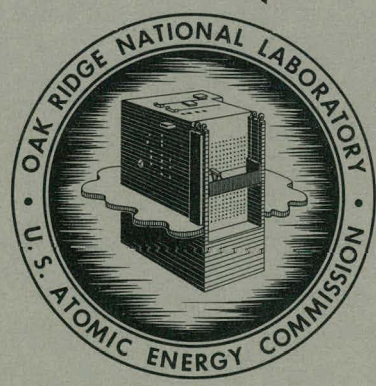ORNL-3585
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PROPOSED HEAD-END TREATMENTS OF

PUREX-1WW WASTE FOR FISSION PRODUCT

RECOVERY BY ION EXCHANGE

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operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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JUNE 1964

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W. C. Yee   and   W. Davis, Jr.

ABSTRACT

Two methods are described for preparing Purex 1WW radio-active waste for recovering strontium and/or rare earths by cation exchange. One method involves (1) complexing the major cationic impurities with citrate ion at pH 2.5, and (2) processing a twentyfold diluted and treated waste solution through a column of resin (pre-equilibrated to pH 2.5 with ammonia) where the uncomplexed alkaline earth and rare earth elements are sorbed. The other method involves (1) precipitating sulfate ion (as ferric sulfate) from Purex 1WW waste at 55 to 60% HNO_3, and (2) precipitating strontium nitrate from the resulting nearly-sulfate-free solution from 85% HNO_3. Cation exchange is used to purify this precipitate further.

Pretreatment (complexing) with citrate ion results in a fourfold and threefold improvement in resin capacity for strontium and rare earths, respectively, over that for un-treated and tenfold diluted waste. Less than 1% of the ferric ion in the waste is sorbed on the resin. Pretreatment by a double precipitation concentrates the strontium by a factor of 2.5 to 3.0 and reduces by more than 200-fold the ratio of total trivalent cationic impurities to strontium. Resin capacity for strontium is improved by a factor of 20 over that for the citrate-treated waste.

Radiation degradation of the resin in both processes is discussed in terms of expected resin life. If citrate complexing is used as the basis for separating strontium and/or rare earth elements from impurity ions, then operating time to 10% resin capacity loss would be about 2500 hr or 100 hr, depending on whether just strontium or strontium and rare earth elements were recovered. If the head-end precipitation process is used for removing impurities, then the time to 10% loss of resin capacity in the final purification would be only about 15 and 10 hr, respectively, depending on whether strontium or strontium and rare earth elements were recovered.

1. INTRODUCTION

The principle purpose of this report is to describe two preparatory procedures for separating strontium and/or rare earth elements from the major cationic impurities in Purex 1WW waste solution. One of these procedures is based on the use of citrate to complex the cationic impurities (iron, chromium, and aluminum) prior to separating them from strontium and the rare earths. The second preparatory procedure involves a double precipitation in which first sulfate is removed and then strontium nitrate is precipitated nearly free of the cationic impurities. A second purpose of this report is to indicate how these materials that are nearly free of the cationic impurities may then be further processed by ion exchange in order to obtain more or less pure fractions of strontium and rare earths.

One of the most significant wastes from nuclear fuel processing operations is a Purex 1WW waste. In this waste, concentrations of radio-isotopes are small, about 10^3 to 10^4 curies per tonne* of uranium, or 0.1 to 1.0 gram per liter of waste solution. Associated with the fission products, amongst other things, are about 30 g of trivalent cationic impurities (iron, chromium, and aluminum) that greatly interfere with the separation of strontium and rare earth elements from this solution by ion exchange. In addition, there is about one mole of sulfate ion per liter of solution that prevents the use of precipitation to separate strontium as the nitrate from these impurities. Because ion exchange offers a rather simple process to recover fission products in the absence of sulfate and the cationic impurities, some effort has been spent to eliminate them.

The scope of this report includes the description of an ion exchange process in which the cationic impurities of Purex 1WW waste are complexed with citrate and then passed through a column of Dowex 50W cation resin where the uncomplexed alkaline earth and rare earth elements are sorbed.

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* A "tonne" is a metric ton, 10^3 kg.

It also includes the description of a method for removing sulfate from the waste by a precipitation process, and a subsequent precipitation of strontium nitrate from the resulting nearly-sulfate-free solution. Also included is a discussion of how presently available ion exchange technology can be applied for further purification of strontium and rare earths after either of the preliminary purification procedures.

2. FLOWSHEETS

Two flowsheets are given as alternative methods of cleaning up Purex 1WW waste in order subsequently to process it by cation exchange for recovery of the fission products, strontium and/or rare earths. The composition of the waste solution is given in Table 1, which includes the major cationic impurity concentrations corresponding to Hanford Purex 1WW supernatant.[1,2] Fission product yields were calculated from the data of Blomeke and Todd[3] on the basis of about a tenth of Yankee Atomic Power Reactor conditions, which correspond to a burnup of about 8000 Mwd/tonne of 3.5% U^{235} and a cooling time of 100 days.[4]

2.1 Waste Treatment by Citrate Complexing

One simple and effective method of waste treatment is to complex the major trivalent cationic impurities by adding citrate ion in the ratio of 1.5 moles for each mole of ferric, chromic, and aluminum ion in the filtered waste. The pH of the solution is adjusted to 2.5 with ammonium hydroxide and heated to 90°C for 0.5 hr. Subsequent cation exchange processing is accomplished by passing a twentyfold diluted and treated waste solution through a column of Dowex 50W X-8 (100 to 200 mesh) resin which has previously been converted to the ammonium form at pH 2.5. A linear flow rate of about 1 cm/min is used. The flowsheet for this procedure is given in Fig. 1.

Laboratory tests with simulated Purex 1WW indicated that up to 3 and 5 volumes of original filtered waste (equivalent to 60 and 100 volumes of twentyfold diluted waste) can be processed for strontium and rare earths (RE's), respectively, per volume of Dowex 50W in the ammonium form.

PUREX 1WW
WASTE → FILTER →

PUREX 1WW SOLN

Sr^{2+}	0.18 mg/ml
RE (Ce^{3+})	1.61 mg/ml

CITRIC ACID

1.5 mole per mole of
$Fe^{3+} + Cr^{3+} + Al^{3+}$

SOLUTION ADJUSTMENT

Heat to 90°C-0.5 hr
Sr Recovery - 60 vol
RE Recovery - 100 vol

RESIN PRETREATMENT SOLUTION

0.5 $\underline{M}$ NH_4NO_3-0.05 $\underline{M}$ NH_4 citrate

NH_4OH

to pH 2.5

H_2O

To make 20X-diluted
PUREX 1WW

CATION EXCHANGE RESIN COLUMN

H^+ form   100-200 mesh

1 vol

WASTE

Fe	> 99%
Sr	< 5%
RE's	< 5%
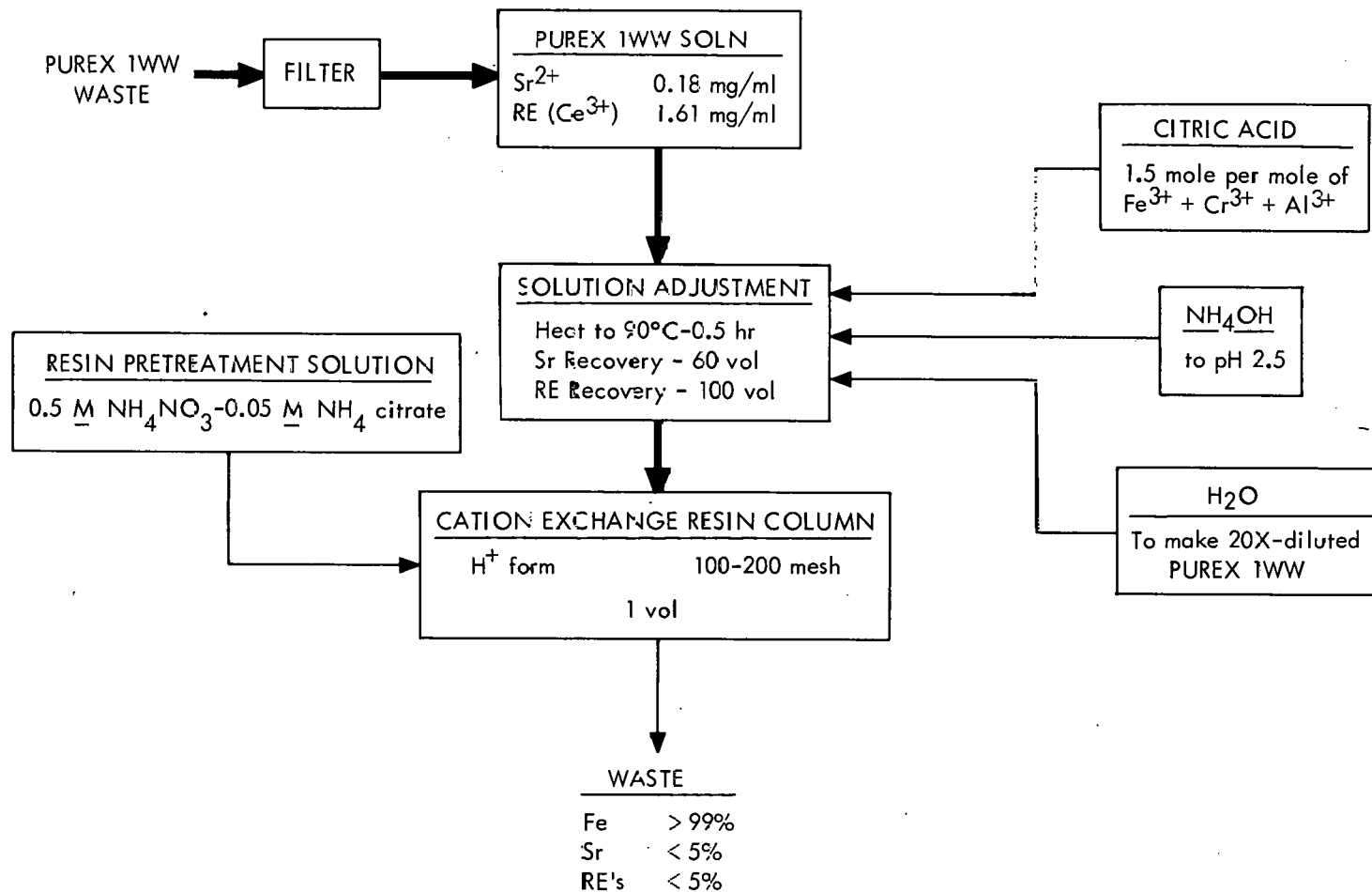
Fig. 1. In this Flowsheet, the Trivalent Cationic Impurities (Fe^{3+}, Cr^{3+}, and Al^{3+}), after being Complexed with Citrate, Pass through the Ion Exchange Column while Strontium and Rare Earth Cations are Sorbed on the Resin.

