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**D2EHPA EXTRACTION RECOVERY
OF NEPTUNIUM AND PLUTONIUM
FROM PUREX ACID SLUDGE SOLUTIONS**

W. W. SCHULZ

MARCH, 1968

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March 1968

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ABSTRACT

A batch D2EHPA solvent extraction process for recovery of neptunium and plutonium values from Purex Acid Sludge solution has been developed. This process recovers 95 to 98% of both actinides in a small volume (concentration factor of about 9000) of product solution and purifies them from essentially all contaminants except for small amounts of iron and uranium.

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D2EHPA EXTRACTION RECOVERY
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FROM PUREX ACID SLUDGE SOLUTIONS

W. W. Schulz

INTRODUCTION

A large fraction of the sludge now contained in self-boiling tanks at Hanford was derived from waste (1WW solution) produced before the startup of neptunium recovery operations in the Purex plant. Considerable ^{237}Np and plutonium, the latter from normal small Purex process losses, accumulated in the sludge. ^{237}Np is the starting material for production of ^{238}Pu , an isotopic power source currently of interest. Therefore, recovery of ^{237}Np from the stored sludge is desirable.

Current Hanford Waste Management plans include removing the sludge from underground storage tanks by sluicing with water. Undissolved solids will then be leached (in stainless steel equipment) with HNO_3 to recover ^{90}Sr in a HNO_3 solution [Purex Acid Sludge (PAS) solution]. A process flowsheet for the water sluicing and HNO_3 leaching operations for ^{90}Sr recovery was established previously. A modified leach procedure to ensure recovery of the bulk of the sludge neptunium and plutonium in the PAS solution has been developed recently. ⁽¹⁾

A batch solvent extraction process for recovery and purification of neptunium and plutonium from PAS solution has been developed and is described in this report. This solvent extraction process uses D2EHPA [di(2-ethylhexyl)phosphoric acid] as the extractant.

SUMMARY AND CONCLUSIONS

A chemical flowsheet for batch D2EHPA solvent extraction recovery of neptunium and plutonium from PAS solution is presented and discussed. The process involves a recovery and purification D2EHPA extraction - oxalic acid strip cycle to recover neptunium and plutonium and to free them from most of the associated contaminants in PAS solution. The extraction process has been demonstrated successfully with both synthetic and actual PAS solutions; overall recoveries of neptunium and plutonium are typically 95 to 98%.

PROCESS CONCEPT

The concept of the batch extraction process for recovery of neptunium and plutonium from PAS solution is illustrated schematically in Figure 1.

Core of the process is a sequence of extraction-strip batch contacts. The first pair of contacts recovers neptunium and plutonium from the PAS solution by D2EHPA extraction followed by oxalic acid stripping. These first contacts also free the plutonium and neptunium from most of the radioactive and inert contaminants present in the PAS solution; uranium and iron remain as the principal contaminants after the first contacts.

Neptunium and plutonium are extracted again into the D2EHPA extractant to provide further decontamination from uranium, iron, and other contaminants. Feed for this purification contact is prepared by destroying oxalate in the first oxalic acid strip solution by reaction with H_2O_2 and HNO_3 . (A ninefold evaporative volume reduction during destruction of the oxalate is made to concentrate the plutonium and neptunium.) Plutonium and neptunium are again removed from the organic phase by stripping with oxalic acid. This final strip is treated with HNO_3 and H_2O_2 and concentrated to yield a solution suitable for final separation and purification of the neptunium and plutonium in other facilities. It is estimated⁽²⁾ that the plutonium and neptunium from each 9000 gal of PAS solution can be accumulated in 5 gal of final product solution.

PROCESS CHEMISTRY AND LITERATURE REVIEW

D2EHPA EXTRACTION CHEMISTRY

General reviews of reaction mechanisms and other fundamentals involved in D2EHPA extraction systems have been given by several authors.^(3, 4) More specifically, Weaver and Horner⁽⁵⁾ have investigated in great detail, the D2EHPA extraction of plutonium and neptunium from HNO_3 and HNO_3 -nitrate solutions. Highlights of their findings are:

- The order of extraction of plutonium in different oxidation states is $\text{Pu(IV)} > \text{Pu(VI)} \gg \text{Pu(III)}$. Similarly, the order of extraction of neptunium is $\text{Np(IV)} > \text{Np(VI)} \gg \text{Np(V)}$.

- Extraction of Np(IV) from HNO_3 is inversely proportional to the square of the acidity above about 1M HNO_3 and directly proportional to acidity below 1M HNO_3 .
- Addition of neutral nitrates to 1M (or higher) HNO_3 solutions does not affect extraction of Np(IV). Below this acidity, extraction from salted solutions increases to a maximum at about 0.3M HNO_3 .
- Extraction of Pu(IV) from nitrate solutions is somewhat similar to that of Np(IV), but distribution ratios are several times as high.
- Dilute oxalic acid is an effective reagent for stripping plutonium and neptunium from D2EHPA solutions.

Weaver and Horner found that in the range from 10^{-4} to 10^{-2}M D2EHPA, extraction of Pu(IV) from 1M HNO_3 was proportional to the square of the uncomplexed D2EHPA concentration. On the other hand, Peppard and co-workers⁽⁶⁾ found that in the D2EHPA (toluene) versus (perchlorate + nitrate) system, the Np(IV) extracted species contained one nitrate group. They suggest that the extraction reaction is

where $(\text{HR})_2$ is dimerized D2EHPA.

Experimental evidence indicated that in actual PAS, plutonium is present as Pu(IV), but neptunium is present in the inextractable quinquevalent state. Therefore, a key point in the development of the extraction process was the need to establish both plutonium and neptunium in the quadrivalent state to permit extraction of both elements into the same organic phase. Initially, attempts were made to find a combination of oxidizing or reducing agents which would establish both plutonium and neptunium simultaneously in the quadrivalent state in the PAS solution. These attempts failed as they did previously with Purex Acid Waste solution.⁽⁷⁾

Since techniques for obtaining both neptunium and plutonium in PAS in the plus four oxidation state were not found, alternate procedures for extracting both into the same organic phase were explored. A successful procedure consists of extracting Pu(IV) into the D2EHPA

FIGURE 1. Batch D2EHPA Np-Pu Recovery Process Concept

phase and, after allowing the two phases to separate but without removing the organic phase, treating the aqueous phase with ferrous sulfamate and hydrazine to attain Np(IV) . Recontact of aqueous and organic phases then extracts the Np(IV) . Satisfactory recovery of both actinides depends on the great affinity of D2EHPA for Pu(IV) so that serious back-extraction of plutonium does not occur during valence adjustment and extraction of neptunium.

