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RECOVERY AND PURIFICATION OF TECHNETIUM-99 * FROM NEUTRALIZED PUREX WASTES

by

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I. INTRODUCTION

Technetium-99 has until recently been neglected by researchers because of its limited availability and high cost. It is known that pertechnetate ion is a superior corrosion inhibitor for steel(1) and may have application as such in closed systems such as boiling water reactors. Also, technetium metal is a superconductor(2) at low temperatures. Undoubtedly more uses for this unusual element will come to light as the supply and cost become more favorable.

The major source at present for technetium is the fluorination ash from the uranium reprocessing plant at Paducah. The technetium is recovered there along with neptunium(3). Siddall(4) has shown by laboratory studies that as much as 40 percent of the technetium may follow the uranium in a Purex plant. Most of the remaining technetium is found in the high-level wastes. Thus the waste represents a much higher source for technetium than the uranium product.

The Purex wastes are neutralized with sodium hydroxide prior to storing. The ferric hydroxide precipitate formed carries most of the radioactivity with the exception of that due to cesium-137. Technetium is present as pertechnate and remains in the supernate. Table I shows the composition of a typical Purex neutralized waste supernate.

TABLE I

COMPOSITION OF PUREX NEUTRALIZED WASTE SUPERNATE

Constituent	Concentration
$NaNO_2$	4.2 M
$NaNO_3$	2.6 M
Na_2CO_3	1.0 M
Na_3PO_4	0.02 M
Na_2SO_4	0.07 M

The purpose of the work described in this report was to study the behavior of technetium in purex neutralized wastes with anion exchange resins and to develop and demonstrate an economical ion-exchange process to recover the technetium.

II. SUMMARY

Technetium recovery from neutralized Purex waste supernate by ion exchange was studied on laboratory and pilot plant scales. The pertechnetate ion was shown to be absorbed from slightly acid, neutral, or basic solutions at concentrations as high as 7.5 M in nitrate by a variety of strong-base anion exchange resins.

Several grams of technetium were recovered from plant waste supernate in three runs using a single five liter anion exchange bed. The recovered technetium was further purified by oxidation of ruthenium to RuO_4 and precipitation of the ruthenium on a cation exchange bed to give a technetium product of high

purity. The technetium was subsequently precipitated as technetium sulfide. The results obtained show that technetium can be economically recovered from neutralized purex wastes by a single stage ion-exchange process with over-all yields greater than 80 percent. The technetium can be obtained with a chemical and radiochemical purity greater than 99 percent.

III. DISCUSSION

The absorbtion of the pertechnetate ion (TcO_4^-) on strong base anion exchangers is a well known phenomenon and has been used in the separation of trace amounts of technetium from molybdenum, rhenium, and fission products(5). It was observed in this laboratory in 1960 that pertechnetate is strongly absorbed on Dowex 1 from neutral or basic solutions containing high concentrations of nitrate and nitrite salts.(6) Laboratory experiments showed that fifty column volumes of the neutralized Purex waste supernate could be passed through Dowex 1 without significant technetium breakthrough. The technetium could be completely removed from the resin with strong nitric acid. Substantial decontamination from fission products was obtained and the technetium was concentrated by a factor of 30. As a result of these observations it was concluded that a very simple and economical ion-exchange process to recover and purify technetium from these wastes was available.

In the following discussion, some batch distribution measurements are presented which are intended to show the behavior of technetium under various conditions. Three pilot-scale recovery runs made in our shielded ion exchange facility and a final purification run are described. Also the removal of nitric acid from the product and the precipitation of technetium heptasulfide (Tc_2S_7) are discussed.

A. Batch Distribution Measurements

Batch distribution measurement were made under conditions of varying NO_3^-, NO_2^-, $CO_3^=$, OH^-, and H^+ concentrations. Also several anion exchange resins were evaluated. All batch measurements were made by equilibrating 10 ml of an aqueous phase containing known amounts of technetium with 0.5 g of vacuum dried resin in the nitrate form. The aqueous phase was then analyzed for technetium by extracting into hexone, mounting, and counting on a beta proportional counter. The distribution coefficient was defined as:

$$K_d = \frac{\text{Amount of Tc in Resin}}{\text{Amount of Tc in Solution}} \times \frac{\text{Ml solution}}{\text{Grams Resin}}$$

Since the neutralized Purex waste supernate is composed chiefly of sodium nitrate, sodium nitrite, and sodium carbonate (see Table I), distribution measurements were made to find the effect of each of these or combinations of these salts on the distribution. Concentrations were chosen to approximate those found in the waste. The pH was adjusted to 10 by addition of sodium hydroxide or nitric acid prior to equilibration. Table 2 shows the results found with Dowex 1 X-8 resin.

