

FEB 16 1962

HW-SA-2396

MASTER

UNCLASSIFIED

SOLVENT EXTRACTION RECOVERY AND PURIFICATION OF STRONTIUM-90*

by

Wallace W. Schulz, John E. Mendel, and Gerald L. Richardson

HANFORD LABORATORIES OPERATION
GENERAL ELECTRIC COMPANY
RICHLAND, WASHINGTON

December 13, 1961

Facsimile Price \$	3.60
Microfilm Price \$	1.19
Available from the Office of Technical Services Department of Commerce Washington 25, D. C.	

* For presentation at ACS National Meeting, Washington, D.C.,
March, 1962

This paper was submitted for publication in the open literature at least 6 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

UNCLASSIFIED

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:
A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or
B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.
As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

000 001

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TITLE SOLVENT EXTRACTION RECOVERY AND PURIFICATION OF STRONTIUM-90
AUTHORS Wallace W. Schulz, John E. Mendel, and Gerald L. Richardson
PLACE WORK
WAS DONE Hanford Atomic Products Operation
General Electric Company
Richland, Washington

A solvent extraction process was developed to produce high purity Sr^{90} from an irradiated uranium reprocessing waste solution. The extractant is D2EHPA diluted with TBP and Shell Spray Base.

The process uses an acetic acid-acetate buffered aqueous phase which is countercurrently contacted with the D2EHPA organic phase. Calcium and some Ce^{144} extract with the Sr^{90} ; extraction of other contaminants (Zr^{95} , Nb^{95} , Ru^{106} , and inert lead and iron) is prevented by adding either DTPA or EDTA to the feed solution. Decontamination from calcium and Ce^{144} is provided by back extraction of the Sr^{90} into an aqueous 1M citric acid solution.

The process was used to isolate and purify about one megacurie of Sr^{90} for subsequent use in the fabrication of thermoelectric power generators as part of the Systems for Nuclear Auxiliary Power (SNAP) program.

WALLACE W. SCHULZ, JOHN E. MENDEL, and GERALD L. RICHARDSON

Hanford Atomic Products Operation, General Electric Co., Richland, Wash.

SOLVENT EXTRACTION RECOVERY AND PURIFICATION OF STRONTIUM-90

This liquid-liquid extraction process uses:

- ▶ An acetate buffered aqueous phase containing DTPA or EDTA to suppress extraction of contaminants.
- ▶ A citrate buffered strip solution to partition Sr⁹⁰ from co-extracted inert calcium and fission product rare earths.

A solvent extraction process has been developed for the recovery of Sr⁹⁰ from Hanford Purex plant crude Sr⁹⁰ concentrate solution (Table I). It involves extraction of Sr⁹⁰ into di(2-ethylhexyl) orthophosphoric acid (D2EHPA) diluted with tri-n-butylphosphate (TBP) and Shell Spray Base. The process was used in the Hanford Hot Semiworks (HSW) plant to produce approximately one megacurie of highly purified Sr⁹⁰ for use by the Martin Company in fabrication of thermoelectric power generators as part of the Systems for Nuclear Auxiliary Power (SNAP) program.

This article describes the laboratory experiments which formed a basis for the chemical flowsheets used in the HSW. The production runs made in the HSW and the chemical flowsheet modifications that were necessary because of equipment limitations in the HSW have been summarized by Burns and others (1).

Process Description

The solvent extraction process described in this article was designed to produce a Sr⁹⁰ product meeting certain purity specifications. These specifications evolved through discussions with the Martin Company and were established specifically to permit the use of Hanford Sr⁹⁰ product in SNAP-7 (2) generators. Specifications for radiochemical purity imposed by shielding

requirements called for a product containing less than 0.0045 curie of hard gamma (>2 MEV.), less than 0.015 curie of intermediate gamma (1-2 MEV.), and less than 0.15 curie of soft gamma (0.2-1 MEV.) per gram of Sr^{90} , respectively. For the composition of plant crude Sr^{90} concentrate listed in Table I, these specifications correspond to required decontamination factors of about 500 to 5000 for Ce^{144} , about 80 to 3000 for $\text{Zr}^{95}\text{-Nb}^{95}$, and 10 to 200 for $\text{Ru}^{106}\text{-Rh}^{106}$. It was further specified that of the cations (excluding sodium ion) present in the product, not more than 25 wt. % should be stable isotopes other than stable strontium isotopes.

The chemical flowsheet developed to isolate Sr^{90} meeting these requirements is shown in Figure 1. Principal features of the flowsheet are:

- Strontium and inert calcium are extracted with D2EHPA from an aqueous feed solution buffered at pH 4.7.
- Addition of either tetrasodium ethylenediaminetetraacetate (Na_4EDTA) or pentasodium diethylenetriaminepentaacetate (Na_5DTPA) to the feed solution serves to suppress almost completely the extraction of iron, lead, and fission product $\text{Zr}^{95}\text{-Nb}^{95}$ and $\text{Ru}^{106}\text{-Rh}^{106}$. Some decontamination from fission product rare earths is also achieved by the use of these complexing agents.
- An aqueous citrate solution is used in the scrub section of the extraction column to remove most of the extracted sodium ion from the organic phase and to reduce entrainment of feed solution.
- Strontium is stripped into 1M citric acid in a partition column. Decontamination from co-extracted inert calcium and fission product rare earths is obtained in this step by operating at pH 1.5 to 2.0.
- An eleven-fold increase in strontium concentration over that in the original crude concentrate is achieved by proper selection of aqueous and organic phase flow ratios.

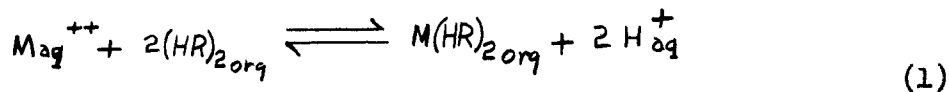
Solvent extraction feed solution is prepared from crude Sr⁹⁰ concentrate by adjustment of acidity and addition of buffering and complexing agents. The acid adjustment consists of neutralizing the crude concentrate with NaOH to a pH of 4.7. The acetic acid-sodium acetate system serves as a convenient system to supply the required buffering. Acetate concentrations of 0.4 to 0.5M are sufficient to maintain pH within the necessary limits when the flow ratios shown in Figure 1 are used.

