APPLICATION OF AMBERLITE XE-270 RESIN
TO PURIFICATION OF NEPTUNIUM

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ABSTRACT

Amberlite XE-270, a macroreticular weak-base ion exchange resin made by the Rohm and Haas Company, was used successfully over an eight-month period in the Hanford Purex plant to purify about eight kg of neptunium-237. Details of the plant experience as well as the many laboratory-scale tests which preceded plant-scale operation are described. For routine purification of ^{237}Np the Amberlite XE-270 resin provides four important advantages over conventional microreticular strong base resins used heretofore:

- *Greatly improved thorium decontamination performance.*
- *A much sharper neptunium elution band.*
- *Operation at 25 °C rather than at 40 or 50 °C.*
- *Five-fold lower resin cost.*

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APPLICATION OF AMBERLITE XE-270 RESIN TO PURIFICATION OF NEPTUNIUM

INTRODUCTION

Conventional, microreticular strong-base (quaternary ammonium) anion exchange resins have been used for several years at both the United States Atomic Energy Commission Hanford and Savannah River Purex plants to recover and/or purify neptunium-237. Details of the neptunium ion exchange processes and equipment used at these sites have been reported elsewhere.^[1-3]

The strong-base exchangers have generally provided adequate service in recovery and decontamination of neptunium; yet for this application they do have several disadvantages. Foremost of these is their inability to separate neptunium cleanly from thorium. Feed to the Hanford Purex plant ion exchange purification unit contains, typically, less than 1 g/liter thorium; but, in some cases, as after a preceding Thorium Campaign,^[4] can contain as much as 50 to 100 g/liter thorium. With strong-base exchangers which have a relatively high affinity for thorium, time-consuming and expensive special loading and elution procedures are required for production of specification grade (≤ 3 wt% Th) neptunium from such high-thorium feeds; adequate separation is achieved only at the expense of large (*e.g.*, 65%) neptunium losses.

Other disadvantages of the strong-base exchangers include their relatively high cost and the "tailing" which occurs during elution of neptunium. Neptunium in these tail fractions must be recycled for recovery. Failure of the neptunium to elute in a sharp band makes it difficult for process

operators at Hanford to judge when to start and stop collection of concentrated product.

Substitution of Amberlite[®] XE-270 resin, a macroreticular weak-base (tertiary amine) exchanger made by the Rohm and Haas Company, for the strong-base resins largely overcomes the disadvantages of the latter for neptunium purification. The Amberlite XE-270 resin was developed originally for improved recovery of uranium from sulfate leach liquors.^[5] This paper describes batch and column tests with the Amberlite XE-270 resin which led to its eventual use in the Hanford Purex plant. Plant-scale experience with Amberlite XE-270 resin over an eight-month period is also summarized.

NEPTUNIUM PURIFICATION FLOWSHEET

Typical flowsheet conditions for fixed-bed anion exchange resin purification of ^{237}Np recovered in the Hanford Purex plant are listed in Table I. (Early laboratory work which provided the technological basis for selection of these flowsheet conditions was performed by Ryan^[6] and Burney^[7].) The ion exchange system is currently operated at 25 °C with 25-50 mesh Amberlite XE-270 resin; previously the process was operated at 40 °C with 50 to 100 mesh Dowex 21K resin, a typical strong-base exchanger made by Dow Chemical Company. Except as noted in the subsequent discussion, the flowsheet conditions shown in Table I apply equally well, generally, to both resins and differ only slightly from those previously published.^[1,2] One important change is the omission of a reducing wash to remove plutonium; adequate decontamination from plutonium is now obtained in the preceding solvent-extraction cycles.

TABLE I
HANFORD ANION EXCHANGE
NEPTUNIUM PURIFICATION FLOWSHEET

Operation	Stream Composition	Column Volumes	Process Rate
Pretreatment	6M HNO ₃ 0.1M N ₂ H ₄	2	2-3 ml cm ⁻² min ⁻¹
Loading ^a	6-7M HNO ₃ 0.1M N ₂ H ₄ 6 g/liter Np(IV)	4-8	8 mg Np cm ⁻² min ⁻¹
Fission Product Scrub	7.5M HNO ₃ 0.05M N ₂ H ₄ ~0.01M NaF	3-10	2-3 ml cm ⁻² min ⁻¹
Fluoride Removal	7.0-8M HNO ₃ 0.1M N ₂ H ₄	1.5-5	2-3 ml cm ⁻² min ⁻¹
Elution:			
Forecut	0.35M HNO ₃	1-2	1 ml cm ⁻² min ⁻¹
Product cut	0.35M HNO ₃	0.5-1	1 ml cm ⁻² min ⁻¹
After cut	0.35M HNO ₃	1	1-2 ml cm ⁻² min ⁻¹

^aFeed also contains from <1 to as much as 100 g/liter ²³²Th and 0.2-1.5 g/liter U plus varying amount of ¹⁰⁶Ru-¹⁰⁶Rh, ⁹⁵Zr-⁹⁵Nb, ²³³Pa, and ²³⁴Th.