OXIDATION OF OXALIC ACID

Destruction of oxalic acid in strip solutions is mandatory before satisfactory concentration and purification of the neptunium-plutonium fraction can be accomplished either in the D2EHPA purification cycle or in subsequent final purification operations. Many familiar oxidizing agents (e.g., KMnO_4 , $\text{Ce(SO}_4)_2$, etc.) can be used to destroy oxalic acid, but their use would introduce metallic impurities into the neptunium-plutonium product. Introduction of metallic contaminants can be avoided by oxidizing oxalic acid with HNO_3 according to the reactions:

Kinetics of the oxidation of oxalic acid with HNO_3 at 97 °C in 0.1 to 12.7M HNO_3 solutions containing 0.2 to 1.0M oxalic acid have been studied in detail by Russian workers.⁽⁸⁾ Additional kinetic data are presented in this report (See page 28). Both investigations have shown that the reaction is first order with respect to oxalic acid. A major disadvantage in the use of HNO_3 to oxidize oxalic acid is the very slow rate of reaction at HNO_3 concentrations below about 9M. ✓3

In dilute acid solution, H_2O_2 is a powerful oxidizing agent and is the preferred reagent for destroying oxalic acid in strip solutions. (The use of H_2O_2 to oxidize citric acid in solutions containing ^{90}Sr is a well-established practice at Hanford.)⁽⁹⁾ Hydrogen peroxide reacts with oxalic acid according to the reaction:

Harber⁽¹⁰⁾ initially studied this reaction since then, various AEC investigators⁽¹¹⁻¹²⁾ have made use of it.

EXPERIMENTAL

MATERIALS

Synthetic Purex Acid Sludge (PAS) Solution

Some experiments were made with PAS solution derived from actual stored sludge. In the majority of the experimental studies, however, laboratory-prepared PAS solution of the composition shown in Table I was used. The concentration of certain of the inert and radioactive fission products in actual PAS was approximated by adding inert strontium, zirconium, cerium, and lanthanum to the laboratory-prepared waste solution. For convenience only, zirconium was added as $\text{Zr}(\text{SO}_4)_2$; the exact chemical specie(s) of zirconium in PAS is not known.

TABLE I. Composition of Synthetic PAS Solution

<u>Component^(a)</u>	<u>Concentration, M</u>
$\text{Al}(\text{NO}_3)_3$	0.55
NaNO_3	0.42
$\text{Fe}(\text{NO}_3)_3$	0.36
HNO_3	0.28
H_3PO_4	0.057
H_2SO_4	0.026
$\text{UO}_2(\text{NO}_3)_2$	0.023
$\text{Cr}(\text{NO}_3)_3$	0.021
$\text{Ni}(\text{NO}_3)_2$	0.021
$\text{Mn}(\text{NO}_3)_2$	0.01
$\text{Zr}(\text{SO}_4)_2$	0.004
$\text{Sr}(\text{NO}_3)_2$	0.0017
$\text{La}(\text{NO}_3)_3$	0.001
$\text{Ce}(\text{NO}_3)_3$	0.001

(a) Actual PAS solutions are expected to be about 1.6×10^{-5} M Np and about 4.64×10^{-5} M Pu.

For convenience also, the synthetic PAS solution as initially prepared contained neither plutonium nor neptunium. As required, appropriate amounts of HNO_3 stock solutions of either (or both) $\text{Pu}(\text{NO}_3)_4$ or NpO_2NO_3

were added. These stock solutions had been purified by anion exchange resin techniques and were shown to be radiochemically pure by alpha pulse height analysis.

Chemical and radiochemical analyses of actual Tank-241-A-103 sludge have been made.⁽¹³⁾ Estimates of the total volumes of sludge and liquid in the various storage tanks have also been made. Combination of these data with the proposed sludge leach flowsheet conditions enabled P. W. Smith⁽²⁾ to arrive at the PAS composition shown in Table I. Although this is regarded typical of the actual PAS to be produced, variations in sludge composition from tank to tank and in leach conditions can result in some deviations from the composition listed.

Actual PAS Solutions

Samples of stored sludge from Tanks 241-A-101 and 241-A-104 were leached with water and HNO_3 to produce actual PAS solutions. Two water leaches at 80 °C dissolved most of the soluble NaNO_2 , NaNO_3 , and Na_2CO_3 . Each of the water leaches was cooled to 25 °C and, without removal from the solid residue, NaOH was added to a terminal concentration of 1 or 2M. The resulting slurry was stirred 30 min at 25 °C, centrifuged, and the alkaline leach liquor removed. Addition of NaOH to the water leaches was necessary to destroy soluble carbonate complexes of uranium, plutonium, and neptunium. The solid residue from the water leaches was leached at 80 °C with HNO_3 to obtain PAS solutions.

Extractant

Extractant compositions used were 0.04M D2EHPA-0.02M TBP-Soltrol-170, 0.06M D2EHPA-NPH*, and 0.1M D2EHPA-0.1M TBP-NPH. Extractants were prepared by diluting as-purchased (Union Carbide Co.) D2EHPA with appropriate volumes of TBP (Commercial Solvents Corp.) and either NPH or Soltrol-170 (Phillips Petroleum Co.). The D2EHPA contained 94.9% D2EHPA, 1.93% mono(2-ethylhexyl)phosphoric acid, and 1.3% 2-ethylhexanol. Some pyro-esters as well as traces of iron were

* NPH is the Hanford designation for a mixture of normal paraffin hydrocarbons, principally C_{10} through C_{13} . A mixture made by the South Hampton Co., Houston, Texas was used in this study.

also present. Prior to use, extractants were washed successively with equal volumes of 4.8M NaOH, 6M HNO₃, and water.

Radioisotopes

Extraction of elements other than plutonium and neptunium was followed with the aid of the radioisotopes listed in Table II.

TABLE II. Radioisotopes Used in This Study

<u>Isotope</u>	<u>Chemical Form</u>
²³³ U	UO ₂ (NO ₃) ₂ in HNO ₃
⁹⁵ Zr	Zr(IV) in 10M HNO ₃
⁵⁹ Fe	FeCl ₃ in HCl
⁸⁸ Y	YCl ₃ in HCl
¹⁵²⁻¹⁵⁴ Eu (a)	EuCl ₃ in HCl
¹⁰⁶ Ru- ¹⁰⁶ Rh (a)	RuCl ₃ in HCl
¹⁴⁴ Ce- ¹⁴⁴ Pr	CeCl ₃ in HCl
⁵¹ Cr	CrCl ₃ in HCl
²⁴¹ Am	Am(NO ₃) ₃ in HNO ₃
⁸⁵ Sr	Sr(NO ₃) ₂ in HNO ₃
⁵⁴ Mn	MnCl ₂ in HCl
¹³⁷ Cs	CsCl in HCl

(a) Referred to in this report as ¹⁵²Eu, ¹⁰⁶Ru, and ¹⁴⁴Ce, respectively.