Aqueous solutions of either Na₄EDTA or Na₅DTPA are added to provide 0.05 to 0.10 mole per liter of free complexing agent. Free complexing agent is defined as that concentration of agent present in excess of the concentration required to complex the iron and lead in the solution assuming formation of 1:1 complexes.

Theoretical

Separation of various actinides, lanthanides, and fission products by solvent extraction processes which utilize the liquid ion exchange characteristics of D2EHPA have been described (3,4,5). In general, trivalent cations are more efficiently extracted than are divalent cations, which, in turn, are more efficiently extracted than monovalent cations.

In many instances the extracting cation associates with dimers of D2EHPA. Extraction of a divalent cation, such as Sr⁺⁺, may then be represented by the following reaction:



where (HR)₂ is dimerized D2EHPA, M⁺⁺ is the extracted ion, and the subscripts refer to the aqueous and organic phases, respectively. Using concentrations rather than activities, the equation for the distribution coefficient (K_d) of the divalent ion can be derived from Equation 1:

$$K_d = \frac{[M(HR_2)_2]}{[M^{++}]} = \frac{K_{eq} [(HR)_2]^2}{[H^+]^2} \quad (2)$$

The degree of separation of cations M_a and M_b (charges not specified) which can be obtained in a solvent extraction process is a function of the ratio of their respective K_d 's. In some cases the degree of separation can be increased by addition of a complexing agent which forms more stable complexes in the aqueous phase with cation M_b than with cation M_a . If cation M_b reacts with ligand L to form a 1:1 complex of the type M_bL , then, as a first approximation, the distribution coefficient of M_b can be shown (6) to be given by the expression:

$$K_d = \frac{K_d^0}{1 + k_b [L']} \quad (3)$$

where K_d^0 is the distribution coefficient in the absence of complexing agent, k_b is the conditional stability constant (7) of the complex M_bL , and $[L']$ represents not only the concentration of the free ligand but the concentration of all species of the complexing agent not bound to the metal. A similar expression involving the conditional stability constant for the complex M_aL can be written for the distribution coefficient of cation M_a .

The distribution coefficient of a divalent cation forming a 1:1 complex with ligand L is then obtained by combining Equations 2 and 3:

$$K_d = \frac{K_{eq} [(HR)_2]^2}{[H^+]^2} \cdot \frac{1}{1 + k_b [L']} \quad (4)$$

Theoretically, it is possible to determine K_{eq} and k_b experimentally, after which K_d can be predicted for any condition of solvent loading, acidity, and complexing agent concentration. This approach to the design of chemical flowsheets for D2EHPA solvent extraction systems is now being investigated in this laboratory. A more empirical approach was followed in the work reported in this article, however, because of the need to define a satisfactory chemical flowsheet in a short time.

As is apparent from Equation 4, extraction of a divalent ion such as Sr^{++} is directly proportional to the square of the free D2EHPA concentration and inversely proportional to the square of the hydrogen ion concentration of the aqueous phase. Both of these variables are of importance in the design of a satisfactory chemical flowsheet for the extraction of Sr^{90} . The free D2EHPA concentration is determined by the extent to which the solvent is loaded with all extracting cations, including sodium. Flow ratios must thus be selected such that the K_d of the desired extracting cation is not reduced below design requirements.

In both the extraction and partition steps of the flowsheet shown in Figure 1, transfer of cations to or from the organic phase is accompanied by a corresponding transfer of hydrogen ions from or to the aqueous phase. Control of aqueous phase pH between rather narrow limits is necessary to maintain desired K_d relationships. Mixtures of organic acids and their sodium salts were used for pH control in this work.

Experimental.

Materials.

Typical plant-produced crude concentrate has the composition shown in Table I. Also shown is the composition of the laboratory-prepared concentrate used in the majority of the experimental studies. Chemical flowsheets used in preparing batches of crude Sr^{90} concentrate from Hanford Purex plant acidic waste have been described by Bray and Van Tuyl (8). Inert strontium isotopes and Sr^{89} are also present in the crude concentrate so that the total strontium concentration is about 0.0025M.

Although not indicated in Table I, plant concentrate contains, in addition to Ce^{144} , stable and radioactive isotopes of other rare earths as well as of yttrium produced in the fission of U^{235} . Most of the radioactive isotopes have half-lives shorter than that of Ce^{144} (258 days), while those with longer half-lives either emit lower energy gamma rays or are pure beta emitters. As a consequence, Ce^{144} is the only isotope of the yttrium-rare earth group of importance in the separation and decontamination of Sr^{90} from crude concentrate solution. Lanthanum nitrate was added to the laboratory-prepared concentrate to simulate the behavior of rare earths other than cerium.

The D2EHPA (Union Carbide Chemicals Co.) contained about 91.5% D2EHPA plus undetermined amounts of mono(2-ethylhexyl) phosphoric acid and pyro esters. Traces of iron were also present. A solvent composition of 0.37M D2EHPA-0.2M TBP-Shell Spray Base was used throughout. It was prepared by diluting the as purchased D2EHPA with appropriate volumes of TBP (Commercial Solvents Co.) and Shell Spray Base (Shell Chemical Co.). Dilution with an inert kerosene-type hydrocarbon such as Shell Spray Base was necessary to improve hydraulic properties of the solvent in the sieve-plate pulse columns of the HSW. TBP was added to the solvent to promote solubility of the extracted cations in the organic phase (5).

Stock solutions of 1.3M Na_4EDTA and 1.05M Na_5DTPA were obtained from the Dow Chemical Co. All other chemicals used were of reagent grade quality.

Except in those experiments with actual plant concentrate, the extraction and decontamination of strontium was followed with the aid of the radioactive isotopes Sr^{85} , Ce^{144} , Ca^{45} , Fe^{59} , Na^{22} , Zr^{95} - Nb^{95} , Ru^{106} - Rh^{106} , and $Eu^{152-154}$. Sodium-22 was obtained from Abbot Laboratories; the other isotopes were obtained from Oak Ridge National Laboratory (ORNL).