The feed adjustment procedure to establish Np(IV) involves simply adding hydrazine to the 6 to 7M HNO₃ solution obtained from the preceding solvent extraction purification cycles and heating for an hour at 60 °C. The resulting feed batch, containing typically 1500 to 2000 grams of neptunium, is passed downflow through the 50-liter (six-inch diameter) resin bed at a rate of about 1.4 ml cm⁻² min⁻¹. [About 2 column volumes of 6M HNO₃-0.1M N₂H₄ solution are passed through the bed immediately prior to the load cycle to condition the resin for sorption of Np(NO₃)₆²⁻.] Reflecting its greater selectivity for neptunium over thorium the Amberlite XE-270 resin can be loaded to neptunium concentrations as high as 30 to 40 g/liter even from feedstocks

containing as much as 100 g/liter thorium. Similar high neptunium loadings cannot be achieved with Dowex 21K and other strong-base resins from 100 g/liter thorium feeds without excessive loss of neptunium.

The loaded resin bed is washed with 3 to 10 column volumes of 7.5M HNO₃-0.01M NaF-0.05M N₂H₄ solution to scrub ⁹⁵Zr, ⁹⁵Nb, and other contaminants. With Amberlite XE-270 resin, 3 to 5 column volumes of the fluoride scrub provide adequate removal of fission products with satisfactorily low neptunium loss. From 5 to 10 column volumes of fluoride scrub can be used with Dowex 21K resin to obtain satisfactory purification from fission products without experiencing significant neptunium loss. Following the fission product scrub step, 1.5 to 5 column volumes of 7.0-8M HNO₃-0.1M N₂H₄ solution are passed through the column to wash the resin free of fluoride.

Neptunium is eluted from the resin bed with about three column volumes of 0.35M HNO₃. These are divided approximately equally into a forecut, a product cut, and an aftercut. Neptunium elutes in a much sharper band from the Amberlite XE-270 resin than from the Dowex 21K exchanger. Typical product solutions from the Dowex 21K and Amberlite XE-270 resins contain, respectively, 25 and 40 g/liter neptunium. Because of the "tailing" which occurs during elution of the Dowex 21K resin, the forecut and aftercut solutions contain significant amounts of neptunium which must be recycled to the next loading cycle for recovery. The forecut and aftercut solutions from elution of the Amberlite XE-270 resin are also recycled to the next loading cycle but do not contain large amounts of neptunium.

Waste solutions from the loading and washing steps are normally routed to underground storage. When these wastes

contain significant quantities of neptunium, however, they are routed to the back-cycle waste stream for recovery.

Data illustrating plant-scale recovery and decontamination performance of both the Amberlite XE-270 and Dowex 21K resins are presented and discussed later.

EXPERIMENTAL

MATERIALS

Ion exchange resins used in this work are listed in Table II; a more detailed description of the macroreticular Amberlite XE-270 resin is given in Table III.

TABLE II
LIST OF ION EXCHANGE RESINS

Property	Resin			
Designation	Amberlite XE-270	Dowex 21K	Amberlyst A-21	FPS-4024L
Manufacturer	Rohm and Haas Company	Dow Chemical Company	Rohm and Haas Company	Dow Chemical Company
Type	Weak-base	Strong-base	Weak-base	Weak-base
Active group	Tertiary amine	Quaternary ammonium	Tertiary amine	Tertiary amine
Structure	Macroreticular	Microreticular	Macroreticular	Macroreticular
Particle size ^a	25-50 ^b	50-100 ^b	14-50 ^b	20-50 ^c
Ionic form ^d	Hydroxide	Chloride	Hydroxide	Hydroxide

^aU.S. standard screen.

^bDry basis.

^cWet basis.

^dAs-received.

TABLE III
SELECTED PROPERTIES OF AMBERLITE XE-270 RESIN

Property	Value ^a
Manufacturer	Rohm and Haas Company
Resin type	Weak base
Skeletal structure	Styrene-divinyl-benzene
Functional group	Tertiary amine
Physical structure	Macroreticular
Shape	Spherical Beads
Porosity ^b , %	48
Particle size	25-50 mesh (U.S. Standard Screen)
Ionic form	Free base
Swelling (OH + NO ₃), %	40
Moisture content, %	46-54
Ion exchange capacity meq/ml wet resin	1.4
Maximum operating temp., °C	100
Shipping weight, lb/ft ³	42
Price ^c , \$/ft ³	74.50

^aTaken mainly from References 5 and 8.

^bTrue porosity as measured in dry state.

^cFor 1-39 cubic-foot lots as of March, 1973.