²³³U obtained from ThO₂ irradiated at Hanford was purified by appropriate TBP extraction cycles in the Hanford Purex Plant and further purified by anion resin techniques. ²⁴¹Am, obtained from Hanford Recuplex⁽¹⁴⁾ process waste, was purified by appropriate ion exchange cycles. ⁹⁵Zr, obtained from ORNL as an oxalic acid solution of the equilibrium mixture of ⁹⁵Zr and ⁹⁵Nb, was purified from ⁹⁵Nb, as required, by TTA (thenoyltrifluoroacetone) extraction according to the method of Rais, Kyras and Caletka.⁽¹⁵⁾ ⁸⁸Y was obtained from Nuclear Science and Engineering Co.; ⁵⁴Mn was obtained from New England Nuclear Co. All other radioisotopes were obtained from ORNL.

Radioisotopes were added to synthetic PAS in the form received (Table II). We believe that the resulting oxidation states of the radiotracers

were the same as those of the inert and active isotopes of the same metal ions in actual PAS. This may not have been true, however, for ^{106}Ru and ^{95}Zr . Some caution should be used, therefore, in extrapolating tracer data to the behavior of ruthenium and zirconium in actual PAS.

Other Chemicals

The following stock solutions were obtained:

- 11M Hydrazine, from the Olin Mathieson Chemical Co.
- 1.57M Na_3HEDTA (trisodium N-hydroxyethylethylenediaminetriacetate), from the Dow Chemical Co.
- 3.25M ferrous sulfamate (FS), from the Mallinckrodt Co.

Hydrogen peroxide used to destroy oxalate in strip solutions was procured from two sources. Chemically stabilized 30% H_2O_2 solution (General Chemical Co.) was used in most of the experiments; some experiments were performed with a 3.7M H_2O_2 (unstabilized) solution obtained from the Pittsburgh Plate Glass Co. All other chemicals used were of reagent grade quality.

PROCEDURES

Distribution Ratio Measurements

The distribution ratio, E_a^O , is defined as the ratio of the concentration of the element of interest in the organic phase to the concentration of the element in the aqueous phase after equilibration of the two sensibly immiscible liquids. Phases were equilibrated by mechanical stirring; all contacts were at room temperature (24-26 °C) unless otherwise noted. Phases were separated by centrifugation.

Kinetics of Destruction of Oxalic Acid

Experiments were performed to study the rates at which oxalic acid is destroyed in HNO_3 and in $\text{HNO}_3\text{-H}_2\text{O}_2$ solutions. In the former case, kinetics of the reaction were studied at boiling temperature in 7 to 11M HNO_3 solutions containing initially about 0.1 mole oxalic acid per liter. To study the reaction of H_2O_2 with nitric-oxalic acid solutions, 25 ml of 3.7 to 7.8M H_2O_2 was added to 200 ml of boiling 0.1M oxalic acid-0.1 or 0.5M HNO_3 solution. In some experiments, small concentrations of Mn(II) ,

U(VI), or Fe(III) were also present in the nitric-oxalic acid solutions. In all cases, samples were taken at appropriate intervals, immersed in an ice bath, and analyzed for oxalate content.

ANALYSES

Neptunium and plutonium in aqueous solutions were determined by sequential triisooctylamine and TTA extractions, and alpha counting.⁽¹⁶⁾ Neptunium and plutonium in D2EHPA solutions were determined by direct alpha counting of aliquots. ²³³U and ²⁴¹Am in synthetic process aqueous solutions and in D2EHPA phases derived therefrom were also determined by direct alpha counting of aliquots. Alpha pulse height analyses were also performed where required.

Gamma energy pulse height analyses were performed to determine the concentration of radioisotopes of interest in samples derived from both actual PAS solutions and from solutions containing only a single radioisotope.

Oxalic acid solutions obtained in experiments with actual PAS solutions were analyzed by emission spectroscopy to determine the nature and approximate concentration of metallic impurities. Chemical analyses of these solutions were also made to determine concentrations of iron, uranium, zirconium and aluminum. After destruction of oxalate with boiling 15.6M HNO₃, iron was determined spectrophotometrically as the orthophenanthroline complex,⁽¹⁷⁾ and uranium was determined by X-ray fluorescence techniques.⁽¹⁸⁾ Inert zirconium was determined by the trioctylphosphine oxide (TOPO) extraction procedure of Young and White.⁽¹⁹⁾ Aluminum in acidified strip solutions and also in D2EHPA solutions was determined by the procedure of Case⁽²⁰⁾ which involves addition of hydroxyquinoline to a HNO₃ solution to develop the aluminum complex after prior TOPO extraction of interfering uranium and iron. D2EHPA solutions were stripped successively with Na₂CO₃, NaOH, and water solutions to remove aluminum and other metallic ions. The resulting alkaline solutions were acidified, composited, concentrated, and diluted to known volume.

Oxalate in nitric-oxalic acid solutions was analyzed by reaction with an excess of standard $\text{Ce}(\text{SO}_4)_2$ and back titration of the excess with FeSO_4 . Hydrogen peroxide, when present in the nitric-oxalic acid solution, was destroyed by catalytic (osmic acid) decomposition in alkaline solution prior to determination of oxalate.

RESULTS AND DISCUSSION

RECOVERY CYCLE

Extraction of Plutonium and Neptunium from Synthetic PAS

Tables III and IV summarize data for the extraction of plutonium and neptunium from synthetic PAS solutions. These experiments demonstrated an excellent extraction of plutonium and neptunium in a single extraction contact with either 0.04 or 0.1M D2EHPA extractant.

Ferrous sulfamate, either by itself or in combination with hydrazine, efficiently and rapidly reduces Np(V) to Np(IV) . Hydrazine by itself is inadequate for this purpose. The combination of FS with hydrazine is preferable over FS alone because of its additional capacity to destroy the nitrite ion, thereby preventing nitrite-catalyzed HNO_3 oxidation of Fe(II) . Concentrations of both reductants in the range of 0.01 to 0.05M are adequate for neptunium reduction. Satisfactory reduction of Np(V) to Np(IV) is achieved at 25 °C in as little as 10 min.

