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RECOVERY OF FISSION PRODUCTS FROM WASTE SOLUTIONS BY SOLVENT EXTRACTION

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OAK RIDGE NATIONAL LABORATORY
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ABSTRACT

Increasing industrial, military, and space requirements for certain fission products place emphasis on new and large-scale methods for their recovery from waste liquors produced by the fuel recovery processes. With recent developments of new organic extractants for separating and recovering these fission products, solvent extraction offers a versatile alternative to ion-exchange, precipitation, and crystallization procedures heretofore used for small-scale recoveries.

A process flowsheet has been developed for the recovery of strontium and mixed rare earths from adjusted Purex 1WW solution by the use of di(2-ethylhexyl)phosphoric acid (D2EHPA). After adding tartrate to complex the iron and caustic to adjust the pH to 6, strontium and rare earths are co-extracted and then co-stripped with nitric acid in the first cycle. In additional D2EHPA extraction cycles, they are isolated as concentrated fractions. The mixed rare earths from this process can be treated by tributyl phosphate (TBP) extraction to separate the individual rare earth elements of which promethium and cerium are of greatest interest. Zirconium-niobium also may be recovered with D2EHPA from acidic waste liquors.

An amine pretreatment extraction process has been developed for removing nitric acid, iron sulfate, zirconium-niobium, and ruthenium from waste solutions to furnish a feed liquor more amenable to subsequent processes for recovering fission products. The separate recovery of ruthenium, zirconium-niobium, and rare earths may also be possible by amine extraction.

A process based on the use of substituted phenols has been developed for recovering cesium from alkaline waste solutions. These compounds are selective extractants for cesium, giving high decontamination from other fission products and sodium, and they are readily stripped with dilute nitric acid.

Previous studies have also outlined methods for recovering neptunium, plutonium, and technetium with solvents similar to those described here. When appropriately combined, these developments offer a versatile integrated solvent extraction flowsheet for the recovery of all important fission products and other components from waste liquors.

1. INTRODUCTION

Large demands for certain radioactive fission products, Sr^{90}, Ce^{144}, Pm^{147}, Cs^{137}, etc., are anticipated for industrial, space, and other uses. Although small-scale recoveries of these materials, principally by precipitation, have been conducted for many years, attention has been given only recently to methods more adaptable to production of large commercial quantities. At the Oak Ridge National Laboratory attention has centered on the use of versatile solvent extraction methods for recovering the fission products from reactor fuel process waste liquors. Processes have been developed through laboratory scale for strontium and mixed rare earth recovery by extraction with di(2-ethylhexyl)phosphoric acid and its sodium salt,[1-11] individual rare earth separations with tributyl phosphate,[12-16] zirconium-niobium recovery by extraction with di(2-ethylhexyl)phosphoric acid,[17] and cesium recovery by extraction with selected substituted phenols.[8,9,18] Feed pretreatment methods using amine extraction have also been developed to remove bulk impurities such as nitric acid, sulfate and iron, and certain fission products such as zirconium-niobium and ruthenium.[9,19] Such pretreatment produces feed solutions more amenable to the subsequent recovery of other fission products and might also be adapted to the isolation of zirconium-niobium, ruthenium, and possibly rare earths. These combined developments afford solvent extraction methods for recovering most of the valuable fission products from waste liquors. Previous studies also suggested solvent extraction methods for recovering other valuable components such as neptunium, plutonium, and technetium.[20,21]

This paper describes the highlights of the developments along with the pertinent process chemistry and controlling variables, with references to reports from Oak Ridge National Laboratory and elsewhere, describing much of the chemistry and developmental studies in greater detail. The names, structures, and sources of the less common extractants and diluents used are given in Table 1.

2. COMPOSITION OF FEED LIQUORS

Nearly all the studies reported here were made with simulated Purex 1WW waste of composition similar to that currently produced at the

Table 1. Reagents and Diluents Used for the Solvent Extraction of Fission Products

Compound	Structure	Source[a]	Availability[b]
Di(2-ethylhexyl)phosphoric Acid (D2EHPA)	Self-evident	Union Carbide; Virginia-Carolina Co.	C
Primene JM	$H_2N-C(R)(R')(R'')$; $R+R'+R''$ = 18-24 carbon atoms	Rohm and Haas Co.	C
p-Dodecylphenol (PDP)	dodecyl = mixed isomers	Rohm and Haas Co.	C
o-Phenylphenol (OPP)	Self-evident	Dow Chemical Co.	C
4-Chloro-2-phenylphenol (PCOPP)	Self-evident	Matheson, Coleman and Bell	E
4-Sec-butyl-2(α-methyl)benzylphenol (BAMBP)	Self-evident	Dow Chemical Co.	E
Santophen-1	4-chloro-2-benzylphenol	Monsanto Chemical Co.	C
Mono-heptadecylphosphoric Acid	heptadecyl = 1-(3-ethylpentyl)-4-ethyloctyl	Dow Chemical Co.	E
Amsco 125-82	Refined aliphatic petroleum fraction	American Mineral Spirits Co.	C
Diisopropyl benzene	Mixed isomers	Dow Chemical Co.	C

[a] Source of particular reagents used; in many cases other suppliers are available.

[b] C represents commercial quantities; E represents experimental quantities.

Hanford plant.[22] Tracer quantities of the appropriate radioisotopes were added in most experiments for analytical purposes. Purex 1WW waste is the evaporation-concentrated aqueous raffinate from the tributyl phosphate-nitric acid extraction process used to recover plutonium and uranium from spent uranium reactor fuel. It is about 4 M in HNO_3, 1 M in SO_4^{2-}, 0.5 M in Fe^{3+}, 0.1 M in Al^{3+}, and contains smaller amounts of fission and corrosion products (Solution A, Table 2). Waste from the Savannah River plant is of somewhat similar composition but contains much less iron and no sulfate.

The strontium and cesium recovery processes subsequently described require prior neutralization of the waste solution with caustic. To prevent the precipitation of iron and other hydrolyzable metals, an aqueous complexing agent is added. Tartrate has been used most extensively, although other complexants such as citrate, etc., are also effective.[3] The addition of about 2 moles of sodium tartrate per mole of iron, coupled with dilution of the neutralized liquor to about three times its initial volume, produces stable feeds. Larger amounts of tartrate would not significantly interfere with the recovery processes, but decreasing the ratio appreciably can result in precipitation of hydrous iron oxide.[11] For the strontium recovery process the pH of the feed solution is adjusted to 4.5 to 6 (Solution B, Table 2). In the cesium recovery process the pH is adjusted to ≥ 12, resulting in a somewhat greater concentration of sodium ion (Solution C, Table 2).

Process changes are expected at Hanford wherein the free acid content of the Purex 1WW will be reduced to about 0.5 M during the decomposition of nitrate with formaldehyde.[23] Neutralization of this waste, designated Purex FTW, will give solutions lower in sodium ion concentration. Tests of cesium recovery have been made with wastes of this type adjusted by adding caustic and tartrate (Solution D, Table 2). In the future, other changes are planned, such as replacing ferrous sulfamate with U(IV) nitrate as a plutonium reductant, which will decrease the iron concentration and eliminate sulfate from the waste.[23] These less contaminated feeds, with less iron to be complexed and less sodium to compete for the extractant, will respond even better to the processes described here than the feeds used in the current tests.

Table 2. Approximate Composition of Simulated Waste and Feed Solutions

Solution A	Purex 1WW contains, in moles/liter: 4.0 H^+, 1.0 SO_4^{2-}, 4.5 NO_3^-, 0.6 Na^+, 0.5 Fe^{3+}, 0.1 Al^{3+}, 0.01 Cr^{3+}, 0.01 Ni^{2+}, 0.005 UO_2^{2+}, 0.002 Sr^{2+},0.003 Cs^+, 0.006 Sm^{3+} (see footnote a), 0.003 Ce^{3+}, 0.003 Ru, and small amounts[b] of Zr, Si, and PO_4^{3-}.
Solution B	Strontium-Rare Earth Recovery Feed: Purex 1WW (Solution A), tartrate-complexed (2 moles/mole Fe), adjusted with NaOH to pH 4.5-6, and diluted 3-fold. Contains, in moles/liter: 0.33 SO_4^{2-}, 1.5 NO_3^-, 2.7 Na^+, 0.17 Fe^{3+}, 0.033 Al^{3+}, 0.0033 Cr^{3+}, 0.0033 Ni^{2+}, 0.0016 UO_2^{2+}, 0.0007 Sr^{2+}, 0.001 Cs^+, 0.002 Sm^{3+} (see footnote a), 0.001 Ce^{3+}, 0.001 Ru, and small amounts of Zr, Si, and PO_4^{3-}.
Solution C	Cesium Recovery Feed: Same as Solution B adjusted with additional NaOH to pH 12-13 (excess NaOH above pH 7 = 0.1-0.6 M; Na = 2.9-3.4 M).
Solution D	Adjusted Formaldehyde-Treated Purex 1WW (FTW): Composition and pH range same as Solution C, except Na^+ ~1.7-2.2 M and NO_3^- ~ 0.2 M.
Solution E	Tank Waste Supernate contains, in moles/liter: 0.001 Cs^+, 8.0 Na^+, 3 NO_3^-, 3 NO_2^-, 1 CO_3^{2-} (original pH ~10) adjusted to pH 12-13 (0.1-0.4 M additional NaOH). In some cases diluted two-fold prior to NaOH addition.

Note: Radioisotopes were added in many experiments for analytical expediency. These included Sr^{85}, Cs^{134}, $Zr\text{-}Nb^{95}$, Ru^{103}, $Eu^{152-154}$, Ce^{144}, Y^{91}, Pm^{147}, Ca^{45}, Ba^{133}, Rb^{86}, and mixed fission products.

[a] Sm used to represent ΣRE's (total rare earths) excluding Ce.

[b] 0.01 M PO_4^{3-}, 0.02 M Si, and 0.006 M Zr added but were mostly precipitated on aging. This simulates plant practice where most of these components in the original process raffinate are precipitated during evaporation.

Another waste liquor containing appreciable amounts of cesium is the Hanford tank farm supernatant liquid which is produced by neutralizing the Purex 1WW liquor and some of the other plant waste liquors with caustic prior to tank storage. Most of the polyvalent metals are precipitated, but the alkaline supernatant liquid contains nearly all the original cesium and trace quantities of other radioactive components. The approximate bulk composition is, in moles/liter: 8 Na^+, 1 CO_3^{2-}, 3.0 NO_3^-, 3.0 NO_2^-; pH about 10 (Solution E, Table 2).