Macroreticular ion exchange resins are prepared by a variation of the polymerization technique used for the conventional gel-like (microreticular) resins.^[9] Such resins consist of an agglomerate of randomly packed microspheres (with normal gel porosity) with a continuous non-gel pore structure extending through the agglomerate; pore diameters of the macroreticular resins are several hundred angstroms. In all other respects the macroreticular resins are identical to their microreticular counterparts. Burney and Thompson^[10] have reported results of laboratory studies of the application of a macroreticular strong-base resin for separation of ²³⁷Np from ²³⁸Pu.

Differential thermoanalytical data for nitrate-form Amberlite XE-270 and Dowex 21K resins are shown in Figure 1. The former resin is characterized by a large exotherm at

about 180 °C and a smaller one at about 420 °C. Exotherms for nitrate-form Dowex 21K resin occur at about 236, 265, and 385 °C. Since these exotherms correspond to temperatures at which various resin degradation reactions occur, thermal stability of the nitrate-form Amberlite XE-270 resin is slightly less than that of nitrate-form Dowex 21K resin. This decreased thermal stability of the Amberlite XE-270 resin is not a serious deterrent to its use, however, since process operating temperatures (≤ 40 °C) are far removed from 180 °C. The data in Figure 1 were obtained with a Mettler Company Thermoanalyzer; 0.36-gram resin samples were heated in air at a rate of 4 °C per minute.

Feedstock for many of the batch and column tests was prepared by appropriate addition of stock HNO_3 , N_2H_4 , $\text{Th}(\text{NO}_3)_4$, and ferrous sulfamate (FeSA_2) solutions to concentrated and highly purified Hanford Purex plant neptunium product solutions. These latter solutions contained, typically, 33 g/liter ^{237}Np as NpO_2NO_3 . [Ferrous sulfamate was added to reduce Np(V) to Np(IV)]. In some column runs the feedstock was spiked with a small amount of Purex plant dissolver solution to supply fission product activity.

Feed for some column runs was also prepared by appropriate dilution of actual Purex plant neptunium ion exchange column feed solution. This latter 7M HNO_3 solution contained 7.8 g/liter ^{237}Np , 65 g/liter Th , 1100 $\mu\text{Ci/liter } ^{233}\text{Pa}$, and $1.2 \times 10^5 \mu\text{Ci/liter } ^{234}\text{Th}$.

Except for the neptunium stock solutions, reagent-grade chemicals were used throughout.

PROCEDURES

Distribution Ratios

Nitrate-form XE-270 and Dowex 21K (20 to 50 mesh) resins were prepared by contacting (30 min at 25 °C) about 400 ml of as-received resin with alternate liter-portions of 5M NaOH and 5M NaNO₃ solutions. After five such cycles the resin was washed five times with fresh 1.5-liter portions of water and then air-dried. A weighed portion of the air-dried resin was heated in a vacuum at 60 °C to constant weight. From the loss in weight, a factor for calculating vacuum-dried weights from air-dried weights was determined.

One-quarter gram amounts of the nitrate-form XE-270 and 21K resins were contacted 48 hr at 26 °C with 10-ml portions of 4 to 9M HNO₃-0.012M Th(NO₃)₄ solutions. Following the contact period, the resin beads were collected on a sintered glass filter, and the concentration of thorium in the filtrate was measured. Subsequently, the resin beads were contacted twice (10 min at 26 °C) with fresh 10-ml portions of 0.25M HNO₃ to elute sorbed thorium; the composite eluate was analyzed for thorium. From these measurements the grams of thorium sorbed per gram of vacuum-dried resin were determined. The thorium distribution ratio, K_d , is defined as the ratio of the concentration of thorium in the resin to that in the solution in equilibrium with the resin; *i.e.*,

$$\text{Th } K_d = \frac{\text{g Th/g oven-dried resin}}{\text{g Th/ml solution}}$$

A procedure similar to that just described was followed to determine distribution of ²³⁷Np between Amberlite XE-270 and Dowex 21K resins and 4 to 9M HNO₃-0.5 g/liter Np(IV)-0.05M FeSA₂-0.01M N₂H₄ solutions. Contact times ranged from 10 minutes to 10 days at 26 °C. The grams of neptunium

sorbed on the resin were determined by analysis of the aqueous solution before and after contact with the resin. The neptunium distribution ratio is defined as

$$\text{Np } K_d = \frac{\text{g Np/g oven-dried resin}}{\text{g Np/ml solution}}$$

Column Runs

Ion exchange column runs with XE-270 and the other resins listed in Table II were performed under downflow conditions at either 25 or 50 °C. Jacketed, glass columns containing a sintered glass frit to support the resin beads were used throughout. The resin bed (nitrate-form) in most tests was 1 cm in diameter and 12.7 cm high (10-ml bed volume).

Conditions employed in the loading, wash, and elution cycles corresponded approximately to those listed in Table I; exact conditions are specified in later tables and discussion. Solutions were either pumped (Fluid Metering, Inc.) or gravity-fed to the ion exchange column. Effluent was collected manually, usually in one-column volume samples.

