\text{Pu}(\text{NO}_3)_4$ and/or NpO_2NO_3 stock solutions.

Extractant Components

DBBP extractants were prepared by diluting as-purchased DBBP (Virginia Carolina Co.) with either NPH or, in a few experiments, Soltrol-170 (Phillips Petroleum Co.). Gas chromatographic analyses of the commercial DBBP made in another study⁽⁵⁾ indicate it contains, typically, 82 to 83% DBBP, about 15% dibutylmethyl phosphonate, and about 2 to 3% low-boiling fractions. Extractant DBBP concentrations quoted in this report refer to the volume percent of the commercial mixture in the kerosine diluents.

Radioisotopes

Decontamination of plutonium and neptunium from various contaminants in synthetic 1WW solutions was followed with the aid of the radioisotopes listed in Table 2.

^{59}Fe , ^{88}Y , and ^{85}Sr were obtained from the Nuclear Science and Engineering Co. ^{233}U , ^{241}Am , ^{234}Th , and ^{95}Zr were obtained as described below; all other listed isotopes came from the Oak Ridge National Laboratory (ORNL). ^{233}U , from irradiated ThO_2 , was purified by TBP extraction in the Hanford Purex plant and further purified before use by ion exchange resin techniques. ^{241}Am , obtained from Hanford Recuplex⁽⁶⁾ process waste, was purified by appropriate ion exchange procedures. ^{234}Th was prepared from natural uranium by the ion exchange procedure outlined by Phillips.⁽⁷⁾ Finally, a 10M HNO_3 solution of the

equilibrium mixture of ^{95}Zr and ^{95}Nb was prepared by destruction of oxalate in the oxalic acid solution supplied by ORNL. As required, ^{95}Zr was purified from ^{95}Nb by the procedure of Rais, Kyrs, and Caletka.⁽⁸⁾

TABLE 2. *Radioisotopes Used in This Study*

<u>Isotope</u>	<u>Chemical Form</u>
^{233}U	UO_2^{+2} in HNO_3 Solution
^{234}Th	Th^{+4} in HNO_3 Solution
^{59}Fe	Fe^{+3} in HCl Solution
^{88}Y	Y^{+3} in HCl Solution
$^{152-154}\text{Eu}$	Eu^{+3} in HCl Solution
$^{144}\text{CePr}$	Ce^{+3} in HCl Solution
^{241}Am	Am^{+3} in HNO_3 Solution
^{85}Sr	Sr^{+2} in HCl Solution
^{137}Cs	Cs^{+1} in HCl Solution
^{95}Zr	Zr^{+4} in 10M HNO_3 Solution
$^{95}\text{ZrNb}$	in 10M HNO_3 Solution

Radioisotopes were added to synthetic 1WW in the chemical form listed in Table 2. It is believed that in each case the resulting oxidation state of the radioisotope was the same as that of the inert and/or radioactive isotopes of the same metal ions in actual 1WW solution.

Other Chemicals

Hydrazine was obtained from the Olin Mathieson Chemical Co. as an 11M stock solution. All other chemicals used in this study were of reagent quality.

PROCEDURES

Distribution Ratio Measurements

Distribution ratios are listed in many tables. The distribution ratio is defined as the ratio of the concentration of the element of interest in the less dense organic phase to the concentration of the element in the more dense aqueous phase after equilibration of the two essentially immiscible liquids.

Unless otherwise indicated, a standard 10-min contact period (mechanical stirring) at about 25 °C was allowed for attainment of equilibrium. Phases were separated by either centrifugation (synthetic 1WW) or gravity settling (plant 1WW).

ANALYSES

Neptunium and plutonium in aqueous solutions were determined by sequential triisooctylamine and thenoyltrifluoroacetone extraction and alpha counting. When present singly in DBBP solutions, either neptunium or plutonium was determined by direct alpha counting of aliquots. ^{233}U and ^{241}Am in simulated process aqueous solutions, and DBBP phases derived therefrom, were also determined by direct alpha counting of aliquots.

The concentrations of various gamma emitters in aqueous and DBBP solutions obtained from experiments with both plant and synthetic 1WW solutions were determined by gamma-energy pulse height analyses.

RESULTS AND DISCUSSION

The bulk of the extraction-scrub-strip experiments were performed with synthetic 1WW solution or DBBP phases derived from contact thereof. These results are summarized in Tables 3 through 12. For purposes of comparison and illustration appropriate results obtained with plant 1WW solutions are also included in some of these tables. However, because the experiments with plant 1WW were made to demonstrate the overall

extraction-scrub-strip cycle, the complete results with plant 1WW solutions are collected in Tables 13 through 15 and are further discussed at that point in the text.

EXTRACTION CONTACT

Valence Adjustment Step

From its manner of preparation and composition and from known aqueous actinide chemistry, Purex plant 1WW solution would be expected to contain plutonium in the +4 state. The ready extraction of plutonium from unadjusted plant 1WW solution into either DBBP (Table 3) or TLA⁽³⁾ extractants testifies that this expectation is realized. More significantly, from 85 to 90% of the neptunium in plant 1WW solution also exists in a readily extractable state, presumably as either Np(IV) or Np(VI) or both (Table 3). Neptunium(IV) and (VI) in 1WW solution probably arise from disproportionation of Np(V) according to the reaction

The disproportionation reaction⁽⁹⁾ is favored in those aqueous solutions containing sulfate or fluoride ions and/or which are strongly acidic--all three of these features being characteristic of 1WW solution. The first experimental data listed in Table 3 provide evidence for the occurrence of the disproportionation of Np(V) in 1WW solution. In the case referenced, the neptunium was initially added all as Np(V), but over 80% of the neptunium extracted when the 1WW solution was later (1 to 2 days) contacted with the DBBP solvent. Only a negligible extraction of neptunium would be expected if the neptunium remained largely as Np(V).

A valence adjustment step to convert all the neptunium in the 1WW solution to extractable species is required to permit an extraction of 95 to 99% of the neptunium in a single-batch

extraction contact. A suitable valence adjustment is accomplished by adding hydrazine to the 1WW solution (Table 3). Hydrazine, like most reductants (e.g., ferrous sulfamate) that reduce Np(V) to Np(IV), is thermodynamically capable of reducing Pu(IV) to Pu(III). Although hydrazine rapidly reduces Np(V) to Np(IV), the rate of reduction of Pu(IV) to Pu(III) in 1WW solution at 25 °C is apparently very slow. Burney⁽¹⁰⁾ has also noted the low rate of hydrazine reduction of Pu(IV) in HNO₃ solutions. Thus, an advantage can be taken of the difference in reduction kinetics to establish both elements in the quadrivalent state. A concentration of hydrazine in the range 0.02 to 0.05M is satisfactory.

TABLE 3. *Adjustment of Neptunium Valence*

Conditions: Portions of synthetic 1WW-1 solution [containing added Pu(NO₃)₄ or NpO₂NO₃] or plant 1WW solution were made indicated concentration of hydrazine and were allowed to stand at 25 °C for indicated time. Resulting solutions were then contacted for times indicated with a double volume portion of 25% DBBP-NPH.