3. GENERAL EXPERIMENTAL PROCEDURES

In batch extraction tests, the organic and aqueous phases were contacted either by mixing in an open separatory funnel with a high-speed interface stirrer or in separatory funnels mounted in a Burrell wrist-action shaker. Continuous tests were made in Knolls-type mini-mixer-settlers. Di(2-ethylhexyl)phosphoric acid (D2EHPA), as received, normally contains small amounts of iron and other impurities. The D2EHPA-TBP-Amsco solvent (composition below) was cleaned prior to use by alternate contacts with 0.5 vol of 6 $\underline{M}$ HNO_3, 0.5 vol of 2 $\underline{M}$ NaOH, and 2 vol of 0.5 $\underline{M}$ HNO_3.

4. RECOVERY OF STRONTIUM AND RARE EARTHS

Di(2-ethylhexyl)phosphoric acid (D2EHPA) and its sodium salt (NaD2EHP) are versatile cation exchangers which, depending upon the chosen conditions, can extract various metals in various degrees.[24] A general reaction may be written as

$$M_{aq}^{+b} + b[HX]_{2_{org}} \rightleftharpoons MX_b[HX]_{b_{org}} + bH_{aq}^{+} \quad , \qquad (1)$$

where X represents the di(2-ethylhexyl)phosphate anion, $[HX]_2$ the dimer form in which the acid exists in hydrocarbon diluents, and the subscripts aq and org refer to the aqueous and organic phases, respectively. With sodium-form reagent, Na^+ would replace H^+. This equation is somewhat oversimplified* but is suitable for the present discussion. Hydrocarbons such as kerosenes or Amsco 125-82 are satisfactory diluents for D2EHPA and many of its metal complexes in equilibrium with acid solutions, but modification of the diluent with, for example, tributyl phosphate (TBP) is needed to maintain the miscibility of NaD2EHP in the solvent phase.[25]

4.1 Strontium Extraction and Stripping

Since hydrogen ions are more tightly bound by the D2EHP anions than strontium ions, extractions are slight from acid solution but become appreciable from liquors at higher pH. As shown in Fig. 1, the maximum extraction from the adjusted Purex waste liquors is obtained at pH 4.6 to 6. This means also that strontium is easily stripped from the solvent with dilute acid.

The strontium extraction coefficient depends, of course, upon the extractant concentration[4,11] (see also Eq. 1 and footnote). Adequate extractions ($E_a^o > 5$) have been obtained with 0.3 M extractant (Fig. 1) and this concentration has been used in the process tests. Specifically, owing to the marked change of strontium extraction with pH, the process solvent composition has been set at 0.2 M D2EHPA—0.1 M NaD2EHP—0.15 M TBP** in Amsco 125-82. This NaD2EHP/D2EHPA ratio provides a buffered

---

*Although Eq. 1 holds for extraction of several metals from acidic solutions[24,26,27] it does not give a representative picture of Sr^{2+} extraction[26] and especially over an extended pH range. Recent results of McDowell[28] suggest a general equation, $Sr^{2+} + n/y(ZX)_y \rightleftharpoons SrX_2 \cdot (ZX)_{n-2} + 2\,Z^+$, where Z = H or Na and X = di(2-ethylhexyl)phosphate. Reagent dependence given by slopes n/y of log $[H^+]^2_{aq}\,E_{Sr}$ plotted vs log [total ZX] at constant % NaD2EHP have varied from ~3 at 100% D2EHPA to 0.95 at 100% NaD2EHP. This suggests an initial reaction $Sr^{2+} + 3(HX)_2 \rightleftharpoons SrX_2 \cdot 4HX + 2\,H^+$ (in agreement with Peppard, et al) with diminishing values of n/y reflecting changes in n or y or both as more of the reagent is converted to the sodium salt. It is known that polymerization beyond dimerization occurs as the percent of reagent in the sodium form increases.[1] Equation (1) represents satisfactorily extraction of rare earths from acidic liquors,[26] but the reaction is probably more complicated in high pH regions where much of the reagent is in the sodium form.

**This concentration of TBP is sufficient for miscibility of NaD2EHP in the solvent.[25]

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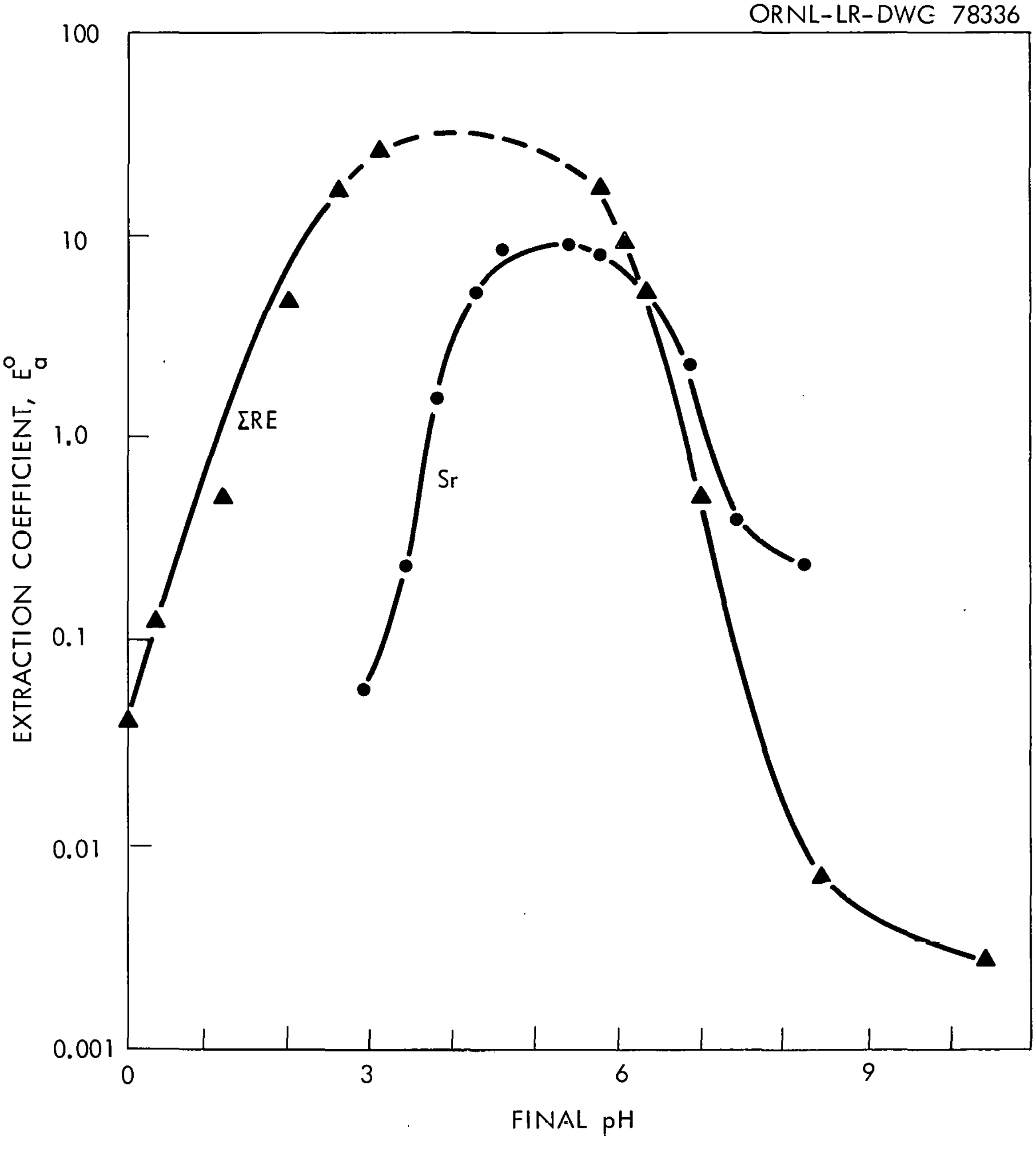

Fig. 1. Extraction of Rare Earths and Strontium from Adjusted 1WW Solution. Aqueous: same as Solution B except adjusted with caustic to various initial pH levels; traced with mixed fission products. Organic: 0.2 $\underline{M}$ D2EHPA—0.1 $\underline{M}$ NaD2EHP—0.15 $\underline{M}$ TBP in Amsco 125-82. Phase ratio: 1/1. Contact time: 10 min.

solvent that minimizes Na^+-H^+ transfer between the organic phase and low acid aqueous phase and simplifies maintaining the pH between 4.5 and 6.

Except for the rare earths, described below, other fission products, including Ru, Zr-Nb, and Cs are not appreciably extracted from the waste liquors under conditions optimized for strontium. Extractions of chromium are also inappreciable. Most of the trace uranium and some iron and aluminum are extracted, the latter two slowly, but all are easily separated during stripping (see below). Calcium, if present, and nickel are extracted, but, these elements, as noted later, can be separated in subsequent operations. Although the extraction coefficients for sodium are low, the large concentration of this ion in the aqueous phase affords significant competition with strontium (and rare earths) for the extractant. Liquors containing greater amounts of sodium than those tested, or expected in practice, could be handled but with some loss in strontium extraction efficiency.[11] On the other hand, better extractions would be obtained from the Purex process waste liquors expected in the future which, after adjustment, will have a lower sodium content. Variations in sulfate concentration of the liquor have little effect on the extraction process.[3,11]

4.2 Rare Earths Extraction and Stripping

The fission product rare earths are extracted more strongly than strontium from tartrate-complexed Purex 1WW at pH's less than 6. Their coefficients are much larger at pH less than 4, becoming approximately equal to those for strontium at pH 6 to 7 and finally smaller than those for strontium at higher pH's (Fig. 1). Versatile opportunities are thus presented for separate extraction of strontium and rare earths, co-extraction and stripping, or co-extraction with partitioning in the strip cycle, through use of pH and phase ratio changes. In contrast to rapid strontium extraction (equilibrium reached within a minute), the approach to equilibrium is slow for the extraction of rare earths and yttrium from adjusted Purex 1WW solution. As shown in Fig. 2, the coefficients are still increasing beyond 30 min of contact time. However, since the mass transfer in 1 min is 90 to 95% of that in 30, good recovery of rare earths can be obtained with reasonable contact periods. The order of extractability from the tartrate-complexed solution at pH 6, up to 30 min of