ANALYSES

X-Ray fluorescence, alpha counting and energy analysis, and gamma energy analysis [Ge(Li) detector] procedures were all used to determine the ^{237}Np concentration of various feed, wash, and elution solutions. X-Ray fluorescence techniques were also used to measure the concentration of ^{232}Th in such solutions. In column runs with plant feed solutions the behavior of ^{234}Th , ^{233}Pa , and various fission products was followed by gamma energy analysis of appropriate samples.

A spectrophotometric procedure using Thoron indicator was used to analyze for thorium in HNO_3 solutions obtained in batch distribution ratio experiments.

The HNO_3 concentration of solutions used in both batch- and column-experiments was determined by potentiometric titration with NaOH after addition of potassium oxalate to complex neptunium and iron(II).

RESULTS AND DISCUSSION

BATCH STUDIES

Distribution Ratios

Amberlite XE-270 resin sorbs the $\text{Np}(\text{NO}_3)_6^{2-}$ ion from 6 to 9 HNO_3 solutions less efficiently than does Dowex 21K resin (Figure 2). Even so, at these HNO_3 concentrations neptunium distribution ratios with the Amberlite XE-270 resin are still sufficiently high (≥ 800) to insure excellent neptunium recovery.

Affinity of the Amberlite XE-270 resin for sorbing thorium from 6 to 9M HNO_3 solutions is less than half that of the Dowex 21K resin (Figure 3). Reflecting this behavior, the Amberlite XE-270 resin selectively sorbs neptunium even from HNO_3 solutions containing very high concentrations of thorium. Data plotted in Figure 3 for Dowex 21K resin are in excellent agreement with thorium distribution ratios measured by Ryan^[11] and Carroll^[12] for other strong-base exchangers.

Paralleling the ion exchange data presented here, solvent extraction results also demonstrate that quaternary ammonium reagents extract thorium from HNO_3 solution more strongly than do tertiary amine extractants. For example, distribution ratios for thorium between 5 volume percent (in xylene) Aliquat 336 (a quaternary ammonium extractant made by General Mills, Inc.) and 1 to 8M HNO_3 solutions range from about 10 to 50.^[13] Conversely, distribution

ratios for thorium between 10 volume percent (in xylene) tri-n-octylamine and 1 to 8M HNO₃ solutions are less than one. [14]

Kinetics of Neptunium Sorption

Results plotted in Figure 4 show that the equilibrium distribution of Np(IV) between 7.2M HNO₃ and Amberlite XE-270 resin is attained in about three hours at 26 °C. With Dowex 21K resin at this temperature, however, equilibrium distribution of neptunium is not attained even after contacting resin and solution for 1000 minutes. The more rapid uptake of neptunium by the Amberlite XE-270 resin is a consequence, presumably, of its macroreticular structure.

COLUMN RUNS

Load Cycle Parameters

Effects of changes in load cycle conditions upon breakthrough of thorium and neptunium were studied with a 10-ml bed of Amberlite XE-270 resin. Except in two cases the feed was a 6.3M HNO₃-0.01M FeSA₂-0.01M N₂H₄ solution containing 25.9 g/liter thorium and 5.1 g/liter neptunium; two runs were made with 7.0 and 8.0M HNO₃ feeds, respectively. Runs were made at either 25 or 40 °C at flow rates in the range 1.05 to 2.10 ml cm⁻² min⁻¹. In each run 90 ml (9 column volumes) of the feed solution were passed downflow through the resin bed; each column volume of effluent was analyzed to determine its neptunium and thorium content. Following each load cycle 2 column volumes of 7M HNO₃, 5 column volumes of 0.35M HNO₃, and 5 column volumes of 6.3M HNO₃ were passed in succession through the resin bed to prepare it for the next load cycle.

Results of the various load cycle runs are tabulated in

Table IV and plotted in Figures 5 through 7. For this particular range of experimental conditions, sorption and breakthrough behavior of thorium is relatively insensitive to changes in column temperature, feed acidity, or feed flow rate. Conversely, as would be expected for the major species sorbed by the resin, changes in all these parameters affect sorption and breakthrough behavior of neptunium. For example, corresponding to the distribution data shown in Figure 2, neptunium loads more efficiently from 7 and 8M HNO_3 feeds than from the 6.3M HNO_3 solution (Figure 5b). Also, reflecting beneficial kinetic effects, low feed flow rates (Figure 6b) and higher bed temperatures (Figure 7b) are both conducive to increased loading of neptunium.

A second series of load cycle runs identical to the first except with feeds containing only 2.45 g/liter thorium was made. Results for neptunium were similar to those plotted in Figures 5 through 7. At this lower thorium concentration, however, retention of thorium by the Amberlite XE-270 resin also increased as feed acidity and column temperature increased and as feed flow rate decreased.