TABLE II

DISTRIBUTION OF TECHNETIUM ON DOWEX 1 FROM SOLUTIONS OF VARYING COMPOSITION

Concentration of Anions, Moles/Liter			K_d
NO_3^-	NO_2^-	$CO_3^=$	
0	0	1	1026
0	3	1	410
0	3	0	240
3	3	1	220
3	0	1	165
3	3	0	144
3	0	0	96

These data show that the presence of carbonate enhances the absorbtion of technetium and that nitrate reduces the absorbtion.

The effect of hydrogen ion concentration on absorbtion of technetium was also determined. Again batch distribution techniques were employed. In this case no measurements on solutions containing the weak acids, carbonate and nitrite, were made so that meaningful data across a wide range of hydrogen ion concentration could be obtained. Instead solutions containing sodium nitrate, nitric acid, or sodium hydroxide were used.

In the first experiment solutions containing a constant 7.5 M nitrate concentration but with the hydrogen ion varying from 0 to 7.5 M were equilibrated with IRA 401 resin. The data obtained (Fig. 1) show that the distribution for technetium increases sharply as the hydrogen ion concentration falls below 0.5 M. The distribution of technetium is effected much less by changes in the hydrogen ion concentration in the range of pH 1 to pH 11 as is shown in the next experiment. In this case solutions were made up to known sodium nitrate concentrations and pH. The pH values shifted in the unbuffered aqueous phase after equilibrations so the pH was measured before and after contact with the resin. The data obtained (Table III) show the distribution coefficient to be nearly independent of the pH.

TABLE III

TECHNETIUM DISTRIBUTION WITH IRA 401 RESIN IN $NaNO_3$ SOLUTIONS OF VARYING pH

Solns. made up to nominal pH of	~7.5 M $NaNO_3$		4 M $NaNO_3$		1 M $NaNO_3$	
	Obs. pH	K_d	Obs. pH	K_d	Obs. pH	K_d
1	1.71	124	1.2	136	1.0	319
2	5.45	145	2.95	149	2.0	482
3	6.73	126	6.10	135	4.65	319
4	7.0	131	6.50	142	6.25	358
5	7.0	130	6.60	149	6.20	358
6	6.9	131	6.10	135	6.25	261
7	6.7	131	6.0	135	6.40	274
8	6.65	138	6.3	142	6.50	287
9	6.5	137	6.55	126	6.30	284
10	8.75	139	7.0	136	6.65	287
11	10.7	131	10.65	135	9.88	307

The distribution of technetium from solutions of nitric acid was measured to find optimum concentrations for washing the resin and for elution of the technetium. Solutions of known nitric acid concentrations were contacted with Dowex 1 x-8 resin, and the distribution coefficients were measured as before. The data (Fig. 2) indicate the resin can be washed with nitric acid concentrations as high as 1.0 M without loss of technetium, and elution will be rapid at concentrations above 4 M.

A number of commercially available anion exchange resins were tentatively evaluated for their applicability for the proposed process of technetium recovery by measuring technetium distribution from simulated neutralized Purex waste supernate. The simulated supernate was made up to correspond to that shown in Table I. This was diluted to varying degrees with water and contacted with the resins. The distribution coefficients were obtained as before and are shown in Table IV.

TABLE IV

TECHNETIUM DISTRIBUTION ON COMMERCIAL RESINS FROM SIMULATED PUREX WASTE SUPERNATE AT VARIOUS DILUTIONS

	TECHNETIUM K_d IN SUPERNATE OF STRENGTH:				
	100%	75%	67%	50%	25%
Duolite A 101	373	335		389	529
Duolite A 102	194	213		209	294
Duolite A 30B	23	25		22	27
Dowex 1 x 7.5, 20-50 mesh	340	299	290	271	448
Dowex 2 x 7.5, 20-50 mesh	220	226		218	320
Dowex 21K, 20-50 mesh	186	202		156	202
Dowex 3 20-50 mesh	50	61		78	112
IRA 400	414	318		271	440
IRA 401			325		
IRA 45	139	138		147	178
Permutit S-2	226	193		201	297
Permutit SK 20-50 mesh	118	92	88	85	116

All of the resins tested showed high distribution coefficients except the weak base resins, Dowex 3 and Duolite 30B. Some other experiments showed that IRA 401 resin had a slightly more favorable rate of absorbtion of technetium than other resins. For this reason it was selected for use in the subsequent pilot-scale recovery runs.

B. Pilot-Scale Technetium Recovery Runs

Three technetium recovery runs were made using actual neutralized Purex waste supernate as feed to demonstrate the process on a pilot-plant scale. The ion-exchange equipment in the High Level Radiochemical Facility was used. This equipment, originally designed for the recovery of promethium-147 and used for the isolation of 75,000 curies of purified strontium-90, has been described in detail(7). At the time of the technetium runs several leaks in the valving and lines of the equipment were known to exist. Also, no attempt was made to thoroughly decontaminate the facility prior to the technetium runs. As a result indeterminate liquid losses and contamination during the technetium runs gave lower technetium recovery and radiochemical purity than might be expected under more favorable conditions.