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Table 1. Approximate Composition of Purex 1WW Waste Solution

| | Concentration | |
Ion	Molarity	Gram/liter
Major Impurities[a]		
H^+	5.6	
NO_3^-	6.1	
SO_4^{2-}	1.0	
Fe^{3+}	0.5	
Al^{3+}	0.1	
Cr^{3+}	0.01	
Ni^{2+}	0.01	
Na^+	0.6	
UO_2^{2+}	0.01	
PO_4^{3-} [b]	0.01	
$SiO_2 \cdot xH_2O$ [b]	0.02	
Fission Products[c]		
Ba^{2+}		0.18
Sr^{2+}		0.18
Ca^{2+}		0.72
Ce		0.47
Zr-Nb[b]		0.63
Rare earths		0.93
Cs^+		0.43
Ru		0.25

[a] Same as Hanford Purex 1WW waste supernatant.

[b] As precipitate.

[c] Concentrations based on 0.1 of Yankee Atomic Power Reactor conditions, which correspond to a burnup of 8000 Mwd/tonne of 3.4% U^{235}, and 100 days of cooling time.

Greater than 95% of the strontium and rare earths are retained on the resin bed while greater than 99% of the ferric ion in the waste is removed by citrate complexing.

2.2 Waste Treatment by Nitric Acid Precipitation

The nitric acid treatment of Purex 1WW waste consists of a double precipitation in which sulfate ion is precipitated as ferric sulfate in 55 to 60% HNO_3 and then strontium is recovered by precipitation in 85% HNO_3. The procedure follows the flowsheet shown in Fig. 2.

1. Add ferric ion to Purex 1WW, as freshly precipitated $Fe_2O_3 \cdot xH_2O$ or partially dehydrated $Fe(NO_3)_3 \cdot 9H_2O$ (boiling temperature of about 135°C).

2. Add 90% HNO_3 to increase the acidity to 55 to 60% HNO_3 in order to precipitate sulfate as $Fe_2(SO_4)_3$.

3. Filter and evaporate filtrate until the temperature reaches 135°C.

4. Make 85% in nitric acid with 90% HNO_3 to precipitate strontium.

5. Hold at about 70°C to 12 hr[5] to minimize coprecipitation of the remaining iron and aluminum and then filter at temperature.

6. Dissolve the strontium precipitate in water for ion exchange processing.

7. Add citrate ion in the ratio of 3 moles per mole of remaining ferric, chromic, and aluminum ions in this solution; adjust the pH to 2.5 with ammonium hydroxide and process through a column of Dowex 50W X-8 (100 to 200 mesh) which has been converted to the ammonium form at pH 2.5.

Laboratory studies with simulated Purex 1WW show that the double precipitation procedure yields a solid product containing 75 to 80% of the original strontium and less than 1% each of the major cationic impurities, ferric, aluminum, and sodium ions and sulfate. Subsequent cation exchange processing of this product indicates an improvement in resin capacity of over 20 times that of the citrate waste treatment procedure (Sec 2.1); that is to say, the equivalent of almost 67 volumes of original Purex 1WW could be processed per volume of Dowex 50W resin in the ammonium form, with greater than 95% of the strontium retained on the resin bed. Rare earth recovery is not improved by this treatment because only partial precipitation occurs in the 85% HNO_3 solution.

3. PROCESS CHEMISTRY STUDIES

The initial objective was direct ion exchange processing of diluted, acid Purex 1WW waste by cation exchange, but this approach had to be
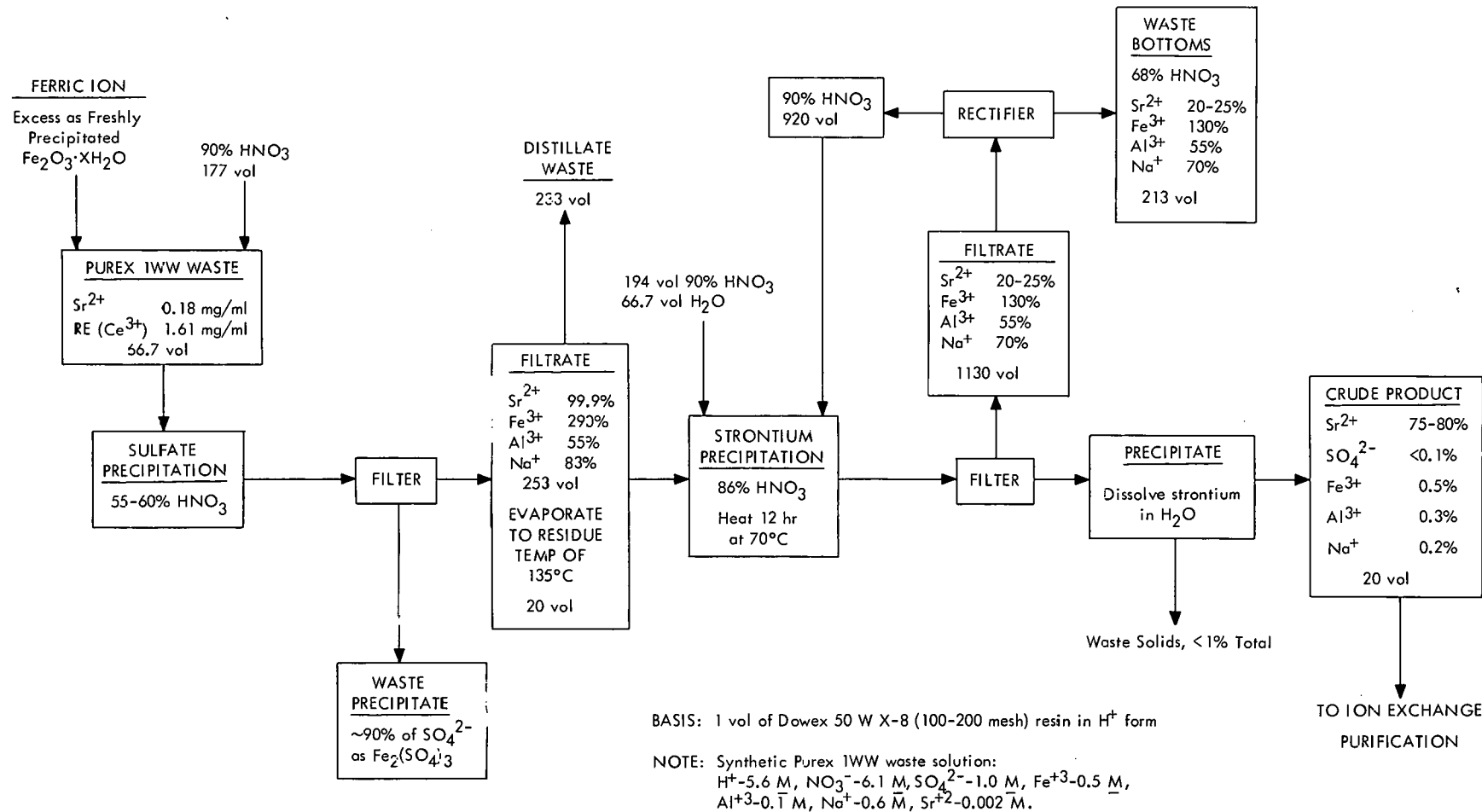
FERRIC ION

Excess as Freshly
Precipitated
$Fe_2O_3 \cdot XH_2O$

90% HNO_3
177 vol

PUREX 1WW WASTE

Sr^{2+} 0.18 mg/ml
RE (Ce^{3+}) 1.61 mg/ml
66.7 vol

SULFATE
PRECIPITATION

55-60% HNO_3

FILTER

WASTE
PRECIPITATE

~90% of SO_4^{2-}
as $Fe_2(SO_4)_3$

DISTILLATE
WASTE

233 vol

FILTRATE

Sr^{2+} 99.9%
Fe^{3+} 290%
Al^{3+} 55%
Na^+ 83%
253 vol

EVAPORATE
TO RESIDUE
TEMP OF
135°C

20 vol

194 vol 90% HNO_3
66.7 vol H_2O

STRONTIUM
PRECIPITATION

86% HNO_3

Heat 12 hr
at 70°C

90% HNO_3
920 vol

RECTIFIER

WASTE
BOTTOMS

68% HNO_3

Sr^{2+} 20-25%
Fe^{3+} 130%
Al^{3+} 55%
Na^+ 70%

213 vol

FILTRATE

Sr^{2+} 20-25%
Fe^{3+} 130%
Al^{3+} 55%
Na^+ 70%

1130 vol

FILTER

PRECIPITATE

Dissolve strontium
in H_2O

Waste Solids, <1% Total

CRUDE PRODUCT

Sr^{2+} 75-80%
SO_4^{2-} <0.1%
Fe^{3+} 0.5%
Al^{3+} 0.3%
Na^+ 0.2%

20 vol

TO ION EXCHANGE
PURIFICATION

BASIS: 1 vol of Dowex 50 W X-8 (100-200 mesh) resin in H^+ form

NOTE: Synthetic Purex 1WW waste solution:
H^+-5.6 M, NO_3^--6.1 M, SO_4^{2-}-1.0 M, Fe^{+3}-0.5 M,
Al^{+3}-0.1 M, Na^+-0.6 M, Sr^{+2}-0.002 M.