Fission Product Wash Cycle Studies

An HNO_3 -HF scrub solution is used in the Hanford neptunium purification flowsheet (Table I, page 3) to remove ^{95}Zr , ^{95}Nb and other fission products from the loaded bed prior to elution of the neptunium. Thorium and small amounts of neptunium are also scrubbed from the resin bed during this fission product wash cycle. Table V and Figures 8 and 9 present conditions and results of several column runs made to study how changes in acidity and flow rate of the fluoride scrub and in bed temperature influence scrubbing of thorium and neptunium.

TABLE IV
LOAD CYCLE BEHAVIOR OF NEPTUNIUM AND THORIUM

A. RUN CONDITIONS

Run No.	HNO ₃ M	Feed ^a		Temperature °C.	Flow Rate ml cm ⁻² min ⁻¹
		Np g/liter	Th g/liter		
10	6.3	5.1	25.9	25	1.58
11	7.0	5.1	25.9	25	1.58
12	8.0	5.1	25.9	25	1.58
13	6.3	5.1	25.9	25	2.10
14	6.3	5.1	25.9	40	1.05
15	6.2	5.1	25.9	40	2.10
16	6.3	5.1	25.9	25	1.05

^aOther conditions given on p. 11.

B. RESULTS

Column Volumes	C/C ₀ ^a													
	Run 10		Run 11		Run 12		Run 13		Run 14		Run 15		Run 16	
	Np	Th	Np	Th	Np	Th	Np	Th	Np	Th	Np	Th	Np	Th
1	<0.004	<0.004	<0.004	<0.004	<0.004	<0.003	<0.004	<0.004	<0.004	<0.003	<0.004	<0.003	<0.004	<0.003
2	<0.004	0.021	<0.004	0.047	<0.004	<0.018	<0.004	<0.004	<0.004	<0.003	<0.004	0.021	<0.004	0.024
3	<0.004	0.259	<0.004	0.348	<0.004	0.183	<0.004	0.442	<0.004	0.071	<0.004	0.181	<0.004	0.215
4	<0.004	0.522	<0.004	0.647	<0.004	0.634	0.052	0.704	<0.004	0.454	<0.004	0.634	<0.004	0.582
5	0.019	0.919	0.005	0.968	0.019	0.953	0.097	0.897	<0.004	1.02	0.022	1.03	0.006	0.949
6	0.088	1.03	0.033	1.06	0.045		0.160	1.07	<0.004	1.19	0.051	1.12	0.037	1.08
7	0.141	1.12	0.067	1.10	0.108	1.15	0.240	1.16	0.030	1.22	0.096	1.12	0.050	1.10
8	0.202	1.10	0.141	1.14	0.145	1.13	0.291	1.12	0.032	1.21	0.147	1.14	0.094	1.10
9		1.02	0.178	1.11	0.198	1.12	0.339	1.12	0.102	1.20	0.210	1.13	0.156	1.10

^aC/C₀ = concentration in effluent/concentration in influent.

TABLE V
BEHAVIOR OF THORIUM AND NEPTUNIUM IN FISSION PRODUCT WASH CYCLE

A. RUN CONDITIONS^a

Run No.	Scrub		Temperature °C	Flow Rate ml cm ⁻² min ⁻¹
	HNO ₃ M	NaF M		
1	7.0	0.01	25	1.05
2	7.0	0.01	40	1.05
3	7.0	0.01	25	2.10
4	7.0	0.01	40	2.10
5	8.0	0.01	25	1.05
6	8.0	0.01	40	2.10
7	8.0	0.01	25	2.10
8	8.0	0.01	40	2.10

^aOther condition on p. 15.

B. RESULTS

Column Volumes	Cumulative Percent Removed											
	Run 1		Run 2		Run 3		Run 4		Run 5	Run 6	Run 7	Run 8
	Np	Th	Np	Th	Np	Th	Np	Th	Th	Th	Th	Th
1	5.31	42.6	5.54	43.3	5.13	49.0	5.06	43.2	41.6	43.5	39.1	37.5
2	8.71	54.9	8.39	64.3	8.24	65.7	8.71	63.8	68.2	65.7	57.8	55.3
3	10.6	69.2	11.0	77.4	11.1	77.5	12.1	75.8	8.13	78.4	67.4	68.5
4	12.9	78.2	13.5	86.4	13.9	85.3	15.2	82.8	89.4	87.0	74.5	77.6
5	15.7	84.2	16.2	90.8	16.7	72.2	18.7	88.3	98.8	92.4	79.9	8.51
6	19.0	88.8	18.9	94.2	19.5	96.1	22.2	91.5	97.5	95.8	84.2	90.4
7	22.4	91.2	21.6	96.9	22.6	98.4	25.7	97.2	99.4	97.9	87.5	94.0
8	29.4	93.9	24.6	98.6	25.5	101.	29.3	99.1	100.	99.0	90.0	96.5
9	29.4	96.6	27.8	99.3	28.4		32.7	99.5		99.5	93.0	97.1
10	32.8	98.1	30.7	100.	31.2		35.9			99.6	95.4	98.7

