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Macroreticular Anion Exchange Cleanup Of TBP Solvent

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MACRORETICULAR ANION EXCHANGE RESIN
CLEANUP OF TBP SOLVENTS

By

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May 15, 1972

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ABSTRACT

Strong base macroreticular anion exchange resins (e.g., Amberlyst A-26) remove fission products, dibutyl phosphoric acid, and diluent degradation products from used TBP extractants. Application of these resins in routine cleanup of such solvents is potentially attractive to eliminate or, at least, minimize the large volumes of radioactive waste generated by presently used solvent wash procedures.

Column tests with both unwashed Hanford Purex plant 30% TBP-NPH and Plutonium Reclamation Facility 20% TBP-CCl₄ solvents demonstrate the high capacity of A-26 resin for sorbing solvent impurities. Chemical and physical properties of resin-treated solvent, according to various solvent quality indices and mixer-settler tests, are comparable with those of carbonate-washed extractant. Resin beds used to treat Purex process solvent can be regenerated by successive treatment with 3M HNO₃-0.025M HF and 1M NaOH solutions. Alternatively, spent resin can be disposed of by incineration at 750 °C. Conceptual flowsheets for resin cleanup of typical TBP extractants are described.

MACRORETICULAR ANION EXCHANGE RESIN CLEANUP OF TBP SOLVENTS

INTRODUCTION

Tributyl phosphate (TBP) solvent extraction processes are extensively used in both U.S. and foreign nuclear industry. Typical applications include purification of aqueous uranium feedstocks in uranium refineries,^[1] recovery of uranium and/or plutonium from metallurgical scrap^[2,3] and, most importantly, the Purex process for reprocessing all kinds of irradiated nuclear reactor fuels.^[4]

Plants which use TBP extraction processes routinely perform "solvent treatment" operations to maintain extractant quality. Such treatments conventionally involve a combination of alkaline and acid washes, sometimes in conjunction with alkaline permanganate solutions, to remove dibutyl phosphoric acid (HDBP); residual fission products and uranium and plutonium, if present; and, at least partially, degradation products of the hydrocarbon mixture used to dilute the TBP. Chemical and radiolytic degradation of TBP extractants and solvent treatment procedures have been reviewed by several authors.^[5-8]

Sustained, satisfactory operation of various Purex and other TBP extraction plants in the U.S. and elsewhere attests to the efficiency of present-day solvent washing techniques. A major disadvantage of these methods, however, is that they generate large volumes of aqueous waste. Spent wash solution in the case of Purex plants must be stored or otherwise treated as a high-level radioactive waste. Development of an alternative solvent treatment

procedure which does not generate such waste (or, at least, minimizes its volume) is both economically and environmentally desirable.

Encouraging results have been obtained in this direction utilizing the properties of macroreticular ion exchange resins. Such resins are identical to their conventional microreticular counterparts except for having much larger pore diameters. These large pores do not disappear when the swelling solvent, water, is removed; hence, macroreticular resins are especially suited for use with non-aqueous, even non-polar, solutions.^[9,10]

Initial tests of macroreticular ion exchange resin cleanup of Hanford Purex process solvent were summarized previously.^[11] These tests have now been extended to include cyclic load-elution capacity runs as well as determination of the effects of flow rate and solution residence time on resin performance and behavior of resin-treated solvent under countercurrent Purex process-type conditions. Application of macroreticular resins to routine treatment of Hanford's Plutonium Reclamation Facility (PRF) 20% TBP-CCl₄ solvent has also been investigated. (A reflux solvent extraction process is used in the PRF to recover and purify plutonium from a wide assortment of metallurgical scrap.^[2]) Progress and findings of these latest resin solvent treatment studies are highlighted in this paper.

SYNOPSIS OF PREVIOUS WORK

Japanese workers^[12,13] and British scientists^[14] before them applied microreticular ion exchange resins for removal of various acidic components from degraded TBP-diluent solutions. Significant findings of our initial

experiments with Rohm and Haas Company macroreticular resins and Hanford Purex plant unwashed first cycle solvent (1CW solution) included:^[11]

- . Strong base (A-26 and A-29) resins sorbed HDBP and fission product ^{106}Ru , ^{95}Zr , and ^{95}Nb much more strongly than did either Amberlyst A-21 (weak base) or Amberlyst 15 (cation exchanger) resins. [Amberlyst A-26 resin was selected for further study because of its slightly greater stability at elevated temperatures.]
- . Affinity of hydroxide-form A-26 resin for radioruthenium was slightly greater than that for ^{95}Zr , ^{95}Nb , or HDBP; however, batch distribution ratios for all these solutes were greater than 500.
- . Kinetics of sorption of fission products and HDBP from used Purex solvent by A-26 resin were significantly faster at 40 °C than at 25 °C. Kinetics of fission product and HDBP uptake by A-26 resin also increased with decreasing resin particle size.
- . Of many reagents tested for this purpose, 1 to 4M NaOH and 1 to 3M HNO₃-0.05M HF solutions were best for eluting fission products and HDBP from A-26 resin.
- . High capacity of A-26 resin for sorbing extractant impurities was indicated in very preliminary column runs. Physical and chemical properties of the effluent solvent in these runs were equal to or superior to those of Hanford Purex plant carbonate-washed material.

EXPERIMENTAL

MATERIALS

Important properties of Amberlyst A-26 resin are listed in Table I. As-received Cl-form A-26 resin was converted to the OH-form by treatment with excess 4M NaOH, washed with water, and dried in air. The density of the dried 14 to 50 mesh (U.S. Standard Screen Series) OH-form resin is about 39 lb/ft³; an 80% increase in volume occurs when the dry resin is wet with water. As required, CO₃-form A-26 resin was prepared by washing the OH-form material with excess 1M Na₂CO₃.

Macroreticular anion exchange resin obtained from the J. T. Baker Company (A-641 resin) was used in one experiment with Purex process solvent. Prior to use, the as-received 16 to 50 mesh Cl/SO₄-form was converted to the OH-form by washing with 4M NaOH.

TABLE I
PROPERTIES OF AMBERLYST A-26 RESIN^a

<u>Property</u>	<u>Typical Value</u>
Appearance	Hard, spherical, light-tan, water-saturated beads ^b
Functional group	Quaternary ammonium
Ion exchange capacity:	
meq/gram	4.1-4.4
meq/ml	0.95-1.1
Density, lb/ft ³	39-43
Average pore diameter, A	400-700
Maximum operating temperature	60 °C ^c
Price, \$/lb	1.56 ^d

^a Taken from Reference 10.

^b For chloride-form.

^c For hydroxide-form.

^d 40 to 9999 lb lots.

Unwashed Hanford Purex plant first cycle solvent (1CW solution) was used in capacity and flowrate tests. This pale-yellow material contained, nominally, 30 vol% TBP; and, depending on plant performance and the type of fuel processed (*i.e.*, Al-clad U, Zr-2-clad U, or Al-clad ThO₂), from 0.05 to 1100 $\mu\text{Ci/liter}$ ⁹⁵Zr-⁹⁵Nb and from 70 to 380 $\mu\text{Ci/liter}$ ¹⁰⁶Ru-¹⁰⁶Rh. [The ratio of ⁹⁵Zr to ⁹⁵Nb in the various batches of 1CW solvent ranged from 2:1 to 1:1.] Small amounts of ¹⁰³Ru were also present. Plutonium Retention Numbers (an empirical measure of HDBP concentration, see p. 8) were generally in the range 2000 to 10,000 but, in some cases, were as high as 59,000. [The HDBP concentration of 1CW solvents with Pu Retention Numbers of 2,000 to 5,000 was below $5 \times 10^{-5}M$, the lower limit of the analytical method used.] Various batches of 1CW were titrated with NaOH; no HNO₃ was detected in any of them.

One capacity test was performed with Hanford Purex plant carbonate- and HNO₃-washed solvent. This material, as received, contained 3 $\mu\text{Ci/liter}$ ⁹⁵Zr-⁹⁵Nb, 55 $\mu\text{Ci/liter}$ ¹⁰⁶Ru-¹⁰⁶Rh, and 0.005M HNO₃; its Pu Retention Number was 93,000. This high Pu Retention Number was attributed to the presence of HDBP produced by acid hydrolysis of TBP when the acidified solvent was allowed to sit. Prior to use in resin tests the acidified TBP was washed twice with one-fifth volume portions of water to remove the HNO₃.

Both water- and carbonate-washed PRF 20% TBP-CCl₄ solvents were used. Respectively, these solutions contained, typically, 0.00056 and 0.00014M HDBP and 0.11 and 0.50 mg/liter Pu, their Pu Retention Numbers were, respectively, 93,000 and 13,000. No HNO₃ was present in the plant water-washed solvent.

Soltrol 170, a mixture of 100% branched paraffins, was obtained from the Phillips Petroleum Company. This material

was degraded by heating 6 hours at 70 °C while in stirred contact with an aqueous 6M HNO₃-0.05M NaNO₂ solution.