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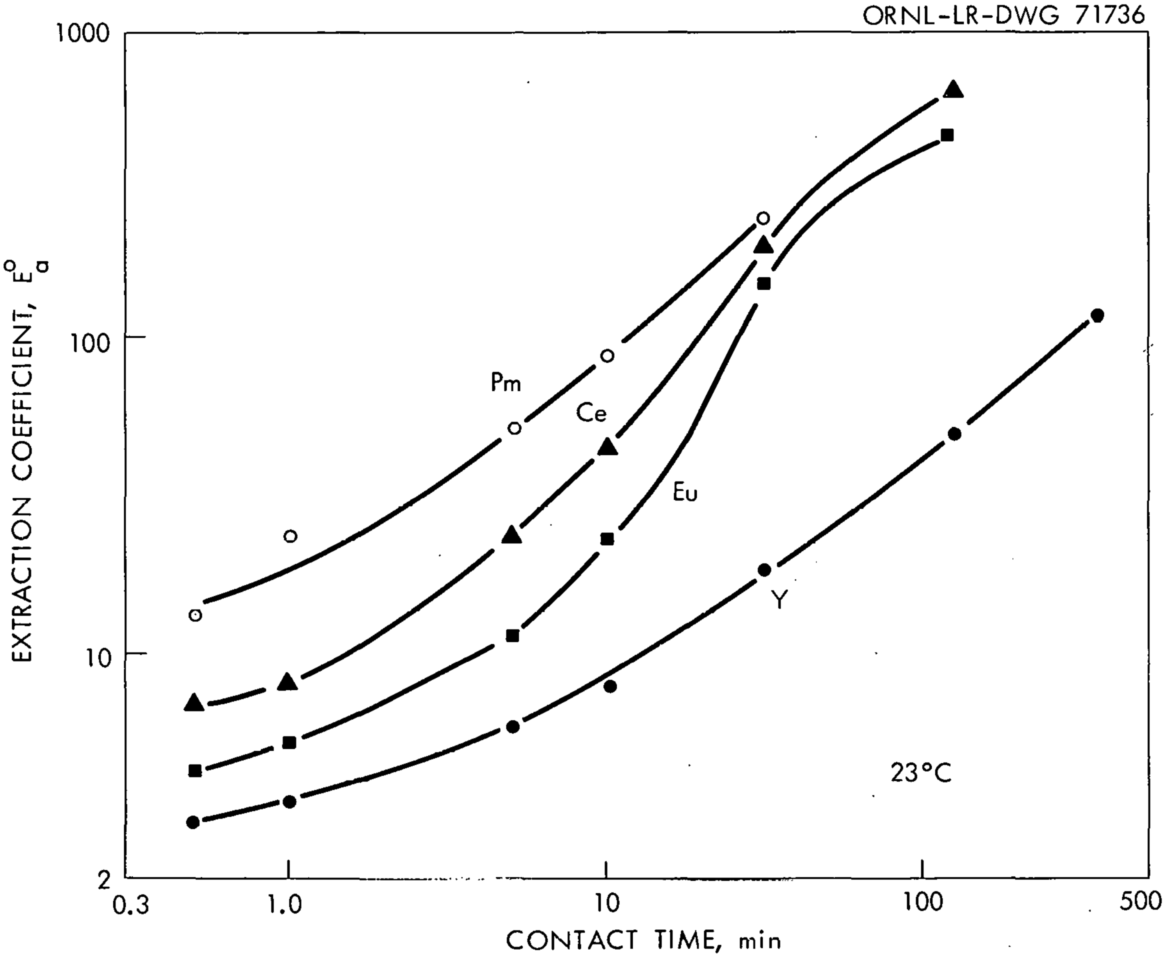

Fig. 2. Rate of Rare Earths and Yttrium Extraction from Adjusted 1WW Solution at Initial pH 6. Aqueous: Solution B with appropriate tracers and 0.04 g/liter each of Y and Eu. Organic: 0.2 M D2EHPA—0.1 M NaD2EHP—0.15 M TBP in Amsco 125-82. Organic/aqueous phase ratio: 2/1.

contact time, is Pm > Ce > Eu > Y. On the other hand, from noncomplexed sodium nitrate solution (corresponding to the second cycle feed in the flowsheet described below), equilibrium is reached rapidly, and the order of extractability is Y >> Eu > Pm > Ce (Fig. 3). Using 0.2 M D2EHPA—0.1 M NaD2EHP—0.15 M TBP in Amsco 125-82, extraction coefficients for cerium are about 10 at pH 1 and increase to about 100 at pH 1.5. Efficient stripping of the rare earths, but not yttrium, is obtained with 1 to 2 M HNO_3 (Fig. 4), and, as expected, the stripping order is inverse to that in extraction from the simple acid nitrate solution: Ce, Pm > Eu >> Y. The complete stripping of yttrium requires larger aqueous volumes or more concentrated acid. This behavior affords a convenient method for separating yttrium from the rare earths at this point.

4.3 Flowsheet for the Recovery of Strontium and the Rare Earths

Many different arrangements of a process for recovery, separation, and purification of strontium and rare earths are possible. Other than the versatility offered by pH control, different organic complexants can be added to the aqueous feed or strip solutions to change the degree[29] and order[*] of extractability of different metals. Since the amount of study required to examine all process arrangements is formidable, emphasis has been placed on a particular flowsheet (Fig. 5) that includes a first cycle for co-extraction and stripping of strontium and rare earths to give separation from the bulk of the 1WW components, a second cycle for separating the strontium from the rare earths, and a third cycle for further purifying and concentrating the strontium. This flowsheet was based on batch, batch-countercurrent, and continuous-countercurrent tests with simulated waste solutions.[1-11] It was subsequently tested (see below) on a sample of actual Purex 1WW obtained from the Hanford plant.[8] Figure 5 shows data on the flow ratios, the ideal stage requirements, and the separation of the metals[**] of principal importance. The solvent used in all

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[*] Strontium is more strongly extracted than calcium by D2EHPA from EDTA-complexed solutions, in contrast to stronger extraction of calcium than strontium from other solutions such as nitrate, acetate, tartrate, etc.[30]

[**] Calcium was not added to the simulated solutions used in these tests since it was originally thought to be an insignificant component of the Purex 1WW liquor.

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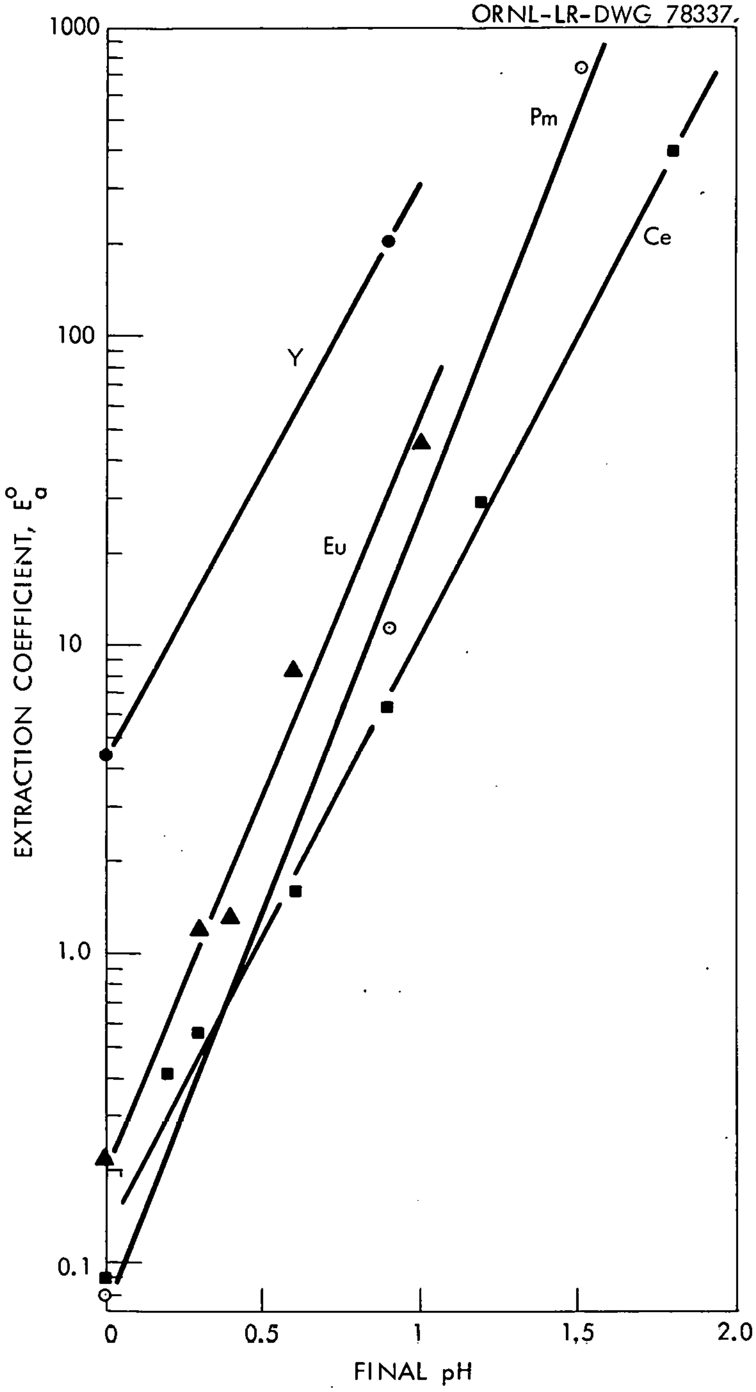

Fig. 3. Extraction of Rare Earths and Yttrium from Sodium Nitrate-Nitric Acid Solution (2 M ΣNO_3^-). Aqueous: 0.5 g/liter each of Ce, Eu, and Y in $NaNO_3$-HNO_3 solution with appropriate tracers. Organic: 0.2 M D2EHPA—0.1 M NaD2EHP—0.15 M TBP in Amsco 125-82. Organic/aqueous phase ratio: 2/1. Contact time: 6 min.