TABLE III. Extraction of Plutonium from Synthetic PAS Solution

Conditions: Synthetic PAS (Table I) was adjusted to $2.7 \times 10^{-5}\text{M Pu}(\text{NO}_3)_4$ and contacted 10 to 30 min at 25 °C with an equal volume of D2EHPA extractant indicated. Without phase separation FS and/or N_2H_4 was added to aqueous phase to indicated concentration and allowed to stand at 25 °C for time indicated. Finally aqueous and organic phases were recontacted for 30 min at 25 °C.

Extractant (a)		Reduction Conditions			Pu E_a^0 (b)	Pu not Extracted, %
D2EHPA, M	TBP, M	FS, M	N_2H_4 , M	Time Stand, min		
0.04	0.02	0.0	0.0	60	2740	0.034
0.04	0.02	0.01	0.01	60	2500	0.039
0.04	0.02	0.01	0.0	60	2200	0.044
0.04	0.02	0.025	0.025	60	1250	0.078
0.04	0.02	0.05	0.05	60	1030	0.095
0.10	0.05	0.01	0.01	30	1230	0.078

(a) Diluent was either Soltrol-170 or NPH.

(b) After final contact.

TABLE IV. Extraction of Neptunium from Synthetic PAS Solution

Conditions: Same as those listed in Table III except synthetic PAS was adjusted to $2.9 \times 10^{-5} \text{M NpO}_2\text{NO}_3$ before contact with extractant.

Extractant ^(a)		Np Reduction Conditions			Np $E_a^{0(b)}$	Np not Extracted, %
D2EHPA, M	TBP, M	FS, M	N ₂ H ₄ , M	Time stand, min		
0.04	0.02	0.0	0.05	60	-	35.4
0.04	0.02	0.01	0.0	10	>85	<0.94
0.04	0.02	0.01	0.0	30	>110	<0.85
0.04	0.02	0.01	0.0	60	-	1.24
0.04	0.02	0.01	0.01	10	>110	<0.86
0.04	0.02	0.01	0.01	30	>90	<1.0
0.04	0.02	0.01	0.01	60	-	1.8
0.04	0.02	0.025	0.0	10	>120	<0.79
0.04	0.02	0.025	0.0	30	>130	<0.70
0.04	0.02	0.025	0.025	10	>130	<0.71
0.04	0.02	0.025	0.025	30	>160	<0.63
0.04	0.02	0.05	0.0	10	>100	<0.89
0.04	0.02	0.05	0.0	30	>120	<0.79
0.04	0.02	0.05	0.05	10	>110	<0.88
0.04	0.02	0.05	0.05	30	>160	<0.57

(a) Diluent was either Soltrol-170 or NPH.

(b) After second contact.

Extraction of Plutonium and Neptunium from Actual PAS

Satisfactory extraction of plutonium and, to some extent, neptunium from actual PAS solution (Table V) required that the extractant be at least 0.1M D2EHPA. This is a significant difference from results with synthetic PAS. The reason for the poorer plutonium extraction is obscure. Procedures were conducted to improve extraction of plutonium from PAS solution derived from Tank 241 A-104 sludge by using a double volume of 0.04M D2EHPA or by adding NaNO_2 to convert any Pu(III) to Pu(IV), but these attempts failed.

The poor extraction of neptunium when FS and hydrazine were not added to the actual PAS solutions constitutes evidence that neptunium is present largely as Np(V) in such solutions.

In the experiments listed in Table V, phases were allowed to disengage (gravity settling) for 10 to 30 min. Clean, sharp interfaces were

obtained in all cases. There was no evidence of emulsions even though the PAS solutions contained soluble silicates to the extent of 0.2 to 0.5 g/liter silicon.

TABLE V. Extraction of Np and Pu from Actual PAS Solutions

Conditions: PAS solutions obtained in laboratory sludge leaching experiments were contacted 30 min with an equal volume of indicated D2EHPA-TBP-diluent solution. Then (unless otherwise indicated), without phase separation, aqueous phase was adjusted to 0.01M N_2H_4 and 0.01M FS and allowed to stand 30 min at 25 °C. Finally, aqueous and organic phases were recontacted 30 min.

PAS Description ^(a)		D2EHPA, TBP,		FS,	N_2H_4	Not Extracted, %	
Sludge from PAS	H^+ , M	M	M	M	M	Np	Pu
Tank No.							
241-A-101	4.48 ^(b)	0.10	0.10	0.01	0.01	0.32	0.39
241-A-101	3.05 ^(b)	0.10	0.10	0.01	0.01	1.42	0.65
241-A-101	2.24	0.06	0.06	0.01	0.01	6.56	33.5
241-A-101	0.72	0.04	0.02	0.01	0.01	14.9	57.1
241-A-101	0.72	0.04	0.02	0.00	0.00	52.9	81.8
241-A-104	0.50	0.10	0.05	0.01	0.01	0.1	1.11
241-A-104	0.83	0.10	0.05	0.01	0.01	5.08	1.42
241-A-104	0.50	0.10	0.05	0.00	0.00	74.7	0.84
241-A-104	0.61	0.06	0.06	0.01	0.01	0.88	1.29
241-A-104	0.50	0.04	0.02	0.01	0.01	2.11	5.47
241-A-104	0.50	0.04	0.02	0.00	0.00	94.8	1.5
241-A-104	0.59	0.04	0.02	0.01	0.01	6.55	22.6
241-A-104	0.59	0.04	0.02	0.00	0.00	47.5	16.8
241-A-104	0.59	0.04 ^(c)	0.02	0.00	0.00	81.4	17.2
241-A-104	0.59	0.04 ^(d)	0.02	0.00	0.00	42.9	10.3
241-A-104	0.92	0.04	0.02	0.01	0.01	2.05	13.7
241-A-104	0.92	0.04	0.02	0.00	0.00	99.2	15.9
241-A-104	1.17	0.04	0.02	0.01	0.01	9.88	18.8
241-A-104	1.17	0.04	0.02	0.00	0.00	56.2	9.84
241-A-104	1.97	0.04	0.02	0.01	0.01	10.6	24.8
241-A-104	1.97	0.04	0.02	0.00	0.00	99.3	10.6

(a) See page 6 for description of preparation procedure.

(b) Adjusted to 1.0M H^+ by addition of NaOH before contact.

(c) PAS made 0.01M $NaNO_2$ before extraction contact.

(d) Two volumes of extractant and one volume of PAS used.

