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HOT SEMIWORKS STRONTIUM-90 RECOVERY PROGRAM

BASED ON WORK BY

CHEMICAL DEVELOPMENT OPERATION
CHEMICAL LABORATORY

JULY 17, 1963

HANFORD LABORATORIES

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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for Plutonium and Uranium
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HOT SEMIWORKS STRONTIUM-90 RECOVERY PROGRAM

Based on work by

Chemical Development Operation
Chemical Laboratory
Hanford Laboratories

July 17, 1963

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HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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SECTION 1. PROGRAM SYNOPSIS

G. L. Richardson and A. M. Platt

INTRODUCTION

In July, 1960, the Hanford Atomic Products Operation was asked by the AEC to undertake the recovery and purification of approximately 1 Mc of Sr^{90}. This long-lived, heat-generating fission product was needed for a series of prototype thermoelectric power units which were being developed by the Martin-Marietta Corporation for the AEC's Division of Reactor Development.[20] The units were basically similar in design (Figure 1.1) and consisted of an encapsulated strontium titanate heat source powering lead telluride thermocouples.

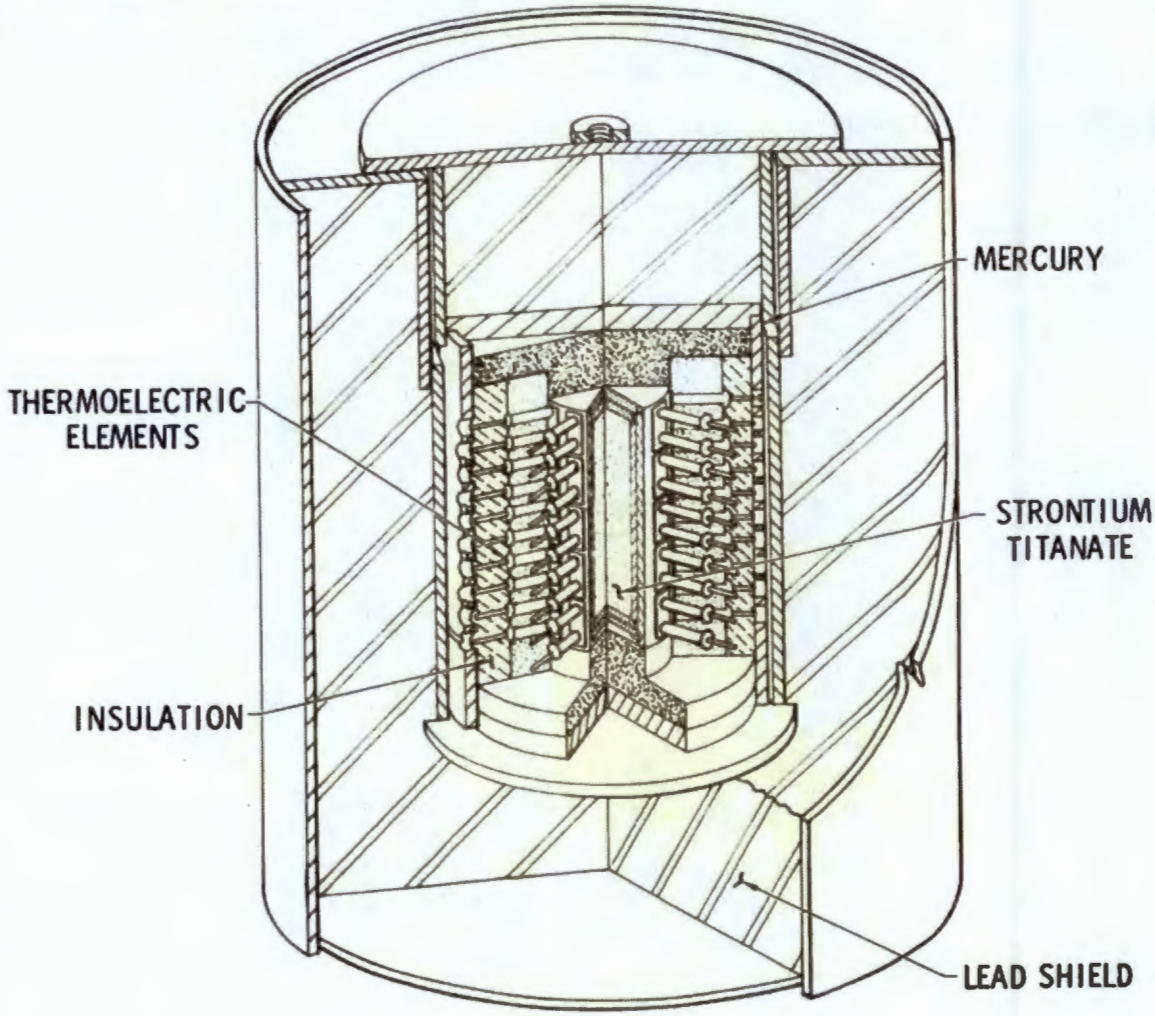

FIGURE 1.1

Artist's Conception of 5-Watt Sr^{90} Generator for Arctic Weather Station

Five units were involved: a small, 5-watt (electrical) Weather Bureau Unit, two 10-watt SNAP-7 units (SNAP, an acronym of systems for nuclear auxiliary power), and two 60-watt SNAP-7 units for the Navy and Coast Guard. The two smaller SNAP-7 generators each required 40,700 curies of Sr^{90} and the two larger units 245,000 curies for a total of about 650,000 curies. The work locations for the units are:

5 watt unit - Axel Heiberg, Northern Canada (a weather station)

10 watt unit - Minna Bluff, McMurdo Sound, Antarctica (a weather station)

10 watt unit - Curtis Bay, Maryland (a flashing light navigation buoy)

60 watt unit - Gulf of Mexico (a Navy boat-type weather station)

60 watt unit - Chesapeake Bay (a 250-watt flashing light navigation buoy)

Hanford's contribution to the general program consisted of (1) recovery of a crude strontium concentrate from Purex Plant waste[7] (see Figures 1.2 and 1.3) (2) purification of 72 kilocuries of this crude material by ion exchange in Hanford's High Level Radiochemistry Cells,[28] (3) purification of 740 kilocuries of Sr^{90} by solvent extraction in the Hot Semiworks, and (4) design and fabrication of product shipping casks,[26] shown in Figures 1.4, 1.5, 1.6, and 1.7.

The Oak Ridge National Laboratory prepared, on an interim basis, the strontium titanate pellets for use in generators designed and built by the Martin-Marietta Corporation. It was necessary to meet tight schedules in the overall program to assure delivery of the two Arctic units during accessible periods in 1961.

This report describes the laboratory studies, radioactively cold development studies and radioactively hot development-recovery activities involved in the Hot Semiworks operations. Details are presented on the D2EHPA (di-2-ethylhexl phosphoric acid) extraction process successfully used in Hanford's Hot Semiworks and the development studies on solvent extraction, ion exchange and precipitation leading to the recovery and purification of nearly a megacurie of Sr^{90} during the Hot Semiworks Interim Program.

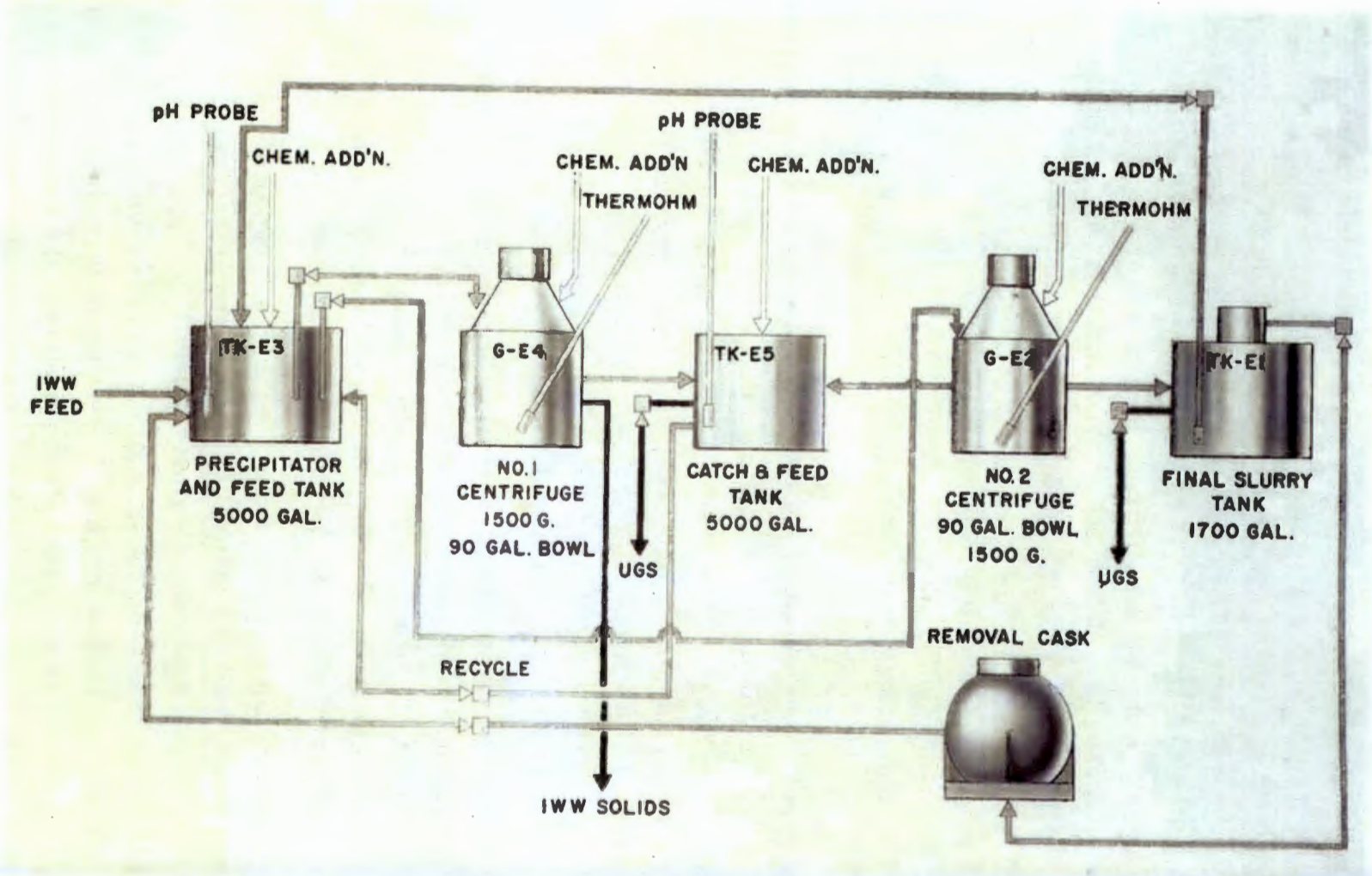

FIGURE 1.2

Fission Product Recovery-Purex Plant

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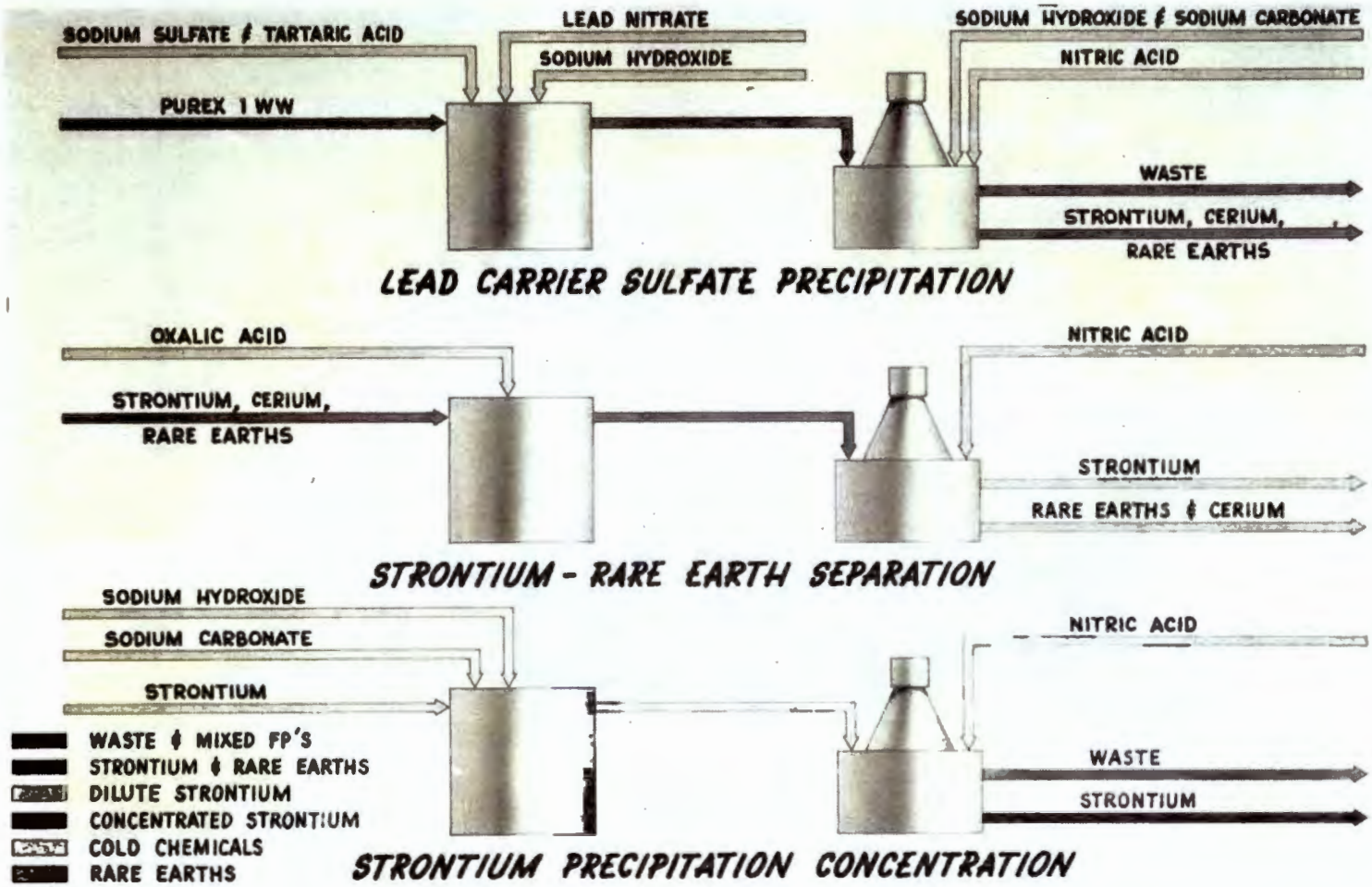

FIGURE 1.3

Purex Sr^{90} Recovery Flowsheet

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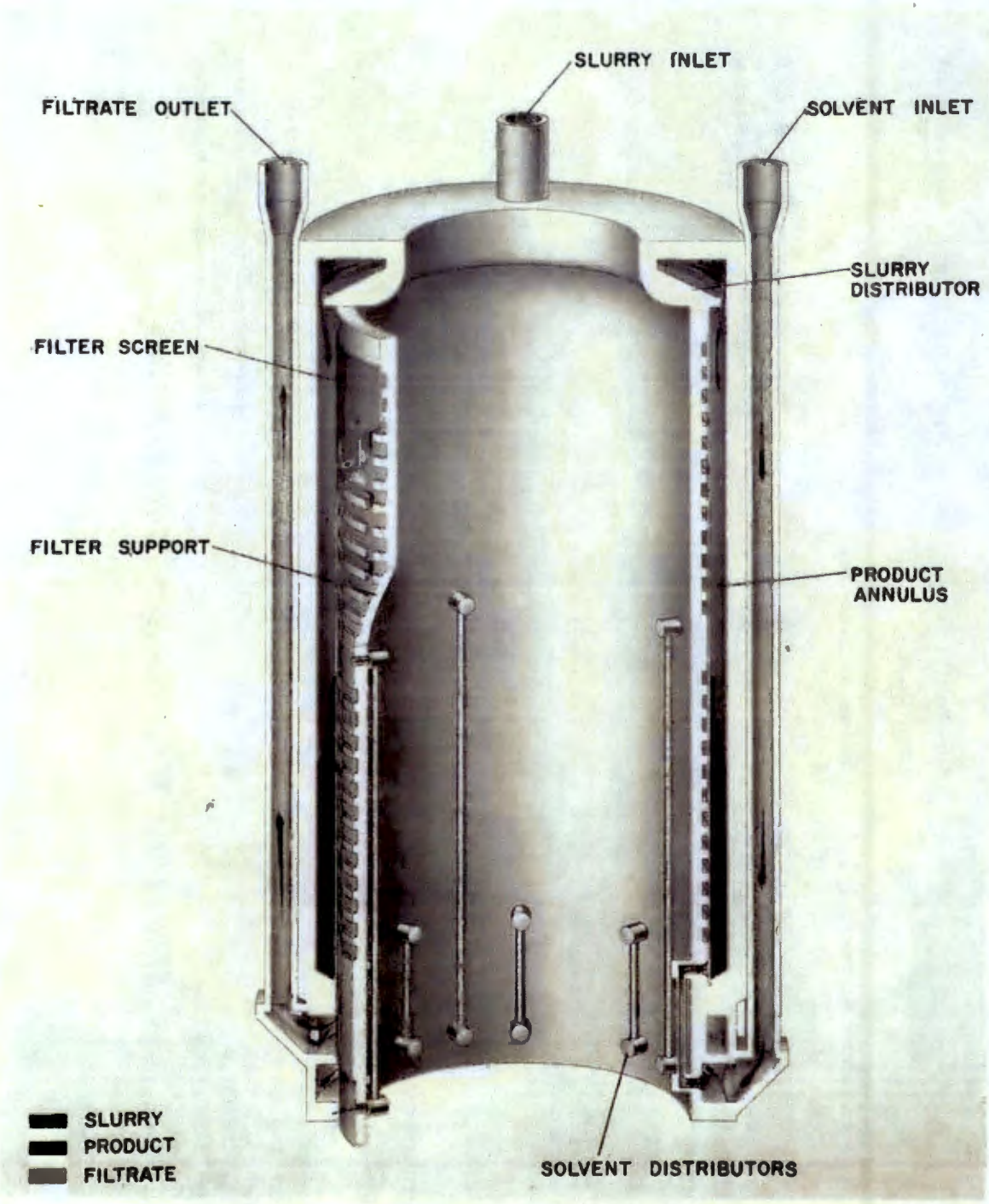

FIGURE 1.4
HAPO II Filter-Container

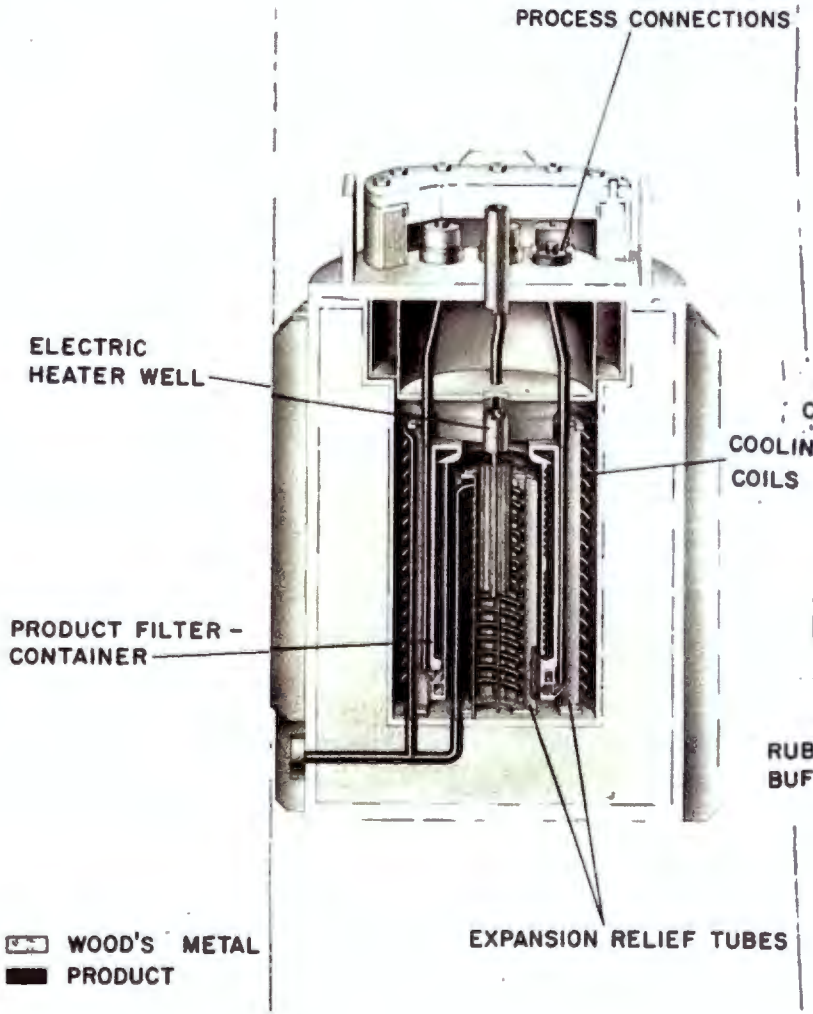

FIGURE 1.5

HAPO II Cask

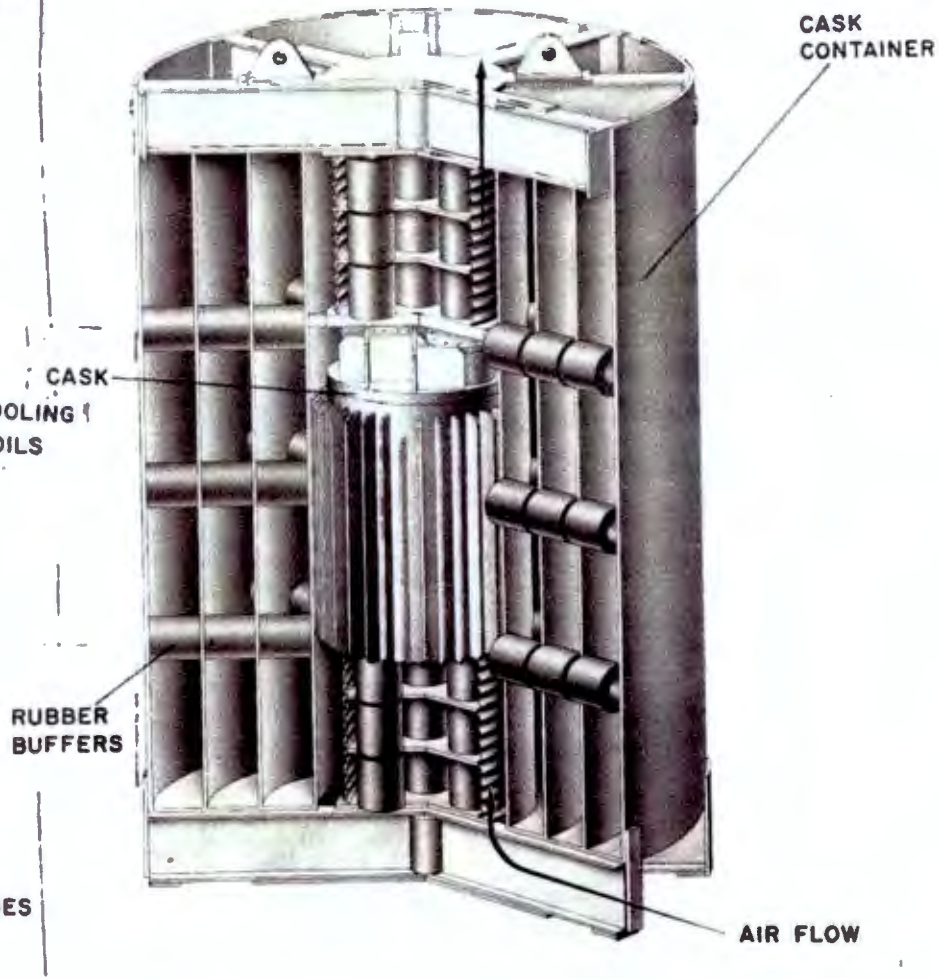

FIGURE 1.6

HAPO II Cask Container

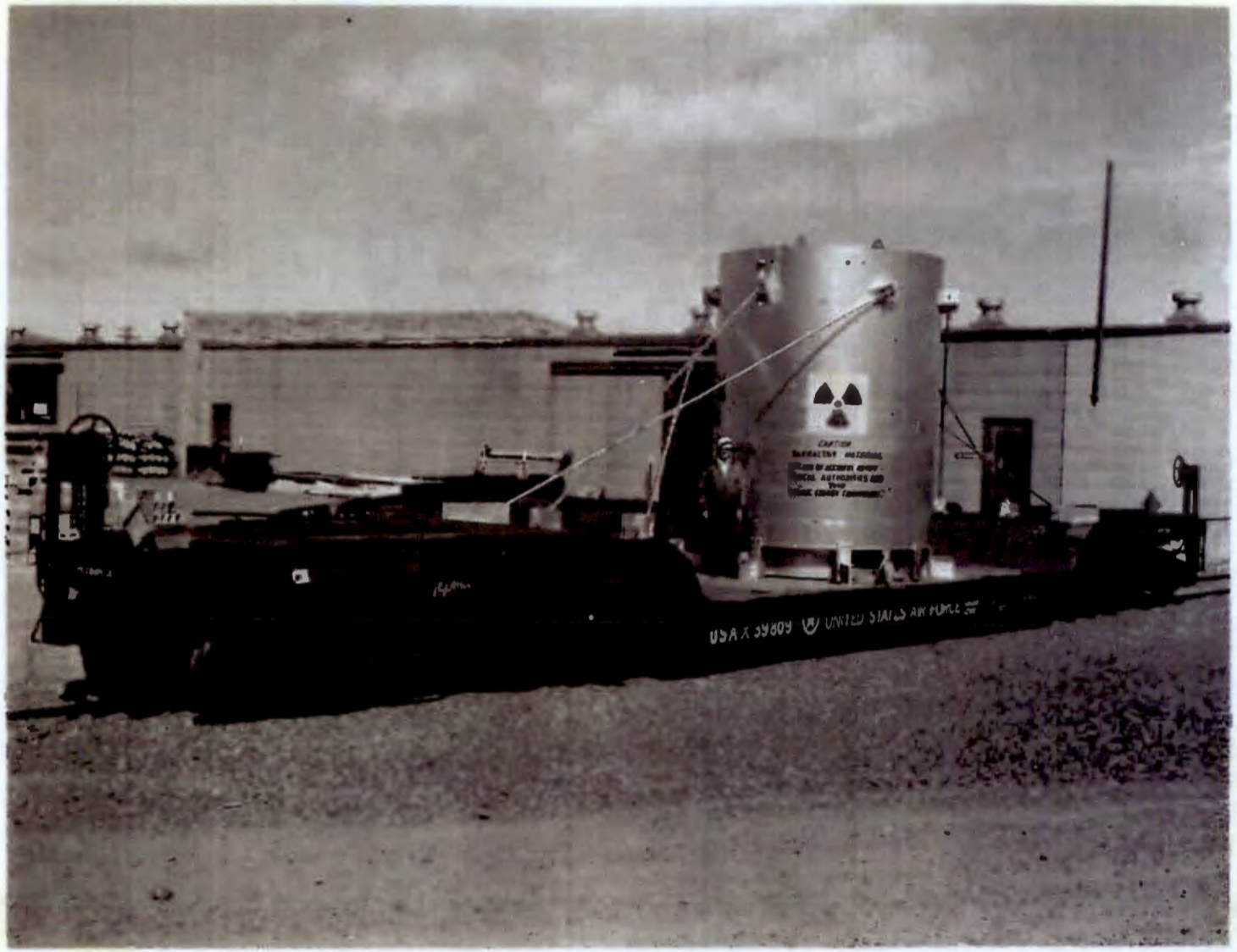

FIGURE 1.7

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OVERALL PROGRAM SUMMARY

Four runs, each processing 210 to 480 kilocuries of Sr^{90}, were made in the Hot Semiworks between May and October, 1961; each lasted about 2 weeks. A total of 744 kilocuries of purified Sr^{90} was isolated for shipment out of a total input of 1180 kilocuries. The overall material balance for the program is presented in the following table:

	Kilocuries of Sr^{90}			
Run No.	Crude Input	Total Input	Specification Product	Shipped or Stored Product
Sr-4	212	212	150	118
Sr-5	191	223[a]	169	375[b]
Sr-6	363	363	305	
Sr-7	418	478[a]	251[c]	251[c]
Total	1184	1276[a]	875[c]	744[c]

a. Includes rework material

b. Estimated by heat balance and material balance

c. Does not include an additional 169 kilocuries of stored out-of-specification product

The plant and process performance met expectations, and the process demonstrated fully the feasibility of using solvent extraction on a large scale for removing strontium from radioactive waste solutions. The flowsheet demonstrated in run Sr-6 has, with slight modification, been used successfully in a continuing program of Sr^{90} purification in the Hot Semiworks, now renamed the Strontium Semiworks.

The final run of the series also demonstrated the possibility of coextracting cerium and other rare earths with strontium, a possible objective of future waste management or fission product programs.

PRODUCT PURITY

Strontium-90 was the favored heat source for the generators because of its long half-life (28 years), adequate specific power (0.5 thermal watts per gram of total strontium), and the fact that the radiation from Sr^{90} and its short-lived Y^{90} daughter are almost entirely beta emitters with little or no associated gamma activity requiring extensive biological shielding.

To take advantage of the lower biological shielding requirements, the gamma emitters must be removed to a level insignificant in comparison to the associated bremmstrahlung radiation. Thus, the specifications for each gram of purified Sr^{90} permitted less than 0.0015 gamma curie of gamma emitters with energies greater than 2 Mev, less than 0.015 curie in the 1 to 2 Mev range, and less than 0.15 curie in the 0.2 to 1 Mev range. This corresponds to separation factors on the order of 10^4 to 10^5 from Ce^{144}, $ZrNb^{95}$, Ru^{106}, and most other gamma emitting fission products.

In addition, a high degree of purification from inert contaminants was also required so that the specific heat-generating rate of the strontium titanate would equal or exceed the design criteria of the generators (0.5 watts/cc). Thus, the non-strontium impurities had to be less than 25 wt% of the total cation weight and the Sr^{90} content had to be greater than 36% of the total cation weight. The crude feed stock prepared in the Purex Plant had up to 0.1M iron, 0.03M lead, and 0.005M calcium plus barium. Decontamination factors* as high as 400 for iron and lead, and 5 for calcium and barium were required.

The strontium produced in uranium fission contains only about 57 wt% Sr^{90}. The remainder consists of inactive strontium isotopes and the short-lived, high-energy Sr^{89} isotope. Since Sr^{89} has a half-life of only 51 days, it was removed by natural decay. The removal of Sr^{89} helps

---

* Defined as the ratio of initial to final weight per gram of Sr^{90}.

stabilize the generator temperatures to match the narrow operating temperature range of the lead telluride thermocouples. Minimization of the content of the HAPO product required storage for aging and a subsequent careful segregation of individual batches of Sr^{90} through all stages of purification.

SECTION 2. TECHNICAL BASES

G. L. Richardson, W. W. Schulz

INTRODUCTION AND SUMMARY

The theoretical basis for the D2EHPA solvent extraction of strontium from Purex plant crude Sr^{90} solution is discussed in this section. Of central interest is a method for estimating strontium distribution ratios in the presence of certain aqueous phase complexing agents and in the presence of competing extractable cations. The calculation method outlined is still considered to be in a somewhat primitive stage, but it should be useful in establishing new strontium recovery flowsheet concepts.

An ion exchange process suggested by Bray[6] for final purification of the Sr^{90} product is also discussed. Correlations for estimating the strontium capacity of Dowex 50W x 12 resin and the rate of elution of strontium from the resin are presented.

D2EHPA SOLVENT EXTRACTION OF STRONTIUM

LITERATURE REVIEW

The extractant D2EHPA has been used for several years in the Dapex process for uranium ore refining.[3, 4, 5, 15] Its chemical properties have been extensively investigated by Peppard and coworkers[25] at Argonne National Laboratory and by Baes,* Brown, Gillette, and associates[1, 8, 9, 10, 18, 29] at Oak Ridge National Laboratory.

Physical Properties of D2EHPA

Pure D2EHPA is a colorless liquid of formula weight 322.4 with the following physical properties:

---

*The recent review paper by Baes[1] is particularly useful.

SELECTED PHYSICAL PROPERTIES OF D2EHPA

Density	0.9770 g/ml, 20/20 C
Freezing Point	-60 C (glass formation)
Viscosity	53.0 centipoise at 20 C
Flash Point	385 F, Cleveland Open Cup
Solubility in Water	0.01 wt% at 20 C
Solubility of Water in D2EHPA	2.4 wt% at 20 C

Commercially available D2EHPA, as used at HAPO, generally contains only 91 to 94% D2EHPA. Impurities present include mono-2-ethylhexyl phosphoric acid, 2-ethylhexanol, pyroesters, and iron. Because of its high density and viscosity, D2EHPA must be diluted with an inert diluent to be usable in countercurrent liquid-liquid solvent extraction systems. Common kerosene type diluents have been widely used.

Sodium Salt of D2EHPA

The sodium salt of D2EHPA (NaD2EHP) can be prepared by neutralization of the acid form with NaOH or Na_2CO_3 solutions. The salt is soluble in water (a 25 wt% solution in water is available commercially) but only sparingly soluble in aqueous solutions which contain sodium ion. The solubility of NaD2EHP in Na_2CO_3 solutions, for example, decreases from 325 mg/liter at 0.38 M Na^+ to 7 mg/liter at 2.8 M Na^+.[8b]

The sodium salt also has limited solubility in common kerosene-type diluents. A modifier such as TBP (tributyl phosphate) must be added to the diluent to prevent formation of a NaD2EHP-rich third phase. The minimum amount of TBP required to prevent third phase formation in the presence of 10% Na_2CO_3 is given by the formula:[4, 5]

$$\underline{M}\ \text{TBP required} = 0.063 + 0.20\ (\underline{M}\ \text{D2EHPA in kerosene})$$

(Caution: Recent work has demonstrated that this recipe may not prevent third phase formation at lower aqueous phase sodium concentrations.)

Extraction at Low Solvent Loading

Reaction Mechanism - The existence of D2EHPA as a hydrogen-bonded dimer in most organic solvents has been well substantiated.[1, 5, 25b, 25d] The general extraction reaction of a metal ion M^{+z} at low solvent loadings may be represented as

$$M_a^{+z} + z\,(HR)_{2_o} \rightleftharpoons M(HR_2)_{z_o} + z\,H_a^+ \qquad (1)$$

where R represents the di-2-ethylhexyl phosphate anion; $(HR)_2$ represents dimerized D2EHPA; and the subscripts a and o refer to aqueous and organic phases, respectively. According to Baes,[1] this simple cation exchange reaction, leading to the formation of a complex in which only half the acidic hydrogen of the extractant is replaced, has been found to be quite common at low loadings.

The equilibrium constant, K_{eq}, for the reaction represented by Equation (1) is given in terms of concentrations by

$$K_{eq} = \frac{[M(HR_2)z]_o\,[H_a^+]_a^z}{[M^{+z}]_a\,[(HR)_2]_a^z} \,. \qquad (2)$$

In the absence of aqueous phase complexing agents the distribution ratio, K_d, of the metal ion may be defined as

$$K_d = \frac{[M(HR_2)_z]_o}{[M^{+z}]_a} \,. \qquad (3)$$

Using this definition, Equation (2) may be rearranged to

$$K_d = \frac{K_{eq}\,[(HR)_2]_o^z}{[H_a^+]_a^z} \,. \qquad (4)$$

According to Equation (4), therefore, the distribution ratio is increased by increasing the D2EHPA concentration of the organic phase and decreasing the hydrogen ion concentration of the aqueous phase (or equivalently, by raising the pH of the aqueous phase).

Effect of Ion Charge and Size - In general the larger the charge on the metal cation the greater the magnitude of K_{eq} as expressed by Equation (2): that is to say, quadrivalent ions are extracted more strongly than trivalent ions which in turn are extracted more strongly than divalent ions, etc. A partial list of the affinity of metal ions for D2EHPA is Zr(IV) ≃ Ce(IV) > Y > Eu > Fe(III) > Pm > Ce(III) > La > Ca > Al > Mn(II) > Ru(III) > Sr > Ba > Na > Cs.[18b]

Dyrssen[17] has pointed out that for the trivalent ions of Group III (the lanthanide and actinide ions) log K_{eq} appears to vary inversely with ion radius. There is a similar correlation for the alkali and alkaline earth ions.[1] In all of these groups, the smaller the metal ion the more strongly is it extracted.

It should be noted that UO_2^{++}, PuO_2^{++}, and NpO_2^{++} are by far more strongly extracted than other divalent cations.[1] These cations appear to hold a unique position in the affinity series. It is also of interest that UO_2^{++} is extracted at high nitric acid concentrations by forming complexes analogous to the $UO_2(NO_3)_2$-TBP complex.[3]

Kinetics of Extraction - No systematic study of the extraction kinetics of metal ions into D2EHPA-containing phases has been made. Results obtained at both HAPO and ORNL indicate the reaction between strontium and D2EHPA is complete within about a minute. Recent work at HAPO indicates that rare earth ions extract more slowly than strontium ions.

Extraction of ions undergoing hydrolysis, such as Fe(III), Zr(IV), and Al(III), can be especially slow. Up to several hours may be required to attain equilibrium at room temperature.[3, 9a, 9c, 9g] The back extraction of these ions with nitric acid is also exceedingly slow. Effective removal of iron and aluminum from the solvent within a practical time requires the use of alkaline solutions or solutions containing complexing agents.

Effect of Diluent Modifier - Diluent modifiers such as TBP may also have an effect on the D2EHPA extraction of metal ions. Depending on the particular metal ion, the diluent modifier may either increase or

decrease the distribution ratio. For example, in the presence of TBP, uranium (VI) extraction is strongly increased whereas extraction of iron (III) is decreased.[5] Some preliminary HAPO evidence indicates that strontium and possibly rare earth ion extraction is also improved by the presence of TBP.

In spite of much investigation, the effects of diluent modifiers in D2EHPA extraction systems are still not completely understood. It is generally agreed that, in the case of a beneficial effect, a mixed complex, involving the metal ion (D2EHPA) and diluent modifier, is formed. However, the exact type of complex formed and the manner in which the modifier is held in the complex are still in doubt.