Fig. 2.   In this Flowsheet, First Sulfate Is Removed by Precipitation from Simulated Purex
1WW Waste as $Fe_2(SO_4)_3$ from 55 to 60% HNO_3, then $Sr(NO_3)_2$ is recovered by Precipitation from
85% HNO_3.

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abandoned. Early work by others[6] with a waste somewhat similar to a tenfold diluted Purex 1WW indicated that a volume distribution coefficient of nearly 200 could be expected for strontium. However, in the present experiments with a waste that closely simulated the diluted Purex 1WW, a value of 7.5 was found because of the overwhelming amount of iron, chromium, and aluminum in this waste.[7] The distribution coefficient for rare earths was found to be about 17. Furthermore, a cation-resin-selectivity scale published by Strehlow[8] confirmed that relatively little strontium could be sorbed under these conditions and that there was little hope of improved strontium recovery by using either more concentrated or more dilute waste solutions. Thus, it was necessary to develop procedures to overcome the adverse effects of the major cation impurities.

3.1 Addition of Complexing Agent, pH Adjustment, and Ion Exchange Separation

Citrate complexes of iron,[9] chromium,[10] and aluminum[9] have been reported to be stable at pH values as low as 3 if 1.5 moles of citrate are added for each mole of trivalent ion. However, at this pH level the rare earths are also known to form citrate complexes[11] and therefore would not be separated from the waste. Hence, a lower pH range was investigated to see if both strontium and the rare earths could be separated from the trivalent cationic impurities.

Exploratory tests showed that this separation could be achieved at pH 2.5. Distribution coefficients were then determined for rare earths (Ce^{3+}), strontium, and iron (Fe^{3+}) as a function of Purex 1WW dilution in order to find the optimum conditions for column operation at this pH value. For these experiments, Dowex 50W X-8 (100 to 200 mesh) resin was converted to the ammonium form prior to its use by equilibrating with a 0.5 $\underline{M}$ HNO_3--0.05 $\underline{M}$ ammonium citrate solution at pH 2.5. The waste solution was prepared for use by adding 1.5 moles of citrate per mole of combined Fe^{3+}, Al^{3+}, and Cr^{3+}, by neutralizing to pH 2.5 with concentrated ammonia, by heating to 90°C for half an hour to ensure complete complexing of the chromic ion,[10] and by diluting with water to the desired values. Experimental data (Fig. 3) indicated that the
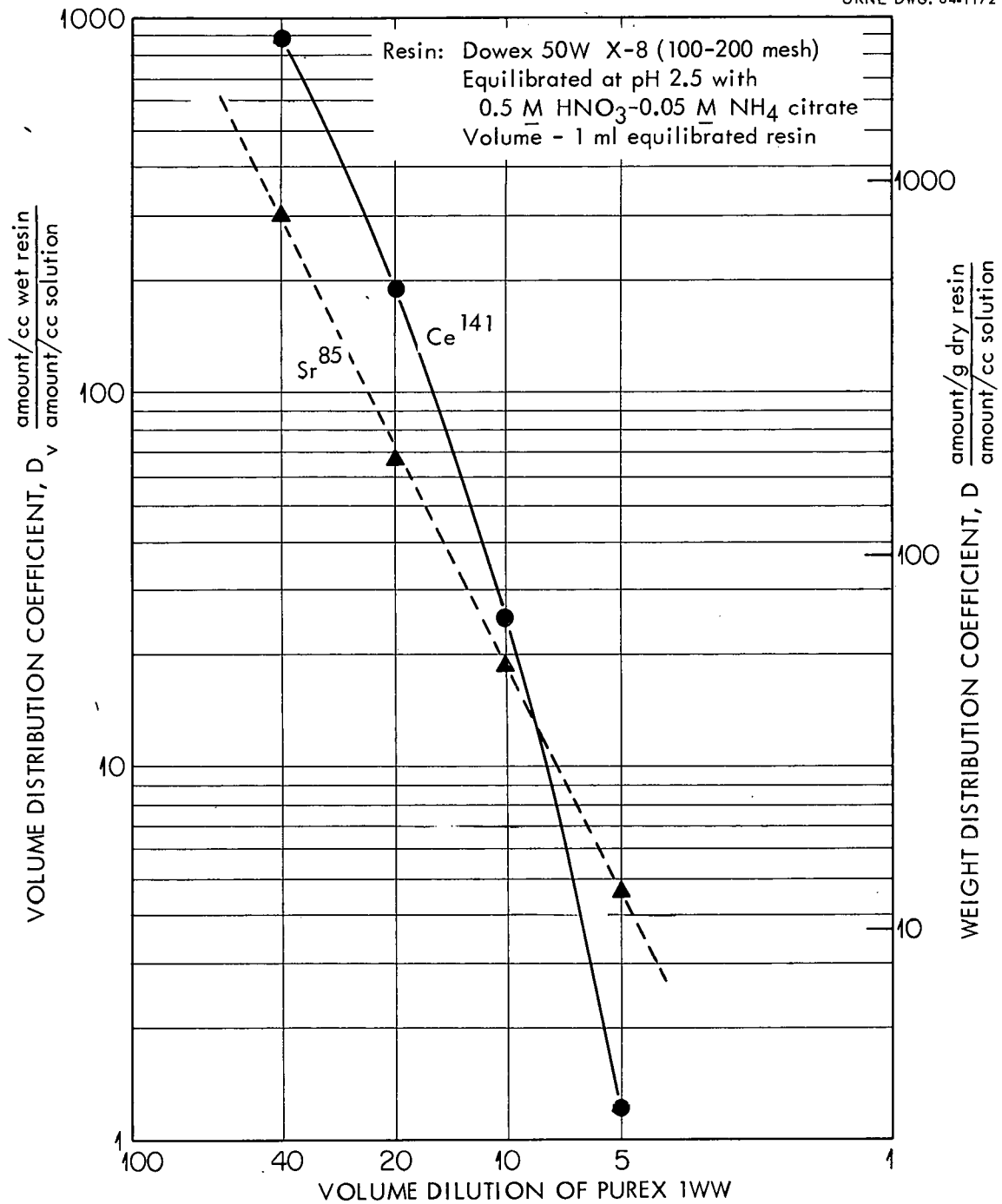
Fig. 3. The Distribution Coefficients of Ce^{141} and Sr^{85} Increase as the Solution is Diluted. The distribution coefficient for iron (Fe^{59} tracer) did not change even when the Purex waste was diluted with 400 parts of water. The points are not shown in the graph. (1.5 moles of citric acid per mole (Fe^{3+} + Al^{3+} + Cr^{3+}) were added to one volume of 1WW solution. The pH was adjusted to 2.5 with NH_4OH, and this solution was then diluted to the indicated value.)

major cationic impurities were retained as strong citrate complexes, even in greatly diluted waste solutions; the volume distribution coefficient values for iron were less than 0.3 for both 40- and 400-fold diluted Purex 1WW waste. Resin capacity for strontium and rare earths was observed to increase as the extent of water dilution was increased. For column operations a reasonable dilution factor of 20 was selected, and the separation factors were then determined to be as follows: D^{Sr}/D^{Fe}, more than 200; D^{Ce}/D^{Fe}, more than 600; and D^{Ce}/D^{Sr}, about 3.

Treated waste at this twentyfold dilution was run through a column (0.5-in.-ID x 6-in.-long) of cation resin in the ammonium form (15 ml) to obtain kinetic sorption data. A linear flow rate of 0.73 cm/min was used. Resin capacity for strontium, rare earths, barium, and calcium was obtained by the use of Sr^{85}, Ce^{141}, Ba^{133}, and Ca^{47}-Sc^{47}; the isotope Fe^{59} was also added to observe the ability of citrate to complex ferric ion. Each resin volume of effluent was collected and counted on a 200-channel gamma-ray scintillation spectrometer. A least-squares analysis was made of these data with the aid of the Control Data Corp. 1604-A computer to solve for the amount of activity in each solution. From this analysis, a plot was made of the sorption cycle, that is, the activity of each isotope relative to the concentration in the original feed solution, $(\frac{C}{Co})$, as a function of resin volumes of effluent (Fig. 4). A more detailed discussion of the method of analysis is given in the Appendix.