Determination of Distribution Coefficients.

A standard 10-minute contacting period (mechanical stirring) at 25-26°C. was allowed for attainment of equilibrium. Phases were separated by centrifugation. The pH of the equilibrium aqueous phase was measured. Unless otherwise noted, equal volumes of aqueous and organic phases were used.

Flowsheet Test Procedure.

Chemical flowsheets were tested with feeds prepared both from actual plant concentrate and from laboratory-prepared concentrate in 12-stage mixer-settlers. These units were Hanford-designed versions of a type developed at the Knolls Atomic Power Laboratory by Coplan and others (9).

In testing the flowsheets, mixer-settlers were operated with the particular feed, scrub, and organic solutions required until a steady state in the effluent streams was reached. Flow rates were maintained either with metering pumps or by a syringe-drive feed system. Samples of the effluent streams were taken hourly and analyzed to determine when steady state was reached. Waste losses and decontamination factors were computed from analyses of steady-state effluent streams.

Mixer-settlers were operated under extraction column conditions with seven extraction and five scrub stages. Only five of the 12 mixer-settler stages were used in partition column runs. In testing chemical flowsheets with feeds derived from laboratory-prepared concentrate, separate mixer-settler runs, each with a different radioisotope added to the feed, were made for each flowsheet tested.

Analyses.

In those solutions which contained only one radioisotope the concentration of this isotope was determined by gamma scintillation counting or, in the case

of Ca^{45} , by beta counting techniques. More involved procedures were required for analysis of solutions derived from plant concentrate. In particular, because of the bremsstrahlung radiation produced by Sr^{89} and Sr^{90} in such solutions, it was necessary to remove radioactive strontium before the concentration of other radioactive constituents could be determined. Separation of radioactive strontium was accomplished by addition of inert $\text{Sr}(\text{NO}_3)_2$ to an aliquot of solution followed by repeated precipitation of $\text{Sr}(\text{NO}_3)_2$ with fuming HNO_3 . The concentration of other radioactive constituents was then determined by analysis of a portion of the supernatant liquid with a 256-channel gamma-energy-pulse-height analyzer. A different procedure (on a separate portion of the solution) involving successive precipitation of the strontium as $\text{Sr}(\text{NO}_3)_2$ and SrCO_3 was used to determine the total concentration of radioactive strontium.

Results and Discussion.

Distribution Coefficients.

Extraction Column.

Distribution coefficients of various constituents of crude Sr^{90} concentrate from feed solutions containing either Na_4EDTA or Na_5DTPA are presented in Table II and Figure 2. To obtain these data 100 ml. portions of laboratory-prepared concentrate were diluted to 135 ml. by addition of 35 ml. of sodium acetate- Na_4EDTA (or Na_5DTPA)- NaOH solution. The composition of the additive solution was selected in each case to prepare 0.45M sodium acetate and 0.19M Na_4EDTA or 0.15M Na_5DTPA solutions at pH's in the range 3.5 to 5.5. Portions of these latter solutions were contacted with one-fifth volume portions of solvent.

Distribution coefficients for iron, ruthenium, and zirconium (Table II) with Na_4EDTA added to the feed solution were all uniformly low at all

equilibrium aqueous phase pH's in the range 2.9 to 5.4. Because no radioactive lead isotope of sufficiently long half-life was available, a systematic attempt to determine distribution coefficients for lead was not made. However, X-ray fluorescence analyses of some of the organic solutions obtained in the experiments listed in Table II indicated lead was extracted to about the same extent as iron.

With either Na_4EDTA or Na_5DTPA added to the feed, the cerium K_d decreased as pH increased. Distribution coefficients for $\text{Eu}^{152-154}$ (the radioisotope used to determine the behavior of rare earths other than Ce) from solutions containing Na_4EDTA also decreased with increased pH, and, over the pH range investigated, were less than those of cerium. Thus, the extraction behavior of Ce^{144} limits the degree of decontamination from radioactive rare earth isotopes obtainable in the extraction column.

For the conditions used (Figure 2) EDTA and DTPA have about the same effect on the strontium K_d . However, at approximately equal concentrations, DTPA complexes cerium more strongly than EDTA. This observation is in agreement with the results reported by Catsch (10). The effect of addition of Na_5DTPA on the distribution coefficients of other constituents of crude Sr^{90} concentrate was not measured. It was assumed from tabulated stability constants (7) that these would be complexed to at least the same extent as by the addition of Na_4EDTA . The validity of this assumption was substantiated in subsequent HSW runs with feeds containing DTPA.

Data in Figure 2 indicate that operation of the extraction column with high pH (pH \geq 5) feeds is desirable to minimize contamination of the Sr^{90} product with Ce^{144} . However, complexing of strontium by either EDTA or DTPA begins to occur at about pH 4 and increases at higher pH's. The choice of a

suitable feed pH must thus be a compromise between the need for satisfactory extraction of Sr^{90} and maximum decontamination from Ce^{144} . A feed pH of 4.7 is considered optimum and is so specified in the chemical flowsheet.

Calcium distribution coefficients were higher than those of strontium for all cases studied. Hence, essentially all of the inert calcium in the crude Sr^{90} concentrate is extracted with the strontium.

Distribution coefficients for sodium between solvent and aqueous solutions of the composition 0.5M sodium acetate - 0.5M NaNO_3 - 0.10M Na_4EDTA - 0.05M $\text{Sr}(\text{NO}_3)_2$, adjusted to pH's in the range 3.0 to 5.5 with HNO_3 , were measured (Figure 3).

Because of the high concentration of sodium ions in the aqueous feed solution, the organic phase at the feed point of the extraction column can be almost 50% loaded with sodium even though the sodium K_d is considerably smaller than either the strontium or calcium K_d . For example, for the flowsheet conditions shown in Figure 1, the organic phase at the feed point of the extraction column contains about 0.13 mole per liter of sodium. Unless somehow removed in the extraction column, almost all of this sodium will transfer from the organic phase to the aqueous phase at pH's below 2.5 in the partition column. Hydrogen ion, equivalent to the decrease in organic phase sodium concentration, must be supplied from the aqueous phase to preserve electroneutrality. This puts a heavy burden on the buffering capacity of the aqueous partitioning solution, particularly so if small flows of the partitioning solution are used. Partial removal of sodium from the organic phase prior to partition column operation is accomplished by using 0.6M citric acid adjusted to pH 2.6 with 19M NaOH as an extraction column scrub stream.