To obtain ¹³¹I₂, a 3M HNO₃ solution was spiked with an Na¹³¹I solution obtained from the Pacific Northwest Laboratory. Molecular iodine thus obtained was extracted into either 1CW solvent or into laboratory-prepared 30% TBP-NPH solution.

Synthetic PRF 20% TBP solvent was prepared by diluting as-received TBP (Commercial Solvents Corporation) with CCl₄. This solvent was washed with Na₂CO₃ and HNO₃ solutions; subsequently, HDBP (Victor Chemical Company) purified from monobutylphosphoric acid, was added to a concentration of about 0.002M.

PROCEDURES

Column loading tests with 1CW solution were all performed at 40 °C under downflow conditions. [Jacketed, glass columns containing either a sintered glass frit or a fine mesh stainless steel screen to support the resin beads were used throughout.] In most capacity and cyclic load-elution tests the initial A-26 resin bed was 1.9 cm in diameter by 7.6 cm high (21.5 ml bed volume). This height:diameter ratio of 4 was selected as typical of that which might be used in plant-scale equipment. This same bed height:diameter ratio was used in short (50 to 100 bed volumes) column runs to study effects of flow rate and residence time on A-26 resin cleanup of Purex process solvent. Prior to use with 1CW solution, all resin beds were classified by upflow of water.

Loaded A-26 resin beds obtained in cyclic load-elution tests with 1CW solvent were eluted with alternate small volume (6 to 8 bed volumes) portions of 3M HNO₃-0.025 or 0.05M HF and 1 or 4M NaOH solutions. Between successive

HNO₃ and NaOH eluents 1 to 2 bed volumes of water were passed through the resin bed. One elution cycle was performed at 25 °C; all others were done at 40 °C. Considerable gassing occurred when HNO₃ was first passed through the loaded A-26 resin. To accommodate this gas, all HNO₃ elutions were performed under upflow conditions. Both upflow and downflow conditions were used with NaOH eluents. Final eluted resin beds were washed upflow with several column volumes of water before use in the next load cycle.

With PRF solvent A-26 resin bed loading tests were performed at both 25 and 40 °C under both up- and downflow conditions. [Upflow of the dense CCl₄ solvent is preferable for best hydraulic operation.] An 0.5-foot diameter by 5.5-foot high resin bed is projected for plant-scale resin treatment of PRF solvent. This height:diameter ratio was approximated in many of the laboratory studies which employed a 1.5-cm diameter by 8.8-cm high resin bed. Other height:diameter ratios were used in flowrate and residence time tests. Water-classified resin beds were used throughout. No attempt was made to elute any of the resin beds used with PRF solvent.

To determine affinity of OH-form A-26 resin for I₂, two-gram portions of air-dried 14 to 50 mesh A-26 resin were first contacted (30 min, 25 °C) twice with fresh 10-ml portions of laboratory-prepared 30% TBP-NPH. Subsequently, the resin was contacted (60 min, 40 °C) either with ICW containing ¹³¹I₂ or laboratory-prepared 30% TBP-NPH containing ¹³¹I₂. [All liquid-solid separations were by centrifugation.] Initial and final liquid phases from the last contact were analyzed for ¹³¹I. Distribution ratios (K_d) were calculated as

$$K_d = \frac{\mu\text{Ci } ^{131}\text{I on resin per gram of resin}}{\mu\text{Ci } ^{131}\text{I per ml of solution}}$$

ANALYTICAL

Concentrations of fission products in LCW solvent, before and after resin treatment, and in eluate solutions were determined by gamma pulse height analyses using both NaI(Tl) and Ge(Li) detectors. The total alpha content (principally plutonium) of PRF solvents was measured by standard counting techniques.

An infrared spectroscopic method was used to analyze PRF solvent for HDBP.^[15] Test solvents were contacted with 1.0M Na₂CO₃-0.1M NaF solution to transfer the HDBP to an aqueous phase. After scrubbing twice with CCl₄ to remove any TBP, the aqueous solution was adjusted to 1.0M HCl, and the HDBP extracted into CCl₄. Absorbance of the HDBP in the extract was measured at 1036 cm⁻¹ using 1.0 mm thick Irtran-2 cells. By proper choice of phase volumes in the various steps of the procedures HDBP concentrations as low as 5 x 10⁻⁵M could be measured.

Plutonium retention tests involved contacting (5 min, 25 °C) the TBP phase with one-fifth volume of 3M HNO₃-0.001 Pu(NO₃)₄ solution; the resulting organic phase was scrubbed three times with fresh double-volume portions of 0.01M HNO₃. The Pu Retention Number was calculated by multiplying the molarity of plutonium in the final organic phase by 10⁹. Like the analogous "Z" and "H" Numbers,^[8] the Pu Retention Number has traditionally been regarded as a sensitive measure of the presence of HDBP and/or deleterious diluent degradation products in used Purex process solvent. For example, the Pu Retention Number of undegraded, carbonate-washed 30% TBP-NPH is about 25 while that of carbonate-washed Hanford Purex plant first cycle solvent is typically 50 to 100.

Differential thermal analysis of OH-form A-26 resin was performed with a Mettler Company Thermoanalyzer; 5-mg

samples were heated in air at a rate of 4 °C/min.

RESULTS

PUREX PROCESS SOLVENTS

Flow Rate Tests

Table II summarizes conditions and results of column runs made to study effects of flow rate and solution residence time on A-26 resin cleanup of Purex process solvent. With one exception, these runs were made at a bed height:diameter ratio of 4. Resin bed performance is primarily a function of solution residence time rather than flow rate; this is demonstrated by the correlations plotted in Figure 1. Solvent cleanup is excellent at residence times of 10 to 30 minutes (2 to 6 bed volumes per hour).

TABLE II

A-26 RESIN TREATMENT OF PUREX PROCESS SOLVENT-- EFFECTS OF FLOW RATE AND RESIDENCE TIME

Data are for passage at 40 °C of 50 to 100 column volumes of Purex ICW solution through indicated beds of 14-50 mesh, OH-form A-26 resin.

Bed Dimensions		Flow Rate		Residence Time min	Average Effluent Solvent		
Diam cm	Height cm	Col. Vol. hr ⁻¹	Gal. ft ² hr ⁻¹		C/C ₀ ^a		Pu Retention Number
					⁹⁵ Zr- ⁹⁵ Nb	¹⁰⁶ Ru- ¹⁰⁶ Rh	
2.54	10.2	2.0	5.0	30.	0.0027	0.0031	63
2.54	10.2	4.32	10.8	14.6	0.0062	0.0026	35
1.90	7.6	6.0	11.3	10.0	0.0081	0.0194	41
2.54	10.2	8:26	20.8	7.65	0.0257	0.0202	140
1.10	4.5	9.0	10.	6.68	0.0272	-	-
1.10	61.4	15.1	228.	4.0	0.053	0.052	-

^a Concentration in ICW/Concentration in effluent.