Effect of Diluent - Many prospective diluents have been tested but only aliphatic or kerosene-type diluents are considered suitable. Others, such as CCl_4, $CHCl_3$, benzene, long-chain alcohols, etc., evidently interact with D2EHPA to reduce metal distribution coefficients.[3]

Extraction at High Solvent Loadings and/or High pH

The complex $M(HR_2)_z$ (see Equation (1)) occurs only in organic solutions in which there is a sufficient excess of D2EHPA. At higher loadings it is often found that more of the metal cation is extracted than corresponds to this composition. In the case of UO_2^{++}, evidence[1] indicates chain polymer formation as follows:

$$HR_2(UO_2)R_2H \rightarrow HR_2(UO_2)R_2(UO_2)R_2H \rightarrow HR_2\,[(UO_2)R_2]_n\,(UO_2)R_2H.$$

This process proceeds to a limiting composition UO_2R_2.

The limiting composition MR_z has also been noted by Peppard and coworkers.[25b] They have prepared a number of D2EHPA salts, including KR, NaR, LiR, UO_2R_2, ScR_3, ThR_4, and HfR_4.

Investigators at ORNL have published equilibrium data for the extraction of strontium ions from sodium nitrate solutions by the sodium salt of D2EHPA.[8b] Their data, obtained at pH's above 7, can be

correlated by the equation

$$\frac{(Sr)_o}{(Sr^{++})_a} = 25\left[\frac{(Na)_o}{(Na^+)_a^2}\right]^{0.76} \tag{5}$$

where the terms in parentheses represent molarities. This equation has the general form of the expression of the equilibrium constant for the reaction

$$Sr_a^{++} + (NaR)_{2_o} \rightleftarrows SrR_{2_o} + 2Na_a^+ . \tag{6}$$

A similar linear dependency on solvent concentration was observed when extracting strontium from a Na_2SO_4 solution with Na D2EHP.[9c] One interpretation of this behavior suggests that the extraction of metal ions by D2EHPA proceeds stepwise, as typified by the following postulated reactions with strontium:

$$Sr^{++} + 2(HR)_2 \rightleftarrows Sr(HR_2)_2 + 2H^+ \tag{7}$$

and

$$Sr^{++} + Sr(HR_2)_2 \rightleftarrows 2\ SrR_2 + 2H^+. \tag{8}$$

The analogous reactions of D2EHPA with sodium would form successively $NaHR_2$ and the dimeric species $(NaR)_2$, shown in Equation (6).

The transition between the two postulated strontium complexes, $Sr(HR_2)_2$ and SrR_2, is illustrated qualitatively in Figure 1. This figure, obtained from ORNL data,[8c] represents the effect of pH on the extraction of tracer strontium from 0.5M $NaNO_3$ into 0.1M D2EHPA - 3% TBP solution. The initially rising strontium K_d with rising pH is attributed to the extraction of Sr^{++} as $Sr(HR_2)_2$. The K_d reaches a maximum at about pH 5. This limit is attributed primarily to increased loading of the solvent with sodium. The decreasing K_d between pH 5 and pH 7 probably represents a transition zone in which the formation of SrR_2 becomes increasingly important. The level zone beyond pH 7 implies the existence of only SrR_2 and $(NaR)_2$.

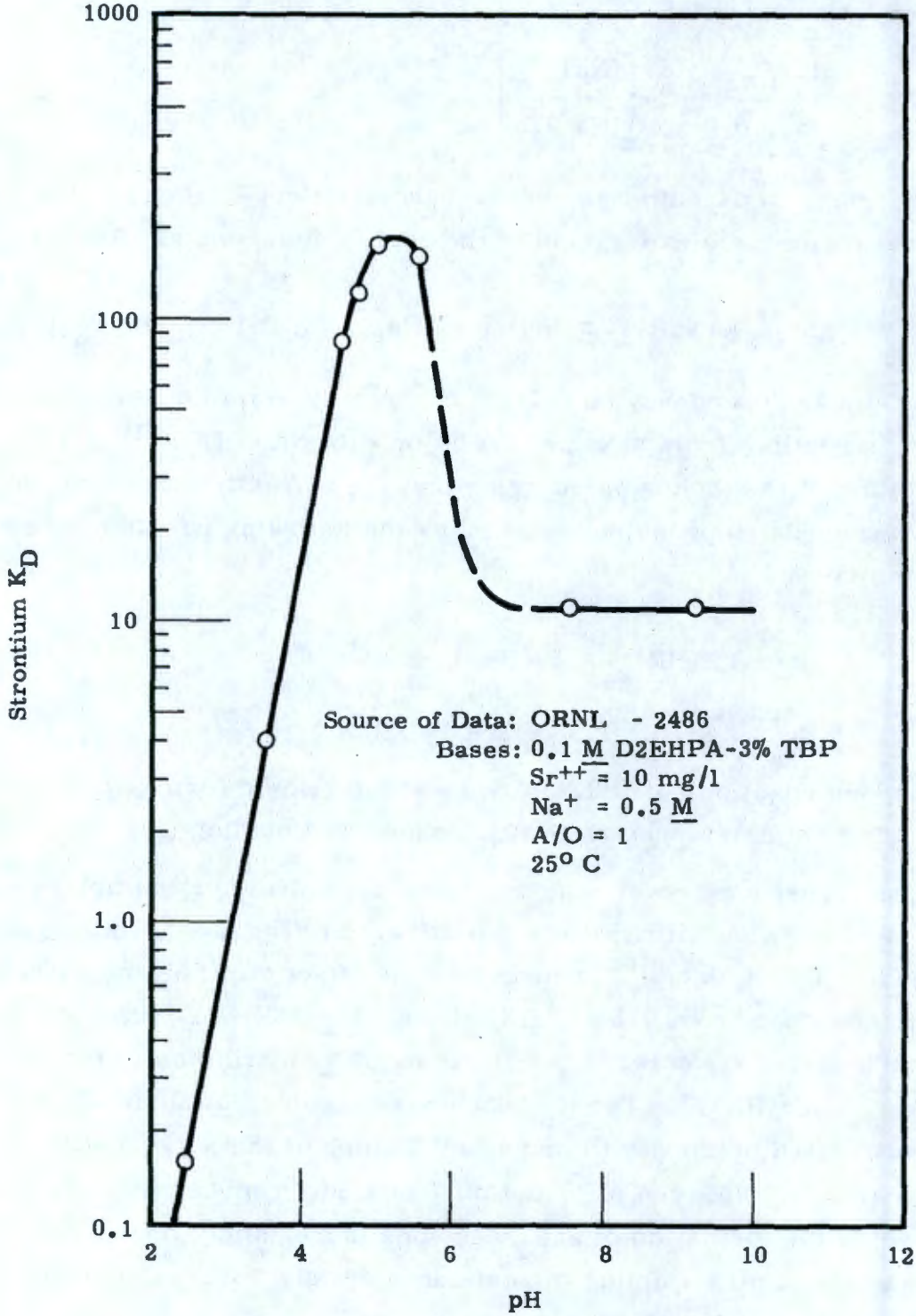

FIGURE 2.1

Effect of pH on Strontium Extraction

PROCEDURE FOR ESTIMATING STRONTIUM DISTRIBUTION RATIOS

In D2EHPA solvent extraction processes for recovering and purifying Sr^{90}, whether it be from Purex plant crude concentrate solution or (as now contemplated) from Purex plant formaldehyde-treated waste, it is obviously desirable to be able to predict quantitatively the effect of flowsheet variables on strontium distribution ratios. In such processes (as presently operated or envisioned) there are three principal factors which affect the strontium distribution ratio: (a) the pH of the aqueous feed, (b) the presence in the feed of other extractable metal ions which compete with strontium for the solvent, and (c) the presence in the aqueous phase of ligands such as acetate ion, EDTA, etc., which can form inextractable complexes with strontium. The ligands are added for pH control and to suppress extraction of undesirable inert and fission product elements.

A procedure for estimating the strontium distribution ratios which takes into account the three factors mentioned above is outlined in the following procedure. In many respects this procedure follows the steps outlined by Morrison and Freiser[24] for quantitative treatment of extraction data. However, because of the nonideality of the solutions involved and the lack of knowledge of certain aspects of D2EHPA extraction systems the procedure given here does necessarily deviate somewhat from the Morrison-Freiser procedure. In spite of this shortcoming, the procedure is a workable one for testing the feasibility of different flowsheet concepts.

Estimation of Strontium K_d in Absence of Aqueous Phase Complexing Ligands

A procedure for estimating Sr K_d for this system will be considered first for a D2EHPA-TBP-hydrocarbon diluent solution in contact with an aqueous solution containing small concentrations of strontium and other divalent and trivalent metal ions and up to 1.5M Na^+. Subsequently, the effects of aqueous phase complexing agents which lower the Sr K_d will be considered.

In treating this system any effects of TBP and of the hydrocarbon diluent on the extraction reactions will be neglected. It is assumed that the pH is so adjusted that Sr^{++} and the other divalent and trivalent ions are extracted according to the mechanism shown in Equation (1), that is, as the species $M(HR_2)_z$. Because of its high concentration, Na^+ may be extracted as $(NaR)_2$ as well as $NaHR_2$.

The equilibrium constants for the reactions of interest, expressed in molar concentrations, are

$$Sr\ K_{eq} = \frac{[Sr(HR_2)_2]\ (H^+)^2}{(Sr^{++})\ [(HR)_2]^2}, \tag{9}$$

$$Na\ K_1 = \frac{(NaHR_2)\ (H^+)}{(Na^+)\ [(HR)_2]}, \tag{10}$$

and

$$Na\ K_2 = \frac{[(NaR)_2]\ (H^+)^2}{(Na^+)^2\ [(HR)_2]^2}. \tag{11}$$

Using the definition of K_d from Equation (3), Equation (9) can be rearranged to

$$Sr\ K_d = \frac{Sr\ K_{eq}\ [(HR)_2]^2}{(H^+)^2}. \tag{12}$$

The extent to which the solvent is loaded with other extractable ions must be considered in determining the value of $[(HR)_2]$ to be used in solvent Equation (12). Since extraction of trivalent and divalent ions has been assumed to occur by the mechanism shown in Equation (1), it follows that a suitable solvent loading correction for such ions in the solvent is given by

$$\underline{M}\text{"free D2EHP"} = 2[(HR)_2]_o + 2(NaHR_2)_o + 2[(NaR)_2]_o = R - 4(\Sigma \underline{M}\ M^{+2})_o + 6(\Sigma \underline{M} M^{+3})_o \tag{13}$$

where R represents the initial D2EHPA molarity (formula weights of D2EHPA/liter). Equation (13) defines the "free D2EHP" as that amount of solvent not associated with divalent and trivalent ions.

To obtain a suitable correction for sodium loading, Equations (10) and (11) are rearranged to give

$$(NaHR_2)_o = \frac{Na\ K_1\ [(HR)_2]\ (Na^+)}{(H^+)} \tag{14}$$

and

$$[(NaR)_2]_o = \frac{Na\ K_2\ [(HR)_2]\ (Na^+)^2}{(H^+)^2}\ . \tag{15}$$

Substitution of these values of $(NaHR_2)$ and $[(NaR)_2$ in Equation (13) and rearranging slightly leads to

$$2[(HR)_2]\left[1 + Na\,K_1\,\frac{(Na^+)}{(H^+)} + Na\,K_2\,\frac{(Na^+)^2}{(H^+)^2}\right] = \underline{M}\ \text{free D2EHP.} \tag{16}$$

Hence

$$[(HR)_2] = \frac{\underline{M}\ \text{free D2EHP}}{2\left[1 + \frac{Na\ K_1(Na^+)}{(H^+)} + \frac{Na\ K_2(Na^+)^2}{(H^+)^2}\right]}\ . \tag{17}$$

Finally, substituting this value of $[(HR)_2]$ into Equation (12), the expression for the Sr K_d is

$$Sr\ K_d = \frac{Sr\,K_{eq}(\underline{M}\ \text{free D2EHP})^2}{4(H^+)^2}\ .\ \frac{1}{\left[1 + Na\,K_1\frac{(Na^+)}{(H^+)} + Na\,K_2\frac{(Na^+)^2}{(H^+)^2}\right]^2} \tag{18}$$

Equation (18) can be solved explicitly for the Sr K_d; use of this equation, however, requires a knowledge of the equilibrium constants for strontium and sodium. Tentative values of these constants, calculated from data listed in Table 2.2, are given in Table 2.1* Equilibrium constants for several other ions of interest in the strontium recovery program are also listed; these latter values were calculated from data presented in Table 3.22, Section 3. It must be emphasized that these constants

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*See Appendix for Tables

were derived from data obtained in experiments not specifically designed to measure equilibrium constants. Values of Sr K_{eq} and Na K_1 obtained by Kimura and Lamb in the absence of TBP have been reported by Baes.[1] Kimura's values obtained with toluene as the diluent differ significantly from those of Lamb obtained with Amsco 125-80 as a diluent. Both sets of data differ from the values given in Table 2.1.*

Because of the uncertainties and discrepancies in available equilibrium constants, an alternative to their substitution in Equation (18) is desirable to estimate the Sr K_d in the absence of aqueous phase complexing agents. In the alternative procedure presented here, experimentally obtained values of $\frac{(\text{Sr } K_d)(H^+)^2}{(\underline{M} \text{ free D2EHP})^2}$ are plotted versus the ratio $\frac{(Na^+)}{(H^+)}$ in Figure 2.2.

The same data are shown in Figure 2.3 with the ratio Sr K_d $(\underline{M}$ free D2EHP$)^2$ plotted versus the pH and with the sodium concentration appearing as a parameter. (Similarly, experimental values of $\frac{(\text{Na } K_d)(H^+)}{(\underline{M} \text{ free D2EHP})}$ versus $\frac{(Na^+)}{(H^+)}$ are plotted in Figure 2.4.) The method of plotting is consistent with the form of Equation (18) but avoids the necessity of specifying the equilibrium constants. The data used for the above curves are listed in Table 2.2. Only those data points obtained in the absence of complexing agents (other than acetate ion) were used. Strontium K_d's obtained in the presence of acetate ion were corrected for the effect of acetate complexing by use of the relations described on page 2.17.

Estimation of the Sr K_d by the use of Figures 2.2 and 2.3 is presently considered not only easier but more reliable than by the use of Equation (18). Nevertheless, until the chemistry of D2EHPA extraction systems is better understood, caution should be exercised in extrapolating the curves in Figures 2.2, 2.3, and 2.4 to conditions far removed from those used in their derivation.

*See Appendix for Tables

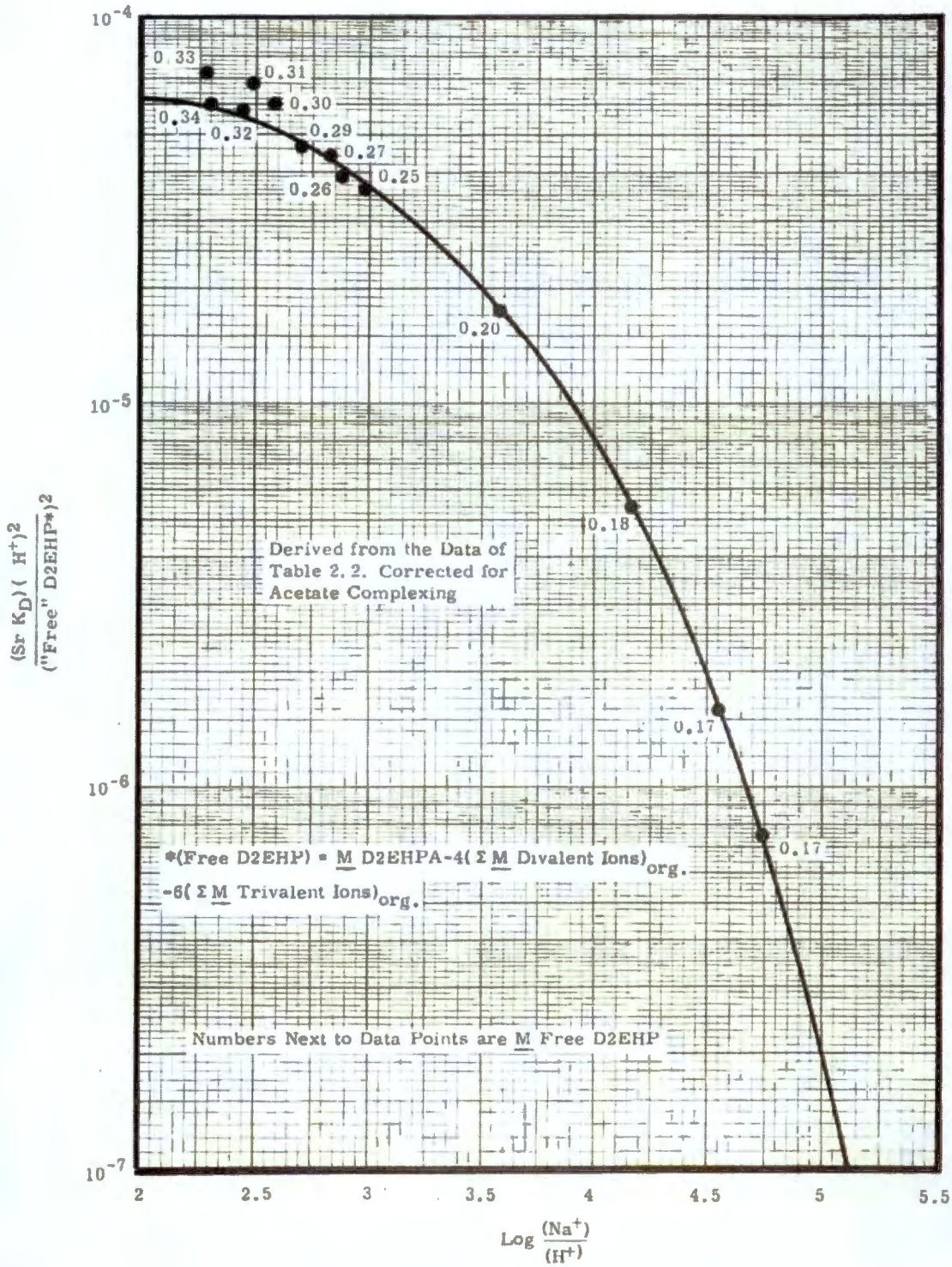

FIGURE 2.2

Preliminary Correlation of D2EHPA-Strontium Extraction Data

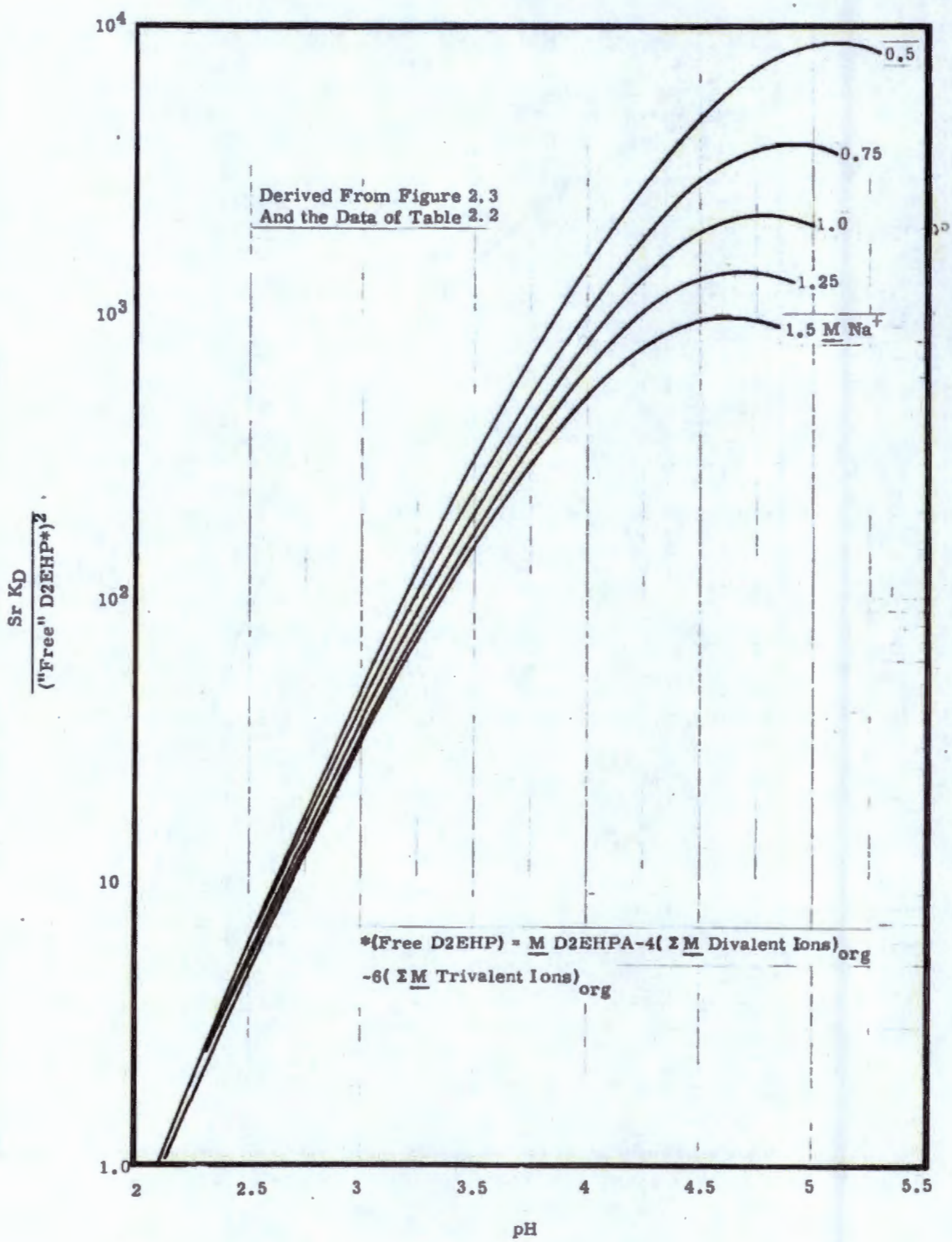

FIGURE 2.3

Correlation Curves for Estimating Strontium Distribution Ratios

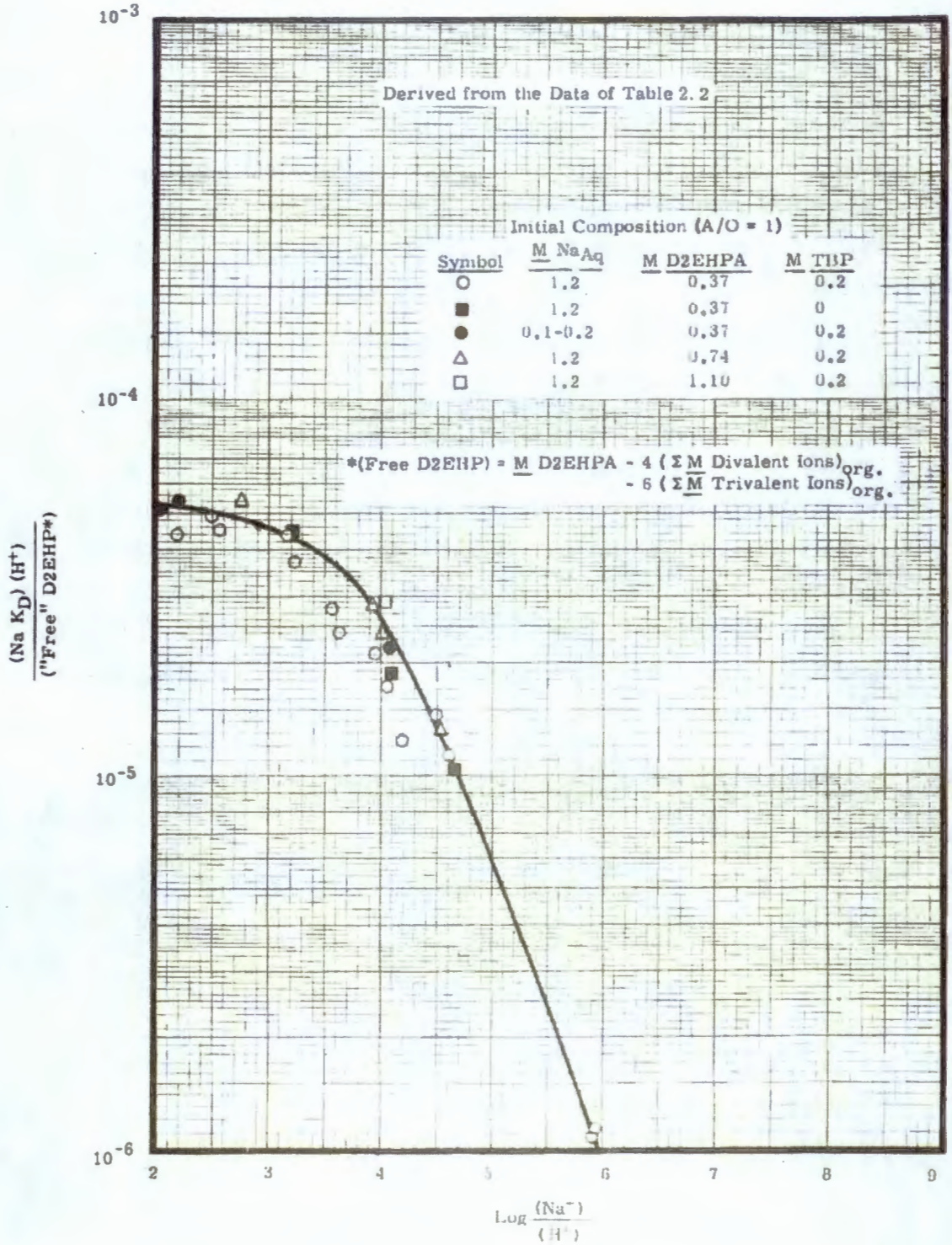

FIGURE 2.4

Preliminary Correlation of D2EHPA-Sodium Extraction Data

Effect of Aqueous Phase Complexing Agents on Strontium Distribution Ratios

Ligands such as acetate, EDTA, etc., which are added to the aqueous phase to control pH or to suppress extraction of undesirable inert and fission product elements,form complexes with strontium which lower the Sr K_d. A method of correcting the Sr K_d for the effect of such complexing agents is considered below.

The essential points in the derivation of the correction factor are:

(1) Consider a system which contains the ligands L_1, $L_2 \ldots L_n$ in the aqueous phase which form with Sr^{++} only inextractable 1:1 complexes of the type SrL_1, $SrL_2 \ldots SrL_n$. Assume, for the time being, that there are no other metal ions present which will form complexes with these ligands; the effect of the presence of other metal ions will be considered later. The reaction between the general ligand L_n and Sr^{++} can be represented (omitting for simplicity the charges of the ligand and of the complex formed) as

$$Sr^{++} + L_n \rightleftarrows SrL_n. \tag{19}$$

(2) In concentration units define

$$Sr\ E_a^o = \frac{(Sr)_o}{(Sr)_a} = \frac{\text{Concentration of all Sr species in organic phase}}{\text{Concentration of all Sr species in aqueous phase}}$$

$$= \frac{(Sr)_o}{(Sr^{++})_a + (SrL_1) + (SrL_2) + \ldots + (SrL_n)} . \tag{20}$$

(3) At any given pH the "conditional stability constant" for the complex SrL_n can be expressed as

$$K_n' = \frac{(SrL_n)}{(Sr^{++})(L_n)} . \tag{21}$$

In Equation (21), (L_n) represents not only the concentration of free ligand but the concentration of all species of the complexing agent not bound with Sr^{++} or other metal ions; that is, (L_n) includes the concentrations of the various protonated species of the ligand. (For example, in the case of EDTA, (L_n) represents the combined concentrations of the HY^{-3}, H_2Y^{-2}, H_3Y^{-1}, and H_4Y species in addition to the free Y^{-4} ligand.) The relative concentrations of the protonated and unprotonated ligands depends on the acidity (pH) of the solution; and, in consequence, the extent of complexing of Sr^{++} by the ligand L_n is pH dependent. This dependency on pH is expressed by using conditional stability constants rather than thermodynamic stability constants. A more complete description of conditional stability constants and their uses is given in Reference 21.

(4) From Equation (21), at any given pH

$$(SrL_n) = K'_n\,(Sr^{++})\,(L_n). \tag{22}$$

Substitution of this value of SrL_n and the analogous values of SrL_1, SrL_2, etc. into Equation (20) gives

$$Sr\,E^{\circ}_a = \frac{(Sr)_o}{(Sr^{++}) + K'_1(L_1)(Sr^{++}) + K'_2(L_2)(Sr^{++}) + \ldots + K'_n(L_n)(Sr^{++})}$$

$$= \frac{(Sr)_o}{(Sr^{++})\,[1 + K'_1(L_1) + K'_2(L_2) + \ldots + K'_n(L_n)]}\,. \tag{23}$$

(5) If, as has been assumed earlier, the only species of strontium present in the organic phase is the complex $Sr(HR_2)_2$, then by Equation (3)

$$\frac{(Sr)_o}{(Sr^{++})} = \frac{[\,Sr\,(HR_2)_2\,]}{(Sr^{++})} = Sr\,K_d.$$

Hence,

$$Sr\ E^{\circ}_{a} = \frac{Sr\ K_d}{1 + K'_1(L_1) + K'_2(L_2) + \ldots + K'_n(L_n)} . \qquad (24)$$

Equation (24) is the relationship desired to permit calculation of the strontium extraction coefficient in the presence of aqueous phase complexing agents. Application requires a knowledge of the values of the various K' and (L) terms and a knowledge of the Sr K_d. The latter value is obtained by the graphical procedure given in the preceeding section.

Conditional stability constants calculated for the various ligands studied in this program are presented in Figure 2.5. Except for acetate these were calculated from the experimental data included in Table 2.2. The constants for acetate were calculated from published values of the dissociation constant of acetic acid and the thermodynamic stability constant of the strontium acetate complex. Ideally, K' values for the other ligands could be calculated similarly using the calculation techniques discussed in Reference 17, pages 564-567. The complexity of dissociation of multibasic acids, the possibility of complex formation with protonated ligands, and the unavailability of certain of the thermodynamic stability constants made the experimental method of determining K' values more convenient. Typical published thermodynamic stability constants and acid dissociation constants are presented in Table 2.3.

Note in Figure 2.5 that the conditional stability constants for EDTA, (ethylene diamine tetra-acetic acid) DTPA (diethylene triamine penta-acetic acid), and HEDTA (hydroxyethylethylene diamine triacetic acid) were obtained using solutions which also contained acetate. The constants calculated for these ligands have been corrected for the effects of acetate in complexing strontium.

Estimation of the (L_n) values to use in Equation (24) requires a knowledge of the metal ions other than strontium ion which are present in the aqueous phase and the extent and manner in which these other metal

ions react with the various complexing ligands. The sample flowsheet calculation shown below illustrates how (L_n) values are calculated.

Sample Calculation of Strontium Extraction Flowsheets

With the above correlation for estimating strontium distribution ratios, it is now possible to determine the feasibility of a given flowsheet to quantitatively extract strontium. The following steps can be used for this purpose:

(1) Determine the feed composition, including the concentration of both the extractable ions (strontium, calcium, sodium, etc.) and those ions which will be essentially completely complexed by ligands (iron, lead, cerium, etc.). If a scrub stream is used, assume that it is stoichiometrically combined with the feed to establish the total concentration of ligands and metal ions entering the extraction section at the feed point.

(2) Select a feed pH. This will normally be in the range of pH 3.5 to 5, high enough to prevent extraction of undesired, complexed metals (such as iron or cerium) but not high enough for sodium extraction to depress strontium extraction. If the system is adequately buffered (see Page 2.23), the equilibrium pH will be essentially the same as the feed (or combined feed plus scrub) pH.

(3) Select a solvent concentration and a solvent-to-feed flow ratio. Assume that the more extractable ions, and only these ions (such as calcium and strontium), are completely extracted. Calculate their concentrations in the product solvent and use the values to determine the free D2EHP concentration in the product (Equation 13). This will be the minimum value of free D2EHP in the system.

(4) Assume that the equilibrium sodium concentration in the aqueous phase at the feed point is the same as the stoichiometric sodium concentration in the combined feed plus scrub. This will be approximately true if sodium extraction is minimized by selection

of a low feed pH, a low solvent-to-feed flow ratio, or the use of a scrub stream which returns extracted sodium to the extraction section.

(5) Calculate the Sr K_d using Figure 2.2 or 2.3 and the values of free D2EHP, pH, and (Na^+) determined above.

(6) Establish the ligand concentrations in the feed and scrub according to the requirements of the process (see Sections 3, 4, and 5 of this report series). Calculate the concentrations of uncomplexed or free ligands in the combined feed-plus-scrub. If only 1:1 complexes are formed, this will be equal to the total ligand concentration minus the total molarity of metal ions complexed by that ligand. (In a mixture of metal ions and ligands, the complexes with the greatest stability constants would preferentially be formed. Thus in a mixture of ferric and lead ions and EDTA and citrate ligands, the ferric-EDTA complex would form first; any excess EDTA would then complex the lead. Citrate would form complexes only if there were insufficient EDTA to complex all of the iron and lead.) Assume that only negligible quantities of the extracting ions (strontium, calcium, etc.) are complexed (this will be true if the concentrations of extractable components are small and if the distribution ratios are relatively high).

(7) Determine the ligand-complexing correction factor $[1 + K_1'(L_1) + K_2'(L_2) \ldots + K_n'(L_n)]$, from Figure 2.5, using the above values of free ligand concentrations and the feed pH to determine individual K'(L) values.

(8) Calculate the actual strontium E_a° by dividing the Sr K_d, determined in Step 5, by the ligand-complexing correction factor (see Equation (24)).

To insure adequate strontium extraction, the calculated distribution ratio should be at least twice the assumed aqueous-to-organic flow ratio. If not, a new flow ratio or a more favorable pH should be assumed

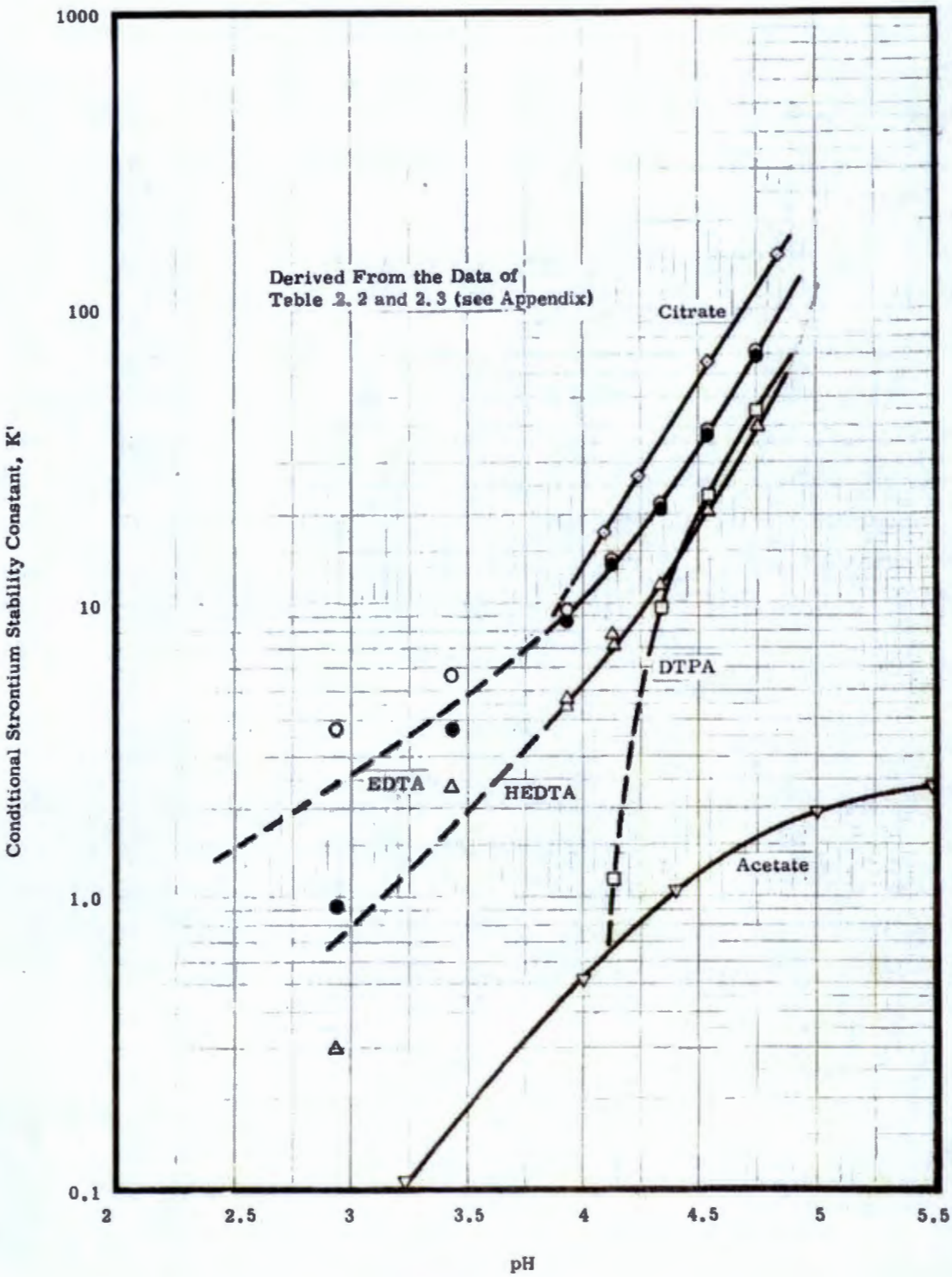

FIGURE 2.5

Effect of pH on Conditional Strontium Stability Constants

and the calculation repeated. At least a 40% safety margin should be allowed for flowsheet conditions differing from those listed in Table 2.2 which were used to derive the correlation. A sample calculation, employing the flowsheet conditions recommended in Section 4 is presented in Table 2.4 in the Appendix.

Decontamination Potential

No theoretical study was made of the decontamination potential obtainable with the various complexing agents. Generally, any of the complexing agents - citrate, HEDTA, EDTA, and DTPA - would essentially prevent extraction of iron, lead, zirconium-niobium, and ruthenium. Their ability to suppress extraction of cerium and other rare earths increased in approximately the order shown. Citrate and HEDTA permitted quantitative extraction of cerium, EDTA suppressed extraction of cerium sufficiently to provide a modest decontamination factor, while DTPA was very effective in preventing rare earth extraction. Empirical decontamination performance is presented in Section 3.

