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operated by
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U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

A solvent extraction flowsheet was developed for recovery of strontium-90 and mixed rare-earth fission products from adjusted Purex 1WW waste solution by di(2-ethylhexyl)phosphoric acid (D2EHPA) in Amsco 125-82 modified with tributyl phosphate (TBP). First cycle feed is prepared by adding tartrate and caustic to the waste solution to complex the iron and adjust the pH. Strontium and rare earths are co-extracted with D2EHPA-TBP-Amsco and stripped with nitric acid in the first cycle, and then isolated as concentrated product solutions by processing through additional solvent extraction cycles. Satisfactory product recoveries and physical operation were demonstrated in bench-scale batch and continuous countercurrent tests with simulated, unirradiated, feed solutions.

CONTENTS

1.0 INTRODUCTION

Megacurie quantities of fission products, such as strontium and rare earths, will be required in the future for industrial applications. To meet this demand, it appears likely that the simpler and more versatile solvent extraction and ion exchange process technologies will be preferred over batch precipitation techniques, which have been used ordinarily for production of relatively small amounts of fission products.

Di(2-ethylhexyl)phosphoric acid (D2EHPA) and its sodium salt (Na-D2EHP) are versatile liquid ion exchange reagents that effectively extract many cations from slightly acidic or alkaline solutions, according to either or both of the reactions[1]

$$M^{Z+}(a) + Z/2[HX]_2\,_{(o)} \rightleftharpoons MX_{Z(o)} + ZH^+_{(a)}$$

$$M^{Z+}(a) + Z[HZ]_2\,_{(o)} \rightleftharpoons MX_Z(HX)_{Z(o)} + ZH^+_{(a)}$$

where subscripts (a) and (o) indicate the aqueous and organic phases, X^- represents the di(2-ethylhexyl)phosphate anion, and $[HX]_2$ represents the dimer form in which the acid exists in hydrocarbon solution. For sodium and strontium,

$$2Na^+_{(a)} + [HX]_2\,_{(o)} \rightleftharpoons 2NaX_{(o)} + 2H^+_{(a)}$$

$$Sr^{++}_{(a)} + 2[HX]_2\,_{(o)} \rightleftharpoons SrX_2(HX)_2\,_{(o)} + 2H^+_{(a)}$$

$$Sr^{++}_{(a)} + 2NaX_{(o)} \rightleftharpoons SrX_2\,_{(o)} + 2Na^+_{(a)}$$

Details of the sodium-strontium-D2EHP equilibria are being determined.[2] Hydrocarbons such as kerosenes or Amsco 125-82 are satisfactory diluents for D2EHPA and many of its metal complexes in equilibrium with acidic solutions, but modification of the diluent with, for example, tributyl phosphate (TBP) is needed to maintain miscibility of NaD2EHP.[1]

Preliminary tests showed that strontium and rare earths were extracted with D2EHPA from $NaNO_3$ systems,[3] but were not appreciably extracted from acidic or neutralized Purex waste solutions principally because of interference of iron.[4] Tartrate added to Purex waste, however, effectively complexed the relatively large quantities of iron and, at the same time, did not seriously inhibit strontium and rare earth extraction with D2EHPA.[4,5] This concept was used in the development of a D2EHPA solvent extraction process in which strontium and rare earths can be isolated from a tartrate and caustic-adjusted Purex waste. The flowsheet is described in Sect. 2, and countercurrent tests are reported in Sect. 3. The detailed studies on which the flowsheet was based, and further tests of some of the variables, are reported in Sect. 4.

The authors express appreciation to K. B. Brown for helpful suggestions, to W. B. Howerton and M. D. Bartlett for laboratory assistance, and to the ORNL Analytical Chemistry Division for analytical services. In the mini mixer-settler tests particular acknowledgment is made to J. R. Flanary, F. H. Goode, and L. A. Byrd for assistance in assembly and operation of the equipment and to John Peele for analytical services.

2.0 FLOWSHEET

Based on laboratory tests with simulated solutions, a process for recovering strontium and the rare earths from Purex wastes is proposed (Fig. 2.1).

Feed Preparation. Purex waste[6,7] (designated 1WW) is the concentrated aqueous raffinate from the TBP-HNO_3 process by which plutonium and uranium are recovered from plutonium production reactor fuel. The significant concentrations of ionic contaminants (Table 2.1), such as iron, sulfate, and sodium, and the small amounts of the desired fission products complicate fission product separation processes. Caustic addition to the waste co-precipitates strontium with the iron at pH 2 or greater, but a complexing agent such as tartrate yields stable solutions throughout the pH range 0-12 and does not interfere markedly with D2EHPA extraction of strontium and rare earths.

The waste is made initially 1 M in tartrate ion to prevent iron precipitation and then adjusted to pH 5.5 ± 0.5 with caustic. The resulting feed solution (Table 2.1) is about 3 times more dilute than the original waste, with a final tartrate concentration of about 0.33 M. Throughout the experimental program the siliceous and phosphate solids normally present in the waste showed no interference with the extraction. Filtration or centrifugation of the waste or adjusted feed prior to processing appears to be optional.

First Cycle: Co-extraction of Strontium and Rare Earths. The strontium and rare earths are co-extracted from the adjusted solution by countercurrent contacting with the solvent, 0.3 M D2EHPA (0.21 M D2EHPA--0.09 M NaD2EHP)--0.15 M TBP in Amsco 125-82. (After extraction, the D2EHPA/NaD2EHP ratio in the solvent may vary since the relative amounts of sodium and acid form of the reagent are dependent on the acid and sodium concentrations of the equilibrating aqueous phase.) The strontium, rare earths, and sodium (from the NaD2EHP) are stripped from the solvent with 2 M HNO_3.

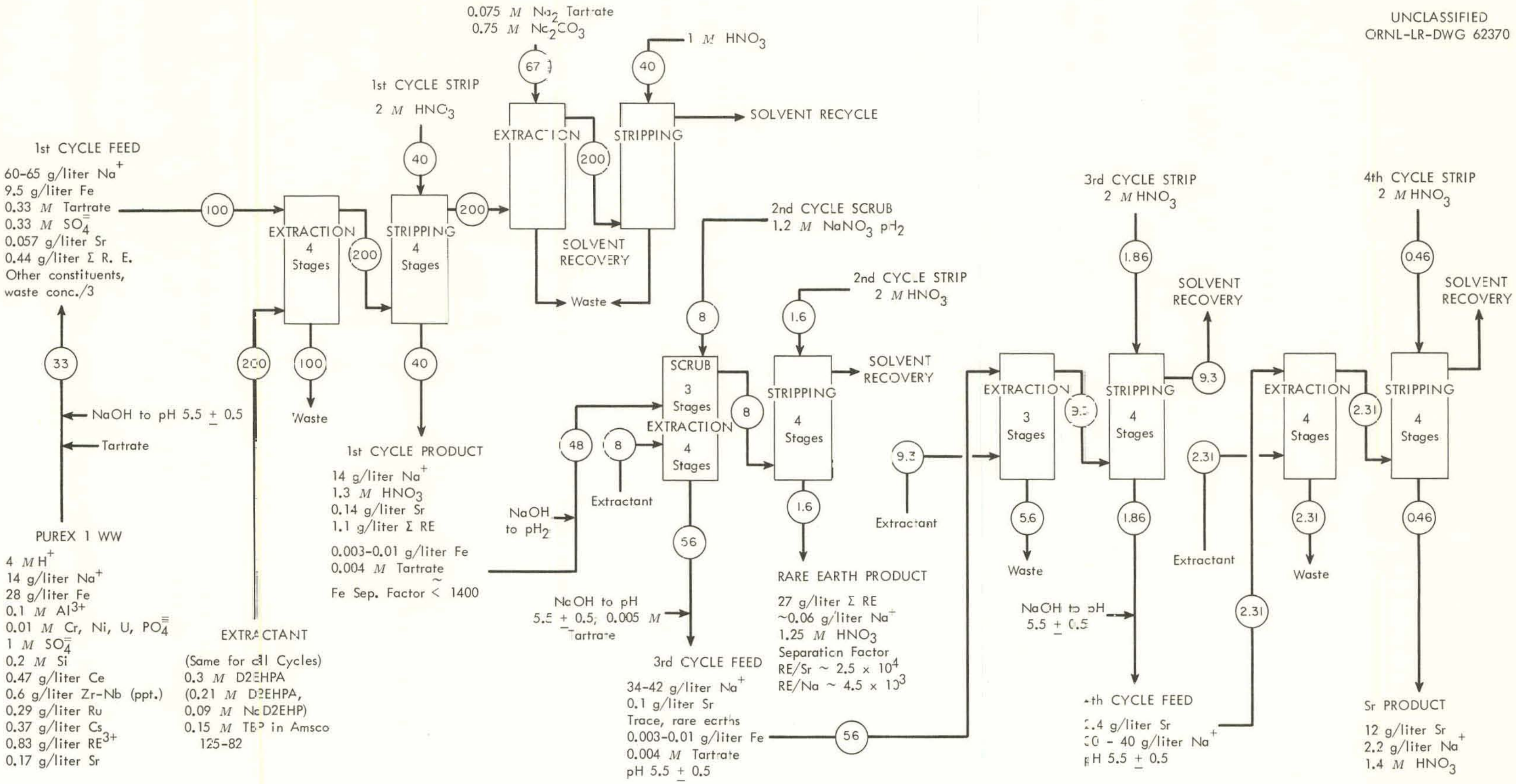

Fig. 2.1. Recovery of strontium and rare earths by solvent extraction with D2EHPA. Data reported here were obtained principally from batch countercurrent tests described in Section 3.1.

Table 2.1. Approximate Composition of Purex Waste

Constituent	Concentration: Original 1WW M	Original 1WW g/liter	After Adjustment to Feed Conditions M	After Adjustment to Feed Conditions g/liter
H^+	4.0	-	pH 5.5±0.5	-
$C_4H_4O_6^{=}$	-	-	0.33	-
Na^+	0.6	14	~2.7	60-65
Fe^{3+}	0.5	-	~0.15	8-9
Al^{3+}	0.1	-	0.033	-
Cr^{3+}	0.01	-	0.0033	-
Ni^{2+}	0.01	-	0.0033	-
U	0.005	-	0.002	-
NO_3^-	4.5	-	1.5	-
$SO_4^{=}$	1.0	-	0.33	-
$PO_4^{\equiv}$	0.01*	-	0.003*	-
Si	0.02*	-	0.007*	-
Sr^{2+}	-	0.17	-	0.057
Ce	-	0.47	-	0.16
Zr-Nb	-	0.60*	-	0.2*
R.E.	-	0.83	-	0.28
Cs^+	-	0.37	-	0.12
Ru	-	0.29	-	0.10

*As ppt.

Although an appreciable portion of the iron in the feed may be extracted into the solvent, only a small amount is stripped into the first cycle product. Less iron is extracted if the phase contact times are held to a minimum. Decontamination from ruthenium, zirconium-niobium, and cesium is appreciable.

Second Cycle: Strontium—Rare Earths Partitioning. The second cycle feed is the first cycle strip product made 0.004 M in tartrate (to complex traces of iron) and adjusted to pH 2 with NaOH. The rare earths are extracted into solvent of the same composition as in the first cycle, the solvent is scrubbed with 1.2 M $NaNO_3$ at pH 2, and the rare earths are then stripped into 2 M HNO_3. The aqueous raffinate contains strontium plus sodium and other contaminants but is essentially free of rare earths. The rare earth strip solution product (~20 g RE/liter) is essentially free of strontium.

Since the magnitudes of both the strontium and rare earth extraction coefficients are very pH dependent, large aqueous pH changes in the second cycle are avoided by using a low o/a phase ratio to minimize Na^+ - H^+ transfer. It is also helpful that the separation factor between rare earths and strontium is approximately constant over the pH range 0.5-3 (Sect. 3.1).

Third and Fourth Cycles: Strontium Separation and Concentration. The feed to the third cycle is the aqueous raffinate from the second cycle adjusted to pH 6. Strontium is extracted by solvent of the same composition as used in previous cycles and (with sodium) stripped with 2 M HNO_3.

If desired, the strontium can be further concentrated in a fourth cycle, similar to the third. The feed is the strip solution from the third cycle adjusted to pH 6. In the fourth cycle product the strontium concentration is a factor of 70 greater than that of the original waste.

Solvent Recovery: Removal of Iron. More than 99% of the iron is removed from the used solvent by contacting countercurrently for several stages with 0.75 M Na_2CO_3—~0.075 M $Na_2C_4H_4O_6$, O/A = 3/2. The tartrate prevents subsequent iron precipitation. The recovered solvent, after partial acidification to the original composition, is recycled to the extraction step.

3.0 FLOWSHEET TESTS

Batch countercurrent and continuous countercurrent experiments were made to test the chemical and physical operability of the flowsheet (Fig. 2.1). Decontamination factors and ultimate product purity were not demonstrated absolutely since facilities were not available for operation on a sufficiently high activity feed. Equipment operation was satisfactory with pulsed columns, mixer-settlers, or a combination of these devices for the separate operations.

3.1 Batch Countercurrent Experiments

Batch countercurrent tests were made of each process cycle.

First Cycle: Strontium and Rare Earth Co-extraction and Stripping. In laboratory batch countercurrent tests of the first cycle extraction and stripping, the distribution of tracer Ce-144 and Sr-85 (Table 3.1) showed that >99% of the strontium and ~98% of the rare earths were extracted and stripped. Iron distribution data (Table 3.2) showed that, although about 28% of the iron in the feed was extracted, only 0.17% was stripped. The strip product contained 0.14 g Sr, 1.1 g R.E., 13 g Na, and 0.039 g Fe per liter and 1.2 M HNO_3. The distribution of other

Table 3.1. First Cycle: Co-Extraction and Stripping of Strontium and Rare Earths

Organic phase: 0.21 M D2EHPA—0.09 M NaD2EHP—0.15 M TBP in Amsco 125-82

Aqueous phase: synthetic Purex waste (composition as shown in Table 2.1) adjusted to 0.33 M $Na_2C_4H_4O_6$ and to pH 6.0 with NaOH, plus tracer Ce-144 and Sr-85; dilution factor 3

Strip: 2 M HNO_3

Batch countercurrent runs, 4 extraction stages, 4 strip stages

Feed/extractant/strip phase ratio: 10/20/4

Stage	Aqueous Equil. pH	Ce-144 γ, c/m. ml		E_a^o Ce	Sr-85 γ, c/m. ml		E_a^o Sr
		Org	Aq		Org	Aq	
Feed	6.0	-	9.95×10^4	-	-	8.68×10^4	-
Ext-1	4.6	4.96×10^4	5.52×10^3	9.0	4.53×10^4	6.88×10^3	6.6
-2	4.4	2.71×10^3	2.68×10^3	1.01	3.62×10^3	5.3×10^2	6.7
-3	4.2	8.7×10^2	1.64×10^3	0.53	2.5×10^2	1.5×10^2	1.7
-4	4.1	2.4×10^2	1.27×10^3	0.19	50	80	0.63
Str-1		1.71×10^4	2.62×10^5	0.065	2.2×10^2	2.25×10^5	0.001
-2		7.3×10^2	3.41×10^4	0.021	20	3.79×10^3	0.005
-3		2.1×10^2	3.44×10^3	0.061	20	7.2×10^2	0.028
-4		1.2×10^2	4.3×10^2	0.28	Bkgd	60	-

fission product activities in the first cycle was shown with feed spiked with fission products from a Purex HAW solution (Table 3.3). Decontamination factors were 24 from Ru, 9 from Zr-Nb, and 26 from Cs.