Effect of PAS Acidity on Extraction of Plutonium and Neptunium

The synthetic PAS used in the bulk of the experimental work contained 0.5 mole per liter hydrogen ion. Because of variations in sludge composition and leaching procedures, the acidity of actual PAS solution

may range to higher values. Data in Table VI demonstrate adequate reduction of Np(V) to Np(IV), and coextraction of plutonium and neptunium into 0.1M D2EHPA can be obtained at PAS acidities as high as 2M.

TABLE VI. Effect of PAS Acidity on Extraction of Plutonium and Neptunium

Conditions: Synthetic PAS was adjusted to either 7.6×10^{-5} M $\text{Pu}(\text{NO}_3)_4$ or 1×10^{-4} M NpO_2NO_3 and adjusted to acidity as shown by addition of 15.6M HNO_3 . Resulting solutions were contacted 10 min with an equal volume of 0.1M D2EHPA-0.1M TBP-NPH. Without phase separation aqueous phase was adjusted to 0.025M FS and 0.025M N_2H_4 and allowed to stand 30 min at 25 °C. Finally, aqueous and organic phases were recontacted 30 min.

Acidity, M	Plutonium		Neptunium	
	E_a^0	Not Extracted, %	E_a^0	Not Extracted, %
0.75	480	0.21	580	0.18
1.0	460	0.21	290	0.36
1.5	390	0.27	230	0.44
2.0	330	0.32	130	0.74

Kinetics of Plutonium Extraction

Data in Table VII demonstrate that Pu(IV) extracts very rapidly from PAS solution; over 99.8% of the plutonium extracts in one minute of vigorous agitation. Similar studies with Np(IV) were not performed, but it is believed neptunium extraction equilibrium is also attained rapidly.

TABLE VII. Kinetics of Plutonium Extraction

Conditions: Synthetic PAS was adjusted to 2.7×10^{-5} M $\text{Pu}(\text{NO}_3)_4$ and contacted for the times indicated with an equal volume of 0.04M D2EHPA-0.02M TBP-Soltrol-170.

Contact Time, min	Pu E_a^0	Pu not Extracted, %
0.5	150	0.56
1.0	1870	0.051
3.0	3300	0.029
5.0	1640	0.059
10.0	2400	0.040

Effect of Added Complexants on Extraction of Plutonium and Neptunium

Extraction recovery of plutonium and neptunium from synthetic PAS was not hindered by addition of various complexing agents (Table VIII). In earlier extraction studies⁽¹⁾ addition of complexing agents decreased extraction of inert zirconium into D2EHPA extractants. Addition of complexing agents to PAS solutions for the same purpose was initially thought necessary and desirable, but subsequent results (see page 18) showed adequate decontamination from zirconium could be obtained in their absence.

TABLE VIII. Effects of Complexing Agents on Extraction of Plutonium and Neptunium from Synthetic PAS Solution

Conditions: Synthetic PAS was adjusted to either $2.7 \times 10^{-5} \text{M Pu(NO}_3)_4$ or $2.9 \times 10^{-5} \text{M NpO}_2\text{NO}_3$ and then adjusted to either 0.016 or 0.05M in complexant shown. Resulting solutions allowed to stand 24 hr at 25 °C and then contacted 30 min with an equal volume of 0.04M D2EHPA-0.02M TBP-Soltrol-170. Without phase separation aqueous phase was adjusted to 0.025M N_2H_4 and 0.025M FS and allowed to stand one hr at 25 °C. Finally, aqueous and organic phases were recontacted for 30 min.

Complexant		E_a^0 (a)	Not Extracted, %	
Type	Conc., M		Np	Pu
None	-	1080	0.63	0.091
Citric Acid	0.016	1010	0.59	0.19
Citric Acid	0.05	840	0.72	0.21
Tartaric Acid	0.016	490	0.72	0.089
Tartaric Acid	0.05	480	0.41	0.13
Na_3HEDTA	0.016	700	0.12	0.12
Na_3HEDTA	0.05	740	0.12	0.12

(a) After final 30 min contact.

Oxalic Acid Strip of Plutonium and Neptunium

Aqueous-soluble oxalate complexes of both Pu(IV) and Np(IV) are well known.⁽²¹⁾ Depending on conditions (acidity, oxalate concentration, etc.) one or more of the complexes $\text{M(C}_2\text{O}_4)_1^{+2}$, $\text{M(C}_2\text{O}_4)_2$, $\text{M(C}_2\text{O}_4)_3^{-2}$, and $\text{M(C}_2\text{O}_4)_4^{-4}$ may be formed where M = Pu(IV) or Np(IV). Formation constants for these complexes are so high that, under proper conditions, dilute oxalic acid solutions quantitatively strip Pu(IV) and Np(IV) from the D2EHPA extractant. Data illustrating this point are presented in Table IX.

TABLE IX. Oxalic Acid Stripping of Plutonium and Neptunium

Conditions: Organic D2EHPA-TBP-diluent solutions which were either $2.7 \times 10^{-5} \text{M}$ Pu(IV) or $2.9 \times 10^{-5} \text{M}$ Np(IV) were prepared by contact with synthetic PAS. Resulting organic solutions were contacted with $\text{H}_2\text{C}_2\text{O}_4$ solutions according to conditions listed.

Organic Composition		Strip Conditions				E_a^0		Not Stripped, %	
D2EHPA, M	TBP, M	$\text{H}_2\text{C}_2\text{O}_4$, M	Time min	Temp, °C	Vol Ratio Aq/Org	Pu	Np	Pu	Np
0.10	0.05	0.1	30	25	1:1	0.0021	0.0011	0.22	0.11
0.10	0.05	0.25	30	25	1:1	0.0007	0.0004	0.078	0.037
0.10	0.05	0.1	30	50	1:1	0.17	-	16.3	-
0.10	0.05	0.1	30	50	1:2	1.0	-	74.0	-
0.04	0.02	0.1	30	25	1:1	<0.010	<0.0022	<1.1	<0.24
0.04	0.02	0.25	30	25	1:1	<0.0079	<0.0011	<0.86	<0.13
0.04	0.02	0.1	30	50	1:2	<0.0058	<0.0037	<1.24	<0.84

Based on these data, a single equal volume contact at 25 °C with 0.1M $\text{H}_2\text{C}_2\text{O}_4$ is specified in the chemical flowsheets for stripping plutonium and neptunium. Plutonium(IV) is stripped less efficiently at 50 °C than at 25 °C. Higher temperatures favor oxalic acid stripping of iron (see page 18) and should be avoided for this reason also.