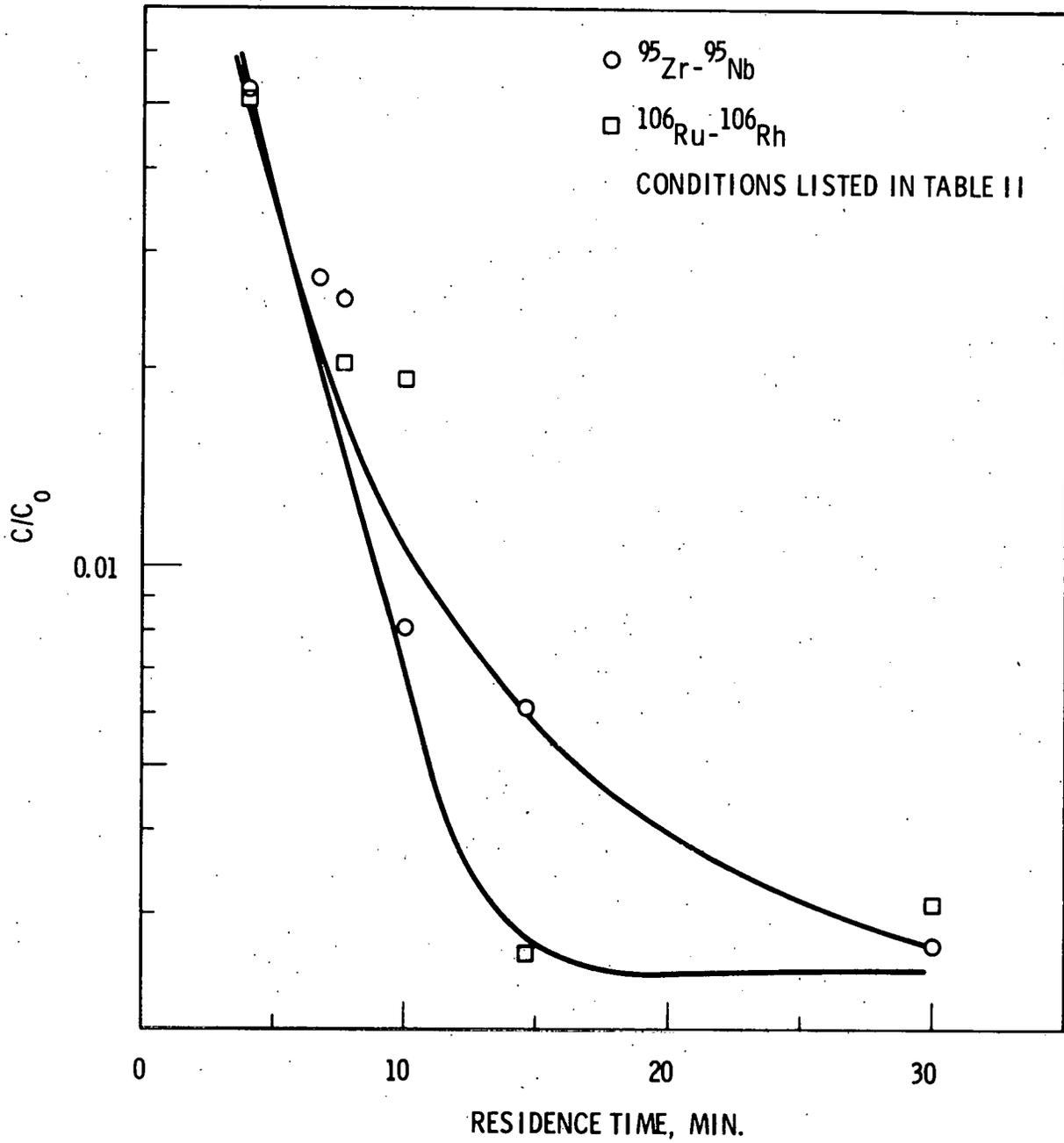


FIGURE 1
EFFECTS OF RESIDENCE TIME
ON A-26 RESIN SORPTION OF FISSION PRODUCTS

Capacity Tests

Results of several column runs to establish capacity of A-26 resin for sorbing fission products from Purex process solvents are summarized in Table III. Such capacity depends very strongly on the HDBP concentration (as measured by Pu Retention Number) of the solvent. For feed containing little HDBP (low Pu Retention Number) as much as 10,000 to 15,000 μCi of ^{95}Zr - ^{95}Nb and ^{106}Ru - ^{106}Rh could be loaded without significant breakthrough of any radioisotope (*e.g.*, Run 1). Conversely, with a feed whose Pu Retention Number was a high 90,000 (Run 6) 17% breakthrough of ^{106}Ru - ^{106}Rh occurred after only 960 μCi of ^{106}Ru - ^{106}Rh were loaded!

Table IV and Figure 2 present detailed information on the progress of the capacity test cited as Run 1 in Table III. Concentrations of ^{106}Ru - ^{106}Rh and ^{95}Zr - ^{95}Nb in the effluent solvent ranged from 3.7 to 9.7 $\mu\text{Ci/liter}$ and from 0.07 to 20.4 $\mu\text{Ci/liter}$, respectively. In contrast, concentrations of ^{106}Ru - ^{106}Rh and ^{95}Zr - ^{95}Nb in Hanford Purex plant carbonate-washed solvent produced over the same time period ranged from 48 to 96 $\mu\text{Ci/liter}$ and from 2.6 to 33 $\mu\text{Ci/liter}$, respectively. Effluent solvent produced in Run 1 was typical of that generated in the other capacity runs up to the breakthrough point.

The Pu Retention Number of all the effluent solvent produced in Run 1 was less than 100, comparable to that of carbonate-washed used solvent. Resin-treated solvent generated in some of the other capacity tests (*e.g.*, Run 6, Table III) had Pu Retention Numbers in the range 1600 to 4000. However, such solvent was produced only after breakthrough of fission product activity.

The minimum in the ^{95}Zr - ^{95}Nb curve shown in Figure 2

TABLE III
 A-26 RESIN TREATMENT
 OF PUREX PROCESS SOLVENT--CAPACITY TESTS

Property	Run No. ^a					
	1	2	3	4	5	6 ^b
Column Volumes	2,200 ^c	1,465 ^c	1,360 ^c	1,300 ^c	1,650 ^c	1,590 ^c
μCi loaded:						
⁹⁵ Zr- ⁹⁵ Nb	15,500	50	1,160	4,740	10,800	55
¹⁰⁶ Ru- ¹⁰⁶ Rh	10,500	4,420	5,100	2,360	6,400	960
Influent solvent:						
⁹⁵ Zr- ⁹⁵ Nb, μCi/liter	17-1,100	0.05-1.5	16-164	12-506	120-570	3.4
¹⁰⁶ Ru- ¹⁰⁶ Rh, μCi/liter	86-340	71-223	87-320	8-166	160-380	55.
Pu Retention No.	500-3,800	1,880-11,900	2,280-59,400	6,600-85,400	6,600-23,500	93,000

^a Downflow at 40 °C and 4-5 column volumes/hr through 21.5-ml resin bed for all
^b With water-washed Hanford Purex plant G-5 solution; all others with LCW solution.
^c Breakthrough data were:

Run No.	% Breakthrough	
	⁹⁵ Zr- ⁹⁵ Nb	¹⁰⁶ Ru- ¹⁰⁶ Rh
1	5.	4.
2	<1.	1.3
3	25.	10.
4	7.	10.
5	5.	11.
6	8.	17.

TABLE IV
TYPICAL LOAD CYCLE DATA FOR A-26 RESIN TREATMENT
OF PUREX PROCESS SOLVENT

Data are for Run 1, Table III.

Column Volumes	Feed			Effluent		
	⁹⁵ Zr- ⁹⁵ Nb μCi/liter	¹⁰⁶ Ru- ¹⁰⁶ Rh μCi/liter	Pu Number	⁹⁵ Zr- ⁹⁵ Nb μCi/liter	¹⁰⁶ Ru- ¹⁰⁶ Rh μCi/liter	Pu Number
0-130	105.	248	2800	0.658	3.67	78
131-277	40.9	323	1670	0.355	4.96	29
278-424	16.6	336	1550	0.070	4.75	18
425-491	20.2	324	1210	0.094	4.75	66
492-637	55.2	322	1560	0.161	5.33	49
638-788	1050.	228	1820	3.18	4.92	25
789-939	1000.	233	1810	5.91	4.71	34
940-1085	1115.	217	1820	-	4.92	30
1086-1233	123.	206	2650	2.10	4.35	41
1234-1386	122.	212	450	3.19	5.55	76
1387-1538	425.	209	510	-	5.43	60
1539-1576	298.	241	1370	2.79	6.11	18
1477-1758	61.	86	1335	-	7.46	48
1759-1906	195.	196	1730	7.64	6.92	52
1907-2052	313.	194	1040	20.4	9.74	37
2053-2199	240.	191	2020	12.9	7.56	25

reflects preferential sorption of ⁹⁵Zr over ⁹⁵Nb for the first 700 or so column volumes; beyond this point both isotopes were sorbed with about equal efficiency. Similar behavior was observed in other capacity runs.

Some resin bed shrinkage occurred in all the capacity tests. In Run 1 (Table III), for example, the final resin bed volume was about 88% of the starting volume. [The original volume was used in all bed volume calculations.]

Cyclic Load-Elution Tests

Sequential load-elution tests were performed to study A-26 resin performance and life under such cyclic conditions and to evaluate effectiveness of various elution schemes for removing fission products. Data for the three load cycles in one such test are summarized in Table III (Runs 3,