Table 3.2. First Cycle: Extraction of Sodium, Acid, and Iron

Conditions same as in Table 3.1

Stage	Fe, mg/ml		Na, mg/ml		H^+		
No.	Org	Aq	Org	Aq	Org, M	Aq pH	Aq, M
Feed	-	9.2	-	59	-	6.0	
Ext-1	1.31	8.9	2.2	60	0.15	4.6	
-2	1.06	8.2	1.70	60	0.18	4.4	
-3	0.70	7.6	1.72	64	0.20	4.2	
-4	0.34	6.9	1.76	59	0.22	4.1	
Str-1	1.30	0.039	0.025	12.9	0.30		1.17
-2	1.30	0.005	0.018	0.28	0.32		1.99
-3	1.28	0.004	0.015	0.05	0.32		2.1
-4	1.28	0.004	0.018	0.027	0.33		2.1

Second Cycle: Rare Earth--Strontium Partitioning. The second cycle feed was the strip product from cycle 1 adjusted to 0.004 M tartrate (to complex traces of iron stripped in the first cycle) and to pH 2 with NaOH. Ce-144 and Sr-85 tracer distribution data (Table 3.4) showed a rare earth/Sr separation factor in the second cycle of $\sim 2.5 \times 10^4$ and a rare earth/Na separation factor of $\sim 4.5 \times 10^3$. The product from this cycle contained 28-30 g of rare earths and 0.06-0.07 g of Na per liter and 1.25 M HNO_3. The overall concentration factor for the rare earths from the original waste to the second cycle strip product solution is 20. The strontium/rare earth separation factor through the second cycle (based on the original waste) is estimated to be at least 2.5×10^3, but its precise value could not be determined because of limited analytical accuracy in determining the rare earth concentration in the second cycle raffinate.

The strontium and rare earth distribution coefficients change markedly under second cycle conditions as a function of the aqueous pH (Fig. 3.1). However, pH control is not difficult because a large amount of Na^+ or H^+ does not transfer between the organic and aqueous phases at the low o/a ratio (1/6) used. The buffering effect is almost entirely associated with the organic phase, i.e., the balance between NaD2EHP and D2EHPA, since the aqueous phase is essentially a simple sodium nitrate system. The rare earth E_a^o/strontium E_a^o ratio is approximately constant over the pH range 0.5-3, so that different operating conditions could be chosen, if desired, without affecting the rare earth-strontium separation.

Table 3.3. First Cycle: Extraction of Mixed Fission Products

Conditions same as in Table 3.1 except feed spiked with mixed fission products (Purex HAW solution) and 3 extraction and 3 strip stages

	Ru γ, c/m. ml			Zr-Nb γ, c/m. ml		
Stage No.	Org	Aq	E_a^o Ru	Org	Aq	E_a^o Zr-Nb
Feed	-	2.31×10^{6}	-	-	8.3×10^{5}	-
Ext-1	4.76×10^{4}	2.30×10^{6}	0.021	7.2×10^{4}	9.6×10^{5}	0.075
-2	2.19×10^{4}	2.39×10^{6}	0.009	1.74×10^{4}	7.95×10^{5}	0.022
-3	2.38×10^{3}	2.33×10^{6}	0.001	1.07×10^{4}	6.3×10^{5}	0.017
Str-1	880	2.40×10^{5}	3.7×10^{-3}	2.90×10^{4}	2.3×10^{5}	0.13
-2	580	4.47×10^{4}	1.3×10^{-2}	2.31×10^{4}	3.5×10^{4}	0.66
-3	680	1.47×10^{4}	4.6×10^{-2}	2.13×10^{4}	3.3×10^{3}	6.5
	Cs γ, c/m. ml			Total RE β, c/m. ml		
	Org	Aq	E_a^o Cs	Org	Aq	E_a^o RE
Feed	-	1.48×10^{6}	-	-	6.29×10^{6}	-
Ext-1	2.40×10^{4}	1.49×10^{6}	0.016	3.0×10^{6}	2.88×10^{5}	10.4
-2	1.79×10^{4}	1.48×10^{6}	0.012	1.54×10^{5}	9.0×10^{4}	1.71
-3	1.67×10^{4}	1.38×10^{6}	0.012	3.66×10^{4}	7.0×10^{4}	0.52
Str-1	<100	1.4×10^{5}	$<7 \times 10^{-4}$	5.38×10^{5}	1.51×10^{7}	0.036
-2	<50	7.59×10^{3}	$<7 \times 10^{-3}$	1.76×10^{5}	2.10×10^{6}	0.084
-3	<50	924	$<5 \times 10^{-2}$	8.92×10^{4}	3.71×10^{5}	0.24

Table 3.4. Second Cycle: Partitioning of Rare Earths from Strontium

Organic phase: 0.21 M D2EHPA-0.09 M NaD2EHP--0.15 M TBP in Amsco 125-82

Aqueous phase: synthetic first cycle product—0.6 M $NaNO_3$, 0.8 M HNO_3, 0.13 g Sr/liter, 0.40 g Ce/liter, 0.70 g Sm/liter; adjusted to 0.004 M tartrate and to pH 2 with NaOH (dilution factor 1.2) plus tracer Ce-144 or Sr-85

Scrub: 1.2 M $NaNO_3$, pH 2

Strip: 2 M HNO_3

Batch countercurrent runs, 4 extraction stages, 3 scrub stages, 3 strip stages
Feed/extractant/scrub/strip phase ratio: 30/5/5/1

Stage	Aqueous equil. pH	Ce-144 γ, c/m. ml		E_a^o Ce	Sr-85 γ, c/m. ml		E_a^o Sr
		Org	Aq		Org	Aq	
Org Feed	-	2.65×10^5					
Str-3	-	1.12×10^3	2.91×10^4	0.04			
-2	-	6.31×10^3	2.38×10^5	0.03			
-1*	-	3.96×10^4	$1.34\times10^{6*}$	0.03			
Feed	2.0	-	8.31×10^4	-	-	1.07×10^5	-
Scr-3	2.0	5.95×10^5	3.05×10^3	195	29	3	9.7
-2	2.0	5.95×10^5	4.75×10^3	125	29	22	1.3
-1	1.8	6.02×10^5	1.01×10^4	60	44	2.58×10^3	0.02
Ext-1	1.7	5.90×10^5	3.17×10^4	19	197	9.40×10^4	0.002
-2	1.6	2.63×10^5	3.44×10^4	7.7	7.63×10^2	9.32×10^4	0.008
-3	1.6	2.64×10^4	2.39×10^2	110	9.20×10^2	9.45×10^4	0.01
-4	1.8	2.72×10^3	7	390	3.05×10^3	9.40×10^4	0.03

*Strip product: 9.1-9.5 g Ce/liter, 19-21 g Sm/liter, 0.06-0.07 g Na/liter, 1.25 M HNO_3.

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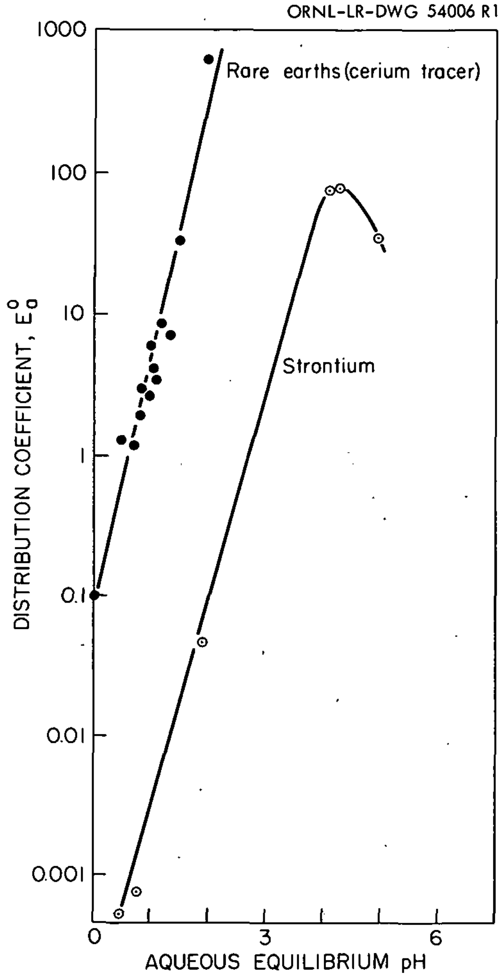

Fig. 3.1. Distribution coefficients of strontium and rare earths under second cycle conditions, showing large separation factor. Organic phase: 0.3 *M* D2EHPA (0.21 *M* D2EHPA—0.09 *M* NaD2EHP)—0.15 *M* TBP in Amsco 125-82; aqueous phase: 1.15 *M* $NaNO_3$, 0.11 g Sr and 0.97 g total rare earths per liter, pH adjusted as shown; o/a phase ratio 1/5.

Third Cycle: Strontium Extraction and Stripping. Essentially all the strontium was recovered in the third cycle strip product, containing 3.2 g of Sr and 8-9 g of Na per liter and 1.3 M HNO_3 (see Table 3.5 for data). This is a strontium concentration factor of 20 over the original waste.

Fourth Cycle: Strontium Extraction and Stripping. The fourth cycle product contained 12.7 g of Sr and 2.9 g of Na per liter, and 1.4 M HNO_3, which represent strontium/sodium separation factors of ~400 based on the original waste, or ~5000 based on the prepared feed, and an overall strontium concentration of 70. Strontium distribution data are given in Table 3.6. The overall strontium/rare earth separation through the fourth cycle should be as large as or larger than the estimated strontium/rare earth separation factor through the second cycle as reported above.

Table 3.5. Third Cycle: Strontium Extraction and Stripping

Organic phase: 0.21 M D2EHPA-0.09 M NaD2EHP—0.15 M TBP in Amsco 125-82
Aqueous phase: second cycle aqueous raffinate, ~0.1 g Sr and 34 g of Na per liter, adjusted to pH 6 with NaOH
Strip: 2 M HNO_3
Batch countercurrent runs, 3 extraction stages, 2 strip stages
Feed/extractant/strip phase ratio: 30/5/1

Stage	Aqueous Equil. pH	Sr-85, γ c/m. ml		E^o_a Sr
		Org	Aq	
Feed	6.0	-	$3.97x10^4$	-
Ext-1	4.1	$2.56x10^5$	$3.37x10^3$	76
-2	4.1	$2.61x10^4$	$8.9x10^2$	28
-3	4.1	$2.42x10^3$	54	45
Str-2	-	66	$1.38x10^4$	0.005
-1	-	640	$1.24x10^6$	0.0005

Table 3.6. Fourth Cycle: Strontium Extraction and Stripping

Organic phase: 0.21 M D2EHPA-0.09 M NaD2EHP--0.15 M TBP in Amsco 125-82
Aqueous phase: third cycle strip product, 3.2 g Sr and 8-9 g of Na per liter, 1.3 M HNO_3, adjusted to pH 6 with NaOH. Dilution factor 1:1
Strip: 2 M HNO_3
Batch countercurrent runs 3 extraction stages, 2 strip stages
Feed/extractant/strip phase ratio: 5/5/1

Stage	Aqueous Equil. pH	Sr-85, γ c/m. ml		E^o_a Sr
		Org	Aq	
Feed	6.8	-	$1.03x10^3$	-
Ext-1	3.9	$1.04x10^5$	$4.44x10^3$	23.5
-2	4.1	$6.22x10^3$	$1.1x10^2$	56.5
-3	4.1	$1.2x10^2$	27	4.45
Str-2	-	$1.5x10^2$	$3.24x10^4$	0.005
-1	-	$4.31x10^3$	$5.33x10^5$	0.008

Solvent Recovery. Iron remaining in the first cycle waste solvent was easily removed by contacting with 0.75 M Na_2CO_3--~0.075 M $Na_2C_4H_4O_6$ solutions, then with 0.5 vol of 10% NaOH, followed by another 0.5 vol of 6 M HNO_3 to remove insolubles. Half the prepared solvent was then converted to the sodium form with 10% NaOH, and equal volumes of acid-form (containing excess nitric acid extracted by the TBP) and sodium-form solvent were combined to give 0.21 M D2EHPA--0.09 M NaD2EHP.

Although this batch solvent treatment proved satisfactory in small-scale tests, continuous methods would be preferable in plant operation. The acid solvent would be contacted with 0.75 M Na_2CO_3—0.075 M $Na_2C_4H_4O_6$ in 2-3 stages, o/a = 3/2, and subsequently acidified to 0.21 M D2EHPA—0.09 M NaD2EHP--0.15 M TBP in Amsco 125-82.

Solvent Makeup. Di(2-ethylhexyl)phosphoric acid, as received, normally contains iron and other impurities which, when contacted with caustic, form precipitates. In laboratory tests the solvent, 0.3 M D2EHPA--0.15 M TBP in Amsco 125-82, was ordinarily pretreated by contacting with 0.5 vol of 6 M HNO_3.

3.2 Pulsed Column Tests of First Cycle Strontium Extraction

A continuous pulsed column test of the first cycle strontium extraction (Fig. 2.1) was made to evaluate the operability of aqueous-continuous phase contacting in this equipment and to obtain preliminary data on stage heights, strontium recovery, and iron extraction. The Sr-85 data (Table 3.7) show that the system approached steady state rapidly and did not fluctuate significantly after about one column volume throughout. In general, material balances for strontium and iron were 100 ± 1% based on analyses of the organic product and aqueous raffinate streams. Nearly all the strontium and only a small percentage of the iron were extracted. In batch tests with the same aqueous and organic feed solutions, 5-6 times as much iron was extracted during a 10-min equilibration as during a 1-min equilibration (Table 3.8). No significant difference was observed between the amounts of strontium extracted in the 1- and 10-min contacts. About 50% less iron was extracted in the pulsed column than in 60-sec batch contacts at a phase ratio (o/a) of 2. This is apparently due to more efficient phase contacting in the batch tests than in the pulsed column.