If desirable for some reason, other complexants such as carbonate, citrate, EDTA, etc. could probably be used successfully to strip plutonium and neptunium from the D2EHPA phase. Oxalic acid, however, is smoothly and readily destroyed by reaction with H_2O_2 and/or HNO_3 and can be used without any danger of precipitating plutonium such as might occur during neutralization of alkaline solutions.

Yellow solids precipitate within 24 to 48 hr when $0.1\text{M H}_2\text{C}_2\text{O}_4$ strip solution from the recovery cycle is allowed to stand at 25°C .

These solids have been tentatively identified as iron(III) oxalate. Their formation can be prevented by adjusting the strip solution to 0.1M HNO_3 . Addition of this much HNO_3 to the strip solution is required also to provide the required media for destruction of oxalate by H_2O_2 and to prepare a satisfactory feed for the purification cycle (see page 19).

Extraction-Strip Behavior of Contaminants

Data illustrating the extraction and strip behavior of various metallic impurities in synthetic PAS are presented in Tables X and XI, respectively. Besides Np(IV) and Pu(IV), only uranium, zirconium, and iron extract into the D2EHPA solvent to any extent. As is to be expected, extraction of uranium and iron is greater into 0.1M D2EHPA than into 0.04M D2EHPA ; presumably the same is true of zirconium.

TABLE X. Extraction of Contaminants—Synthetic PAS

Conditions: Synthetic PAS solution spiked with various radioisotopes was contacted 60 min with equal volume of extractant as indicated.

Radioisotope	0.04M D2EHPA-0.2M TBP-Soltrol-170			0.1M D2EHPA-0.1M TBP-NHP		
	E_a^0	Extracted, %	DF ^(a)	E_a^0	Extracted, %	DF
^{233}U	3.18	77.8	-	38.7	97.7	-
^{95}Zr	-	-	-	6.7	86.0	-
^{59}Fe	0.0220	-	46	0.108	9.7	-
^{88}Y	0.0169	-	60	0.0055	-	180
^{152}Eu	0.0053	-	185	0.0010	-	970
^{106}Ru	0.0027	-	360	-	-	-
^{144}Ce	0.0018	-	620	0.00029	-	3460
^{51}Cr	<0.0015	-	>680	-	-	-
^{241}Am	0.00010	-	9700	-	-	-
^{85}Sr	<0.00002	-	>4900	-	-	-
^{54}Mn	<0.00001	-	>10000	-	-	-
^{137}Cs	0.000005	-	21000	-	-	-

(a) Decontamination Factor

TABLE XI. Oxalic Acid Stripping of Contaminants

Conditions: Synthetic PAS, traced with appropriate radioisotope, was contacted 60 min with an equal volume of indicated extractant. Portions of resulting organic phase then were contacted 30 min with oxalic acid under conditions indicated.

Extractant		Strip		Temp, °C	E_a^0			Stripped, %		
D2EHPA, M	TBP, M	H ₂ C ₂ O ₄ M	Vol Ratio Aq/Org.		²³³ U	⁵⁹ Fe	⁹⁵ Zr	²³³ U	⁵⁹ Fe	⁹⁵ Zr
0.1	0.1	0.1	1	25	26.4	2.95	13.5	4.8	25.6	6.9
0.1	0.1	0.25	1	25	8.9	0.487	5.48	12.5	67.4	15.2
0.1	0.05	0.25	1	50	6.07	-	-	19.8	-	-
0.1	0.05	0.25	0.5	50	8.72	-	-	7.0	-	-
0.04	0.02	0.1	1	25	1.75	0.638	-	36.6	60.8	-
0.04	0.02	0.25	1	25	0.98	0.225	-	49.5	84.0	-
0.04	0.02	0.1	0.5	50	1.45	<0.014	-	25.4	~100.	-

The results in Table XI demonstrate that considerable decontamination from extracted iron, uranium, and zirconium is obtained during the oxalic acid strip. Again 0.1M D2EHPA extractant retains uranium and iron more tenaciously than the 0.04M D2EHPA solvent. Considerably more uranium and iron strip at 50 °C and with 0.25M H₂C₂O₄ than do under the preferred (equal volume strip with 0.1M oxalic acid at 25 °C) strip conditions.

The excellent decontamination performance observed in recovery extraction-strip contacts (performed according to the flowsheet conditions shown in Figure A-I) with actual PAS solutions substantiates the results with synthetic PAS. For example, an oxalic acid strip solution obtained with a PAS solution from Tank-241-A-104 sludge contained 0.16 g/liter uranium, 0.51 g/liter iron, and less than 0.02 g/liter inert zirconium. A similar solution obtained with a PAS solution from Tank-241-A-101 sludge contained 0.57 g/liter uranium, 0.19 g/liter iron, and less than 0.02 g/liter inert zirconium. Predicted values for the composition of the oxalic acid strip solution from results in Tables X and XI are 0.24 g/liter uranium, 0.52 g/liter iron, and 0.02 g/liter inert zirconium. The strip solutions in the experiments with the Tank-241-A-104 and 241-A-101 PAS solutions each contained only a trace (<0.01%, spectroscopic analysis) each of aluminum, chromium, magnesium, manganese,

nickel, and silicon. Chemical analysis of the oxalic acid strip solution from the Tank-241-A-101 sludge indicated the aluminum concentration was 0.00017M .

British workers report⁽²²⁾ substantial extraction of molybdenum from HNO_3 solutions into D2EHPA extractants can occur under certain conditions. The molybdenum content of actual PAS solutions has not been established; however, spectroscopic analysis of oxalic acid strip solutions from Tank-241-A-104 and Tank-241-A-101 PAS solutions indicated the presence of less than 5ppm molybdenum.

The D2EHPA extractant from the experiment with PAS obtained from Tank-241-A-104 sludge, after oxalic acid stripping, contained 0.02 moles uranium per liter. In the similar experiment with PAS from Tank-241-A-101 sludge, the stripped organic was 0.046M uranium. A uranium concentration of 0.02M is predicted from experiments (Tables X and XI) with synthetic PAS. The former organic solution also contained 3 uCi/liter ^{95}Zr - ^{95}Nb , 210 uCi/liter ^{106}Ru and 850 uCi/liter ^{90}Y activity. No gamma emitters were detected in the stripped organic from the experiment with PAS from Tank-241-A-101 sludge, but this organic phase contained 6620 uCi/liter of ^{90}Y activity.

PURIFICATION CYCLE

The initial extraction-strip contacts discussed in the preceding sections recover the neptunium and plutonium and free them from the bulk of the contaminants with which they are associated in PAS solution. Further purification, and also concentration, is necessary and desirable, however, to provide a small volume of purified material for final separation and purification.