1WW Type	N ₂ H ₄ , M	Reduction Time, min	Contact Time, min	E _a ^o		Not Extracted, %	
				Pu	Np	Pu	Np
Synthetic 1WW-1	0.0	-	10	62.0	3.58	0.77	12.6
Plant	0.0	-	10	-	-	1.4 to 3.6 ^(a)	7 to 15 ^(a)
Synthetic 1WW-1	0.05	30	10	61.8	25.4	0.77	1.17
Synthetic 1WW-1	0.02	30	10	65.6	38.1	0.76	1.40
Plant	0.05	30	10	-	-	1.0	-
Synthetic 1WW-1	0.05	-	5 ^(b)	-	39.1	-	1.36
Synthetic 1WW-1	0.05	-	15 ^(b)	-	52.7	-	1.07
Synthetic 1WW-1	0.05	-	30 ^(b)	-	53.1	-	1.03
Plant	0.05	-	30 ^(b)	-	-	1.81	4.0
Synthetic 1WW-1	0.02	-	30 ^(b)	57.9	38.4	0.86	1.40

(a) See results in Table 13.

(b) Contacted with extractant immediately after addition of hydrazine.

In most of the extraction experiments, the 1WW solution, after addition of N_2H_4 , was allowed to stand 30 min at 25 °C before contact with the DBBP extractant--a technique used for convenience only. Data in Table 3 show that reduction and extraction of neptunium can be accomplished simultaneously. To shorten process time cycles, immediate contact of aqueous and organic phases after hydrazine addition may be desirable in plant operation of the DBBP extraction contact.

Extraction of Neptunium and Plutonium

Experiments (Table 4) were performed to study DBBP extraction of neptunium and plutonium from synthetic 1WW solutions of various compositions. In each instance, plutonium extracted better than neptunium; the greater affinity of DBBP for Pu(IV) over that for Np(IV) was demonstrated earlier by Siddal.⁽¹¹⁾ An extractant composition of 25% DBBP is required, at an aqueous-to-organic ratio of 1:2, to extract more than 98% of the neptunium in 1WW solution of the estimated current composition (1WW-1).

As might be expected, elimination of sulfate from the 1WW-5 solution aids DBBP extraction of both neptunium and plutonium (Table 4); however, with 1WW-5 solution, elimination of both the iron and sulfate is detrimental to extraction of neptunium. The possibility that iron(III) enters into the reaction between hydrazine and neptunium(V) was considered but not pursued. Results for 1WW-2 and 1WW-3 solutions show that both neptunium and plutonium extractions fall off slightly as the 1WW HNO_3 concentration is increased or decreased below that estimated for typical current 1WW solution. However, for the range of acidities tested, over 94% of the neptunium was extracted in a single contact. The results in Table 4 thus demonstrate that the DBBP extraction process will provide satisfactory neptunium recovery over a wide range of 1WW compositions.

TABLE 4. *DBBP Extraction of Neptunium and Plutonium from Synthetic 1WW Solutions*

Conditions: Portions of various synthetic 1WW solutions [containing either $\text{Pu}(\text{NO}_3)_4$ or NpO_2NO_3] were adjusted to the N_2H_4 concentration and were allowed to stand 30 min at 25 °C. Resulting solutions were then contacted with a double volume portion of indicated DBBP extractants.

1WW No. (a)	DBBP, vol%	Plutonium			Neptunium		
		N_2H_4 , M	E_a^o	Not Extracted, %	N_2H_4 , M	E_a^o	Not Extracted, %
1WW-1	5	0.05	7.19	6.36	0.022	1.81 ^(b)	21.3
1WW-1	10	0.05	18.7	2.50	0.022	5.99 ^(b)	7.38
1WW-1	20	0.05	45.6	1.05	0.022	16.4 ^(b)	2.78
1WW-1	25	0.05	61.8	0.77	0.022	25.4 ^(b)	1.17
1WW-1	25	-	-	-	0.022	22.9	1.96
1WW-4	25	0.05	254.0	0.19	0.05	77.4	0.64
1WW-2	25	0.05	15.4	3.07	0.05	12.1	4.01
1WW-3	25	0.05	39.7	1.21	0.05	8.2	6.24
1WW-5	25	0.05	91.5	0.53	0.05	0.98	34.5

(a) For identification purposes, see Table 1.

(b) Diluent was Soltrol-170 in these runs, and NPH in all other experiments.

Results of contacting one portion of DBBP extractant successively, without intervening scrub or strip contacts, with six fresh portions of 1WW solution, are presented in Table 5. Such an extraction scheme has been suggested⁽¹²⁾ for use in the plant application of the DBBP extraction process. Its chief disadvantage, which follows from the constancy of the neptunium distribution ratio, is that the percent of neptunium not extracted increases from contact to contact.

TABLE 5. *Successive DBBP Batch Extractions of Neptunium*

Conditions: Synthetic 1WW-1 solution made 0.022M N_2H_4 and was allowed to stand 30 min at 25°C . One portion of 25% DBBP-NPH was then contacted with successive 1/2 volume portions of the 1WW solution.

<u>Contact No.</u>	<u>E_a^0</u>	<u>Not Extracted, %</u>
1	30.1	1.77
2	33.3	3.20
3	40.2	4.18
4	39.8	5.56
5	43.1	6.25
6	34.4	8.16

Finally, results in Table 6 show that plutonium-extraction equilibrium is attained in 1 to 3 min of vigorous agitation. It is believed neptunium-extraction equilibrium is attained equally rapidly.

TABLE 6. *Kinetics of Extraction of Plutonium*

Conditions: Portions of synthetic 1WW-1 solution [containing $\text{Pu}(\text{NO}_3)_4$] were contacted at 25°C for times indicated with double volume portions of 25% DBBP-NPH.

<u>Contact Time, min</u>	<u>$\text{Pu } E_a^0$</u>
0.5	18.5
1.0	55.5
3.0	62.0
5.0	62.5
10.0	62.0
30.0	65.3

Extraction of Contaminants

Small amounts of uranium and thorium(UX_1), present in 1WW solution, coextract with neptunium and plutonium (Table 7). Of the gamma-emitting fission products in plant 1WW solution,

only $^{95}\text{ZrNb}$, $^{144}\text{CePr}$, and $^{106}\text{RuRh}$ appear to extract to any extent. Distribution ratio data for ^{85}Sr and ^{137}Cs for synthetic 1WW-1 are in agreement with this result.

TABLE 7. *Extraction of Contaminants*

Conditions: Plant or synthetic 1WW-1 solution (the latter containing the indicated radioisotopes) was contacted with a double volume portion of unirradiated 25% DBBP-TBP.