By correlating the strontium distribution coefficient of 7.6 from the batch tests, at a phase ratio (o/a) of 2 and 1 min phase contact, with the strontium losses in the pulsed column, the stage height for strontium extraction in the pulsed column was calculated to be 21.4 in.; thus, the 33-in. pulsed column contained 1.54 extraction stages.

Table 3.7. First Cycle: Pulsed Column Demonstration of Strontium Recovery

Organic phase: 0.21 M D2EHPA—0.09 M NaD2EHP—0.15 M TBP in Amsco 125-82
Nonradioactive aqueous phase: synthetic Purex waste, 0.5 M Fe^{3+}, 1 M $SO_4^=$, 0.1 M Al^{3+}, 0.01 M Ni^{2+}, Cr^{3+}, $UO_2{}^{2+}$, 0.17 g Sr^{2+} per liter, adjusted to 0.33 M $Na_2C_4H_4O_6$, and to pH 5.9 with 5 M NaOH; dilution factor = 3
Radioactive aqueous phase: Same as above but containing 1.09×10^5 Sr-85 γ c/m. ml
O/a phase ratio: 2/1

	Organic Product				Aqueous Raffinate			
Time Elapsed, hr	Sr-85, γ c/m. ml	Fe, mg/ml	% Extracted[a] Sr	Fe	Sr-85, γ c/m. ml	Fe, mg/ml	% Not Extracted[a] Sr	Fe
0.75	5.0×10^4	0.146	91.4	3.14	4×10^1	9.0	0.037	97
1.25	5.4×10^4		98.8		3.7×10^2		0.338	
1.75	5.4×10^4		98.8		8.2×10^2		0.75	
2.25	5.6×10^4		102.5		1.5×10^3		1.35	
2.75	5.5×10^4	0.165	101.0	3.55	1.5×10^3	9.1	1.37	98
3.25	5.4×10^4		99.5		1.5×10^3		1.34	
3.75	5.5×10^4		100.0		1.5×10^3		1.35	
4.25	5.4×10^4		99.5		1.4×10^3		1.31	
4.75	5.4×10^4		99.5		1.6×10^3		1.46	
5.25	5.4×10^4	0.153	99.5	3.29	1.5×10^3	8.9	1.33	96

[a] Based on analysis of aqueous feed and the flow ratio of the respective solutions.

The 0.75-in.-dia glass pulsed column consisted of 33 in. of pulse plates spaced on 1-in. centers with 9-in.-high by 1.75-in.-o.d. enlarged sections on both top and bottom of the column. The inlet and exit tubes for the organic and aqueous streams were welded into the enlarged sections. The organic extractant stream, 0.09 M NaD2EHP—0.21 M D2EHPA—0.15 M TBP in Amsco 125-82, was pulsed at 72 cycles/min at an amplitude of 1/16 in. with a Research Appliance stainless steel bellows pump and fed into the lower enlarged section. In addition to the pulser on the organic extractant stream, the entire column was pulsed at 29 cycles/min with an amplitude of 1/4 in. to provide adequate phase mixing. The aqueous feed was metered into the upper enlarged section above the pulse plates by a sigma pump powered by a 0.5-hp electric motor through a hydraulic transmission.

Table 3.8. Batch Distribution Data for Strontium and Iron between Organic and Aqueous Feed Solutions

Organic and aqueous phases identical to those given in Table 3.6

Vol Ratio, o/a	60 sec Contact						10 min Contact					
	Sr-85, γ c/m. ml		E_a^o Sr	Fe Conc, mg/ml		E_a^o Fe	Sr-85, γ c/m. ml		E_a^o Sr	Fe Conc, mg/ml		E_a^o Fe
	Org	Aq		Org	Aq		Org	Aq		Org	Aq	
1	9.44×10^4	1.45×10^4	6.5	0.51	8.4	0.061	9.65×10^4	1.21×10^4	8.0	2.42	6.7	0.36
2	5.14×10^4	6.7×10^3	7.6	0.31	8.2	0.038	5.0×10^4	8.1×10^3	6.2	1.27	6.7	0.19
3	3.5×10^4	4.4×10^3	8.0	0.18	8.7	0.020	3.49×10^4	5.3×10^3	6.6	0.83	6.7	0.124

After the column had operated smoothly for several hours, a synthetic feed that contained 1.09×10^5 Sr-85 γ c/m. ml was substituted for the nonradioactive feed. After 3/4 hr operation with this feed, the organic product and the aqueous raffinate streams were sampled and analyzed. Sr-85 was determined in samples of the product and raffinate streams at 0.5-hr intervals for 4.5 hr, and iron was determined at 0.75, 2.75, and 5.25 hr.

The volumes of the plate section of the column and the enlarged sections were measured and found to be:

Lower enlarged section up to 1st plate	200 ml
Body of column, pulse plate section	275
Upper enlarged section from top of pulsed plate section to interface position	100
Total aqueous volume, not including organic volume during operation	575 ml

The organic extractant and aqueous feed rates were 800 and 400 ml/hr, respectively. These flow rates were based on measurements of the organic product and aqueous raffinate flow rates to eliminate the need for rotameters on the feed and extractant streams. Under these conditions, 1.44 hr was required for each aqueous column volume change.

3.3 Iron Extraction and Stripping in the First Cycle in Pulsed Columns and Mixer-Settlers

Both pulsed columns and mixer-settler contactors were operated successfully in laboratory-scale tests of the first cycle. That the type of mixing was not critical was shown by the good physical operability with organic-continuous mixing in mixer-settlers and with aqueous-continuous mixing in small pulsed columns. In a continuous countercurrent experiment, to study the physical and chemical operability of the first cycle with particular emphasis on iron extraction, a pulsed column was used for the extraction section and four mixer-settler units for the stripping section. The unclarified feed was contacted by the solvent in the aqueous-phase—continuous column, o/a = 2. The organic phase was stripped with 2 M HNO_3 in organic phase—continuous mixer-settlers, o/a = 5/1. Analyses of end stream samples (Table 3.9a) showed that only 0.013% of the iron in the feed was subsequently stripped into the strip section aqueous product. This compares to 0.17% found in batch countercurrent experiments (Sect. 3.1).

When the pulsed column was replaced with four mixer-settler units and four mixer-settler units were used for the stripping section, the organic-continuous system operated smoothly with the same solutions. However, 0.44% of the iron in the feed was subsequently stripped into the first cycle strip product (Table

3.9b), giving a higher iron concentration than in the pulsed column product. This increased extraction of iron is due to the longer residence time in the mixers and possibly also to aqueous entrainment in the organic phase between the extraction and strip sections.

Table 3.9. Continuous Countercurrent Extraction and Stripping of Strontium and Rare Earths

	Conc, g/liter				H^+,
Sample	Sr	Rare Earths[x]	Na^+	Fe	M
a. Pulsed-column extraction section, mixer settlers stripping section					
Feed	0.057	0.44	65	9.2	pH 6
Extractant	-	-	1.9	-	0.23
Extraction column Product (org)	-	-	-	0.182	-
Extraction column Raffinate (aq)	-	-	-	8.2-9.3	-
Strip section Product (aq)	0.11-0.13	0.8-0.93	12-15	0.003	1.0-1.2
Strip section Raffinate (org)	-	-	-	0.17-0.19	0.36

	Conc, g/liter				H^+,
Sample	Sr	Rare Earths[x]	Na^+	Fe	M
b. Mixer settlers for both extraction and stripping sections					
Feed	0.057	0.44	65	9.0	pH 6
Extractant	-	-	1.9	-	0.23
Ext. section Product (org)	-	-	-	1.86	-
Ext. section Raffinate (aq)	-	-	-	5.4	-
Strip section Product (aq)	-	-	12-15	0.08-0.1	0.9-1.2
Strip section Raffinate (org)	-	-	<0.05	1.7	0.3

[x] Rare earth determination of questionable accuracy.

3.4 Flowsheet Tests in Miniature Mixer-Settlers

As soon as containment changes have been made in Bldg. 4507 at ORNL, the proposed solvent extraction process for strontium and rare earth recovery from Purex waste will be tested in miniature mixer-settlers on actual plant high activity feed. In preparation for these experiments, the mixer-settler equipment was tested through three cycles with nonradioactive simulated feed solutions using the chemical flowsheet shown in Fig. 2.1.

The apparatus consisted of three banks of Knolls-type mini mixer-settlers, one of which was held in standby. The extraction and extraction-scrub banks contained 16 stages and the strip bank 8 stages. All entering streams were metered with Lapp Pulsafeeder pumps. End-stream samples were taken at about 4-hr intervals during single 8-hr shifts. For the nonradioactive tests, the apparatus was assembled and run in the operating area of Bldg. 4507. The equipment was then reassembled for high-activity experiments in cell 2, Bldg. 4507 (Fig. 3.2).

3.4.1 First Cycle Demonstration

Feed Preparation. Simulated Purex waste (Table 2.1) was made initially 1 M in tartrate and then adjusted to pH 6 with 5 M NaOH; the overall dilution factor was 3 with a final tartrate concentration of about 0.33 M. The prepared feed (Table 2.1) was filtered through glass wool to remove traces of siliceous and phosphate solids which otherwise might have plugged the capillary tubing in the mixer-settler apparatus.

Extraction and Stripping. The solvent (1AX), 0.21 M D2EHPA—0.09 M NaD2EHP—0.15 M TBP in Amsco 125-82, and the adjusted feed (1AF) were metered into the first and eighth stages, respectively, of the 16-stage bank at an o/a phase ratio of 2. The remaining eight stages in the extraction section were used as a flow line to the stripping section (Fig. 3.3) and not as extractors. Data from batch countercurrent experiments indicated that four stages in each section would provide efficient extraction and stripping. Operating experience,[8] however, showed that the mini mixer-settler stages are about 50% efficient and the actual number of stages was accordingly increased in all three cycles. The organic stream (1AP) from the extraction section was cascaded to the eight-stage stripping bank and contacted with 2 M HNO_3 (1BX) at an o/a phase ratio of 5/1. Stream flow rates were maintained at: 1AF, 1 ml/min; 1AX, 2 ml/min; 1BX, 0.4 ml/min.

Partial analyses of the first cycle feed and end stream samples (Table 3.10) showed better iron separation than was expected. Even though the amount of iron that was extracted and subsequently stripped into the first cycle product increased slightly throughout the 17 hr operating time, it only reached 4.8% of that in the feed extracted and 0.02% stripped, a separation factor of 4.4×10^3. The quantities after the first 3 hr of operation were 3.3% extracted and 0.01% stripped into the product (Table 3.11).

Because of analytical difficulty[9] with both strontium and rare earths in feed samples, and to some extent in the product samples, data on recovery of these metals in this run were not dependable.

Phase separation and general operation of the equipment with these synthetic solutions were excellent; end streams showed no evidence of phase entrainment, precipitates, or emulsions.

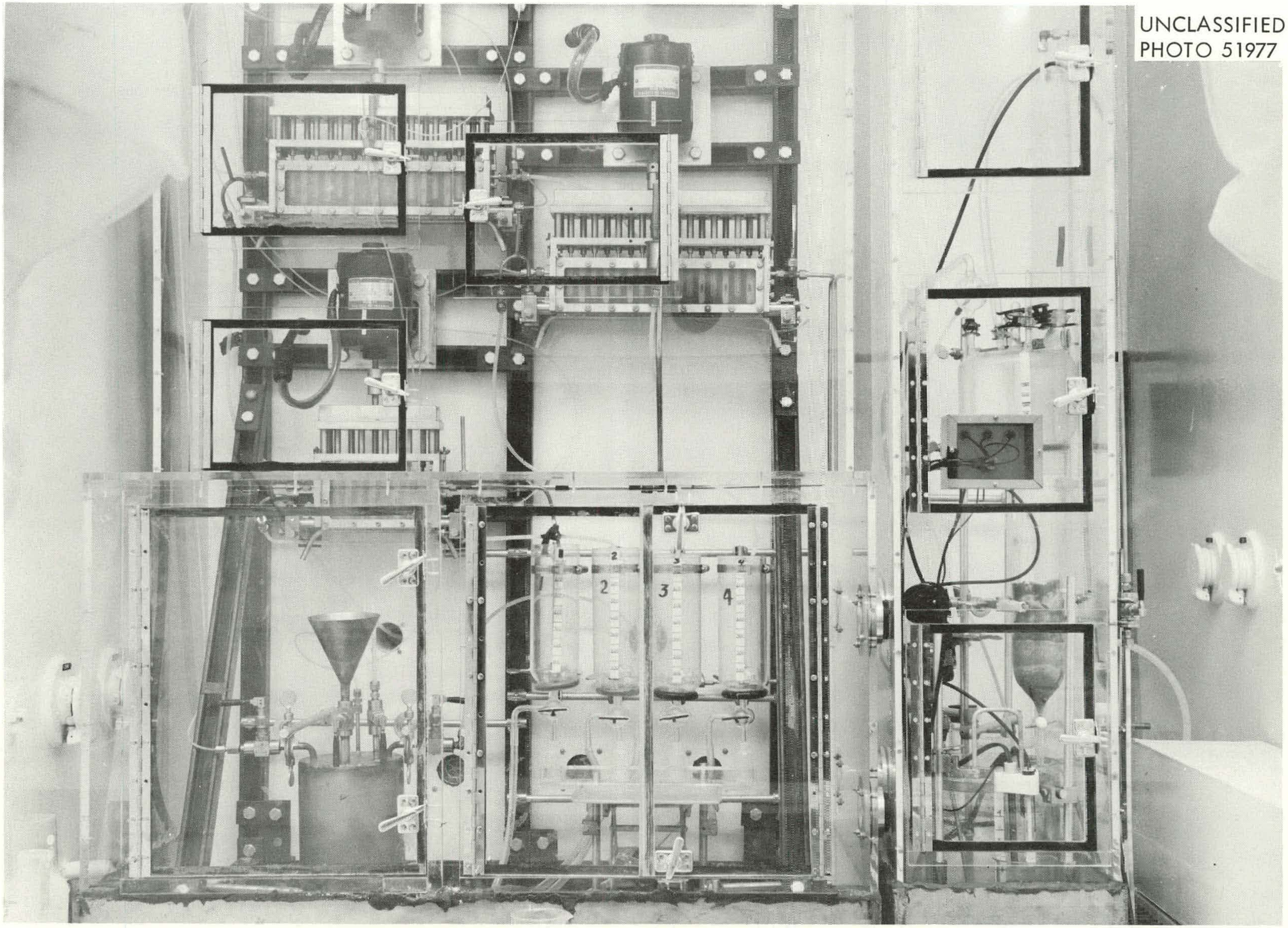

Fig. 3.2. Miniature mixer-settler apparatus assembled in hot cell, Bldg. 4507.