ION EXCHANGE

Ion exchange using Dowex 50W x 12 cation resin was proposed by Bray[6] for use as a final purification step for strontium. The feed for this column would be derived from the 1M citric acid solvent extraction product stream and would contain some sodium and calcium in addition to strontium. Bray's loading studies on sodium-form resin are summarized below:

Feed				Column Loading at 100% Breakthrough, M Sr/L Resin
M Sr	M Ca	M Na	pH	
0.05	0.01	0.14	2.0	0.80
0.05	0.01	0.32	2.45	0.48
0.05	0.01	0.5	2.8	0.40
0.05	0.01	1.0	3.5	0.22

For estimating column capacity with other flowsheet variations, the above values were extrapolated by use of the mass action law. The equilibrium reaction of strontium with the resin can be written as:

$$Sr^{++} + 2\ NaR \rightleftarrows SrR_2 + 2Na^+, \tag{25}$$

and

$$K_{eq} = \frac{[SrR_2]\,[Na^+]^2}{[Sr^{++}]\,[NaR]^2} \tag{26}$$

The value of K_{eq} derived from the above loading data (assuming about 1.9 equivalents per liter of resin and neglecting the effect of citrate complexing and calcium loading) is about two in molar units. Loading curves based on this equation are shown in Figure 2.6. Actual capacity at 10% breakthrough is about 90% of the loaded value.

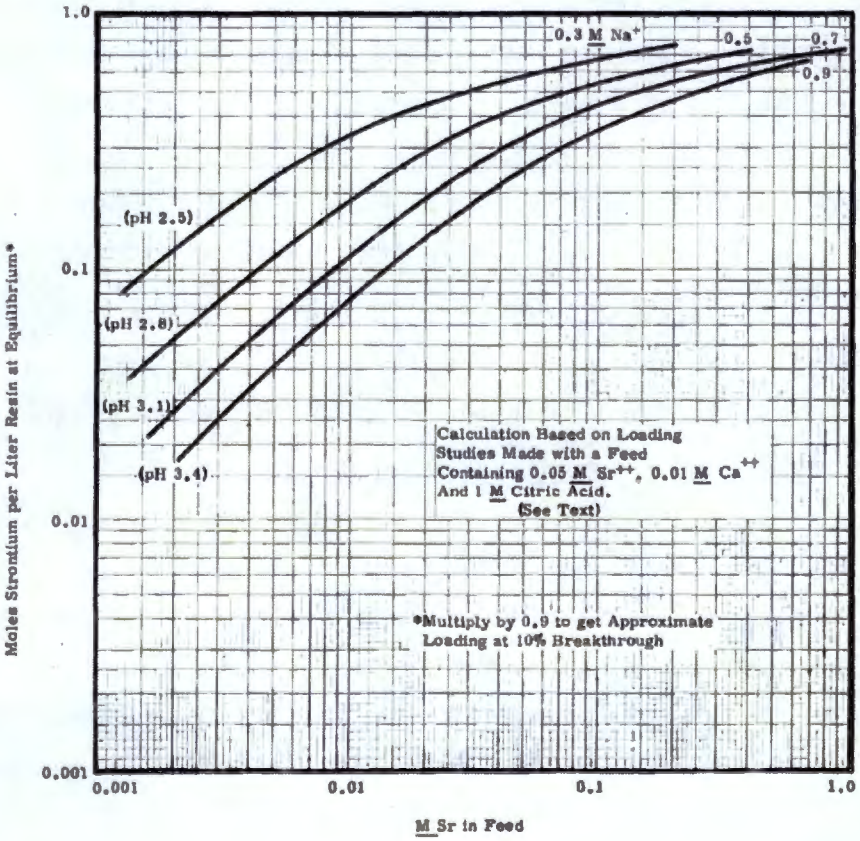

FIGURE 2.6

Calculated Maximum Strontium Loading on Dowex 50W x 12 Cation Resin

No theoretical analysis was made of the scrubbing studies, reported in Section 3. Generally, adequate decontamination from cerium with minor strontium loss could be achieved by passing several column volumes of 1M citric acid at a pH of 3.0 through the loaded column.

The rate of elution with various elutants could be expressed in the form of a first order reaction; that is, the rate at which strontium was being eluted was proportional to the quantity of strontium left on the column. Typical elution curves using this method of correlation are shown in Figure 2.7. The elutant flow was about 2 to 5 ml/min-cm^2.

HYDROGEN ION CONTROL AND ADJUSTMENT

Hydrogen ion control in the pH-sensitive portions of the separations process was achieved by the use of buffer agents. A sufficient amount of buffer reagent was added so that the pH change through hydrogen ion exchange would have only a minor effect on the strontium distribution coefficients or decontamination potential. Acetic and citric acid buffer systems were usually employed, but the buffering capacities of the complexing ligands EDTA, DTPA, and HEDTA were also considered.

Typical titration curves used for the buffer calculations are shown in Figure 2.8. These curves were derived from published values of the acid dissociation constants (see Table 2.4) and agree reasonably well with experimental data.

Although not tested in this program, pH control in the D2EHPA extraction step can be achieved without buffer addition by partially preneutralizing the solvent with sodium hydroxide so that the extracting ion will exchange with the sodium ion rather than hydrogen ion.[29] A precise balance between the extent of preneutralization and the moles of cation to be extracted is not required since the solvent itself will tend to act as a buffer. A feed buffer may still be required to prevent an acidic scrub from excessively lowering the feed point pH.

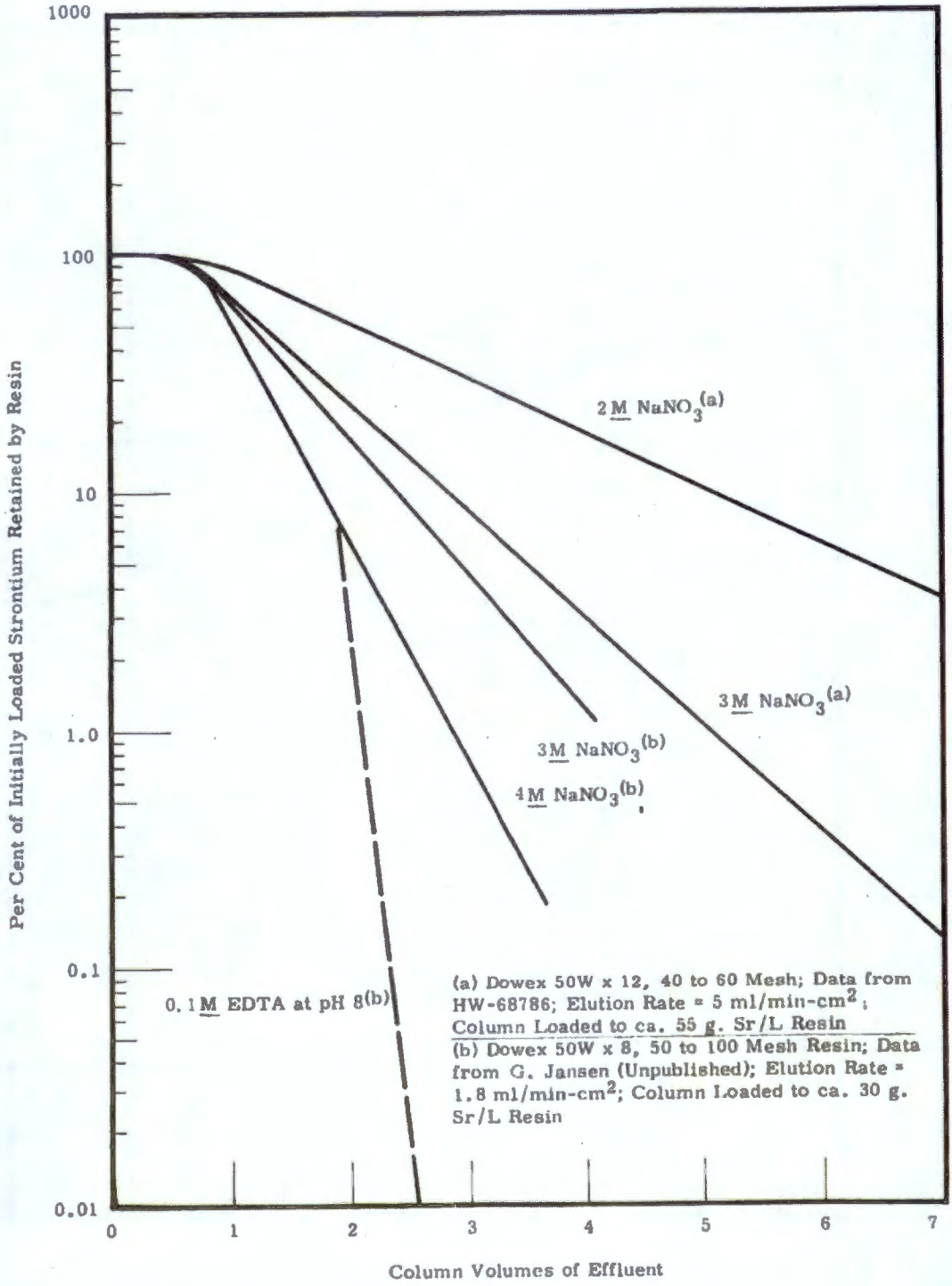

FIGURE 2.7

Strontium Elution From Dowex 50W Resin

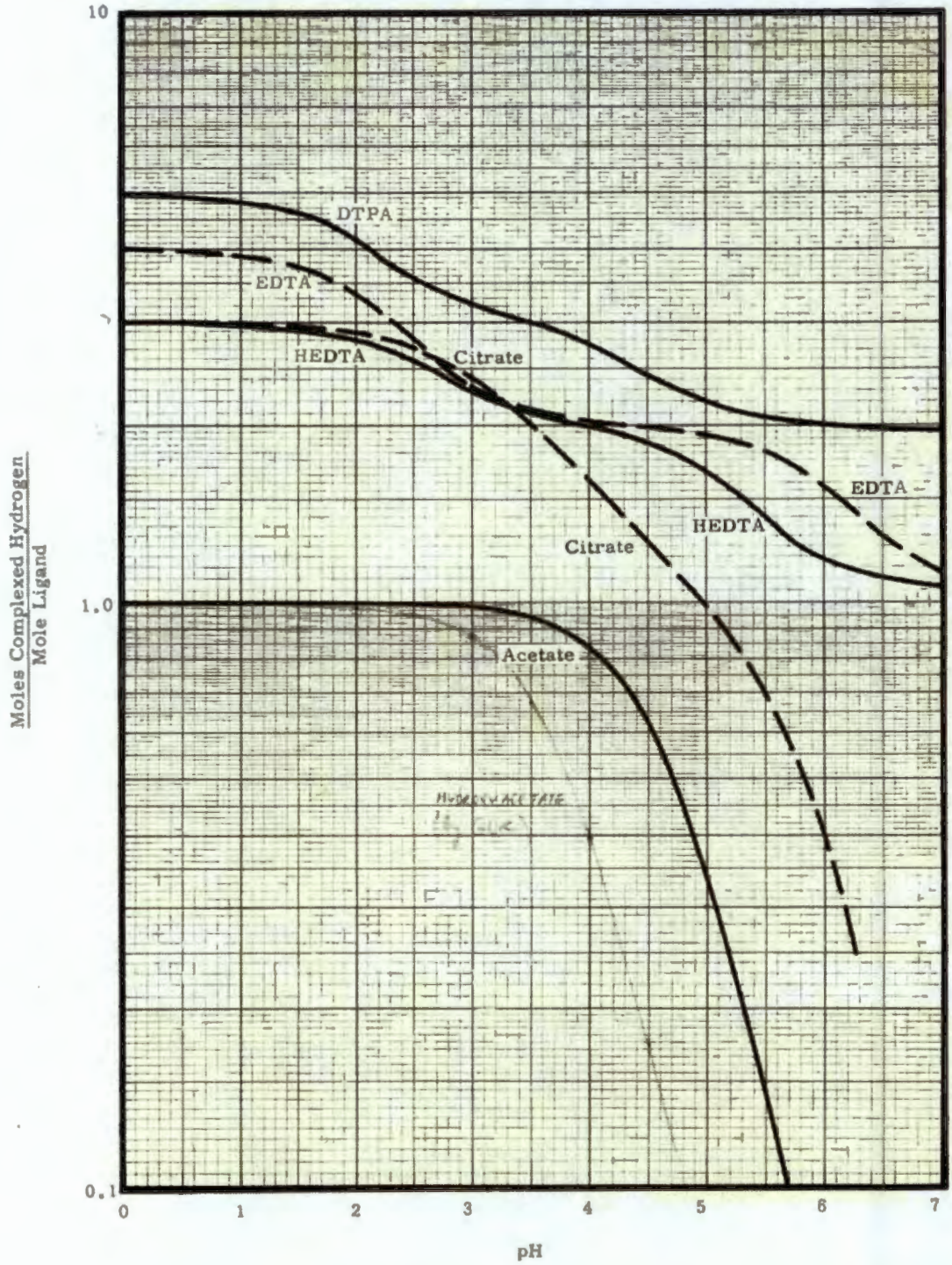

FIGURE 2.8

Hydrogen Ion Complexing by Ligands

SECTION 3. LABORATORY STUDIES

W. W. Schulz, J. E. Mendel

INTRODUCTION AND SUMMARY

Bench-scale investigations conducted to aid in the development of technology required for satisfactory recovery, purification, and packaging of Sr^{90} in the Hot Semiworks (HSW) are discussed in this Section. Batch and continuous countercurrent extraction studies performed with crude concentrate solutions to develop and demonstrate chemical flowsheets for the D2EHPA extraction and purification of Sr^{90}, Ce^{144}, and Pm^{147} are described in detail. The work was carried out in close cooperation with the pilot plant work described in Section 4. Also discussed are results obtained in studies of the tail-end cation exchange resin purification of the solvent extraction Sr^{90} product from Ce^{144}, as well as on precipitation and filtration of the Sr^{90} product.

SOLVENT EXTRACTION STUDIES

EXPERIMENTAL

Materials

Synthetic and Plant Crude Concentrate Solutions - The composition of the synthetic crude concentrate used in the majority of the laboratory extraction studies is listed in Table 3.1. Three different one-liter batches of actual, full-level plant concentrate of the composition shown in Table 3.1 were used in several continuous countercurrent extraction runs.

The following points are of significance with respect to the composition of the synthetic concentrate:

(1) The concentrations of HNO_3 and $Fe(NO_3)_3$ were based on analyses of plant concentrate produced early in the Sr^{90} recovery program. Batch 3 of the plant concentrate was typical of this material.

TABLE 3.1

COMPOSITION OF SYNTHETIC AND PLANT CRUDE CONCENTRATE SOLUTIONS

Synthetic Concentrate	
Component	Concentration, M
HNO_3	1.0
$Fe(NO_3)_3$	0.10
$Pb(NO_3)_2$	0.004
$Sr(NO_3)_2$	0.0025
$ZrO(NO_3)_2$	0.001
$RuCl_3$	0.00002
$Ce(NO_3)_3$	0.001
$Ca(NO_3)_2$	0.003
$La(NO_3)_3$	0.0025

Plant Concentrate			
	Composition		
Component	Batch 1	Batch 2	Batch 3
HNO_3, M	0.057	0.062	1.12
$Fe(NO_3)_3$, M	0.005	0.021	0.12
$Pb(NO_3)_2$, M	0.028	0.011	0.049
$Sr^{89} + Sr^{90}$, c/1*	259	328	27
$Zr^{95} + Nb^{95}$, c/1	291	221	3
$Ru^{103} + Ru^{106}$, c/1	2	0.8	---
Ce^{144}, c/1	186	228	244

*Curies/liter

Subsequent improvements in the plant procedure used to prepare crude concentrate resulted in material containing less HNO_3 and $Fe(NO_3)_3$. Batches 1 and 2 were typical of this latter concentrate.

(2) Inert strontium isotopes as well as Sr^{89} and Sr^{90} are also present in the crude concentrate so that the total strontium concentration is about 0.0025M.

(3) Although not indicated in Table 3.1, plant concentrate also contains calcium and barium. Concentrate processed in the HSW was about 0.005M $Ca(NO_3)_2$ and 0.0004M $Ba(NO_3)_2$ (cf. Table 5.1, Appendix). The synthetic concentrate used in these studies was 0.0025M $Ca(NO_3)_2$ and did not contain barium.

(4) Plant concentrate contains, in addition to Ce^{144}, stable and radioactive isotopes of other rare earths as well as of yttrium produced in the fission of U^{235}. Lanthanum nitrate was added to the synthetic concentrate to approximate the bulk organic phase loading of the fission product rare earths other than cerium. The extraction behavior of these other rare earths was followed radiometrically with trace concentrations of $Eu^{152-154}$.

(5) For convenience, zirconium and ruthenium were added to the synthetic concentrate as $ZrO(NO_3)_2$ and $RuCl_3$. The exact chemical species of radioactive zirconium and ruthenium in plant concentrate are not known.

All batches of plant concentrate appeared visibly clear when received. Subsequent centrifugation of small portions revealed, however, the presence of white solids, believed to be $Ce_2(C_2O_4)_3$, in Batch 1 and brown solids, believed to be hydrous ferric oxide, in Batch 2. No solids were found in Batch 3. Before use in continuous countercurrent extraction runs, Batches 1 and 2 were adjusted to about 1.0M HNO_3 by addition of 15.7M HNO_3 and then digested 2 hours at 65-75 C. This treatment dissolved the brown solids but not the white solids. The acidified concentrates were not centrifuged before use in mixer-settlers.

Extractant - The D2EHPA contained about 91.5% D2EHPA plus undetermined amounts of mono(2-ethylhexyl)-phosphoric acid and pyro esters. Traces of iron were also present. An extractant composition of 0.37M D2EHPA-0.2M TBP-Shell Spray Base (SSB) was used throughout. In some instances the extractant was washed with successive half-volume portions of 3.7M NaOH and 6M HNO_3. Extractant treated in this manner is designated washed extractant.

Tracers - Except in those experiments with actual plant concentrate, the extraction and decontamination of strontium was followed with the aid of radioactive isotopes. The isotopes used and their chemical form are listed in Table 3.2.

TABLE 3.2

RADIOACTIVE TRACERS USED IN THIS STUDY

Isotope	Chemical Form
Cs^{137}	CsCl in HCl
Sr^{85}	$Sr(NO_3)_2$ in HNO_3
Ce^{144}	$CeCl_3$ in HCl
Ca^{45}	$CaCl_2$ in HCl
Fe^{59}	$FeCl_3$ in HCl
Pm^{147}	$PmCl_3$ in HCl
$Eu^{152-154}$	$EuCl_3$ in HCl
$ZrNb^{95}$	Oxalic Acid Solution
Ru^{106}	$RuCl_3$ in HCl

Other Chemicals - Commercially available solutions of 1.3M Na_4EDTA, 1.05M Na_5DTPA, and 1.57M Na_3HEDTA were used. All other chemicals used were of reagent grade quality.

Equipment and Procedures

Determination of Distribution Ratio - The distribution ration, E_a^o, is defined in this paper as the ratio of the concentration of the element in the less dense organic phase to the concentration of the element in the more

dense aqueous phase after the equilibration of the two immiscible liquids. A standard 10-minute contacting period at room temperature by mechanical stirring was used. After this contacting period, phases were centrifuged 5 minutes before separation. Except for manganese the concentration of elements of interest was determined radiometrically.

Miniature Mixer-Settler Runs - Chemical flowsheets for the recovery and decontamination of Sr^{90} were tested in 12-stage mixer-settlers with feeds prepared from both synthetic and plant concentrate. These units were Hanford-designed versions of a type developed at the Knolls Atomic Power Laboratory by Coplan and others.[14]

In testing the flowsheets, mixer-settlers were operated until a steady state in the effluent streams was reached. Samples of the effluent streams were taken hourly and analyzed to determine when steady state was reached. Waste losses and decontamination factors were computed from analyses of steady-state effluent streams.

Mixer-settlers were operated under extraction (1A) column conditions with seven extraction and five scrub stages. Only five of the 12 mixer-settler stages were used in partition (1B) column runs. In testing chemical flowsheets with feeds derived from synthetic concentrate, separate mixer-settler runs, each with a different radioisotope added to the feed, were made for each flowsheet tested.

Further details and results of mixer-settler runs are described on page 3.24.

Miniature Pulse Column Runs - Two miniature pulse columns were used in 1B column flowsheet demonstration studies with tracer levels of radioactivity. Both columns were 0.23 inch in diameter and contained sieve plates spaced at 0.25 inch intervals. The stainless steel sieve plates had 0.02 inch holes uniformly spaced to give 23% free area.

One column was fitted for sampling both phases at points one-third and two-thirds of the distance up from the bottom of the column. The cartridge length between sample ports was 6 inches, or 18 inches overall. This cartridge was operated with the aqueous phase continuous.

The second column, which was used for most of the runs, contained a much more efficient "zebra" cartridge which provided alternating aqueous-continuous and organic-continuous operation throughout the length of the column. The length of this cartridge was 16 inch. Further details of these columns, designed and constructed by O. H. Koski, are given in HW-39938.[22]

Analyses

In those solutions which contained only one radioisotope, the concentration of this isotope was determined by gamma scintillation counting, or, in the cases of Ca^{45} and Pm^{147}, by beta counting techniques. More involved procedures were required for analysis of solutions derived from plant concentrate. In particular, because of the bremsstrahlung radiation produced by Sr^{89} and Sr^{90} in such solutions, it was necessary to remove radioactive strontium before the concentration of other radioactive constituents could be determined. Separation of radioactive strontium was accomplished by addition of inert $Sr(NO_3)_2$ to an aliquot of solution; this procedure was followed by repeated precipitation of $Sr(NO_3)_2$ with fuming HNO_3. The concentration of other radioactive constituents was then determined by analysis of a portion of the supernatant liquid with a 256-channel gamma energy pulse-height analyzer. A different procedure (on a separate portion of the solution) involving successive precipitation of the strontium as $Sr(NO_3)_2$ and $SrCO_3$ was used to determine the total concentration of radioactive strontium.

Organic solutions containing manganese were contacted with 1M HNO_3 to transfer manganese to the aqueous phase. Manganese(II) was oxidized to the permanganate ion by treatment with KIO_4; the concentration of the permanganate ion was determined spectrophotometrically. Citric acid solutions containing manganese(II) were treated with HNO_3, H_2SO_4, and $(NH_4)_2S_2O_8$ to destroy citrate ion. Manganese(II) was then oxidized to the permanganate ion with KIO_4 and determined spectrophotometrically.

Sodium in organic solutions was determined by flame photometer procedures.

RESULTS

Extraction of Strontium from Crude Concentrate

Results of batch and continuous counter current extraction studies conducted to develop a chemical flowsheet for the recovery of only Sr^{90} from crude concentrate are discussed here. Results of studies conducted to develop technology for the simultaneous recovery of Sr^{90}, Ce^{144}, and Pm^{147} from concentrate solution are discussed separately (cf. p. 3.30).

First Cycle Extraction Column - Comparison of Complexants - Results of experiments performed to compare the effectiveness of various aqueous phase complexants in their ability to complex iron(III) and trivalent rare earth ions are given in Table 3.3.

TABLE 3.3

COMPARISON OF COMPLEXING AGENTS

Type	Conc., M	Equil. Aq. pH	Distribution Ratio Fe	Sr	Ca	Ce	Eu
DTPA	0.15	4.6	---	15	---	0.07	---
EDTA	0.19	4.4	0.0002	10	100	0.70	0.15
HEDTA	0.20	4.6	0.005	23	1500	12	1.10
Citric Acid	0.20	4.6	0.043	14	1900	280	400
Tartaric Acid	0.20	4.6	1.3	13	2600	120	110

To obtain these data, 100 ml portions of synthetic concentrate were made 0.45M sodium acetate (NaOAc) and 0.15 to 0.20M complexing agent. In all cases sufficient 19M NaOH and water were added to give 135 ml of solution at pH 4.7. Portions of these solutions were traced with the appropriate radioisotope and then contacted with one-fifth-volume portions of washed extractant. Under the experimental conditions, EDTA and DTPA were clearly superior to the other complexants in suppressing extraction of trivalent ions.

Additional data relative to the distribution coefficients of various constituents of laboratory concentrate from feed solutions containing either EDTA or DTPA are presented in Table 3.4 and Figure 3.1. To obtain these data, 100 ml portions of synthetic concentrate were diluted to 135 ml by addition of 35 ml of NaOAc-Na_4EDTA (or Na_5DTPA)-NaOH solution. The composition of the additive solution was selected in each case to prepare 0.45M acetate and 0.19M EDTA or 0.15M DTPA solutions at pH's in the range 3.5 to 5.5. Portions of these latter solutions were contacted with one-fifth volume portions of washed extractant.

TABLE 3.4

EXTRACTION COLUMN DISTRIBUTION COEFFICIENTS

(Initial aqueous solutions were all 0.45M acetate and 0.19M EDTA.)

Equilibrium Aqueous pH	Distribution Coefficient				
	Ca	Fe	Ru	ZrNb	Eu
2.9	580	0.0006	0.0003	---	8.8
3.6	1800	0.0009	0.0012	<0.0001	---
4.4	500	0.0002	0.0024	0.0017	0.27
4.9	27	0.0001	0.0010	<0.0002	0.076
5.4	1.7	0.0014	0.0006	0.0038	0.0074

Distribution coefficients for iron, ruthenium, and zirconium (Table 3.4) with EDTA added to the feed solution were all uniformly low at at all equilibrium aqueous phase pH's in the range 2.9 to 5.4. Because no radioactive lead isotope of sufficiently long half-life was available, a systematic attempt to determine distribution coefficients for lead was not made. However, X-ray fluorescence analyses of some of the organic solutions obtained in the experiments listed in Table 3.4 indicate lead was extracted to about the same extent as iron.

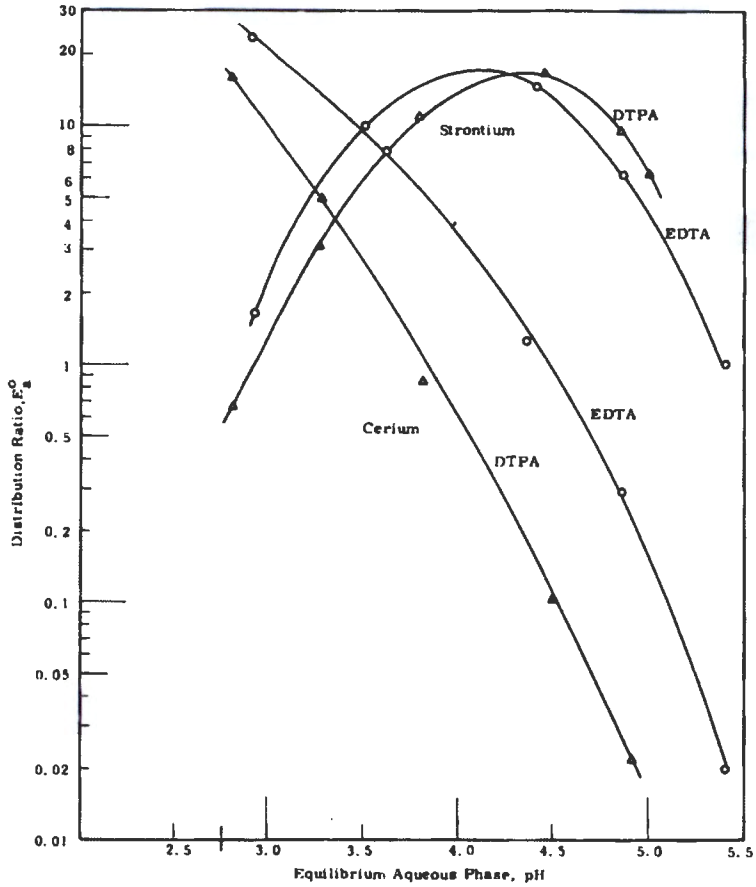

FIGURE 3.1

Comparison of DTPA and EDTA as Complexing Agents for Cerium and Strontium

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

EDTA and DTPA had about the same effect on strontium E_a^o. However, at approximately equal concentrations, DTPA complexed

cerium more strongly than EDTA. This observation is in agreement with the observations of Catsch.[11] The effect of DTPA on the distribution coefficients of other constituents of crude concentrate was not measured. It was assumed that these would be complexed to at least the same extent as by EDTA.

Data in Figure 3.1 indicate that operation of the extraction column with high pH feeds is desirable to minimize contamination of the Sr^{90} product with Ce^{144}. However, complexing of strontium by either EDTA or DTPA begins to occur at about pH 4 and increases at higher pH's. The choice of a suitable feed pH must thus be a compromise between the need for satisfactory extraction of Sr^{90} and maximum decontamination from Ce^{144}. A feed pH of 4.7 is considered optimum.

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

- Effect of EDTA Concentration on Distribution Ratios -

A synthetic concentrate of the composition given in Table 3.1, except that the $Fe(NO_3)_3$ concentration was 0.025M, was prepared. One hundred ml portions of this concentrate were made 0.05 to 0.30M EDTA and 0.45M acetate and adjusted to pH 4.7 by addition of 19M NaOH. In all cases the final solution volume was 135 ml. Portions of these solutions were contacted with one-fifth volume portions of washed extractant. The equilibrium aqueous phase pH in all cases was 4.4. Results of these experiments are given in Table 3.5.

TABLE 3.5

EFFECT OF EDTA CONCENTRATION ON DISTRIBUTION RATIOS

EDTA	Distribution Ratio					
M	Sr	Ca	Ce	Fe	Ru	ZrNb
0.05	38	450	1.4	---	0.00048	0.00057
0.10	27	260	1.5	0.0077	0.00030	0.00070
0.15	20	110	1.1	0.0011	---	0.00010
0.20	--	57	---	0.00005	0.00004	0.00005
0.25	11	52	0.73	0.00007	---	---
0.30	7.9	45	0.39	0.00005	---	---

All distribution ratios decreased with increased complexant concentration. In the case of cerium and strontium the logarithm of the distribution ratio decreased linearly with increased total EDTA concentration (Figure 3.2). Attempts to derive an equation which predicts a linear relationship between total complexant concentration and the logarithm of the distribution ratio were unsuccessful.

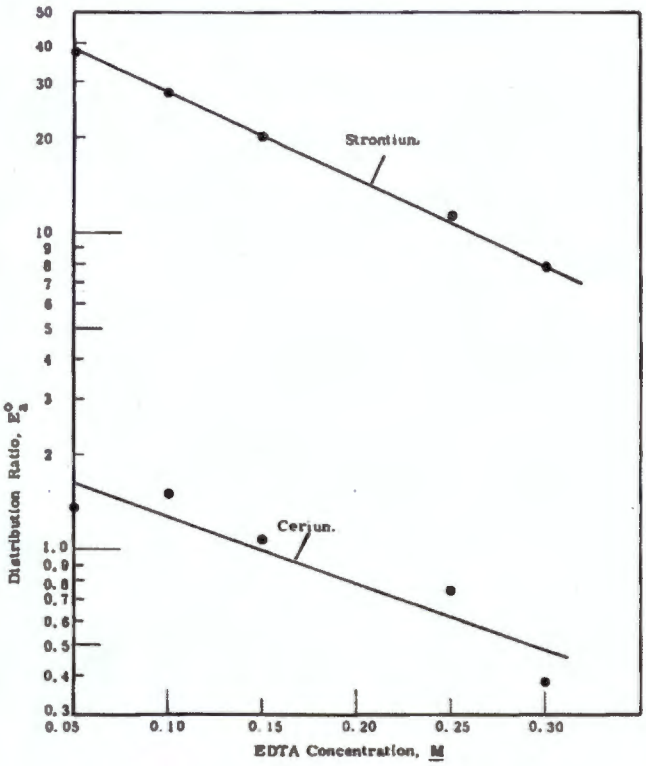

FIGURE 3.2

Effect of EDTA Concentration on Distribution Ratios of Strontium and Cerium

- Stability of Feed Solution to Radiation - Some studies were made to determine the effect upon solution stability of the high radiation fields which exist in the feed solutions. Of particular interest were the rate of change of solution pH induced by radiation and the rate at which complexing agents were decomposed.

Synthetic extraction column feed solutions were prepared and irradiated in vented glass containers by Co^{60} sources. The activity levels of the Co^{60} sources used were 1 and 4 x 10^6 r/hr.

The following conversion factors were used to estimate the radiation dose rate of process solutions:

Isotope	Total Watts/Kilocurie of Parent Isotope
Sr^{89}	3.4
Sr^{90}	6.7[a]
Y^{91}	3.6
$ZrNb^{95}$	4.85[b]
Ru^{106}	9.7[a]
Ce^{144}	8.05[a]
Pm^{147}	0.42

a - Total watts includes contribution of short-lived daughter.
b - Based on total kilocuries of $ZrNb^{95}$ prorated to reflect the equilibrium ratio of 2.1 curies Nb^{95}/curie Zr^{95}.

The activity level in feed solutions derived from plant concentrate varied with cooling time but was typically about 1×10^6 r/hr when calculated in this manner.

Based on the results shown in Table 3.6 and the estimated dose rate of 1×10^6 r/hr, radiolysis effects in feed solutions containing either EDTA or DTPA would not be expected to become apparent for at least 2 days, except for some increase in cerium distribution ratio. Cerium decontamination in the IA column would be completely lost after feeds containing DTPA had been exposed to 7.5×10^7 r (perhaps 3 days standing).

After Solution II had been exposed to 2.61×10^8 r, a small amount of strontium had precipitated and sufficient EDTA had been destroyed to allow iron to be extracted with a distribution ratio greater than one. It was demonstrated that this radiolytically damaged feed could be readjusted so that normal extraction behavior was restored. It was acidified to a pH of 0.5 with 15.7M HNO_3 (requiring 1.3M HNO_3) and readjusted by adding 3 parts 1.27M NaOH-1.81M NaOAc -0.69M Na_4EDTA to 10 parts acidified feed. Strontium and iron distribution ratios then measured 11.8 and 0.00091, respectively, at an equilibrium pH of 4.30.

- Back Cycle of Citric Acid Product Solution. - Batch extraction experiments were performed to determine the effects on distribution ratios of recycle of partition column citric acid product solution (1BP solution) to the extraction column. Such recycle was necessary in HSW operation because of the limited volume of the tank used to collect 1BP

TABLE 3.6

RADIOLYSIS OF SYNTHETIC FEED SOLUTIONS

Component, M	Solution I	Solution II	Solution III
$Sr(NO_3)_2$	0.0019	0.00169	0.0054
$Ca(NO_3)_2$	0.0031	0.0028	0.0030
$Fe(NO_3)_3$	0.021	0.074	0.0186
$Pb(NO_3)_2$	0.004	0.0035	---
$Ba(NO_3)_2$	9.1×10^{-5}	7.4×10^{-5}	---
$NaNO_3$	1.11	1.26	---
$ZrO(NO_3)_2$	8.6×10^{-6}	7.35×10^{-6}	---
$RuCl_3$	1.3×10^{-5}	1.18×10^{-5}	---
$Ce(NO_3)_3$	9.5×10^{-5}	8.1×10^{-5}	0.0011
$La(NO_3)_3$	0.00019	1.7×10^{-5}	0.00045
Acetate	0.482	0.45	0.50
HEDTA	0.042	---	---
EDTA	---	0.18	---
DTPA	---	---	0.075
pH	5.0	4.30	4.6

Radiation Dose, r	Solution I Solids	Solution I pH	Solution II Solids	Solution II pH	Strontium in Solution	Strontium E_a^o (a)	Iron E_a^o (a)	Equilibrium Aqueous pH	Solution III pH	Cerium E_a^o (c)	Equilibrium Aqueous pH (c)
0	None	5.0	None	4.30	100%	7.86	<0.00029	4.30	4.60	0.059	4.20
1.92×10^7	None	---	None	4.52	101.5	7.30	<0.00029	4.32	---	---	---
2.50×10^7	---	---	---	---	---	---	---	---	4.60	0.198	4.32
7.43×10^7	---	---	None	4.72	100	10.0	0.00031	4.50	---	---	---
5.00×10^7	---	---	---	---	---	---	---	---	4.71	0.210	4.32
7.5×10^7	---	---	---	---	---	---	---	---	4.88	15.0	4.40
8.0×10^7	Trace	---	---	---	---	---	---	---	---	---	---
2.60×10^8	---	---	Trace	6.42	93.3	4.0	1.90	5.63	---	---	---
3.72×10^8	~15 vol%	---	---	---	---	---	---	---	---	---	---
5.90×10^8	~15 vol%	8.0	---	---	---	---	---	---	---	---	---

(a) Aqueous/organic ratio was 5/1
(b) After extraction contact
(c) Aqueous/organic ratio was 1/1

HEC-66 RICHLAND WASH

solution. A synthetic feed simulating blending of 1 part 1BP with 8.3 parts 1AF was prepared. The normal 1AF solution was prepared by addition of 31 ml of 0.73M Na_4EDTA-1.03M NaOH solution to 100 ml of synthetic concentrate. The resulting solution at pH 4.7 was 0.41M acetate and 0.17M EDTA. Individual portions of the extraction column feed solution were traced with $ZrNB^{95}$, Ce^{144}, Ru^{106}, and Sr^{85}. The synthetic 1BP solution contained 1.0M citric acid-0.035M $Sr(NO_3)_2$-0.055M $NaNO_3$-0.0075M $Ca(NO_3)_2$-0.003M $Ce(NO_3)_3$. A liter of this solution was adjusted to pH 2 by addition of 12.2 ml of 19.1M NaOH. A portion of the 1BP at pH 2 was then adjusted to pH 4.7 by addition of 0.9 ml of 19.1M NaOH per 10 ml of 1BP solution. One ml portions of the 1BP solution at pH 4.7 were then mixed with 8.3 ml portions of the traced 1AF. The final solutions contained 0.097M citrate.

The solutions were contacted with one-fourth volume portions of unwashed extractant. In all cases the equilibrium aqueous phase pH was 4.6. Distribution ratios for $ZrNb^{95}$, Ru^{106}, Sr^{85}, and Ce^{144} were 0.0365, 0.00057, 7.46, and 0.136, respectively. In comparison, distribution ratios in the absence of 1BP solution were (in the same order) 0.0034, 0.0033, 17.6, and 0.480.

The presence of 0.097M citrate significantly repressed extraction of cerium, strontium, and ruthenium. Extraction of $ZrNB^{95}$, however, significantly increased. Possibly, negatively charged or neutral polymeric species of zirconium and/or niobium were converted to positively charged ions.

These results indicated that recycle rates as high as one volume of 1BP solution per eight volumes of extraction column feed could be tolerated without adversely affecting recovery of strontium. In actual HSW operation one volume of 1BP solution was combined with about 22 volumes of extraction column feed (Section 5, p. 5.81).