Radioisotope	E_a^0	
	Synthetic 1WW	Plant 1WW(a)
^{233}U	35.9	
^{234}Th	16.1	
^{95}Zr	2.18	
$^{95}\text{ZrNb}$		0.15 to 0.25
$^{144}\text{CePr}$	0.020	0.33 to 0.53
$^{106}\text{RuRh}$		0.10 to 0.26
$^{152-154}\text{Eu}$	0.17	
^{88}Y	0.14	
^{241}Am	0.0046	
^{59}Fe	0.0016	
^{85}Sr	10^{-4}	
^{137}Cs	10^{-5}	

(a) *Typical values for current plant 1WW (see Tables 14 and 16).*

Extraction of ^{95}Zr is particularly severe (80 to 90%) from both plant and synthetic 1WW solutions. (In this connection, detailed resolution of the gamma energy spectra of DBBP extracts from plant 1WW shows little, if any, ^{95}Nb present.) Pronounced extraction of zirconium by DBBP solutions was also observed in earlier studies of Siddall.⁽¹¹⁾

One peculiarity of the data listed in Table 7 is that considerably more $^{144}\text{CePr}$ extracts from plant 1WW than from the synthetic 1WW. This apparent discrepancy has not been resolved;

duplicate measurements confirm the difference in distribution ratios. It is noteworthy, however, that the $^{144}\text{CePr } E_a^{\text{O}}$ with plant 1WW is in line with those for yttrium and europium with the synthetic 1WW.

SCRUB CONTACTS

^{95}Zr is the principal radioactive contaminant in the DBBP phase resulting from the extraction contact with 1WW solution. Unless removed before hand, practically all the zirconium reports to the oxalic acid strip used to remove neptunium and plutonium from the organic phase. Recycle of such a strip solution, after oxalate destruction, to the Purex process HA column would eventually result in a greatly increased steady-state concentration of ^{95}Zr in the HA column. This in turn would undoubtedly be reflected in decreased (probably intolerably so) decontamination of the plutonium and uranium products from ^{95}Zr . A convenient way to avoid these difficulties is to scrub zirconium from the organic phase prior to the strip contact. Scrubbing of the DBBP extract with 1/10 volume of a dilute oxalic acid solution removes over 80% of the ^{95}Zr and only negligible amounts of neptunium and plutonium. (Scrubbing of ^{95}Zr is subsequently discussed in detail.)

Significant amounts of radiocerium and radoruthenium are also present in the DBBP solution after the extraction contact. The small volume of oxalic acid solution used to scrub zirconium removes only minor amounts of these contaminants. However, contact of the DBBP solution with a small volume of 4 to 6M HNO_3 effectively scrubs cerium activity. Such a HNO_3 scrub also benefits ruthenium decontamination because it apparently removes most of that small fraction of the ruthenium activity which normally transfers to the oxalic acid strip solution. Ruthenium decontamination is better when the HNO_3 scrub follows the oxalic acid scrub; conversely, $^{95}\text{ZrNb}$ scrub behavior does not depend on scrub order.

HNO₃ Scrub Contact

The effectiveness of HNO₃ scrubbing of ¹⁴⁴CePr from DBBP extractant is well illustrated by the data listed in Table 8. It is evident that cerium removal decreases as scrub acidity decreases. Nevertheless, a single contact of the organic phase with 1/4 volume of 4 to 6M HNO₃ at either 25 or 50 °C removes over 80% of the extracted ¹⁴⁴CePr. Under these conditions, only small amounts of plutonium and neptunium are scrubbed from the DBBP solution.

TABLE 8. Nitric Acid Scrub Data

Conditions: Synthetic 1WW-1 solution [containing either ¹⁴⁴CePr, Pu(NO₃)₄ or NpO₂NO₃] made 0.05M N₂H₄ and was allowed to stand 30 min at 25 °C. It was then contacted with a double volume portion of 25% DBBP-NPH. Portions of resulting organic solutions were contacted 10 min with indicated HNO₃ solutions.

HNO ₃ , M	Temp, °C	Volume Ratio A/O(a)	E _a ^o			% Scrubbed		
			¹⁴⁴ CePr	Np	Pu	¹⁴⁴ CePr	Np	Pu
0.5	25	1/4	0.295			44.7		
1.0	25	1/4	0.248			48.6		
2.0	25	1/4	0.169			58.3		
4.0	25	1/4	0.0592	197	108	80.0	0.52	0.92
6.3	25	1/4	0.0216	191	104	92.8	0.53	0.97
0.5	50	1/4	0.132			64.4		
1.0	50	1/4	0.108			68.8		
2.0	50	1/4	0.0790			74.9		
4.0	50	1/4	0.0269	147	105	89.7	0.70	0.95
6.3	50	1/4	0.0115	144	90	95.7	0.71	1.1
0.5	25	1/8	0.200			37.0		
1.0	25	1/8	0.178			40.4		
2.0	25	1/8	0.128			49.5		
4.0	25	1/8	0.0537			70.2		

(a) Aqueous to Organic Volume Ratio

Nitric acid solutions and HNO_3 solutions containing various additives were screened for their action in scrubbing zirconium activity from the DBBP phase (Table 9). Only negligible amounts of zirconium were removed by HNO_3 solutions or by HNO_3 solutions containing either inert zirconium, H_3PO_4 , or complexants such as citrate or tartrate. However, HNO_3 solutions containing either oxalic acid or, particularly, fluoride ion removed zirconium very smoothly and efficiently. (The results with HNO_3 -oxalic acid solutions led to the experiments reported in the next section and eventually to selection of 0.1M oxalic acid as the preferred reagent for zirconium scrubbing.) However, nitric acid-fluoride scrub solutions have two disadvantages: they are corrosive to stainless steel, and they scrub relatively large amounts of neptunium from the organic phase. For example, the contact of a 25% DBBP-NPH extractant containing Np(IV) with one tenth volume of a 5M HNO_3 -0.05M NH_4F solution removed about 5% of the neptunium.

Oxalic Acid Scrub Contact

Contact of the DBBP extract with a small volume of dilute oxalic acid solution is a very efficient way of scrubbing ^{95}Zr from the organic phase (Table 10). Preferred flowsheet scrub conditions (1/10 volume of 0.1M oxalic acid) remove over 80% of the extracted ^{95}Zr and only small amounts of neptunium and plutonium.

TABLE 9. *Scrubbing of Zirconium with Nitric Acid Solutions*

Conditions: Synthetic 1WW-1 solution (containing either ^{95}Zr or $^{95}\text{ZrNb}$) was contacted with a double volume portion of 25% DBBP-NPH. Portions of resulting organic solutions were contacted with HNO_3 solutions indicated.