The three runs were made by passing the feed through a glass column two inches in diameter filled to a depth of eight feet with IRA 401 anion exchange resin until the effluent technetium concentration reached about 50 percent of the feed concentration. The column was then washed with an appropriate solution and the technetium eluted with 8.0 M nitric acid.

The feed for all runs was Purex 103A tank supernate. It was centrifuged at the Purex plant to remove the solids and transferred to the 325A facility in a shielded cask. During the course of the various transfers the feed underwent jet dilutions. The as-received feed was therefore somewhat less than half as concentrated as the original waste supernate.

The absorbtion cycle for Run 1 was conducted at a flow rate of 6.1 ml/min. cm^2 and at ambient cell temperature (30-35° C). The as-received feed was not altered in any way prior to being pumped through the resin. After 448 liters of feed effluent had been collected the column was washed with 30 liters of water. The technetium was then eluted with 8.0 M nitric acid and collected in four-liter fractions.

Run 2 was similar to Run 1. The absorbtion-cycle flow rate was reduced to 3.1 ml/min. cm^2 in an attempt to sharpen the breakthrough. Dilute nitric acid was substituted for water in the wash cycle to improve decontamination from other fission products. The elution was again with 8.0 M nitric acid.

The feed for Run 3 was adjusted by adding 10 percent sodium hydroxide to the as-received feed to give an excess of two moles of sodium hydroxide per liter. Preliminary laboratory data had shown that somewhat higher distribution coefficients were obtainable with excess caustic. The loading, wash, and elution cycles were identical to Run 2. Table V summarizes the data obtained from Runs 1, 2, and 3.

TABLE V

SUMMARY OF TECHNETIUM RECOVERY RUNS 1, 2, and 3

LOADING CYCLE	Run 1	Run 2	Run 3
Feed Composition			
pH	9.9	9.9	~ 12
$NaNO_3$	1.34 M	1.34 M	1.12 M
$NaNO_2$	2.13 M	2.13 M	1.77 M
Na_2CO_3	0.5 M	0.5 M	0.4 M
NaOH	~ 1.0 M	~ 1.0 M	3.0 M
Feed Volume	448 liters	553 liters	498 liters
Feed Adjustment	None	None	Add 2 moles NaOH/liter
Flow Rate	6.1 ml/min. cm^2	3.2 ml/min. cm^2	3.1 ml/min. cm^2
Effluent Volume at 50% breakthrough	425 liters	450 liters	450 liters
WASH CYCLE			
Wash solution	H_2O	0.25 M HNO_3	0.25 M HNO_3
Volume	30 liters	31 liters	41 liters
ELUTION CYCLE			
Eluting solution	8 M HNO_3	8 M HNO_3	8 M HNO_3
Flow rate	1.4 ml/min. cm^2	1.1 ml/min. cm^2	1.1 ml/min. cm^2
PRODUCT			
Volume	12 liters	12 liters	12 liters
% Tc recovered	80%	80%	75%
DECONTAMINATION FACTORS			
Cs-Ba-137	67	21000	15200
Ru-Rh-106	57	190	187
Ce-Pr-144	(Not detectable)	(Not detectable)	218
Zr-Nb-95	67	280	500

The breakthrough data on Runs 1, 2, and 3 are plotted in Figure 3. This data shows that the slower flow rate used in Runs 2 and 3 does sharpen the breakthrough, but the addition of caustic in Run 3 resulted in lower capacity because of the dilution. Actually, these loading capacities (about 80 column volumes of feed to 50 percent breakthrough) are very adequate. Coupled with the excellent elution behavior (Figure 4), a considerable degree of concentration is achieved. However, further decontamination is necessary (and further concentration is desirable) before the product can be handled in unshielded laboratory facilities.

C. SECOND CYCLE PURIFICATION OF TECHNETIUM

The product of Runs 1, 2, and 3 consisted of several grams of technetium in 37 liters of 8.0 molar nitric acid. The major contaminants were Ru-Rh-106, Ce-Pr-144 and Zr-Nb-95. Experiments showed that the Ce-Pr-144 and the Zr-Nb-95 activity could be removed by a single ferric hydroxide scavenge but that the Ru-Rh-106 remained in the supernate with the technetium. A second cycle ion exchange step was devised and aimed primarily at removing the Ru-Rh-106.

Laboratory experiments indicated that the ruthenium species present could be converted to ruthenium tetroxide by contacting with solid argentic oxide in a neutral or basic solution. The ruthenium tetroxide could then be absorbed on a bed of organic cation exchange resin, presumably by reduction to an insoluble ruthenium oxide. Since technetium is not absorbed by cation exchangers, this technique could be used to remove the ruthenium. The technetium could again be absorbed on an anion exchanger and eluted with a small volume of nitric acid. Essentially all of the remaining zirconium-niobium and cerium would also be removed in this cycle, part absorbing on the cation column and the remainder passing through the anion column.