- Boil-Down of Extraction Column Aqueous Raffinate - Flowsheet No. 1 conditions (cf. Table 3.11) were employed in a mixer-settler run with synthetic concentrate to prepare 350 ml of aqueous waste at steady-state conditions. This quantity of waste was boiled down to 50 ml. Boiling point, density, and pH as a function of the degree of boil-down are listed in Table 3.7.

TABLE 3.7

BOIL-DOWN OF EXTRACTION COLUMN AQUEOUS WASTE

Volume, ml	Concentration Factor	pH, @ 25 C	Boiling Point, °C	Density g/ml, @25 C
350	1.00	4.50	104.1	1.092
300	1.17	---	105.1	---
250	1.40	4.60	105.3	1.129
200	1.75	4.65	106.1	1.159
150	2.33	4.72	107.0	1.204
125	2.80	4.82	108.1	1.249
100	3.50	4.92	109.8	1.304
75	4.67	5.20	112.1	1.398
50	7.00	---	113.0	---

The waste solution was free of solids both at boiling temperature and at 25 C when concentrated to 75 ml. Crystalline solids precipitated at boiling temperature at some undetermined point between this volume and the final volume of 50 ml. These solids were not identified but were thought to be $NaNO_3$. There was no evidence of any precipitation of iron as the hydroxide.

First Cycle Partition Column - Distribution Ratio Data - Distribution ratios of strontium, calcium, and cerium between extractant and 1.0M citric and tartaric acids as a function of equilibrium aqueous phase pH are given in Figure 3.3 and Table 3.8. The variation in distribution of strontium and cerium with citric acid concentration is also shown in Figure 3.3. Distribution ratios of strontium and cerium between extractant and other candidate partitioning agents, monochloroacetic and dichloroacetic acids, are also shown in Table 3.8.

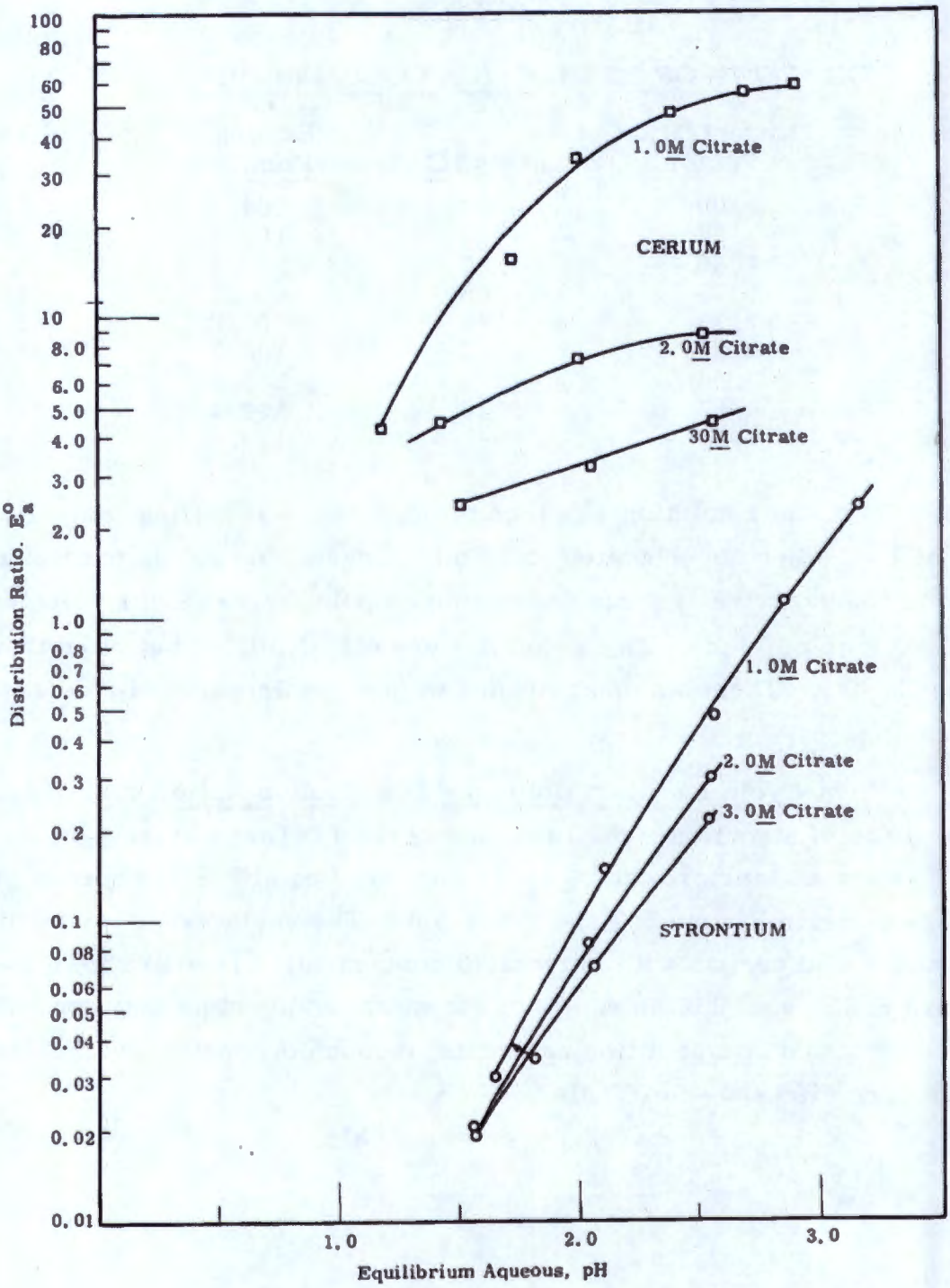

FIGURE 3.3

Partition Column Distribution Ratios

TABLE 3.8

PARTITION COLUMN DISTRIBUTION RATIOS

A. Citric Acid

Initial Aqueous Phase Composition		Strontium		Cerium		Calcium	
Citrate, M	Na^+, M	Equil. pH	E_a^o	Equil. pH	E_a^o	Equil. pH	E_a^o
0.833	0.588	3.2	2.3	2.9	57	2.8	29
0.870	0.460	2.9	1.1	2.7	53	2.7	15
0.909	0.321	2.6	0.48	2.4	46	2.3	6.6
0.952	0.168	2.1	0.15	2.0	33	1.9	2.5
0.976	0.086	1.8	0.034	1.7	15	1.6	1.2
0.988	0.044	1.7	0.030	---	--	1.5	0.67
1.00	0.00	---	---	1.2	4.4	---	---
1.88	0.963	2.5	0.28	2.5	8.7	---	---
1.92	0.456	2.0	0.083	2.0	7.4	---	---
1.94	0.148	1.6	0.02	1.4	4.4	---	---
2.48	1.62	2.6	0.22	2.6	4.4	---	---
2.71	0.939	2.0	0.07	2.1	3.2	---	---
2.74	0.41	1.6	0.02	1.5	2.4	---	---

B. Tartaric Acid

Tartrate, M	Na, $^+$M						
0.833	0.588	2.9	0.7	2.8	32	2.8	21
0.870	0.460	2.7	0.38	2.6	42	2.6	9.6
0.909	0.321	2.4	0.17	2.3	23	2.3	4.5
0.952	0.168	2.0	0.055	1.9	12	1.9	1.6
0.976	0.086	1.7	0.022	1.7	6.6	1.6	0.79
0.988	0.044	1.6	0.011	---	---	1.4	0.45
1.00	0.00	---	---	1.2	2.0	---	---

C. Dichloroacetic Acid

Dichloro-Acetate, M	Na^+, M						
0.794	0.728	3.1	11	3.1	11000	---	---
0.820	0.637	2.6	1.4	2.6	150	---	---
0.866	0.474	1.9	0.12	1.9	5.5	---	---

D. Monochloroacetic Acid

Monochloro-acetate, M	Na^+, M						
0.905	0.335	2.6	2.3	2.6	>1000	---	---
0.952	0.168	2.1	0.5	2.1	>1000	---	---
0.995	0.018	1.5	0.074	1.5	>1000	---	---

The procedure used to obtain data for tartaric acid partitioning was typical of that used with the other acid partition agents. Solutions of the composition 1.0M tartaric acid - 0.01M $Sr(NO_3)_2$, 1.0M tartaric acid - 0.0005M $(Ce(NO_3)_3$, and 1.0M tartaric acid - 0.05M $Ca(NO_3)_2$ were prepared and traced with Sr^{85}, Ce^{144}, and Ca^{45}, respectively. Portions of the traced solutions were adjusted to pH's in the range 2 to 4 by addition of 3.53M NaOH and contacted with an equal volume of unwashed extractant. Sodium and acid anion concentrations are listed in Table 3.8.

Cerium distribution ratios decreased as citrate concentration increased, indicating formation of a cerium citrate complex. Strontium distribution ratios decreased also as citrate concentration increased but to a lesser extent. One molar citric acid was chosen for use in the partition column since this concentration supplied sufficient buffering capacity and permitted a larger strontium-cerium separation than would have higher citrate concentrations. When 1.0M citric acid is used as the partitioning agent it is desirable to operate the partition column so that the pH at the bottom of the column does not exceed 2.25 in order to prevent excessive strontium loss. Operation at lower pH's tends to decrease cerium decontamination, however, and optimum operation requires balancing these two considerations.

Alternate partitioning agents investigated were tartaric acid, dichloroacetic and monochloroacetic acids, and maleic acid. The behavior of tartaric acid was quite similar to that of citric acid, and tartaric acid should be a satisfactory partitioning agent. The distribution ratio data indicate that excellent cerium decontamination could be obtained with monochloroacetic acid. Radiolytic decomposition and the attendant chloride ion corrosion problems, which might be expected, were not investigated. Maleic acid was investigated briefly because it offered a high buffering capacity in the desired pH range. The monosodium salt of maleic acid begins to precipitate at about pH 1.5, however. The volume of solids formed appeared so large as to preclude use of maleic acid in the partition column.

- Control of pH in the Partition Column - At pH's in the range 1.5 to 2.25 in the partition column, strontium and any extracted sodium transfer to the aqueous phase while cerium and calcium remain largely in the organic phase. To preserve electroneutrality hydrogen ion equivalent to the amount of strontium and sodium ions removed must be supplied from the aqueous phase to the organic phase. The titration curves in Figure 3.4 show the amounts of hydrogen ion which can be furnished by either 1.0M citric acid or 1.0M tartaric acid in the pH range of interest.

Data in Table 3.9 illustrate the partition column pH profile obtained at two different flow ratios with 1.0M citric acid as the partitioning agent. These data were obtained with the profile-type miniature pulse column. The organic feed solution was the extraction column organic product obtained in Cold Semiworks Run 42 (cf. Table 4.3, Appendix). This feed solution was 0.210M hydrogen-form D2EHPA. The pH's of the aqueous effluent streams in these runs were calculated from data in Figure 3.4 to be 2.32 and 2.47, respectively. Experimental values were in excellent agreement with the calculated values.

TABLE 3.9

PARTITION COLUMN pH PROFILE

	Run 1	Run 2
Flow Ratio: Aqueous/Organic	0.234	0.147
pH, Top of Column	1.50	1.36
pH, 1/3 Down Column	1.82	1.84
pH, 2/3 Down Column	2.00	2.10
pH, Aqueous Effluent	2.29	2.40
H^+, Organic Raffinate	0.268M	0.257M

- Stability of Partition Column Product Solution to Radiation - Bray[6] reported the results of some Co^{60} irradiation studies on partially neutralized citric and tartaric acid solutions. Further studies of the irradiation of simulated partition column product solutions are described here.

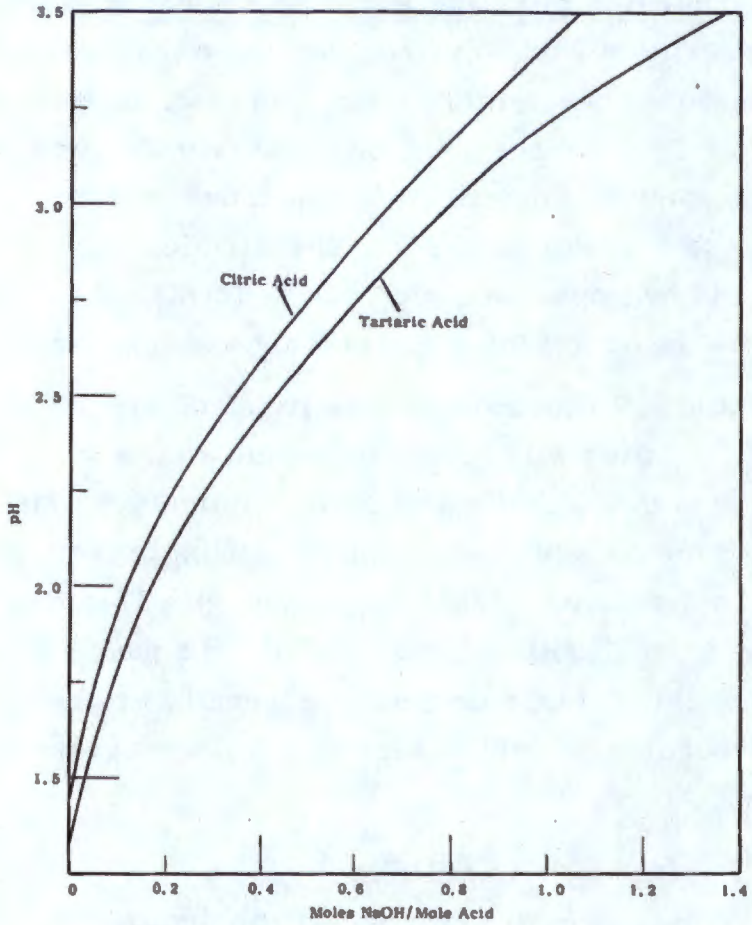

FIGURE 3.4

Variation in pH as Function of Neutralization of Citric and Tartaric Acids

Upon irradiation, the pH of citrate solutions containing strontium rises ultimately to about pH 8, and precipitates form which carry strontium almost completely. Although the precipitates are soluble in HNO_3, dissolution in HNO_3 is undesirable for two reasons. First, it has been plant and laboratory experience that gross foaming occurs when acid is added to irradiated citric acid solutions; the foaming is of such a magnitude that it can be difficult to control. Second, it is necessary to neutralize all of the added HNO_3 when strontium is precipitated as $SrCO_3$ during final product load-out. If the neutralization is done with NaOH, undesirably high sodium concentrations in the load-out solution can result.

An optimum method for storing citrate solutions containing strontium would involve addition of HNO_3 to maintain a pH sufficiently low that strontium doesn't precipitate. Ideally, the HNO_3 addition should be planned so that the excess HNO_3 has been radiolytically decomposed at the time the final product load-out is made. The HNO_3 could be added in one batch or in smaller increments at various time intervals.

A series of irradiations were made in which HNO_3 was added in various amounts, and at various time intervals, to simulated partition column citrate solutions irradiated in the Co^{60} facility. Details of these experiments and the results obtained are shown in Table 3.10. When the total dose received by the solution was not more than 8×10^8 r, less than 10% of the strontium precipitated when no HNO_3 was added. Addition of HNO_3 greatly increased the amount of strontium precipitation unless enough acid was added to maintain the pH below 0.0. Large quantities of HNO_3 were required to meet this pH requirement. When the solution was made 4.0M initially, 90% of the strontium had precipitated after an irradiation dose of 8×10^8 r; when the solution was made 6.0M HNO_3 initially, none of the strontium precipitated after a dose of 8×10^8 r, but more than 99% had precipitated after a dose of 1.6×10^9 r.

The data in Table 3.10 indicate the radiolytic destruction of citrate is a first order reaction with a dosage of 8×10^8 r corresponding to one half-life. The addition of HNO_3 decreased the citrate half-life somewhat (by about 40% when 3.6M HNO_3 was added); but because of the simultaneous destruction of HNO_3 and the undetermined nature of the reaction, only a qualitative statement can be made. It should be emphasized that the citrate analyses upon which the preceding statements are based were actually titrations of the reducing power of the solutions. Some of the radiolytic degradation products were probably also titrated by this procedure.

Since these radiolysis studies were made it has become HSW practice to treat the partition column product stream with H_2O_2. The use of 2.5 moles of H_2O_2 - 0.75 moles of HNO_3 per mole of citrate completely destroys the citrate, thus eliminating radiolysis problems.

TABLE 3.10

STABILITY OF PARTITION PRODUCT SOLUTION TO RADIATION

Solution[1]	HNO_3 M	Accumulative Dose, r	Precipitate, Vol%	pH	% Sr in Solution	Citrate, M[2]	Specific Gravity
A	0.0	0.0		0.90	100.0	1.96	
	0.0	4×10^8	0.0	1.92	98.9	1.51	
	0.0	8×10^8	trace	2.40	99.3	0.996	
	0.0	12×10^8	trace	2.70	97.3	0.678	
A	0.0	0.0		0.90	100.0	1.96	
	0.0	8×10^8	trace	2.28	96.8	0.971	
	0.0	16×10^8	1.9	3.10	90.6	0.588	
B	0.0	0.0		0.70	100.0	(2.20)	1.189
	0.0	8×10^8	0.32	3.40	90.5	1.01	1.109
	0.0	16×10^8	8.8	5.55	9.2	nil	1.046
	0.0	24×10^8	7.7	7.70	7.6	nil	1.035
B	6.0	0.0		<0.0	100.0	(1.60)	1.282
	6.0	8×10^8	0.0	0.0	98.7	0.47	1.121
	6.0	16×10^8	4.1	8.0	0.24	nil	1.015
	6.0	24×10^8	4.6	8.30	0.25	nil	1.017
B	4.0	0.0		<0.0	100.0	(1.75)	1.263
	4.0	8×10^8	2.9	0.75	10.5	0.42	1.095
	(8.0)[3]	16×10^8	3.5	3.40	19.3	nil	1.024
B	3.0	0.0		<0.0	100.0	(1.85)	1.253
	3.0	8×10^8	3.7	1.70	3.52	0.63	1.076
	(6.0)	16×10^8	3.8	8.15	0.24	nil	1.022
A	2.0	0.0		0.0	100.0	2.10	
	2.0	8×10^8	1.1	1.90	1.49	0.97	
	(4.0)	16×10^8	0.9	4.00	5.87	0.23	
A	2.0	0.0		0.0	100.0	2.10	
	2.0	4×10^8	0.0	0.25	101.5	1.48	
	(4.0)	8×10^8	0.8	0.44	66.1	1.13	
	(6.0)	12×10^8	0.45	0.26	60.4	0.298	
A	1.0	0.0		0.0	100.0	2.10	
	1.0	8×10^8	0.6	2.50	28.3	1.14	
	(2.0)	16×10^8	2.0	4.70	2.81	0.426	
A	1.0	0.0		0.0	100.0	2.10	
	1.0	4×10^8	0.0	0.67	99.6	1.48	
	(2.0)	8×10^8	0.8	0.82	45.3	0.96	
	(3.0)	12×10^8	1.9	2.20	0.85	0.62	
A	0.5	0.0		0.14	100.0	1.99	
	0.5	8×10^8	0.6	2.65	68.6	1.17	
	(1.0)	16×10^8	8.4	4.30	52.6	0.449	
A	0.5	0.0		0.14	100.0	1.99	
	0.5	4×10^8	0.6	1.64	81.3	1.48	
	(1.0)	8×10^8	trace	2.11	60.5	0.947	
	(1.5)	12×10^8	8.0	2.95	35.5	0.491	

(1) Solutions coded A contained 2.0M citric acid - 0.075M $Sr(NO_3)_2$, plus 15.7M HNO_3 to make HNO_3 concentration shown. Irradiated in a field of 1×10^6 r/hr.
Solutions coded B contained 2.0M citric acid - 0.2M $Sr(NO_3)_2$ - 0.2M $NaNO_3$ - 0.02M $Ca(NO_3)_2$, plus 15.7M HNO_3 to make HNO_3 concentrations shown. Irradiated in a field of 4×10^6 r/hr.

(2) Analyses by ceric titration procedure; some of the radiolytic degradation products were probably also titrated by this procedure.

(3) In some of the tests HNO_3 was added incrementally during the irradiation. The accumulative total HNO_3 concentration added is shown in parentheses.

Second Cycle Extraction Column - Batch contacts were made to determine the feasibility of using a second cycle of solvent extraction in lieu of a tail-end ion exchange column to provide additional decontamination of the Sr^{90} product from Ce^{144}.

The starting feed solution for these studies was the synthetic 1BP solution already described (cf. p. 3.14). Thirty-five ml portions of the 1BP solution at pH 2 were adjusted to pH's 3.0, 3.5, 4.0, 4.5, and 5.0 by addition of 1.1, 1.9, 2.8, 3.5, and 4.4 ml, respectively, of 19.05M NaOH. Individual portions of the resulting solutions were traced with Ce^{144} and Sr^{85} and then contacted with an equal volume of unwashed solvent. In other experiments, 4.2 ml of 1.3M Na_4 EDTA was added to 50 ml of the synthetic 1BP. Twelve ml portions of the resulting solution at pH 2.7 and 0.1M EDTA were adjusted to pH's 3.0, 4.0, and 5.0 by addition of 0.2, 0.6, and 1.3 ml, respectively, of 19.05M NaOH. Individual portions of the final solutions were traced with Ce^{144} and Sr^{85} and contacted with an equal volume of unwashed solvent.

Results of these studies (Figure 3.5), showed maximum strontium extraction was achieved at about pH 4.0. Even at pH 4 the strontium E_a^o at an aqueous/organic volume ratio of one was only about two. The presence of a complexing agent such as EDTA (or, presumably DTPA) was required to obtain decontamination from cerium. Strontium E_a^o's were not affected by the presence of as much as 0.1M EDTA in this system.

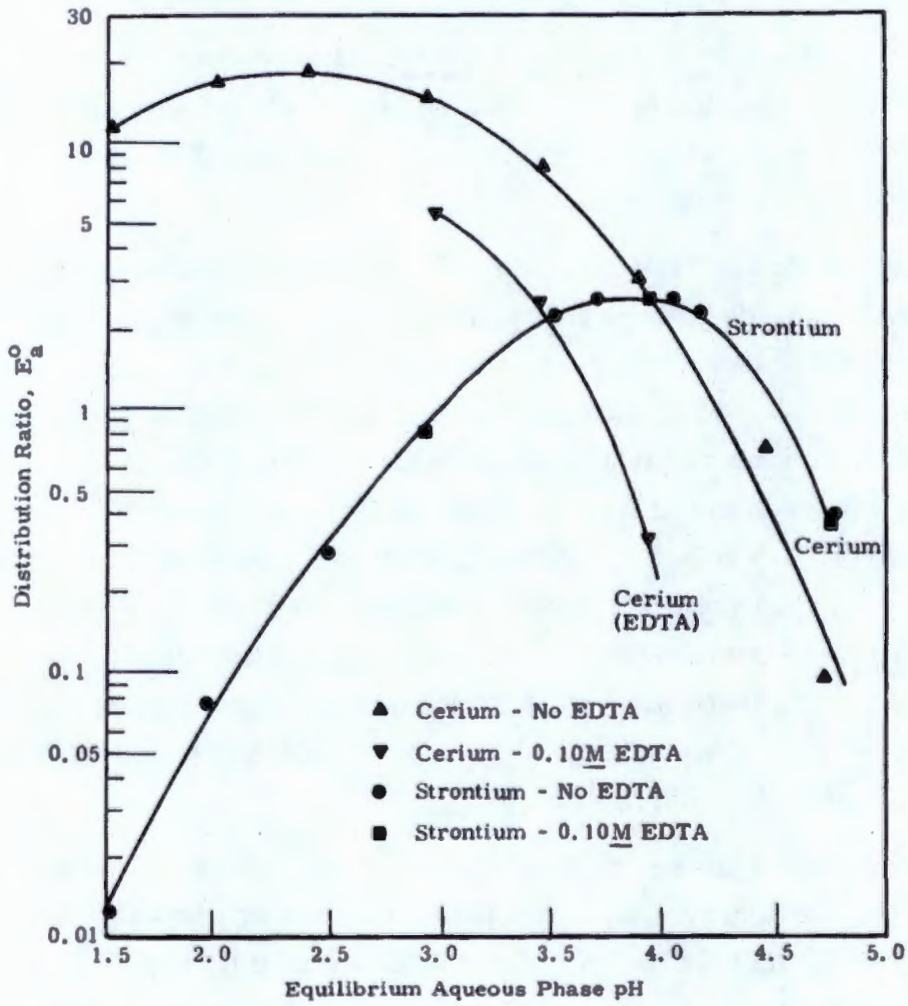

FIGURE 3.5

Extraction of Strontium from Partition Column Product Solution

Continuous Countercurrent Runs - First Cycle Extraction Column - Conditions and results of the many mixer-settler extraction column runs made with synthetic concentrate are summarized in Table 3.11. Except for the absence of back-cycle of the partition column product solution, the conditions shown for Flowsheet No. 1 in Table 3.11 were essentially those subsequently employed in the first HSW run, Run Sr-4 (cf. Section 5, p. 5.8). The other flowsheet conditions tested were earlier versions of the HSW start-up flowsheet suggested by laboratory and Cold Semiworks studies.

TABLE 3.11

FIRST CYCLE EXTRACTION COLUMN MIXER-SETTLER RUNS WITH SYNTHETIC CONCENTRATE

Feed: Synthetic concentrate (Table 3.1) made 0.18M EDTA and 0.41M acetate and adjusted to pH indicated by addition of 3.1 ml of 1.73M NaOAc - 0.74M EDTA - 1.0 to 1.2M NaOH per 10 ml of concentrate. Resulting solution spiked with appropriate radioactive tracer.

Scrub: Composition indicated

Extractant: 0.368M D2EHPA - 0.2M TBP - SSB

Flows: As indicated

	Run 1	Run 2[a]	Run 3[b]	Run 4	Run 5	Run 6
Flowsheet No.	1	2	2	3	4	5
Feed pH	4.7	4.2	4.2	4.2	4.2	4.2
Extractant Treatment[c]	Unwashed	Washed	Washed	Unwashed	Washed	Washed
Scrub Composition						
$NaNO_3$, M	0.0	0.5	0.5	0.0	0.5	0.0
Citrate, M	0.6	0.0	0.0	0.6	0.0	0.0
EDTA, M	0.0	0.02	0.02	0.0	0.02	0.0
pH	2.6	3.6	3.6	2.6	3.6	---
Relative Flows						
Feed	1.0	1.0	1.0	1.0	1.0	1.0
Extractant	0.27	0.21	0.21	0.27	0.27	0.25
Scrub	0.054	0.040	0.040	0.054	0.054	0.0
Sr Loss, %	3.8	1.7	<3.5	<0.01	0.01	---
Ce^{144} DF	19	13	11	4	14	13
$Zr\text{-}Nb^{95}$ DF	580	2310	---	---	---	---
Ru^{106} DF	1040	930	---	---	---	---
M Na in Organic Product	0.007	0.07	---	0.004	---	---
Raffinate pH	4.5	4.0	4.0	3.5	3.9	4.0

(a) Decontamination factor for Fe^{59}, Cs^{137}, $Eu^{152-154}$, and Ba^{133} were $>2 \times 10^4$, 3.3×10^4, 200, and 1.2, respectively.

(b) Solvent irradiated to a total exposure of 1.77×10^7 r before use

(c) See page 3.4 for washing treatment.

Results of these runs were in good agreement with those expected from batch contact data. Strontium losses were low under all conditions tested. The addition of EDTA to the feed suppressed almost completely extraction of inert iron and lead and radiozirconium, niobium, and ruthenium. Cerium DF's were increased by operation of the extraction section of the column at high pH's. The more efficient removal of sodium from the organic stream by scrubbing with 0.6M citric acid at pH 2.6 rather than with 0.5M $NaNO_3$ at pH 3.6 was also demonstrated. One run also showed that irradiation of the solvent to a total dose of 10^7 r had no appreciable effect on strontium recovery or cerium decontamination.

Certain of the extraction column flowsheets were also tested with actual plant crude concentrate. Conditions and results of these mixer-settler runs are listed in Table 3.12. In several of these runs acidified plant crude was diluted with synthetic concentrate. The iron and lead concentrations of the synthetic concentrates were those corresponding to the actual plant crude concentrate (cf. Table 3.1). In all cases the synthetic concentrate was also 1.0M HNO_3, 0.005M $Sr(NO_3)_2$, and 0.003 M $Ca(NO_3)_2$.

Flowsheet performance with feeds prepared from plant concentrate duplicated that with feeds prepared from synthetic concentrate in most respects. Some disparity was noted in the behavior of Ru^{106} and $ZrNb^{95}$. This is due in part to the difficulty encountered in obtaining reliable analyses for small concentrations of these two constituents in the presence of high concentrations of Sr^{90} and Ce^{144}. Another reason may be that chemical species of ruthenium and zirconium in plant concentrate are different from those of the radioactive tracers used with synthetic concentrate.

The Ce^{144} DF in Run 3 under Flowsheet No. 1 conditions was five to six times lower than that in Runs 1 and 2 (Table 3.12). Run 3 was made with the third batch of plant concentrate while Runs 1 and 2 were made with the second batch of plant concentrate. As indicated in Table 3.1, the iron and lead concentrations of the third batch of concentrate were considerably

TABLE 3.12

FIRST CYCLE EXTRACTION COLUMN MIXER-SETTLER RUNS WITH PLANT CONCENTRATE

Feed: Acidified plant concentrate (diluted with synthetic concentrate in some cases) adjusted to acetate and EDTA concentrations and pH indicated by addition of 310 ml NaOAc-Na_4EDTA-NaOH solution per liter of concentrate.

Scrub: Composition indicated

Extractant: 0.368M D2EHPA - 0.2M TBP - SSB

Flows: Feed/Extractant/Scrub:: 1.0/0.25/0.05

	Run 1	Run 2	Run 3	Run 4	Run 5[a]
Flowsheet No.[b]	1	1	1	2	3
Concentrate Batch No.[c]	2	2	3	2	1
Percent Activity Level[d]	12	40	100	12	100
Feed Composition					
Acetate, M	0.40	0.40	0.37	0.40	0.45
EDTA, M	0.15	0.15	0.16	0.15	0.10
pH	4.7	4.7	4.7	4.3	4.2
Scrub Composition					
$NaNO_3$, M	0.0	0.0	0.0	0.5	0.0
Citric Acid, M	0.6	0.6	0.6	0.0	0.6
EDTA, M	0.0	0.0	0.0	0.02	0.0
pH	2.6	2.6	2.6	3.6	2.6
Sr Loss, %	0.73	0.68	1.6	0.03	(10.0)
Ce^{144} DF	15	19	3.0	11	2.0
$ZrNb^{95}$ DF	1600	1620	----	920	675
Ru^{106} DF	>140	250	----	----	----
Raffinate pH	4.5	4.5	4.3	4.2	3.5

(a) Washed extractant used in this run; unwashed extractant used in all other runs.

(b) Flowsheet numbers correspond to those in Table 3.11.

(c) Batch numbers correspond to numbers in Table 3.1.

(d) As explained in text, in some runs plant concentrate was diluted with synthetic concentrate.

than those of Batches 1 and 2. One explanation for the poor Ce^{144} DF in Run 3 may be that the concentration of EDTA not complexed by iron and lead was insufficient to depress the cerium E_a^o to the same extent as in Runs 1 and 2.

- First Cycle Partition Column - Continuous countercurrent partition column runs were made in both mixer-settlers and in a miniature pulse column. Data from the former runs are given in Table 3.13 and from the latter in Table 3.14.

TABLE 3.13

MIXER SETTLER RUNS - FIRST CYCLE 1B COLUMN

Feed (1BF): Organic product (1AP) solutions obtained at steady state from mixer-settler extraction column runs under Flowsheet 1 conditions, Tables 3.11 and 3.12.

1BX: 1M citric acid

Flows: 1BF/1BX 1.0/0.26

Feed Derived From	1BP pH	% Sr Loss	Ce^{144} DF
Lab Concentrate	1.8	4.8	43
Plant Concentrate*	2.0	3.6	45

*Organic product from Run 3, Table 3.12.

The chemical flowsheet conditions employed in the mixer-settler runs and in miniature pulse column Runs 3-5 were essentially identical to those employed in HSW Runs Sr-4 and Sr-5 (cf. Section 5). Comparison of loss and decontamination performance is shown in Table 3.15.

TABLE 3.14

MINIATURE PULSE COLUMN 1B COLUMN RUNS

	Run 1	Run 2	Run 3	Run 4	Run 5
1BF Source	Batch Contact[a]	Batch Contact[a]	Mixer-Settler[b]	Mixer-Settler[c]	Mixer-Settler[d]
1BX Composition	1.0M Citric Acid	2.0M Citric Acid	1.0M Citric Acid	1.0M Citric Acid	1.0M Citric Acid
Aqueous/Organic Flow Ratio	0.234	0.147	0.234	0.234	0.234
Flow, Combined Phases, gal/hr sq ft	150	150	100	104	140
Pulse Frequency, cycles/min	78	78	86	95	86
1BF H^+, M	0.248	0.293	0.328	---	0.334
1BW H^+, M	0.304	0.340	0.346	---	0.352
1BP pH	2.5	2.25	1.75	--	1.85
% Sr Loss	11.5	0.50	0.30	---	---
Ca DF	---	505	12	---	---
Ce DF	---	324	11	9	55

(a) The 1BF (0.004M Sr - 0.008M Ca - 0.005M Ce and traced with either Sr^{85} or Ce^{144} was prepared by batch contacts of extractant and appropriate aqueous phases.

(b) Organic product streams from mixer-settler extraction column runs with synthetic concentrate using conditions of Flowsheet 3, Table 3.11.

(c) Same as (b) except 1BF was spiked with organic product from mixer-settler extraction column Run 5 (Table 3.12) with plant concentrate.

(d) Organic product from mixer-settler extraction column run with laboratory concentrate using conditions of Flowsheet 1, Table 3.11.

TABLE 3.15

COMPARISON OF LABORATORY AND HSW PARTITION COLUMN RESULTS

1BX: 1.0M Citric Acid

Aqueous/Organic Flow Ratio = 1.0/0.23-0.26

	Mixer-Settler	Miniature Pulse Column	HSW Sr-4	HSW SR-5
% Sr Loss	3.6 - 4.8	0.3	1.0	0.2
Ca DF	---	12	9	19
Ce DF	44	10-55	55	72

Strontium losses in the miniature pulse column were comparable to those experienced in the HSW runs. The higher losses noted in mixer-settler stages for strontium transfer. The calcium DF obtained in the miniature pulse column runs also compared favorably to those observed in HSW runs.

The cerium DF observed in mixer-settler runs with feeds derived from both plant and laboratory concentrate was approximately the same as noted in the HSW runs. The cerium DF in miniature pulse column Run 5 also agreed with the HSW and mixer-settler data. No explanation could be found for the lower cerium DF's found in Runs 3 and 4.

Operation of the miniature pulse column to produce 1BP solutions at pH's in the range 2.25-2.50 (Runs 1 and 2, Table 3.14) resulted in better decontamination from calcium and cerium at the expense of greater strontium loss. These findings were in agreement with those predicted from the batch contact data shown in Figure 3.3.

Simultaneous Recovery of Sr^{90}, Ce^{144}, and Pm^{147} from Crude Concentrate

Flowsheet Concept - As noted in Section 5 of this report, HSW Run Sr-7 had the dual objectives of recovering Sr^{90} and also of investigating some of the technology involved in recovering Ce^{144} and a cerium-free Pm^{147} fraction. Laboratory studies conducted to aid in the development of a chemical flowsheet for this HSW run are presented here.

The basic steps in the flowsheet investigated in the laboratory were:

1. Co-extract Sr^{90}, inert calcium, Pm^{147}, Ce^{144}, and other fission product rare earths at pH 3.5 to 4.0 from an acetate buffered crude concentrate containing complexant(s) to suppress extraction of iron, lead, $Zr\text{-}Nb^{95}$, and Ru^{106}.
2. Partition Sr^{90} from other extractables into 1M citric acid.
3. Strip calcium and rare earths from organic solution from Step 2 with 1-2M HNO_3.

4. Oxidize Ce^{144} in HNO_3 solution from Step 3 to the tetravalent state with $KMnO_4$ and batch extract into a D2EHPA-TBP-SSB solution. (An alternative approach involving separation of trivalent cerium and promethium by D2EHPA extraction was briefly investigated.)
5. Adjust the aqueous phase from Step 4 to 0.25 - 0.5M citric acid at pH 1-2 and batch extract Pm^{147} and other rare earths from manganese(II) and calcium.
6. Strip extracted Pm^{147} from the organic phase in Step 5 with 1-2M HNO_3.

Only steps 1, 4, and 5 of the above flowsheet were investigated in the laboratory. It should be noted that the final flowsheet used in HSW Run Sr-7 to recover Sr^{90}, Ce^{144}, and Pm^{147} differed somewhat from that presented here (cf. Section 5, p. 5.23).

Coextraction of Strontium and Rare Earths from Concentrate - Batch Extraction Data - Laboratory-prepared crude concentrates of three different compositions (Table 3.16) were used. These solutions differed principally in $Ce(NO_3)_3$ and $La(NO_3)_3$ (stand-in for other rare earths in plant concentrate) concentrations. At the time of these studies there was considerable uncertainty as to the concentrations of the various rare earth ions in plant concentrate; Solution 3, was believed to be the closest approximation to actual plant crude rare earth composition. The $Sr(NO_3)_2$ concentration of this solution was also increased from 0.0025M to 0.0072M to correspond to that prevailing in HSW operation when the 1BP stream was recycled to the extraction column. Iron and lead concentrations of these solutions corresponded to values found for plant concentrate and were lower than those used in earlier laboratory studies (cf. Table 3.1, p 3.2).

Extraction column feed solutions (0.5M acetate and either 0.05M HEDTA or 0.05 to 0.1M EDTA) at pH's in the range from 2 to 4 were prepared from the various laboratory concentrates. In all cases the concentrate was diluted to 1.34 times its original volume. Portions of the

final aqueous solutions were spiked with appropriate tracers and contacted with unwashed extractant at various phase ratios. Distribution ratios of iron were very low under all conditions tested. Distribution ratios of other constituents of crude concentrate are presented in Figures 3.6 - 3.10.