Table 3.10. Composition of End Stream Samples: First Cycle of Fission Product Recovery Flowsheet

		Conc, g/liter				
Sample	Operating Time, hr	Sr	Rare Earths	Na	Fe	H, M
1WW	-			10.6	29	
1AF	-			55	9.6	
1AX	-			1.80	0.011	0.24
1AP-1	3			2.5	0.157	
-2	8.5			2.5	0.162	
-3	12			2.6	0.194	
-4	17			2.6	0.23	
1AW-1	3			60	9.3	
-2	8.5			59	9.2	
-3	12			63	9.1	
-4	17			56	8.9	
1BP-1	3			11.8	0.0026	
-2	8.5			14.0	0.0027	
-3	12			12.2	0.0037	
-4	17			12.2	0.0055	
1BP Comp-1	3-8 hr interval	0.098	0.84	12.6	00.0027	
-2	12-16 hr interval	0.085	0.82	11.6	0.0043	1.37
1BW-1	3			0.025	0.159	
-2	8.5			0.015	0.125	
-3	12			0.025	0.182	
-4	17			0.050	0.20	

Table 3.11. Strontium-Iron Separation in First Cycle

	% of Fe initially in Feed Solution		
Operating Time, hr	Extracted into 1AP	Stripped into 1BP	Sr/Fe Separation Factor
3	3.3	0.01	9.25×10^3
8.5	3.4	0.01	
12	4.0	0.02	
17	4.8	0.02	4.36×10^3

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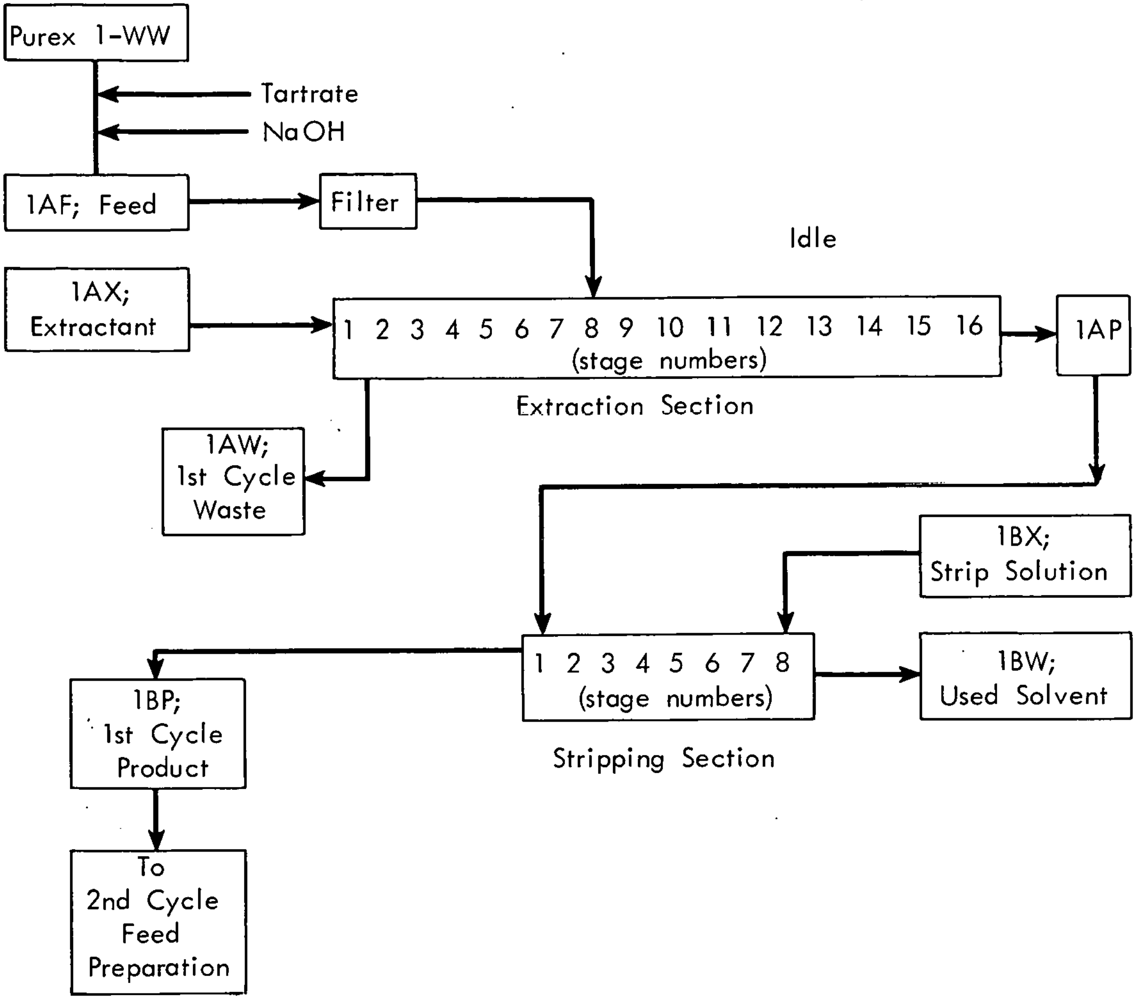

Fig. 3.3. Nomenclature of streams and sketch of mini mixer settler apparatus used in nonradioactive tests of first cycle Sr-RE recovery flowsheet.

3.4.2 Second Cycle Demonstration

Rare Earth—Strontium Partitioning. After completion of the first cycle experiment, the equipment was cleaned and used for the second cycle (Fig. 2.1). The same arrangement of apparatus was used except that a scrub stream was added to the extraction section (Fig. 3.4). The 16-stage bank was divided into eight extraction and eight scrub stages; the strip section contained eight strip stages.

Feed Preparation. A simulated first cycle strip product (1BP) was adjusted to 0.004 M tartrate and then to pH 2 with NaOH for makeup of the second cycle feed (2AF), which contained 0.083 g of Sr, 0.91 g of RE, 33 g of Na, and 0.013 g of Fe per liter and 0.003 M tartrate.

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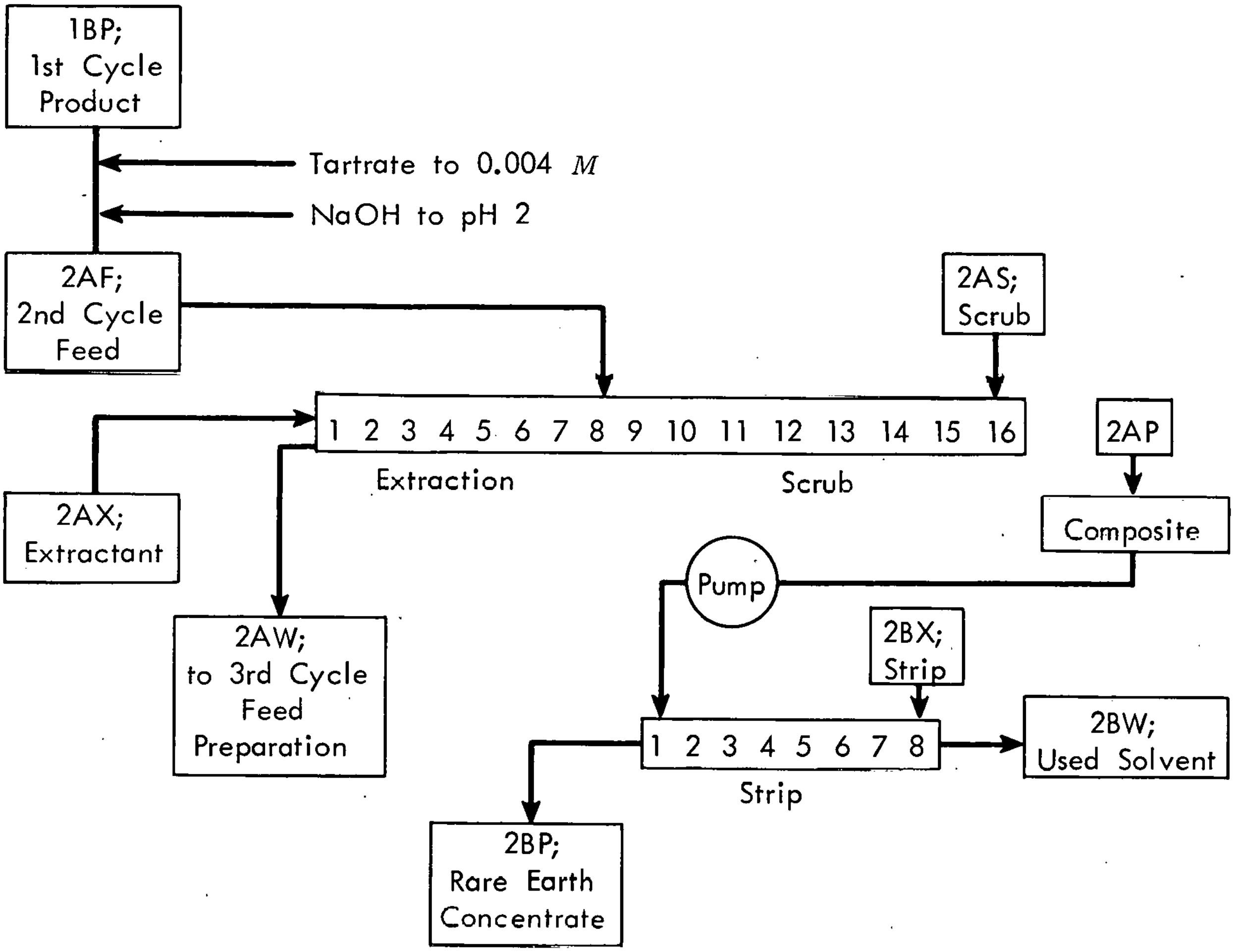

Fig. 3.4. Nomenclature of streams and sketch of mini mixer settler apparatus used in nonradioactive tests of second cycle of Sr-RE recovery flowsheet.

<u>Extraction, Scrubbing, Stripping</u>. The rare earths were selectively partitioned from strontium and other components by contacting the feed (2AF) with the solvent (2AX) and scrubbing the extract with 1.2 M $NaNO_3$, pH 2 (2AS). The organic product (2AP) was collected for subsequent feed to the strip section, where the rare earths and traces of sodium were stripped with 2 M HNO_3 (2BX). Because of flow rate limitations, the strip section mixer-settlers and pumps could not be operated simultaneously with the extraction-scrub section. The stripping section was run later with the flow rates shown in Table 3.12. The equipment is limited in that the minimum flow for any given pump is 0.25 ml/min. In the planned high-activity-level experiments, to allow simultaneous operation of the extraction-scrub and strip section the strip section will be run at an o/a phase ratio of 2 rather than the flowsheet ratio of 5. This

change will result only in a dilution of the second cycle rare earth product.

Table 3.12. Stream Flow Rates for Second Cycle

Stream	Flow Rate, ml/min
Feed (2AF)	3.0
Extractant (2AX)	0.5
Scrub (2AS)	0.5
Strip section feed (2AP)	3.0
Strip (2BX)	0.6

Operation of the stripping section was determined by analyses of end stream composites (Table 3.13). The rare earths initially in the stripping section organic feed were 98.2% stripped into the 2BP, leaving 1.8% in the solvent raffinate (2BW).

Table 3.13. Composition of End Stream Samples: Second Cycle of Fission Product Recovery Flowsheet

Sample	Operating Time, hr	Conc, g/liter				H, M
		Sr	Rare Earths	Na	Fe	
2AF	-	0.083	0.91	33	0.013	
2AP-1	6	<0.05	6.5	0.029	0.048	
-2	9.5	<0.05	5.7	0.026		
-3	13.6	<0.05	5.4	0.023	0.048	
-4	17	<0.05	5.8	0.014		
-5	21.3	-	5.7	0.018	0.047	
-6	25.5	<0.05	5.1	0.014		
-7	28.5	<0.05	5.2	0.014	0.048	
-8	32.5	<0.05	5.4	0.013		
-9	36.5	<0.05	5.4	0.016	0.046	
2AW-1	5.5	0.082	<0.005	35		
-2	9.3	0.064	<0.005	35		
-3	13.5	0.078	<0.01	34		
-4	16.8	0.058	<0.01	33		
-5	21	0.067	<0.01	32		
-6	25	0.075	<0.01	32		
-7	28	0.070	<0.01	34		
-8	32	0.071	<0.005	38		
-9	36	0.078	<0.005	37		
2AP*	36.5	<0.05	5.5	0.029	0.047	0.12
2BP*	4	<0.05	27	0.019	0.003	1.43
2BW*	4	<0.05	0.099	0.009	0.041	0.40

*Composites of flowing streams.

The rare earth/sodium separation factor over the entire second cycle was 5×10^4, the rare earth/iron separation factor was 130, and the rare earth concentration factor was 30. Rare earth/strontium separations are not reported since strontium concentrations in the rare earth product were below detection limits. Rare earth losses to the solvent raffinate (2BW) could be nearly eliminated, if desired, by adding additional strip stages or, alternatively, by decreasing the o/a phase ratio.