In each of the runs listed in Table V, 90 ml (9 bed volumes) of a 6.3M HNO_3 -0.1M FeSA_2 -0.01M N_2H_4 solution containing 27 g/liter thorium and 5.5 g/liter neptunium were passed downflow at 25 °C and at a rate of 1.05 ml cm^{-2} min^{-1} through a 10-ml bed of Amberlite XE-270 resin. Subsequently, 10 column volumes of 7 or 8M HNO_3 -0.01M NaF solution were passed downflow through the bed at either 25 or 40 °C and at a rate of either 1.05 or 2.10 ml cm^{-2} min^{-1} . Each column volume of wash solution was collected separately and analyzed for thorium and, in some cases, for neptunium. Following the fluoride scrub step the bed was washed with 2 column volumes of 7M HNO_3 and 5 column volumes of 0.35M HNO_3 . Effluent from the latter steps was also analyzed for neptunium and thorium.

Each column volume of the fluoride fission product scrub solution (after the first) removes about three percent of the neptunium loaded onto the Amberlite XE-270 resin (Figure 9). Such losses do not occur with strong-base resins, thus reflecting the stronger affinity of quaternary over tertiary amine groups for neptunium. Neptunium lost to the fission product wash cycle effluent must be recycled for recovery; to minimize such recycle it is desirable to limit the volume of the fluoride fission product scrub solution to the minimum required for satisfactory removal of fission products and/or thorium. In the Hanford plant-scale application of Amberlite XE-270 resin (discussed on page 19), approximately three column volumes of the 7 to 8M HNO_3 -0.01M NaF scrub solution provide adequate removal of contaminants. This volume of scrub solution, as the results plotted in Figure 8 show, removes about 75 percent of the thorium left on the resin after the load cycle is completed. Changes in scrub acidity, temperature, and flow rate affect to some extent the amounts of thorium and neptunium removed by the

HNO₃-NaF scrub; but, at least over the range of conditions tested, no really significant trends with any of these variables is apparent.

Elution Cycle Studies

Mention has already been made that neptunium elutes in a much sharper band from Amberlite XE-270 resin than from strong-base resins. Data which illustrate this point are plotted in Figure 10; at either 25 or 40 °C one-half to one column volume of dilute HNO₃ elutes 90 to 95 percent of the neptunium from loaded Amberlite XE-270 resin. With Dowex 21K and other strong-base resins, however, "tail" fractions of the eluate contain up to 10 to 20 percent of the eluted neptunium.

Decontamination Performance

Several column runs were made to compare the performance of the Amberlite XE-270 and Dowex 21K resins in purifying neptunium from thorium and other contaminants. Runs were made at both 25 and 40 °C with the stream compositions and flows indicated in Table VI. Various wash cycle combinations (Table VII) were tested with a uniform five-column volume elution cycle. In each test all the second column volume of eluate was arbitrarily taken as the neptunium product. Judging from subsequent plant-scale experience, more careful fractionation of the eluate in these laboratory-scale runs would have yielded a somewhat purer neptunium product, particularly from the Dowex 21K resin.

Easily the outstanding result of these experiments (Table VII) was the much superior thorium decontamination provided by the Amberlite XE-270 resin over that obtained with Dowex 21K resin. The Amberlite XE-270 resin also

TABLE VI
DECONTAMINATION STUDIES--
STREAM COMPOSITIONS AND FLOWS

Stream	Flow ml/min	Composition					
		HNO ₃ M	Np g/liter	Th g/liter	FeSA ₂ M	N ₂ H ₄ M	NaF M
Feed 1 ^{a,b}	0.5	6.3	5.5	0.1	0.1	0.1	0.0
Feed 2 ^{c,d}	0.5	6.3	5.5	45.	0.1	0.1	0.0
Wash 1	2.0	6.7	0.0	0.0	0.1	0.1	0.0
Wash 2	2.0	7.0	0.0	0.0	0.0	0.05	0.01
Wash 3	2.0	8.0	0.0	0.0	0.0	0.0	0.0
Eluent	1.0	0.3	0.0	0.0	0.0	0.0	0.0

^aAlpha energy analysis was 95.9% ²³⁷Np, 2.95% ²³⁹Pu, and 1.3% ²⁴¹Am.

^bSpiked to contain, typically, 750 μ Ci/liter ⁹⁵Zr-⁹⁵Nb and 12,000 μ Ci/liter ¹⁰⁶Ru-¹⁰⁶Rh.

^cPrepared from Hanford Purex plant ion exchange column feed.