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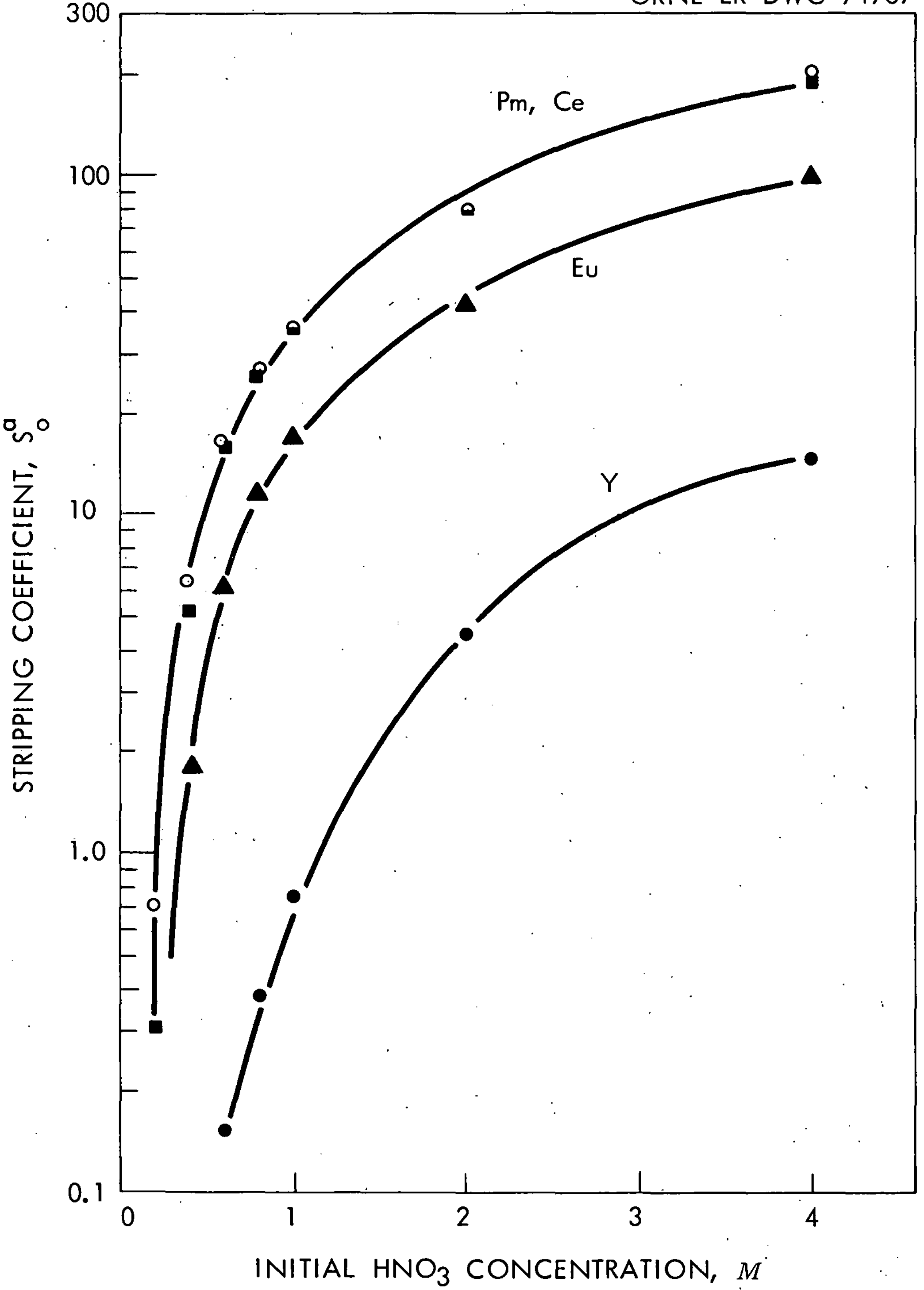

Fig. 4. Stripping of Rare Earths and Yttrium with Nitric Acid. Organic: 0.2 M D2EHPA—0.1 M NaD2EHP—0.15 M TBP in Amsco 125-82 containing extracted rare earths with appropriate tracers. Phase ratio: 1/1. Contact time: 5 min.

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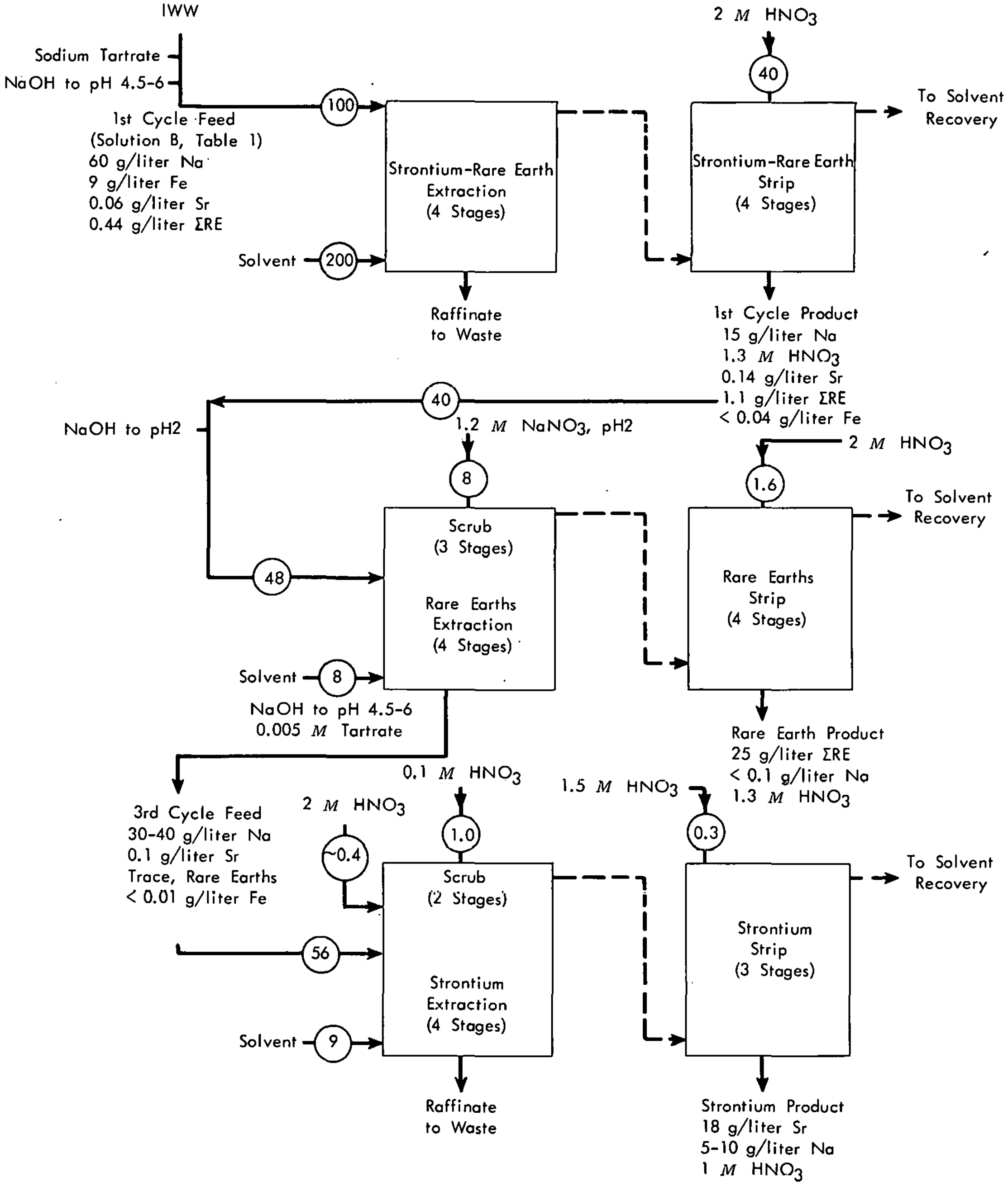

Fig. 5. Flowsheet for Recovery of Strontium and Rare Earths from Adjusted 1WW. Numbers in circles denote relative volume flows.

three cycles is 0.2 $\underline{M}$ D2EHPA—0.1 $\underline{M}$ NaD2EHP—0.15 $\underline{M}$ TBP in Amsco 125-82. As noted previously, this proportion of the acid and salt forms of the extractant prevents excessive pH change in the extraction system, which is especially important in cycles 1 and 3 for maintaining the efficiency of the strontium extraction.

In the first cycle, more than 99% of the strontium and more than 95% of the rare earths are recovered from the tartrate-complexed feed at pH 4.5 to 6 by countercurrent extraction at an organic/aqueous ratio of 2/1. The first-cycle product is obtained by co-stripping with 2 $\underline{M}$ HNO_3 at an organic/aqueous ratio of 5/1. Fission-product decontamination factors measured over this cycle are about 25 from ruthenium, 10 from Zr-Nb, and 25 from cesium. Although most of the uranium, 5 to 25% of the iron, and some aluminum are extracted, these elements are not stripped by the 2 $\underline{M}$ HNO_3 but are removed from the solvent in a subsequent solvent recovery step. Less iron and aluminum are extracted if phase contact times are held to a minimum.[3]

Second-cycle feed is prepared by adjusting the first-cycle strip product to pH 2 with caustic. The rare earths are extracted at this pH while strontium remains in the aqueous phase.[6] To aid this separation, the extract is scrubbed with one-fifth its volume of 1.2 $\underline{M}$ $NaNO_3$ (pH 2). The strontium in the aqueous raffinate is almost free of rare earths. The rare earths are stripped from the scrubbed extract with 2 $\underline{M}$ HNO_3 to give a product solution nearly free of strontium and containing about 25 g of rare earths per liter.

The second-cycle raffinate is adjusted to pH 6 with caustic for the third cycle, the purpose of this cycle being to concentrate the strontium and to further separate it from sodium and radioactive contaminants. Scrubbing with a controlled amount of nitric acid to give a pH of 3 to 4 in the scrub system greatly improves the separation from sodium.[9] Stripping with 1.5 $\underline{M}$ HNO_3 yields a strontium product solution containing 18 g of strontium and less than 10 g of sodium per liter.

4.3.1 Solvent Recovery

Iron, uranium, aluminum, and other extracted elements are removed from the used solvent by contacting with sodium carbonate solution (about 1 $\underline{M}$) containing sodium tartrate. After partial acidification to the original composition, the recovered solvent is recycled to the extraction step.[11]

4.4 Demonstration Runs

The three-cycle process was successfully demonstrated in miniature mixer-settlers, first with simulated Purex 1WW,[7] and finally in a hot cell, with a sample of actual Purex 1WW liquor from the Hanford plant.[8] The results of the hot-cell tests were in good agreement with data from prior batch and continuous tests.