3.4.3 Third Cycle Demonstration

Strontium Extraction and Concentration. The second cycle aqueous raffinate (2AW) was adjusted to pH 6 with 5 M NaOH to provide third cycle feed (3AF). The third cycle used eight extraction stages and eight strip stages (Fig. 3.5). Strontium was extracted (Fig. 2.1) by a solvent of the same composition as that in the first and second cycles. The strontium-bearing organic phase was then cascaded to the stripping section where strontium and sodium (from NaD2EHP) were co-stripped with 2 M HNO_3. The organic stream (3AP) from the extraction section was

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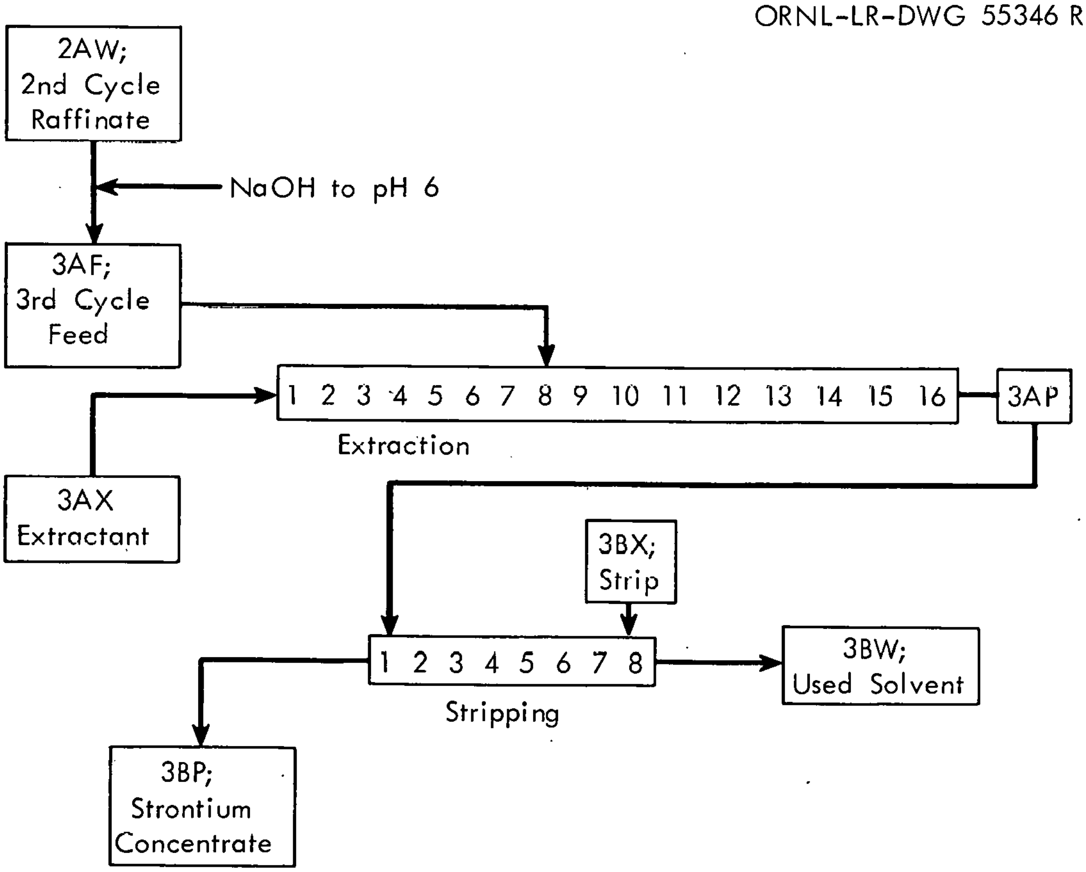

Fig. 3.5. Nomenclature of streams and sketch of mini mixer settler apparatus used in nonradioactive tests of third cycle of Sr-RE recovery flowsheet.

composited for subsequent feed to the stripping section. As discussed above, this technique allowed the stripping section to be run at an o/a phase ratio of 5. In high-activity-level experiments the stripping section will be run at an o/a phase ratio of 2 so that the organic stream (3AP) can be cascaded directly to the stripping section rather than composited. The flow rates used for this experiment are shown in Table 3.14.

Table 3.14. Stream Flow Rates for Third Cycle

Stream	Flow Rate, ml/min
Feed (3AF)	3.0
Extractant (3AX)	0.5
Strip section feed (3AP)	3.0
Strip (3BX)	0.6

Analyses of the end stream from the third cycle (Table 3.15) show high strontium losses to the raffinate (3AW) during startup; however, after 19 hr of operation, strontium losses were below analytical detection limits.

Table 3.15. Composition of End Stream Samples: Third Cycle of Fission Product Recovery Flowsheet

Sample	Operating Time, hr	Conc, g/liter Sr	Na	Fe	H, M
3AF		0.078	35	0.005	-
3AP-1	6	0.43	1.50		
-2	10.6	0.44	1.53		
-3	15.3	0.43	1.54		
-4	19.2	0.44	1.54		
-5	23.5	0.40	1.35		0.24
-6	28	-	-		0.24
-7	32	0.41	1.38		0.24
-8	34.7	0.39	1.57		-
3AW-1	6	0.080	37		
-2	10.6	0.077	38		
-3	15.3	0.026	38		
-4	19.2	<0.02	38		
-5	23.5	<0.01	35		-
-6	28	<0.01	35		-
-7	32	<0.02	32		-
-8	34.5	<0.02	34		-
3AP*		0.47	1.55	0.037	0.086
3BP-1*	3.8	2.3	7.6	0.001	1.45
-2*	4.3	2.4	8.8	0.001	1.45
3BW-1*	3.3	<0.02	<0.01	0.031	0.17
-2*	4	<0.02	<0.01	0.026	0.16

*Composites of flowing streams.

In the stripping section essentially all the extracted strontium was recovered in the product (3BP); strontium losses to the used solvent (3BW) were below detection. About 0.8% of the iron in the third cycle feed was present in the strontium product, giving a strontium/iron separation factor of 108. The strontium/sodium separation factor was 130 and the strontium concentration factor was 30.

4.0 PROCESS CHEMISTRY STUDIES

It has been reported[10] that strontium can be extracted by di-2-ethylhexyl phosphate from very weak acidic or alkaline solutions. In first attempts to apply this system to strontium recovery from Purex wastes, tests were made in which (1) the waste was neutralized and the iron hydroxide and other insoluble hydroxides were filtered off prior to strontium extraction[4] and (2) the waste was neutralized and the resulting slurry was extracted directly. However neither method was attractive from a process standpoint. In agreement with previous work[11-13], in method 1, the voluminous hydroxide precipitate carried a large part of the strontium as well as placing other fission products in a form less suitable for subsequent recovery. The second method suffered from the same disadvantages and was also subject to slow phase separations and emulsions during the extraction step.

In further tests the addition of complexing agents to the waste prevented precipitation during pH adjustment and extraction and established the basis for a workable recovery process.

4.1 Addition of Complexing Agents

Tartrate, citrate, thiocyanate, and salicylate present in sufficient concentration before Purex waste[4] was neutralized with NaOH prevented precipitates over the pH range 2-12. The tartrate ion was selected as the additive to be used in further process studies although there appeared to be little difference in the complexing ability and operation of the tartrate- and citrate-complexed systems. Further studies may show still other complexing systems to be as good as or superior to tartrate.

4.2 Effect of pH on Strontium Extraction

When the aqueous phase was neutralized with 5 M NaOH (curve A , Fig. 4.1), the strontium distribution coefficient increased from 0.06 at pH 2.9 to a maximum of 9.5 at pH 5.3 and decreased to 0.23 at pH 8.2. When it was neutralized with 19 M NaOH (curve B), the strontium distribution coefficients were about a factor of 3 lower for a given equilibrium aqueous pH, probably because of the higher Na^+ concentration which competes with strontium for the extractant. These aqueous solutions were also more viscous and the phases separated more slowly than in

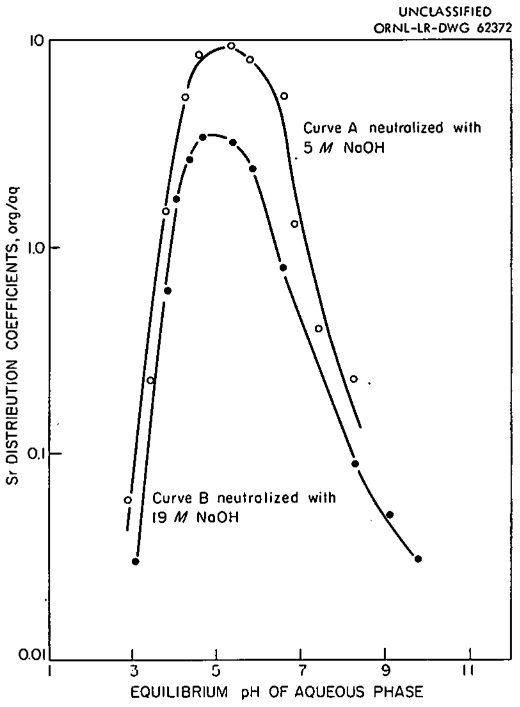

Fig. 4.1. Strontium distribution from tartrate-complexed synthetic Purex waste as function of equilibrium pH. Organic phase: 0.3 *M* D2EHPA—0.15 *M* TBP in Amsco 125-82; aqueous phase: synthetic Purex waste, tartrate-complexed and neutralized to various pH's with 5 *M* and 19 *M* NaOH; o/a phase ratio: 1.0.

the first series. From a process standpoint, the extraction of strontium by D2EHPA is about optimum from a tartrate-complexed waste solution neutralized and diluted a factor of 2.5-3 with 5 M NaOH to an aqueous pH between 4.2 and 6.5. Strontium E_a^o's were ≥5 over this pH range (Table 4.1). The pH can be easily controlled in the pH range 4.2-6.5 since the NaD2EHP-D2EHPA in the organic phase gives good buffering supplemented by some buffering from tartrate in the aqueous phase.

In these experiments a series of synthetic waste samples, initially 1 M in tartrate ion and containing Sr-85, were adjusted over the pH range 3-10 with 5 M NaOH. Another series was prepared by adjusting the pH with 19 M NaOH. These solutions were then batch-equilibrated for 10 min with an equal volume of solvent containing ~0.3 M D2EHPA and 0.15 M TBP in Amsco 125-82.

4.3 Effect of Sulfate Concentration on Strontium Extraction

The sulfate ion concentration in Purex waste has been reported to vary between 0.75-1.5 M. Since sulfate might be expected to have significant affinity for strontium, the extraction of strontium tracer by D2EHPA was studied as a function of the aqueous sulfate ion concentration, but extraction of strontium tracer by D2EHPA from a mixed $NaNO_3$-Na_2SO_4 aqueous phase

Table 4.1. Distribution Coefficients (org/aq) for Sr-85 between D2EHPA-TBP and Adjusted Synthetic Purex Waste

Organic phase: 0.3 M D2EHPA (mixture of NaD2EHP + D2EHPA), 0.15 M TBP, Amsco 125-82 diluent
Aqueous phase: synthetic Purex waste adjusted to 0.42 M $Na_2C_2H_4O_6$ and various initial pH's with 5 M NaOH and to 0.67 M $Na_2C_4H_4O_6$ and various initial pH's with 19 M NaOH
O/a phase ratio: 1.0
Equilibration time: 10 min
Sr-85 determined by deep-well γ-scintillation technique

Waste Neutralized with 5 M NaOH, Dilution Factor ~2.4		Waste Neutralized with 19 M NaOH, Dilution Factor ~1.5	
Equilibrium pH of Aqueous Phase	Sr E_a^o (tracer only)	Equilibrium pH of Aqueous Phase	Sr E_a^o (initial Sr Conc 0.17 g/liter)
0.93	<0.02	-	-
2.1	<0.002	-	-
2.9	0.06	-	-
3.4	0.23	3.1	0.03
3.7	1.5	3.8	0.62
4.2	5.3	4.0	1.7
4.5	8.6	4.3	2.6
5.3	9.5	4.6	3.4
5.7	8.2	5.3	3.2
6.5	5.5	5.8	2.4
6.8	1.3	6.5	0.79
7.4	0.40	8.1	0.09
8.2	0.23	9.1	0.05
12.8	<0.001	9.8	0.03

was essentially the same as when extracted from a $NaNO_3$ solution free of sulfate (Table 4.2). Similar to previous tests, in both the presence and absence of sulfate, the strontium distribution coefficients increased rapidly as the aqueous pH increased from ~2 to ~5. The distribution coefficient was maximum at about pH 5, and then decreased to a constant value over the pH range of 8-12. The constancy of the coefficient over the pH range 8-12 is in contrast to the continued decrease in strontium coefficient in the tartrate-complexed system (Sect. 4.2). Increasing the D2EHPA concentration from 0.1 to 0.3 M increased the strontium distribution coefficients by a factor of about 3.

In order to minimize the number of variables, the initial aqueous solutions were HNO_3 or HNO_3-H_2SO_4 mixtures and did not contain any of the other usual components of the waste. Three acid solutions were prepared with sulfate concentrations of 0.0 M, 0.5 M, and 1.0 M and HNO_3 to give a total acid concentration of 4 M. Aliquots containing Sr-85 tracer with no tartrate ion added were neutralized with 5 M NaOH to different aqueous pH values.

The respective sulfate-ion concentrations were 0.0, 0.25, and 0.52 M after neutralization.

Table 4.2. Extraction of Sr-85 by D2EHPA from $NaNO_3$-Na_2SO_4 Solutions

Aqueous phase: three stock solutions, total H^+ = 4 M;
0.0 M, 0.50 M, and 1.0 M $SO_4^=$, respectively; Sr-85 tracer, distilled water, and 5 M NaOH added to adjust pH and decrease the $SO_4^=$ concentration to 0.0 M, 0.25 M, and 0.52 M, respectively
O/a phase ratio: 1.0
Equilibration time: 10 min

0.0 M $SO_4^=$		0.25 M $SO_4^=$		0.52 M $SO_4^=$	
Equil. pH	Sr E_a^o	Equil. pH	Sr E_a^o	Equil. pH	Sr E_a^o
Extractant: 0.1 M D2EHPA — 0.1 M TBP — Amsco 125-82 diluent					
2.2	0.01	2.2	0.003	2.0	0.005
4.4	13.0	4.4	10.1	3.6	0.18
5.2	9.2	4.7	9.1	3.7	0.92
5.4	1.9	5.0	6.8	4.2	7.8
7.6	0.63	5.2	3.9	4.3	9.6
8.8	0.62	6.2	2.9	4.5	8.3
9.3	0.61	8.7	0.45	7.7	0.38
10.1	0.55	10.0	0.47	9.7	0.38
Extractant: 0.3 M D2EHPA — 0.15 M TBP — Amsco 125-82 diluent					
2.2	0.07	2.2	0.005	2.0	0.29
3.2	48.5	2.9	1.26	2.6	0.35
3.8	21.2	3.6	10.0	3.3	3.7
4.6	25.7	4.4	19.2	4.1	15.4
5.4	6.3	5.0	13.6	4.6	18.6
6.1	4.0	5.3	4.8	5.8	4.4
11.3	3.4	11.2	2.6	7.7	2.1
11.6	3.1	11.7	2.5	11.8	2.0

The respective sulfate-ion concentrations were 0.0, 0.25, and 0.52 M after neutralization.