A second-cycle purification run was made utilizing this ruthenium oxidation-cation exchange-anion exchange process (Figure 5). Two of the 2-inch glass columns connected in series were used. The first column contained 4.5 liters of Dowex 50 X-8 resin in the sodium form. The second contained 1.5 liters of IRA 401 resin in the nitrate form. The feed was prepared by neutralizing most of the combined product from Runs 1, 2, and 3 with 10 M sodium hydroxide. Carrier ruthenium was added to give a concentration of 0.1 g ruthenium per liter. About two grams per liter of solid argentic oxide were added, and the mixture was air sparged for thirty minutes. The feed was prepared in several batches of 15 to 20 liters and fed to the ion-exchange column system. A total of 65 liters of effluent from the loading cycle were collected. Ten liters of water were then passed through the system. The anion exchange column was washed with 15 liters of 0.5 M nitric acid. Finally, the technetium was eluted with 8.0 M nitric acid and removed from the cell. Table VI shows the results obtained from the run. The technetium product had a radiochemical purity greater than 98 percent. Spectrographic analysis showed it to contain only trace amounts of metallic impurities ($< 0.5\%$).

TABLE VI

TECHNETIUM RECOVERY - SECOND CYCLE RESULTS

FEED CYCLE

Volume of Adjusted Feed	65 liters
Composition of Adjusted Feed	
$NaNO_3$	4.0 M
NaOH	0.5 - 1.0 M
pH	11.3 - 11.6
Resin Bed Volumes	
Cation exchanger	4.5 liters
Anion exchanger	1.5 liters
Flow rate	1.5 ml/min. cm^2

WASH CYCLE

1. 10 liters distilled water through cation and anion exchangers
2. 15 liters 0.5 M HNO_3 through anion exchanger

DESORBTION CYCLE

Desorbing solution	8.0 M HNO_3
Volume	8 liters
Flow rate	1.0 ml/min. cm^2

PRODUCT

Volume	8 liters
Tc recovered	98%
Decontamination factors	
Cs-Ba-137	Greater than 5000
Ru-Rh-106	1200
Ce-Pr-144	800
Zr-Nb-95	Greater than 5000

D. Preparation of Technetium Sulfide

The precipitation of technetium sulfide, which is insoluble in acids, is a useful method for final isolation of technetium and is a good starting point for the preparation of the metal and other technetium compounds. The product from the runs described above consisted of the technetium in eight liters of 8.0 molar nitric acid. The nitric acid had to be removed prior to precipitation of the sulfide to prevent troublesome formation of free sulfur. The following procedure was used to prepare technetium sulfide.

The product solution was concentrated by distillation until technetium was detected in the distillate. At this point the volume was less than one liter, and the nitric acid concentration was 14.4 molar. Hydrochloric acid was added to the solution to give a concentration of three molar, and a volume of 1500 ml. The solution was heated to boiling under reflux, and formaldehyde was slowly added until evolution of nitrogen oxides stopped. The solution was then concentrated by distillation to a volume of one liter to remove volatile organic material. Initial attempts to precipitate technetium sulfide from the solution gave only a small amount of precipitate. This was probably because of reduction of pertechnetate to some lower valence state by traces of organic material present.

The technetium was reoxidized to pertechnetate by adding 5.0 g/l ammonium persulfate and heating to boiling. Technetium sulfide was then precipitated by passing hydrogen sulfide gas into the solution for 90 minutes. The precipitate formed was finely divided and could not be filtered, but on heating to 80°C for 30 minutes a coarse precipitate was formed which was easily filtered on a coarse glass filter. Ninety-five percent of the technetium was recovered as a highly purified sulfide. Gamma energy analysis and beta absorbtion measurements showed the technetium to be 99.9% radiochemically pure. This is of substantially higher purity than technetium obtained from Oak Ridge National Laboratory.

CONCLUSIONS

A simple and efficient ion-exchange process has been developed and demonstrated which can be used for the recovery of multi-kilogram amounts of technetium from readily available Purex wastes. The technetium can be obtained as a crude product by simply passing the untreated alkaline waste supernate through a bed of strong base anion exchanger and elution with nitric acid. This crude, which would contain the techneium concentrated by a factor of 35 and less than 10^{-5} of the other fission products initially in the waste, could either be concentrated further by evaporation or could be further purified and concentrated by the second-cycle ion-exchange process described here. In either case the nitric acid in the product can be destroyed by formaldehyde treatment without significant loss of technetium.

This process is favorable from the standpoint of waste management because the alkaline wastes can be returned to storage unchanged in any way after removal of the technetium. Also, this process can be integrated with the present cesium recovery operation with little additional operating cost.