Partition Column

In the partition column 1M citric acid is used to separate Sr^{90} from co-extracted Ce^{144} and inert calcium (Figure 4). Solutions of the composition 1M citric acid - 0.01M $\text{Sr}(\text{NO}_3)_2$, 1M citric acid - 0.05M $\text{Ca}(\text{NO}_3)_2$, and 1M citric acid - 0.0005M $\text{Ce}(\text{NO}_3)_3$, after addition of 19M NaOH to adjust pH to the desired value, were used to obtain distribution coefficient data. In agreement with earlier ORNL results (11), partitioning is most effective in the pH range 1.5 to 2.5. Any complexing of Ce^{144} and calcium by citrate ions which occurs in this pH range is not sufficient to impair the favorable K_d relationship between these elements and Sr^{90} . Provided sodium has been adequately removed from the organic feed solution in the extraction column, 1M citric acid furnishes sufficient buffering capacity to operate the partition column in the desired pH range with an organic flow four times the aqueous flow.

Flowsheet Demonstrations

Feed solutions for extraction column mixer-settler runs (Tables III and IV) were prepared by addition of 310 ml. of 1.74M sodium acetate - 0.73M Na_4EDTA - 1.0 to 1.2M NaOH solution to a liter of concentrate. Prior to feed make-up, plant concentrate was diluted two to five times with a synthetic concentrate of the composition 1.0M HNO_3 - 0.005M $\text{Sr}(\text{NO}_3)_2$ - 0.003M $\text{Ca}(\text{NO}_3)_2$ - 0.01 to 0.02M $\text{Fe}(\text{NO}_3)_3$ - 0.01 to 0.03M $\text{Pb}(\text{NO}_3)_2$. Iron and lead concentrations of this latter solution were selected so as to be equal to those in the undiluted plant concentrate. Certain of the organic product solutions from extraction column mixer-settler runs (Flowsheet 1, Table III) were used as feed solution in mixer-settler partition column runs (Table V).

The effects of increased feed pH on Ce^{144} decontamination and of scrub composition and pH on the sodium concentration of the organic product observed

in extraction column mixer-settler runs paralleled closely those to be expected from batch distribution data. Note also that under the same flowsheet conditions similar waste losses and decontamination factors were obtained regardless of whether the feed solution was prepared from plant or laboratory concentrate. The greatest disparity was noted in the behavior of Ru^{106} - Rh^{106} and Zr^{95} - Nb^{95} . Part of this discrepancy is attributed to the difficulty of obtaining reliable analyses for small concentrations of these two constituents in the presence of high concentrations of Sr^{90} and Ce^{144} . Another reason may be that chemical species of ruthenium and zirconium in plant concentrate are different from those in the radioactive tracer solutions used with laboratory-prepared concentrate.

Flowsheet 1 conditions listed in Table III are essentially those specified in the process chemical flowsheet (Figure 1). Required decontamination from Ru^{106} - Rh^{106} and Zr^{95} - Nb^{95} was obtained in the extraction column with EDTA as the complexant under these flowsheet conditions. However, the over-all (plant concentrate to citric acid product solution) Ce^{144} decontamination factor was about 850, 3-4 times lower than required to meet, routinely, radiochemical purity specifications. HSW experience indicates the desirability of adding Na_5DTPA rather than Na_4EDTA to the extraction column when using feeds having high Ce^{144} concentration. In the only such run made in the HSW all purity specifications were met in a single extraction and partition cycle.

Additional Purification Cycles

If necessary, either an ion exchange cycle or an additional solvent extraction cycle may be used to provide additional decontamination from Ce^{144} and other contaminants (Figure 5). Both methods employ the citric acid partition column product solution as feed. Technology for the ion exchange resin

procedure has been developed by Bray (12); the flowsheet shown in Figure 5 is adapted from his work.

Distribution coefficients were determined for strontium and cerium (Figure 6) between solvent and a simulated partition column product solution of the composition $0.035M Sr(NO_3)_2 - 0.0075M Ca(NO_3)_2 - 0.0003M Ce(NO_3)_3 - 1.0M$ citric acid. Portions of this latter solution were adjusted to pH's in the range 2.0 to 5.0 by addition of $19M NaOH$. In some cases $1.3M Na_4EDTA$ was added to obtain solutions containing 0.1 mole Na_4EDTA per liter.

The pH range 3.5 to 4.5 is optimum for extraction of strontium from partition column product solution. However, even at this pH range, the strontium K_d is not much greater than one. Hence, the organic flow must be at least equal to the aqueous flow to recover strontium adequately. It is also apparent that addition of a complexing agent such as Na_4EDTA is required to obtain any appreciable decontamination from Ce^{144} in this pH range.

In the solvent extraction flowsheet shown in Figure 5, $0.2M HNO_3$ is used to strip strontium from the organic phase. Alternatively, partition column conditions (Figure 1) can be used to remove strontium from the organic phase. This latter method provides even further decontamination from Ce^{144} .

Acknowledgement

Grateful acknowledgement is made to L. C. Neil, D. G. Bouse, and M. M. Darby for their assistance in performing much of the experimental work.

Work performed under Contract No. AT(4501)-1350 between the Atomic Energy Commission and General Electric Company.