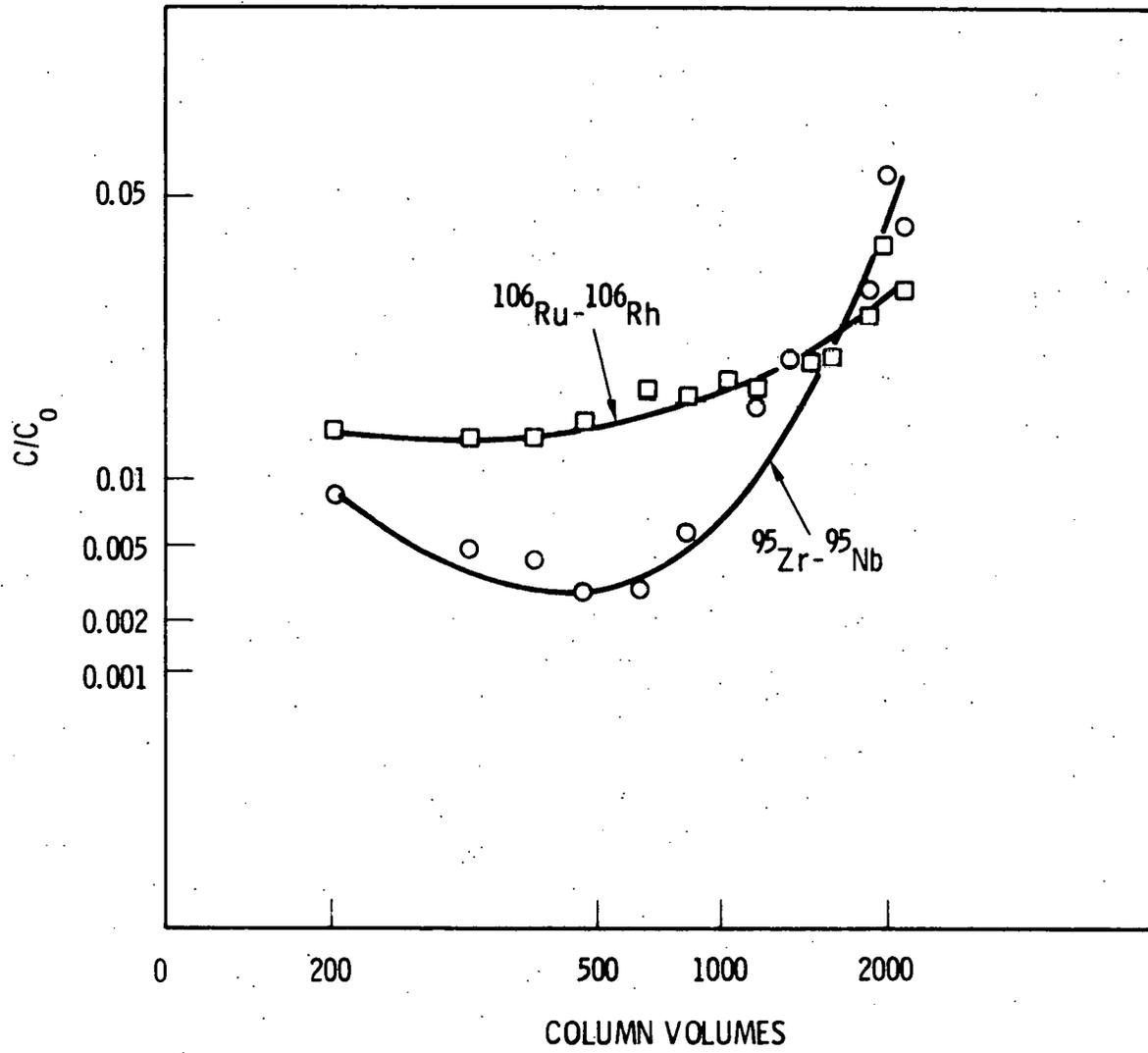


FIGURE 2

A-26 RESIN TREATMENT OF PUREX PROCESS ICW SOLVENT
Data are for Run 1, Table III

4, and 5); elution cycle data for this test are listed in Table V.

TABLE V
ELUTION OF LOADED A-26 RESIN BEDS

Conditions: Loaded A-26 resin beds (Runs 3-5, Table IV), eluted upflow at 40 °C and at about 2 column volumes/hr with indicated HNO₃-HF and NaOH solutions.

	<u>Elution Cycle No.</u>		
	<u>1^a</u>	<u>2^b</u>	<u>3^c</u>
Total bed volumes 3M HNO ₃ -0.025M HF	7.1	8.2	8.6
Total bed volumes 3M HNO ₃	14.2	0	0
Total bed volumes 1M NaOH	11.8	8.3	8.6
Percent removed:			
⁹⁵ Zr- ⁹⁵ Nb	45.	56.	59.
¹⁰⁶ Ru- ¹⁰⁶ Rh	90.	100.	77.

- a* In succession--7.1 col. vol. 3M HNO₃-0.025M HF, 6.7 col. vol. 1M NaOH, 14.2 col. vol. 3M HNO₃, and 5.1 col. vol. 1M NaOH.
- b* Two successive cycles of 4 col. vol. 3M HNO₃-0.025M HF and 4 col. vol. 1M NaOH.
- c* Four successive cycles of 2 col. vol. 3M HNO₃-0.025M HF and 2 col. vol. 1M NaOH.

No truly effective eluent for removing all the fission product activity from A-26 resin has been found. But a combination of 8 to 9 column volumes each of 3M HNO₃-0.025M HF and 1M NaOH solutions removes 55 to 60% of the ⁹⁵Zr-⁹⁵Nb and 80 to 100% of the ¹⁰⁶Ru-¹⁰⁶Rh. Removal of this much activity still permits highly satisfactory load cycle performance as shown, for example, by results of Run 5, Table III. The low Pu Retention Numbers of the effluent solvent in subsequent load cycles indicate that the

combination of HNO_3 -HF and NaOH eluents also provides satisfactory removal of HDBP.

In plant-scale operation, eluates resulting from regeneration of A-26 resin beds would become, after evaporation, part of the Purex process high-level liquid waste stream. To prevent undue increase in the volume of this stream, resin application schemes which minimize regeneration frequency and eluate volume are desirable. Calculations to establish economically permissible frequency and volume have not been made, however.

High-level waste from commercial reprocessing plants in the U.S. will be calcined or otherwise solidified. Because of its volatility and corrosivity in the solidification process, HF is an undesirable constituent of Purex process waste.^[16] Attempts to find an alternative to HNO_3 -HF solutions for removing ^{95}Zr and ^{95}Nb from A-26 resin have not been fruitful. Dilute (*e.g.*, 0.25M) oxalic acid solutions are fairly effective for this purpose, but conversion of oxalate-form A-26 resin to NO_3 - or OH-forms is difficult and apparently incomplete with dilute HNO_3 and NaOH solutions. Although not examined in detail, A-26 resin properties do not appear to deteriorate upon alternate load-elution cycles. At the end of a load cycle resin beads, particularly at the top of the bed, collect in clumps as if bound by some organic "glue." The HNO_3 and NaOH eluents remove this "glue" (see p. 19) and restore the resin to its original discrete bead form.

Mixer-Settler Tests with Resin-Treated Solvent

That decontamination and physical performance of resin-treated LCW solvent under continuous countercurrent conditions should be comparable to that of carbonate-washed

extractant was indicated in early batch tests. This expectation has now been realized utilizing both conventional and centrifugal mixer-settlers.

Centrifugal contactors were employed by G. L. Richardson of the Westinghouse Hanford Company to determine performance of a TBP extractant under conditions simulating the first cycle of a Purex-type flowsheet for processing irradiated Liquid Metal Fast Breeder Reactor fuel. The control solvent in these runs was 15 vol% TBP-n-dodecane. Solvent for one run was A-26 resin-treated virgin 15% TBP-NPH while that for another was resin-treated Hanford Purex plant LCW solution diluted with resin-treated NPH to 15% TBP. Results obtained with the resin-treated solvents were equal to or better than those with the n-dodecane diluent. Richardson concludes,^[17] "Routine use of resin treatment, together with or in place of carbonate washing, should provide n-dodecane decontamination performance with the much cheaper NPH diluent."

Countercurrent runs in standard mixer-settlers simulated flowsheet conditions of the Hanford Purex plant first cycle coextraction (HA) column. Three extractants were tested: A-26 resin-treated LCW solvent, plant carbonate-washed LCW solvent, and laboratory-prepared and -washed 30% TBP-NPH. Performance of the former extractant equalled or exceeded that of the latter two on all counts.

Miscellaneous Observations and Tests

Resin Type and Form. We have emphasized application of OH-form Amberlyst A-26 resin for cleaning up used Purex process solvent. But other macroreticular strong base anion exchange resins (*e.g.*, Amberlyst A-29, J. T. Baker Company A-641, etc.) can also be used for this purpose. Approximately 75 column volumes of typical LCW were passed downflow

(at 40 °C and 4 column volumes/hr) through a 12.5-ml bed of 16 to 50 mesh OH-form A-641 resin. The resin bed removed 98 to 99% of all the fission products in the influent solvent; all the effluent was water-white and its Plutonium Retention Number was about 50.

In the as-received Cl-form A-26 resin does not efficiently sorb fission products from Purex 1CW solvent (Table VI). Limited test data shown in Table VI suggest, however, that CO₃-form A-26 resin is as effective as OH-form resin for this purpose. Further testing is needed to establish advantages and disadvantages of CO₃-form over OH-form resin.

TABLE VI
EFFECTS OF RESIN FORM ON A-26 RESIN CLEANUP
OF PUREX PROCESS SOLVENT

Conditions: Typical 1CW solvent passed downflow (at 40 °C and 4 column volumes/hr) through 21.5-ml beds of A-26 resin in form shown.