The desired purification is accomplished by a further extraction-strip cycle using essentially the same conditions employed in the initial recovery contacts. Feed for the purification cycle extraction contact is prepared by accumulating (after concentration and destruction of oxalate described on page 22) the neptunium and plutonium from several batches of PAS solution in a 1M HNO_3 solution. It is estimated this feed solution will also be about $0.09\text{M Fe(NO}_3)_3$ and $0.01\text{M UO}_2(\text{NO}_3)_2$; smaller ($<0.01\text{M}$) amounts of other contaminants (aluminum, zirconium, yttrium, etc.) may also be present.

Batch contact of the acid feed with an equal volume of 0.1M D2EHPA-0.1M TBP-NPH solvent serves to extract the Pu(IV). To recover the neptunium the aqueous phase (without phase separation) is made 0.01 to 0.05M in both FS and hydrazine to reduce Np(V) to Np(IV). Subsequent recontact of the aqueous and organic phases then extracts the Np(IV) without significant loss of Pu(IV) to the aqueous phase as illustrated by the data in Table XII.* Essentially all of the uranium and about 15% of the iron are coextracted with the neptunium and plutonium.

TABLE XII. Purification Cycle-Extraction Contact

Conditions: Synthetic feed^(a) was contacted 30 min at 25 °C with an equal volume of 0.1M D2EHPA-0.1M TBP-NPH. Without phase separation, aqueous phase was adjusted to 0.01M ferrous sulfamate and 0.01M hydrazine and allowed to stand 30 min at 25 °C. Aqueous and organic phases then were recontacted 30 min at 25 °C.

Element	Distribution Ratio, E_a^0	
	First Contact	Second Contact
Plutonium	1500	980
Neptunium	0.234	2620
Uranium	137	113
Iron	0.111	0.176

(a) 1.0M HNO₃-0.089M Fe(NO₃)₃-0.01M UO₂(NO₃)₂-0.002M Zr(SO₄)₂-0.08M Al(NO₃)₃-4.1 x 10⁻⁴M Pu(NO₃)₄-1.4 x 10⁻⁴M NpO₂NO₃.

To complete the purification cycle the extracted plutonium and neptunium are costripped into an equal volume of 0.1M oxalic acid just as in the recovery cycle (See Table IX). Results in Table XIII indicate about 4 and 84% of the extracted uranium and iron, respectively, will accompany the plutonium and neptunium into the strip solution. The oxalic acid solution is treated with HNO₃ and H₂O₂ (See page 24) to destroy the oxalate and then concentrated to yield a small volume of product for final separation and purification of the recovered neptunium and plutonium.

* As noted in Table XII the synthetic feed solution used in the recycle extraction contact experiments was 0.08M Al(NO₃)₃; this solution was prepared before it was realized very little aluminum would be present in the oxalic acid strip from the recovery cycle.

TABLE XIII. Purification Cycle-Strip Contact

Conditions: Portions of organic phases obtained in contacts listed in Table XII were contacted 30 min at 25 °C with equal volume of oxalic acid solution as indicated.

Oxalic Acid, <u>M</u>	<u>Uranium</u>		<u>Iron</u>	
	E_a^O	Stripped, %	E_a^O	Stripped, %
0.10	22.4	4.3	0.209	84.4
0.25	11.7	7.7	0.0155	97.7

SOLVENT TREATMENT

The stripped 0.1M D2EHPA extractant from both the recovery and purification cycles is expected to contain about 2 to 5 g/liter uranium and 0.1 to 1 g/liter iron. Smaller amounts of the other inert contaminants (zirconium, aluminum, etc.) in PAS solutions will also be present in the used extractant. Radioactive contaminants will include ^{90}Y and, from the younger sludges, small amounts of ^{95}Zr - ^{95}Nb and ^{106}Ru .

Routine removal of uranium and iron from the solvent is necessary to prevent overloading the extractant and thereby impairing extraction recovery of neptunium and plutonium. Uranium, as well as zirconium and yttrium, can be readily removed from the D2EHPA solvent by washing with Na_2CO_3 -sodium citrate (or tartrate) solutions as illustrated by the data in Table XIV.

Sodium hydroxide solutions could also be used to wash contaminants from the 0.1M D2EHPA extractants. With NaOH washes, however, uranium precipitates as the diuranate even in the presence of citrate or tartrate. Precipitation of uranium is avoided with carbonate washes because of the formation of soluble uranium carbonate complexes. Addition of citrate or tartrate to the Na_2CO_3 solution prevents precipitation of hydrated iron(III) oxide.

Two organic phases formed when 0.1M D2EHPA-0.05M TBP-NPH solutions were contacted with 0.5 to 1.0M Na_2CO_3 solutions. When the TBP concentration was increased to 0.1M a third phase did not form if the Na_2CO_3 concentration was 1.0M or greater. Because of this restriction on Na_2CO_3 concentration it is economically desirable to use only a

TABLE XIV. Solvent Wash Studies

Conditions: 0.1M D2EHPA-0.1M TBP-NPH extractant from extraction-strip contacts with synthetic and actual PAS solutions were washed (15 min, 25 °C) with indicated solutions.

Wash Composition			Vol Ratio Aq/Org	E_a^0		Not Removed, %		
Na_2CO_3 , M	$\text{Na}_2\text{Tar.}^{(a)}$ M	$\text{Na}_3\text{Cit.}^{(b)}$ M		U	^{95}Zr	U	^{95}Zr	$^{90}\text{Y}^{(c)}$
1.0	0.1	0.0	1:5	0.0062	-	3.7	-	-
1.0	0.1	0.0	1:3	0.0084	-	2.8	-	-
1.0	0.1	0.0	1:1	0.0125	<0.0008	0.89	<0.09	-
1.0	0.0	0.1	1:5	0.0062	-	3.5	-	-
1.0	0.0	0.1	1:3	0.0089	-	2.9	-	-
1.0	0.0	0.1	1:1	0.021	<0.0008	1.4	<0.09	-
1.5	0.0	0.1	1:5	0.0067	-	3.4	-	5.7
1.5	0.0	0.1	1:3	0.0063	-	2.1	-	7.0
1.5	0.0	0.1	1:1	0.011	0.0011	0.69	0.11	5.4

(a) Sodium Tartrate.

(b) Sodium Citrate.