Literature Cited

1. Burns, R. E., Moore, R. L., Platt, A. M., and Swift, W. H., AIChE meeting, Los Angeles, 1962.
2. West, W. L., U. S. At. Energy Comm. Rept. MND-P-2483-1, 1961.
3. McHenry, R. E., Posey, J. C., Ind. Eng. Chem. 53, 647-650 (1961).
4. Peppard, D. F., Ferraro, F. R., Mason, G. W., J. Inorg. & Nuclear Chem. 7, 231-4 (1958).
5. Blake, C. A., Crouse, D. J., Coleman, C. F., Brown, K. B., Kelmers, A. D., U. S. At. Energy Comm. Rept. ORNL 2172, January, 1957.
6. White, J. M., Tang, P., Li, N. C., J. Inorg. & Nuclear Chem. 14, 255-61 (1960).
7. Ringbom, A., "Treatise on Analytical Chemistry." I. M. Kolthoff, P. J. Elving, eds., Part I, Vol. I, Chap. 6, Interscience Encyclopedia, Inc., New York, 1959.
8. Bray, L. A., Van Tuyl, H. H., U. S. At. Energy Comm. Rept. HW-69534, May, 1960.
9. Coplan, B. V., Davidson, J. K., Zebroski, E. L., U. S. At. Energy Comm. Rept. AECU-2639, Aug. 8, 1953.
10. Catsch, A., in "Health Physics in Nuclear Installations Symposium May, 1959," p 379, Organization for European Economic Cooperation, Risø, Denmark, 1959.
11. Brown, K. B., U. S. At. Energy Comm. Rept. ORNL-CF-60-3-136, April, 1960.
12. Bray, L. A., U. S. At. Energy Comm. Rept. HW-68786, March, 1961.

Table I. Composition of Crude Sr⁹⁰ Concentrate Solution

Solvent extraction process feeds were prepared from the crude concentrate

<u>Typical Plant Concentrate</u>		<u>Laboratory Concentrate</u>	
<u>Component</u>	<u>M curies/liter</u>	<u>Component</u>	<u>M</u>
HNO ₃	0.80	HNO ₃	1.0
Fe(NO ₃) ₃	0.025	Fe(NO ₃) ₃	0.10
Pb(NO ₃) ₂	0.020	Pb(NO ₃) ₂	0.004
Ca(NO ₃) ₂	0.005	Ca(NO ₃) ₂	0.003
Sr ⁹⁰	17-24	La(NO ₃) ₃	0.0025
Ce ¹⁴⁴	40-260	Sr(NO ₃) ₂	0.0025
Zr ⁹⁵ -Nb ⁹⁵	0.5-40	Ce(NO ₃) ₃	0.0001
Ru ¹⁰⁶ -Rh ¹⁰⁶	0.1-2.0	ZrO(NO ₃) ₂	0.001
		RuCl ₃	0.00002

Table II. Extraction Column Distribution Coefficients

Test solutions were 0.19M Na₄EDTA and 0.5M sodium acetate

<u>pH</u>	<u>Distribution Coefficient</u>				
	<u>Ca</u>	<u>Fe</u>	<u>Ru</u>	<u>Zr</u>	<u>Eu</u>
2.9	577	0.0006	0.0003		8.75
3.6	1770	0.0009	0.0012	<0.0001	
4.4	500	<0.0002	0.0024	0.0017	0.274
4.9	27.3	<0.0001	0.0010	<0.0002	0.0763
5.4	1.7	0.0014	0.0006	0.0038	0.0074

Table III. These Extraction Column Flowsheets Were Tested in Mixer-Settler Units

Flowsheet	Concentrate Source	Feed pH ^a	Scrub Composition			
			NaNO ₃ M	Na ₄ EDTA M	Citric acid M	pH
1	Lab Prepared	4.7	0.0	0.0	0.6	2.6
1	Plant	4.7	0.0	0.0	0.6	2.6
2 ^b	Lab Prepared	4.2	0.5	0.02	0.0	3.5
2 ^b	Plant	4.2	0.5	0.02	0.0	3.5
3	Lab Prepared	4.2	0.0	0.0	0.6	3.6
3 ^b	Plant	4.2	0.0	0.0	0.6	3.6

^a All feeds were 0.41M sodium acetate and 0.15 to 0.17M Na₄EDTA.

^b Relative volume flows of feed, extractant, and scrub were 1.0/0.21/0.04; in all other runs relative flows were 1.0/0.24/0.05.

Table IV. Extraction Column Flowsheet Performance

Flowsheet	Concentrate Source	Aqueous Raffinate pH	Na in Organic Product M	% Sr Loss	Decontamination Factors		
					Ce ¹⁴⁴	Ru ¹⁰⁶ -Rh ¹⁰⁶	Zr ⁹⁵ -Nb ⁹⁵
1	Lab Prepared	4.5	0.007	3.9	19	1040	600
1	Plant	4.5		0.68	19	250	1620
2 ^a	Lab Prepared	4.0	0.07	1.7	14	925	2300
2	Plant	4.2		0.74	10		920
3	Lab Prepared	3.8	0.004	0.01	4		
3	Plant	3.5		0.96	2		

^a Decontamination factors for Fe⁵⁹ and Eu¹⁵²⁻¹⁵⁴ were 20,000 and 200, respectively for these flowsheet conditions.

Table V. Partition Column Flowsheet Performance

Relative volume flows: Organic/aqueous : 1.0/0.28
Partition Solution : 1M citric acid

<u>Organic Feed Source</u>	<u>Aqueous Product pH</u>	<u>% Sr Loss</u>	<u>Decontamination Factors</u>	
			<u>Ce¹⁴⁴</u>	<u>Ca</u>
Lab Prepared	2.0	3.6	45.3	12.4
Plant	1.8	4.8	42.9	

000 021

Figure 1. This chemical flowsheet was used to recover and purify about one megacurie of Sr⁹⁰.