TABLE 3.16

LABORATORY CONCENTRATES USED IN STUDIES OF COEXTRACTION OF STRONTIUM AND RARE EARTHS

Component	Solution 1, M	Solution 2, M	Solution 3, M
HNO_3	1.0	0.50	0.80
$Fe(NO_3)_3$	0.025	0.025	0.025
$Pb(NO_3)_2$	0.02	0.02	0.025
$Ca(NO_3)_2$	0.003	0.0038	0.0040
$Sr(NO_3)_2$	0.0025	0.0025	0.0072
$Ce(NO_3)_3$	0.0025	0.0040	0.0015
$La(NO_3)_3$	0.0025	0.0105	0.0006
$Ba(NO_3)_2$	-----	0.0015	-----
$Nd(NO_3)_3$	-----	-----	0.0001
$RuCl_3$	-----	0.000016	-----
$ZrO(NO_3)_2$	-----	0.001	-----

Significant aspects of these data were:

1. Higher distribution ratios for strontium and rare earths were obtained with HEDTA than with EDTA as the complexant for inert iron and lead. (However, the required amount of HEDTA was not available in the HSW; and, because of the necessity of meeting Sr^{90} production commitments, it was decided to use the less desirable EDTA as the complexant.)
2. Extraction of Pm^{147} was increased by reducing the aqueous/organic flow ratio and by decreasing the total EDTA concentration.
3. A pH of 3.5 was optimum for coextraction of strontium and rare earths.

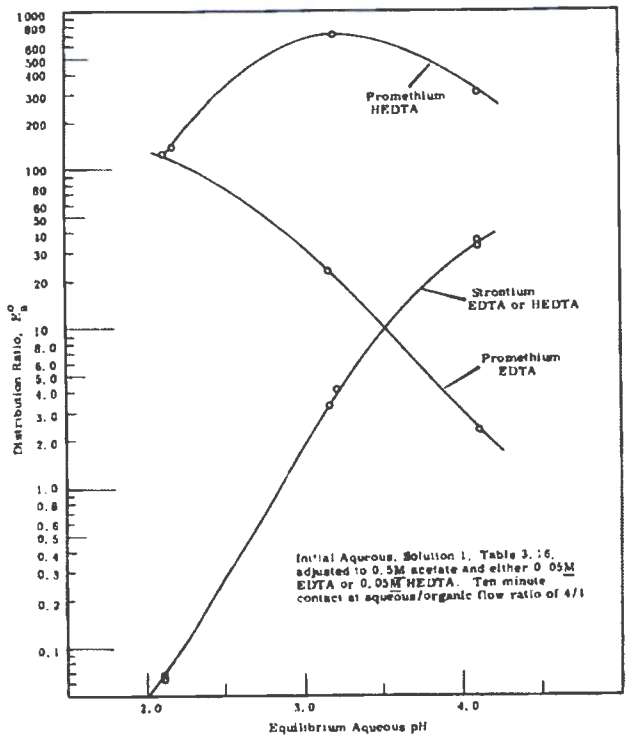

FIGURE 3.6

Effect of Complexing Agents on Promethium and Strontium Distribution Ratios

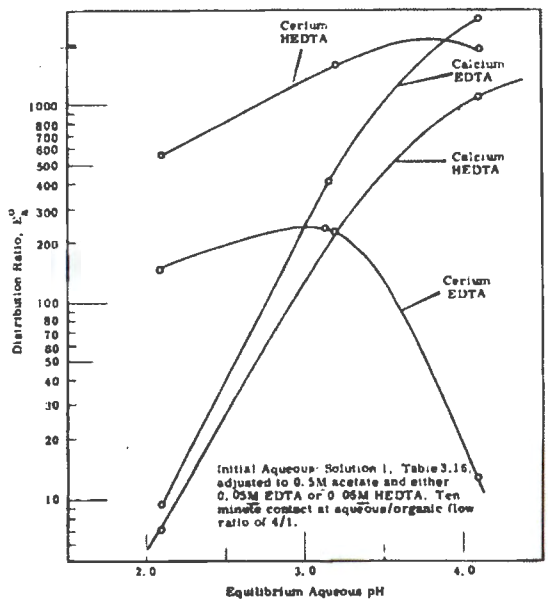

FIGURE 3.7

Effect of Complexing Agents on Calcium and Cerium Distribution Ratios

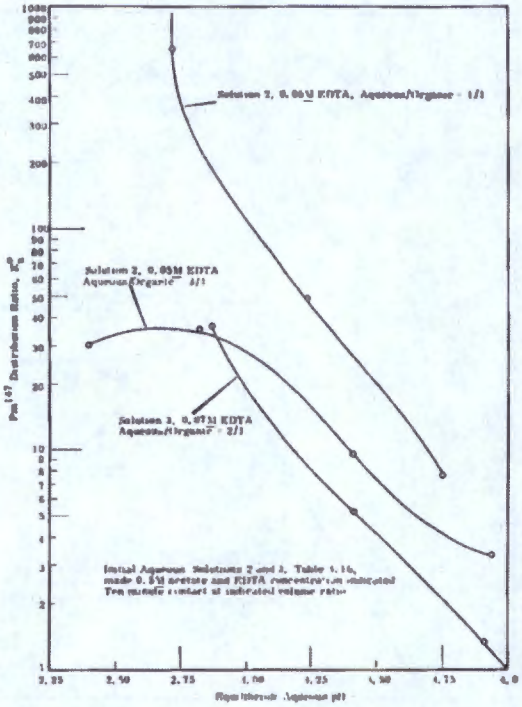

FIGURE 3.8

Effect of Aqueous/Organic Ratio on Promethium Distribution Ratio

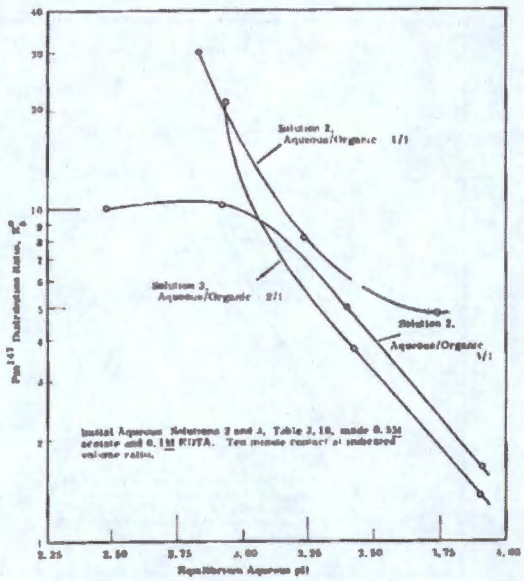

FIGURE 3.9

Effect of Aqueous/Organic Flow Ratio on Promethium Distribution Ratio

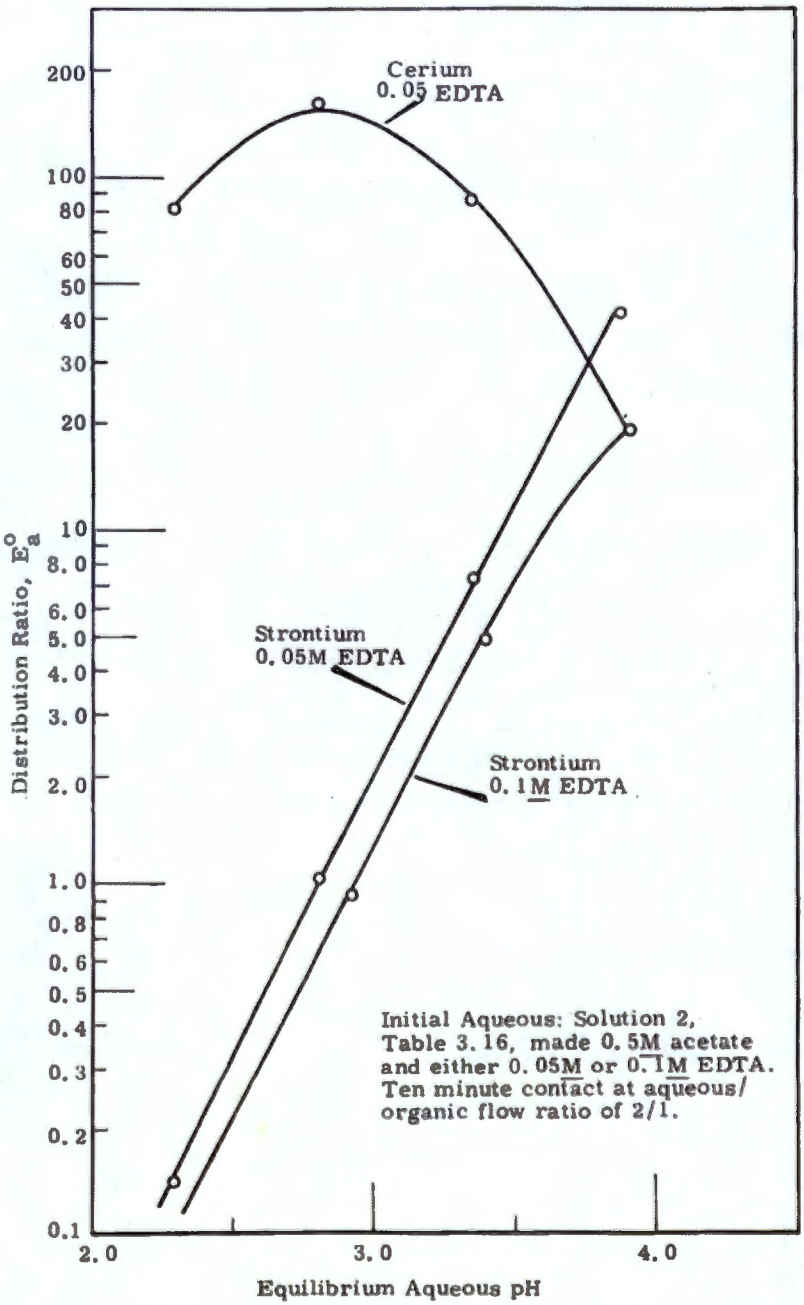

FIGURE 3.10

Coextraction of Strontium and Cerium from Feed Containing EDTA

- Mixer-Settler Runs - Two unsuccessful mixer-settler runs to extract Pm^{147} from laboratory concentrate were made (Table 3.17). The feed/extractant flow ratio and feed and raffinate pH's were near optimum according to batch contact data. Failure to recover significant amounts of Pm^{147} was ascribed to excessive complexing of Pm^{147} by the high concentrations of EDTA employed. Partly as a result of these data, the EDTA concentration used in the HSW Run Sr-7 was greatly reduced (cf. Section 5, p. 5.23). Because of HSW scheduling, no further mixer-settler runs were made to develop a satisfactory extraction column flowsheet.

TABLE 3.17

EXTRACTION OF Pm^{147} FROM LABORATORY CONCENTRATE - MIXER-SETTLER RUNS

Feed: Run 1: Solution 2, Table 3.16, traced with Pm^{147} and made 0.5M acetate and 0.10M EDTA
Run 2: Solution 3, Table 3.16, traced with Pm^{147} and made 0.5M acetate and 0.07M EDTA.

Extractant: Unwashed 0.368M D2EHPA - 0.2M TBP - SSB

Scrub: Indicated composition

Flow Ratios: Feed/extractant/scrub::2.08/1.0/0.105

Stages: 7 extraction, 5 scrub

Run No.	Feed pH	Scrub Composition $NaNO_3$ M	Scrub Composition Acetate M	Scrub Composition pH	Raffinate pH	% Pm Extracted
1	3.70	0.5	0.05	3.5	3.40	5.0
2	3.62	0.25	---	3.5	3.38	21.0

Separation of Cerium as Cerium(III) - The feasibility of separating cerium from promethium and other rare earths by preferential stripping of promethium from the partition column organic phase after removal of strontium was investigated. In this flowsheet version, cerium and calcium would be left in the organic phase and could be stripped from it in a subsequent operation. Alternatively, calcium and rare earths might be

stripped from the organic phase with dilute HNO_3. Then, after appropriate solution adjustments, the cerium would be extracted into a D2EHPA - TBP - SSB solution leaving promethium in the aqueous raffinate.

Another mode of operation in the HSW to recover Sr^{90}, Ce^{144}, and a cerium-free Pm^{147} fraction might be to extract only Sr^{90} and calcium leaving the rare earths in the aqueous raffinate. A second extraction of the aqueous phase could be made to remove Ce^{144} preferentially leaving the remaining rare earths in the raffinate. A third extraction of the aqueous phase would remove Pm^{147} along with other rare earths.

Conditions and results of batch contacts made to investigate these routes to the separation of Ce^{144} from Pm^{147} are summarized in Tables 3.18 and 3.19. Both EDTA and DTPA were tested as complexing agents to produce a differential between Ce^{144} and Pm^{147} extraction. The differences in E_a^o for cerium and promethium shown in Tables 3.18 and 3.19 indicate promise for separating these two rare earths in multistage solvent extraction systems. However, due to equipment limitations in the HSW, which did not permit retention of the extraction column raffinate and which made difficult the collection of the partition column organic stream for successive column operations, these approaches were dropped in favor of separating cerium from other rare earths following oxidation to cerium(IV).

TABLE 3.18

DISTRIBUTION OF CERIUM AND PROMETHIUM VERSUS pH AND FLOW RATIO

Aqueous solution of the composition 0.005M $Ce(NO_3)_3$ - 0.006M $Ca(NO_3)_2$ - 0.01M $La(NO_3)_3$ - 0.4M acetate - 0.13M DTPA at pH 4.5 was prepared and adjusted to the desired pH with concentrated HNO_3 or NaOH (dilution in all cases was less than 2.5%). Solutions traced with either Ce^{144} or Pm^{147} and contacted with indicated volume of extractant.

Equilibrium Aqueous pH	Distribution Ratios*			
	Aqueous/Organic = 1.0		Aqueous/Organic = 4.0	
	Ce	Pm	Ce	Pm
2.5	8	1.1	1.7	0.25
3.0	4.2	0.5	1.2	0.21
3.5	2	0.2	0.75	0.15
4.0	0.7	0.08	0.35	0.07
4.5	-	--	0.1	0.025

*Values taken from plots of E_a^o versus equilibrium aqueous pH.

TABLE 3.19

DISTRIBUTION OF CERIUM AND PROMETHIUM VERSUS pH AND COMPLEXING AGENT

Aqueous solution of the composition 1.0M HNO_3 - 0.025 M $Fe(NO_3)_3$ - 0.02M $Pb(NO_3)_2$ - 0.0025M $Ce(NO_3)_3$ - 0.0025M $La(NO_3)_3$ traced with Ce^{144} or Pm^{147} and made 0.4M Acetate and 0.13M in complexing agent and adjusted to pH's in range 2 to 5. Portions of final solutions contacted with one-fourth volumes of extractant.

Equilibrium Aqueous pH	Distribution Ratios[a]			
	DTPA		EDTA	
	Ce	Pm	Ce	Pm
2.5	18	3	--	--
3.0	9	0.8	45 [b]	5 [b]
3.5	3.5	0.25	37	4
4.0	1.2	0.08	15	2
4.5	0.25	0.03	--	--

(a) Values taken from a plot of E_a^o versus equilibrium aqueous pH

(b) Values at pH 3.25. Precipitation of EDTA occurred at lower pH's.

Separation of Cerium as Cerium(IV) - Oxidation of Cerium(III) to Cerium(IV) - Cerium(IV) is known to be readily extracted into D2EHPA solutions from strongly acid solutions while the rare earths in the tervalent oxidation state are not. It was proposed to oxidize cerium in the aqueous strip solution used to remove calcium and the rare earths from the partition column organic stream following strontium removal. The oxidized acidic solution would be contacted with D2EHPA to remove cerium(IV). Promethium would be recovered from the aqueous phase and purified by subsequent solvent extraction procedures.

The major problem in this approach was to oxidize cerium and keep it oxidized during contact with the organic phase. Oak Ridge National Laboratory personnel had studied the use of permanganate for this purpose.[5] They found it necessary to keep adding some permanganate during the contact to assure an excess of oxidant.

Limited testing of oxidants other than permanganate was done. Those tried were $(NH_4)_2S_2O_8$, $NaBrO_3$, and PbO_2. The most promising of these was $(NH_4)_2S_2O_8$. However, this reagent is an effective oxidant for cerium only at or near the boiling point. There are sufficient oxidizable components in the D2EHPA extractant that appreciable reduction of cerium occurs during contact of aqueous and extractant phases. Consequently, although complete oxidation of cerium could be obtained with persulfate ion at 90-100 C, some cerium was reduced and not extracted in subsequent contact of the cerium(IV) aqueous solution with extractant.

Most attention was given to oxidizing cerium with permanganate to adapt the ORNL procedure to the HSW flowsheet. A serious disadvantage of permanganate for this purpose is that solid MnO_2, formed as permanganate is reduced, interferes with phase separation. Citric acid, however, may be added to the aqueous phase after oxidation and extraction is complete to dissolve the manganese dioxide.

- Extraction of Cerium(IV) - A series of experiments was performed to study the effects on the oxidation and extraction of cerium of initial permanganate concentration, oxidation time, time of contact with organic phase, time of contact after adding citrate to the aqueous phase, and the organic to aqueous volume ratio. The aqueous phase simulated the nitric acid strip solution anticipated as a result of stripping the partition column organic phase. Lanthanum was used as a stand-in for promethium. Cerium distribution was followed by tracing the solution with Ce^{144}. Table 3.20 shows cerium distribution as a function of the above variables.

Several of the sets of conditions produced E_a^o's high enough to indicate that removal of greater than 99% of the cerium from the strip solution with a single batch contact was possible (E_a^o greater than 100 at aqueous/organic volume ratio of 1). The effect of prolonged contact time after adding citric acid in reducing E_a^o is clearly evident.

TABLE 3.20

OXIDATION AND EXTRACTION OF CERIUM

Initial Aqueous: For all designated[1]: 1.0M HNO_3, 0.012M $Ca(NO_3)_2$, 0.010M $La(NO_3)_3$, 0.010M $Ce(NO_3)_3$; For all others: 1.0M HNO_3, 0.012M $Ca(NO_3)_2$, 0.010M $La(NO_3)_3$, 0.033M $Ce(NO_3)_3$

Organic/Aqueous Volume Ratio	$KMnO_4$ M	Time, Minutes: Oxidation	Organic-Aqueous Contact	After Citric Acid Addition	Ce E_a^o
1:1	0.050	0	30	10	110
1:1	0.050	5	30	20	440
1:1	0.050	15	30	20	140
1:1	0.050	30	30	20	150
1:1	0.050	60	30	20	100
1:1	0.050	20	30	10	84
1:1	0.050	20	30	20	130
1:1	0.050	20	30	40	260
1:1	0.050	20	30	80	15
1:1	0.025	0	30	10	65 (180)[a]
1:1	0.025	5	30	10	88
1:1	0.025	15	30	10	58
1:1	0.025	15	30	10	610
1:1	0.025	30	30	10	140
1:1	0.025	60	30	10	21
1:1	0.025	0	5	10	19
1:1	0.025	0	30	20	360
1:1	0.025	0	30	60	42
1:1	0.025	0	30	120	10
1:4	0.025	0	5	10	7
1:4	0.025	0	30	10	13 (17)[a]
1:4	0.025	15	15	10	6
1:1	0.025	15	15	10	31
1:1	0.025	15	15	60	57
1:1	0.025	20	30	30	64
1:1	0.050 (1)	0	30	10	(b)
1:1	0.050 (1)	0	30	20	560
1:1	0.050 (1)	0	30	30	410
1:1	0.050 (1)	0	30	60	590
1:1	0.050 (1)	0	10	30	580
1:1	0.050 (1)	0	20	30	(b)
1:1	0.025 (1)	0	30	10	260
1:1	0.025 (1)	0	30	20	140
1:1	0.025 (1)	0	30	30	240
1:1	0.025 (1)	0	30	60	27
1:1	0.025 (1)	0	10	30	160
1:1	0.025 (1)	0	20	30	150
1:1	0.025	0	30	10	8[c]
1:1	0.025	5	30	10	9[c]
1:1	0.025	30	30	10	32[c]
1:1	0.025	0	30	30	48[c]
1:1	0.025	0	30	60	17[c]

(a) Two successive contacts; numbers in parentheses represent combined E_a^o's for both extractions.

(b) Cerium not detected in aqueous phase, $E_a^o > 600$.

(c) TBP not present in extractant

Equipment limitations in the HSW precluded preoxidation in the absence of any organic phase. Successive oxidation and extraction were possible. The one simulated successive oxidation and extraction experiment done at an organic to aqueous volume ratio of 1:1 indicated that satisfactorily high cerium extraction could be achieved by such successive treatment.

- Effect of Hot Semiworks Solvent on Extraction of Cerium(IV) - Nitric acid washed D2EHPA-TBP-SSB solvent from a HSW strontium recovery run was available for testing. Batch contact experiments of cerium(IV) extraction similar to those listed in Table 3.20 were performed using this solvent. Physical behavior of organic and aqueous phase was essentially the same as when using fresh solvent. In tests where the initial aqueous permanganate concentration was 0.05M or greater, cerium distribution compared favorably with that when fresh solvent was used. However, at 0.025M initial permanganate concentration, the permanganate was consumed about 50% more rapdily than with fresh solvent. Typical cerium(IV) E_a^o's with 0.05M permanganate were around 100 as compared to 200 when using fresh solvent.

- Effect of Citrate in the Aqueous Phase on Cerium(IV) Extraction - It was anticipated that the aqueous phase from which cerium was to be extracted would contain some citrate due to entrainment of aqueous in the organic phase during partitioning of strontium in the partition column. Estimates by HSW personnel placed the citrate concentration in the cerium strip solution as high as 0.05M. In a typical batch contact experiment in which the aqueous phase was initially 0.1M $KMnO_4$, 0.05M citric acid, 0.012M $Ca(NO_3)_2$, 0.007M $Ce(NO_3)_3$ and 0.024M other rare earths, the cerium distribution ratio was 10.7 as compared to >200 in the absence of citrate. The presence of citrate in the cerium strip solution has a deleterious effect on oxidation and extraction of cerium and must be counteracted by an increased permanganate concentration.

- Stripping of Cerium(IV) - Cerium which has been extracted as cerium(IV) into D2EHPA solutions can be removed most readily by contact with an aqueous phase containing a reductant which will reduce the cerium to

the trivalent state. A convenient reductant to use is H_2O_2. Table 3.21 shows distribution coefficients obtained on contacting extractant containing cerium(IV) with equal volumes of HNO_3-H_2O_2 solutions. The organic phases used were those obtained in the batch extraction experiments shown in Table 3.20. Oxalic acid was included in some of the strip solutions to see if it would aid in removing cerium from the organic.

TABLE 3.21

REMOVAL OF CERIUM(IV) FROM D2EHPA-TBP-SSB SOLVENT

HNO_3, M	H_2O_2, %	$H_2C_2O_4$, M	Ce E_a^o
1	2	0.01	0.018
1	1	0.01	0.033
5	2	0.10	0.025
5	1	0.10	0.016
2	2	0.10	0.032
2	1	0.10	0.023
1	1	0.10	0.102
5	2	0.0	0.022
5	1	0.0	0.056
2	2	0.0	0.022
2	2	0.0	0.014
1	1	0.0	0.039
4	2	0.0	0.018
4	1	0.0	0.048
1	2	0.0	0.008
5	2	0.0	0.006
2	2	0.0	0.026
1	1	0.0	0.017
4	2	0.0	0.004

The relatively low E_a^o's obtained in most of these experiments indicate very effective removal of cerium in a countercurrent strip column and adequate removal in one, or at most two, batch contacts at a 1:1 organic to aqueous volume ratio. Oxalic acid did not lower the cerium E_a^o's.

Isolation and Purification of Pm^{147} - The aqueous phase following oxidation and extraction of cerium(IV) is about 1M in nitric acid and contains non-cerium rare earths (particularly promethium), $Ca(NO_3)_2$, $Mn(NO_3)_2$, and some citric acid. In the flowsheet proposed for HSW use, this solution

was to be adjusted to pH 1-2, and the rare earths were to be extracted away from as much of the calcium and manganese as possible. Batch experiments were performed to determine conditions for this separation.

Since the exact composition of the aqueous phase which would result from the cerium extraction step was not known, two different synthetic solutions were prepared representing the expected concentration range. The composition of these solutions is shown in Table 3.22. Portions of these solutions were made 0.1 to 0.5M in citric acid and adjusted to pH's in the range 1 to 3. They were spiked with Ca^{45} and Pm^{147} to permit determination of distribution coefficients for these elements and contacted with an equal volume of unwashed extractant. Manganese(II) distribution coefficients were determined in separate contacts. Table 3.22 shows promethium, calcium, and manganese distribution coefficients obtained. From the standpoint of Hot Semiworks Operation, it was desirable that:

1. At least 90% of the promethium be recovered in a single batch contact.
2. Separation of promethium from calcium and manganese be as high as possible.
3. Citrate concentration be as high as possible to allow for possible error in addition of NaOH solution for pH adjustment.

Examination of the data in Table 3.22 indicates that, to obtain best overall performance in terms of these criteria, promethium and other rare earths should be extracted at pH 1.5 to 2.0 from a feed solution 0.25 to 0.50M in citric acid. Below this pH range, promethium E_a^o's are too low to attain 90% recovery in a single batch contact at an aqueous/organic volume ratio of 1.0. Above this pH range and at citrate concentration above 0.25M, the promethium E_a^o's decrease because of complexing. At any given pH, promethium E_a^o's decrease with increasing citrate concentration. At pH 2, 90% of the promethium could be extracted in a single equal-volume contact at 0.5M citrate. If greater promethium recovery is desired, one must go to a lower citrate concentration. Buffering capacity appears adequate at 0.25 to 0.50M citrate.

TABLE 3.22

SEPARATION OF NON-CERIUM RARE EARTHS FROM MANGANESE AND CALCIUM

Test Solution Used*	Initial Aqueous Citric Acid M	Initial Aqueous $NaNO_3$ M	pH Initial	pH Equilibrium	E_a^o Mn	E_a^o Ca	E_a^o Pm	% Pm Not Extracted
Mn-1	0.5	0.72	1.1	1.1	0.027	0.120	4.94	18.0
Mn-1	0.5	0.92	2.0	2.0	0.188	2.05	17.1	5.9
Mn-1	0.5	1.31	3.1	3.1	3.82	12.5	4.24	21.1
Mn-2	0.5	0.72	1.0	1.05	0.026	0.141	6.36	15.2
Mn-2	0.5	0.92	2.1	2.05	1.07	4.12	26.6	3.79
Mn-2	0.5	1.18	3.1	3.0	---	39.3	24.7	4.30
Mn-1	0.25	0.66	1.05	1.05	0.009	0.061	4.27	18.7
Mn-1	0.25	0.82	2.0	1.80	0.167	1.08	34.1	3.1
Mn-1	0.25	1.07	3.0	2.80	1.24	12.5	15.8	5.6
Mn-2	0.25	0.66	0.90	1.0	---	0.091	4.37	18.7
Mn-2	0.25	0.84	2.0	1.80	0.429	2.30	116.0	0.89
Mn-2	0.25	1.02	3.05	2.90	7.50	42.5	75.7	1.45
Mn-1	0.10	0.63	1.05	1.0	0.006	0.055	3.19	26.7
Mn-1	0.10	0.81	2.05	1.6	0.063	0.456	29.3	3.9
Mn-1	0.10	0.89	3.0	2.4	0.667	4.38	68.0	1.6
Mn-2	0.10	0.65	0.95	1.02	0.012	0.103	6.58	13.9
Mn-2	0.10	0.77	2.05	1.62	0.167	1.24	148.0	0.68
Mn-2	0.10	0.86	2.95	2.32	1.50	9.05	415.0	0.26

* Test Solution Composition:

Mn-1	Mn-2
0.042M $La(NO_3)_3$	0.0205M $La(NO_3)_3$
0.015M $Ca(NO_3)_2$	0.0075M $Ca(NO_3)_2$
0.05M $Mn(NO_3)_2$	0.05M $Mn(NO_3)_2$
0.05M Citric Acid	0.05M Citric Acid
1.00M HNO_3	1.00M HNO_3

Through citric acid addition and adjustment to pH these solutions were diluted such that at contact manganese, calcium, and lanthanum concentrations were 0.72 of those shown.

Solvent Washing Studies

Limited studies were made of wash procedures for removing Ce^{144} and $ZrNb^{95}$ from HSW extractant. Solvent from the first cycle of HSW Run Sr-5 was used in these studies. This solvent originally contained about 200 curies/liter of Ce^{144} and received about 300 watt-hr/liter of radiation before plant washing operations were initiated. The first attempt at washing in the HSW involved successive contacts with a 4.4M NaOH - 0.1M EDTA solution and a 4.4M HNO_3 solution in the HSW A and B columns (cf. Section 5,p 5.31). The column operation was difficult to control and resulted in a cerium DF of only 10.

Portions of the solvent, after this treatment, were used in laboratory studies; this solvent is designated HSW Solvent 1. Subsequently, this solvent was successively batch-washed in the HSW with 1.0M NaOH - 0.1M EDTA and 1.0M HNO_3-0.5M oxalic acid solutions. Portions of the solvent after these batch washes were also used in laboratory studies; this solvent is designated HSW Solvent 2.

Laboratory washing studies with these solvents (Tables 3.23 and 3.24) were not sufficiently extensive to define an optimum wash composition for removing activity from D2EHPA solutions. These meager data did indicate, however, that 1M oxalic acid and alkaline solutions containing either EDTA or DTPA were very effective in removing Ce^{144} and $ZrNb^{95}$ activity. Since these results were obtained, chemical flowsheets for the D2EHPA extraction of Sr^{90} and fission product rare earths from Purex Plant formaldehyde-treated waste have been investigated. These latter studies have substantiated the utility of oxalic acid wash solutions in removing various inert and radioactive elements from used solvent. The wash procedure currently favored consists of one or more batch contacts with an equal volume of 0.25 to 0.5M oxalic acid at 60 C.

TABLE 3.23

RELATIVE EFFECTIVENESS OF SOLVENT WASH SOLUTIONS

Initial Organic: HSW Solvent 1: 19,300 μc/ml Ce^{144}, >41 μc/ml $ZrNb^{95}$

10 minute contact (25 C) at 1:1 organic to aqueous phase ratio

Wash Solution Composition	Decontamination Factors		
	Gross γ	Ce^{144}	$ZrNb^{95}$
1.0M Oxalic Acid	360	1930	21
1.0M Acetate - 0.2M DTPA, pH 7	160	840	10
1.0M Acetate - 0.2M EDTA, pH 7	360	330	46
1.0M Acetate - 0.2M DTPA, pH 12	220	330	41
6.0M HNO_3	59	79	5
15.0M HNO_3	47	72	6
1.0M H_2O_2 - 1.0M HNO_3	2	23	4
1.0M Citric Acid	10	14	6
1.0M H_3PO_4	4	4	--
0.5M NH_4F	42	---	--
1.0M Tartaric Acid	2	--	--

TABLE 3.24

SOLVENT WASH STUDIES

Initial Organic: HSW Solvent 2: 700 μc/ml Ce^{144}, 0.264 μc/ml $ZrNb^{95}$

10 minute contact (25 C) at 1:1 organic to aqueous phase ratio

Wash Solution Composition	Decontamination Factors		
	Gross γ	Ce^{144}	$ZrNb^{95}$
2M NaOH - 0.50M Tartaric Acid	130	15	75
3M NaOH - 0.50M Tartaric Acid	200	23	--
2M NaOH 0.75M Tartaric Acid	140	17	200
3M NaOH 0.75M Tartaric Acid	180	23	--
2M HNO_3	56	7.8	200
3M HNO_3	82	10	--
4M HNO_3	140	19	5
5M HNO_3	230	33	4
0.5M EDTA, pH 7.1	1200	230	--
0.5M EDTA, pH 12	600	70	--
0.5M EDTA - 0.2M NaOH	900	140	--
0.5M EDTA - 1.4M NaOH	25	3.9	--
0.5M DTPA, pH 4.2	3.2	11	--
0.5M DTPA, pH 7.0	-	230	--
0.5M DTPA, pH 12	1100	230	--
0.5M DTPA - 0.2M NaOH	1500	--	--

ION EXCHANGE PURIFICATION OF STRONTIUM PRODUCT

The feasibility of using a cation exchange resin bed for final purification of HSW solvent extraction Sr^{90} product from Ce^{144} was demonstrated by Bray.[6] Additional ion exchange experiments performed as part of the present investigation are discussed in this section.

EXPERIMENTAL

Materials

The resin used in all experiments was 40 to 60 mesh Biorad Dowex* 50W-X12. Unless otherwise noted, the resin was in the sodium form.

Equipment and Procedures

Batch Contacts - Batch contacts were made by placing a sample of resin in a polythene bottle, adding a solution of the desired composition and

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*Trademark of Dow Chemical Company.

shaking the combination for 48 hours. The ratio of resin weight to solution volume varied depending upon the amount of transfer to the resin phase expected to occur. The liquid phase was analyzed before and after the contact, and the amount of transfer to the resin phase was determined by difference. The distribution ratio, D, of component M was calculated as D = grams M per gram dry resin/grams M per ml solution. Dry resin refers to resin dried to constant weight at 60 C in a vacuum oven. Air-dried resin was used for the actual determinations, with a correction factor applied to convert the D value to the dry resin basis. The correction factor was determined by drying samples of each batch of resin to constant weight in the vacuum oven.

Column Experiments - Glass columns of several different sizes were used. Feed to the columns was metered by constant flow gravity systems. Dimensions of the individual columns are included with the experimental data.

RESULTS

Loading Studies

Batch Contacts - Distribution ratios obtained under conditions representative of loading the resin bed are given in Table 3.25. From these data, equilibrium constants (Ke) were calculated for the reaction:

$$M^{+n} + n\ NaR \rightleftharpoons MR_n + n\ Na^+. \qquad (1)$$

In these calculations the bulk density of the resin was taken to be 0.5 g/ml and the resin capacity was assumed to be 1.9 equivalents/liter. The equilibrium constant for strontium was about two, similar to the value given in Section 2 (p. 2.22) calculated from column loading data. Citrate complexing of strontium was neglected in calculating equilibrium constants.

TABLE 3.25

ION EXCHANGE BATCH CONTACTS - LOADING STUDIES

Aqueous Phase Composition					Equilibrium	Strontium		Cerium
Citric Acid M	$Sr(NO_3)_3$ M	$Ce(NO_3)_3$ M	EDTA M	Na^+ M	pH	D	Ke	D
1.0	0.05	0.0001	0.0	0.39	2.50	94.6	2.22	20.0
1.0	0.05	0.0001	0.0	0.72	3.00	23.6	1.88	0.35
1.0	0.05	0.0001	0.0	1.07	3.42	7.8	1.95	0.40
1.0	0.05	0.0001	0.01	0.75	3.00	28.8	---	0.40
1.0	0.05	0.0001	0.001	0.72	3.00	22.0	---	0.40

A rough index to column capacity may be obtained from the batch contact data. If a symmetrical breakthrough curve is assumed, then the capacity of the column in bed volumes is approximately equal to D multiplied by the density of the dried resin.

The strontium D is inversely proportional to the square of the aqueous phase sodium concentration. With a given partition column product stream as feed and with the requirement that the pH be about 3.0, sodium concentration can be lowered only by diluting the solution. This also lowers the strontium and citrate concentrations. In Table 3.26 distribution ratios obtained from batch contacts are given which show that strontium D's are increased by decreasing solution concentration and that the increase is in agreement with that which would be predicted. The cerium D's increased even more markedly greater than would be predicted from a third power sodium dependency.

TABLE 3.26

ION EXCHANGE BATCH CONTACTS - EFFECT OF SODIUM CONCENTRATION ON LOADING

Aqueous Phase Composition				Equilibrium	D	
Citric Acid, M	$Sr(NO_3)_2$ M	$Ce(NO_3)_3$ M	Sodium M	pH	Strontium	Cerium
1.0	0.05	1×10^{-4}	0.72	3.0	16.3	0.63
0.4	0.02	4×10^{-5}	0.25	3.0	112	14
0.2	0.01	2×10^{-5}	0.11	3.0	383	382

Column Experiments - From the D's shown in the previous section, it can be predicted that at pH 3.0, 50% column breakthrough will occur after about ten bed volumes have been processed, assuming a bulk density of 0.5 g/ml for the resin in the column. In laboratory tests breakthrough occurred somewhat sooner, probably because of kinetic considerations. The D's were obtained from 48-hour batch equilibrations while solution residence time during the column experiments was between 15 and 30 minutes.

The results of column loading experiments at two different flowrates are shown in Table 3.27. In both runs 50% strontium breakthrough occurred at eight column volumes; however, at the slower feed rate the breakthrough was sharper and the column was loaded more efficiently.

TABLE 3.27

ION EXCHANGE COLUMN LOADING STUDIES

Column Dimensions	1 x 62 cm (48 ml volume)	
Feed Composition	0.0625M strontium 0.0075M calcium 5×10^{-5} M cerium 1.0M citrate 0.7M sodium pH = 3.02	
Results		
Feed rate	2.5 ml/min-cm^2	5.0 ml/min-cm^2
Column volumes:		
to 10% breakthrough	6.9	5.4
to 50% breakthrough	8.0	8.0
Column loading		
at 10% breakthrough	37.8 gram Sr/liter	34.5 gram Sr/liter

Washing Studies

A washing step is included between the bed loading and elution steps to achieve increased cerium decontamination by preferentially eluting cerium. Cerium and strontium distribution ratios obtained with candidate washing solutions are shown in Table 3.28.

TABLE 3.28

ION EXCHANGE BATCH CONTACTS - WASHING STUDIES

Aqueous Phase						D	
Acetate M	EDTA M	HEDTA M	Strontium M	Cerium M	Equilibrium pH	Strontium	Cerium
0.2	0.01	0.0	0.05	1×10^{-4}	3.0	259	11.6
0.2	0.01	0.0	0.05	1×10^{-4}	3.93	208	0.15
0.2	0.01	0.0	0.05	1×10^{-4}	4.98	163	< 0.10
0.2	0.0	0.10	0.05	1×10^{-4}	3.18	181	8.11
0.2	0.0	0.10	0.05	1×10^{-4}	4.10	164	0.37
0.2	0.0	0.10	0.05	1×10^{-4}	5.02	125	0.07

It can be seen that either EDTA or HEDTA solutions are good washing solutions at pH 4.0. In order to change the pH of the column from 3.0 to 4.0 a buffering agent, such as acetate, must be included in these washing solutions. An alternate washing agent, and the one used successfully in the first HSW run, is 1.0M citric acid adjusted to pH 2.8-3.0.

Elution Studies

Batch Contacts - The washing step is followed by a water flush, after which the bed is ready for elution. The eluting agents investigated (Table 3.29) were $NaNO_3$, HNO_3, and EDTA.