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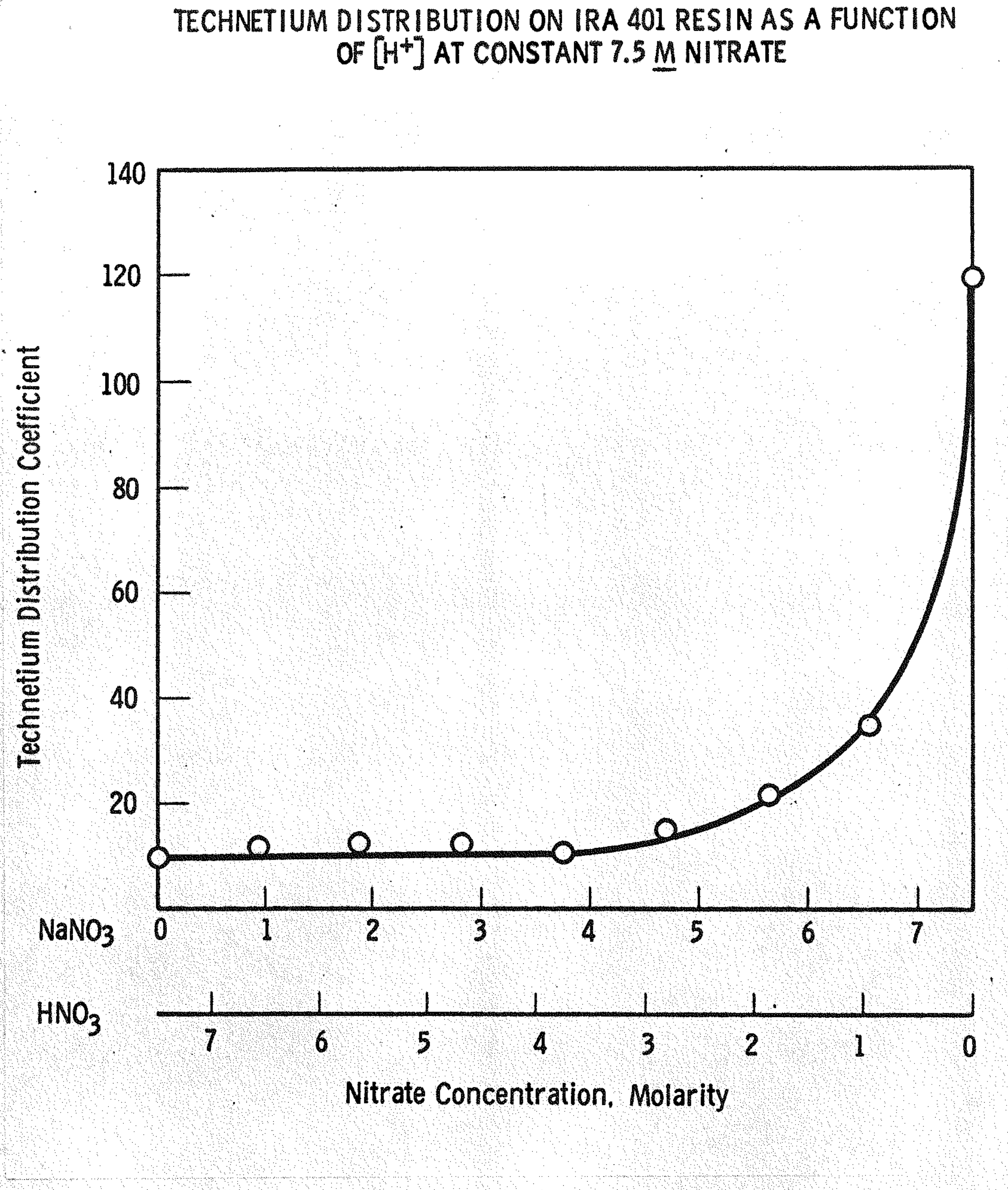

FIGURE 1

Technetium Distribution on IRA 401 Resin as a Function of $[H^+]$ at Constant 7.5 M Nitrate