Scrub Composition	Volume Ratio, A/O	E_a^0	
		$^{95}\text{ZrNb}$	^{95}Zr
4.0M HNO_3	1/4	137.	-
6.3M HNO_3	1/4	204.	-
4.0M HNO_3 -0.01M Citric Acid	1/4	21.0	-
4.0M HNO_3 -0.01M Tartaric Acid	1/4	22.9	-
4.0M HNO_3 -0.01M Oxalic Acid	1/4	1.52	-
6.0M HNO_3 -0.01M Citric Acid	1/4	28.0	-
6.0M HNO_3 -0.01M Tartaric Acid	1/4	36.9	-
6.0M HNO_3 -0.01M Oxalic Acid	1/4	1.91	-
5.0M HNO_3 -0.005M NH_4F	1/5	-	3.35
5.0M HNO_3 -0.01M NH_4F	1/5	-	1.42
5.0M HNO_3 -0.05M NH_4F	1/5	-	0.158
5.0M HNO_3 -0.1M NH_4F	1/5	-	0.0360
4.0M HNO_3 -0.005M $\text{ZrO}(\text{NO}_3)_2$	1/5	-	297.
4.0M HNO_3 -0.1M H_3PO_4	1/5	-	11.0
2.0M HNO_3 -0.1M KMnO_4	1/5	-	1.0
2.0M HNO_3 -0.1M $\text{KMnO}_4^{(a)}$	1/5	-	28.0

(a) MnO_2 at interface dissolved with H_2O_2 before phase separation.

TABLE 10. *Oxalic Acid Scrub Data*

Conditions: Synthetic 1WW-1 solution [containing either ^{95}Zr , $\text{Pu}(\text{NO}_3)_4$, or NpO_2NO_3] made 0.05M N_2H_4 and was contacted with a double volume portion of 25% DBBP-NPH. Portions of resulting organic phase were contacted with indicated oxalic acid solutions.

Oxalic Acid, <u>M</u>	Volume Ratio, <u>A/O</u>	E_a^{O} ^{95}Zr	% Scrubbed		
			^{95}Zr	<u>Np</u>	<u>Pu</u>
0.005	1/5	1.24	13.1	-	-
0.01	1/5	0.438	31.5	-	-
0.05	1/10	0.0683	58.8	0.35	0.495
0.10	1/10	0.0107	83.3	0.89	1.07
0.25	1/10	0.00392	96.2	3.77	3.93

STRIP CONTACTOxalic Acid Costrip of Neptunium and Plutonium

Neutral and anionic oxalate complexes of quadrivalent plutonium and neptunium are well known.⁽¹³⁾ Formation constants of such complexes are so high that dilute oxalic acid solutions can be used to costrip 85 to 95% of both actinides in a single batch contact of the DBBP phase (Table 11). Besides stripping plutonium and neptunium efficiently and rapidly, oxalic-acid strip solutions have two other desirable characteristics: they contain no cations other than hydrogen ions, and oxalate can be readily oxidized to CO_2 and water by HNO_3 or $\text{HNO}_3\text{-H}_2\text{O}_2$ solutions. The latter property makes it easy to prepare suitable neptunium-plutonium product solutions for recycle to the mainline Purex process.

TABLE 11. Oxalic Acid Stripping of Neptunium and Plutonium

Conditions: Synthetic 1WW-1 solution [containing either Np(V) or Pu(IV)] made 0.022M N_2H_4 and was allowed to stand 30 min at 25 °C before contact with a double volume portion of 25% DBBP-NPH. Portions of resulting organic solutions were contacted at 25 °C as indicated with oxalic acid strip solution.

Oxalic Acid, M	A/O	Contact Time, min	E_a^o		Not Stripped, %	
			Pu	Np	Pu	Np
0.25	2/1	10	0.0235	0.0216	1.19	1.10
0.25	1/1	10	0.0544	0.0289	5.25	2.85
0.1	2/1	10	0.0612	0.0210	3.06	1.08
0.1	1/1	1	0.0874	0.0734	8.26	7.12
0.1	1/1	3	0.0896	0.0733	8.32	7.13
0.1	1/1	5	0.0923	0.0752	8.69	7.36
0.1	1/1	10	0.101	0.0740	9.18	7.15
0.1	1/1	30	-	0.0699	-	6.82

Stripping of Contaminants

The oxalic acid strip contact provides excellent decontamination of the neptunium and plutonium from coextracted thorium and uranium (Table 12). Conversely, coextracted fission-product zirconium (especially) and cerium largely accompany the neptunium and plutonium into the strip solution. The need to provide decontamination from these latter contaminants thus motivates incorporation of scrub contacts into the DBBP recovery process.

Oxalic acid strip behavior of fission product ruthenium is complex and depends, among other factors, upon the prior treatment of the DBBP phase. Further comments on the extraction, scrub, and strip behavior of ruthenium are made in the next section.

TABLE 12. Stripping of Contaminants

Conditions: Plant or synthetic 1WW-1 solution, (the latter containing the indicated radioisotopes) was contacted with a double volume portion of 25% DBBP-NPH. The resulting organic phases were then contacted with an equal volume of 0.1M oxalic acid.

Contaminant	E_a^o	
	Synthetic 1WW	Plant 1WW ^(a)
^{234}Th	44.3	
^{233}U	8.19	
^{95}Zr	0.0055	
$^{95}\text{ZrNb}$		0.0059 to 0.0097
$^{144}\text{CePr}$	0.073	
$^{106}\text{RuRh}$		12 to 13 ^(b) 2.8 to 4.9 ^(c)

(a) Typical values; see Table 14.

(b) Organic phase scrubbed with 1/4 volume of 6M HNO_3 prior to oxalic acid strip.

(c) Organic phase not scrubbed with HNO_3 .

PATH OF ACID IN DBBP PROCESS

Transfer of HNO_3 to, or from, the DBBP extractant occurs in the various portions of the batch recovery process. Typically, the acid concentration of the final oxalic acid strip product and the DBBP phase in equilibrium with it will be about 0.8 and 0.3M, respectively (Table 13).

TABLE 13. *Acid Distribution in DBBP Process*

Conditions: Extraction-scrub-strip contacts were performed with synthetic 1WW-1 solution according to conditions shown in Figure 2.

<u>Contact Type</u>	<u>A/O</u>	<u>H⁺, M in final</u>	
		<u>Aqueous Phase</u>	<u>DBBP Phase</u>
Extraction	1/2	-	0.908
0.1M oxalic acid scrub	1/10	2.65	0.651
6M HNO ₃ scrub	1/4	5.12	0.886
0.1M oxalic acid strip	1/1	0.815	0.277

PROCESS TESTS WITH PLANT 1WW SOLUTION

Extraction-Scrub-Strip Contacts

Both current (~1 week old) and aged (~1 year old) plant 1WW solutions were used in tests of the overall DBBP recovery process (Tables 14 and 15). Some additional extraction contacts of current plant 1WW with irradiated DBBP extractants were made* and the results are given in Table 16.