4.4 Effect of Tartrate Concentration on Strontium Extraction

Strontium extraction decreased with increasing aqueous tartrate concentration, at constant pH, Na^+, and D2EHPA (Fig. 4.2). This indicates appreciable competition for strontium between tartrate in the aqueous phase and D2EHPA in the organic phase. For process purposes the optimum tartrate concentration is set at a $C_4H_6O_6^=$/Fe mole ratio of 2. Thus with the current waste, containing 0.5 M Fe, feed is prepared by adding 1 mole of tartrate per liter prior to pH adjustment. Larger amounts of tartrate would not significantly interfere with the process, but decreasing the above ratio to 1.5 occasionally resulted in precipitation of hydrous iron oxide.

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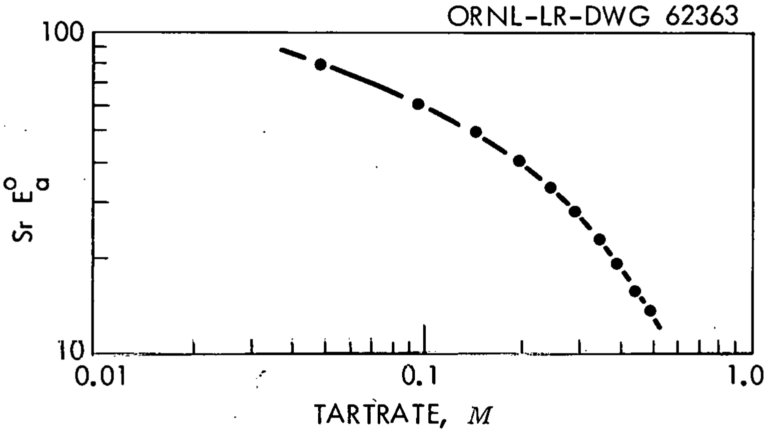

Fig. 4.2. Strontium distribution as a function of aqueous tartrate concentration. Organic phase: 0.3 M D2EHPA—0.15 M TBP in Amsco 125-82; aqueous phase: 0.0 to 1.0 M $NaNO_3$—0.5 to 0.0 M $Na_2C_4H_4O_6$, pH 3.9-4.6; o/a phase ratio 1.0.

4.5 Effect of Aqueous Sodium Concentration on Strontium Extraction

The effect of sodium ion concentration on strontium extraction by D2EHPA was examined briefly in extractions from 0.3 to 5.0 M $NaNO_3$ solutions, pH 5, containing Sr-85 tracer. The strontium distribution coefficient decreased as the sodium ion concentration increased according to the relation $Sr_a^o \approx [Na^+]^{-1.6}$ (Table 4.3, Fig. 4.3). Even in fairly concentrated sodium ion solutions, however, the strontium distribution coefficient is sufficiently large for good recovery.

Table 4.3. Strontium Extraction as a Function of Sodium Concentration

Organic phase: 0.21 M D2EHPA—0.09 M NaD2EHP—0.15 M TBP in Amsco 125-82; ~0.03 g Sr/liter; ~4.5×10^4 Sr-85 γ c/m. ml
Aqueous phase: 0.3-5.0 M $NaNO_3$, pH 5
O/a phase ratio: 1

Aqueous $NaNO_3$, M	Sr E_a^o
0.3	835
0.5	500
1.0	111
2.0	31
5.0	12

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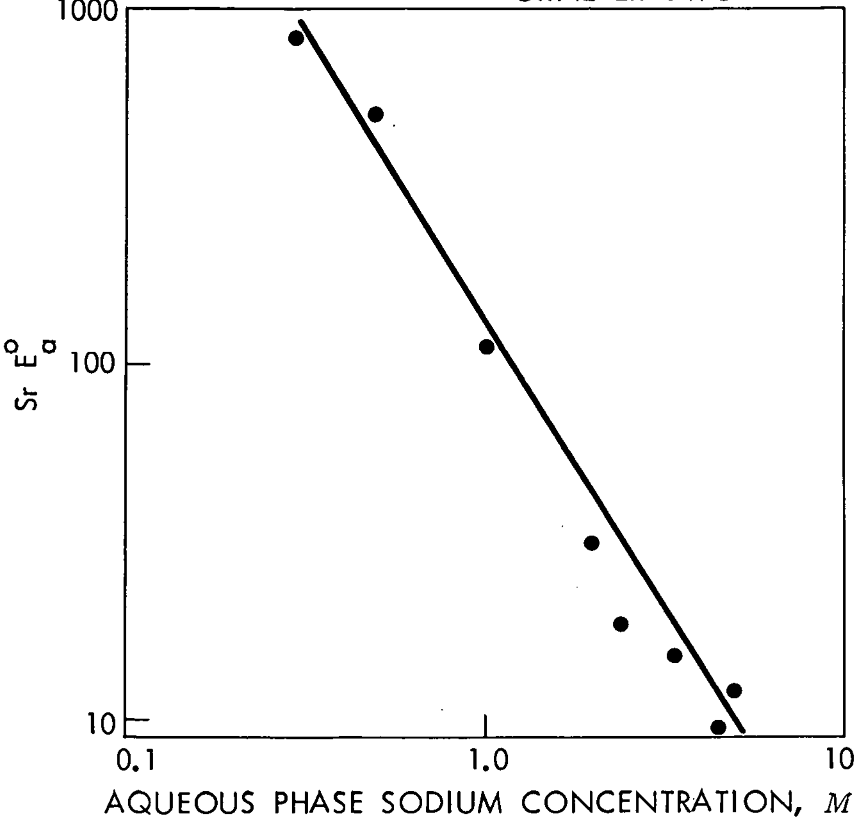

Fig. 4.3. Strontium distribution as a function of aqueous sodium concentration. Organic phase: 0.3 *M* D2EHPA—0.15 *M* TBP in Amsco 125-82; aqueous phase: 0.3 to 5 *M* $NaNO_3$—0.03 g Sr/liter, equilibrium pH 5; o/a phase ratio: 1.0.

4.6 Effect of Iron on the Strontium Extraction from Na_2SO_4-$Na_2C_4H_4O_6$ Solutions

In cursory studies the effect of iron on strontium extractions by solvent of the usual composition was examined by comparing extractions from solutions containing 2.4 M Na^+, 1 M $SO_4^=$, 0.2 M $C_4H_4O_6^=$ with and without the presence of 0.1 M $Fe(NO_3)_3$. Sr-85 tracer was added to each solution to give a counting rate of ~10^4 γ c/m. ml. When no iron was present there was a sharp strontium extraction maximum, which upon addition of iron was broadened over several pH units (Fig. 4.4, Table 4.4). Without iron in the aqueous phase, the strontium distribution coefficient was almost constant over the pH range 7-12, but when iron was present it continued to decrease from the maximum of ~8 at pH 5.5 to 0.05 at pH 12. This curve for extraction from the Na^+, $SO_4^=$, $C_4H_4O_6^=$, Fe^{3+} solution closely approximates that for extraction of strontium by D2EHPA from a NaOH-neutralized tartrate-complexed synthetic Purex waste (Sect. 4.2).

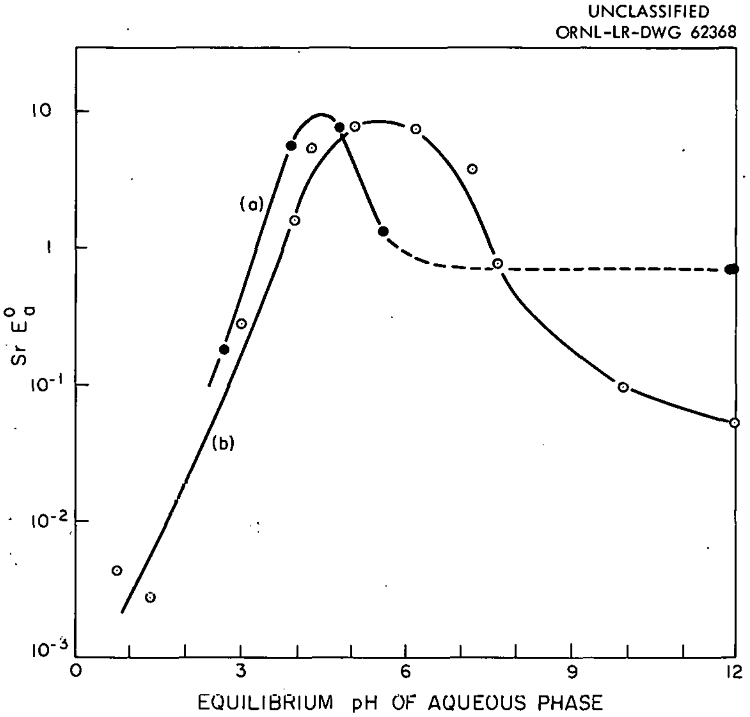

Fig. 4.4. Strontium-85 tracer distribution from Na_2SO_4-$Na_2C_4H_4O_6$ and Na_2SO_4-$Na_2C_4H_4O_6$-$Fe(NO_3)_3$ solutions. Organic phase: 0.3 *M* D2EHPA—0.15 *M* TBP in Amsco 125-82; aqueous phase: (a) 2.4 *M* Na^+—0.2 *M* $C_4H_4O_6^=$—1 *M* $SO_4^=$; (b) same plus 0.1 *M* Fe^{3+}—0.3 *M* NO_3^-; o/a phase ratio: 1.0.

Table 4.4. Effect of Iron on Sr-85 Extraction by D2EHPA from Na_2SO_4-$Na_2C_4H_4O_6$ Solutions over pH Range 1-12

Organic phase: 0.3 M D2EHPA—0.15 M TBP, Amsco 125-82
Aqueous phase: 2.4 M Na^+, 1 M $SO_4^=$, 0.2 M $C_4H_4O_6^=$ for one series and 2.4 M Na^+, 1 M $SO_4^=$, 0.2 M $C_4H_4O_6^=$, 0.1 M $Fe(NO_3)_3$ for the other; Sr-85 ≅ 10^5 γ c/m. ml
O/a phase ratio: 1.0
Equilibration time: 10 min

0.0 M $Fe(NO_3)_3$		0.1 M $Fe(NO_3)_3$	
Equil. pH	Sr-85 E_a^o	Equil. pH	Sr-85 E_a^o
2.65	0.18	0.8	0.004
3.8	5.9	1.4	0.003
4.7	7.5	3.0	0.27
5.5	1.2	3.9	1.3
11.8	0.72; 0.70	4.2	5.3
11.9	0.71	5.0	7.8
		6.1	7.9
		7.1	3.7
		7.6	0.76
		9.9	0.10
		12.0	0.05

The wider maximum in the strontium extraction vs pH curve when iron was present in the aqueous phase may be due to essentially complete complexing of the tartrate by iron, leaving most of the strontium in a noncomplexed, more extractable condition.

4.7 Strontium Extraction Isotherm

A strontium extraction isotherm was obtained by a series of equilibrations of a solvent comprised of 0.3 M D2EHPA (0.21 M D2EHPA and 0.09 M NaD2EHP)--0.15 M TBP in Amsco 125-82 and aqueous solutions containing 1.0-1.3 M $NaNO_3$, 0.011-1.00 M $Sr(NO_3)_2$, and Sr-85 tracer at an initial pH of 6. After equilibrations the pH varied from 4.3 to 5.0. The equilibrium curve, (Fig. 4.5, Table 4.5) leveled off at a solvent loading corresponding to a D2EHP/Sr ratio of 4. This is the expected ratio for strontium complexed by two D2EHPA dimers.

Table 4.5. Extraction Isotherm for Strontium

Organic phase: 0.21 M D2EHPA--0.09 M NaD2EHPA--0.15 M TBP; Amsco 125-82
Aqueous phase: 1.0-1.3 M $NaNO_3$; 0.011-1.00 M $Sr(NO_3)_2$; Sr-85 Tracer, pH 6.0
Variable phase ratios

Strontium Concentration				
Organic Phase		Aqueous Phase		Aqueous Equilibrium pH
g/liter	M	g/liter	M	
0.743	8.48×10^{-3}	0.019	2.17×10^{-4}	4.8
0.993	1.13×10^{-2}	0.014	1.59×10^{-4}	4.8
1.99	2.27×10^{-2}	0.038	4.32×10^{-4}	4.8
1.78	2.03×10^{-2}	0.051	5.82×10^{-4}	4.8
5.70	6.50×10^{-2}	0.156	1.78×10^{-3}	5.0
5.46	6.24×10^{-2}	0.594	6.80×10^{-3}	4.9
5.80	6.62×10^{-2}	0.695	7.93×10^{-3}	4.9
6.72	7.65×10^{-2}	2.26	2.58×10^{-2}	4.9
6.95	7.94×10^{-2}	2.95	3.37×10^{-2}	5.0
6.80	7.75×10^{-2}	3.18	3.62×10^{-2}	5.0
6.75	7.71×10^{-2}	8.28	9.45×10^{-2}	4.7
7.40	8.45×10^{-2}	14.0	1.60×10^{-1}	4.7
6.99	7.98×10^{-2}	23.5	2.68×10^{-1}	4.6
7.24	8.27×10^{-2}	34.2	3.91×10^{-1}	4.6
7.50	8.56×10^{-2}	53.9	6.16×10^{-1}	4.4
6.85	7.82×10^{-2}	75.8	8.66×10^{-1}	4.3

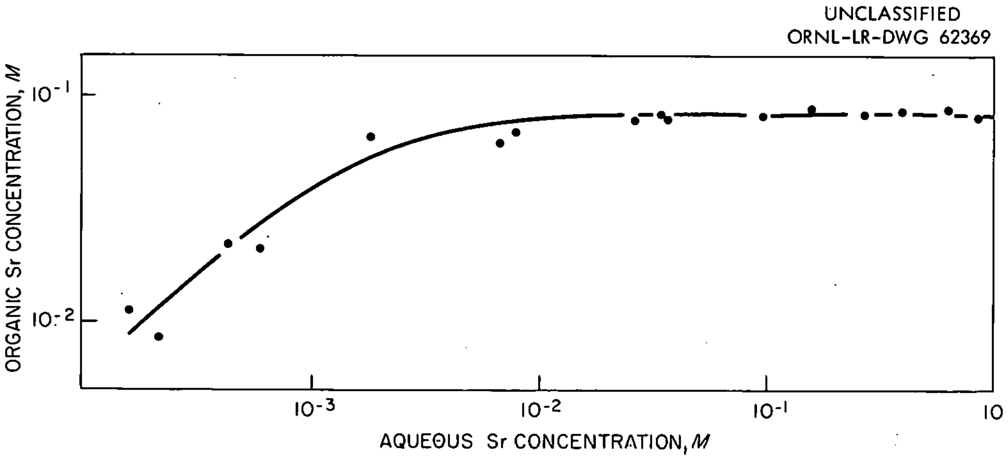

Fig. 4.5. Strontium extraction isotherm. Organic phase: 0.3 *M* D2EHPA—0.15 *M* TBP in Amsco 125-82; aqueous phase: 1.0-1.3 *M* $NaNO_3$, pH 6.