The strontium and rare earths recoveries in the first cycle were 99.7 and 94%, respectively. Greater recoveries of rare earths should be possible by increasing the extraction contact times (Fig. 2). First-cycle decontamination factors were 45 from cesium, 170 from ruthenium, and about 3000 from Zr-Nb, the latter value being much higher than predicted from other tests, probably due to scavenging of these elements by a small amount of precipitate that formed in the adjusted feed.

Nearly all the strontium and rare earths in the first cycle product were recovered in the subsequent cycles. However, the rare earth/strontium decontamination factor for the second cycle was 80, compared with 2.5×10^4 obtained in earlier tests, owing to accidental operation at pH's higher than intended. Overall strontium decontamination factors were better than 1500 from rare earths, about 10^5 from Zr-Nb, about 3×10^3 from cesium, about 10^4 from ruthenium, and more than 2×10^4 from iron. The strontium product solution contained nickel at a concentration approximately equal to the strontium; however, subsequent tests showed that the addition of a small amount of ethylenediaminetetraacetic-acid to the third cycle feed prevents nickel extraction without affecting strontium recovery.

While the results of the calcium analyses of the strontium product solutions were inconclusive, previous data have shown that calcium is extracted more strongly than strontium and should follow strontium through the process. For example, from Solution B at pH 5.6, the extraction coefficients for calcium, strontium, and barium were about 490, 5, and 0.01, respectively.[4] These same data show that calcium-strontium separations can be achieved by D2EHPA extraction. Effective separations have been obtained at Hanford by partitioning in the stripping cycle.[29,31]

McHenry and Posey of the Oak Ridge National Laboratory Isotopes Division have described a calcium-strontium separation process based on a D2EHPA extraction from acetate-buffered solutions.[32]

The duration of the hot-cell test was not sufficient to provide data on stability of the solvent to radiation. However, a modified version of the D2EHPA process has been developed and used at Hanford for routine production of megacurie amounts of Sr^{90} from highly radioactive waste concentrates.[29,31]

5. PROMETHIUM AND RARE EARTH SEPARATIONS

The well-known separability of rare earths by extraction with tributyl phosphate from concentrated acids[12-14] was used in developing a process[15,16] for separating promethium from a mixture of fission-product rare earths such as that obtained from the D2EHPA strontium-rare earth recovery process described above. The two-cycle flowsheet is based on separation factors of about 1.9 between promethium and the adjoining rare earths, neodymium and samarium, when extracting from 12 $\underline{M}$ HNO_3 with 100% TBP. Coefficients at lower acidities are small enough to strip the elements from the organic phase with water or dilute nitric acid. Stream flows and the feed points of the multistage countercurrent partitioning system are chosen so that in the first-cycle promethium and the heavier rare earths are extracted, separating them from neodymium and the lighter rare earths. After being stripped with 2 $\underline{M}$ HNO_3 and concentrated by evaporation, the promethium is isolated in the second-cycle aqueous phase by extracting away yttrium, samarium, and the heavier rare earths. Since this process has been described,[15,16] further details are not presented here.

Cerium may be recovered from the promethium process first-cycle raffinate by extracting with D2EHPA after oxidation to Ce(IV). Recovery processes for cerium (and yttrium) have been developed and used routinely in the ORNL fission product production facilities.[33] Extraction by D2EHPA is also a potential alternate to TBP extraction for the separation of promethium and other rare earths.[26,34]

6. CESIUM RECOVERY

A new method was developed for recovering cesium from alkaline waste solutions by extraction with substituted phenols in a suitable diluent.[8,9,18] Most studies were made with tartrate-complexed simulated Purex 1WW (Solution C, Table 2) and tartrate-complexed formaldehyde-treated Purex 1WW (Solution D, Table 2) but the process is also applicable to the treatment of Hanford-tank-farm supernatant liquids (Solution E, Table 2). Of the compounds examined thus far, best results were obtained with p-dodecylphenol (PDP) and especially o-phenylphenol (OPP), 4-chloro-2-phenylphenol (PCOPP), 4-sec-butyl-2-(α-methylbenzyl)phenol (BAMBP), and 4-chloro-2-benzylphenol (Santophen-1).

Superficially at least, alkali metal extraction by the phenols may be considered as cation exchange between alkali metal ion M^+ and the hydrogen of the phenol, as represented by the general equation,

$$aM^+_{aq} + bRH_{org} \rightleftharpoons [M_aR_bH_{b-a}]_{org} + aH^+_{aq} \quad , \qquad (2)$$

where RH is a substituted phenol and the subscripts aq and org refer to the aqueous and organic phases, respectively. Cursory tests confirm that one H^+ is released for each Cs^+ extracted. From the simplest stoichiometry both a and b would be expected to equal 1. However, reagent-dependence tests indicate that b is larger than 1. For example, a log-log plot of the cesium extraction coefficient versus free phenol (PDP and BAMBP) concentration in diisopropylbenzene from tracer solution at pH 11.7 to 11.8 gave a slope of about 3, indicating that b is about 3 (ref 9). In other experiments, a maximum loading of about 1 mole of cesium per 6 moles of phenol was obtained by contacting 0.5 M or 1.0 M BAMBP in diisopropylbenzene with concentrated $CsNO_3$-CsOH or CsOH solutions at pH about 13.5 (ref 9). The phenols showing the best extraction properties are extremely weak acids so that, in addition to sensitivity to pH change, appreciable cesium extractions are obtained only from highly alkaline liquor. As expected, the extracted cesium is easily stripped by very dilute acids. Cesium transfer during both extraction and stripping is rapid (equilibrium attained in less than a minute).

In contacting highly alkaline (NaOH) liquors, appreciable quantities of some phenols are transferred from the solvent to the aqueous phase, with an accompanying decrease in aqueous pH. This is presumably due to the partial conversion of the phenol to the sodium phenate salt which distributes almost completely to the aqueous solution. The amount converted depends upon the aqueous caustic concentration, the organic/aqueous phase ratio, and the phenol structure. With 1.0 M OPP in diisopropylbenzene, distribution to Solution C is negligible below equilibrium pH 10 and small at pH 11, but increases rapidly thereafter with increasing caustic concentration (Fig. 6). At equilibrium pH 13, about two-thirds of the OPP distributes to the aqueous at a phase ratio of 1/1. The behavior of PCOPP and Santophen-1 is similar, although losses are lower at comparable pH's. By contrast, the distribution of BAMBP to the same solution is less than 1 g/liter, even at pH 13. The reaction of this reagent with caustic is low, and there is little pH change in the aqueous phase.[9] High losses of extractant from the solvent have a large depressing effect on the cesium extraction coefficient owing to its high power dependence on phenol concentration. However, it is important to note that such solvents can still be used effectively in countercurrent extraction by adding acid to the final stages to lower the pH slightly, for example, to 10 or 11 (Fig. 6). This regenerates the aqueous-phase sodium phenate to the phenol, which then returns to the organic phase.[8] Acid addition is essential with OPP and PCOPP but not with BAMBP and probably not essential with Santophen-1 provided that the extractions are conducted at a pH less than 12. The more aqueous-soluble reagents do impose an upper limit on feed pH and sodium concentration to avoid emulsion, probably caused by third-phase formation.

The dependence of the cesium extraction coefficient from adjusted Purex 1WW (Solution C, Table 2) on final pH is shown in Fig. 7 for 1 M solutions of phenols in diisopropylbenzene. With BAMBP, the coefficient is about 2 at equilibrium pH 12, increasing to 6 at pH 12.5, and 22 at pH 13. With OPP, PCOPP, and Santophen-1, the coefficients increase with increasing pH up to pH 12 to 12.3 and then decrease. The decrease at the higher pH's is due to the loss of phenol from the solvent phase. At pH values lower than 12, where the effect of extractant loss on the

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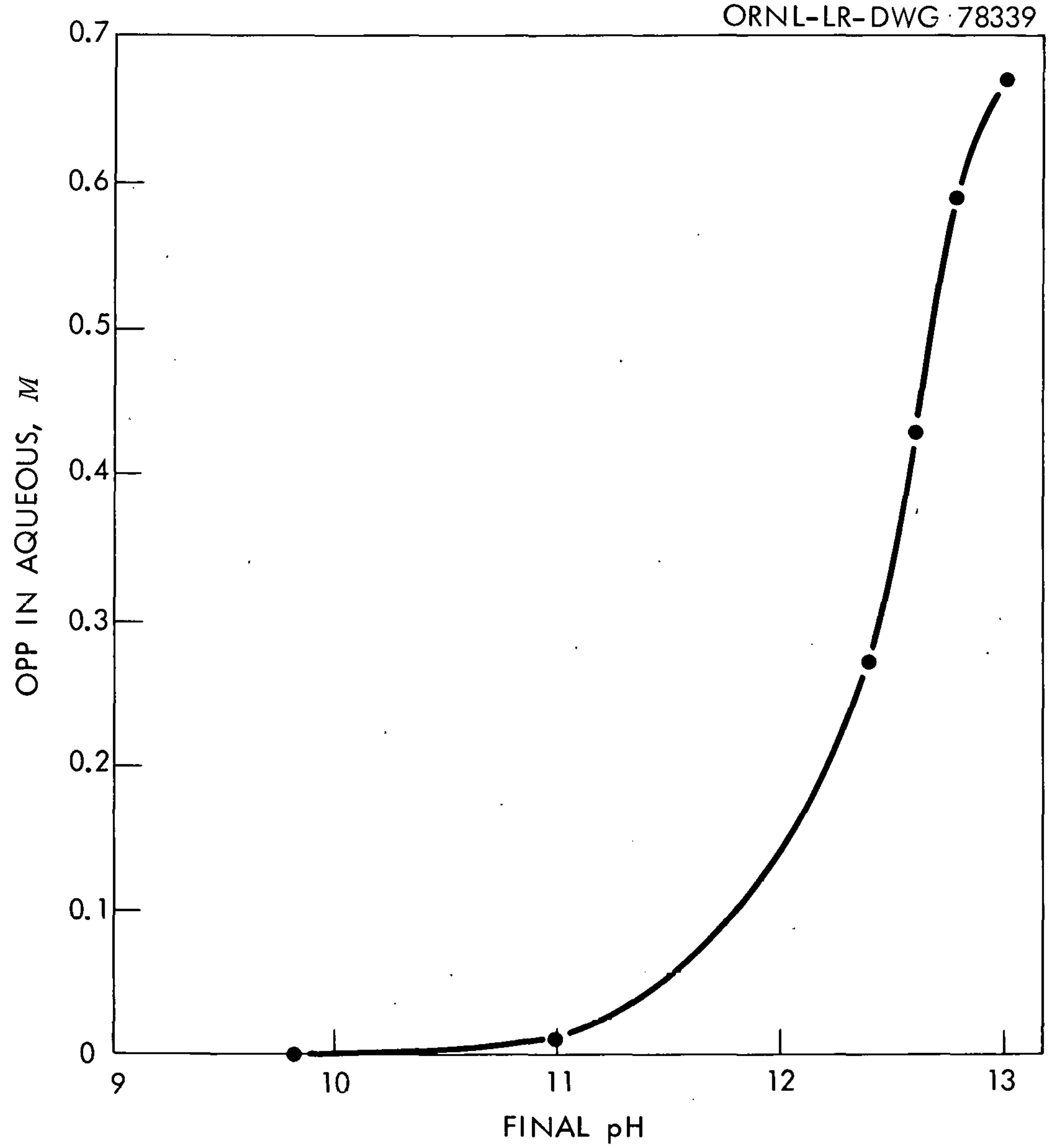

Fig. 6. Loss of o-phenylphenol to the Aqueous Phase. Aqueous: Solution C adjusted to various pH levels ranging 10 to 13.6. Organic: 1 M OPP in diisopropylbenzene. Organic/aqueous phase ratio: 1/1.