Since most of the principal conclusions from these studies have been cited and discussed earlier, they require only mention here. Thus, neptunium and plutonium extraction recoveries were both excellent when hydrazine was added to the 1WW solution. In some cases, as shown in Table 16, as much as 93% of the neptunium extracts even without hydrazine addition. Approximately 17 to 32% of the ¹⁰⁶RuRh, 46 to 12% of the ¹⁴⁴CePr, and 27 to 40% of the ⁹⁵ZrNb, depending upon solvent irradiation dose, in 1WW solution accompany neptunium and plutonium into the DBBP phase. Satisfactory decontamination from the latter two contaminants (Table 15) is provided by the nitric and oxalic acid scrub

* Work done by J. Anderson, Atlantic Richfield Hanford Co.

contacts even for highly irradiated DBBP extractant. Scrub contact $^{144}\text{CePr}$ and $^{95}\text{ZrNb}$ distribution ratios obtained in the studies with plant 1WW solutions are in excellent agreement with those observed in tracer scale scrub experiments.

In the oxalic acid strip contact, radioruthenium favors the DBBP phase much more strongly than does either zirconium or cerium. Additional ruthenium decontamination is provided by the nitric acid scrub which removes a large portion of the ruthenium activity that normally reports to the oxalic acid strip. Conversely, the oxalic acid scrub provides only little decontamination from ruthenium. The results in Table 15 also show that ruthenium decontamination is slightly higher when the nitric acid scrub is performed after the oxalic acid scrub. However, the order of the scrub contacts did not affect the zirconium decontamination factor.

The extraction contact $^{95}\text{ZrNb } E_a^0$ for Experiment 1 in Table 14 appears anomalously high compared to the values observed in Experiments 2, 4, and 5. Outside of this anomaly, irradiated DBBP extractants extract more $^{95}\text{ZrNb}$ but less $^{144}\text{CePr}$ than does unirradiated solvent. This conclusion is apparent both from our results in Table 14 as well as those obtained in Table 16. Tracer level studies with synthetic 1WW solutions (discussed later, p. 37) also demonstrated that irradiation increases the capacity of the DBBP solvent to extract zirconium. The effect of radiation in decreasing the cerium extraction capacity of the DBBP extractant appears well substantiated, but the reason for the decreased extraction is not readily apparent. Finally, ruthenium distribution ratios are well scattered and do not correlate with either solvent radiation history or, as might be expected,⁽¹⁴⁾ with the age of the 1WW solution.

TABLE 14. Extraction-Scrub-Strip Studies with Plant 1WW Solutions

	Experiment No.					
	1 (a)	2 (a)	3A (a,b)	3B (a,c)	4 (a)	5 (d)
<u>Extraction Contact: (e)</u>						
$^{95}\text{ZrNb } E_a^o$	0.558	0.176	0.703	(m)	0.127	0.249
$^{106}\text{RuRh } E_a^o$	0.170	0.208	0.128	0.140	0.359	0.095
$^{144}\text{CePr } E_a^o$	(m)	0.528	0.090	0.071	0.327	(m)
% Not Extracted, Pu	(m)	1.0	0.91	(m)	1.8	(m)
% Not Extracted, Np	(m)	(m)	(m)	(m)	4.0	(m)
<u>Oxalic Acid Scrub: (f)</u>						
$^{95}\text{ZrNb } E_a^o$	0.0104	Not made	Not made	0.0033	(i,j) 0.0066	Not made
$^{106}\text{RuRh } E_a^o$	1.07			0.665	0.787	
$^{144}\text{CePr } E_a^o$	(m)			0.080	0.139	
<u>HNO₃ Scrub: (f)</u>						
	Part A	Part B				
$^{95}\text{ZrNb } E_a^o$	(m)	Not made	41.7	31.1	1.4	(i,k) (m)
$^{106}\text{RuRh } E_a^o$	0.128		0.237	0.131	0.125	0.084
$^{144}\text{CePr } E_a^o$	(m)		0.047	(m)	0.032	0.034
<u>Oxalic Acid Strip: (g)</u>						
$^{95}\text{ZrNb } E_a^o$	0.057	(h)	(h)	0.0097	(h)	(h)
$^{106}\text{RuRh } E_a^o$	12.3	2.81	13.3	13.3	11.3	4.9
$^{144}\text{CePr } E_a^o$	(m)	(m)	(m)	(m)	(h)	(h)

(a) With ~1 year old 1WW.

(b) Unwashed irradiated ($\sim 10^8$ rad) 25% DBBP-NPH.

(c) Carbonate-washed irradiated extractant.

(d) Current 1WW solution.

(e) 1WW solution made 0.05M N_2H_4 , allowed to stand 30 min at 25 °C, and contacted 10 min with double volume of extractant.

(f) 10 min, 25 °C, A/O = 1/4 (6M HNO_3) or A/O = 1/10 (0.1M oxalic acid).

(g) 10 min, 25 °C, A/O = 1(0.1M oxalic acid).

(h) Not detected in final organic.

(i) HNO_3 scrub made before oxalic acid scrub.

(j) Np and Pu losses were 0.71 and 0.57%, respectively.

(k) Np and Pu losses were 0.74 and 0.12%, respectively.

(m) Data not obtained.

TABLE 15. *Extraction-Scrub-Strip Studies - Fission Product Decontamination Factors*

Experiment No. (b)	Decontamination Factor (a)		
	$^{95}\text{ZrNb}$	$^{106}\text{RuRh}$	$^{144}\text{CePr}$
1A	24	102	36
1B	27	16	47
2	1	210	-
3A	2	220	450
3B	80	160	200
4	32	69	25

(a) *From 1WW solution to oxalic acid strip.*

(b) *See Table 14 for conditions.*

TABLE 16. *Extraction Contacts of Plant 1WW Solution with Irradiated Extractants (a)*

Conditions: Current plant 1WW solution contacted 10 min at 25 °C with double volume portions of various irradiated (^{60}Co) 25% DBBP-NPH solutions.

Solvent Irradiation Dose, W-hr/liter (b)	E_a^0			Not Extracted, %	
	$^{95}\text{ZrNb}$	$^{106}\text{RuRh}$	$^{144}\text{CePr}$	Pu	Np
0	0.154	0.257	0.418	3.6	13
58.7	-	0.104	0.0832	1.4	13
118	0.167	-	0.0710	1.4	6.7
176	0.167	-	0.0624	1.4	6.7
235	0.240	0.100	-	2.6	6.7

(a) *Work done by J. Anderson, Atlantic Richfield Hanford Co.*

(b) *See page 34 for irradiation details.*

Effect of Solids in Plant 1WW Solution

Hanford Purex plant 1WW solutions contain varying amounts of gelatinous solids. Similar solids also precipitate from synthetic 1WW solutions as noted in this and other studies. ⁽¹⁵⁾

Solids form only slowly in synthetic 1WW solutions at 25 °C and, thus, freshly prepared synthetic 1WW contains less solids than aged material. Probably, the same is true of plant 1WW solution.

Only one attempt has been made to characterize the solids in plant 1WW. In 1959, Van Tuyl⁽¹⁶⁾ found one particular batch of aged 1WW to contain about 4 vol% of easily centrifuged solids comprised of approximately 60 wt% $\text{Zr}_3(\text{PO}_4)_4 \cdot x\text{H}_2\text{O}$, 30 wt% $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, and 10 wt% BaSO_4 and PbSO_4 . The silica originates presumably from carry-over of Al-Si bonding material into the uranium dissolver solution.