4.8 Effect of D2EHPA Concentration on Strontium Extraction

With the other variables held constant, the Sr E_a^o from the adjusted Purex solution was proportional to $[D2EHPA]^{1.24}$ (Table 4.6, Fig. 4.6). In these experiments simulated Purex waste solution (containing Sr-85 tracer) was contacted with equal volumes of 0.15 M--0.2 M TBP--Amsco 125-82 containing D2EHPA at concentrations varying from 0.02 to 0.5 M. Because the previous data indicated that the maximum strontium extraction would be at about pH 5, the equilibrium pH was allowed to vary only between 4.5 and 5.4.

Table 4.6. Extraction of Strontium as a Function of Initial D2EHPA Concentration

Organic phase: variable D2EHPA and TBP concentrations, Amsco 125-82 diluent
Aqueous phase: synthetic Purex waste adjusted to 0.42 M $Na_2C_4H_4O_6$ and to various initial pH's with 5 M NaOH, dilution factor 2.4
O/a phase ratio: 1.0
Equilibration time: 10 min
Sr-85 determined by γ-scintillation method

Organic Phase		Equilibrium pH of	
D2EHPA, M	TBP, M	Aqueous Phase	Sr E_a^o
0.02	0.2	5.4	0.38
0.05	0.2	4.5	0.53
0.05	0.2	4.7	0.48
0.10	0.2	4.8	2.7
0.3	0.15	4.5	8.6
0.5	0.2	4.7	10.6

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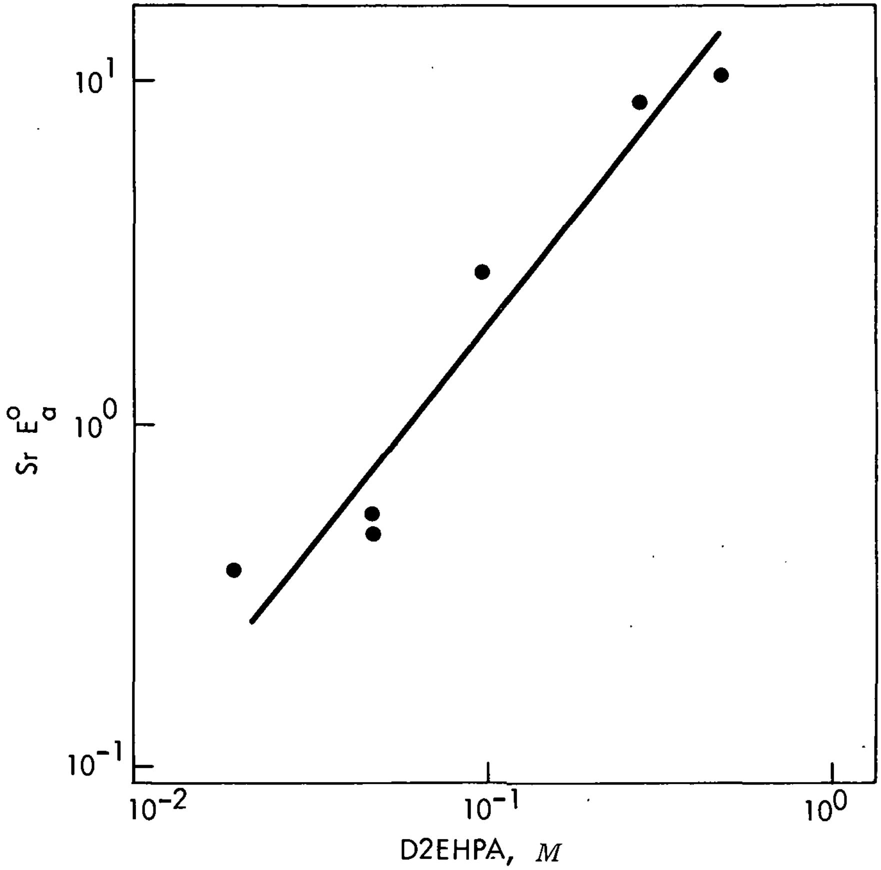

Fig. 4.6. *Strontium distribution as a function of D2EHPA concentration.* Organic phase: 0.02 to 0.5 *M* D2EHPA - 0.2 *M* TBP in Amsco 125-82; aqueous phase: synthetic Purex waste initially 1 *M* in tartrate, NaOH added to equilibrium pH of 4.5-5.4, dilution factor 2.4; o/a phase ratio: 1.0.

The extractant concentration chosen for process use is 0.3 M D2EHPA since this concentration provided large strontium and rare earth distribution coefficients, adequate solvent capacity, and good phase separation. As noted previously the process solvent composition is actually 0.21 M D2EHPA—0.09 M NaD2EHP—0.15 M TBP in Amsco 125-82; this ratio of NaD2EHP/D2EHPA tends to minimize the Na^+-H^+ transfer between the organic phase and low-acid aqueous phase, thus simplifying pH control. Also as mentioned earlier, the TBP is not present in the solvent as an active extractant but only to maintain miscibility of the NaD2EHP in the organic phase.

4.9 Rare Earths Extraction

In the pH range 5-6, the distribution coefficients for europium and for total rare earths were nearly the same. They were a little higher than those for strontium, ensuring rare earth extraction under conditions set for strontium extraction.

In the pH range 2-3 the rare earths were still easily extracted, whereas strontium extraction was negligible. The distribution coefficients for the total fission product rare earths were considerably lower than those for europium, but were still high enough for extraction (E_a^o 5 to 25) and separation from strontium (calculated separation factor 330 at pH 3, Fig. 4.7). The experiments were made with simulated Purex waste with europium tracer (Table 4.7) and mixed fission products (Table 4.8) o/a phase ratio of 1 and 10 min contact time.

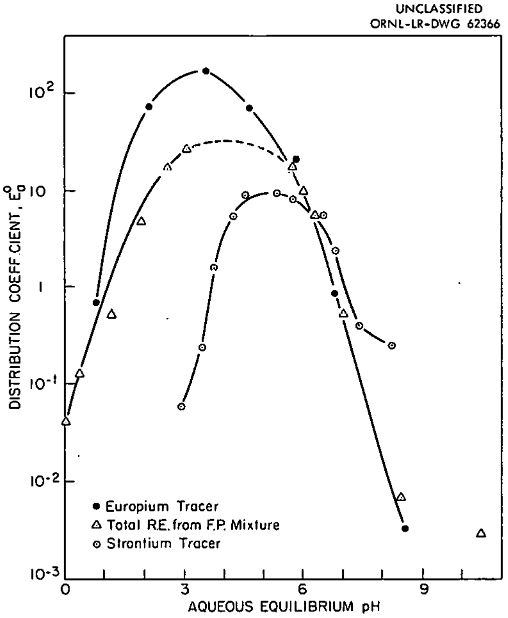

Fig. 4.7. Europium, strontium, and total rare earths distributions from tartrate-complexed synthetic Purex waste as a function of equilibrium pH. Organic phase: 0.3 *M* D2EHPA—0.15 *M* TBP in Amsco 125-82; aqueous phase: synthetic Purex waste, tartrate-complexed and neutralized to various pH's; o/a phase ratio: 1.0.

The data suggest two methods for recovery and separation of strontium and the rare earths: (1) consecutive extractions from the adjusted waste, rare earths at pH 2-3 and then strontium at pH 5-6, or (2) simultaneous extraction of both at pH 5-6 followed by consecutive extractions in a second cycle. The second method was chosen for more intensive study. The advantage of the first is immediate separation of the rare earths and strontium, but the disadvantage is two separate adjustments and extractions of the waste. The two methods would involve about the same number of operations to final purification and should yield approximately the same degree of initial separation.

In further study of the rare earth separation from strontium at pH 3, two batch countercurrent tests were run in parallel, with 4 stages at o/a of 1/5, 1 min contact time. The rare earth distribution was followed in one test by means of europium tracer (Table 4.9a), and the strontium distribution was followed

Table 4.7. Extraction of Europium-152 and -154 by D2EHPA

Organic phase: 0.3 M D2EHPA, 0.15 M TBP, Amsco 125-82
Aqueous phase: synthetic Purex waste adjusted to 0.40 M $Na_2C_4H_4O_6$ and to various pH's with 5 M NaOH, dilution factor = 2.5
O/a phase ratio: 1.0
Equilibration time: 10 min

Aqueous Equil. pH	Eu-152 and -154, γ c/m. ml Organic	Aqueous	Eu E_a^o
0.8	3.02×10^4	4.43×10^4	0.7
2.1	7.52×10^4	1.01×10^3	74
3.5	7.58×10^4	4.5×10^2	170
4.6	7.50×10^4	1.07×10^3	70
5.8	7.19×10^4	3.56×10^3	20
6.8	3.53×10^4	4.00×10^4	0.9
8.6	1.74×10^2	7.58×10^4	~0.002
10.6	1×10^2	7.60×10^4	~0.001

in the other by strontium tracer (Table 4.9b). From the respective distribution coefficients for europium and strontium at the first extraction stage, the Eu/Sr separation factor was calculated to be 115.

Although the aqueous pH did not change markedly, the europium distribution coefficients decreased from 23 at the first stage to 9.9 at the fourth stage. A material balance showed 102% of the europium tracer extracted in the four stages and 1.5% loss to the raffinate. The strontium distribution coefficients were 0.20, 0.34, 0.45, and 0.37 at the first to the fourth stages, respectively, which indicated that the strontium was refluxing to some extent. By material balance, 4.3% of the strontium was extracted and 91.5% was not extracted.

4.10 Zirconium-Niobium Extraction

The distribution behavior of zirconium-niobium tracer between adjusted simulated Purex waste and the D2EHPA solvent was measured in two different acidity ranges: 0.5 to 4 M to examine the possibility of removing zirconium and niobium before strontium or rare earth extraction, and pH 0.4 to 10 to indicate whether there would be serious contamination of strontium and rare earths by zirconium-niobium. Zirconium-niobium extraction was low from the 0.5 to 4 M acid solutions in the absence of tartrate (Table 4.10). The distribution coefficients in all cases were ≤ 0.5 and showed little variation with aqueous acidity. In the presence of 0.25 or 0.4 M tartrate, on the

Table 4.8. Extraction of Total Rare Earths by D2EHPA as a Function of pH

Organic phase: 0.3 M D2EHPA, 0.15 M TBP, Amsco 125-82
Aqueous phase: synthetic Purex waste spiked with Purex waste solution, adjusted to 0.33 M $Na_2C_4H_4O_6$ and to pH values shown with NaOH, dilution factor 3.0
O/a phase ratio: 1.0
Equilibration time: 10 min

Aqueous Equilibrium pH	Total Rare Earths, β c/m. ml Org	Aq	TRE E_a^o
0.4	2.23×10^5	1.87×10^6	0.12
1.2	7.15×10^5	1.43×10^6	0.50
1.9	1.72×10^6	3.57×10^5	4.82
2.5	2.15×10^6	1.21×10^5	17.8
3.0	2.12×10^6	7.84×10^4	26.9
5.7	1.51×10^6	8.38×10^4	18.1
6.0	1.49×10^6	1.57×10^5	9.5
6.3	1.32×10^6	2.36×10^5	5.6
7.0	2.71×10^5	5.33×10^5	0.51
8.5	1.23×10^4	1.76×10^6	0.007
10.5	5.8×10^3	1.74×10^6	0.003

Table 4.9. Batch Countercurrent Extraction of Tracer Europium and Strontium

Organic phase: 0.3 M D2EHPA—0.15 M TBP in Amsco 125-82
Aqueous phase: synthetic Purex waste adjusted to 0.38 M (for Eu) ~0.40 M (Sr) $Na_2C_4H_4O_6$, tracer added, partially neutralized to pH 3.45 (Eu) ~3.0 (Sr) with NaOH, dilution factor 2.6
O/a phase ratio: 1/5
Equilibration time: 1 min
Volume changes: 3

Stage	Activity, γ c/m. ml Org	Aq	E_a^o	Aqueous Equilibrium pH
		a. Eu-152 and 154		
Feed	-	3.68×10^5	-	3.4
1-E	1.91×10^6	8.34×10^4	23.0	3.4
2-E	5.43×10^5	3.12×10^4	17.4	3.4
3-E	1.83×10^5	1.23×10^4	14.9	3.4
4-E	5.39×10^4	5.42×10^3	9.9	3.1

Table 4.9 (Cont'd.)

Stage	Activity, γ c/m. ml		E_a^o	Aqueous Equilibrium
	Org	Aq		pH
		b. Sr-85		
Feed	-	1.40×10^5	-	3.0
1-E	2.82×10^4	1.43×10^5	0.20	3.0
2-E	4.90×10^4	1.46×10^5	0.34	2.95
3-E	6.44×10^4	1.43×10^5	0.45	2.9
4-E	4.82×10^4	1.30×10^5	0.37	2.7

Table 4.10. Extraction of Zirconium-Niobium from 0.6-2.0 M H^+ Purex Waste

Organic phase: 0.3 M D2EHPA—0.15 M TBP in Amsco 125-82
Aqueous phase: synthetic Purex waste adjusted with $Na_2C_4H_4O_6$ and NaOH to conditions shown; Zr-Nb tracer ~5×10^4 c/m. ml
O/a phase ratio: 1.0

Dilution Factor	Phase Contact Time, min	Equilibrium Concentrations, M			Zr-Nb E_a^o
		H^+	Na^+	$C_4H_4O_6^=$	
1.6	10	0.61	2.25	0.0	0.25
1.4	10	1.32	1.86	0.0	0.26
1.2	10	2.54	1.3	0.0	0.21
1.0	10	4.0	0.6	0.0	0.45
2.5	1	0.5	2.3	0.25	0.86
2.5	1	1.0	1.8	0.25	1.0
2.5	1	1.5	1.3	0.25	0.99
2.5	1	2.0	0.8	0.25	1.02
2.5	10	2.0	0.8	0.25	3.27
2.5	10	0.9	1.44	0.4	1.2
2.5	10	1.26	1.04	0.4	1.8
2.5	10	1.53	0.64	0.4	2.2
2.5	10	1.96	0.24	0.4	3.1
2.5	1	0.5	2.8	0.5	0.49
2.5	1	1.0	2.3	0.5	0.74
2.5	1	1.5	1.8	0.5	0.84
2.5	1	2.0	1.3	0.5	0.86

other hand, extractions were higher and were sensitive to the aqueous acidity. From ~1 M and 2 M acid solutions, distribution coefficients were about 1 and 3, respectively. Coefficients in this range are sufficiently large for a Zr-Nb scavenging step.