A comparison of the sorption-cycle data (Fig. 4) with the volume-distribution-coefficient data (Fig. 3) for 20-times diluted Purex 1WW indicated that (1) the strontium 50% breakthrough point of 68 resin volumes was in agreement with that predicted from equilibrium data, (2) the rare earths (Ce^{141}) 50% breakthrough point of 111 resin volumes was lower than the 190 resin volumes predicted, and (3) the iron was effectively complexed by citrate. The apparent 40% decrease in the distribution coefficient value of rare earths is a result of comparing data taken under dynamic conditions with data taken from a batch test in which there was a change in composition of the waste solution; that is to say, under equilibrium conditions (the beaker tests), a large fraction of the
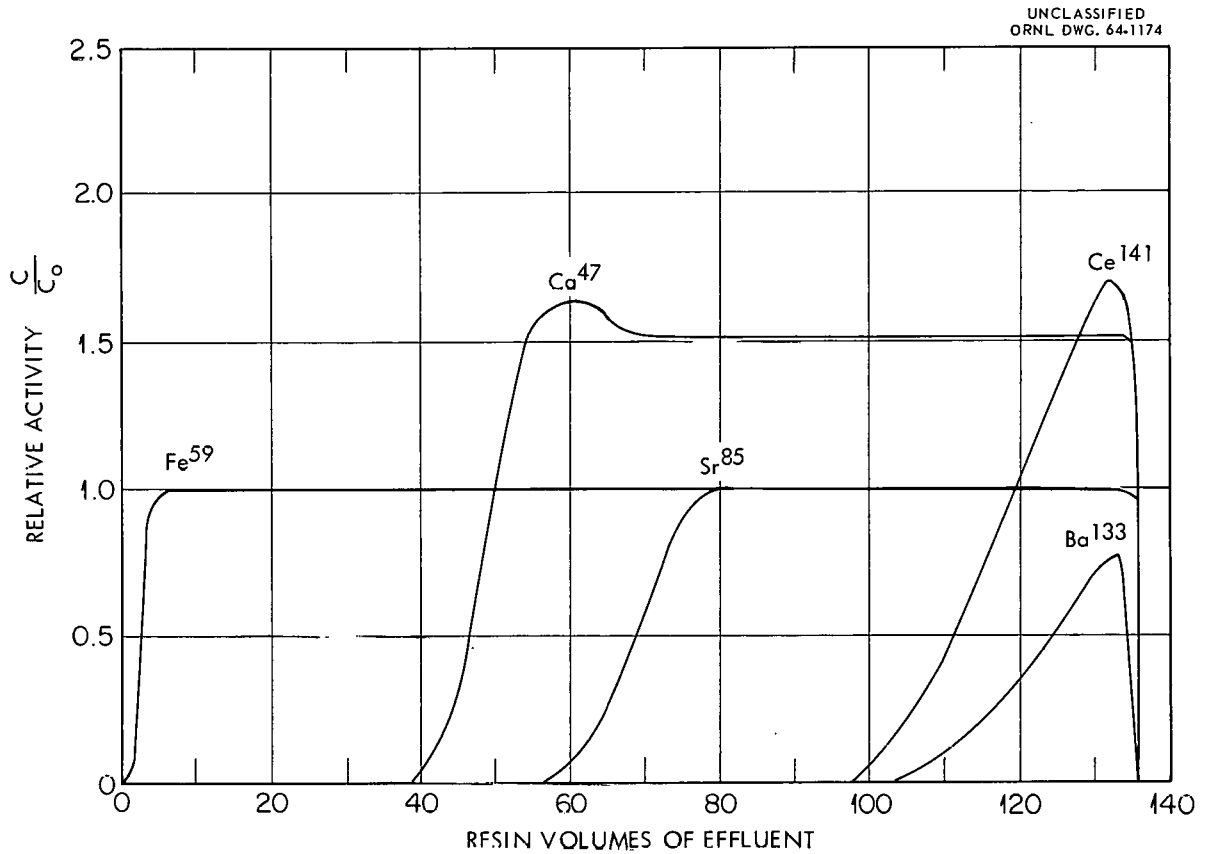
Fig. 4. Sorption Curves. During the sorption cycle with citrate-treated Purex 1WW solution, 50% breakthrough points of strontium and cerium occur at 68 and 111 resin volumes, respectively.

rare earths in solution was sorbed on the resin and thus the concentration of rare earth ions in the waste solution was reduced considerably; under flow conditions this effect was less marked. The calcium and barium 50% breakthrough points occurred at 50 and 125 resin volumes, respectively.

Bulk separation of the sorbed fission products was made by elution with ammonium α-hydroxyisobutyrate according to a procedure published by Wish[12] (Fig. 5). This eluant, though expensive, is reportedly more capable of rapidly eluting the rare earths than ammonium lactate or ammonium citrate and does the job with no significant movement of the strontium and barium sorbed on the cation resin column.[13,14] The eluant also separates strontium from calcium and barium at relatively low pH values and over a small pH range. The use of the less expensive ethylenediaminetetraacetic acid (EDTA) for recovery of strontium from acidic solutions is rather limited because of its low solubility at low pH values (pH 4 to 5); appreciable column loading can lead to precipitation of alkaline earth and other cations on the resin column.[15] A material balance of the resin column experiment (Table 2) gave the following results:

1. The product rare earth stream contained more than 75% of the rare earths sorbed together with 12%, 7%, and 3% of the calcium, strontium, and barium. The calculated decontamination factor (DF) for iron was about 5, based on a 20-fold diluted Purex 1WW feed solution.

2. The product strontium stream contained about 55% of the strontium sorbed together with 31% of the barium and less than 1% each of the rare earths and calcium. An additional 33% of the strontium was found in the calcium product stream. The DF for iron was about 600.

The material balance of each radioactive tracer used ranged from 68% to 78%, with the exception of strontium, which was 95%.

Oxalic acid was also considered as a complexer for the trivalent cationic impurities. Added in a ratio of two moles per mole of Fe^{3+} ion, it effectively complexed iron in the waste solution. However, its use was precluded because of subsequent slow desorption of sorbed rare earths and strontium in the elution cycle.
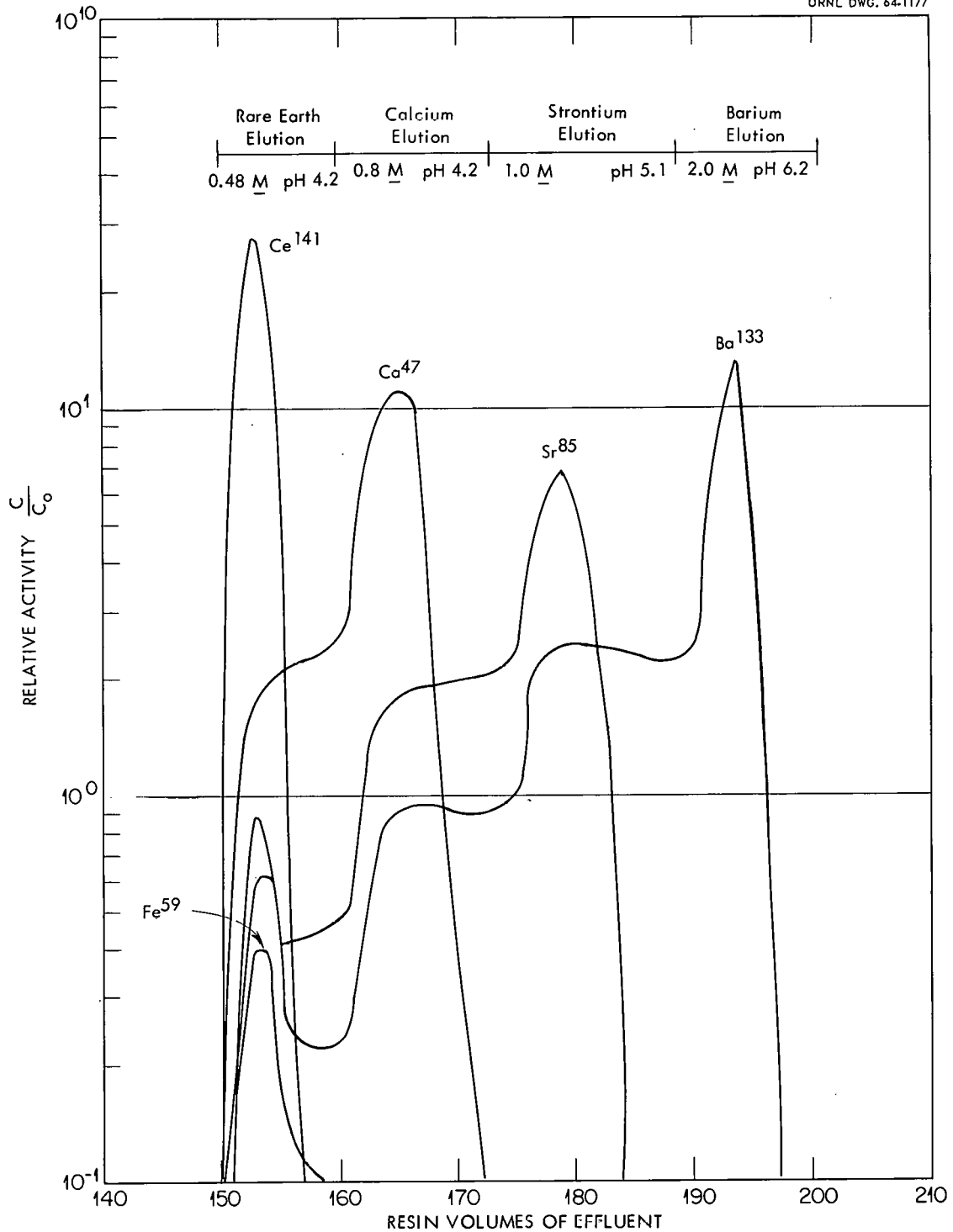
Fig. 5. Elution Curves. During desorption with ammonium α-hydroxy isobutyrate only rough separation of fission products from each other is achieved if the resin colume is fully loaded during sorption. Higher purity products could be obtained if the column were not fully loaded during sorption.