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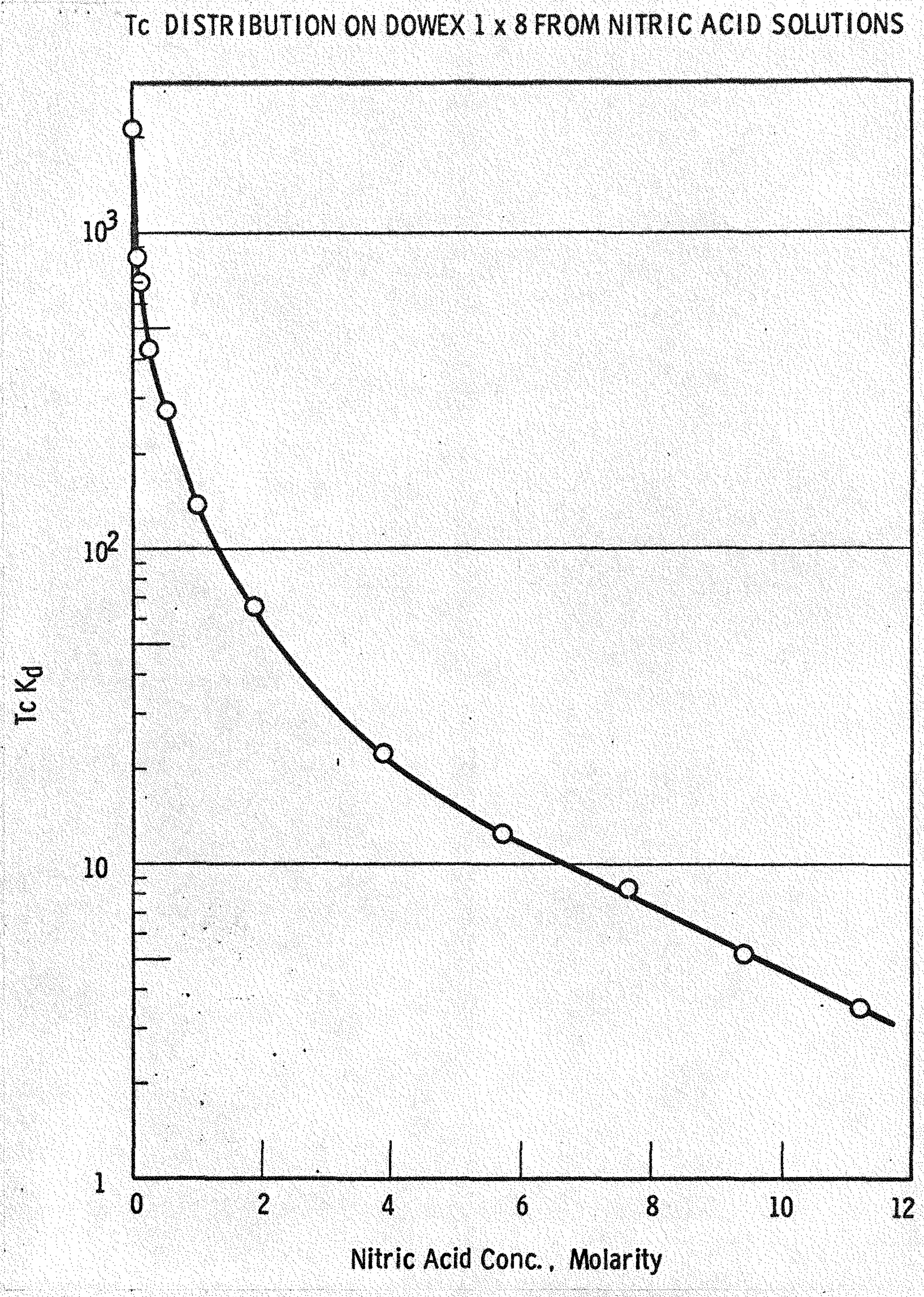