Resin Form	Total Column Volumes	Average Effluent		Pu Retention Number
		C/C ₀		
		⁹⁵ Zr- ⁹⁵ Nb	¹⁰⁶ Ru- ¹⁰⁶ Rh	
Chloride	88	0.733	0.460	-
Carbonate	82	0.0625	0.0328	44
Hydroxide	130	0.0627	0.0147	78

Sorption of Yellow Color Bodies. In addition to sorbing HDBP and fission products from 1CW solvent both OH- and CO₃-form A-26 resin remove yellow color bodies from this TBP solution. Capacity of the OH-form A-26 resin for producing water-white effluent from typical 1CW solvent is about 550 column volumes; a yellow color band moves slowly down the resin bed during the first 500 to 600 column volumes. The

yellow compounds desorb readily when the resin bed is eluted with HNO_3 -HF solution. Additional yellow-colored material elutes when the NO_3 -form resin is converted to the OH-form.

The yellow color bodies are thought to be nitration products of the NPH diluent, but they have not been positively identified as such. Although the exact mechanism is not known, sorption of these yellow colored compounds by A-26 resin is in line with manufacturer's claims for this resin.^[10] In A-26 resin treatment of degraded Purex process solvent it is important to recognize that breakthrough of yellow color occurs long before breakthrough of either HDBP or fission products. Properties, especially Pu Retention Number, of the resin-treated solvent do not appear to be significantly affected by the presence or absence of the yellow-colored compounds.

Resin Treatment of Degraded Diluent. Straight chain paraffin mixtures (*e.g.*, NPH) suitable for use as a diluent for TBP have been commercially available only since about 1966. Before then, commonly used diluents (*e.g.*, Soltrol 170, Shell E-2342, etc.) contained various amounts of branched paraffins, olefins, and naphthenes. Abundant experimental evidence exists^[5-8] to show that nitration products (or compounds derived from them; *e.g.*, hydroxamic acids) of such diluents are responsible for increased fission product retention by washed TBP solvents. Straight chain paraffins are much more resistant to nitration, and their nitration products are not particularly troublesome.^[5-8, 18]

Still, it was of interest to determine if A-26 resin would remove deleterious diluent degradation products. For this purpose 30 column volumes of degraded Soltrol 170 were passed downflow (at 40 °C and 2 column volumes/hr) through a 21.5-ml

bed of OH-form A-26 resin. Influent and effluent Pu Retention Numbers were 1200 and 550, respectively, corresponding to removal of about half of the undesirable ligands.

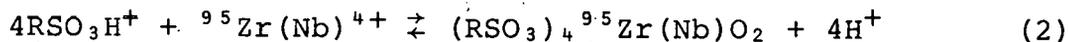
Mechanism of Fission Product Sorption. Neither the chemical form(s) of fission product zirconium, niobium, and ruthenium in Hanford Purex process TBP solutions nor the mechanism by which they are sorbed on A-26 resin has been established definitely. However, Joon, den Boef, and Neefjes^[19] suggest that TBP retention of nitrosylruthenium is due to dimeric species such as $[\text{Ru}(\text{NO})(\text{H}_2\text{O})(\text{NO}_3)_2]_2$, $[\text{Ru}(\text{NO})(\text{H}_2\text{O})(\text{NO}_2)(\text{NO}_3)_2]_2(\text{OH})_2^-$, and $[\text{Ru}(\text{NO})(\text{NO}_2)(\text{NO}_3)_2]_2(\text{OH})_2^-$. Presumably the latter two species might undergo ion exchange with the A-26 resin.

Richardson speculates^[20] that strong sorption of ^{95}Zr and ^{95}Nb from LCW solution onto A-26 resin occurs through neutralization of positively charged colloidal species. Preferential sorption of zirconium over niobium in the early phase of the loading step (see page 13) may be significant in this connection.

Previously, Ohwada^[12] observed strong sorption of zirconium and niobium from degraded 30% TBP solvent onto Amberlyst X120 cation exchange resin. He postulated reactions such as



and



to account for the removal of the zirconium and niobium. Conversely, we find in both batch and column tests that Amberlyst 15 cation exchange resin sorbs zirconium and niobium much less strongly than any of the Amberlyst anion exchange resins.

Sorption of Molecular Iodine. Hydroxide-form A-26 resin appears to have only slight affinity for I_2 in TBP solvents. Distribution ratios for sorption of I_2 from LCW and laboratory-prepared 30% TBP-NPH solvents were only 2.8 and 12.2, respectively.

None of the Hanford Purex process solvents used in this work contained radioiodine. However, TBP extractants used to reprocess high-exposure LWR and LMFBR fuels might contain substantial amounts of radioiodine. Ability of the A-26 resin to remove, even partially, molecular iodine might be an added incentive to its use in routine cleanup of these latter extractants.

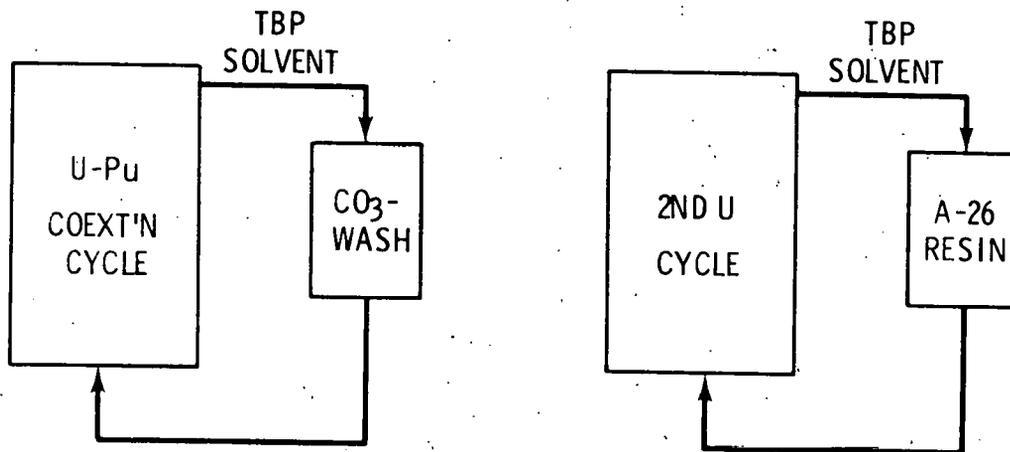
Considerably more work is obviously needed to expand our knowledge of A-26 resin sorption of I_2 . Much of the iodine which may be present in TBP extractants used with high-exposure fuels could be there as organic iodides. Sorption, if any, of these compounds by A-26 resin also needs to be determined.

Resin Application Schemes

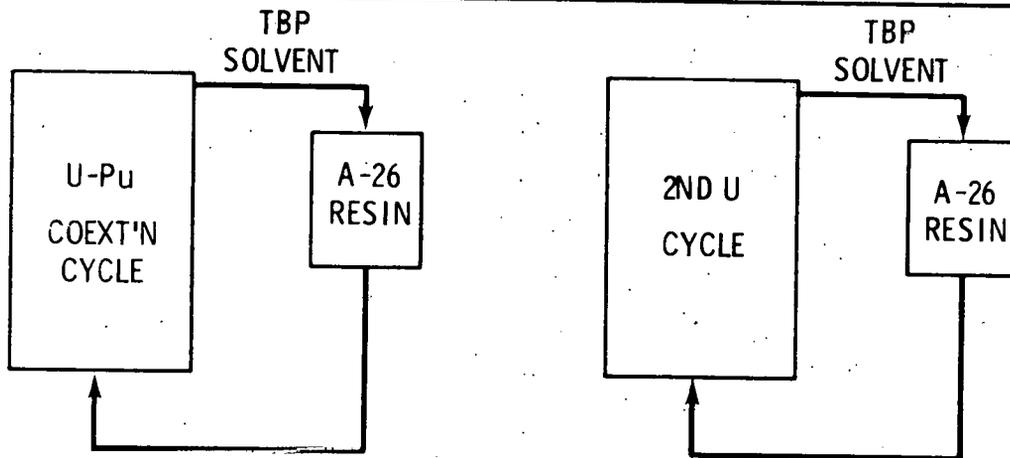
Depending on economic factors and operating philosophies, there may be as many ways to use A-26 resin in cleaning up degraded Purex process solvents as there are Purex plants. Three possible ways are indicated in Figure 3.*

The first of these (Scheme 1) is probably the most conservative way of applying A-26 resin in a plant which uses separate solvent inventories for the coextraction and second

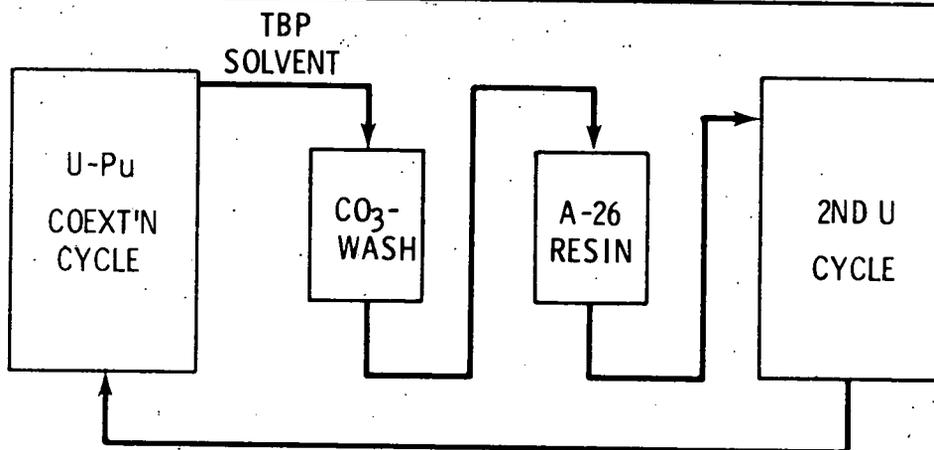
* In all these schemes it is assumed that spent solvent from the second and succeeding Pu cycles is returned to the Pu-U partition column in the coextraction cycle.