85, 070

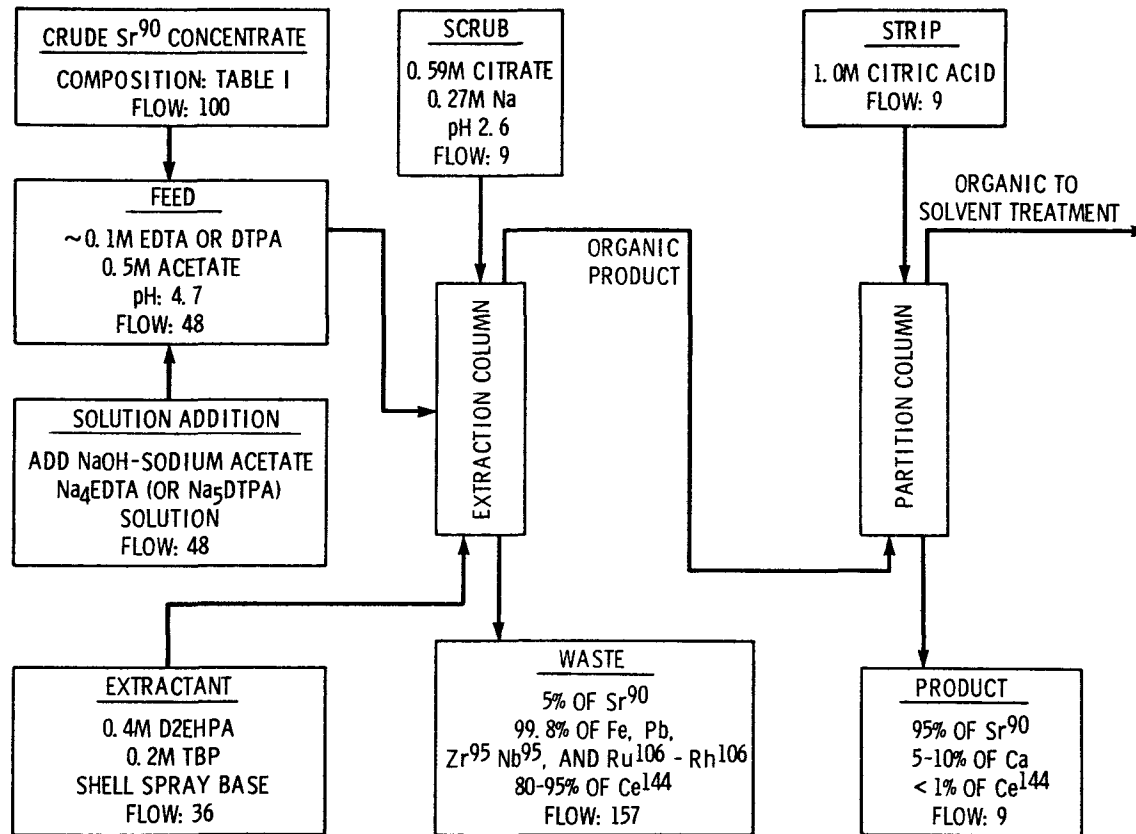
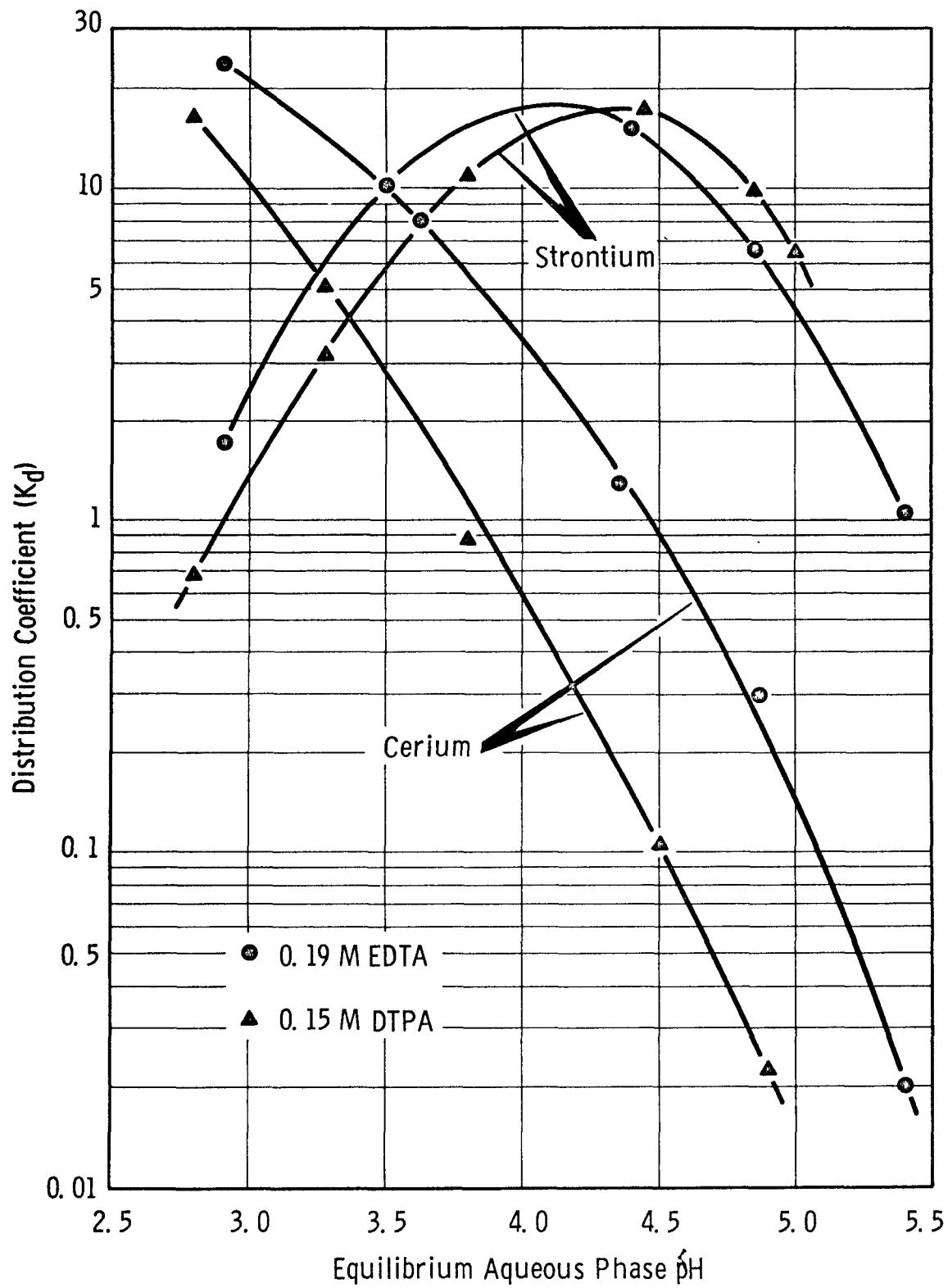


Figure 2. Distribution coefficients for Sr and Ce between 0.37M

D2EHPA and Extraction Column Feed Solutions.