TABLE 3.29

ION EXCHANGE BATCH CONTACTS - ELUTION STUDIES

Initial Resin Form.*	Aqueous Phase Composition			Strontium D
	$NaNO_3$, M	HNO_3, M	$Sr(NO_3)_2$, M	
H	3.0	0.0	Sr^{85} trace only	6.60
H	3.0	0.0	0.01	6.58
H	3.0	0.0	0.10	6.17
Na	3.0	0.0	0.01	6.00
Na	2.0	0.0	0.01	13.3
Na	4.0	0.0	0.01	3.62
H	4.0	0.0	0.01	3.75
H	0.0	3.0	0.01	7.72
Na	2.75	0.25	0.01	5.16
H	2.75	0.25	0.01	4.55
Na	2.50	0.50	0.01	5.16
H	2.50	0.50	0.01	4.55
Na	2.0	1.0	0.01	5.16
H	2.0	1.0	0.01	4.56

*Resin was pre-equilibrated for 16 hours with the given solution minus $Sr(NO_3)_2$.

Distribution ratios were not obtained for EDTA; however, the literature contains many references to strontium elution with EDTA at higher pH's (greater than pH 6.0). Some general conclusions which can be made from the batch contact distribution ratios are:

(1) The efficiency of $NaNO_3$ as an eluting agent increases with concentration.

(2) Sodium nitrate-HNO_3 solutions are slightly better eluting agents than either $NaNO_3$ or HNO_3 alone, at constant nitrate concentrations.

(3) Strontium concentration can be increased by maximum factors of about 1.5, 3.3, and 5.5 through the ion exchange cycle by eluting with 2.0, 3.0, and 4.0M $NaNO_3$, respectively.

Column Experiments - The results of column elution studies also indicated that $NaNO_3$ and HNO_3 are of equal effectiveness as eluting agents. Five column volumes of simulated 1BP solution (0.05M strontium) was fed to a column 13 cm long (column volume = 5 ml). Three column volumes of 1.0M citric acid at pH 3 were used as a wash, followed by ten column volumes of eluting agent. Three eluting agents, 3M HNO_3, 3M $NaNO_3$, and 4M $NaNO_3$ were tested. Losses occurred during both loading and washing steps, evidently because of the small column dimensions. The losses were 3 to 5% during loading and 27 to 29% during the wash. The strontium recovered in the first three column volumes of the elution was 58.9, 60.2, and 63.4% of the total, for 3M HNO_3, 3M $NaNO_3$, and 4M $NaNO_3$, respectively.

In other experiments longer columns (40 ml column volume) were loaded to 100% breakthrough (43.5 grams strontium/liter), rinsed with water and eluted. In one run (Run 1X-2), 85.2% of the strontium was eluted in 4.8 bed volumes with 3.0M $NaNO_3$ and the strontium concentration in the combined elutant was 0.098M. In the other run (Run 1X-1), 86.3% of the strontium was eluted in 2.73 bed volumes with 0.5M Na_4EDTA and the strontium concentration was 0.179M. The elutriant flowrate was about 1.7 ml/min-cm^2 in both runs.

As described in Section 2, (p. 2.23) the elution of the ion exchange columns followed the form of a first order reaction, where the rate at which strontium was being eluted was proportional to the amount of strontium remaining on the resin. Elution curves for the runs described above, plus the demonstration runs described in the next section, are plotted in Figure 3.11.

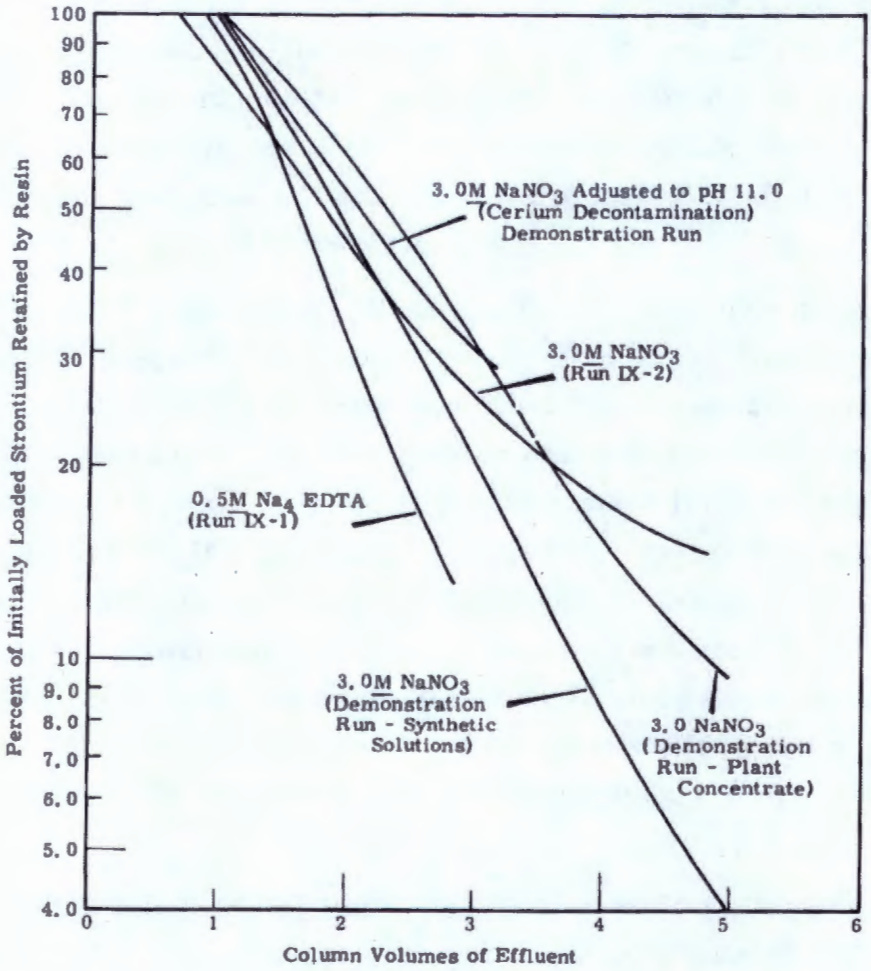

FIGURE 3.11

Elution of Strontium from Dowex 50W Resin

Demonstration Runs

Cerium Decontamination - A demonstration run was made using synthetic 1BP traced with Sr^{85} and Ce^{144}. The general run plan was as follows:

Step I Adjust 1BP to pH 3.0 and load to approximately 50% column capacity.

Step II Wash with two column volumes of 1.0M citric acid at pH 3.0.

Step III Wash with water.

Step IV Elute with 3.0M $NaNO_3$.

A detailed description of the run and the results are given in Table 3.30. The cerium decontamination factor for the run was over 300.

Test with Plant Concentrate - The 1BP from a mixer-settler partition column run with plant crude concentrate (Table 3.13) was loaded on an ion exchange column, washed, and eluted. The results of this test are shown in Table 3.31. Results from an identical run using synthetic solutions are also included. Behavior of the plant solution on the ion exchange column was similar to that of the synthetic solution.

TABLE 3.30

ION EXCHANGE COLUMN STUDIES - CERIUM DECONTAMINATION DEMONSTRATION RUN

Column Dimensions: 1.0 cm diameter, 61 cm long, 47 ml bed volume.

Loading Cycle :	Feed Composition:	0.0625M Strontium 0.0075M Calcium 0.0001M Cerium 1.0M Citrate 0.7M Sodium pH 3.0
	Flowrate:	2.0 ml/min-cm^2
	Throughput:	3.9 bed volumes (resin loading was 21.4 g Sr/liter)
Wash Cycle:	Wash Composition:	1.0M Citric Acid, pH 3.0
	Flowrate:	2.0 ml/min-cm^2
	Throughput:	2.0 bed volumes, followed by 3.7 bed volumes water
Elution Cycle:	Elutriant Composition:	3.0M $NaNO_3$ pH adjusted to 11.0

TABLE 3.30 (contd.)

Effluent Bed Volumes	Strontium, M	% Total Strontium*	Cerium, % of Feed Concentration
0.405	<0.00001	<0.001	0.00062
0.71	0.00076	0.10	0.028
0.83	0.00265	0.21	0.78
0.96	0.0598	3.35	0.25
1.06	0.103	7.84	0.31
1.17	0.116	12.9	0.50
1.38	0.115	23.0	0.16
1.60	0.111	32.5	0.009
1.81	0.099	41.3	0.11
2.06	0.086	50.4	<0.03
2.60	0.064	64.4	<0.03
3.13	0.032	71.2	<0.03

* % of Sr loaded on column.

TABLE 3.31

ION EXCHANGE COLUMN DEMONSTRATION RUNS

Column Dimensions: 1.0 cm diameter 38.2 cm long, 30 ml bed volume.

Feed: 1BP solutions derived from mixer-settler extraction partition column runs.

	1BP from Synthetic Concentrate	1BP from Plant Concentrate
% Sr Loss During Loading	0.025 (4 bed volumes)	0.014 (3 bed volumes)
% Sr loss during wash with 1.0M citric acid at pH 3.0, 2 bed volumes	2.34	0.008
% Sr loss during water flush, 1 bed volume	1.54	0.001
% total Sr recovered by elution with 3.0M $NaNO_3$:		
1 bed volume	3.22	0.81
2 bed volumes	53.5	41.1
3 bed volumes	77.3	70.7
4 bed volumes	88.0	85.5
5 bed volumes	91.9	91.6

PRODUCT PRECIPITATION

STRONTIUM CARBONATE PRECIPITATION

Several strontium compounds, $SrSO_4$, SrC_2O_4, and $SrCO_3$, were considered as final solid forms for HSW Sr^{90} product. Factors such as ease of formation, filterability, ease of drying, and stability to radiation led to the choice of $SrCO_3$ as the product form.

Precipitation of $SrCO_3$ from three different types of solution containing strontium was studied. These solutions were (a) HNO_3 solutions such as might be obtained in two cycles of solvent extraction, (b) $NaNO_3$ solutions such as might be obtained after tail-end cation exchange resin treatment, and (c) citric acid solution such as might be obtained in a single cycle of solvent extraction.

Finely divided, difficultly filterable solid was formed when $SrCO_3$ was precipitated from either HNO_3 or $NaNO_3$ solution by addition of Na_2CO_3 solution. No precipitation condition leading to the formation of readily filterable precipitates was found.

Precipitates with good filtration characteristics were produced from either HNO_3 or $NaNO_3$ solutions by using NH_4OH and CO_2 as precipitating agents. Similarly, readily filterable precipitates were formed when either $NaHCO_3$ or $KHCO_3$ was used as the precipitating agent. The particle size of the solids formed with the latter precipitants was greater than 40-50 mesh; the solids were retained readily without filter aid on Type J "Regimesh"* filter screen.

The most satisfactory procedure found for precipitation of $SrCO_3$ from HNO_3 or $NaNO_3$ solution involves adding either $NaHCO_3$ or $KHCO_3$ to the neutral, hot (80 C) solution until the HCO_3^-/Sr^{++} ratio is two or

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*Trademark of Aircraft Porous Medium Corporation.

greater. The slurry is then digested to coagulate the solid. Ammonium hydroxide, $NaHCO_3$, or $KHCO_3$ can be used to neutralize acidic solutions without adverse effect on the character of the solid. Sodium ion in concentrations up to four molar does not interfere with formation of readily filtered precipitates. The interval between addition of $NaHCO_3$ or $KHCO_3$ and digestion can be at least a week without detrimental effect on precipitate filtration.

Precipitation of $SrCO_3$ by addition of $KHCO_3$ to a 0.2M $Sr(NO_3)_2$ - 0.02M $Ca(NO_3)_2$ - 4M $NaNO_3$ solution was employed to prepare solid for cold testing of the HAPO-II $SrCO_3$ filter cask insert. Potassium bicarbonate was added to 10% excess over the stoichiometric requirements for strontium and calcium. The slurry was digested 2 hours at 80 C and cooled to 25-30 C before filtering. No filter aid was used during filtering of the slurry on the cask insert. Overall recovery of the strontium as filter cake was 99.6%. These latter studies are described in more detail in Reference 16.

Quantitative precipitation of $SrCO_3$ from citric acid solutions containing strontium was difficult to obtain by the bicarbonate procedure. In one test it was necessary to increase the final pH from the usual near 7 to about 8.3 to attain quantitative precipitation. Finely divided or gelatinous precipitates which are not retained on 40 to 50 micron filters or which blind the filters are obtained from solutions which contain citrate. Acetate and tartrate are similarly detrimental to $SrCO_3$ precipitation.

CERIUM DECONTAMINATION BY PRECIPITATION

A brief study was made to determine if additional decontamination of the strontium in HSW ion exchange column or solvent extraction product solutions, particularly from cerium, could be obtained by precipitation techniques. The two obvious courses were considered, namely, (a) precipitate $SrCO_3$ while leaving cerium in solution and (b) precipitate or scavenge cerium from the solution before the final $SrCO_3$ precipitation.

In studies of the first approach, complexing agents agents were added to a synthetic HSW product solution [0.17M $Sr(NO_3)_2$ - 0.017M $Ca(NO_3)_2$ - 0.05M $NaNO_3$ - 0.02M HNO_3 - 9×10^{-6} M $Ce(NO_3)_3$ before $SrCO_3$ precipitation in an attempt to prevent coprecipitation of cerium. Citric acid and EDTA, when added to the product solution in concentrations ranging from 5×10^{-5} to 0.1M, produced no increase in cerium decontamination when $SrCO_3$ was precipitated. Addition of DTPA in concentrations of 0.01 and 0.05M resulted in cerium decontamination factors of 1.8 and 4, respectively. Higher DTPA concentrations did not increase the cerium decontamination.

In the second approach, an attempt was made to take advantage of the much lower solubility of $Ce(OH)_3$ as compared to $Sr(OH)_2$. Inert cerium was added to portions of synthetic HSW product solution to produce total cerium concentrations in the range 1×10^{-5} - 2×10^{-3} M. The pH of these solutions was adjusted to 11.0 - 11.2 at room temperature to precipitate $Ce(OH)_3$. Cerium decontamination factors as high as 65 were obtained with strontium losses no more than 1 - 2%. In similar experiments, $Fe(NO_3)_3$ was added instead of inert cerium to see if cerium would coprecipitate on $Fe(OH)_3$. The cerium decontamination factor was about 30 when the initial Fe^{+3} concentration was 1×10^{-4} M; the strontium loss was 1 - 2%.

SECTION 4. COLD SEMIWORKS STUDIES

G. L. Richardson

INTRODUCTION AND SUMMARY

Concurrent flowsheet development and solvent extraction column design for the Hot Semiworks Strontium Recovery Program were carried out in the 321 Building Cold Semiworks using the pulse-column-equipped Demonstration Unit. The Cold Semiworks studies were instrumental in developing the flowsheet recommended for the Hot Semiworks (see Figure 4.1). The following flowsheet innovations were first tested in the Cold Semiworks:

1. A sodium acetate-acetic acid buffer system was used for pH control.
2. EDTA was used as a complexing agent for all multivalent cations but calcium, barium, and strontium. HEDTA, a weaker complexing agent, was also tested first in the Cold Semiworks.
3. A buffered citric acid scrub was used to remove sodium from the extraction column product.
4. Citric acid was used to selectively strip strontium from the solvent, leaving most of the calcium and rare earths behind. Tartaric acid was also successfully used for this purpose.

In addition, scouting studies were made on flowsheet concepts for coextracting cerium and strontium and for separating cerium from other rare earths by oxidation to cerium(IV) and extraction from acidic solutions. These runs demonstrated that at least 70% of the cerium(III) could be extracted from an EDTA-complexed feed by operating at pH's below 3.8. The attempts to extract cerium(IV) were unsuccessful, probably because of the presence of reducing impurities (citrate, acetate) in the system.

The following pulse column specifications, using Purex-type nozzle plate cartridges, were developed:

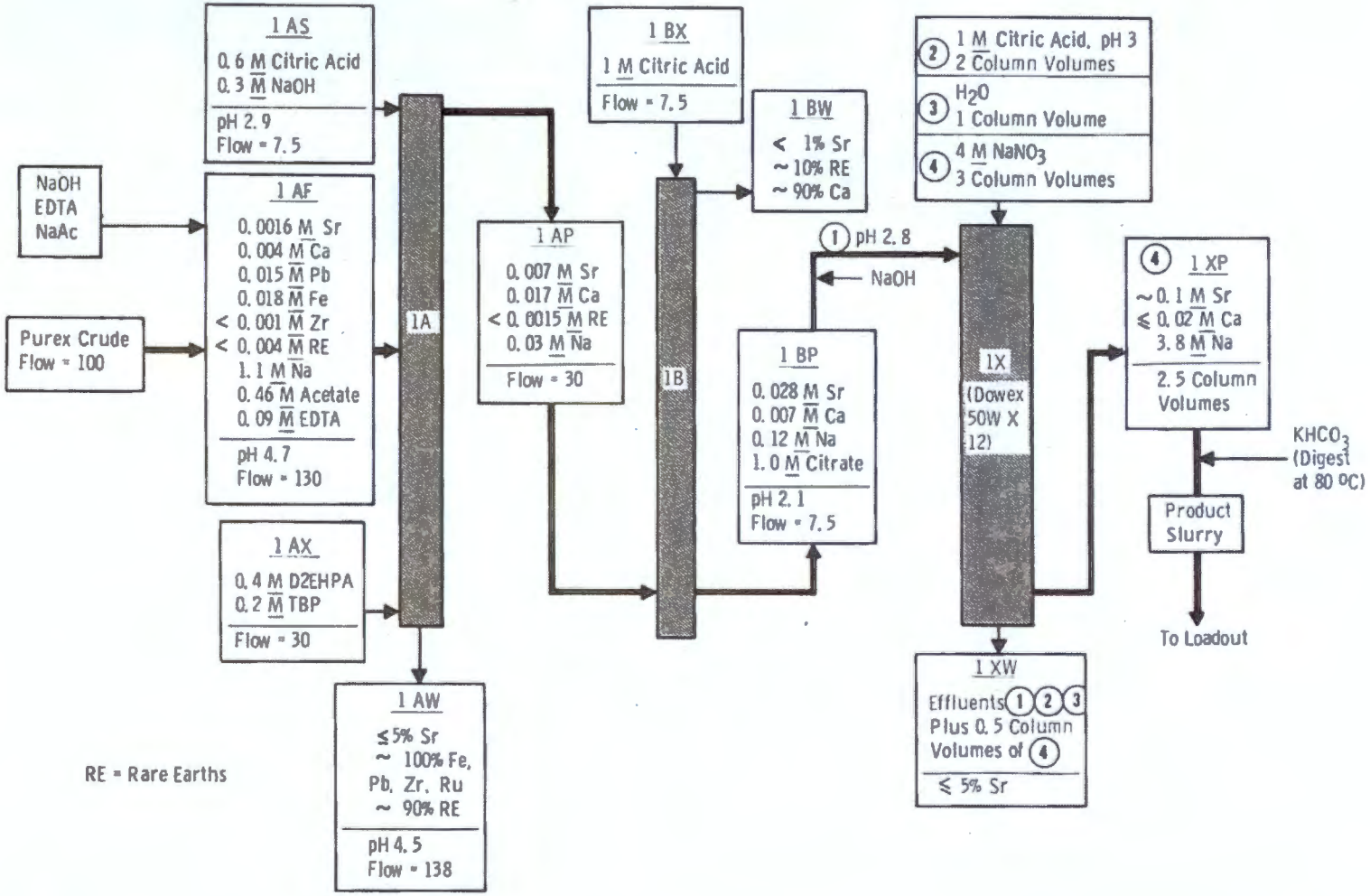

FIGURE 4.1

Proposed Hot Semiworks Flowsheet

	Column		
	1A Extraction	1A Scrub*	1B
Cartridge Height, ft	10	15	16
Diameter, in.	4	4	4
Plate Free Area, %	23	10	10
Hole Diameter, in.	0.188	0.125	0.125
Plate Spacing, in.	4	4	4
Nozzle Depth, in.	≥ 0.04	≥ 0.04	≥ 0.04
Nozzles Point	Down	Down	Up
Pulse Amplitude, in.	0.8	0.8	1.0
Interface Position	Bottom	--	Top

*The scrub section also contained 19% free area louver plates at 3-foot intervals.

Stable superficial volume velocities of the pilot plant columns, using cartridges, flowsheets, and operating conditions similar to those specified for the Hot Semiworks, equaled or exceeded 1080, 350, and 790 gph/ft^2 for the 1A extraction, 1A scrub, and 1B columns, respectively. Optimum operating frequencies ranged from 40 to 80 in the 1A column and 60 to 70 in the 1B column. Flooding in the 1A column seemed to be enhanced by the presence of solids in the feed (probably colloidal ferric hydroxide).

The Cold Semiworks data are reported here more or less in chronological order with brief explanations of why the runs were made and what the results signified. The work was begun in August, 1960, and completed in February, 1961.

EQUIPMENT AND OPERATING PROCEDURE

The Cold Semiworks Demonstration Unit, together with its auxiliaries, was used for the development work. Essentially, this unit consisted of two 3-inch diameter glass pulse columns containing 18 and 10 feet of perforated-plate cartridges, respectively. The taller column was used as the extraction or 1A column and contained a center feed point located variously 6, 9, or 12 feet above the bottom of the cartridge to give various ratios of extraction-to-scrub section heights. The shorter column (1B) was used as the stripping or partition column. It could be operated separately or in cascade with the

1A column. Both columns had enlarged disengagement sections at top and bottom made of standard 4-inch glass tees or crosses. A summary of the plate cartridge designs used in each run is presented in Table 4.1.*

Most of the early steady-state runs lasted 3 or 4 hours, sufficient to provide at least three throughputs of the continuous phase. Periodic sampling indicated that this was sufficient time to reach steady state; however, several runs near the end of the campaign were operated 8 to 24 hours to confirm the reliability of the flowsheets over extended operating periods.

FEED MATERIAL

The composition of the crude feed to be delivered to the Hot Semiworks was still in doubt until the Cold Semiworks program was nearly completed; consequently, only the last few runs used a feed solution comparable to the Hot Semiworks feed. The actual feed and scrub compositions for the development studies are tabulated in Table 4.2.* Of the major constituents in the feed the strontium concentration varied from 0.001 to 0.02M, the calcium from 0.007 to 0.12M, the iron from 0 to 0.1M, the lead from 0 to 0.3M, and the sodium, after feed adjustment, from 0.5 to 2M. Many of the runs contained small quantities (ca 0.001 to 0.005M) of zirconium, barium, cerium, and mixed rare earths. No radioactive tracers were used--a factor that seriously limited analytical accuracy in detecting concentrations below 10^{-4}M. Sodium acetate was added to most of the runs at concentrations from 0.4 to 0.9M for hydrogen-ion buffering. Tartrate, citrate, EDTA, and HEDTA were added as metal-complexing ligands.

The solvent was nominally 0.4M D2EHPA 0.2M TBP in Shell E-2342 diluent. Actual analyses showed only 0.36 to 0.39M D2EHPA present, indicating the stock D2EHPA contained only 90 to 95% pure D2EHPA.

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*See Appendix for Tables

RESULTS

Results are presented in Tables 4.3, 4.4, and 4.5 in the Appendix. The following discussion is a chronological explanation of these results and includes only the more significant observations.

1A COLUMN

Runs 1 Through 16, 22, and 23

The first objective in the program was to determine the behavior of D2EHPA extractant in a pulse column system. These first runs used Cartridges 1 and 2 and Feeds 1, 2, 3, 7, and 8 (all feeds adjusted to a pH of 2 to 2.5) to demonstrate the flowsheet concept in which the extractable impurities are extracted away from strontium. The results of these runs indicated that volume velocities of 800 to 1000 gph/ft^2 were readily obtainable with either top or bottom interface in the column. A foamy "third phase" was observed at the interface in several of the earlier runs with top interface. The third phase disappeared, apparently by dissolving, on standing overnight. It was believed to have been caused by overloading the solvent with metal ions, although TBP was added to prevent such an occurrence; this did not happen in later runs.

The plates became organic-wet in several of the runs with top interface. When this occurred with nozzle plates pointed down, the organic dispersion became frothy and tended to channel up the stainless steel plate support rod. This problem was eliminated by reversing the cartridge so that the nozzles pointed up, in the direction of organic flow. The nozzle orientation had little effect with bottom interface.

Review of extraction data obtained during these runs showed, as expected, that essentially no strontium extracted at the feed pH of 2.5. However, only 30 to 40% of the calcium, less than 20% of the lead and only 70 to 80% of the iron were extracted away from strontium. Essentially no iron was extracted in two runs with 0.2M tartrate present in the feed, and only 10% of the iron was extracted with a citrate-complexed feed at pH 1.9.

Greater than 95% of the zirconium extracted with no complexing agent present, but only about 8% or less extracted with the citrate feed. These results indicated little chance for success in extracting impurities away from strontium; accordingly, the remaining runs were designed to extract strontium away from the impurities.

Runs 17, 18, and 19

These three runs used Feed 4 and demonstrated the effects of operating at a higher feed pH (3.5 to 4.3) and the effects of using the sodium form of D2EHPA as the solvent. Under these conditions, strontium, calcium, and lead extracted almost completely, together with about 70% of the iron. The use of the sodium form of D2EHPA gave waste stream pH's as high as 6.2 as a result of sodium-hydrogen ion exchange. Although the feed was stable, there was some indication that ferric hydroxide was precipitating in the column, as might be expected at the high waste pH with only acetate ion present as a stabilizing ligand. Intermediate samples taken to obtain a pH profile of the column showed that the pH at the feed point in these and most of the other runs was approximately the same as the feed pH (± 10%). The use of either acid or sodium D2EHPA had a significant effect on the pH only in the bottom 3 to 6 feet of the column, the effect decreasing with increasing aqueous to solvent flow ratio.

Runs 20 and 21

These two runs, using Feeds 5 and 6, demonstrated the effect of HEDTA as a complexing agent for iron, lead, and zirconium. In its absence, 70 to 100% of these elements extracted; but when present at 0.066M in excess of stoichiometric requirements, less than 10% of the iron, lead, and zirconium extracted. The solvent, which had been used in earlier runs in the absence of iron complexants, actually contained less iron when leaving than it had on entering (0.21 g/liter reduced to 0.06 g/liter). HEDTA was also effective in dissolving ferric hydroxide formed inadvertently in the feed makeup. The HEDTA had no effect on strontium and calcium extraction.

Runs 24, 25, and 26

These runs were made with simplified feeds containing only strontium, calcium, and sodium acetate (Feed 9) in an attempt to measure HTU's (height of a transfer unit, overall raffinate-film basis) for strontium extraction. Unfortunately, the solvent evidently was loaded excessively, and strontium reflux occurred in the extraction section. Based on intermediate samples, however, the HTU's were estimated to be 1.7 to 1.9 feet, about two-fold higher than obtained for uranium in the Purex-TBP system.

Runs 27 Through 33

These runs, using Feeds 10, 11, and 12, explored the effects of an increased excess of HEDTA on extraction performance, continued the study of hydrogen versus sodium form of D2EHPA, and explored different scrub solutions to improve scrub stability. Results were:

1. An HEDTA concentration as high as 0.094M in excess of that required to complex the iron, lead, cerium, and zirconium had no effect on strontium extraction.
2. Less than 1% of the iron, 3% of the lead and cerium, and 6% of the zirconium were extracted with excess HEDTA present. Addition of HEDTA to the scrub had no discernible effect on decontamination or losses.
3. No significant differences in performance were obtained with the D2EHPA in either the sodium or hydrogen form. The solvent in the lower half of the column, however, had a very milky appearance when introduced in the sodium form. The reason for this was not understood, but was probably connected with sodium transfer from the solvent.
4. Changing the scrub stream from 0.2M acetate to 1M sodium nitrate, both at pH 4, improved the scrub section stability. The internal pH of the scrub section was decreased from 5.4 to 3.9 by the change. Whether the improved stability was caused by increased ionic strength or decreased pH was not determined, but runs much later

in the series used 0.5M $NaNO_3$ without ill effect. It should be noted that at this point the function of the scrub section was primarily to remove feed entrainment from the solvent. Buffering capacity was insufficient to have much effect on mass transfer.

Runs 34 Through 38

A major change in the flowsheet was made at this time. Heretofore, it was assumed that the Purex crude feed to the Hot Semiworks could be concentrated to at least 0.02M before solvent extraction; however, a study of time cycles and available equipment showed that concentration was not feasible. Consequently, these runs and the runs following (with a few exceptions) were made with 0.002M strontium feeds, the approximate concentration of Purex crude. These first runs with the new feed composition (Feed 13) demonstrated excellent strontium recovery (< 5% loss) with the flow ratio adjusted to give the same solvent loading as in the previous runs (ca 0.05M Sr + Ca). Studies of flooding (using Cartridge 2) indicated that stable volume velocities of 1000 and 1300 could be obtained with bottom and top interface positions, respectively--about the same as obtained with the concentrated flowsheet. The net result of the flowsheet change, then, was that the strontium capacity of the 1A column was reduced about threefold. To compensate partially for this reduction, the specified diameter of the Hot Semiworks 1A column was increased from 3 to 4 inches.

Also during these runs, the decision was made to use a bottom interface position. Based on Purex performance, decontamination was expected to be improved by putting the interface at the waste end of the column.

Runs 39 Through 42

These runs, using Feeds 14 and 15, explored the effect of replacing HEDTA with an equivalent concentration of EDTA, a more effective cerium complexing agent. The results with both complexing agents were virtually

identical: less than 2% of the iron, lead, cerium, and zirconium extracted with either 0.12M excess EDTA or 0.11M excess HEDTA. The strontium loss may have been slightly higher with the EDTA feed (5 to 12% versus < 5%). These runs also demonstrated that reducing the sodium nitrate concentration in the 1AS from 1M to 0.5M had no effect on performance.

Runs 42 Through 46

These runs were made with a feed containing 0.09M "free" EDTA (Feed 16) at pH 4.8 - 4.9 to determine how close the proposed aqueous-to-organic flow ratio was to the "pinching" flow ratio. As the flow ratio was increased from 4.0 to 9.0, the strontium recovery decreased from 75 to 18% of the feed. The following equation was derived from the results:

$$\% \text{ Recovery} = \frac{2200\,(\underline{M} \text{ free D2EHP})}{A/O}$$

where

$$\text{"free DEHP"} = \underline{M}\ \text{D2EHPA} - 4(\underline{M}\ \text{Ca} + \underline{M}\ \text{Sr})_{\text{organic}}$$

$$A/O = \text{Aqueous to organic flow ratio}$$

Thus to approach 100% recovery, the ratio of free solvent to A/O had to be equal to or greater than 0.045 in these runs. Actual values ranged from 0.038 to 0.008. This correlation is, of course, dependent on the pH and the concentrations of sodium and complexing agent in the feed, all of which were essentially constant in this run series.

The results of these runs emphasized the great importance of solvent loading on extraction performance. A review of available Purex crude analyses indicated that the calcium molarity would be within a factor of two of the strontium molarity (in place of a Ca/Sr mole ratio of 5 to 6 in these and the preceding runs). Consequently, the Ca/Sr ratio in subsequent runs was corrected to reflect more nearly the expected ratios. With this feed correction, A/O ratios as high as 5 would have provided acceptable strontium recovery in these runs.

Runs 47, 48, and 49

The effect of increased temperature on column performance was investigated. Increasing the temperature 20 C increased the flooding frequency threshold by about 20 cycles/minute (from 85 to about 115 cycles/minute) at 0.5-inch pulse amplitude. At 80 cycles/minute, the strontium losses at both temperatures were less than 5%.

Runs 50 Through 53

These runs, using the more dilute calcium feed (Feed 18), demonstrated the effects of pH and flow ratio on strontium recovery. In two runs at pH 4.75, lowering the A/O ratio from 4.0 to 3.0 apparently reduced the strontium loss from 9% to less than 6%. At pH's of 3.8 and 4.25, strontium losses were less than 6% with A/O ratios as high as 5.4. The feed contained 0.05 to 0.09M excess EDTA. From equilibrium considerations, none of the runs should have been operating near "pinching" conditions.

Runs 54, 55, and 56

Run 54 was operated continuously over a 24 hour period to demonstrate the stability under prolonged operation of a near final version of the Hot Semiworks flowsheet. The feed pH was varied over the range 4.1 to 4.9, and several column upsets were deliberately contrived to determine the effect of these variables on strontium recovery. Test results were highly satisfactory with respect to the 1A column; overall strontium recovery was greater than 95%; floods were readily broken by reducing the frequency; and no abnormal amounts of interface cruds were built up.

The 1B column, which was operated in cascade with the 1A column, had unusually high strontium losses. These were attributed to loss of buffering capacity in the citric acid stripping solution caused by excessive extraction of sodium in the 1A column. Accordingly, emphasis was shifted from extraction flowsheets to flowsheets designed to reduce the sodium concentration in the 1AP.

Runs 55 and 56 were the first step in this direction. These runs, using the same feed as Run 54, showed that about 0.19M sodium was extracted at feed pH's of 4.8 - 4.9, aqueous sodium concentrations of 1.1M, and free solvent molarities of 0.29M. In Run 56, the scrub solution was changed to 0.28M HNO_3. This removed a stoichiometric quantity of sodium from the solvent phase, giving a sodium DF (decontamination factor) of 1.5 in the scrub section.

Runs 57, 58 and 59

The flowsheet for these runs was drastically modified to permit more rapid attainment of steady state in the scrub section. The feed contained only sodium, strontium, and acetate; and the flow ratio was adjusted to give a fourfold higher solvent rate. The variables studied were feed pH and the use of HNO_3 instead of $NaNO_3$ in the 1AS stream.

With 1.5M sodium in the feed, a pH of 4.5 - 4.6, and a free solvent concentration of about 0.30M, the sodium concentration in the product was reduced from 0.14M to 0.10M by changing the 1AS from 0.5M $NaNO_3$ to 0.29M HNO_3. The sodium in the 1AP was reduced to 0.046M by lowering the feed pH to 4.0, still using the acid strip. The sodium DF's were again estimated to represent stoichiometric exchange with the scrub acid.

The strontium HTU was estimated as <2.2 feet.

Runs 60 Through 63

Although the sodium DF's obtained with nitric acid scrub were promising, it was felt that uncontrollable variations in feed pH and hence improper adjustment of 1AS acidity at the Hot Semiworks could occasionally lead to either high strontium reflux or to inadequate sodium DF's. Accordingly, the remainder of the scrub studies were made with buffered scrubs. The four runs in this group again used a special flowsheet, though not as drastically changed as the proceding one.

The 1AS in the initial runs contained 1M acetic acid with 0.2M HNO_3 added. The sodium DF's with this scrub proved to be virtually identical to those obtained with 0.29M HNO_3 alone, with very little indication that

the acetic acid was contributing to sodium-hydrogen exchange. Substitution of 0.2M citric acid for the nitric acid provided no DF at all with a 3.8 pH feed, but gave a sodium DF of 1.5 at pH 4.8.

Reviews of previous runs in the campaign indicated that the extraction flooding frequency was sometimes unusually low. To test the theory that undissolved iron precipitate contributed to the instability, the feed to this series of runs contained 0.03M iron of which about 25% had been precipitated and held at pH 4 for four days before use. The flooding frequency at 0.8 inch pulse amplitude was reduced from about 70 cycles/minute to about 40 cycles/minute with this feed. Flooding characteristics were not extensively explored, but were evidently sensitive to pH, an increased pH favoring greater stability. This observation can probably be explained by increased dissolution of the iron precipitate by EDTA at the higher pH tested.

Runs 64 Through 70

These runs completed the development of the flowsheet and cartridge. The flowsheet development concluded with tests of 1AS containing 0.6M citric acid, neutralized to a pH of 2.3 to avoid accidental strontium reflux at low pH. Cartridge development involved redesign of the scrub section to give improved dispersion characteristics; 1A Cartridges 4, 5, and 6 were tested.

To facilitate development of a suitable scrub flowsheet, an approximate sodium operating diagram, shown in Figure 4.2, was calculated from data presented in Section 2 of this report. This diagram shows that a 0.25 aqueous to-organic flow ratio together with the 0.6M citric acid scrub should reduce the sodium in the product to at least 0.02M with two theoretical extraction stages. When tested with the final scrub cartridge, sodium DF's of 3 to 8 were readily obtained. Typical sodium concentrations in the 1AP were 0.04M with 4.6 pH feed and ≤0.006M with pH 3.8 feed.

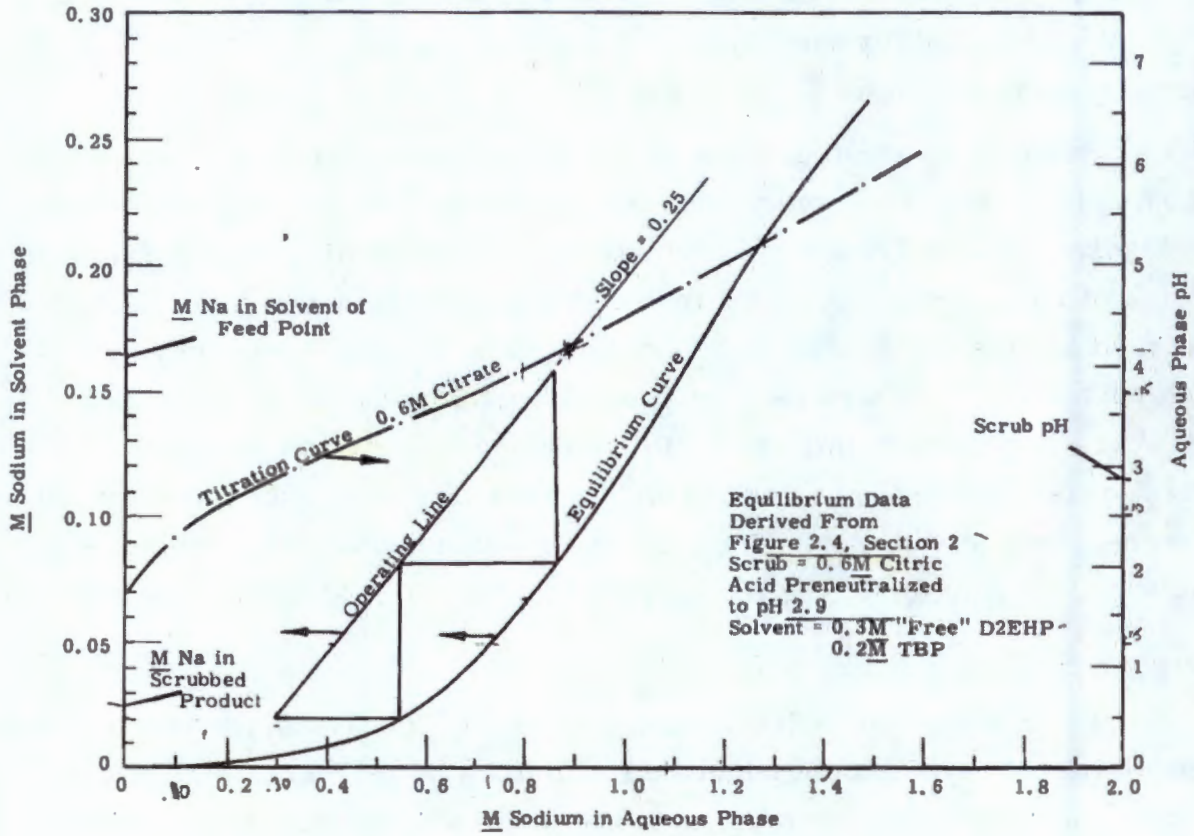

FIGURE 4.2

Operating Diagram for Sodium Scrubbing

Strontium losses in all but one run were ≤3%. In that one run, a combination of low pH (3.65) and a 6-foot extraction section produced a 21% strontium loss. The last two runs of this series contained 0.012M sulfate in the feed, approximately the same concentration as the lead. No effect on strontium extraction was observed.