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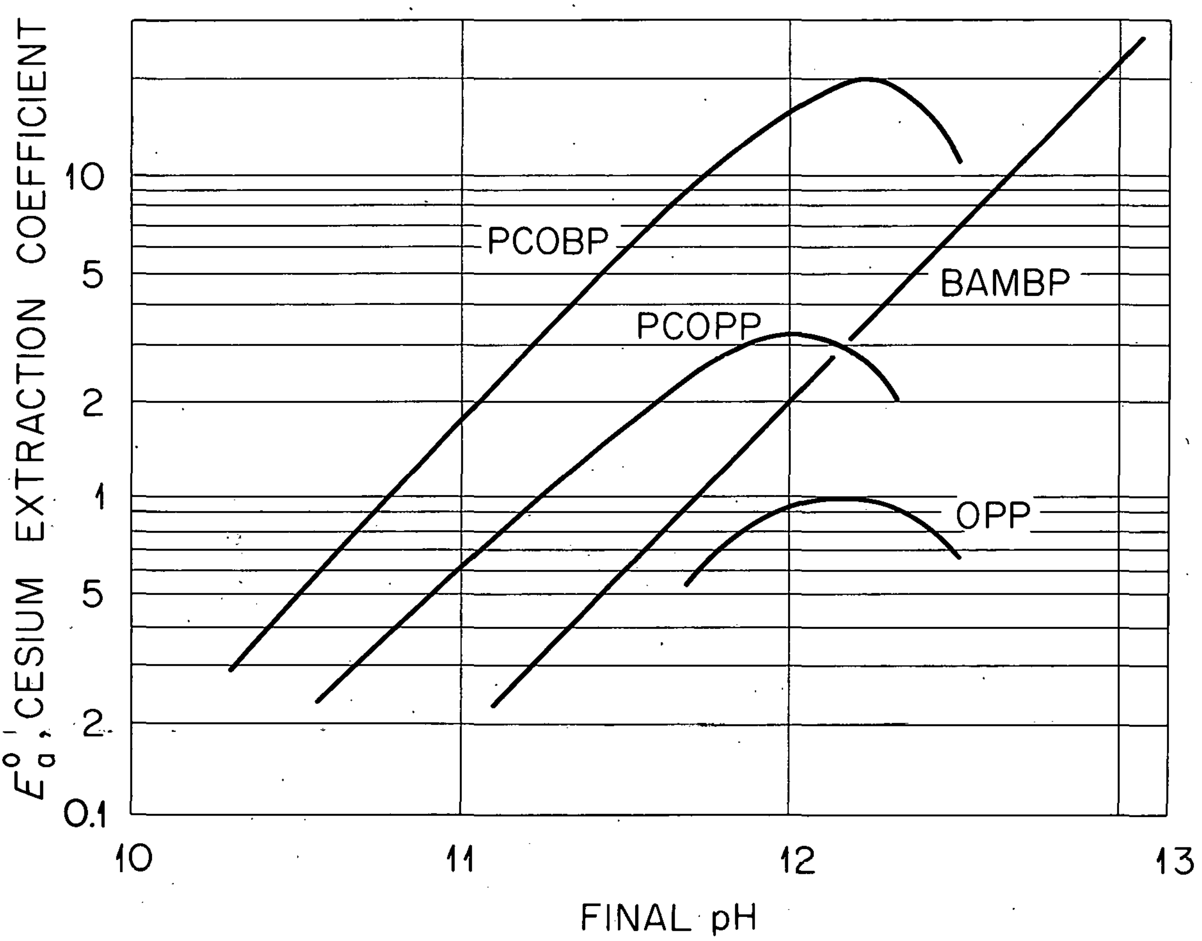

Fig. 7. Extraction of Cesium from Adjusted Purex 1WW Solution.
Aqueous: Solution C adjusted to various pH levels ranging 11 to 13.
Organic: 1 M phenol in diisopropylbenzene. Phase ratio: 1/1.

coefficient is relatively small, coefficients for Santophen-1 and PCOPP are nine times and three times, respectively, higher than those for BAMBP, which in turn are higher than those for OPP.

The affinity of the solvent for cesium is much greater than that for sodium or other alkali metals,[8,9] so that recovery and separation is attained even from the originally highly acid waste liquors that have been neutralized with caustic to give a large concentration of sodium ion. The selectivity of the phenols for cesium over other fission products is also excellent.[8] For example, coefficients for extraction of strontium, ruthenium, Zr-Nb, and europium from Solution C with 1 M OPP in diisopropylbenzene were less than 10^{-3} under conditions where the cesium coefficient was about 1. In addition, the extractions of metals such as iron, aluminum, chromium, and nickel are extremely weak.

Of the diluents tests,[8] best results were obtained for most of the phenols with substituted benzenes, such as diisopropylbenzene. This diluent has a high flash point (about 175°F), is commercially available, and was used throughout most of the experimental studies. Favorable results, with lower cesium extraction coefficients, were obtained with trichloroethylene, carbon tetrachloride, 80% Amsco 125-82—20% tridecanol, and 1,2-dichloroethane. Different results were obtained with BAMBP. In this case, cesium extraction coefficients were considerably higher with aliphatic diluents, for example, with Amsco 125-82 and kerosene, than with diisopropylbenzene.

6.1 Process Tests

A cesium recovery flowsheet (Fig. 8) was evaluated in batch countercurrent tests with simulated Purex waste solutions. Cesium recoveries of 97 to better than 99.8% were demonstrated from Solution D with OPP and from Solution C with OPP, PCOPP, Santophen-1, and BAMBP.[9] The cesium was separated from other components of the waste by extracting in 5 or 6 stages with 1 M substituted phenol in diisopropylbenzene at an organic/aqueous phase ratio of 1/1. The pH in the last extraction stage was adjusted to 10 or 11 to avoid extractant loss, as described above. The extract was scrubbed with dilute caustic at an organic/aqueous ratio of 5/1 to remove entrained liquor and to give still further

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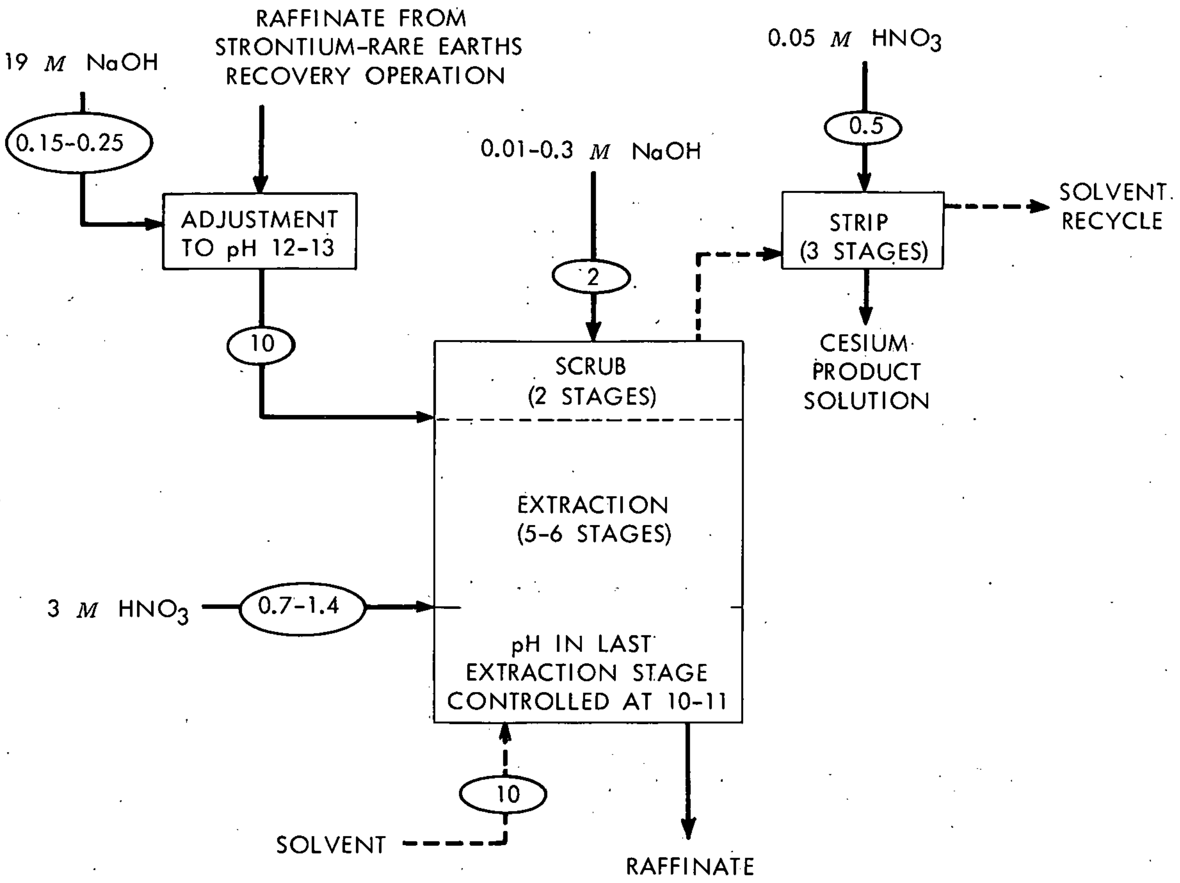

Fig. 8. Flowsheet for Recovery of Cesium from Adjusted Purex 1WW Solution. Solvent: 1 M phenol in diisopropylbenzene. Numbers in circles denote relative volume flows.

decontamination from sodium and other cations. The caustic concentration chosen for scrubbing depends on the phenol used, that is, on the balance between cesium extraction power and reactivity toward sodium hydroxide. With OPP, 0.3 M NaOH is a suitable concentration.[8] At lower concentrations, reflux of cesium to the extractor is excessive. With Santophen-1 and BAMBP, 0.01 M NaOH can be used without excessive refluxing. The extracted cesium was stripped easily with 0.05 M HNO_3. At organic/aqueous phase ratios of 20/1, stripping coefficients were higher than 1000 for OPP, PCOPP, Santophen-1, and BAMBP.