DTPA is superior to EDTA in suppressing extraction of cerium.



600 025

Figure 3. Distribution of sodium between 0.37M D2EHPA and aqueous acetate solution is much lower than strontium distribution.

000 025

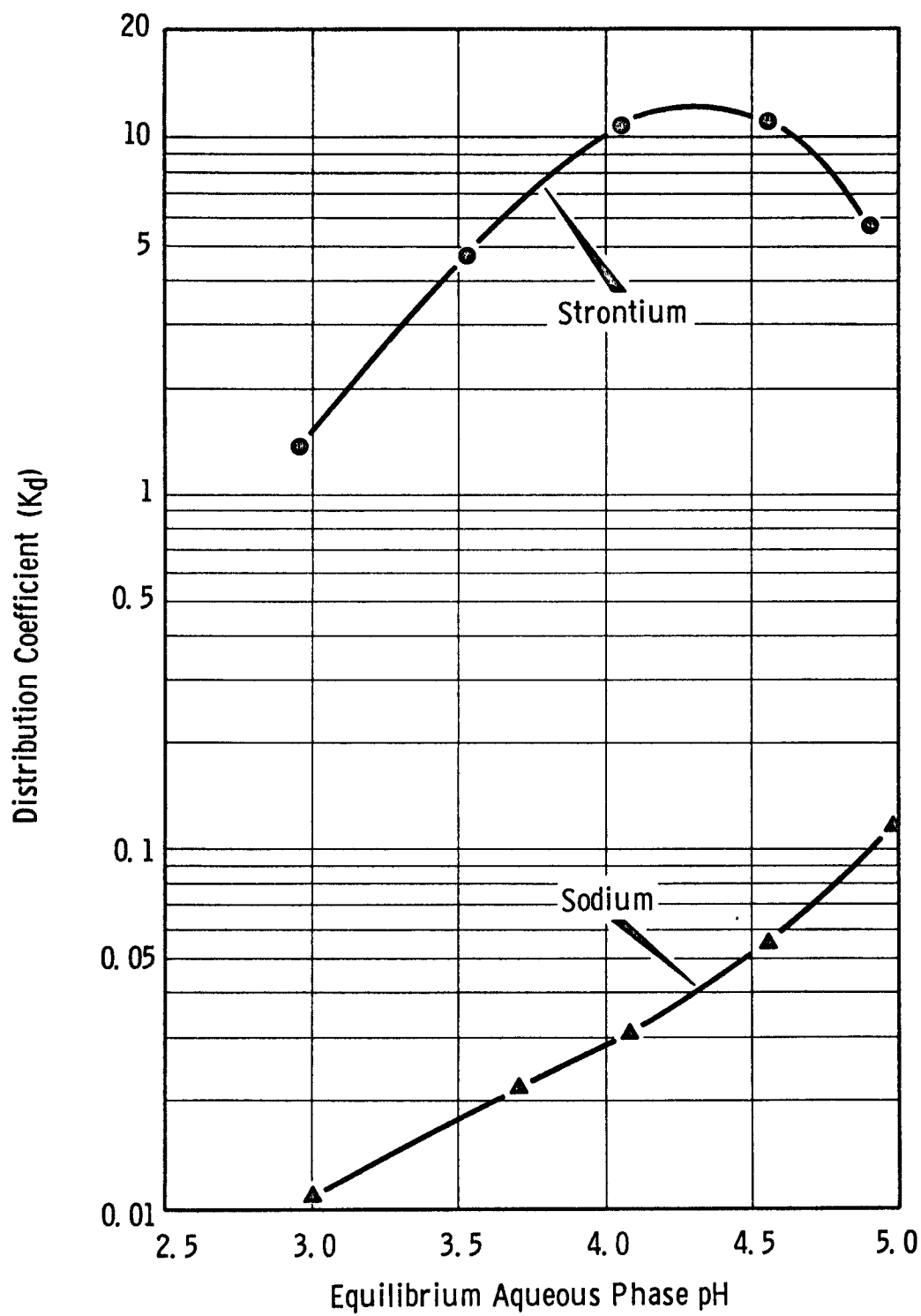


Figure 4. Distribution coefficients of Ca, Sr, and Ce between 0.37M D2EHPA and 1M citric acid. These data were used to define partition column conditions.