Studies (Table 17) were performed with synthetic 1WW solutions to gain some idea of the amounts of neptunium and plutonium associated with the solids precipitated from such solutions. In some experiments Na_2SiO_3 solution was added to the 1WW solution. Plant 1WW solution is estimated to contain 0.01 to 0.02M silicon. A boiling time of 72 hr was used since this is the approximate residence time in the plant 1WW concentrator. Only small amounts of black crystalline solids precipitated from some of the solutions (1WW-1, 1WW-1A, and 1WW-2) during the 72 hr boiling period. In the experiments with solution 1WW-1B (which was initially 0.02M silicon) gray, gelatinous solids precipitated after only 5 hr at boiling or after 12 days at 25 °C.

Generally, in these experiments (Table 17), the plutonium concentration of the 1WW solution decreased slowly while the neptunium concentration either remained constant or increased slightly because of evaporation. Recent results⁽¹²⁾ with actual Purex plant 1WW solution also show that the 1WW solids retain plutonium more tenaciously than neptunium. Thus, examination of three different batches of plant 1WW indicated approximately 65% of the plutonium and 20% of the neptunium were associated with the solids in these solutions. Selective adsorption of plutonium over neptunium on siliceous and phosphate precipitates would appear to be in line with the contention that plutonium in 1WW

solution is largely present as Pu(IV) while neptunium is at least partly present as Np(V) and Np(VI). The consequences of adsorption of neptunium and plutonium on the 1WW solids to the DBBP process and to the overall Purex plant performance have already been discussed. Also, as noted earlier, it has not been established whether at least part of the neptunium and plutonium on the 1WW solids are not extractable into the DBBP solvent.

TABLE 17. *Retention of Neptunium and Plutonium on Solids in Synthetic 1WW Solutions*

Conditions: Freshly-prepared synthetic 1WW solutions [containing added $\text{Pu}(\text{NO}_3)_4$ or NpO_2NO_3] were maintained at either boiling temperature or at 25 °C for times indicated and were analyzed periodically for neptunium and plutonium.

% of Initial Concentration Left in Solution										
Time, days	1WW-1(a,b)		1WW-1A(a,c)		1WW-1B(d,e)		1WW-1B(a,e)		1WW-2(a,f)	
	Np	Pu	Np	Pu	Np	Pu	Np	Pu	Np	Pu
0.21	110	100	94	102			100	100	100	105
1.0	114	98	105	102			100	106	101	100
2.0	123	96	104	88			102	128	101	94
3.0	126	89	-	77			-	-	101	83
5.0					100	100				
12.0					-	30				
22.0					100					

(a) Held at boiling temperature for 3 days.

(b) Initial composition was that listed for solution 1WW-1 in Table 1.

(c) Same composition as 1WW-1 except also made 0.01M Si.

(d) Held at 25 °C for 22 days.

(e) Same composition as 1WW-1 except also made 0.02M Si.

(f) Initial composition was that listed for solution 1WW-2 in Table 1.

The effects of the 1WW solids on the disengaging of 1WW and DBBP phases in plant-scale extractions have not been defined either. Relative to this, solids in current 1WW did not prevent rapid gravity-phase disengagement in any of the experiments shown in Table 14 or Table 16 experiments. However, in some of the experiments with aged 1WW--particularly, those with irradiated extractant--aqueous and organic phases were slow to disengage by gravity settling. Centrifugation in such cases produced clear aqueous-and organic-phases and a layer of interfacial material. Clear liquid phases were also obtained by the addition of small amounts (100 to 200 ppm) of Mistron-25[®] (magnesium silicate) to the aqueous-organic mixture. Plant-scale tests are required to define the magnitude of the phase separation problem, so possible remedies including, possibly, centrifugation of the 1WW feed material, can be considered.

FURTHER PROCESS STEPS

Destruction of Oxalic Acid in Strip Solution

The final product from the DBBP process is a 0.6M HNO_3 -0.1M oxalic acid strip solution containing small concentrations of neptunium and plutonium contaminated with fission product zirconium, ruthenium, and cerium. Concentration and further purification of the neptunium and plutonium can be accomplished most conveniently by recycling the strip solution to an appropriate place in the mainline Purex process (discussed later in more detail). However, because oxalate interferes seriously with TBP extraction of neptunium and plutonium, destruction of oxalic acid in the strip solution is mandatory before such recycle can be permitted.

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Both HNO_3 and $\text{HNO}_3\text{-H}_2\text{O}_2$ solutions can be used satisfactorily to oxidize oxalic acid to water and CO_2 . These oxidizing agents are preferred over reagents such as KMnO_4 to avoid introduction of additional heavy metal cations into the Purex-process denitrated waste (PAW solution). Conditions for oxidation of oxalic acid with HNO_3 and $\text{HNO}_3\text{-H}_2\text{O}_2$ solutions are discussed elsewhere.⁽¹⁷⁾ Both systems appear to follow first-order kinetics with respect to oxalic acid concentration. Half-lives of oxalic acid in boiling 7, 9, and 11M HNO_3 are 125, 55, and 30 min, respectively. The combination of HNO_3 and H_2O_2 permits rapid destruction of oxalic acid at low (0.5 to 1.0M) acidities.

Economic, safety, and other factors dictate the choice between HNO_3 and $\text{HNO}_3\text{-H}_2\text{O}_2$ solutions for plant-scale oxidation of oxalic acid in the strip solution. For present Hanford Purex plant operation, these factors weigh in favor of the use of HNO_3 only⁽¹²⁾--a choice reflected in the chemical flowsheet shown in Figure 2.

Disposition of Neptunium and Plutonium Product

The chemical flowsheet (Figure 2) for the DBBP process anticipates recycle of the neptunium-plutonium product (after oxalate destruction) to the first cycle extraction column in the mainline Purex process. Recycle to this point will ensure adequate capacity for decontamination of the recovered neptunium and plutonium and can probably be accomplished with minimum effects on the overall Purex process performance.

Alternatively, it may prove feasible to by-pass the earlier Purex cycles and route the recovered neptunium and plutonium directly to the 3A-3B column system [J-Cell Package⁽¹⁾]. The fission product content of the strip product from the DBBP process will not likely allow direct use of this material as feed in the lightly-shielded J-Cell Package. However, it may be possible to prepare a satisfactory feed for the accumulation

and decontamination phases of the 3A-3B system by appropriate blending of DBBP process product with mainline Purex process material.

SOLVENT WASH STEP

Essentially all the uranium in the 1WW solution extracts into the DBBP solvent and remains in the organic phase through the scrub and strip contacts; thus, periodic washing of the extractant to remove this uranium is required. Sodium carbonate solutions, particularly 5 to 10 wt% solutions, are eminently suitable for this purpose as well as for removing most of the radoruthenium from both unirradiated and irradiated DBBP extractant (Table 18). Small amounts of $^{95}\text{ZrNb}$, $^{144}\text{CePr}$, ^{234}Th , and neptunium and plutonium, also present in the used DBBP extractant, are also effectively removed by this same method.