Table 2. Material Balance of Strontium and Rare Earth Recovery
from Purex 1WW Waste by Cation Exchange

	Sorption Step	Elution Step: Elutriant-Ammonium α-Hydroxy Isobutyrate				
Radio-active Tracer	Total Ion Sorbed (meq)	Rare Earth (Ce^{3+}) Recovery (%)	Calcium Recovery (%)	Strontium Recovery (%)	Barium Recovery (%)	Material Balance (%)
Sr^{85}	0.12	7	33	55	< 1	95
Ce^{141}	0.91	76	< 1	< 1	< 1	76
Ca^{47}	0.004	12	68	< 1	< 1	78
Ba^{133}	0.24	3	8	31	32	74
Fe^{59}	2.2	68	< 1	< 1	< 1	68

3.2 Precipitation in Nitric Acid and Ion Exchange Separation

Solubility data[16] indicated that, in a nitrate system, the solubility
of strontium ion decreased 1.5 to 2 times faster than either ferric or
aluminum ion as the acid concentration increased to 40% HNO_3. Additional
determinations of the solubility of Fe^{3+}, Al^{3+}, and Sr^{2+} in 50 to 80%
HNO_3 solutions showed that, at 80% HNO_3, almost 90% of the strontium in
Purex 1WW could be precipitated and that less than 20% of the Al^{3+} and
less than 1% of the Fe^{3+} would be in the product (Fig. 6). Since the
solubility of aluminum nitrate rises faster than that of strontium nitrate
with increase in temperature, the solution could be heated to 70°C to
decrease the aluminum impurity to less than 10%.[5]

Similar tests with Purex 1WW, diluted to 60 to 80% HNO_3 by the ad-
dition of 90% HNO_3, indicated that the sulfate in the waste was inter-
ferring with the direct recovery of strontium. Iron and aluminum sulfates
precipitated along with the strontium, as evidenced by (1) the greater
than 90% material balance between the major cationic impurities and the
sulfate in the precipitate (Table 3), and (2) the lower solubility values
of strontium, aluminum, and iron than is predicted for these ions (Table 4).
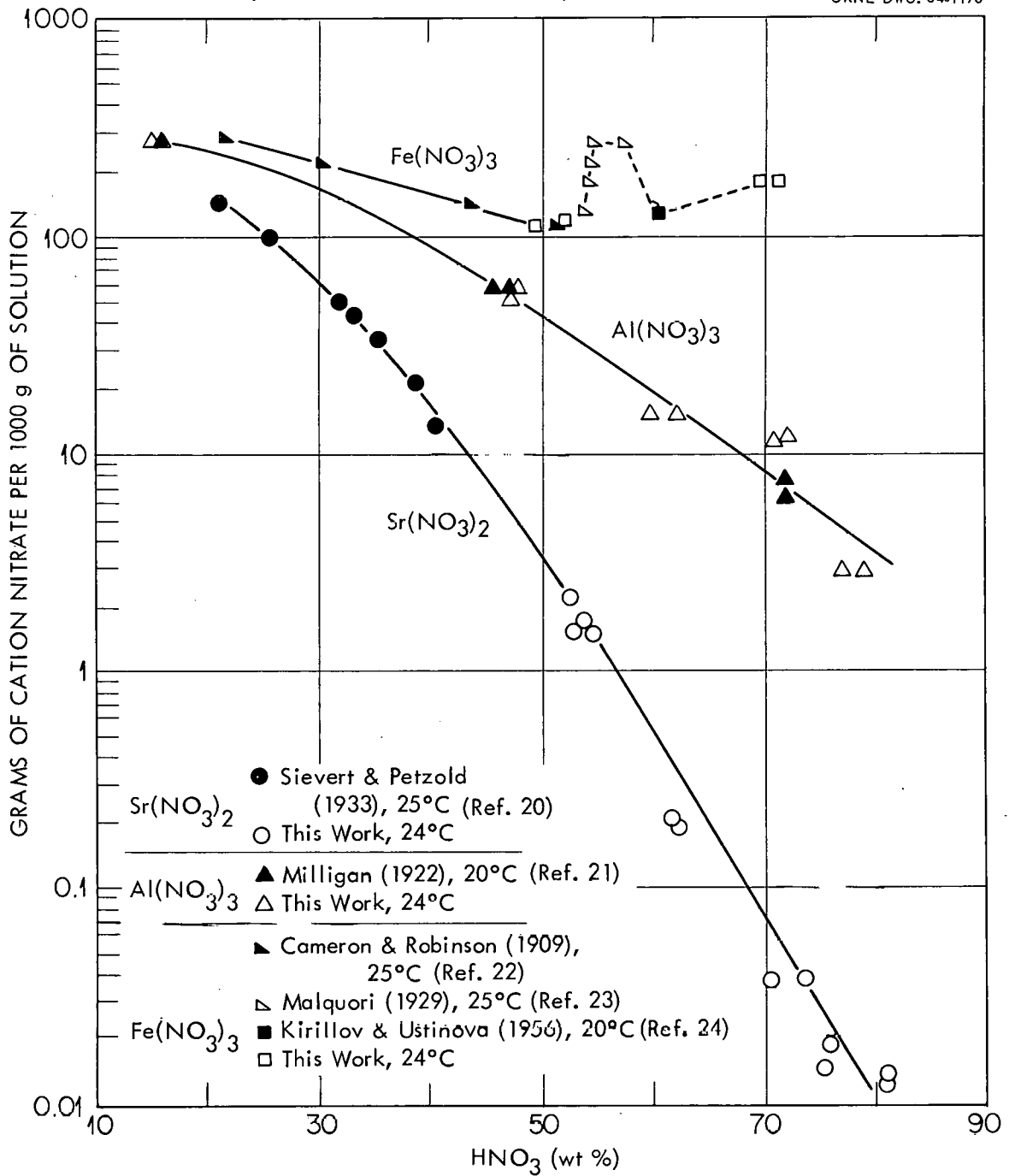Therefore if we want to take advantage of known chemistry of strontium

Fig. 6. The Solubility of Strontium Nitrate in Nitric Acid is Very Significantly Lower than the Solubilities of Aluminum or Ferric Nitrates.

Table 3. Precipitation of Purex 1WW Waste from 60 to 80% Nitric Acid:
Material Balance Between Cations and Sulfate in the Precipitate

Nitric Acid Concentration (wt %)	Amount of Precipitated Cations (meq)					Precipitated Sulfate SO_4^{2-} (meq)
	Fe^{3+}	Al^{3+}	Cr^{3+}	Na^+	Total	
60.9	33.6	1.38	0.109	2.09	37.2	36.2
66.0	99.3	2.67	0.426	11.3	113.8	103.6
68.3	106.5	4.02	0.766	12.7	124.2	116.8
72.4	93.0	2.24	0.552	9.22	105.2	108.2
78.1	88.2	3.15	0.546	6.53	98.7	92.4

in nitrate solutions, removal of sulfate is necessary. Such a separation, however, must be made at a concentration of nitric acid low enough to prevent the precipitation of strontium nitrate.

In tests at 45 to 60% HNO_3, excess ferric ion, in the form of freshly precipitated $Fe_2O_3 \cdot xH_2O$, was added to the waste solution prior to diluting with 90% HNO_3. About 85 to 90% of the sulfate precipitated, while more than 90% of the strontium and about 10% of the rare earths remained in solution at 50 to 60% HNO_3 (Table 5).[17]

A laboratory-scale experiment was performed to test the double precipitation treatment of the waste, that is, precipitation of the sulfate ion at 55 to 60% HNO_3 followed by precipitation of strontium at 85% HNO_3. Radiochemical and wet analyses showed that the product precipitate contained more than 85% of the strontium from the original waste solution together with the following amounts (as percent of that in the feed) of fission product contaminants: barium, more than 85%; calcium, 25%; and rare earths (Ce^{141}), less than 10% (Table 6). In terms of solution concentration, the double precipitation step reduced the amount of cationic impurities--Fe^{3+}, Al^{3+}, and Cr^{3+} -- by a factor of 80 and increased the strontium by a factor of 2.5 to 3.0. Thus, the ratio of total trivalent cationic impurities to strontium was reduced by a factor of about 210.

Table 4. Comparison of the Solubilities of Strontium, Ferric, and
Aluminum Ions in Concentrated Nitric Acid and in lWW Purex-
Nitric Acid Solutions

HNO_3 Conc. (wt %)	lWW-HNO_3 Solution Density (g/ml)[a]	Solubility (grams of cation per 1000 g of solution)	
		In lWW-HNO_3 Solution[b]	In Pure HNO_3 Solution
Strontium (Sr^{2+})			
60.9	1.3954	0.0736	0.200
66.0	1.4081	0.0432	0.0690
68.3	1.4164	0.0183	0.0435
72.4	1.4293	0.0126	0.0190
78.1	1.4475	0.0069	0.0060
Iron (Fe^{3+})			
59.9	--	--	30
60.9	1.3954	1.87	--
66.0	1.4081	0.198	--
68.3	1.4164	0.141	--
69.0	1.5414	--	>44
72.4	1.4293	0.321	--
78.1	1.4475	0.601	--
Aluminum (Al^{3+})			
60.9	1.3954	0.900	2.26
66.0	1.4081	0.862	1.47
68.3	1.4164	0.767	1.21
72.4	1.4293	0.732	0.86
78.1	1.4475	0.332	0.52

[a] At 24 or 25°C.

[b] The solutions were prepared by diluting 100 ml of the synthetic lWW
with 90% nitric acid to the indicated nitric acid concentrations.