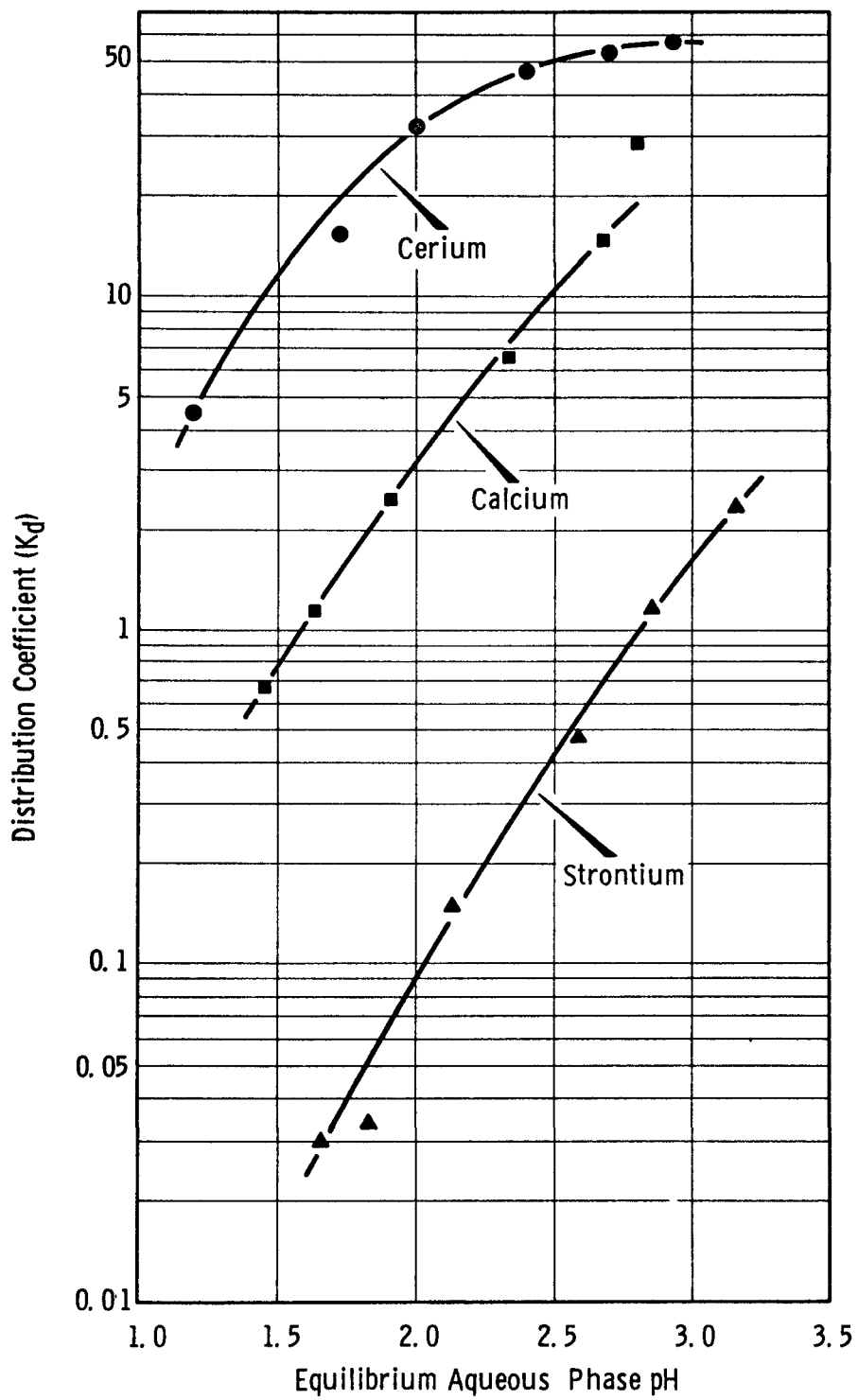
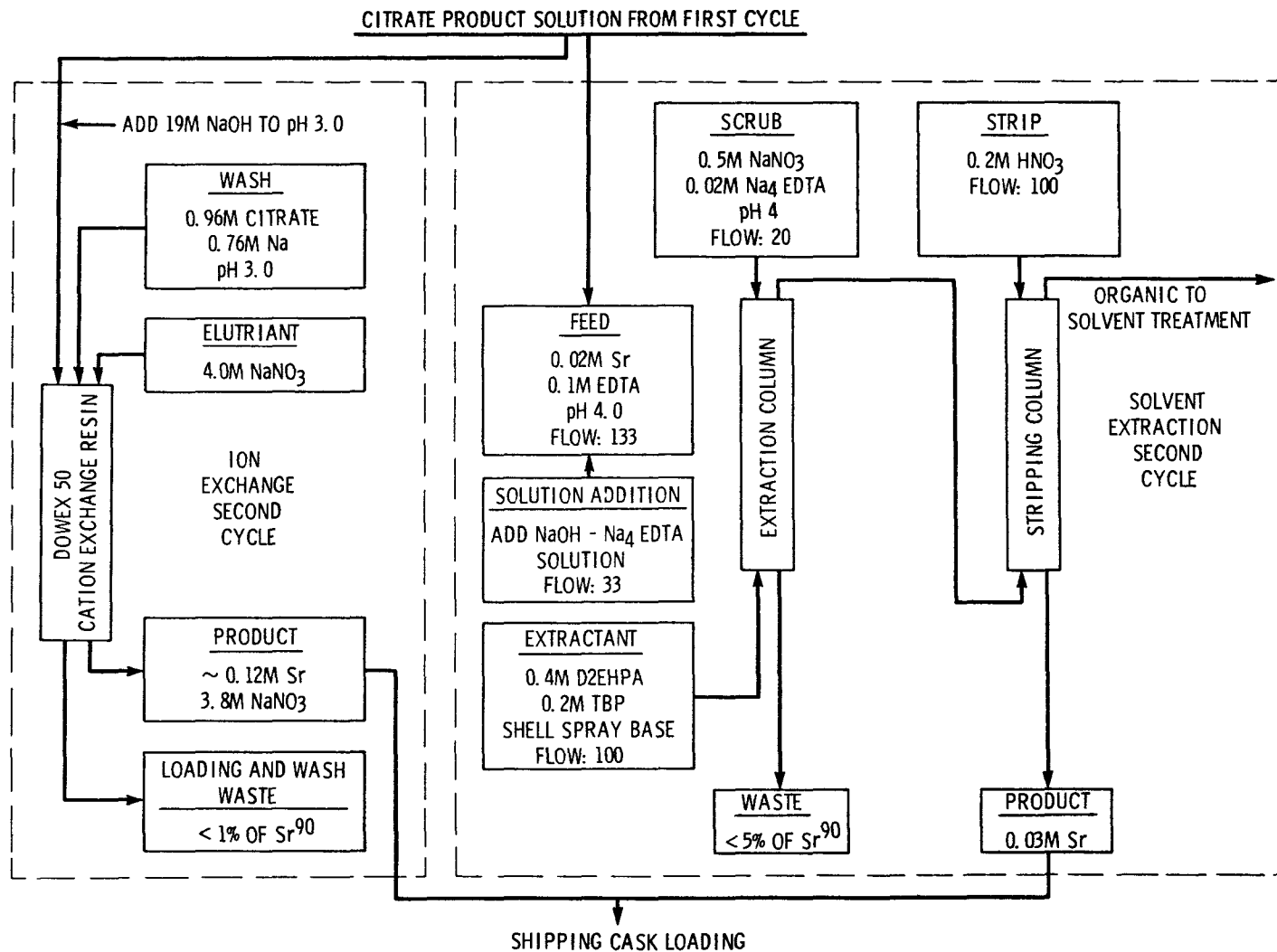


Figure 5. Either of these flowsheets can be used to obtain additional purification of Sr^{90} .



200
 100
 100

Figure 6. Partition column product solution, after pH adjustment and addition of Na_4EDTA , is a suitable feed for a second solvent extraction cycle.

Distribution coefficients were determined with 0.37M D2EHPA solution.