Presently, the carbonate-washing step is believed to be needed only after every fifth or sixth extraction-strip cycle. However, in actual plant operation, more frequent washing of the solvent may prove to be necessary or desirable to remove greater than normal amounts of uranium and/or to minimize solvent radiolysis.

RADIOLYTIC STABILITY OF DBBP EXTRACTANT

When in stirred contact with the highly radioactive 1WW solution, the DBBP-NPH extractant will be irradiated at an estimated rate of 7×10^5 rad/hr. Thus, the effects of such irradiation upon the properties and life of the extractant are of prime concern. To study radiolysis effects, DBBP-NPH extractants were irradiated in a ^{60}Co irradiation facility. The results of these studies demonstrated the excellent radiation stability of the DBBP-NPH extractant.

TABLE 18. Sodium Carbonate Solvent Wash Data

Conditions: 25% DBBP-NPH extractants from extraction-scrub-strip contacts with plant 1WW (Table 14) were contacted 10 min at 25 °C with equal volume portions of indicated Na_2CO_3 solutions.

Solvent No. (a)	Na_2CO_3 , wt%	AT (b)	Uranium	Removed, % (c)		
				$^{95}\text{ZrNb}$	^{103}Ru	$^{106}\text{RuRh}$
2 (d)	1	97.2	30.	-	51.0	54.6
	3	93.4	88.	-	99.2	99.1
	5	99.2	99.	-	99.8	99.7
	10	99.4	99.	-	99.8	99.8
3A (e)	1	87.7	7.	75.7		21.7
	3	85.1	98.	72.9	22.7	55.3
	5	97.4	99.	(f)	64.5	74.9
	10	95.9	99.	(f)	56.9	72.4
5 (d)	10	-	99.	99.8	97.8	98.4

(a) For identification purposes, see Table 14.

(b) Total alpha.

(c) $^{144}\text{CePr}$ not detected in any washed solvents.

(d) Unirradiated extractant.

(e) Irradiated (235 W-hr/liter) extractant.

(f) $^{95}\text{ZrNb}$ not detected in washed solvent.

In initial experiments, portions of 25% DBBP-NPH were irradiated (^{60}Co) in the absence of any aqueous phase at 25 to 30 °C and at 1.15×10^6 rad/hr for periods of time ranging from 24 to 95 hr. All of the irradiated solvents extracted plutonium and neptunium as efficiently as the unirradiated material (Table 19).

TABLE 19. *Extraction of Neptunium and Plutonium by Irradiated Extractants*

Conditions: Portions of synthetic 1WW-1 [containing either $\text{Pu}(\text{NO}_3)_3$ or NpO_2NO_3] made 0.022M N_2H_4 and were allowed to stand 30 min at 25 °C. Resulting solutions were then contacted with double volume portions of each of the irradiated 25% DBBP-NPH solutions.

Solvent Irradiation Dose, W-hr/liter	E_a^0		Not Extracted, %	
	Pu	Np	Pu	Np
0	56.3	27.6	0.81	1.72
58.7	54.2	102.0	0.93	0.58
118.0	72.0	97.3	0.67	0.62
176.0	83.6	107.0	0.57	0.54
235.0	100.0	150.0	0.47	0.39

In another, more definitive experiment, a 25% DBBP-NPH solvent was irradiated to a total exposure of about 327 W-hr/liter while it was in repetitive, stirred contact with a sequence of aqueous solutions. The sequence and composition of aqueous solutions and contact periods used in this experiment (termed cyclic irradiation) are listed in Table 20. These conditions correspond approximately to those listed in Figure 2 for a typical extraction-scrub-strip-solvent wash cycle. A total of 96 irradiation cycles were performed. Properties of the solvent at the end of selected cycles are presented in Table 21.

In the cyclic irradiation experiment the average dose per cycle was about 3.5 W-hr/liter, an approximate exposure anticipated from contact of the extractant with 1/2 volume of plant 1WW solution for 3 hr. Also, the total irradiation dose in each cycle was accumulated in the extraction contact. In plant operation of the DBBP extraction process, it is expected that the majority of the radiation exposure would accrue also in the extraction step.

TABLE 20. Conditions for Cyclic ^{60}Co Irradiation of 25% DBBP-NPH

Contact Type	Aqueous Composition	Flows		Time, min	Solvent Exposure W-hr/liter
		Aqueous	Organic		
Extraction	Synthetic 1WW	100	200	84 - 120 ^(c)	3.3 to 4.0
Scrub ^(a)	6M HNO_3	50	200	5	0
Strip ^(a)	0.1M Oxalic Acid	200	200	5	0
Solvent Wash ^(a,b)	10 wt% Na_2CO_3	200	200	5	0

(a) Done outside ^{60}Co facility.

(b) Performed only after every sixth extraction-scrub-strip cycle.

(c) Adjusted according to exposure dose rate in ^{60}Co facility.

TABLE 21. Selected Properties of Cyclically Irradiated Extractant

Cycle No.	Cumulative Exposure, W-hr/liter	Property ^(a)							
		Density, ^(b) g/ml	Viscosity, ^(c) cP	E_a^0			Extracted, %		
				Pu	Np	^{95}Zr	Pu	Np	^{95}Zr
0	0	0.794	1.649	51.9	41.6	2.49	99.1	98.8	83.3
18	59.2	0.793	1.802	41.3	19.1	3.56	98.8	97.6	87.2
36	118.0	0.796	1.844	33.2	14.5	3.83	98.6	96.6	87.6
54	186.0	0.799	1.901	31.9	13.1	4.55	98.5	96.3	89.4
72	257.0	0.803	1.989	26.2	11.9	-	98.1	95.8	-
96	327.0	0.810	2.123	19.8	12.0	-	97.5	95.8	-

(a) All irradiated solvents washed (10 min, 25 °C) once with an equal volume of 2M HNO_3 and twice with equal volumes of water.

(b) Pycnometric value at 25 °C.

(c) Capillary viscometer at 25 °C.

(d) Synthetic 1WW-1 solution containing either Pu(IV), Np(V) or ^{95}Zr made 0.05M N_2H_4 and allowed to stand 30 min at 25 °C before contact (A/O = 1/2, 10 min, 25 °C) with irradiated solvent.

The data in Table 21 testify to the excellent radiation stability of the DBBP extractant. Thus, even though neptunium and plutonium distribution ratios declined upon irradiation, the solvent after 96 cycles of irradiation still extracted about 96% of each actinide. Further, the irradiated DBBP solution extracted only slightly more zirconium than unirradiated material. As expected, the density and viscosity of the DBBP extractant also increased upon irradiation, but probably not to a prohibitive or intolerable degree.