A strontium HTU of 1 to 2 feet was again measured, this time, in Run 65, using a 6 foot extraction section.

Runs 71, 72, and 73

The conditions and results of these runs are presented in Table 4.5 in the Appendix. They were designed to investigate flowsheet modifications permitting coextraction of cerium and strontium. The feed was

buffered with citric acid to pH's of 3.1 to 3.8 and contained 0.05M free EDTA; aqueous-to-organic flow ratios were about 2.5. Under these conditions, virtually all of the strontium and at least 70% of the cerium was extracted. Average aqueous holdup time was estimated to range from 1 to 2 minutes. The 1B column, operated in cascade, stripped over 90% of the strontium and cerium out of the solvent with 1M HNO_3 at an A/O of 0.2.

This flowsheet demonstrated an acceptable method for extracting two of the long-lived fission products from Purex waste, a goal sought in the Waste Management Program; however, insufficient time was available to develop more optimum flowsheet conditions or to improve cerium extraction. Potential improvements might include: substitution of HEDTA for EDTA, the use of citric acid alone as a complexing agent for iron and zirconium, and increasing the aqueous phase holdup time to overcome a possible kinetic effect in cerium extraction.

Runs 74, 75, and 76

The last runs in this program investigated the possiblility of extracting cerium(IV) out of 1M HNO_3 in the extraction column. Permanganate, dichromate, and persulfate ions were used as oxidizing agents. The results are included in Table 4.5 in the Appendix.

Although the cerium(IV) distribution ratio should have been greater than 100, in all cases less than 40% (perhaps less than 20%) of the cerium was extracted. Much of the difficulty appeared to be the result of the reducing action of small amounts of citrate or acetate left in the system. The intense yellow cerium(IV) color in the persulfate feed, for example, was nearly gone by the time the feed entered the column. The permanganate ion concentration was also reduced from 0.1 to 0.01M in the feed tank. In addition, it is believed that slow extraction kinetics may also have limited cerium(IV) extraction; aqueous holdup time in the system was 2 minutes or less, compared with 10 to 30 minutes usually allowed in batch extraction of permanganate - cerium solutions.

Dichromate (chromate) ion was extractable to some extent in the solvent and in D2EHPA alone. On standing, a green chrome species was formed in the solvent which was extremely difficult to remove. Chromium (III) was extracted into D2EHPA (blue color extracted) and the optical properties of the two species were compared. The spectra were similar, but the spectrum with the green species was displaced toward higher wave lengths. The blue chrome(III) species was readily stripped by dilute HNO_3.

1B COLUMN

Runs 1 Through 6

The first six runs in the 1B column demonstrated the use of 0.1M HNO_3 as the stripping solution (1BX). The feeds for these runs were derived from the first 26 1A runs using Feeds 1 through 9 and contained varying amounts of metal ions (sum of metal equivalents varied from 0.052 to 0.23M exclusive of sodium). The results showed that HNO_3 stoichiometrically stripped out all metal ions but iron and zirconium; less than 10% (probably less than 1%) of these metals were found in the aqueous product.

In the last run of this series, HNO_3 flow was reduced stepwise from 45% to 15% of the stoichiometric requirement for strontium and calcium removal (from a threefold excess to no excess for strontium alone). The strontium recovery decreased from 84% to 45% while the weight ratio of strontium to calcium in the product increased from 0.46 to 0.9 (Sr/Ca = 0.34 in the feed).

Runs 7 and 8

A sieve-plate cartridge was used in the first series of runs. Although the capacity and efficiency were adequate, this cartridge was replaced with

a nozzle plate cartridge for improved flexibility and better operating characteristics. Runs 7 and 8 explored the flooding characteristics of the nozzle plate cartridge with 0.1 to 2M HNO_3 used as 1BX. The flooding frequency at 1 inch pulse amplitude varied from 87 cycles/minute at 400 gph/ft^2 to 65 at 930 gph/ft^2.

The flooding frequency in these runs and in later runs using citric and tartaric acid 1BX streams showed a surprising insensitivity to 1BX composition, flow ratio, and total throughput rate. As a result, all remaining efficiency runs in the 1B column were made at frequencies ranging from 60 to 80 cycles/minute, even though the volume velocities varied from 150 to 800 gph/ft^2.

Runs 9, 10, and 11

These runs explored the use of buffered stripping solutions to selectively strip strontium from the solvent. The three compositions tested were 1 and 1.5 M citric acid and 1M tartaric acid. The following table illustrates the results:

Calcium DF's with Buffered Stripping Solutions

Stripping Solution	A/O	1BP pH	% Sr Loss	Ca DF[a]
1M Citric Acid	0.25	2.3	<2	3.1
	0.17	2.2	<2	4.0
1.5M Citric Acid	1.0	1.9	≤0.3	2.2
	0.44	2.0	0.3	3.3
1M Tartaric Acid	1.1	2.2	0.2	1.5
	0.51	2.1	0.1	3.0
	0.24	2.6	1.4[b]	5.9
	0.13	2.9	1.3[b]	17

(a) Assuming 100% strontium recovery

(b) This loss may not have been at steady state. At the indicated pH's, strontium losses of 10 to 20% would be expected.

The beneficial effect on the calcium DF of reducing the aqueous-to-organic flow ratio is clearly shown. This dependency derives from the theoretical consideration that the DF should approach the value of the extraction factor [E_a^o/(A/O)] whenever the E_a^o exceeds the A/O. The average calcium E_a^o calculated from the results given above was 1.6 with 1M tartrate, 0.7 with 1.5M citrate, and 1.8 with 1.0M citrate. Laboratory data indicate that these values are close to the true values using a 1M citric acid system and a comparable free solvent concentration (Ca E_a^o's ranged from 1 to 3 at pH's from 2.1 to 2.4).

Cascade Runs

The remaining 1B runs were made in cascade with the 1A column to test operability of the entire systems. Only a few of these runs achieved steady state because of the disparity in flow rates in the two columns (the continuous phase flow rate in the 1B column was normally 20 to 25% of that in the 1A column). Highlights of the valid results:

1. No stripping was achieved using 1M $NaNO_3$ as 1BX, nor would any be expected in the light of equilibrium data subsequently obtained.
2. With citric acid 1BX, excessive sodium in the 1B feed would, upon being stripped, neutralize sufficient acid to raise the pH above the maximum allowable for complete strontium stripping. This was first observed in 1A Run 54 and later corrected (as discussed in "Runs 64 Through 70", page 4.12) by using a citric acid scrub in the 1A column for sodium removal. Attempts to improve the 1BX buffering capacity by increasing the citric acid concentration were unsuccessful with 1.1M sodium in the 1BP (2M citric acid) and borderline with 0.5M sodium in the 1BP (1.5M citric acid). The breakpoint with either 1M citric or tartaric acid occurred at 0.3 to 0.4M sodium in the 1BP.

3. Typical calcium DF's obtained with 1M citric acid in the 1BX ranged from 20 to 60 under the flowsheet conditions recommended for the Hot Semiworks (1A Runs 64 through 70). These results may be biased high because of analytical limitations; a real six- to ninefold improvement over the results described earlier would be expected from the extent of lower solvent loading (nearly a threefold higher free solvent concentration at the feed point).
4. Strontium HTU's were estimated to be about 1.4 to 1.6 feet.

SECTION 5. HOT SEMIWORKS STUDIES

C. R. Cooley and G. L. Richardson

INTRODUCTION AND SUMMARY

In 1960, the idle Hot Semiworks pilot plant at Hanford was selected for the strontium program. Previously the contact maintained Semiworks had been used for development work on the Redox and the Purex Processes which required similar solvent extraction equipment. In September 1960, design, construction modifications,and testing started concurrently and continued through to March 1961.

Principal modifications to the facility included provisions for a cross country feed line, product load out cell, and modifications to increase reliability, i.e., duplication of services, adoption of long shaft pulser design, all welded piping and alternate routings to provide multiple cycles of solvent extraction through the same equipment.

Actual hot processing for strontium was initiated in early May and was completed in October of 1961. The process used in the Hot Semiworks was developed by the Cold Semiworks and laboratory studies described in Sections 3 and 4 of this report. Essentially, this process consisted of extracting strontium from a buffered, complexed feed with a D2EHPA solvent, followed by preferential stripping of the strontium from the solvent with 1M citric acid. Additional cycles of solvent extraction or ion exchange were used as needed to provide the necessary product purity.

Approximately 744 kilocuries of Sr^{90} meeting customer purity specifications were produced for shipment from an input of 1184 kilocuries of Purex crude feed. In addition, 169 kilocuries requiring further purification were isolated awaiting product storage space. The total recovery of Sr^{90}, including the impure fraction, was 1044 kilocuries, or 88% of that entering the process. This total includes 131 kilocuries of purified strontium which were lost or otherwise unaccounted for during between-run operations. Four runs comprised the recovery program.

The run flowsheets were based on the Cold Semiworks flowsheet presented in Section 4; however, during the runs, several important modifications were made. These resulted eventually in the demonstration of a satisfactory one-cycle process for producing a specification strontium product and a multicyle process for producing both a strontium and a cerium product. Significant stages in the evolution were:

1. A twofold concentration of the strontium product was achieved with no adverse effects by backcycling about 50% of the first cycle solvent extraction product to the feed. The backcycle concept doubled the amount of product that could be accumulated during a run (without boildown) and, theoretically, provided a twofold improvement in the cerium DF (decontamination factor).
2. Although the ion exchange cycle produced a very high purity product, it was batch-size limited to about 200 kilocuries of Sr^{90} and was replaced by solvent extraction methods after the first run.
3. Two cycles of solvent extraction using EDTA as the complexing agent would provide acceptable cerium DF's only if both cycles used citric acid as the stripping agent. Typical cerium DF's in the extraction (A) columns were only 3 to 10, compared with 40 to 100 in the citrate-stripped partition (B) columns.
4. A one-cycle process was attained by substituting DTPA for EDTA in the feed. The substitution improved the first cycle cerium DF about tenfold without significantly increasing the chemical cost of the process.
5. Over 50% of the cerium and promethium in the feed could be extracted along with the strontium by substituting citric acid for most of the EDTA or DTPA in the feed. However, poor material balances leave some uncertainty about the extent to which rare earths can be routinely extracted from complexed Purex wastes.

One product loadout was made during the program using a bicarbonate precipitation procedure. Inability to slurry all of the precipitate into the filter cask prevented loading more than 120 kilocuries of Sr^{90} out of 150 kilocuries precipitated.

The plant and process as a whole performed exceedingly well. The process fully demonstrated the feasibility of using solvent extraction on a large scale for removing strontium from Purex-treated wastes and tentatively the feasibility of coextracting cerium and other rare earths. For the short-term program the contact-maintained plant was operable about 70% of the time through the addition of all-welded piping, duplication of services, and the use of long vertical-shaft pulsers.

DESCRIPTION OF THE FACILITY

The Hot Semiworks, shown in Figure 5.1, is a miniature processing plant consisting of four basic components: 1) a three cell arrangement of concrete shielding to serve as the hot processing building using contact maintenance, 2) a cold processing building serving as a remote operation center and auxiliary source of services to the hot processing portion, 3) a ventilation and off gas handling building to treat and discharge effluent gases through a 200 foot stack, and 4) general miscellaneous service buildings, i.e., offices, shops, storage, etc., to house supporting personnel and auxiliary functions.

The functions of the three cells were subdivided into: the high level feed, waste and product handling in A Cell (a 22 by 40 foot cell 20 feet high, containing 13 processing tanks with a total of 3500 gallons of storage); the solvent extraction and ion exchange processing in B Cell (a 20 by 38 foot cell 50 feet high); and the solvent treatment and storage plus the condensate storage in C Cell (identical to A Cell but containing 14 processing tanks with a total capacity of 4900 gallons of storage).

The basic flow scheme for the Hot Semiworks processing is shown in Figure 5.2. The crude feed from the Purex plant separations was stored in two 15,000 gallon tanks at C Tank Farm vault. For a run period, the feed was pumped through a 2 inch underground transport line to A Cell in about 500 gallon batches. After feed preparation, it was pumped to B Cell and through the two solvent extraction pulse columns using D2EHPA solvent extraction as described in other portions of this report. Once

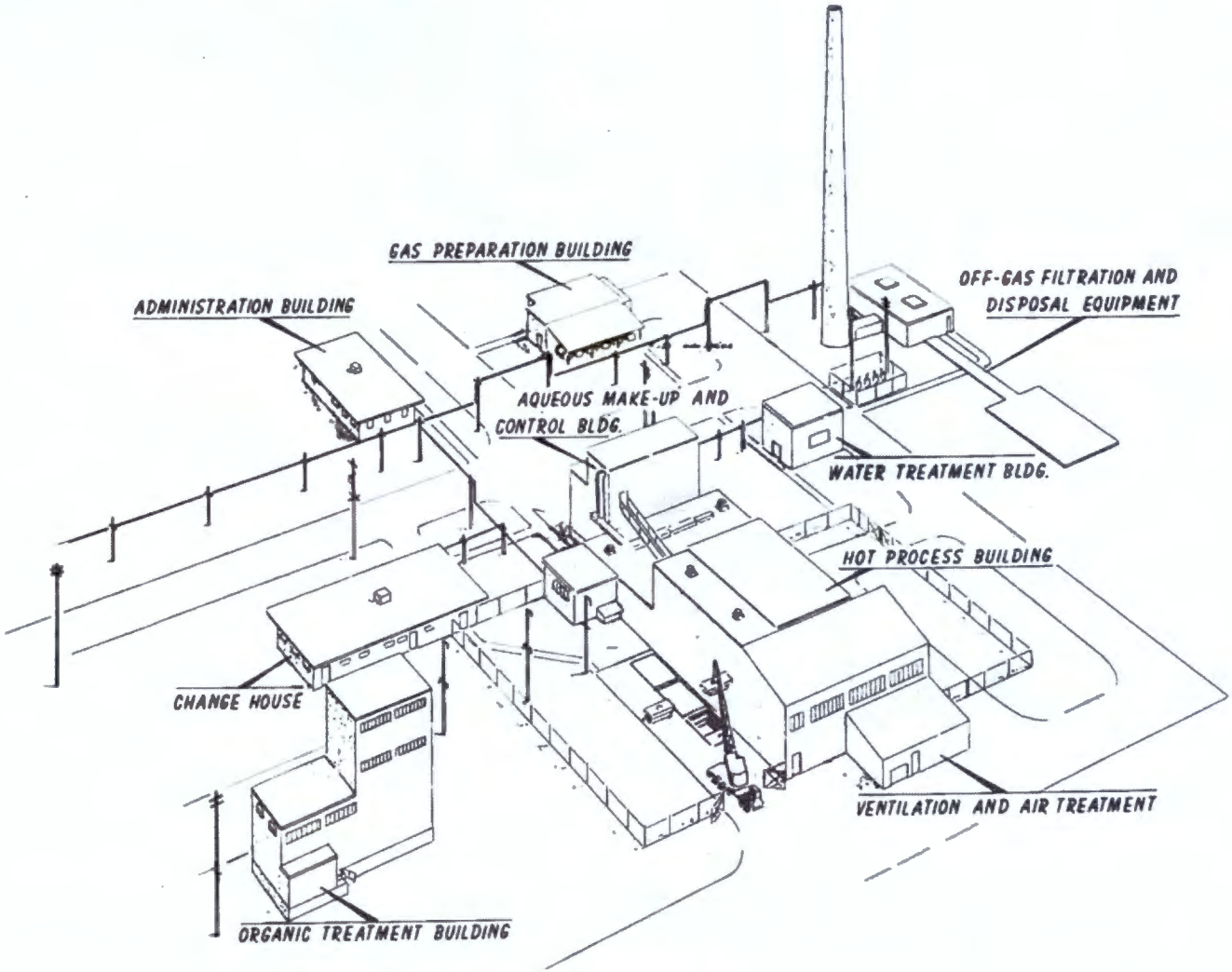

FIGURE 5.1

Hot Semiworks Process Area

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started, a run would continue until the capacity of the receiver tanks or of the ion exchange column was reached. The product was collected in A Cell and stored to await loadout in a slurry filter cask[26] as the carbonate for transcontinental shipment to ORNL or Martin Company. The wastes were concentrated about threefold in A Cell and discharged to C-Farm waste tanks through an existing waste effluent line. Condensates were accumulated in C Cell and periodically discharged. The organic was collected and batch washed in C Cell for recycle. The spent organic was discharged to a specific organic retention crib at the end of the program.

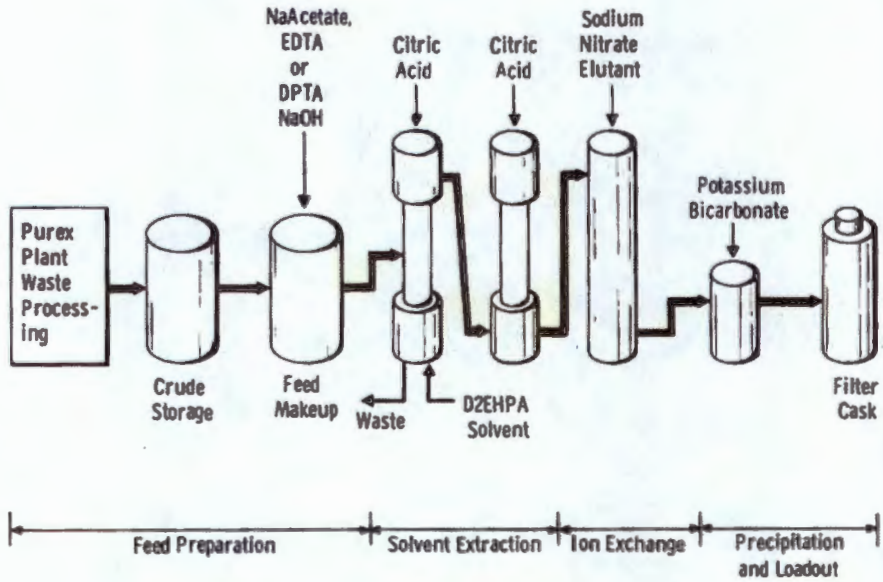

FIGURE 5.2

Simplified Hot Semiworks Strontium Purification

Only two solvent extraction pulse columns and one fixed-bed ion exchange column were installed in this program. This provided equipment simplicity and permitted duplication of services such as feed and waste routes. Considerable operating flexibility and additional reliability was thus attained. Successive passes through the same equipment could be made if additional strontium purification was required for product strontium. In flowsheets describing the runs, the 1A, 2A, and 3A columns are the same columns but refer to the first, second, and third passes.

The compound extraction, or A column, was 4 inches in diameter with a 10 foot extraction section and a 15 foot scrub section. Both disengaging sections were 8 inches in diameter and 5 feet long. The top disengaging section contained a temperature element, interface-specific gravity dip tubes, and a rate indicating overflow orifice. The bottom disengaging section contained an interface jet line, a remote-indicating interface float, a temperature element, a differential pressure cell to indicate column loading (flooding), and the pulse transmission lines from the long vertical shaft piston pulser, as described later. Bottom interface control was used exclusively in the A column to give an organic-continuous column.

The 4 inch diameter stripping, or B column, was 16 feet tall and was operated exclusively aqueous continuous. The disengaging sections were 8 inches in diameter. The top section was 3 feet long and contained dip tubes for interface detection. The bottom section was 5 feet long and contained a temperature element, an interface float (used to detect floods), a differential pressure cell, and the pulse transmission line.

The cartridge assembly for the columns as developed in Cold Semiworks studies (Section 4) is given below:

Nozzle Plate Cartridges

	Column		
	1A Extraction	1A Scrub*	1B Strip
Cartridge Height, ft	10	15	16
Plate Spacing, in.	4	4	4
Hole Diameter, in.	0.188	0.125	0.125
Plate Free Area, %	23	10	10
Nozzle Depth, in.	0.05	0.05	0.05
Nozzle Orientation	Down	Down	Up

*19% free area louver-type redistributor plates inserted at 3-foot intervals.

Flow control to all columns was maintained through remotely operated valves and indicating-controlling rotameters. Cold streams were fed by gravity flow; the feed and solvent streams were pumped with modified canned-rotor-type pumps, described later under equipment performance.

The ion exchange column was a single fixed bed unit containing 100 liters of 50-100 mesh Dowex 50 W x 12 cation exchange resin. The 8 inch diameter, 15 foot high column was serviced by a temperature element, a water cooling jacket,and numerous remotely operated valves. Spent resin was jetted into a filter container for burial.

In addition to the normal cell radiation detection units, three collimated ion chambers were installed on several of the process streams to indicate relative activity readings. A beta and gamma monitor was installed on the effluent line of the ion exchange column to detect Sr^{90} and Ce^{144} breakthrough.

RUN RESULTS

A total of seven runs were made in the Hot Semiworks. The first three runs, using cold and traced feeds, were intended primarily for training and plant shakedown. They satisfactorily demonstrated the operability of the equipment and the Cold Semiworks flowsheet and are not discussed further.

The final four runs, designated Sr-4, 5, 6, and 7 were designed not only to recover Sr^{90} but also to obtain data applicable to the development of improved processes for use in the Waste Management Program at Hanford. The flowsheet for each run contained significant variations from the flowsheets tested in the laboratory and Cold Semiworks. For example, Run Sr-4 demonstrated the feasibility of recycling a portion of the solvent extraction product to the feed stream. Run Sr-5 demonstrated the replacement of the tail-end ion exchange column with a second cycle of solvent extraction. Run Sr-6 demonstrated the use of DTPA in place of EDTA with the elimination of a tail-end cycle. Run Sr-7 attempted the recovery of cerium and promethium together with strontium using a citrate-complexed feed.

The feeds were prepared Purex crude, derived from Purex concentrated waste by the procedure of Bray and Van Tuyl.[7] Detailed feed compositions are presented in Tables 5.1 and 5.2 inthe Appendix. The results of the runs are discussed below.

RUN Sr-4

The flowsheet used in Sr-4 is shown in Figure 5.3. The major features of this flowsheet, which resembles that developed in Cold Semi-works studies, were:

1. The feed was prepared from 12,000 liters of Purex crude by adding sodium acetate for pH control and the sodium salt of EDTA at about 0.06M in excess of stoichiometric requirements as a complexing agent for iron, lead, ZrNb, ruthenium, and rare earths. Additional caustic was required to adjust the pH to 4.7 - 4.8.
2. The scrub stream (IAS) used 0.6M citric acid adjusted to a pH of 2.9 by the addition of caustic. The citric acid concentration, pH, and flow rate were carefully balanced to permit removal of sodium from the solvent phase without causing much strontium reflux.
3. The 1AX was freshly prepared 0.4M D2EHPA -0.2M TBP in Shell E-2342 diluent. The flow rate of this stream relative to the aqueous flow rate was near the practical minimum requirement for strontium recovery.
4. The 1BX stream was 1M citric acid. Its flow rate also was near the minimum required for good strontium stripping. An important factor limiting the flow ratio was the magnitude of pH change caused by the exchange of sodium and strontium with hydrogen ion, which in turn affected the strontium distribution ratio, as discussed in Sections 3 and 4 of this report.
5. About 33% of the 1B column product was backcycled to the feed preparation step during the run. This was done intermittently by adding roughly 90 liter portions of 1BP to four of the six 2000 liter feed batches processed in the run. The maximum effect of this recycle was to approximately double the strontium concentration in the feed. The backcycle concept was used as a means of concentrating the product and, hopefully, of obtaining additional decontamination.

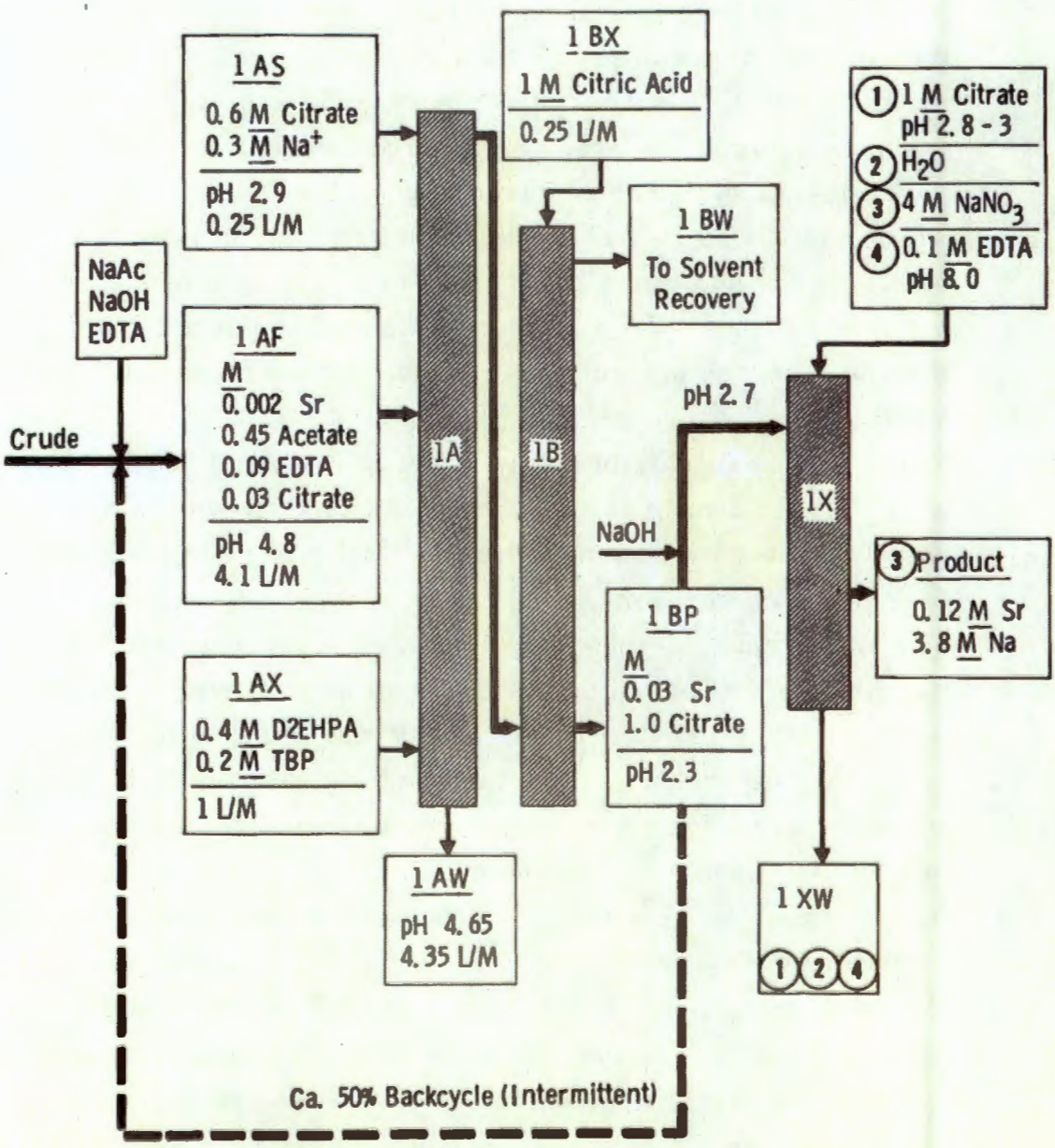

FIGURE 5.3

Sr-4 Flowsheet

6. The final 1B product (about 200 kilocuries of Sr^{90}) was diluted slightly, adjusted to a pH of 2.7, and fed to the ion exchange column at 1.1 liters/minute (3.2 ml/min-cm^2).
7. Ce^{144} was scrubbed from the loaded resin with nearly four column volumes of citric acid at a pH of 2.8 to 3,fed about the same rate as the feed. The citrate solution was then removed by adding a water flush.
8. Eighty percent of the strontium was eluted with about two column volumes of 4M $NaNO_3$, fed at 2 ml/min-cm^2; the remainder by ca 0.1M EDTA at a pH of 8.6. Over three column volumes of EDTA solution were used to assure adequate cleanup of the resin for disposal. The EDTA eluate was held for rework.

The run summary is shown in the following table; details are given in Table 5.3 in the Appendix:

Sr-4 Run Summary

Sr^{90} Input:	210 kilocuries
Sr^{90} Product:	180 kilocuries (including 32 kilocuries requiring rework)

	Solvent Extraction 1A	Solvent Extraction 1B	Ion Exchange	Overall
Strontium Loss, %	6	1	0.5	14*
Strontium Product DF's				
Ce^{144}	~4.5	55	80	$\geq 2 \times 10^4$
$ZrNb^{95}$	≥1400	≤45	--	$\geq 1.2 \times 10^5$
Ru^{106}	≥ 150	≤10	--	$\geq 2.4 \times 10^3$
Calcium	---	9	1.9	17
Barium	≥ 6	--	≤ 5	> 28
Iron	---	--	--	≥ 2000

*Includes 6% unaccounted for

Instantaneous waste losses in both the 1A and 1B columns apparently varied as much as ninefold, but the variation was random and did not coincide with periods of 1BP backcycle. Obviously, backcycle in the fashion shown in the flowsheet could not proceed indefinitely without high loss unless a side product stream were continuously withdrawn to permit attainment of an equilibrium product concentration of the desired magnitude.

The DF's approached expectations, although the Ce^{144} DF in the 1A column was about twofold lower than demonstrated in laboratory studies. All product contaminants were well below Martin specifications, as shown below.

Sr-4 Product Purity

Element	Curies/Curie Sr^{90} Actual	Curies/Curie Sr^{90} Specification	Grams/Gram Sr Total Actual	Grams/Gram Sr Total Specification
Sr^{90}	1	1	0.568	--
Ce^{144}	$\leq 5 \times 10^{-4}$	$\leq 1 \times 10^{-3}$	---	--
$ZrNb^{95}$	$\leq 2 \times 10^{-5}$	$\leq 8 \times 10^{-4}$	---	--
Ru^{106}	$\leq 5 \times 10^{-5}$	$\leq 6 \times 10^{-4}$	---	--
Calcium	---	---	0.05	<0.33
Barium	---	---	<0.01	
Iron	---	---	<0.003	

An ion chamber in the cell provided a measure of the integrated amount of activity absorbed on the ion exchange column and proved very useful in determining the effectiveness of the scrubbing step. For example, the initial scrub pH was 2.8. At the time the ion chamber reading leveled off, the activity left in the column appeared to be significantly greater than the background reading before the column was loaded. At this time, the scrub pH was raised to 3 with a further improvement in DF, as indicated by a decrease in the cell activity reading.

The column capacity for strontium was high enough, as predicted from the correlation presented in Section 2, to hold the entire 1BP strontium product of this run without significant breakthrough. Consequently, the beta and gamma monitors on the effluent stream did not receive a fair test

during loading. During elution, however, integration of the area under the elution curve plotted by these monitors permitted estimation of the percentage of strontium removed from the resin at any given time. The beta monitor curve is shown in Figure 5.4.

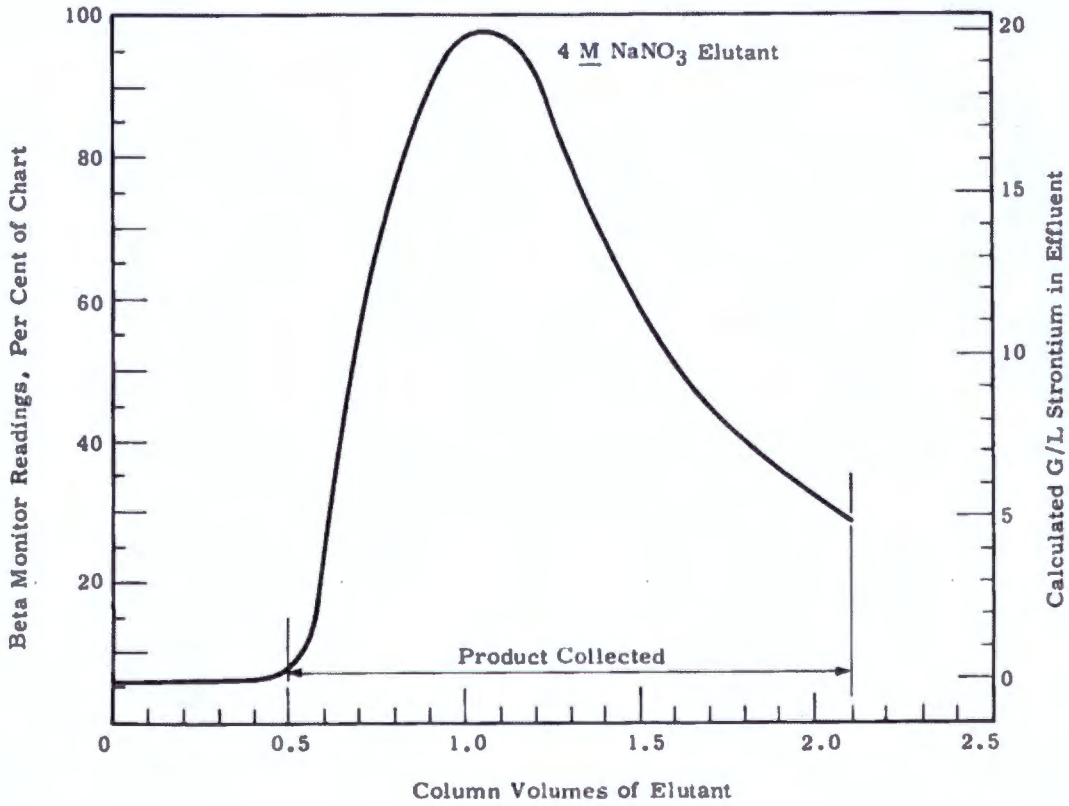

FIGURE 5.4

Ion Exchange Elution Curve Derived from Beta Monitor

The final elution with EDTA cleaned up the resin well enough to permit normal sampling after its transfer from the 1X column to a shielded drum. The used resin was compared in the laboratory with unirradiated resin to determine the extent of resin degradation after an estimated radiation dose of 1000 watt-hours per liter. The data, shown in the table below, indicate a loss in cross linkage of less than 2%.

Moisture Content of Irradiated Resin*

	$\%H_2O$
Fresh Dowex 50	39.5
Fresh Dowex 50W x 12	39.1
HSW Dowex 50W x 12 after 1000 watt-hr/liter	40.6

*Sodium-form, average of duplicate determination

On this basis, the resin would have been usable for several more runs. In the absence of prior experience, however, the resin was discarded after this run.

RUN Sr-5

The flowsheet used in Sr-5 is shown in Figure 5.5. The major differences between this flowsheet and that for Sr-4 were the following:

1. No product backcycle was employed.
2. Used solvent from Sr-4 was used as 1AX.
3. The ion exchange step was replaced by a second solvent extraction cycle for residual cerium decontamination. The feed for this cycle was prepared from the citrate product of the 1B column.

The second cycle concept had not been tested before this run. The critical features--the effect of strontium loading in the solvent and EDTA-citrate complexing in the feed on strontium and cerium distribution ratios in the 2A column--were evaluated in the laboratory in a series of batch equilibrations (see Section 3 of this report). These results dictated the use of a lower feed pH (4.0 to 4.2) and a much lower aqueous-to-organic flow ratio (1.5) for adequate strontium recovery in the 2A column as compared to the 1A. The scrub solution contained 0.02M EDTA, with 0.5M $NaNO_3$ added as an electrolyte to provide better phase disengagement. The 2BX was dilute nitric acid added in a slight stoichiometric excess over that required to strip strontium and sodium from the solvent. These features were expected to give a cerium DF in the range of 10 to 20.

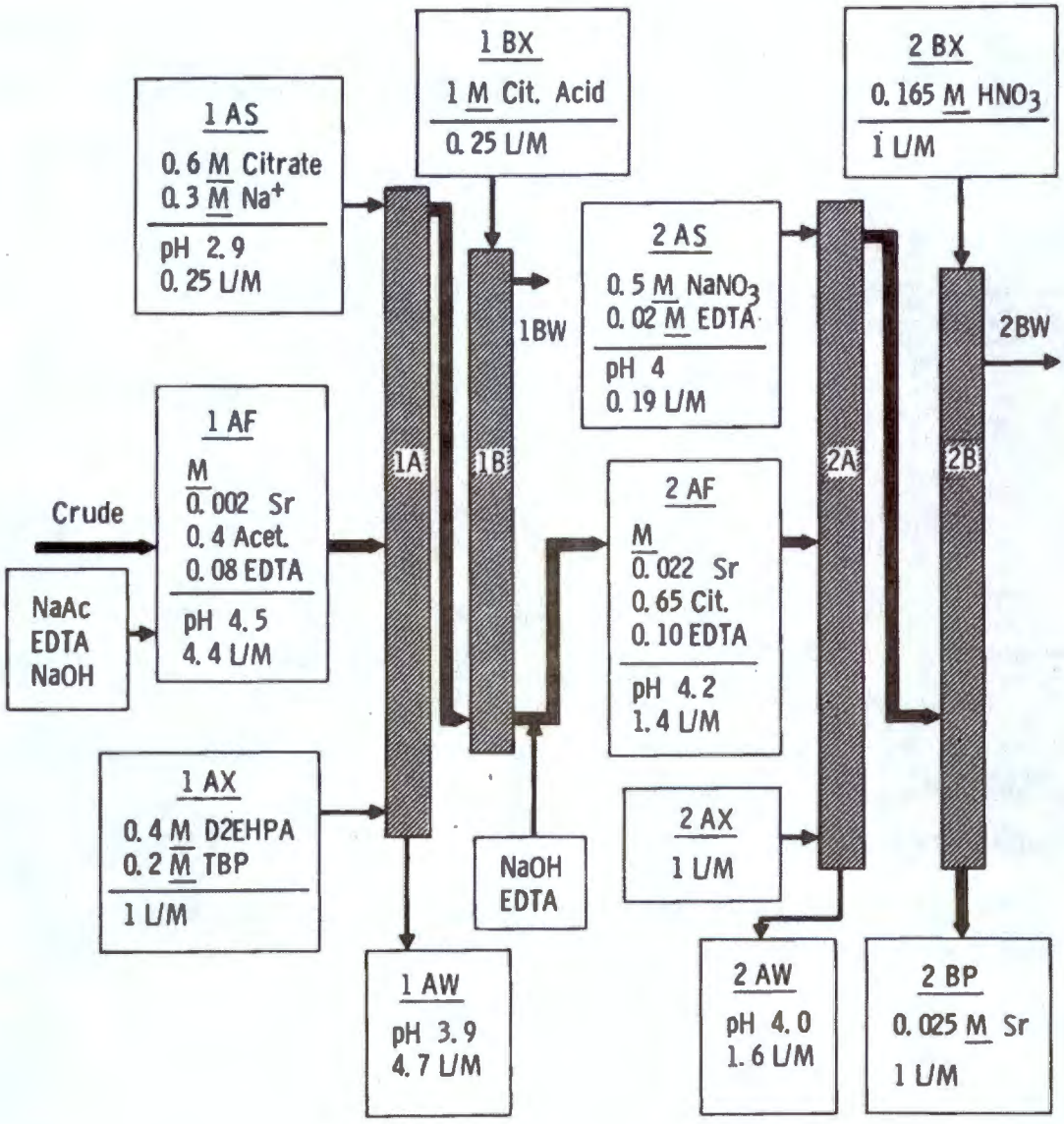

FIGURE 5.5

Sr-5 Flowsheet

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The run summary is presented in the following table; details are given in Table 5.4 in the Appendix.