(c) Solvent from contact PAS from Tank-241-A-101 sludge.

small volume of wash solution in each batch wash. Removal of contaminants is adequate with 1.0 to 1.5M Na_2CO_3 solution at an aqueous-to-organic flow ratio as low as 1 to 5 and this amount of carbonate is still sufficient to prevent precipitation of uranium. Washing of the D2EHPA extractant with a Na_2CO_3 solution converts it to the sodium form. Reconversion to the hydrogen form can be accomplished by washing the extractant with a HNO_3 solution.

DESTRUCTION OF OXALIC ACID

Destruction by Nitric Acid

Typical kinetic data obtained in this investigation for the destruction of oxalic acid by HNO_3 are plotted in Figure 2. That the reaction is first order with respect to oxalic acid concentration has already been discussed. Half lives of oxalic acid at 11, 9, and 7M HNO_3 are about 30, 55, and 125 min, respectively, and are correspondingly longer in more dilute HNO_3 solutions.

FIGURE 2. Destruction of Oxalic Acid by Oxidation with HNO₃

Destruction by Hydrogen Peroxide

The reaction of oxalic acid with H_2O_2 in boiling 0.089M and 0.44M HNO_3 was studied to establish conditions for destruction of oxalate in oxalic acid strip solutions. The reaction is first order in oxalic acid concentration, and its rate increases with both HNO_3 and H_2O_2 concentration (Figure 3). As reported by Blanco and Watson⁽¹¹⁾, Mn(II) catalyzes the reaction (Figures 4 and 5). The data plotted in Figures 3-5 were obtained with H_2O_2 containing a proprietary chemical stabilizer. The results in Figure 6 show that the rate of the reaction between H_2O_2 and oxalic acid was not affected by the presence of this stabilizer.

The extraction-strip conditions shown in Figure A-I were used to prepare an oxalic acid strip solution from synthetic PAS. This strip solution was adjusted to 0.1M HNO_3 by addition of 12.7M HNO_3 , and one portion was also made 0.01M $\text{Mn}(\text{NO}_3)_2$. The results in Figure 7 (Curve 1) show that oxalate was destroyed efficiently and rapidly in boiling 0.1M HNO_3 -0.01M $\text{Mn}(\text{NO}_3)_2$ solution by a single addition of H_2O_2 (unstabilized 3.7M) equivalent to an initial H_2O_2 /oxalic acid mole ratio of about 5. Peroxide oxidation of oxalate in the acidified strip solution proceeded less smoothly when $\text{Mn}(\text{NO}_3)_2$ was not present (Curve II), and addition of two equal portions of 3.7M H_2O_2 was necessary to reduce the oxalate concentration by about a factor of 10. (In the latter experiment the second portion of H_2O_2 was much more effective than the first in destroying oxalate; this peculiar behavior was observed also in a duplicate experiment but is not fully understood.) The final solution obtained in each of the two experiments just described was concentrated ninefold. This concentration step destroyed residual H_2O_2 and yielded 1M HNO_3 solutions containing less than about 0.004M oxalate. Such solutions are considered acceptable feed stocks for subsequent purification D2EHPA cycles.

CHEMICAL FLOWSHEETS

Chemical flowsheets for the recovery and purification cycles are presented in Appendix A, Figures A-I and A-II, respectively. Key flow-sheet features are the specification of a D2EHPA concentration of 0.1M, a

FIGURE 3. Reaction of Oxalic Acid with H_2O_2 —
 Effects of HNO_3 and H_2O_2 Concentration

FIGURE 4. Effect of $\text{Mn}(\text{NO}_3)_2$ Concentration on Reaction of Oxalic Acid with H_2O_2 in 0.089M HNO_3

FIGURE 5. Effect of $\text{Mn}(\text{NO}_3)_2$ Concentration on Reaction of Oxalic Acid with H_2O_2 in $0.44\text{M}\text{HNO}_3$

FIGURE 6. Effect of H_2O_2 Source on Peroxide Destruction of Oxalic Acid

FIGURE 7. Peroxide Destruction of Oxalate in Strip Solutions from Synthetic PAS

single equal volume strip with 0.1M oxalic acid in both the recovery and purification cycles, and the use of Mn(II) as a catalyst in H_2O_2 destruction of oxalate in the strip product from the recovery cycle. To improve product purity, however, peroxide treatment of the strip product from the purification cycle is accomplished without addition of $\text{Mn}(\text{NO}_3)_2$.

DISPOSITION OF NEPTUNIUM-PLUTONIUM PRODUCT

The flowsheet conditions shown in Appendix A provide for recovery of the plutonium and neptunium in each 9000 gal of PAS solution in about 3 to 5 gal of purified product solution. This concentrated product is expected to contain about 5 g/liter neptunium and about 15 g/liter plutonium, and to be about 5M HNO_3 , 0.1M $\text{UO}_2(\text{NO}_3)_2$, and 1 to 2M $\text{Fe}(\text{NO}_3)_3$; small ($<0.01\text{M}$) amounts of aluminum and zirconium also may be present in some cases.

Use of the Hanford Purex plant 3A-3B column system⁽²³⁾ has been considered for final separation and purification of the neptunium and plutonium recovered from PAS solution. Firm plans for the method of processing the recovered neptunium and plutonium through the 3A-3B system have not been established; one attractive scheme is to blend the recovered material with normal Purex plant 3A column feedstock. Such blending would dilute Fe(III) in the PAS neptunium-plutonium product to tolerable levels for FS reduction of Pu(IV) to Pu(III).

The most serious objection to routing plutonium and neptunium recovered from PAS solution to the Purex plant is that D2EHPA may be introduced into the plant 30% TBP extractant. Results obtained by Buckingham⁽²⁴⁾ and Schulz⁽¹⁾ demonstrate that even small concentrations of D2EHPA in the TBP solvent interfere seriously with stripping of plutonium in the Purex 1B column. Since the solubility of D2EHPA in acid aqueous solutions is very low, D2EHPA would not normally be expected to be present in the PAS plutonium-neptunium product. However, variable amounts of D2EHPA might be introduced into each batch of product solution by entrainment during separation of aqueous and organic phases.

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APPENDIX A
CHEMICAL FLOWSHEETS

FIGURE A-I. Chemical Flowsheet for Recovery of Neptunium and Plutonium from Purex Acid Sludge-Recovery Cycle

A-2

BNWL-583

Notes: (a) Organic from Strip Contact in Recovery Cycle (Figure A-9) Washed in Same Way
(b) Product from Treating Six 1500 gal Batches of PAS
(c) Estimated Conditions

FIGURE A-II. Chemical Flowsheet for Recovery of Neptunium and Plutonium from Purex Acid Sludge-Purification Cycle

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