COMPATIBILITY OF DBBP WITH PUREX PROCESS

Incorporation of a DBBP extraction process in the Hanford Purex Purex complex would convert the plant from the traditional one-solvent plant to a two-solvent one. The DBBP process is a low-volume batch operation which, as currently projected, would be performed in a section of the plant isolated from the mainline Purex process solvent. Loss of the entire quantity of 25% DBBP extractant to the TBP solution would be improbable. However, even in such an unlikely event, the Purex process solvent would contain only 2 to 3 vol% DBBP.

This section summarizes results of studies conducted to ascertain the effects, at various points in the Purex process, of the presence of DBBP in the 30% TBP Purex process solvent.

Batch contacts were made to determine the effects of DBBP on the equilibria and kinetics of stripping of uranium and plutonium from 30% TBP-0 to 5% DBBP solutions. Particular concern over these effects was evinced, of course, because DBBP is a more powerful extractant than TBP.

Kinetic data for stripping of plutonium and uranium from TBP-DBBP solutions are shown in Table 22. Following techniques developed by Mendel,⁽¹⁸⁾ these kinetic data were obtained with a dispersion-disengaging apparatus of a familiar type.⁽¹⁹⁾

The presence of 1 to 5 vol% DBBP in the TBP solvent affects the equilibrium distribution of plutonium and uranium but does not appear to have any significant effect upon kinetics of transfer of these elements.

TABLE 22. *Effects of Presence of DBBP in Purex Solvent - Kinetic Measurements*

Solvent No.	(b) DBBP, vol%	Contact time, min	$E_a^{(a)}$		
			Pu		U
			1B Column (c)	2B Column (d)	1C Column (e)
1	0	2	0.0117	0.0159	0.727
		5	0.0187	-	0.804
		10	0.0205	0.0133	0.769
2 (f)	1	2	0.0216	0.0265	0.888
		5	0.0225	-	0.910
		10	0.0214	0.0212	0.853
3 (g)	1	2	0.0288	0.0219	0.860
		5	0.0246	-	0.861
		10	0.0245	0.0226	0.858
4 (f)	5	2	0.0306	0.0724	1.19
		5	0.0284	-	1.22
		10	0.0335	0.0723	1.17

(a) Equal volume contacts at 45 °C.

(b) All solvents were also 30% TBP-NPH.

(c) Initial organic in each case was about 0.32M $UO_2(NO_3)_2$ -0.21M HNO_3 -0.0002M $Pu(NO_3)_4$ while initial aqueous in each case was 0.03M ferrous sulfamate-0.04M sulfamic acid-0.3M HNO_3 .

(d) Initial organic in each case was about 0.18M HNO_3 -0.015M $Pu(NO_3)_4$ while initial aqueous in each case was 0.1M HNO_3 -0.045M H_2SO_4 -0.045M sulfamic acid.

(e) Initial organic in each case was about 0.33M $UO_2(NO_3)_2$ -0.088M HNO_3 while initial aqueous in each case was 0.1M HNO_3 .

(f) Unirradiated DBBP.

(g) Irradiated (~200 W-hr/liter) DBBP.

Multiple batch contact data (Table 23) showed that the presence of even 5 vol% DBBP in the 30% TBP solvent does not interfere with plutonium partitioning or stripping in either the 1B or 2B columns.

TABLE 23. *Effects of Presence of DBBP in Purex Solvent - Multiple Batch Contacts*

Solvent (a,b)		Contact No. (c)	1B Column (d)		2B Column (e)	
No.	DBBP, vol%		Pu E_a	Pu Not Stripped, %	Pu E_a	Pu Not Stripped, %
1	0	1	0.00644	6.13	0.198	38.9
		2	0.0122	0.85	0.0407	5.29
		3	0.0512	0.35	0.00309	0.029
		4	0.293	0.32	0.00238	0.0011
2	1	1	0.00883	8.07	0.287	48.5
		2	0.0162	1.23	0.0386	5.63
		3	0.0443	0.41	0.00906	0.13
		4	0.183	0.28	0.0112	0.0051
3	1	1	0.00971	8.99	0.262	46.0
		2	0.0156	1.30	0.367	5.21
		3	0.0473	0.55	0.0191	0.14
		4	0.175	0.36	0.0230	0.0069
4	5	1	0.0193	16.1	0.706	72.1
		2	0.0221	3.1	0.146	23.3
		3	0.0675	1.87	0.0368	2.18
		4	0.0872	0.91	0.0339	0.22

(a) All solvents were also 30% TBP-NPH.

(b) See Table 22 for further description of these solvents.

(c) All contacts were at 45 °C.

(d) Four successive contacts of organic phases of composition listed in Table 22 with 1/10 volume portions of 0.03M ferrous sulfamate-0.04M sulfamic acid-0.3M HNO_3 .

(e) Four successive contacts of organic phases of composition listed in Table 22 with 1/3 volume portions of 0.1M HNO_3 -0.045M H_2SO_4 -0.045M sulfamic acid.

Laboratory experiments, as well as limited pilot plant scale experiments by G. L. Richardson,⁽²⁰⁾ were performed to determine the effects of DBBP contamination in the Purex solvent on the performance of the 1C uranium stripping column. These studies showed that, although such contamination will increase the 1C column uranium loss, normal losses can be obtained by slight increases in the aqueous-to-organic flow ratio. Richardson found that transfer unit heights under 1C column conditions were virtually unaffected by the presence of DBBP in the TBP solvent. He suggests, therefore, that conventional McCabe-Thiele operating diagrams can be used to set operating conditions for obtaining low uranium losses at any DBBP contamination level up to 5%. The equilibrium distribution data in Table 24 are included for use in the construction of such diagrams.

TABLE 24. Uranium Distribution Ratios for TBP-DBBP Solvents

Conditions: Each of the indicated TBP-DBBP-NPH solutions was contacted twice with fresh portions of 2M $\text{UO}_2(\text{NO}_3)_2$ solution. Portions of the resulting organic phases were contacted (10 min, 45 or 50 °C) with various volumes of 0.01M HNO_3 .

DBBP, vol%	TBP, vol%	Temp, °C	Equilibrium Uranium, M		$\frac{\text{U}}{\text{E}_a}$
			Aqueous	Organic	
0.0	30	45	0.0174	0.00106	0.061
			0.0654	0.0151	0.231
			0.128	0.0616	0.480
		50	0.104	0.0431	0.415
			0.211	0.152	0.719
			0.264	0.210	0.797
			0.314	0.248	0.792
			0.363	0.290	0.797
1.0	28.8	50	0.107	0.0514	0.478
			0.207	0.171	0.824
			0.254	0.227	0.896
			0.314	0.271	0.864
			0.359	0.308	0.858
2.0	27.6	50	0.109	0.0571	0.523
			0.206	0.170	0.826
			0.251	0.223	0.887
			0.317	0.267	0.844
			0.354	0.314	0.886
5.0	24.0	50	0.101	0.0706	0.700
			0.190	0.181	0.950
			0.236	0.226	0.958
			0.298	0.295	0.923
			0.343	0.316	0.921

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