After dissolving in a minimum amount of water, the strontium product
was processed further by complexing the remaining cationic impurities
with citrate ion and by sorbing the fission products on a column of
cation exchange resin in the ammonium form, as described in Sec 3.1.
A least-squares analysis of the radioisotope activity data (Fig. 7)
showed that the capacity for strontium (50% breakthrough) was 23 resin
volumes of feed solution -- the equivalent of 67 resin volumes of Purex
lWW processed. In terms of capacity, this represents a more than

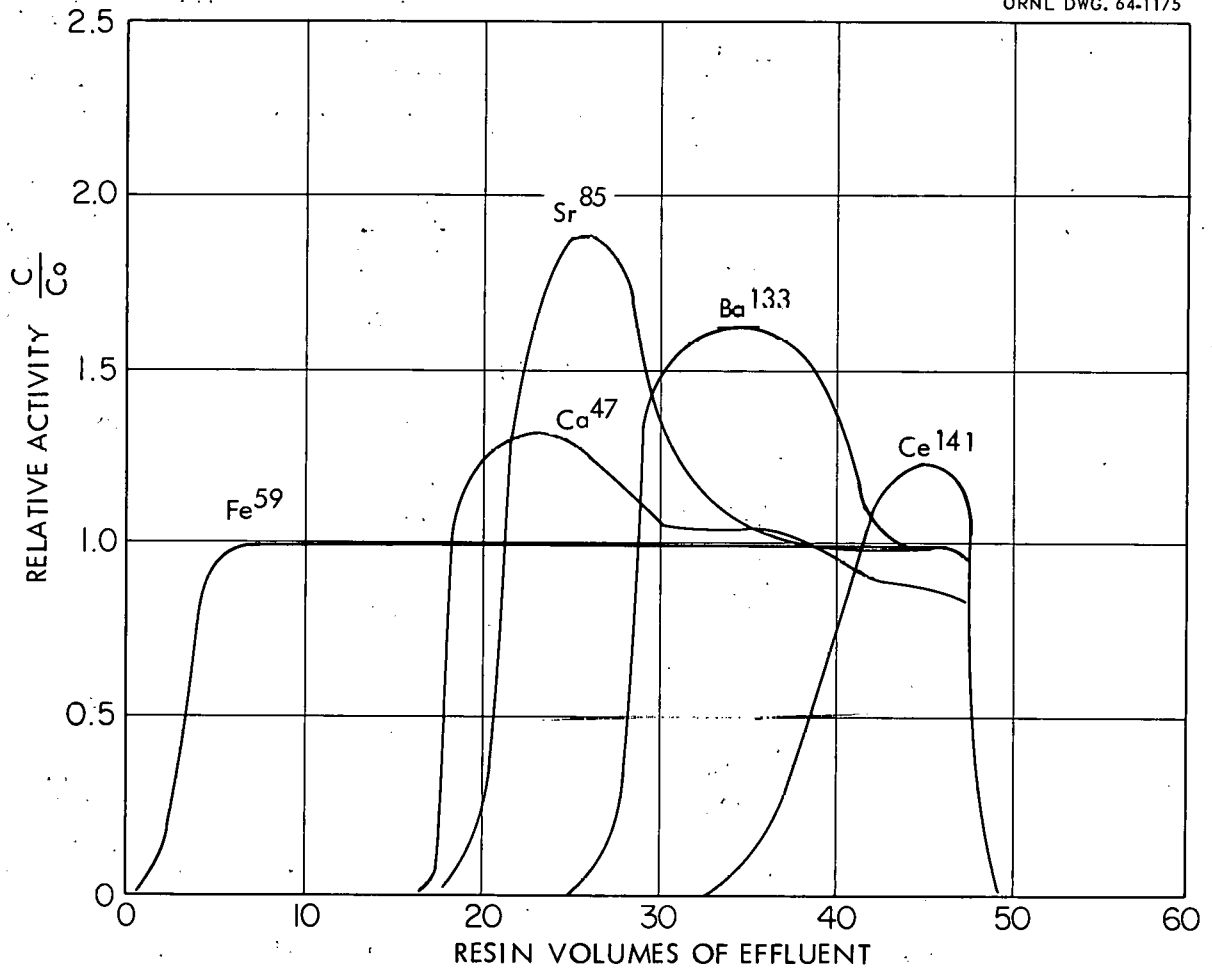Fig. 7. If Fe^{3+}, Al^{3+}, Cr^{3+}, and SO_4^{2-} Impurities are Removed by Precipitation then the Resin column Capacity for Strontium is Increased by a Factor of about 20 to 23 Volumes of Concentrated Solution which was Derived from 67 Volumes of Purex 1WW.

Table 5. Ferric Sulfate Precipitation from Purex 1WW Waste in
which the Nitric Acid Concentrations Ranges from 45 to 60%

A. Sulfate Distribution Between Precipitate and the
Waste Solution - Wet Analysis

HNO$_3$ Conc. (wt %)	SO$_4^{2-}$ Simulated 1WW (moles/liter)	SO$_4^{2-}$ in Products by Wet Analysis		
		Solution (moles/liter)	Precipitate (% Total)	Material Balance (wt %)
46.6	0.987	8.31 x 10^{-2}	42[b]	71
50.9	0.987	2.22 x 10^{-2}	85	93
54.1	0.987	2.16 x 10^{-2}	88	97
54.8	0.987	1.73 x 10^{-2}	89	96
59.0	0.987	1.70 x 10^{-2}	92	99

B. Strontium and Iron Distribution Between the Precipitate and
the Waste Solution - Radioactive Tracer Analysis

HNO$_3$ Conc. (wt %)	Total Activity in Simulated 1WW (cpm)	Cation in Products by Tracer Analysis		
		Total Activity in Solution (%)	Total Activity in Pre-cipitate (%)	Material Balance (wt %)
		Strontium - Sr^{85}		
46.6	4.35 x 10^7	114	4[b]	118
50.9	4.31 x 10^7	102	6	108
54.1	4.54 x 10^7	99	8	107
54.8	4.21 x 10^7	105	9	114
59.0	2.90 x 10^5	100	4	104
		Iron - Fe^{59}		
46.6	1.09 x 10^7	91	17[b]	108
50.9	1.14 x 10^7	81	29	110
54.1	1.29 x 10^7	83	32	115
54.8	1.11 x 10^7	80	31	111
59.0	1.22 x 10^7	83	34	117

[a] Each solution was prepared by (1) adding about 90 g freshly prepared
Fe$_2$O$_3$·xH$_2$O to 100 ml of simulated 1WW, (2) stirring for 24 hr to ensure
the presence of excess Fe^{3+}, (3) diluting with enough 90% nitric acid
to the indicated HNO$_3$ concentration, and (4) stirring for at least 48
hr to approach equilibrium conditions.
[b] Precipitate was only partially recovered.

Table 6. Comparison of Compositions of Purex 1WW and Strontium
Concentrate After Head-End Precipitation

| | Purex 1WW Waste | | Strontium Concentrate[a] | |
Ion	M	g/liter	M	g/liter
H^+	5.6		0.5	
NO_3^-	6.1		0.5	
SO_4^-	1.0		0.002	
Fe^{3+}	0.5		0.007	
Al^{3+}	0.1		0.0009	
Cr^{3+}	0.01		0.0001	
Ni^{2+}	0.01		< 0.0001	
Na^{1+}	0.6		0.0026	
Sr^{2+}		0.18		0.48
Ca^{2+}		0.72		0.46
Ba^{2+}		0.18		0.67
R.E. (Ce^{3+})		1.64		1.01

[a] The head-end precipitation treatment consisted of (1) adding excess
Fe^{3+} to 100 ml of Purex 1WW, (2) precipitating SO_4^{2-} ion at 55 to
60% HNO_3, (3) reducing the volume of filtrate by distillation,
(4) adding 90% nitric acid to the filtrate to precipitate Sr^{2+} at
greater than 85% HNO_3, (5) filtering, (6) dissolving the strontium
precipitate in a minimum amount of water. The volume of strontium
concentrate was 33 ml, ~1/3 the volume of the original Purex 1WW
waste.

twentyfold improvement for strontium sorption over that obtained by using
only citrate complexing to eliminate cationic interference.

The elution data (Fig. 8) and the material balance of this resin
column experiment (Table 7) showed that about 49% of the strontium
sorbed was recovered in the product stream, together with 21% of the
barium and less than 1% each of calcium, cerium, and iron. An additional
38% of the strontium was found in the calcium product stream. The over-
all iron decontamination factor was calculated to be about 5×10^5,
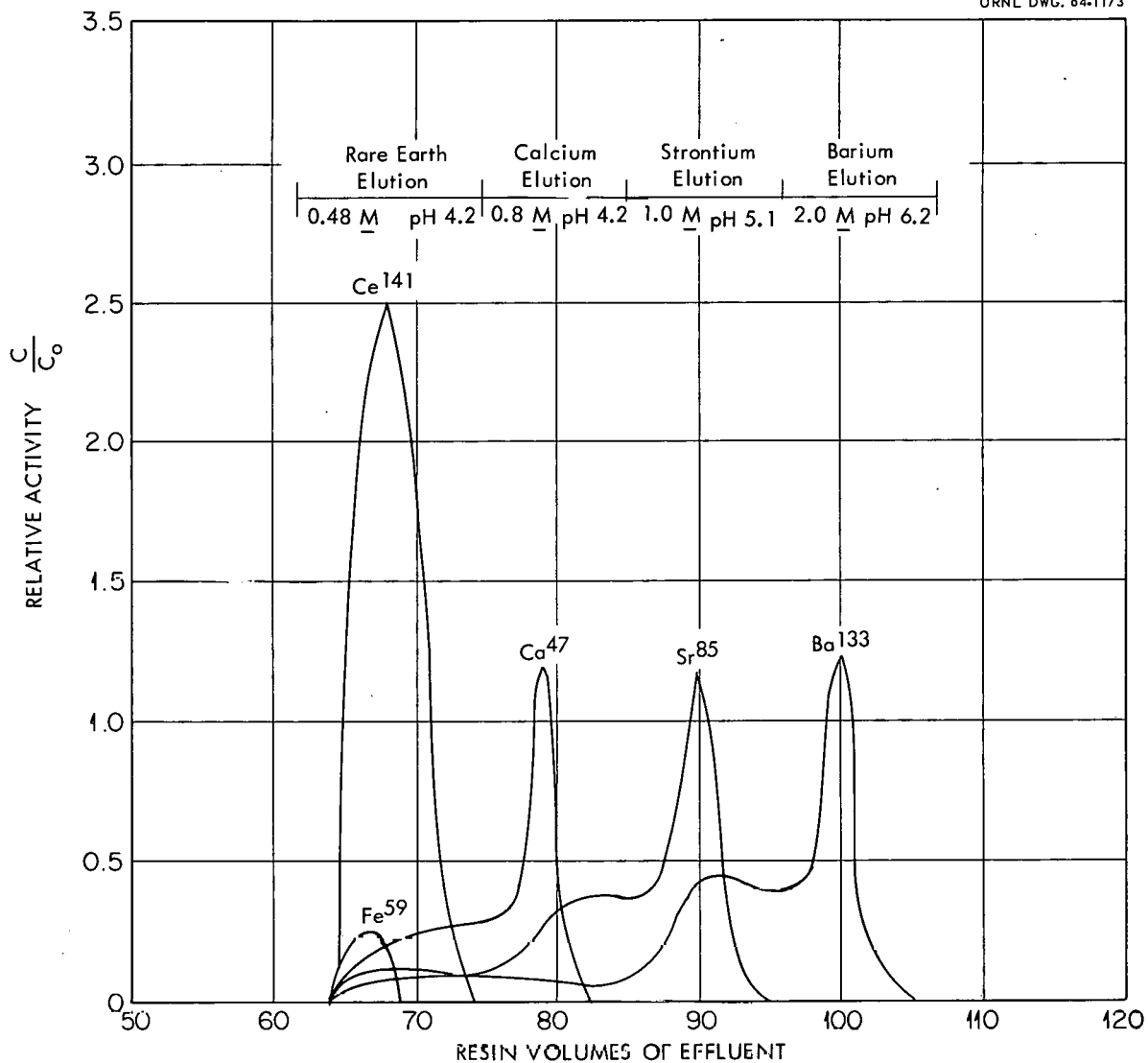based on Purex 1WW waste in its original form.