(a) TWO SOLVENT - ONE RESIN SYSTEM



(b) TWO SOLVENT - TWO RESIN SYSTEM



(c) ONE SOLVENT SYSTEM

FIGURE 3

CONCEPTUAL PUREX PROCESS A-26 RESIN TREATMENT SCHEMES

uranium cycle. In this procedure the A-26 resin is used only to treat solvent from the latter cycle while conventional carbonate washing techniques are used to clean up first cycle solvent. One solvent wash step and its attendant high-level aqueous waste are thus eliminated. Because of its typically low fission product and HDBP content, used second uranium cycle solvent is ideally suited for resin treatment. The A-26 resin bed in this scheme would be expected to have a very long useful life before resin replacement became necessary.

Scheme 2 features resin treatment of both first and second cycle solvents. Elimination of all solvent washing equipment and of the need for disposing of spent wash liquors is certainly desirable. Counterbalancing this advantage, however, is the likely need for frequent resin regeneration and/or replacement of the resin used to treat first cycle solvent. Rapid exhaustion of this resin can be expected from the typical high fission product and HDBP content of Purex process first cycle solvent. Entrained HNO_3 in this solvent could also rapidly use up resin exchange sites. Costs incurred in resin regeneration or replacement could overshadow savings realized by eliminating the solvent wash step. Detailed economic calculations (which have not been made) are required to decide the merit, if any, of Scheme 2.

Application of macroreticular resins in tailend cleanup of carbonate-washed first cycle solvent is, potentially, the most efficient way to take advantage of their favorable properties. In this scheme, as illustrated in Figure 3, resin-treated solvent would be used as the extractant in the second uranium cycle while spent solvent from this cycle would constitute extractant for the coextraction cycle. Such "one solvent" plant operation would eliminate one wash cycle and also would likely provide cleaner solvent to the coextraction

cycle. Carbonate washing prior to resin treatment is an attractive feature of this solvent treatment procedure. Such washing will remove the bulk of the fission product activity, essentially all the HDBP and any entrained HNO_3 , and provide an effective buffer zone to negate effects of periodic coextraction cycle upsets. The overall effect should be to ensure a very long useful life for the A-26 resin bed before its replacement becomes necessary.

Operability of the "one solvent" system, particularly the use of resin-treated first cycle solvent in the second uranium cycle, has not been demonstrated. Still, it is of interest to speculate on the performance of A-26 resin in this system, and this is done in Table VII for a commercial Purex plant processing 5 tonnes of power reactor fuel per day. For the conditions listed a 4-foot diameter by 15-foot high bed of A-26 resin is estimated to have a useful life of almost two years! Resin for this size bed would cost only about \$12,300.

With reference to Table VII, the solvent flow shown is thought typical for a 5 tonne/day plant. Unfortunately, the fission product content of carbonate-washed first cycle solvent from such a plant is not known. Concentrations of ^{95}Zr - ^{95}Nb and ^{106}Ru - ^{106}Rh listed are extrapolated from values for Hanford Purex plant washed solvent. Breakthrough (5 to 10%) capacity of the A-26 resin for sorbing fission products is estimated from Run I, Table III, at about 1.8 Ci of ^{95}Zr - ^{95}Nb and ^{106}Ru - ^{106}Rh each per gallon of resin. The resin-treated solvent would be expected to contain 10 to 20 $\mu\text{Ci/gallon}$ each of ^{95}Zr - ^{95}Nb and ^{106}Ru - ^{106}Rh .

Although they might actually be used, bed dimensions listed in Table VII are primarily for illustrative purposes. Operation of smaller beds at higher flow rates and with more

TABLE VIIRESIN BED PARAMETERS FOR PUREX PROCESS
SOLVENT STREAM

For Scheme C, Figure 3.

SOLVENT^aComposition:

⁹⁵ Zr- ⁹⁵ Nb	190 μCi/gal
¹⁰⁶ Ru- ¹⁰⁶ Rh	190 μCi/gal
Pu Retention No:	100

Flow: 800 gal/hr

RESIN BEDDimensions:

Height	15 feet
Diameter	4 feet
Volume	1,410 gal

Resin:

Weight	7,900 lb
Cost	\$12,300

Capacity:^b

Column vol.	9,300 ^c
Days	680

- a* Carbonate-washed first cycle solvent from 5 tonne/day plant.
b At 1.76 Ci/gallon ⁹⁵Zr-⁹⁵Nb and ¹⁰⁶Ru-¹⁰⁶Rh each.
c At 13.6 column volumes/day.

frequent resin replacement may be advantageous.

Resin replacement rather than regeneration is advocated for Schemes 1 and 3 to avoid the need for disposal of HNO₃-HF and NaOH regenerants. Loaded resin can be incinerated (see p. 33) or destroyed by reaction with HNO₃-H₂SO₄ solutions according to the process being developed by Westinghouse Hanford Company workers.^[21]

PLUTONIUM RECLAMATION FACILITY SOLVENT

Conceptual Resin Solvent-Treatment Schemes

A solvent extraction process involving extensive product reflux is used in Hanford's PRF to recover and purify plutonium from various types of metallurgical scrap. The extractant is 20% TBP-CCl₄.

Figure 4 shows principal features of the chemical flow-sheet currently used with U-Pu feeds.^[3] Uranium and plutonium are coextracted in the CA Column. An HNO₃-HN (HN = hydroxylamine nitrate) solution is used in the CC Column to reduce plutonium to Pu⁺³ and partition it from uranium; about 90% of the plutonium is returned to the CA Column. Subsequently, residual plutonium (held tightly in the solvent as a Pu-DBP complex) is removed in the CO Column with an HNO₃-HF solution. Water is used to strip uranium (and also HNO₃) in the CU Column. The acid-free organic stream (CUW) from the CU Column is washed in the CX Column with an Na₂CO₃-K₂CO₃ solution to remove HDBP and then acidified in the OA Column. Periodic removal of HDBP is essential to prevent buildup of Pu in the organic phase to the point where it precipitates as PuF₄ in the CO Column. Such precipitation tremendously complicates PRF operation.

Two conceptual schemes for routine A-26 resin treatment of PRF solvent are depicted in Figure 5. In the more ambitious one (Scheme 1) the CX and OA Columns would not be operated. Instead, the CUW stream would be passed continuously (at 25 °C) through two 0.5-foot diameter by 5- to 6-foot long A-26 resin beds before recycle to the CA Column. In the other scheme resin solvent treatment is envisioned simply as a tailend step to supplement the relatively inefficient carbonate washing operation. Sufficient resin capacity would be provided in both cases to treat used