^dContained, typically, 85,000 μ Ci/liter ²³⁴Th and 800 μ Ci/liter ²³³Pa.

provided excellent decontamination of neptunium from ²³³Pa and fission product ruthenium; decontamination from ⁹⁵Zr-⁹⁵Nb, although slightly lower than that obtained with Dowex 21K resin, was satisfactorily high also. Neptunium purified with the Amberlite XE-270 resin also contained significantly smaller concentrations of other alpha emitters (americium and plutonium) than did that purified with the strong-base exchanger. In limited tests, changes in column temperature did not significantly affect decontamination performance of the Amberlite XE-270 resin.

Two column runs were made (Table VIII) to evaluate, albeit very briefly, two other weak-base resins (Amberlyst A-21 and FPS 4024L) for their ability to purify neptunium from thorium. In this latter function both resins, although superior to strong-base resins, appear to be inferior to the Amberlite XE-270 resin.

TABLE VII
DECONTAMINATION PERFORMANCE OF AMBERLITE XE-270
and DOWEX 21K RESINS--LABORATORY STUDIES

Load Cycle ^a		Temp.	Wash Cycles ^b			Product		Overall Decontamination Factors ^d				
			Temp.	Wash	Wash	Wash	Np	AEA ^c	232Th	234Th	233Pa	95Zr-95Nb
Feed No. ^b	°C	°C	1	2	3	g/l	% Np					
A. AMBERLITE XE-270 RESIN												
1	25	25	5	5	5	26.3	- ^e	-	-	-	98	7,390
1	25	25	2	3	2	32.1	99.4	-	-	-	35	>360
1	25	25	2	2	2	30.1	99.5	180	-	-	21	2,200
1	25	25	5	0	5	30.4	99.4	-	-	-	9	280
1	40	40	5	0	5	28.9	99.4	-	-	-	9	6,500
2	25	25	5	0	5	31.3	>99.5	29	32	44	-	-
2	25	25	0	10	3	27.6	>99.	140	160	41	-	-
2	25	40	0	10	3	32.5	>99.	87	71	10	-	-
2	25	40	0	5	3	33.4	>99.7	45	-	-	-	-
2	40	40	0	5	3	33.5	-	10	10	78	-	-
2	25	25	0	0	3	30.4	>99.7	16	-	-	-	-
B. DOWEX 21K RESIN												
1	25	25	5	5	5	17.7	98.0	-	-	-	22	58
1	40	40	5	5	5	-	-	1.5	-	-	-	-
1	25	25	5	0	5	26.0	98.2	-	-	-	14	105
1	40	40	5	0	5	28.4	98.3	-	-	-	7	130
2	50	50	0	10	3	13.2	-	3	3	8	117	-

^a7-8 column volumes.

^bComposition listed in Table VI.

^cAlpha energy analysis.

^dDecontamination Factor = $\frac{\text{Np, g/l product}}{\text{Np, g/l feed}} \times \frac{\text{contaminant concentration feed}}{\text{contaminant concentration product}}$

^eSignifies not measured.

TABLE VIII
PURIFICATION OF NEPTUNIUM FROM THORIUM
WITH VARIOUS ANION EXCHANGE RESINS

Property ^a	Resin ^b			
	XE-270	A-21	FPS-4024 L	21K ^c
Np recovery ^d , %	79	44	72	73
Product Np conc., g/liter	27.6	15.8	29.5	13.2
Thorium DF	140	44	25	3

^aConditions:

Load cycle: 9 col vol Feed 2, Table VI.

Wash cycles: 10 col vol Wash 2, Table VI.

3 col vol Wash 3, Table VI.

Elution cycle: 5 col vol 0.3M HNO₃.

^bSee Description in Tables II and III.

^cAt 40 °C; all others at 25 °C.

^dIn second column volume of eluate.

PLANT-SCALE EXPERIENCE WITH AMBERLITE XE-270 RESIN

A 50-liter bed of Amberlite XE-270 resin has been used over an eight-month period in the Hanford Purex plant to purify about 8 kg of neptunium. Plant-scale performance of the Amberlite XE-270 resin has been excellent (Table IX) and on all counts has equaled or exceeded that expected from the laboratory-scale work. Compared with the strong base exchanger (Dowex 21K) used previously, the Amberlite XE-270 resin provides greatly improved decontamination from thorium, satisfactory decontamination from other impurities, and slightly greater overall neptunium recovery. Mechanics of the elution cycle are also much improved with the Amberlite XE-270 resin in that process operators can better judge when to collect the product cut.