Fig. 8. If the Resin Column is Fully Loaded with Product from the Precipitation Process, then only a Rough Separation is Achieved During Desorption with Ammonium α-hydroxy Isobutyrate. Higher-purity products could be obtained if the column were not fully loaded during sorption.

Table 7. Material Balance of Strontium Recovery from Purex 1WW
Waste by the Precipitation-Ion Exchange Process:
Ion Exchange Portion

Radio-active Tracer	Sorption Step Total Ion Sorbed (meq)	Elution Step: Elutriant-Ammonium α-Hydroxy Isobutyrate				
		Rare Earth (Ce^{3+}) Recovery (%)	Calcium Recovery (%)	Strontium Recovery (%)	Barium Recovery (%)	Material Balance (%)
Sr^{85}	1.68	10	38	49	< 1	87
Ce^{141}	9.62	40	< 1	< 1	< 1	40
Ca^{47}	4.15	17	30	< 1	< 1	47
Ba^{133}	13.5	4	9	21	25	55
Fe^{59}	0.04	101	< 1	< 1	< 1	101

4. RADIATION DAMAGE TO THE CATION RESIN

As the composition of the feed solution is modified to achieve greater specific sorption of radioactive fission products on the cation resin, so also does the specific radiation power and the rate of radiation degradation of the resin increase. The extent of this degradation in a process based on either method of strontium and/or rare earth element beneficiation (Sec 2.) will be of considerable significance, as indicated below.

The cation exchange resin Dowex 50W X-8 was exposed[18] in the hydrogen form to a 10,000-curie Co^{60} gamma-ray source in a system of flowing water. After a dose of about 2 whr per gram of dry resin (0.75×10^9 r) the resin had lost about 40% of its strong-acid capacity; sulfonate decomposition products appeared mainly as dissolved sulfate in the flowing water stream. Swelling of the resin beads occurred, as shown by the 10 to 15% increase in specific wet-resin volume. About 20% of the resin volume decomposed and dissolved in the water. Significant breakup of the resin polymer was visible at a dose of about 1.5 whr per gram of dry resin, as evidenced by the turbidity of the column effluent. Thus, at 1 to 2 whr per gram of

dry resin, mechanical difficulties in ion exchange column operation (due to bead swelling and flotation) and loss of capacity will become significant.

The calculation of the rate of capacity loss of Dowex 50W X-8 resin (Table 8) was made assuming the resin to be saturated with strontium or cerium for both the ion exchange and precipitation-ion exchange processes. Further it was assumed that radiation degradation data obtained with de-ionized water apply to the nitrate solutions at this report. Ratios of Sr^{90} to total strontium and Ce^{144} to total cerium and other pertinent nuclear data were obtained from the tables of Blomeke and Todd.[3] In addition, the shapes of the sorption cycle curves* (Figs. 4 and 7) were used as a basis for assuming that both strontium and cerium were uniformly distributed throughout the column in the ion exchange process, while each of the four fission products -- Ca^{2+}, Sr^{2+}, Ba^{2+}, and Ce^{3+} -- was sorbed in a distinct band in the column in the precipitation-ion exchange process.

The calculations showed that: (1) The mass of Sr^{90} ($\tau_{1/2}$ = 28 y) sorbed per curie of radiation is about 25 times that of Ce^{144} ($\tau_{1/2}$ = 285 d) due to the difference in half-lives. Consequently, resin on which cerium is sorbed would be exposed to a correspondingly greater intensity of beta-particle radiation than that on which strontium is sorbed. (2) The fact that the resin (when the head-end purification is based on ion exchange) has a capacity for cerium up to tenfold greater than its capacity for strontium and the fact that Pr^{144} has a higher average beta-particle energy than Y^{90} further differentiate the relative effects of cerium and strontium radiations on the resin. (3) The calculated dose rates, in the ion exchange process, due to Sr^{90}-Y^{90} and Ce^{144}-Pr^{144} were 0.2×10^{-3} and 4.6×10^{-3} watts of beta energy per gram of dry resin, respectively. Assuming a loss of 20% of capacity per watt-hour per gram

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*The sorption of a cation on an ion exchange column was followed by plotting the fraction of the feed solution cation concentration in the effluent (C/Co) vs resin volumes of feed passed through the column. When the characteristic "S"-shaped curve approached unity at 100% breakthrough and leveled off as more feed solution was passed through the column, the cation sorbed was considered uniformly distributed over the entire length of the column. However, when this curve went above unity and then returned asymptotically to unity, as in Fig. 8, then the cation was considered to be concentrated in a band, which occupied only a fraction of the column.

Table 8. Nuclear and Chemical Data on Sr^{90} and Ce^{144} and their
Calculated Effect on Cation Exchange Capacity

A. General Nuclear Data

	Radionuclide	
	Sr^{90}	Ce^{144}
Mass per unit activity, meq/curie	0.156	0.0066
Average energy of β emmitting daughter, Mev[a]	0.73 (Y^{90})	0.97 (Pr^{144})
Energy release per unit activity, (watts/curie) x 10^{-3}	4.32	5.74

B. Calculations Based on Experimental Data[b]

	Process			
	Ion Exchange		Ppt'n-Ion Exch.	
	Sr^{90}	Ce^{144}	Sr^{90}	Ce^{144}
Cation resin capacity, meq/g of dry resin	0.023	0.18	3.52	1.81
Radionuclide mass, meq β emitter/g of dry resin	0.007	0.059	1.17	0.602
Radionuclide energy release, (β-watts/g of dry resin) x 10^{-3}	0.197	4.64	32.5	46.4
Operating time to lose 10% of resin capacity, hr[c]	2540.	108.	15.	11.

[a] From the data of Blomeke and Todd.

[b] Assume resin saturated with either Sr^{90} or Ce^{144}.

[c] Assume capacity loss rate of 20% per watt-hour per gram of dry resin.

of dry resin, the resin could be used in excess of 2500 hr for Sr^{90}-Y^{90}
processing before losing 10% of its capacity. For Ce^{144}-Pr^{144} processing,
this would be reduced to about 100 hr. (4) The calculated dose rates
(in the precipitation-ion exchange process), due to beta emission from
Sr^{90}-Y^{90} and Ce^{144}-Pr^{144}, were 32.5 x 10^{-3} and 46.4 x 10^{-3} watts per gram
of dry resin, respectively. This assumes band-type sorption. The resin
could be used in excess of 15 hr for Sr^{90}-Y^{90} processing or for 10 hr for
Ce^{144}-Pr^{144} processing before losing 10% of its capacity.

5. DISCUSSION OF RESULTS

Pretreatment of Purex-1WW waste with citrate ion at pH 2.5 effectively complexes the major cationic impurities -- Fe^{3+}, Cr^{3+}, and Al^{3+} -- and, upon subsequent cation exchange processing of a twentyfold diluted waste, increases the capacity for strontium to the equivalent of about 3 volumes of original waste per volume of resin -- a fourfold improvement over the processing of an untreated waste which has been diluted by a factor of 10. Resin capacity for rare earths (Ce^{3+}) is increased by a factor of 3 from 1.7 to 5 volumes of original waste per volume of resin.

Pretreatment of Purex 1WW by a double precipitation -- precipitation of sulfate ion at 55 to 60% HNO_3 followed by precipitation of strontium at 85% HNO_3 -- recovers 75 to 80% of the strontium in the waste together with less than 1% each of sulfate ion and the major cationic impurities. This pretreatment concentrates the strontium by a factor of 2.5 to 3.0 and reduces by more than 200-fold the ratio of total trivalent cationic impurities to strontium. This results in a twentyfold improvement in strontium capacity, to 67 volumes of Purex 1WW processed per volume of resin, when the dissolved and citrate-treated precipitate is processed by cation exchange. Rare earth recovery by this treatment is not improved because rare earths are only partially precipitated with strontium.