Typical results are shown in Table 3 for a batch countercurrent run with 1 M BAMBP in diisopropylbenzene to recover cesium from Solution C adjusted to pH 12.6. Cesium recovery was better than 99.8% in five stages. In this particular test, the extract was scrubbed with 0.3 M NaOH although, as mentioned above, 0.01 M NaOH would have been adequate and preferable. Cesium extraction coefficients in the extraction and scrub sections were around 8 and about 33, respectively. The pH in the fifth extraction stage was controlled at 10 to 11 by acid addition to prevent any loss of BAMBP to the raffinate. The cesium was stripped to better than 99.8% in a single stage with 0.05 vol of 0.05 M HNO_3, yielding a product solution containing 2.4 g of cesium, 0.2 g of sodium, and 0.04 g of iron per liter. The overall cesium/sodium decontamination factor was nearly 6000.

Although countercurrent tests have not been made with the simulated Hanford tank waste (Solution E, Table 2), batch extraction tests show that effective cesium recovery could be readily obtained. Cesium extraction coefficients for 1 M BAMBP in diisopropylbenzene at a phase ratio of 1 from Solution E were 6 at initial pH 12.5 and 28 at initial pH 13.1.

Cyclic tests with high-activity waste will be made in order to test the stability of the phenols to radiation degradation. Resistance to chemical degradation of BAMBP was indicated in a batch cyclic test with simulated waste. No significant variation in performance was apparent over 15 extraction-stripping cycles.

Table 3. Batch Countercurrent Recovery of Cesium

Organic: 1 M BAMBP in diisopropylbenzene
Aqueous feed: Solution C adjusted to pH 12.6 with NaOH
Scrub: 0.3 M NaOH
Acid (to 5th extraction stage): 3 M HNO_3
Flow ratios: Organic/feed/scrub/acid = 1/1/0.2/0.075

Stage	pH	Cs γ-Activity (counts min^{-1} ml^{-1}) Organic	Aqueous	Cesium Extraction Coefficient (E_a^o)
Scrub-2	--	1.78×10^5	5.55×10^3	32
-1	--	1.78×10^5	5.27×10^3	34
Aqueous feed	12.6	--	1.76×10^5	--
Extraction-1	12.7	1.80×10^5	2.06×10^4	8.7
-2	12.7	2.62×10^4	3.4×10^3	7.7
-3	12.7	4.4×10^3	6×10^2	7.3
-4	12.6	6×10^2	$<2 \times 10^2$	>3
-5	10.9	--	$<2 \times 10^2$	--

6.2 Other Extractants

Many phenols, other than those mentioned, have been tested and have given inferior performance owing to low extraction power and/or high aqueous solubility.[9] Nevertheless, the considerable variation in extraction behavior of the various phenols has encouraged continuing search for compounds of still better extraction properties.

High-molecular-weight sulfonic acids (and sodium sulfonates), such as dinonylnaphthalenesulfonic acid, extract cesium[18,35,36] from both acid and alkaline solution over the pH range 1 to 12. As to applications to process liquors, these extractants have not been competitive with the phenols owing to relatively poor selectivity and low extraction coefficients.

Sodium tetraphenylboron (usually used in hexone) is a strong and selective extractant for cesium from acid (pH higher than 2) and alkaline waste liquors, but a suitable stripping method has not been found for this reagent.[36-38]

High-molecular-weight monoalkylphosphoric acids, such as monoheptadecylphosphoric acid, extract cesium in preference to sodium from acid (pH 1 to 3) sodium nitrate solutions and show potential utility in separating cesium and sodium from simple solutions.[18] Its application to the highly contaminated waste solutions has been impractical owing to formation of heavy emulsions and poor selectivity.

Promising methods for cesium extraction from waste solutions with dipicrylamine in nitrobenzene have been reported.[31,39-41] Detailed comparisons of this solvent with the phenols have not been made.

7. ZIRCONIUM-NIOBIUM

The high affinity of D2EHPA for tetravalent metal ions[24] can be utilized in recovering Zr-Nb from acidic wastes. With 0.3 M D2EHPA—0.15 M TBP in Amsco 125-82, about 90% of the Zr-Nb was extracted upon contacting an equal volume of acid Purex 1WW (Solution A, Table 2) for 30 min at room temperature (Fig. 9). Approximately the same recovery was achieved in 10 min at 53°C and in 1 min at 83°C. As expected from the large extraction coefficients (E_a^o = 15 to 20) obtained from the highly acid liquor, stripping was ineffective with mineral acids. However, complexants such as oxalic acid were effective stripping agents; more than 99% of the Zr-Nb was removed from the solvent after five 10-min contacts with 1 M oxalic acid at an organic/aqueous ratio of 5. The presence of TBP in the solvent had a large beneficial effect on stripping but no significant effect on extraction.[17]

8. PRETREATMENT OF AQUEOUS FEED WITH AMINES

Preliminary tests[9,19] have shown that large amounts of the major waste components (i.e., nitric acid, iron, and sulfate) can be extracted from simulated Purex 1WW (Solution A, Table 2) with a primary amine. Most of the fission product zirconium-niobium, ruthenium,* and rare earths can also be extracted. Removal of the nitric acid and iron produces a

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*The aqueous chemistry of ruthenium is complex and often depends upon solution history, and the quantitative prediction of its behavior is not always possible with simulated feeds.

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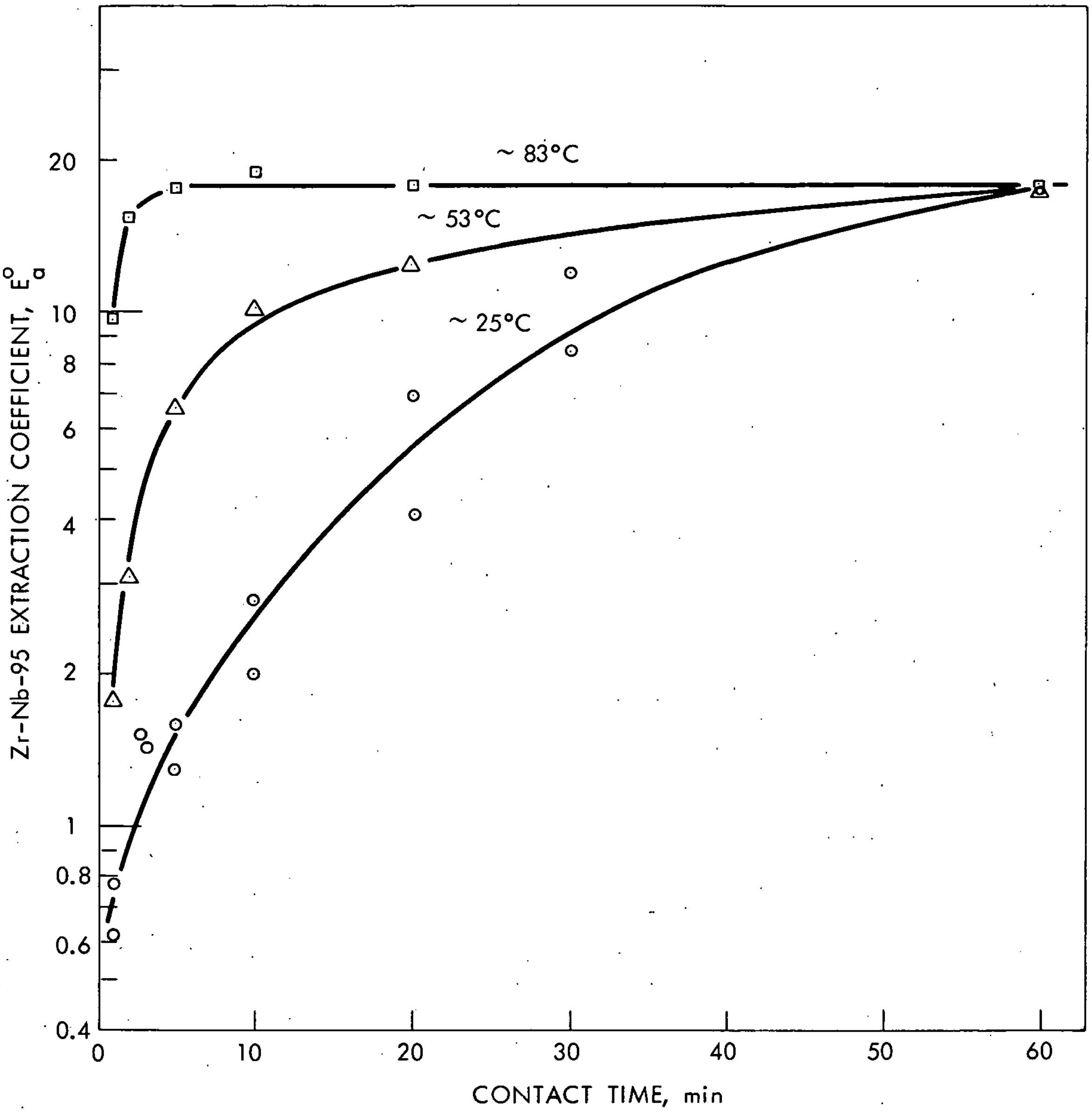

Fig. 9. Rate of Zr-Nb Extraction from Purex 1WW Solution. Organic: 0.3 M D2EHPA—0.15 M TBP in Amsco 125-82. Aqueous: Solution A. Phase ratio: 1/1.

more amenable feed to the strontium and cesium recovery processes due to lower requirements for sodium hydroxide and sodium tartrate in feed adjustment and lower sodium ion concentration in the resulting liquor. The prior removal of some of the other fission products can also be an advantage.