FIGURE 2

Tc Distribution on Dowex 1 x 8 from Nitric Acid Solutions

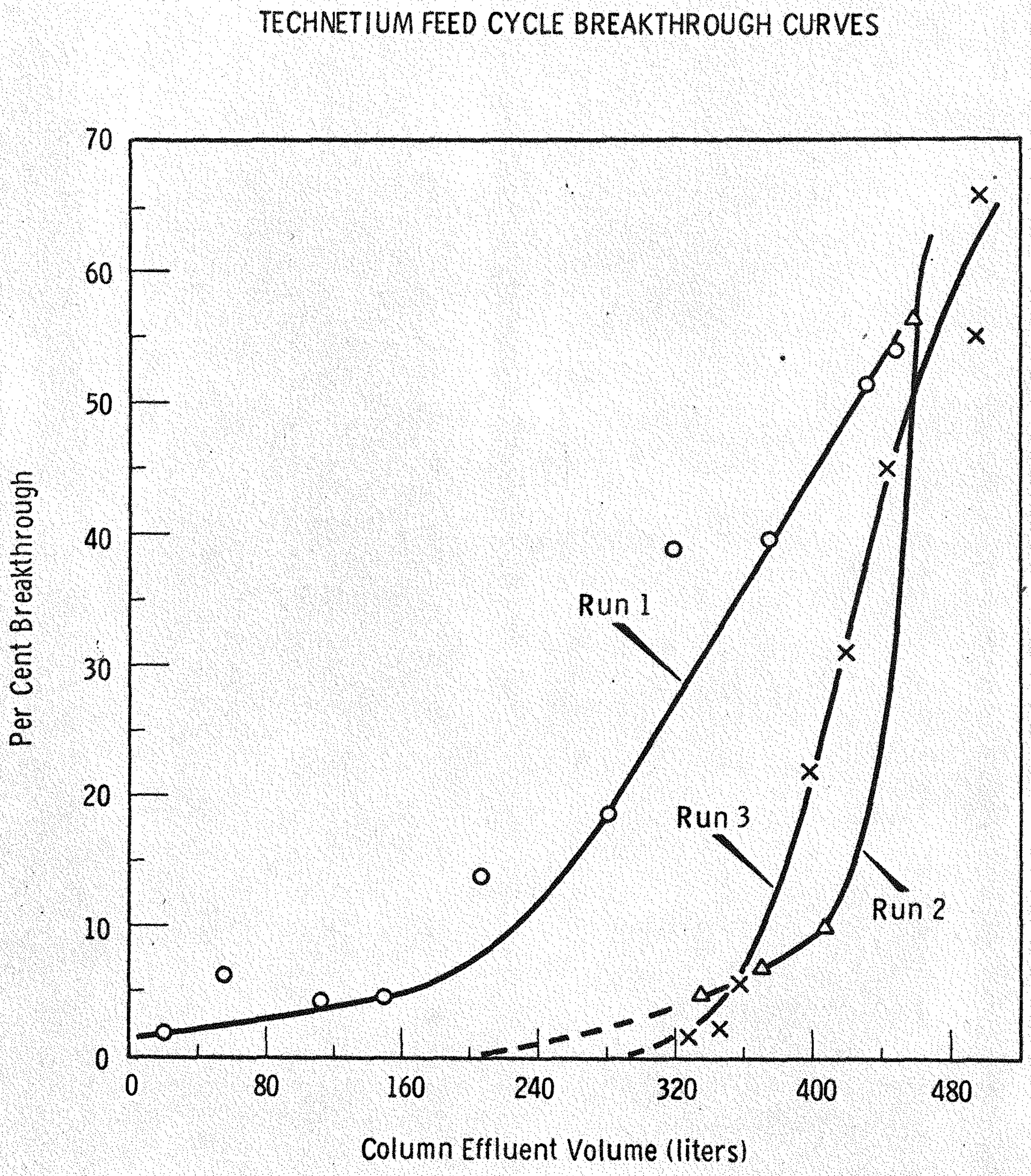

FIGURE 3

Technetium Feed Cycle Breakthrough Curves

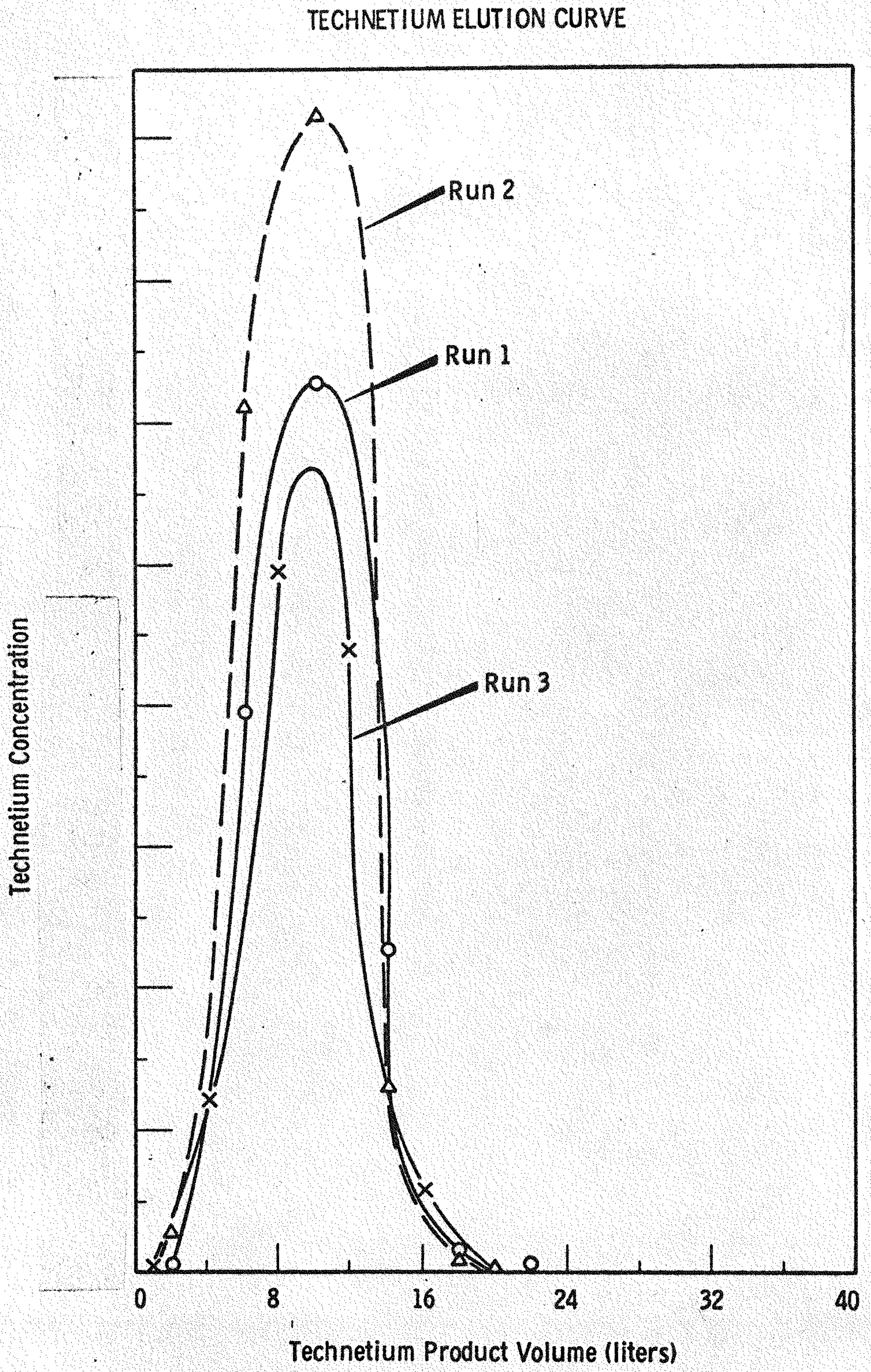

FIGURE 4

Technetium Elution Curve