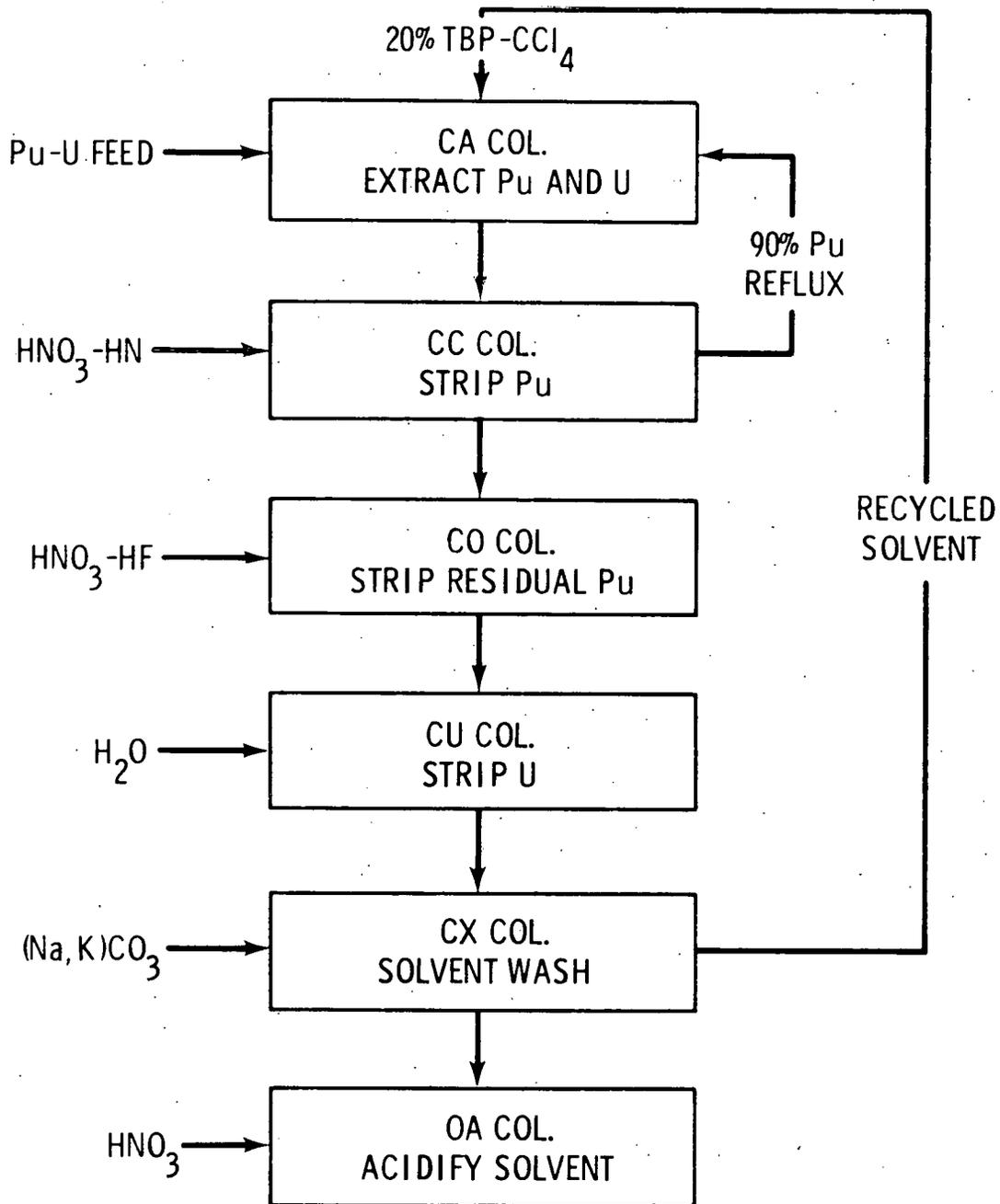


FIGURE 4
CURRENT PRF REFLUX FLOWSHEET

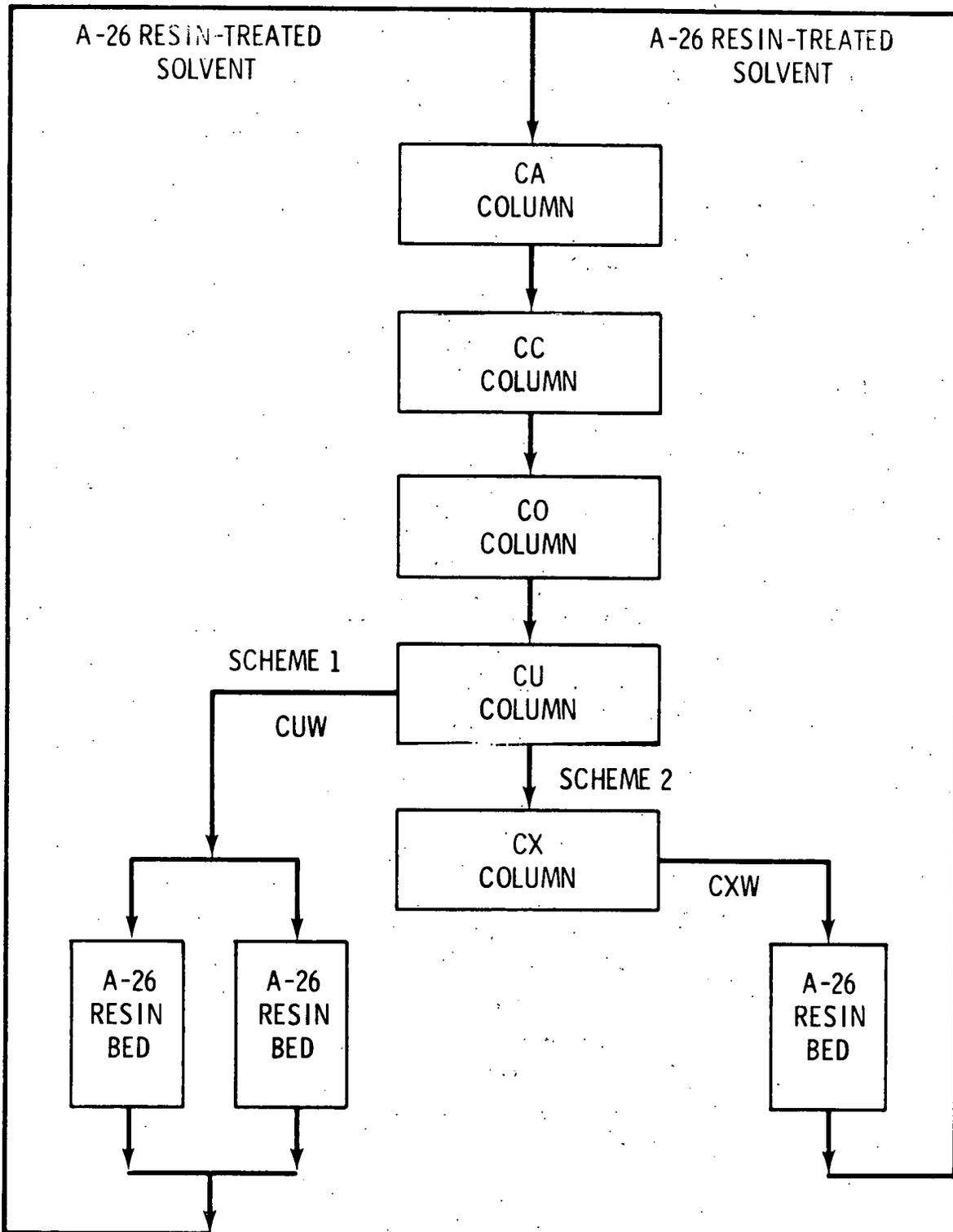


FIGURE 5

CONCEPTUAL PRF RESIN SOLVENT-TREATMENT SCHEMES

solvent for one week before resin replacement. Spent resin would be incinerated at about 760 °C in the present PRF incinerator, [22] and plutonium would be recovered from the ash by standard HNO₃-HF dissolution techniques.

Values of some of the parameters associated with the two resin solvent treatment modes are listed in Table VIII. [Resin capacities are estimated from experimental data presented later.]

TABLE VIII
PARAMETERS FOR CONCEPTUAL A-26 RESIN TREATMENT
OF PRF SOLVENT

Parameter	<u>For Treatment of</u>	
	<u>CUW</u> <u>Stream</u>	<u>CWX</u> <u>Stream</u>
Solvent flow, liters/hour	100	100
Total solvent flow, liters/week ^a	12,000	12,000
Liters A-26 resin required per week ^b	60 ^c	28 ^d
Number A-26 resin beds needed ^e	2	1
Kilogram A-26 resin used per week	40.2	18.8
Cost A-26 resin per week ^f , \$	138.	65.
Cost A-26 resin per year, \$	7,180	2,280

a PRF operates 120 hours per 7-day week.

b Water-wet resin.

c For breakthrough capacity of 200 bed volumes.

d For breakthrough capacity of 500 bed volumes.

e Each bed 0.5-foot diameter by 5.5-feet long.

f At \$1.56 per pound.

Considerably less resin capacity and replacement is required for operation with carbonate-washed feed than with the CUW solvent. Also, carbonate washing provides a buffer zone to ensure removal of HNO₃ and UO₂(NO₃)₂, both of which

rapidly use up resin capacity. For these reasons Scheme 2 (Figure 5) is currently favored for initial application of resin solvent cleanup in the PRF. After sufficient operating experience has been accumulated with this mode resin treatment of the CUW stream may be warranted.

Typical Experimental Data

Capacity Runs. Results of A-26 resin treatment of typical PRF CUW and CXW solvents are shown in Tables IX and X. Both Pu Retention Numbers and HDBP analyses show breakthrough of HDBP occurred after passage of about 200 bed volumes of the CUW solution. Not unexpectedly, however, no indication whatsoever of HDBP breakthrough was apparent after passage of about 200 bed volumes of CXW solvent.

TABLE IX

A-26 RESIN TREATMENT OF PRF CUW SOLVENT

Conditions: Typical PRF CUW solvent passed upflow at 25 °C and 4 bed volumes/hr) through a 15.5-ml (1.5-cm diam x 8.8-cm high) bed of 14-50 mesh, OH-form A-26 resin.