The extraction of Zr-Nb was time-dependent, similar to the previously observed behavior of iron. For example, the distribution coefficients were 1.0 at 1 min and 3.3 at 10 min with 2.0 M acid, 0.25 M tartrate. The relatively long time required for best Zr-Nb extraction would be a detrimental but not a prohibitive factor to the process application of a Zr-Nb scavenging cycle.

From feed of higher pH (1 M tartrate, 10 min contact) Zr-Nb distribution coefficients continue to decrease with increasing pH, e.g., from ~1 at pH 1 to <0.1 at pH 5 and <0.01 at pH 10 (Table 4.11, Fig. 4.8). It is evident that in the

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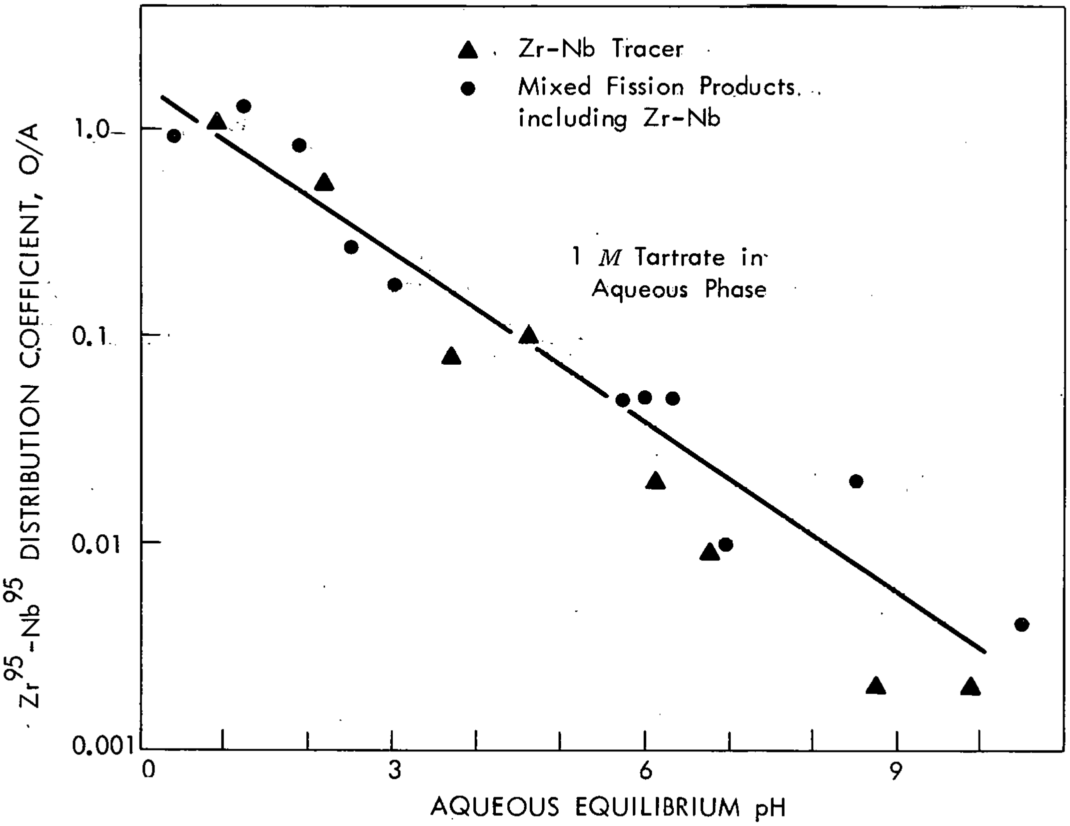

Fig. 4.8. Zirconium-niobium distribution from tartrate-complexed synthetic Purex waste as a function of pH. Organic phase: 0.3 *M* D2EHPA—0.15 *M* TBP in Amsco 125-82; aqueous phase: synthetic Purex waste, tartrate-complexed and neutralized to various pH's; o/a phase ratio: 1.0.

pH range 5-6, which is near optimum for strontium recovery, the coefficient for Zr-Nb is relatively low. Consequently, even though a prior Zr-Nb scavenging cycle is not included in the process, Zr-Nb discard should be possible during the strontium recovery cycle.

Table 4.11. Extraction of Zirconium-Niobium from Purex Waste in the pH Region 0.4-10.5

Organic phase: 0.3 M D2EHPA—0.15 M TBP in Amsco 125-82
Aqueous phase: synthetic Purex waste, Zr-Nb activity as shown, adjusted to 0.40 M $Na_2C_4H_4O_6$, partially neutralized with NaOH to pH shown, dilution factor 2.5
O/a phase ratio: 1.0
Equilibration time: 10 min

Aqueous Equilibrium pH	Zr^{95}-Nb^{95} Activity, c/m. ml		Zr-Nb E_a^o
	Org	Aq	
	Zr-Nb Tracer Only		
0.9	$1.07x10^5$	$9.85x10^4$	1.1
2.2	$7.21x10^4$	$1.31x10^5$	0.55
3.7	$1.36x10^4$	$1.77x10^5$	0.08
4.6	$1.78x10^4$	$1.74x10^5$	0.1
6.1	$4.1x10^3$	$2.0x10^5$	0.02
6.8	$1.74x10^3$	$2.0x10^5$	0.009
8.8	$4.7x10^2$	$2.1x10^5$	0.002
9.9	$3.6x10^2$	$2.1x10^5$	0.002
	Zr^{95}-Nb^{95} in Fission Product Mixture		
0.4	$1.02x10^6$	$1.11x10^6$	0.92
1.2	$1.15x10^6$	$9.22x10^5$	1.25
1.9	$8.9x10^5$	$1.11x10^6$	0.81
2.5	$4.52x10^5$	$1.59x10^6$	0.28
3.0	$2.87x10^5$	$1.73x10^6$	0.17
5.7	$9.36x10^4$	$1.94x10^6$	0.05
6.0	$9.8x10^4$	$1.82x10^6$	0.05
6.3	$9.3x10^4$	$2.0x10^6$	0.05
7.0	$1.92x10^4$	$1.92x10^6$	0.01
8.5	$2.99x10^4$	$1.94x10^6$	0.02
10.5	$8.9x10^3$	$2.27x10^6$	0.004

4.11 Ruthenium Extraction

The extraction of ruthenium activity by the D2EHPA solvent from an adjusted waste solution was studied as a function of the aqueous equilibrium pH under the same conditions as for the previously described zirconium-niobium and rare earth extractions. The ruthenium distribution coefficients were all very low, ranging from 0.04 to 0.005 over the pH range of 0.4 to 10.5 (Table 4.12).

Table 4.12. Extraction of Ruthenium by D2EHPA as a Function of pH

Organic phase: 0.3 M D2EHPA--0.15 M TBP in Amsco 125-82
Aqueous phase: synthetic Purex waste spiked with Purex waste solution, adjusted to 0.33 M $Na_2C_4H_4O_6$ and with NaOH to pH values shown; dilution factor 3.0
O/a phase ratio: 1.0
Equilibration time: 10 min

Aqueous Equilibrium pH	Ruthenium Activity, γ c/m. ml Org	 Aq	Ru E_a^o
0.4	2.71×10^4	7.62×10^5	0.04
1.2	1.17×10^4	7.45×10^5	0.02
1.9	7.75×10^3	7.42×10^5	0.01
2.5	5.73×10^3	7.67×10^5	0.008
3.0	2.72×10^4	7.23×10^5	0.04
5.7	2.21×10^4	7.48×10^5	0.03
6.0	1.72×10^4	7.49×10^5	0.02
6.3	1.65×10^4	7.69×10^5	0.02
7.0	6.36×10^3	7.09×10^5	0.009
8.5	3.29×10^3	7.24×10^5	0.004
10.5	3.53×10^3	7.02×10^5	0.005

4.12 Calcium and Barium Extraction

Calcium was extracted from synthetic Purex waste with a coefficient of 493 at the first extraction stage and >10 at the second stage (Table 4.13). The latter coefficient was probably much greater than 10 but accurate determinations could not be made since the aqueous phase count rate was approaching background. Barium extraction under similar conditions (Table 4.13) was low, the distribution coefficients being 0.1 and 0.03 at the first and second extraction stages, respectively. The organic and aqueous phases were centrifuged to minimize any

Table 4.13. Calcium and Barium Extraction by D2EHPA

Organic phase: 0.15 M NaD2EHP—0.15 M D2EHPA—0.15 M TBP in Amsco 125-82 diluent
Aqueous phase: synthetic Purex waste spiked to (a) ~3×10^5 Ca-45 β c/m. ml, (b) ~4×10^4 Ba-133 γ c/m. ml, and adjusted to 0.33 M $Na_2C_4H_4O_6$ and neutralized with 5 M NaOH to pH 5.6, dilution factor 3.0
Batch countercurrent technique, 2 extraction stages, 5 volume changes
O/a phase ratio: 2

Stage	Activity, c/m. ml		E_a^o
	Org	Aq	
a. Ca-44			
E-1	5.9×10^4	1.2×10^2	493
E-2	5.0×10^2	<50	>10
Feed	-	1.03×10^5	
b. Ba-133			
E-1	1.18×10^3	1.20×10^4	0.099
E-2	7.8×10^2	2.76×10^4	0.029
Feed	-	1.52×10^4	

erroneous count rate due to the presence of $BaSO_4$ precipitate which formed when the feed containing excess barium as a carrier was neutralized to pH 5.6.

These data show that calcium present in Purex waste as an impurity should report to the strontium product solution. When operation is according to the flowsheet in Fig. 2.1, an additional purification cycle for this element will be required. One possible method for separating calcium and strontium by D2EHPA extraction has been proposed by the ORNL Isotopes Division.[14] The presence of barium (from fission), on the other hand, should not present a problem since its low distribution coefficients should allow scrubbing of barium from the organic phase. The data also indicate that D2EHPA extraction is an attractive method for separating the alkaline earth elements. For example, from the adjusted waste solutions under comparable conditions, the distribution coefficients for calcium, strontium, and barium were 493, 5.15, and 0.099, respectively.

4.13 Relative Rates of Iron and Strontium Extraction

As noted previously (Sect. 3.2) the strontium is extracted from the adjusted Purex waste by D2EHPA at a much faster rate than iron. Further data are given in Fig. 4.9. The Sr E_a^o was nearly constant at 6.5-7.3 with phase equilibration times of 1 to 20 min whereas the Fe E_a^o increased from 0.052 after a 1 min-phase equilibration to 0.58 after 20 min contact time. The corresponding Sr/Fe separation factors were 121 after a 1-min phase-contact time and about 13 after 20 min.

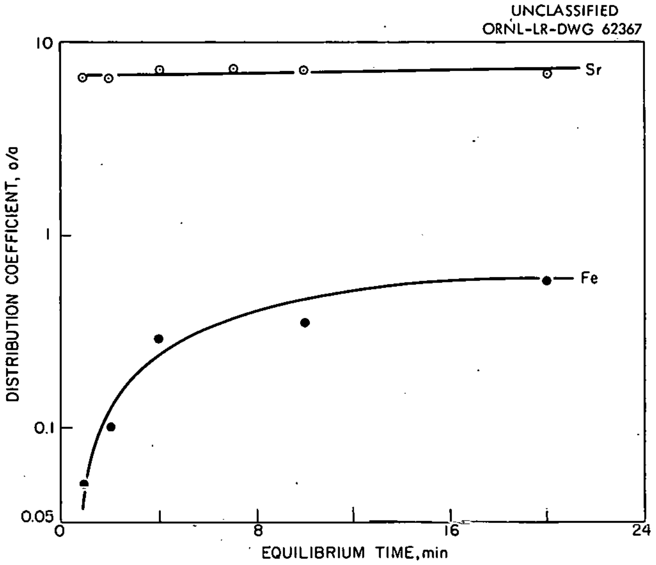

Fig. 4.9. Relative rates of iron and strontium distribution from tartrate-complexed synthetic Purex waste. Organic phase: 0.3 *M* D2EHPA—0.15 *M* TBP in Amsco 125-82; aqueous phase: synthetic Purex waste initially 1 *M* in tartrate, neutralized to pH 5.5 with 5 *M* NaOH, dilution factor 2.5; o/a phase ratio: 1.0.

4.14 Tartrate Extraction from Na_2SO_4-$Na_2C_4H_4O_6$ Solutions

When all the D2EHPA was in the acid form, no detectable tartrate was extracted (Table 4.14). When 30% of the D2EHPA was present as the sodium salt, the tartrate concentration in the organic phase was 0.015 mg/ml. When all the D2EHPA was as the sodium salt, the tartrate concentration was 0.55 mg/ml.

Table 4.14. Tartrate Extraction by NaD2EHP-D2EHPA from Aqueous Na_2SO_4-$Na_2C_4H_4O_6$ Solutions

Organic phase: 0.3 M D2EHPA (varying concentrations of NaD2EHP), 0.15 M TBP, Amsco 125-82 diluent
Aqueous phase: 1 M Na_2SO_4; 0.4 M $Na_2C_4H_4O_6$
O/a phase ratio: 1/4
Equilibration time: 1 hr

NaD2EHP, vol %	D2EHPA, vol %	Tartrate Concentration, mg/ml		Tartrate E_a^o
		Org[a]	Aq[b]	
0	100	0.0	60.0	0.0
30	70	0.015	60.0	2.5×10^{-4}
50	50	0.062	60.0	1.02×10^{-3}
70	30	0.22	59.9	3.68×10^{-3}
100	0	0.55	59.9	9.2×10^{-3}

[a] Analytical method by L. J. Brady.

[b] Calculated value from organic analysis and initial aqueous phase concentration.

In this series of tests aqueous solutions of 1 M $NaSO_4$--0.4 M $Na_2C_4H_4O_6$ were equilibrated 1 hr with D2EHPA-NaD2EHP--TBP—Amsco 125-82 at o/a phase ratios of 1/4. Nitrate solutions were not used in these tests in order to simplify the analytical problems. The amount of the D2EHPA extractant present as the sodium salt was varied from 0-100% and the total reagent concentration held constant at 0.3 M. The TBP concentration was 0.15 M in all cases with Amsco 125-82 as the diluent. Tartrate was determined by reaction with Ce(IV) followed by back-titration of the excess Ce(IV) with standard $FeSO_4$ solution.

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