Feeds used in the first six plant runs with the Amberlite XE-270 resin contained, as noted in Table X, from 13 to 100 g/liter thorium. Even so, all but two of

TABLE IX

NEPTUNIUM PURIFICATION WITH AMBERLITE XE-270
AND DOWEX 21K RESINS--TYPICAL PLANT PERFORMANCE

	Amberlite XE-270 Resin ^a	Dowex 21K Resin ^b
Average Np Recovery, %	82 (72-93)	75 (57-91)
Decontamination Factors:		
Thorium	100-800	10-40
¹⁰⁶ Ru- ¹⁰⁶ Rh	24-530	7-240
⁹⁵ Zr- ⁹⁵ Nb	17-220	28-1600
²³³ Pa	5-25	2-6
Uranium	3.2×10^4 - 1.92×10^5	8.80×10^2 - 1.03×10^5

^aResin bed operated at 25 °C according to flowsheet conditions described in Table I and on pp. 3-4.

^bAverage plant performance over 19-month period prior to change to Amberlite XE-270 resin; bed operated at 40 °C and flowsheet conditions of Table I and pp. 3-4.

the neptunium products met or exceeded the specifications of ≤3 weight percent thorium; the product from Run 1 contained only slightly more than the specification amount of thorium and was shipped on a waiver. Prior to the installation of the Amberlite XE-270 resin, all attempts to prepare specification-grade neptunium product from these high-thorium content feeds using a strong-base exchanger were completely unsuccessful!

Worth calling attention to is that the plant Amberlite XE-270 resin bed was operated at 25 °C rather than the 40 °C temperature used with strong-base resins. Successful operation of the load cycle at 25 °C was possible not only because of the favorable kinetics of the macroreticular resin, but also because of control of neptunium batch size and proper selection of the load-on rate. Operation of the neptunium purification process at 25 °C rather than at an elevated temperature simplifies process control and minimizes any chances of ignition of nitrate-form resin.

TABLE X
PURIFICATION OF ^{237}Np WITH AMBERLITE XE-270 RESIN--
HANFORD PUREX PLANT EXPERIENCE

<u>Feed</u>	<u>Run Number</u>					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Volume, liter	164	336	202	2.90	221	316
Np, g/liter	7.8	4.8	6.8	7.3	8.2	5.4
Th, g/liter	90	55	a	32	100	13
<u>Product</u>						
Volume, liter	27	36	34	31	38	36
Np, g/liter	36	41	36	49	38	37
Th, g/liter	1.2	0.57	3.1	0.82	0.77	0.91
<u>Np Distribution, %</u>						
Pretreatment waste	a	a	a	0.0	0.1	2.7
Loading waste	a	a	a	0.72	0.96	3.9
Fission product wash	a	a	a	0.4	9.3	11.3
Fluoride wash	a	a	a	5.9	2.5	3.3
Elution forecut	a	a	a	0.0	0.3	2.7
Elution aftercut	a	a	a	8.7	7.4	2.8
Elution product	76.3	91.9	89.4	72.0	80.7	77.7
<u>DF's</u>						
Uranium	32,000	192,000	173,000	600	2,580	189,000
^{232}Th	350	800	a	260	630	98
^{234}Th	620	1,360	770	440	120	520
^{106}Ru - ^{106}Rh	530	24	-	-	-	-
^{95}Zr - ^{95}Nb	100	220	17	70	150	30
^{233}Pa	10	14	6	5	100	24

^aData not available.

Overall neptunium recovery in the first six plant runs ranged from 72 to as much as 95 percent. Load cycle neptunium losses were satisfactorily low throughout. In agreement with laboratory experience (p. 15) the bulk (10 to 15 percent) of the product loss occurred in the fission product and fluoride wash steps. Some additional neptunium was lost in the elution aftercut. This latter solution and the wash solutions were recycled to appropriate steps in the solvent extraction or ion exchange processes for recovery of the neptunium.

Following the fifth plant run a sample of the Amberlite XE-270 resin was removed for examination of its physical and chemical properties. Neptunium and thorium distribution ratios for the used resin were comparable to those for new resin. Also, the force required to break a bead of the plant resin was well within the range of forces needed to break beads of unused resin. The empirical force test has long been used at Hanford to indicate deterioration of the strength of resin beads used in plant-scale applications.

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FIGURE 1
THERMOANALYSIS OF NITRATE-FORM AMBERLITE XE-270
AND DOWEX 21K RESINS

FIGURE 2
NEPTUNIUM DISTRIBUTION RATIOS

FIGURE 3
THORIUM DISTRIBUTION RATIOS

FIGURE 4
KINETICS OF NEPTUNIUM SORPTION

FIGURE 5
LOAD CYCLE--EFFECT OF FEED HNO_3 CONCENTRATION

FIGURE 6
LOAD CYCLE--EFFECTS OF FLOW RATE

FIGURE 7
LOAD CYCLE--EFFECT OF TEMPERATURE

FIGURE 8

THORIUM SCRUB BEHAVIOR IN FISSION PRODUCT WASH CYCLE

FIGURE 9
 NEPTUNIUM SCRUB BEHAVIOR
 IN FISSION PRODUCT WASH CYCLE

FIGURE 10
ELUTION OF NEPTUNIUM FROM AMBERLITE XE-270
AND DOWEX 21K RESINS

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