<u>Cumulative Bed Volumes</u>	<u>Effluent^a</u>		
	<u>Pu mg/liter</u>	<u>Pu Retention Number</u>	<u>HDBP M</u>
4.2	0.080	1,240	
89.8	0.060	940	<5 x 10 ⁻⁵
138.	0.038	1,100	
154.	0.038	2,280	<5 x 10 ⁻⁵
169.	0.036	2,190	
185.	0.036	10,600	0.00015
201.	0.032	23,700	0.00015
233.	0.030	75,800	

^a Influent solvent contained 0.11 mg/liter Pu and 0.00056M HDBP; its Pu Retention Number was 93,000.

TABLE X

A-26 RESIN TREATMENT OF PRF CXW SOLVENT

Conditions: Typical PRF CXW solvent passed upflow (at 40 °C and 1.1 bed volumes/hr) through a 15.5-ml bed of 14-50 mesh, OH-form A-26 resin.

Cumulative Bed Volumes	Effluent ^a		
	Pu mg/liter	Pu Retention Number	HDBP.
27.2	0.30		5 x 10 ⁻⁵
36.7	0.30	3,160	
46.2	0.30	2,970	
55.5	0.30	2,530	5 x 10 ⁻⁵
73.4	0.30	2,680	
89.3	-	2,960	5 x 10 ⁻⁵
102.	0.29	2,900	
121.	0.30	2,370	5 x 10 ⁻⁵
142.	0.28	2,350	
162.	0.30	2,030	5 x 10 ⁻⁵
196.	-	2,930	

^a Influent solvent contained 0.50 mg/liter Pu and 0.00031M HDBP; its Pu Retention Number was 13,000.

Over 200 column volumes the A-26 resin bed removed about 60 and 40%, respectively, of the plutonium from the CUW and CXW solvents. The mechanism of plutonium sorption is obscure. It apparently does not involve HDBP, however, since in a 40 column volume run about 80% of the plutonium was sorbed from a laboratory-prepared 20% TBP-CCl₄ solvent containing 5 mg/liter Pu and no HDBP. Reminiscent of the behavior of niobium in Purex process solvent (see p. 13), efficiency of plutonium sorption increases with passage of feed through the A-26 resin bed.

The Pu Retention Numbers of composites of the first 200 column volumes of resin-treated CUW and CXW solvents were each about 2000; HDBP concentration of each composite was

less than $5 \times 10^{-5}M$. No change in Pu Retention Number occurred when the resin-treated CUW composite was passed through a second bed of A-26 resin. Also, the Pu Retention Number of the CUW solvent after washing with successive equal volume portions of 5 wt% Na_2CO_3 , 1M HNO_3 , and water was also about 2000. All these results attest to the efficiency of the A-26 resin for removing HDBP from used PRF solvent.

A-26 resin also sorbs considerable yellow color from both CUW and CXW streams. Still, sorption of yellow color bodies from these TBP- CCl_4 solutions is considerably less than what it is from Purex process TBP-NPH solvent. Even the first portions of resin-treated CUW and CXW were yellow compared with the water-white color of resin-treated LCW solvent.

Flow Rate Effects. Performance of A-26 resin in cleaning up PRF solvent is excellent over a wide range of flow rates and residence times (Table XI). Flow rates in the range 4.5 to 9.0 ml/min/cm² at residence times of 15 to 30 minutes are envisioned in plant applications.

TABLE XI
EFFECTS OF FLOW RATE AND RESIDENCE TIME ON A-26
RESIN TREATMENT OF SYNTHETIC PRF SOLVENT

Data are for downflow of 25 to 50 column volumes of synthetic PRF solvent (containing 0.002 HDBP and 5-6 mg/liter Pu) through indicated beds of OH-form resin.

Bed Ht. ^a cm	Flow Rate ml min cm ²	Residence Time min	Temperature °C	Average Effluent		
				Pu mg/liter	Pu Retention Number ^b	HDBP M
64.8	1.58	40	25	0.86	320	$<5 \times 10^{-5}$
23.0	0.81	28	25	0.92	1,300	$<5 \times 10^{-5}$
56.5	3.6	16	25	1.3	650	$<5 \times 10^{-5}$
58.4	2.0	20	40	0.43	350	$<5 \times 10^{-5}$

^a All beds were 1.1-cm diameter.

^b Pu Retention Number of feed was ca. 150,000.

Resin Incineration. Exotherms occur at about 325 and 500 °C in the differential thermal analysis curve for OH-form A-26 resin (Figure 6); at about 550 °C the resin burns completely to leave a small amount of white ash.

The PRF incinerator operates at 700 to 800 °C with an air inflow of about 0.7 ft³/min; residence time is about 8 minutes.^[22] Combustion behavior of Pu-loaded A-26 resin under these exact conditions has not yet been determined. In scouting tests, however, 1- to 5-gram portions of air-dry OH-form A-26 resin were burned at 760 °C for 0.5 to 2 hours; the white ash in all cases amounted to less than 10 wt% of the original resin.

In one other test, 8 grams of Pu-loaded (~5 mg Pu) A-26 resin resulting from a column test with PRF solvent was burned 30 minutes at 900 °C. Treatment of the resulting black carbonaceous residue with 50 ml of boiling 15M HNO₃-0.6M HF solution for 3.25 hours recovered 98% of the plutonium on the resin.

ACKNOWLEDGMENTS

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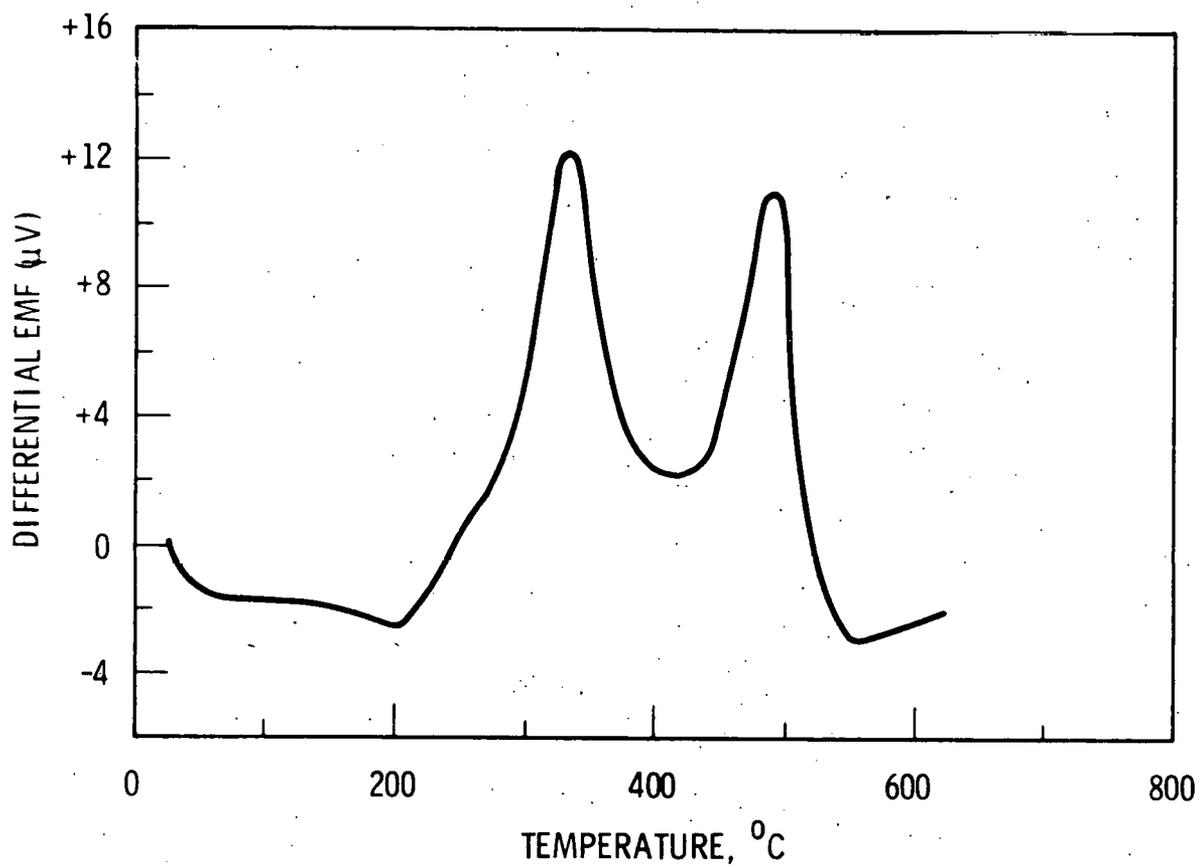


FIGURE 6
DIFFERENTIAL THERMAL ANALYSIS CURVE
FOR OH-FORM A-26 RESIN

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