AEC-GE RICHLAND, WASH.

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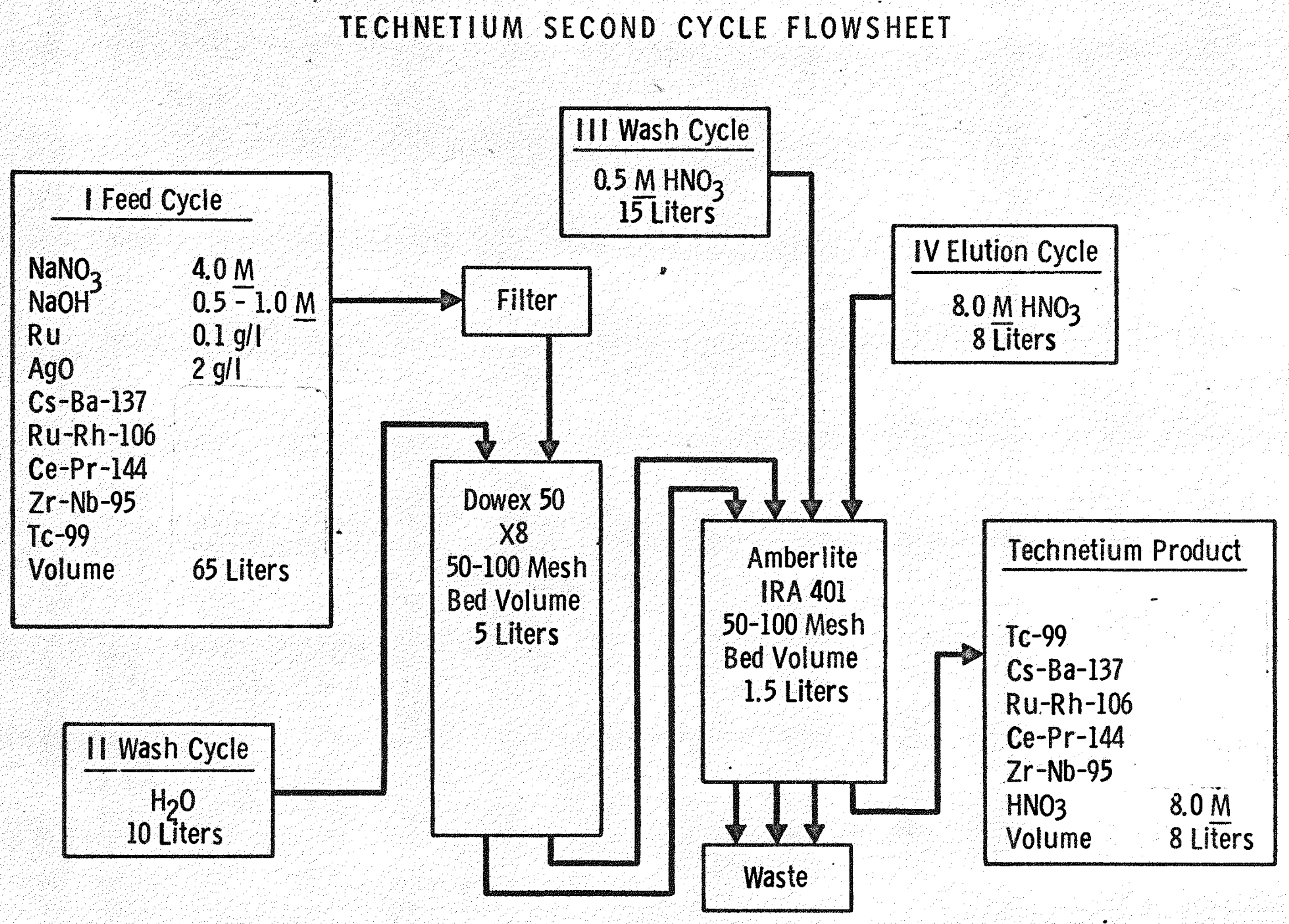

FIGURE 5

Technetium Second Cycle Flowsheet

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