Elution of the sorbed strontium with ammonium α-hydroxyisobutyrate results in the following decontamination factors for ferric ion: 600 for waste pretreated with citrate ion and diluted twentyfold, and 5 x 10^5 for waste pretreated by a double precipitation using nitric acid. Elution of rare earths sorbed from the citrate pretreatment step results in an iron decontamination factor of only 5. However, this factor can probably be improved by eluting ferric ion with citrate to pH 2.5 to 3 before recovering any of the fission products.

Cross-contamination was observed in each of the eluted fission products -- Ce^{141}, Ca^{47}, and Sr^{85} (Figs. 5 and 8). Complete loading of the column to obtain capacity data during the sorption cycle left no reservoir of resin to provide for clean separations during the elution cycle. It was estimated that an additional 0.25 volume of fresh resin

would be ample to prevent the observed cross-contamination. Thus, purer elution products could probably be obtained by either loading to 75% of capacity during the sorption cycle or adding 0.25 volume of fresh resin to the base of a fully loaded column prior to elution.

With the precipitation-ion exchange process, both the resultant volume of liquid waste and the amount of organic chemical in the waste are smaller than in the waste derived from the direct ion exchange process. The volume is about a fourth to a third less. Citrate and α-hydroxyisobutyrate are present in only about 5% of the 500 resin volumes collected from processing 67 volumes of Purex 1WW in the precipitation ion exchange process. On the other hand, in the direct ion exchange process, about 75% of the 1800 resin volumes collected from handling a like amount of Purex 1WW are about 0.05 $\underline{M}$ in citrate; the balance contain α-hydroxyisobutyrate.

Radiation damage to the resin is up to ten times greater when processing Purex 1WW waste for rare earths (Ce^{144}-Pr^{144}) than for strontium (Sr^{90}-Y^{90}). In the direct ion exchange process, the calculated dose rates are 0.2×10^{-3} and 4.6×10^{-3} w of beta energy per gram of dry resin for Sr^{90}-Y^{90} and Ce^{144}-Pr^{144} processing, respectively. At these intensities, it is estimated that strontium and rare earths can be processed in excess of 2500 and 100 hr, respectively, before 10% of the resin capacity is lost. In the precipitation-ion exchange process, capacity is increased a hundredfold, thereby, increasing the dose rate to 32.5×10^{-3} w of beta energy per gram of dry resin from Sr^{90}-Y^{90}. At this dose rate, there would be a 10% loss in resin capacity after about 15 hr of processing time. Obviously, the resin will last about 150 times longer if direct ion exchange is used rather than precipitation-ion exchange. Radiation damage per cycle can be minimized by the use of continuous ion exchange equipment, such as the Higgins contactor.[19]

6. ACKNOWLEDGEMENTS

7. APPENDIX

METHOD FOR ANALYZING A MIXTURE OF GAMMA-EMITTING ISOTOPES BY THE USE OF A MULTICHANNEL GAMMA-RAY SPECTROMETER

This section describes the general procedure used in order to obtain the sorption and elution curves. Since the object of the analysis was to obtain satisfactory data for flowsheet proposals, refinements in the procedure were limited to those necessary for achieving that goal. In order to follow the path of some of the fission products in the processing of Purex 1WW waste by the two procedures described in this report, the gamma-ray emitting isotopes Sr^{85}, Ce^{141}, Ba^{133}, and Fe^{59} were added in tracer quantity to the waste solution. The separation of strontium and rare earths, in the ion exchange step of both processes, required the collection of hundreds of effluent samples. The job of obtaining sorption and elution curves for each of the five isotopes in each of the two runs was simplified by (1) analyzing the gamma spectra of the effluent samples on a 200-channel gamma-ray spectrometer and (2) using the Control Data Corporation 1604-A computer to calculate the activity contribution of each isotope at each channel in a spectrum by a least-squares procedure and to plot the ratio of the individual isotope activities relative to their individual activities in the feed solution to the ion exchange column as a function of resin volumes of liquid passed through the column.

Data obtained by scintillation spectrometry included the gamma spectra of the background and of identical volumes of the feed solution and solutions effluent from the ion exchange column. The feed solution with the concentration of any tracer expressed as C_o was used as a standard for calculating the unknown concentrations C in the effluent samples. Each sample was placed in about the same position on a sodium iodide well-type crystal (3-in. in diameter by 3-in. high), counted, and the time of counting recorded. The multichannel analyzer was set to cover the gamma-

energy range from 0 to 1.6 Mev in 160 channels, or 0.01 Mev per channel. Electronic problems produced a nonlinearity of energy versus channel number at the lower end of the energy spectrum (in the region 0 to 0.2 Mev) and also caused energy-peak shifts to occur during long-term operation of the instrument, wherein the channel-number shift was proportional to energy. The overall effect of these problems was to cause greater inaccuracies at the lower end of the energy spectrum where, characteristically, the activity of a gamma peak would span only about four to five channels, compared with the 15 to 20 channels at greater than 1 Mev.

Of the particular group of isotopes used for the experiments (Table 9) two of them had peaks of almost the same energy level: (1) The daughter product of Ca^{47}, namely Sc^{47}, had an energy peak of 0.157 Mev, compared with 0.145 Mev for Ce^{141}; and (2) the energy peak of Ca^{47} at 1.29 Mev was about the same as the 1.289 Mev peak of Fe^{59}. The interference of Sc^{47} was remedied by repeating measurements for Ce^{141} after the short-lived Ca^{47}-Sc^{47} had decayed. Interference of Fe^{59} in the determination of Ca^{47} was limited to the sorption cycle only; this interference was further minimized because the Fe^{59} activity reached a steady-state value at the beginning of the sorption cycle (iron formed a strong citrate complex and was not sorbed). Thus, when calcium breakthrough occurred, the additional activity was detected without difficulty. Wet analyses of some of the samples containing calcium ion provided an additional check on the radiochemical data.

The resolution of these gamma spectra into individual isotopic activities was done by a least-squares procedure. A correction was made for the channel shift of the energy peaks, proportional to the energy level of the peak. However, the computation assumed linearity over the entire energy spectrum covered, 0 to 1.6 Mev. The FORTRAN code written for the computer is based on the following general solution to the problem.

1. Background. M sets of background counting are obtained. The number of counts collected on channel J is designated as $Y(J,M)$ and the time of counting, T, is represented by $T(M)$.

Table 9. Nuclear Data on Gamma-Emitting Radioisotopes Used in Tracer Quantities in the Reported Experiments

Radioisotope	Half-Life	Energy of Emitted Gamma Radiation (Mev)
Ba^{133}	10.7 y	0.057, 0.082, 0.300, 0.357
Ca^{47}-Sc^{47}	4.5 d Ca^{47} 3.5 d Sc^{47}	1.29 (71%) - Ca^{47} 0.157 (66%) - Sc^{47}
Ce^{141}	32.5 d	0.145 (67%)
Fe^{59}	44.3 d	0.191, 1.098, 1.289
Sr^{85}	64.0 d	0.51

2. Samples. A + N samples are counted of index K. A represents the standard or feed solution, which contains only one isotope; six isotopes were used, so for this problem, A = 1 to 6. N represents the number of unknowns or effluent samples counted. $Y(J,K)$ designates the total counts collected on channel J of sample K. $T(K)$ is the time that the same K is counted.

3. Equations. For the unknown samples (K = A + 1 to A + N corresponding to K = 6 + 1 to 6 + N in the present work), the activity count rate on channel J is the sum of the count rates of the isotopes and of the background, where the count rate of an isotope is expressed as a fraction $[F(I,K)]$ of the count rate $[X(I,J)]$ of the standard. These relations are then summarized for the present report as:

$$Y(K,J) - \sum_{I=1}^{6} F(I,K)\, X(I,J) + \frac{T(K)}{T(M)}\, Y(J,M) , \qquad (1)$$

where

$$
\begin{aligned}
X(1,J) &= Y(1,J) - Y(J,1) , \\
X(2,J) &= Y(2,J) - Y(J,2) , \\
X(3,J) &= Y(3,J) - Y(J,1) , \\
X(4,J) &= Y(4,J) - Y(J,1) , \\
X(5,J) &= Y(5,J) - Y(J,1) , \\
X(6,J) &= Y(6,J) - Y(J,2) .
\end{aligned}
\qquad (2)
$$

F(I,K) is obtained by a least-squares solution of the equation:

$$\sum_{J=1}^{160} \frac{1}{\sigma^2_{Y(K,J)}} \left[Y(K,J) - \sum_{I=1}^{6} F(I,K)\ X(I,J) + \frac{T(K)}{T(M)}\ Y(J,M) \right]^2 = min, \quad (3)$$

where the variance of a count, namely $\sigma^2_{Y(K,J)}$, is equal to the count. That is,

$$\sigma^2_{Y(K,J)} = Y(K,J) .$$

Since all the samples were not analyzed on the spectrophotometer on the same day nor counted for the same length of time, appropriate time corrections had to be made in order to make the activity data significant and comparable. These adjustments were made according to the equation:

$$R(I,K) = F(I,K)\ \left(\frac{T(A)}{T(K)}\right)\ EXP \left[-B(I)\ Z(K)\right] , \quad (4)$$

where

B(I) is the decay constant λ of isotope I,

Z(K) is the elapsed time between counting any sample, K, and its standard,

T(A) is the time of counting the standard,

T(K) is the time of counting the unknown.

Plots of R(I,K) vs resin volumes of liquid passed through the ion exchange column for each of the six isotope tracers are included as Figs. 4, 5, 7, and 8 of this report.

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