As shown in Fig. 10, the extraction of iron and sulfate is negligible until sufficient amine is supplied to extract most of the nitrate. With 0.26 M Primene JM in Amsco 125-82 diluent, 72% of the nitrate, 2% of the sulfate, and less than 1% of the iron were extracted in a single contact at an organic/aqueous phase ratio of 14/1. At a ratio of 26/1, 96% of the iron and nitrate and 43% of the sulfate were extracted. About 99% of the zirconium-niobium, 88% of the ruthenium, and 57% of the cerium were also extracted at the higher ratio, while more than 97% of the cesium and strontium remained in the aqueous phase. In all tests at high phase ratios, to prevent precipitation of remaining hydrolyzable metals, the final aqueous pH was held at 2 or less by supplying a portion of the amine extractant in the sulfate salt form or by adding sulfuric acid to the extractor.

By proper control of flow ratios, the extracted cerium (and presumably other rare earths) can be selectively scrubbed from the solvent and may be combined, if desired, with the strontium-cesium stream.[9] The other extracted metals can be stripped with nitric acid, and the amine nitrate formed can be converted to free amine for recycle by contacting with a base.

Possibilities for using amines to recover fission-product zirconium-niobium, ruthenium, and rare earths are also suggested by the extraction data.

9. CONCLUSIONS

The developments described in this paper offer a versatile, integrated solvent extraction flowsheet for the recovery and purification of nearly all the fission products of principal importance from reactor fuel process waste liquors, including strontium, rare earths (mixed or separated), cesium, and zirconium-niobium. A schematic diagram of such

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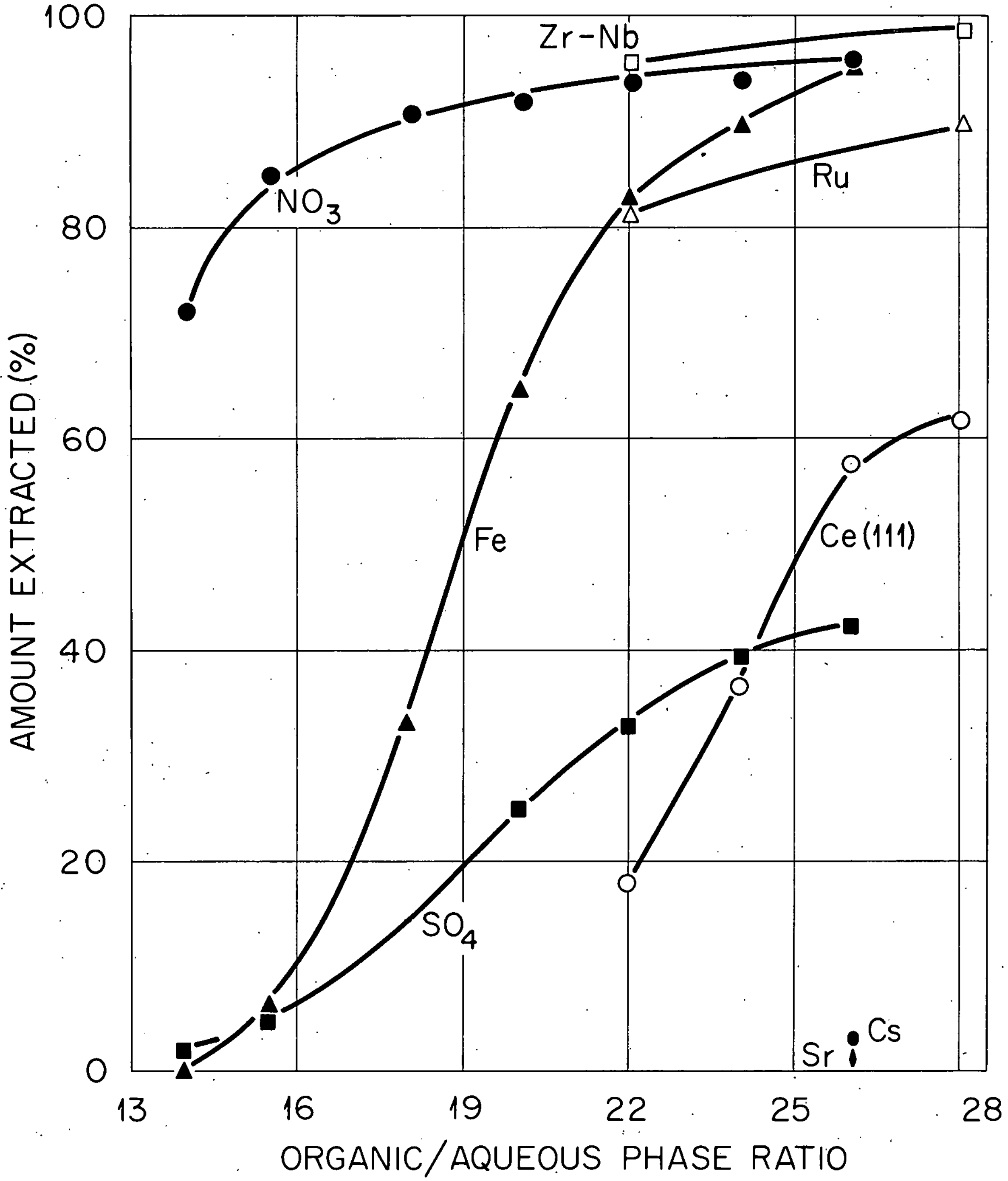

Fig. 10. Extraction of Nitric Acid, Iron, Sulfate, and Fission Products from Purex 1WW Solution with Primene JM. Organic: 0.26 M Primene JM (partially in sulfate salt form at phase ratios eighteen and greater) in Amsco 125-82. Aqueous: Solution A. Contact time: 3 min.

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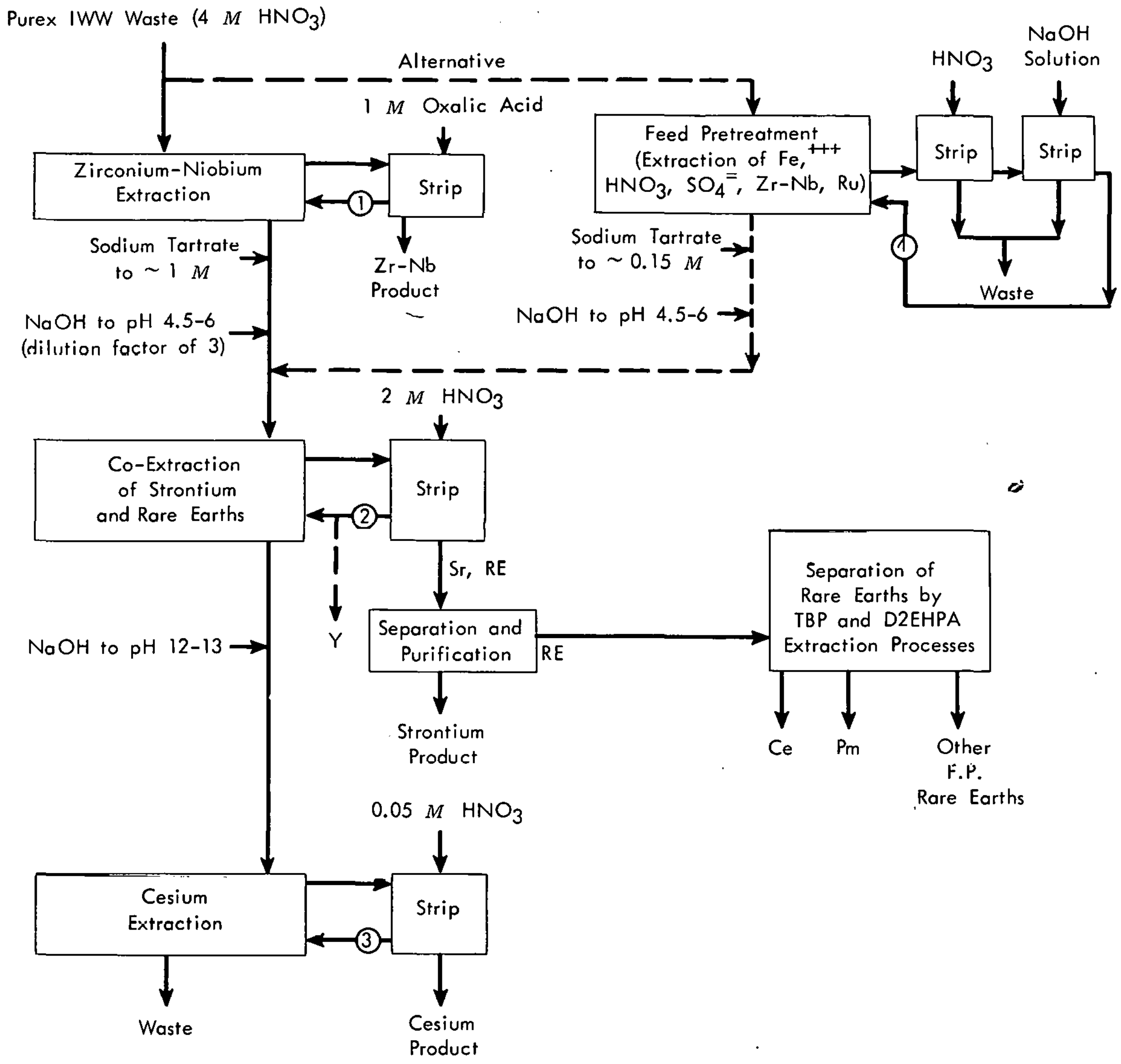

Fig. 11. Integrated Flowsheet for Recovery of Fission Products. Solvent: (1) 0.3 $\underline{M}$ D2EHPA—0.15 $\underline{M}$ TBP in Amsco 125-82; (2) 0.2 $\underline{M}$ D2EHPA—0.1 $\underline{M}$ NaD2EHP—0.15 $\underline{M}$ TBP in Amsco 125-82; (3) 1 $\underline{M}$ BAMBP in Amsco 125-82; (4) 0.25 $\underline{M}$ Primene JM in Amsco 125-82.

a flowsheet is shown in Fig. 11. Previous studies have suggested solvent extraction methods for recovering other valuable components from the waste liquors, including neptunium and plutonium with organonitrogen and organophosphorus compounds,[20] and technetium with organonitrogen compounds.[21]

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