Sr-5 Run Summary

Sr^{90} Input: 220 kilocuries, including 32 kilocuries rework.

Sr^{90} Product: 190 kilocuries, requiring additional cerium DF of 2.

	1st Cycle		2nd Cycle		
	1A	1B	2A	2B	Overall
Strontium Loss, %	3	0.2	10	0.1	14
Strontium Product DF's					
Ce^{144}	3	72	1.3	7	2000
$ZrNb^{95}$	>70	--	--	--	9100
Ru^{106}	> 6	--	--	--	>6900
Calcium	--	19	--	23	45
Barium	2	--	8	--	16

The strontium loss in the 2A column was a little higher than expected, probably an indication that the 2AX flow rate was not quite high enough rather than that the column was operated inefficiently. The 2A pulse frequency was operated just at or below the instability threshold. It was raised first to 70 cyles/minute then reduced to 58 cycles/minute to stabilize the column.

The product met all specifications except that for cerium, as shown in the table below:

Sr-5 Product Purity

	Curies/Curies Sr^{90}		Grams/Grams Sr Total	
Element	Actual	Specification	Actual	Specification
Ce^{144}	6.4×10^{-3}	$\leq 10^{-3}$	---	---
$ZrNb^{95}$	2×10^{-5}	$\leq 8 \times 10^{-4}$	---	---
Ru^{106}	$<7 \times 10^{-6}$	$\leq 6 \times 10^{-4}$	---	---
Calcium	---	---	0.018	>0.33
Barium	---	---	0.015	

The poor cerium DF performance was attributed to four factors:

1. Failure of the feed adjustment pH meter at the start of the run required the use of a lower, more conservative pH in the first cycle to insure adequate strontium extraction (pH was controlled indirectly by monitoring the 1AW pH).
2. Failure of the normal feed pump required the use of the auxiliary feed pump, which in turn prevented the use of the backcycle concept demonstrated in Sr-4.
3. The same columns, tanks, and pumps were used in both cycles with only a brief time available for decontamination between cycles.
4. The Ce^{144}/Sr^{90} ratio in the feed was 40% higher than in Sr-4.

As a result of all these factors, a short rework run, described under "Sr-5 Product Rework" below, was required to purify the cerium contaminated product.

Despite the cerium contamination problem, Run Sr-5 demonstrated that the ion exchange column could be replaced by one or more additional cycles of solvent extraction. This, together with the development of the backcycle concept, permitted increasing the run size from about 200 kilocuries of Sr^{90}, as limited by ion exchange capacity, to nearly 500 kilocuries of Sr^{90}, now limited by product storage capacity.

Sr-5 PRODUCT REWORK

The flowsheet used to rework the product of Sr-5 is shown in Figure 5.6. This run also processed about 13 kilocuries of Sr^{90} from 2300 liters of an aqueous waste solution. The two feeds were not blended but were processed consecutively with appropriate flow adjustments between feeds to compensate for the wide differences in strontium concentration. DTPA was used for the first time as the complexing agent and was added to both the feed and the scrub. Nitric acid was used to strip strontium from the solvent. The concentration and flow rate were adjusted to just provide a stoichiometric exchange of hydrogen ion with strontium and sodium.

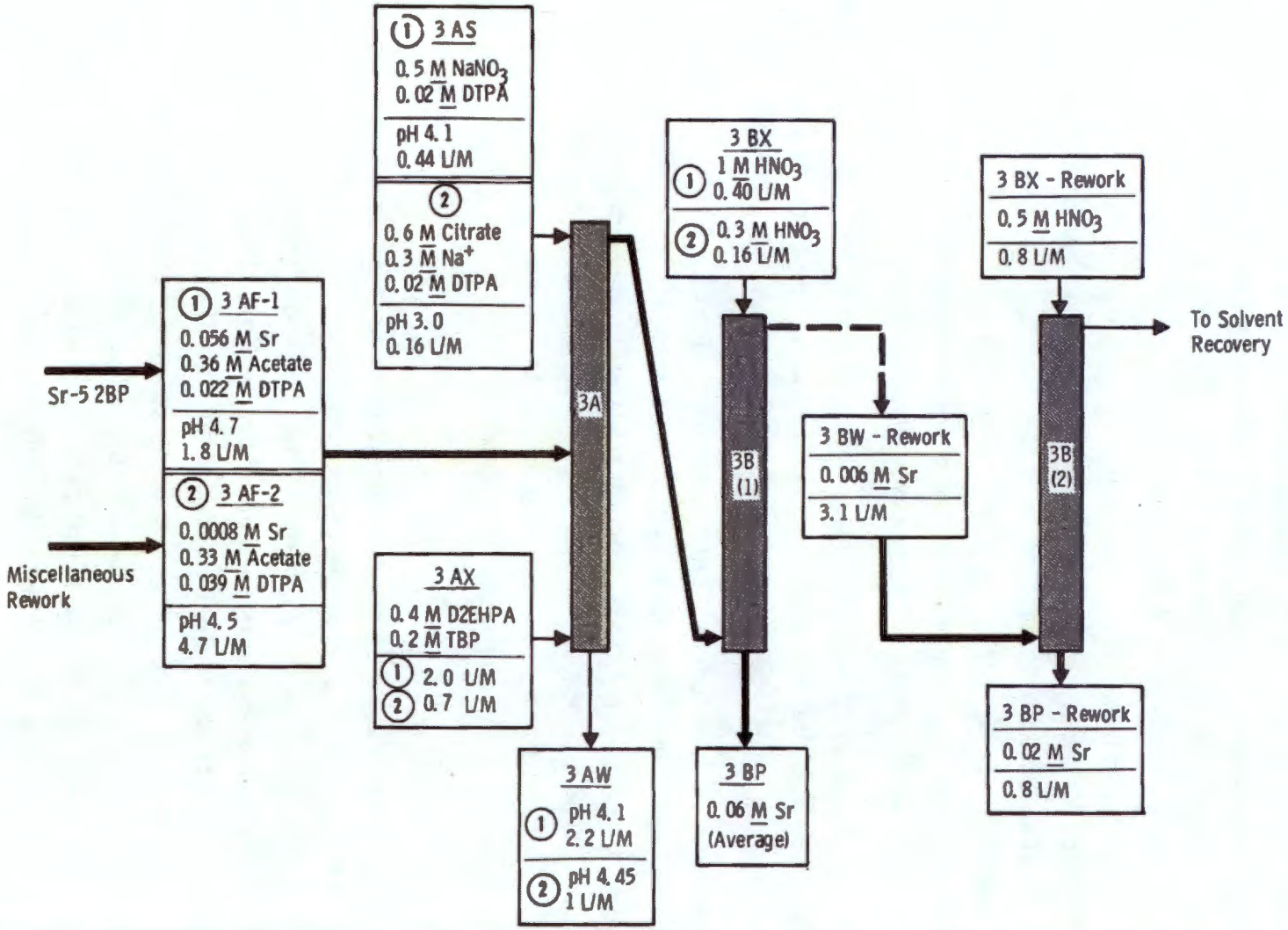

FIGURE 5.6

Sr-5 Third Cycle Flowsheet
(Rework of Sr-5 Product)

ACC-GE RICHLAND, WASH.

This run did not meet expectations. The first part, using the 2BP feed, required less than 4 hours to process nearly 200 kilocuries of Sr^{90}. This short time did not permit the usual adjustments of the pulse frequencies to assure optimum operating conditions. In fact, both the 3A and 3B columns were upset during much of the operating period. This was later found to have contributed to a high strontium loss in the 3B column (ca 25%).

In addition, the instability evidently allowed some cerium to be carried over to the 3BP. Cerium contamination in the 3BP may also have been caused by rework of the dilute waste solution which evidently contained a layer of degraded organic (as shown by variations in cell radiation monitor readings during agitation of the tank).

The strontium which followed the organic 3BW was reworked at the end of the run by passing it back through the 3B column for an additional nitric acid strip. Recovery this time was excellent; however, additional cerium from contamination in the organic storage tank was thus added to the product. Final results of the rework run are summarized below:

Sr-5 Product Rework Run Summary

Sr^{90} Input:	206 kilocuries
Sr^{90} Product:	169 kilocuries

	Column			
	3A	3B	3BW Rework	Overall
Strontium Loss, %	7	18	0.2	24[a]
Ce^{144} DF	8.5	1.8	0.3[b]	5.4[b]
Curie Ratio, Ce^{144}/Sr^{90}	--	--	--	0.0040

(a) Includes 17% not accounted for

(b) Reflects contamination of 3BW with cerium before rework

The cerium in the product still exceeded the specification value; however, permission was obtained from the Martin Company to relax the Ce^{144}/Sr^{90} specification to 0.003, which with Ce^{144} decay would provide

an acceptable product after about 4 months storage. The product was later blended with specification product from Sr-6 to obtain additional product storage space.

RUN Sr-6

The flowsheet for Sr-6 is presented in Figure 5.7. Significant differences from the flowsheet for Sr-4 were the substitution of DTPA for EDTA and the use of only one purification cycle. About 90 liters of 1BP were back-cycled to each 2000 liter feed batch. In addition, the solvent (used in the earlier runs) was continuously washed with a mixture of nitric and oxalic acids and recycled.

This run provided the first valid comparison of DTPA as a complexing agent. Before its use in the HSW, only a few laboratory experiments had been made showing its effect on distribution ratios. These data indicated that a mole per mole replacement of EDTA with DTPA would affect the strontium distribution very little but would depress the cerium distribution ratio about 100-fold at the optimum 4.7 pH. As shown in the run summary, given on page 5.21, definite improvement in cerium DF was obtained. Details are given in Table 5.5 in the Appendix.

First, and most significantly, the product from this one cycle DTPA process was within specifications with respect to all impurities. Second, the strontium losses, though about threefold higher than normal, were not excessive. This performance was achieved despite the use of reused solvent (part of it had received a radiation dose of over 300 watt-hours/liter) and operation at rates 10 to 20% above the rates used in previous runs.

The 1A column efficiency should have given lower strontium losses if flowsheet conditions were optimum. Conceivably the oxalic acid-nitric acid mixture used to wash the solvent during the run may have entrained to some extent with the 1AX and perhaps contributed to the 1A strontium loss through formation of a strontium oxalate precipitate.

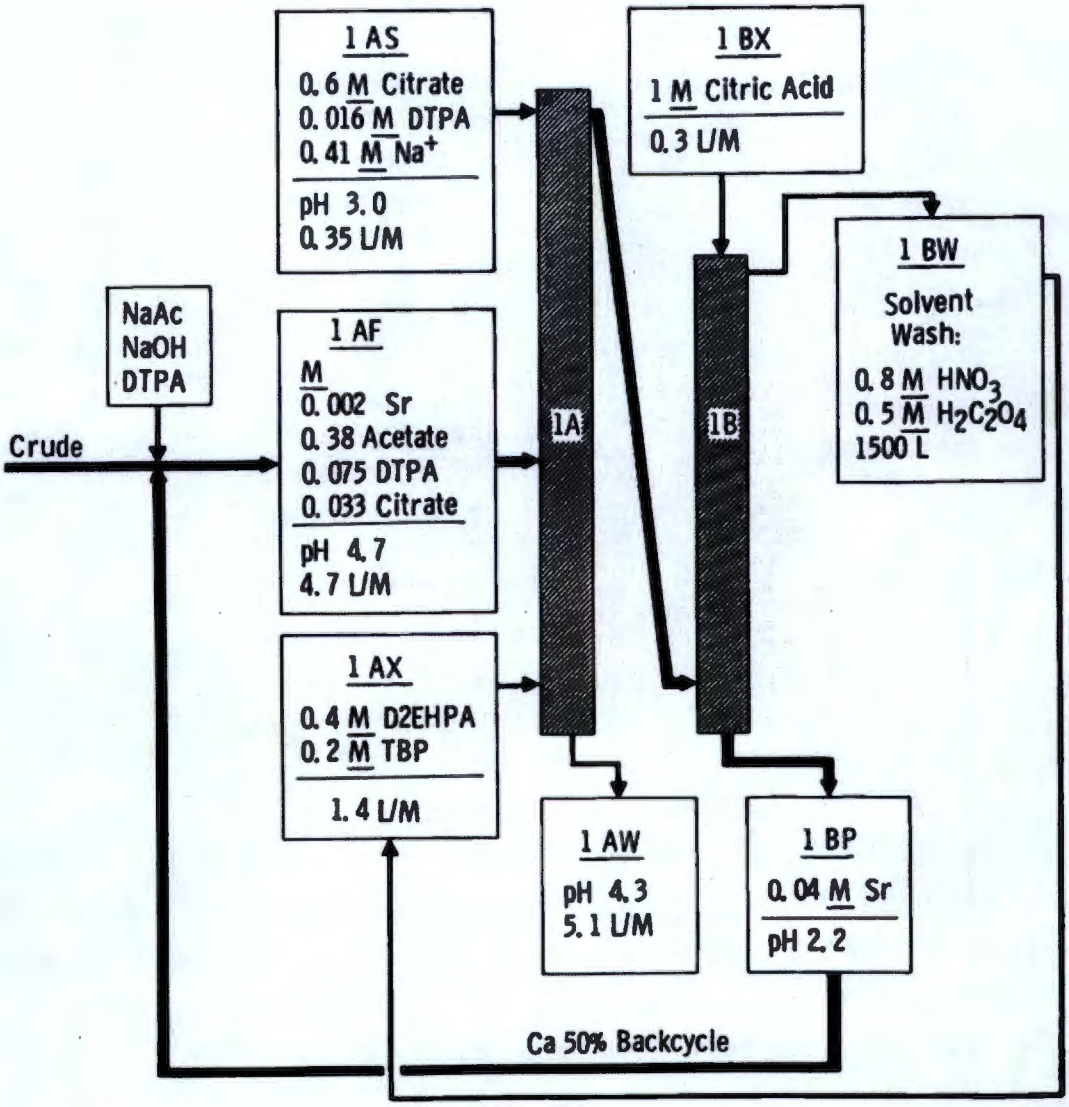

FIGURE 5.7

Sr-6 Flowsheet

Sr-6 Run Summary

Sr^{90} Input:	363 kilocuries
Sr^{90} Product:	305 kilocuries

	Column 1A	Column 1B	Overall
Strontium Loss, %	13	3	16
Strontium Product DF's:			
Ce^{144}	~24	~100	2400
$ZrNb^{95}$	>510	---	>1800
Ru^{106}	>30	---	>90
Calcium	--	40	40
Barium	9.4	---	9.4

Product Purity

Element	Curies/Curies Sr^{90} Actual	Curies/Curies Sr^{90} Specification	Grams/Grams Sr Total Actual	Grams/Grams Sr Total Specification
Ce^{144}	1.1×10^{-3}	$\leq 10^{-3}$	---	---
$ZrNb^{95}$	$<3.5 \times 10^{-5}$	$\leq 8 \times 10^{-4}$	---	---
Ru^{106}	$<7 \times 10^{-5}$	$\leq 6 \times 10^{-4}$	---	---
Calcium	---	---	0.020	<0.33
Barium	---	---	0.020	

At the end of the run, the citric acid product solution was concentrated twofold and allowed to sit undisturbed for about one month. During this period, radiation (which averaged 6.7 watts/liter) was expected to destroy over 99% of the citrate. However, at the end of this period, most of the strontium had precipitated and the system was highly buffered. Eventually, about 1200 gram-moles of nitric acid was added to insure dissolution of the precipitate (indicated by solution pH less than 3). This represented about one mole of nitric acid per mole initial citrate, or nearly four moles per equivalent of metal ion.

Laboratory work completed later (see Section 3) showed that irradiation of citric acid to 2000 watt-hours/liter gave rise to a complex mixture of organic decomposition products which exhibited similar buffer capacity and precipitate formation. Further irradiation to about 5200 watt-hours/liter appeared to convert the citrate completely to a carbonate. This dose for Sr-6 product should have been achieved after 32 days; however the experience described above indicates that the Sr-6 product was not yet to the ultimate carbonate form. The discrepancy between laboratory data and experience may have been due to depletion of radioactivity in the supernatant solution as the strontium precipitated or to the presence of nitrate ion in the laboratory experiment.

A rough calculation of the half-life of citric acid and its intermediate decomposition products was made based on the rate at which the specific gravity of the citric acid product solution decreased to its citrate-free, steady-state value. The plot on which the correlation is based is shown in Figure 5.10. From this, the half-life of the citric acid in the

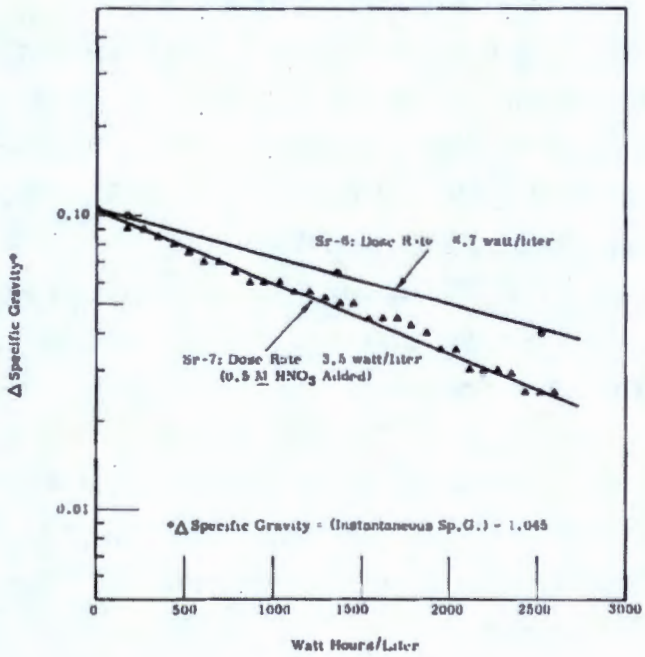

FIGURE 5.8

Estimation of Citric Acid Half-Life in Sr^{90} Product Storage
Initially 2M Citric Acid

product from Sr-6 was estimated to be 2000 watt-hours/liter. The product from Sr-7 was stored similarly but with 0.6M HNO_3 added initially. Its apparent half-life was 1300 watt-hours/liter, possibly indicating that nitric acid or nitrate ion accelerated the decomposition rate. These half-lives agree with those reported in Section 3 (p. 3.21).

RUN Sr-7

This run had the dual objectives of recovering strontium and also investigating some of the technology involved in recovering cerium and a cerium-free rare earth fraction. The flowsheet designed to accomplish this had the following unique features and expectations.

1. Citric acid was employed as the complexing agent for lead and fission products other than strontium and rare earths. Only enough EDTA was added to complex iron. The citric acid was supplied by the 1AS and by product backcycle from the 1BP stream (ca 230 liters per 2000 liter batch). The pH and flow ratios were adjusted so that both strontium and rare earths would be extracted.
2. The D2EHPA concentration was increased to 0.47M, for improved extraction by adding fresh D2EHPA to used solvent.
3. The strontium product from the conventional citric acid strip in the 1B column was diluted, butted with DTPA and acetate, and fed to a second cycle for final purification. A total nitric acid strip was employed in the 2B column.
4. The solvent from the 1B column, containing the rare earths, was batch-stripped with 1.6M nitric acid. Then about 0.07M $KMnO_4$ was added to oxidize cerium to cerium(IV) which was then extracted into fresh solvent (0.4M D2EHPA). Before phase separation, the MnO_2 and excess permanganate ion were killed with citric acid to improve the separation. The final aqueous phase should contain the rare earths (cerium-free) contaminated with considerable calcium and manganese.
5. The solvent phase from above, which should have contained over 99% of the cerium, was contacted with a solution of 1.7M HNO_3 - 0.3M H_2O_2. Under these conditions hydrogen peroxide reduces

cerium(IV) to aqueous-favoring cerium(III). The cerium at this point should be virtually free of all feed impurities with the exception of a small amount of yttrium. The cerium separation steps above were derived from the Oak Ridge National Laboratory procedure.[10]

The above flowsheet, which is presented in Figure 5.9 was operated according to plans; however, some of the results were unexpected and required the operation of three additional cycles for strontium recovery and purification, as shown in Figure 5.10. In particular, maloperation of the 1B column diverted 23% of the strontium to the 1BW, and a similar incident in the second cycle put an additional 37% in the 2BW. The third solvent extraction cycle was added to extract the calcium, manganese, and rare earths away from 1BW strontium (after the cerium removal step) using a pH 2.8 feed buffered with citric acid. The fourth cycle was used to extract and purify the strontium from the third cycle raffinate and from the 2BW solvent wash, using a conventional DTPA-complexed feed and a nitric acid strip. After these steps were completed, it was found that neither of the strontium products met specifications; consequently, a fifth cycle (similar to the fourth cycle except using a citric acid strip) was added to reprocess the combined 2BP and 4BP. New solvent was used in these final cycles.

The overall results of the run are summarized in the table on Page 5.27. Detailed results will be found in Table 5.6 in the Appendix.

Only 40 to 60 kilocuries of Sr^{90} (about 10% of the input) was lost in the aqueous raffinates and discarded. The stripping column losses were recovered in subsequent cycles. They were attributed to inefficient operation of the B column.

The reason for poor recovery of cerium and promethium has not yet been resolved. Evidently only about half of the rare earths extracted in the 1A column; however, no more than 14% of the cerium and promethium was found in the 1AW. The discrepancy may be due to precipitation with some unknown precipitating agent or to laboratory analytical difficulties.

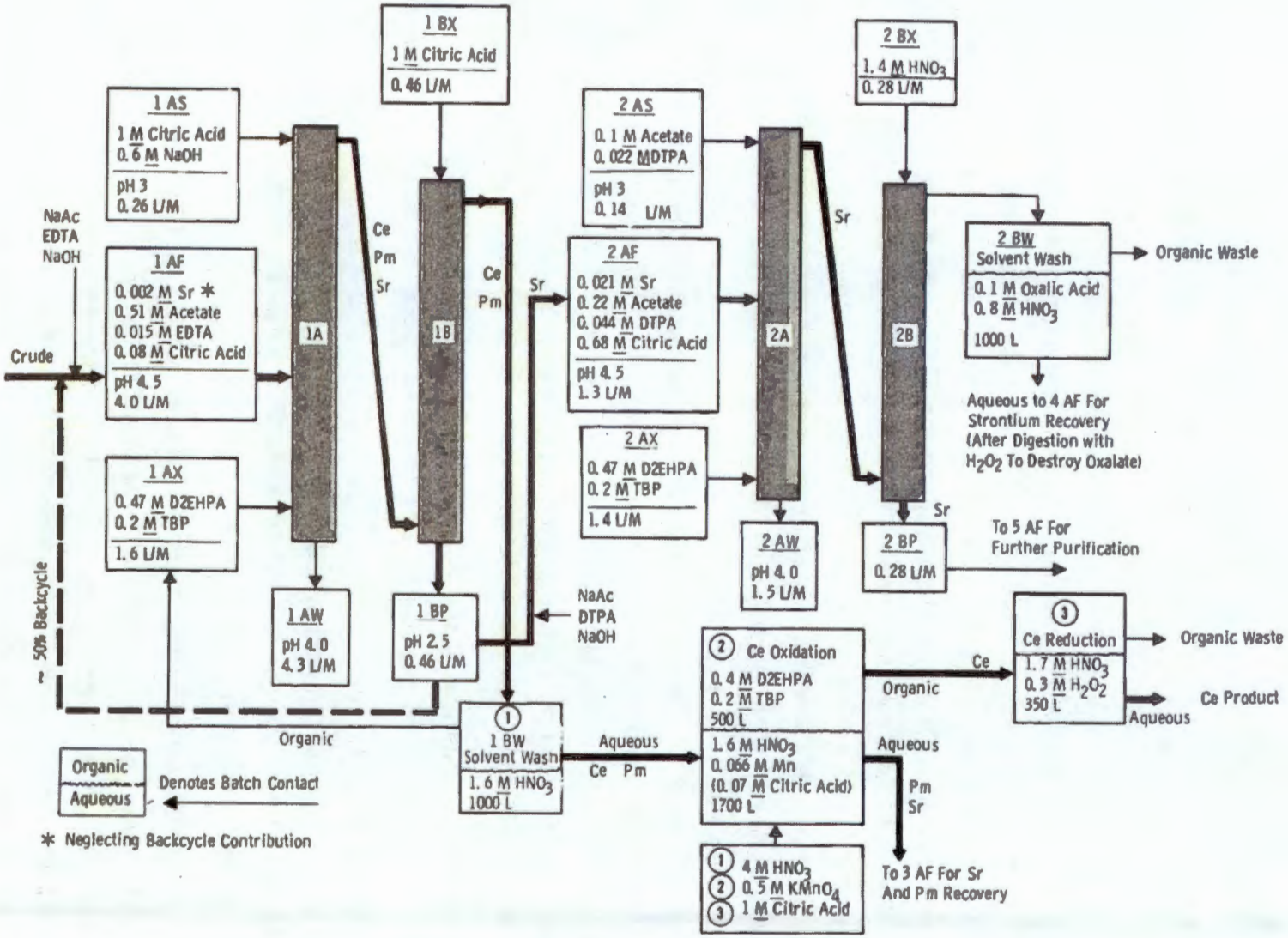

FIGURE 5.9

Sr-7 Flowsheet, Part 1

ASC-GE RICHLAND, WASH.

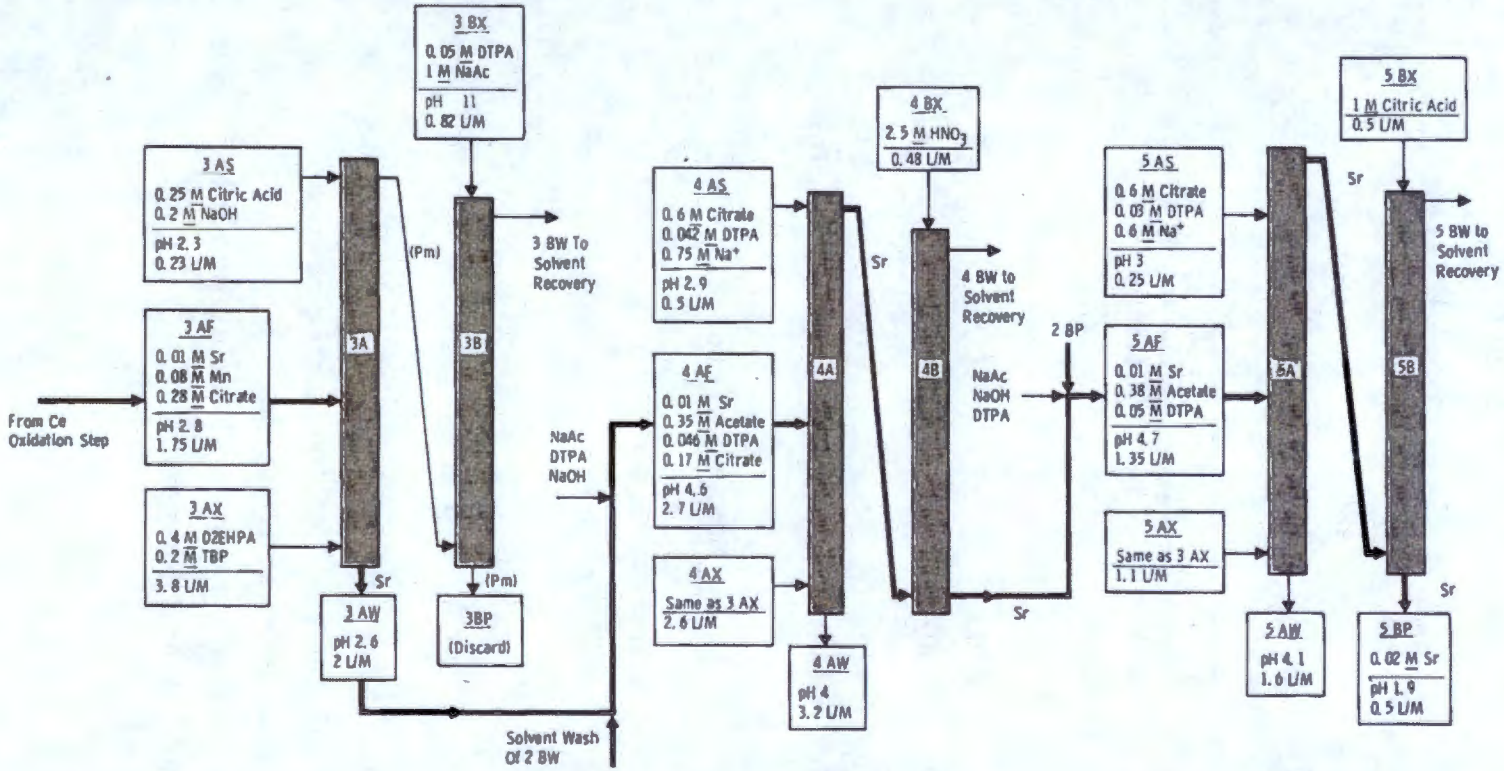

FIGURE 5.10

Sr-7 Flowsheet, Part 2

4-68 PACIFIC, WASH

Sr-7 Run Summary

	Kilocuries		
	Sr^{90}	Ce^{144}	Pm^{147}
Input	480	660	120
Product	420[a]	310	24

	Kilocuries					
Cycle	1	2	Ce[b]	3	4	5
Sr^{90} Input	480	350	(110)	110	260	280
Sr^{90} Product	350	180	110	90	110	250
Sr^{90} Loss[c]	39	4	3	---	7	7
Ce^{144} Input	660	5	(315)	5	60	20
Ce^{144} Product	(330)	---	310	---	---	---
Pm^{147} Input	120	< 1	(60)	24	4	---
Pm^{147} Product	(60)	---	24	(8)	---	---

	Strontium Product DF's					
Cycle	1	2	3	4	5	Overall
Ce^{144}	100	0.4	1.5	1.6	42	780
$ZrNb^{95}$	>400	---	---	---	---	>550
Ru^{106}	---	---	---	---	---	> 7
Calcium	10	2.4	---	---	7.8	70
Barium	(0.09)	2.4	---	---	5	(2)
Manganese	---	---	---	---	15	120

(a) Include 170 kilocuries of Sr^{90} requiring rework

(b) Cerium oxidation-extraction cycle

(c) In aqueous waste stream only. Essentially all Sr^{90} in the organic wastes was reworked or held for rework.

In addition, some of the rare earths (20 to 50%) appeared to be fixed in the solvent and were not removed by the 1.6M HNO_3 wash. A second wash with 3 to 4M HNO_3 removed most of the cerium but evidently little of the promethium.

The permanganate oxidation of cerium was satisfactorily accomplished, giving a DF of 70 from cerium in the promethium fraction. An excess of permanganate was added to compensate for an estimated 0.2% citric acid carry over with the 1BW. The following reactions were assumed:

1. $MnO_4^- + 3\ Ce^{+++} + 4\ H^+ \rightleftharpoons MnO_2 + 3\ Ce^{++++} + 2\ H_2O$
2. $18\ MnO_4^- + 5\ C_6H_8O_7 + 54\ H^+ \rightarrow 18\ Mn^{++} + 30\ CO_2 + 47\ H_2O$
3. $9\ MnO_2 + C_6H_8O_7 + 18\ H^+ \rightarrow 9\ Mn^{++} + 6\ CO_2 + 13\ H_2O$

No difficulties were observed in the subsequent reduction of cerium(IV) with H_2O_2-HNO_3. Because of volume limitations, the 500 liters of cerium(IV)-containing solvent was contacted with four successive portions of the reducing mixture totaling 350 liters. The depleted solvent could not be sampled, but the aqueous strips were believed to have removed over 95% of the cerium.

The third cycle, used to extract the promethium fraction away from the strontium, was also intended to purify the promethium fraction from calcium and manganese. For this purpose, the 3B column used sodium acetate containing DTPA as the stripping agent, self buffered at pH 4.0-4.5. Under these conditions, promethium and rare earths should be stripped preferentially. Unfortunately, the 3B proved to be almost inoperable with this flowsheet because of column flooding, and the attempt to partition promethium was unsuccessful. On a material balance basis, of the 24 kilocuries of promethium entering in the 3BF, 2.5 were found in the 3AW, 8.1 in the 3AP, 7.7 in the 3BW, and only 2.5 in the 3BP. The promethium in the effluent streams added up to only 50% of that entering the system.

The solvent wastes, which made up a large portion of the feed to the fourth cycle, contained oxalic acid which on feed pH adjustment would have

caused strontium precipitation. To prevent this, the oxalate was destroyed by adding 0.4M H_2O_2, digesting the solution at 80 C for 2 hours, and finally boiling for 1 hour. Low waste losses were obtained in the extraction column, but the column was much more frequency sensitive than in previous runs and was finally operated at 27 cycles/minute, about half the expected frequency. Similar behavior was observed in the second cycle using old solvent, and it is possible that the reduced stability was caused by degraded solvent entrained with the solvent washes.

The products from both the second and fourth cycles contained excessive cerium and nonradioactive impurities; consequently, the final cycle was designed for maximum decontamination using DTPA in the feed and a citric acid strip. The following table of product purities demonstrates the performance of this cycle:

Sr-7 Product Purity - Fifth Cycle Performance

	Curies/Curie Sr^{90}			Grams/Grams Sr Total		
Element	Input	Product	Specification	Input	Product	Specification
Ce^{144}	0.100	0.0018	≤0.001	---	---	---
$ZrNb^{95}$	<0.002	<3 x 15^4	≤8 x 10^{-4}	---	---	---
Ru^{106}	<0.004	<5 x 10^{-4}	≤6 x 10^{-4}	---	---	---
Calcium	---	---	---	0.22	0.03	
Barium	---	---	---	0.25	0.05	<0.33
Manganese	---	---	---	0.14	0.009	

The cerium was still slightly high, but with the available decay time it would meet the required specification.

There is no ready explanation for the high impurity contamination in the fifth cycle feed. Evidently, it was picked up from solvent washes and/or from use of contaminated processing equipment or storage tanks. The barium behavior throughout the process was especially mystifying; the first cycle product, for example, contained eight times more barium than was believed to be in the feed.

In addition to the final product, an impure product derived from a 6M HNO_3 wash of the 3BW and 4BW was held for rework. This product had the final composition shown below:

Sr-7 Rework Product Composition

	Kilocuries	Grams
Sr^{90}	165	1160
Ce^{144}	~80	--
$ZrNb^{95}$	< 0.05	--
Ru^{106}	< 0.09	--
Calcium	---	2350
Barium	---	690
Manganese	---	4150
Iron	---	400

The strontium was recovered and purified after the conclusion of the Interim Program by batch solvent extraction.

SOLVENT TREATMENT

During the runs, the solvent was treated in one of three ways. It was either stored without washing or reuse, washed batchwise with 1 to 6M HNO_3, or washed batchwise with a mixture of oxalic and nitric acids (typically 0.2 to 0.5M oxalic acid, 0.5 to 0.8M HNO_3). The latter method provided the best cleanup for cerium activity, but the run (Sr-6) using this method had a strontium loss about threefold higher than normal. Conceivably, this loss could have been caused by oxalate entrainment in the solvent. One factor involving any choice of wash reagent was the ease of recovering strontium from the solvent wash solution if B Column losses were encountered. The difficulty increases with increasing nitric acid concentration and with the addition of complexing reagents such as oxalate. Fortunately, oxalate can readily be destroyed by peroxide digestion, as described in the Sr-7 discussion.

Investigation of other, more severe solvent cleanup methods was restricted to cleanup tests on the solvent waste from Sr 5 (first cycle). This solvent received about 300 watt hour/liter of radiation from cerium before washing operations were initiated. The first attempt at washing involved successive contacts with a 4.4M NaOH - 0.1M EDTA solution and a 4.4M HNO_3 solution in the A and B Columns. The column operation was difficult to control and resulted in a cerium DF of only about 10. Additional consecutive batch washes with 1M NaOH - 0.1M EDTA and with 1M HNO_3 - 0.5M oxalic acid gave additional cerium DF's of 60 and 10, respectively, for an overall DF of 7000.

Laboratory studies (see Section 3) indicated that basic solutions of EDTA and DTPA were very effective washing agents; however, such washes convert the solvent to the sodium form which must then be acidified to the more desirable acid form for reuse. Generally adequate cerium removal could be obtained by using an oxalic acid wash alone. The effectiveness of such a wash was decreased by adding nitric acid to prevent strontium precipitation. The following typical cerium DF's were obtained by equal volume contacts with once-washed Sr 5 solvent; additional washing tests with this same solvent are presented in Section 3.

Results of Laboratory Solvent Washes

Reagent	Cerium DF
2M HNO_3	4.7
1M HNO_3 - 0.5M tartaric acid	26
1M HNO_3 - 0.5M oxalic acid	160
0.5M oxalic acid	800
1.5M oxalic acid	200

Final solvent cleanup at the end of the campaign was satisfactorily carried out using both types of washes. The strontium and cerium activities in the most heavily reused solvent were reduced to less than 0.02 curies/liter, suitable for discharge to specific-retention cribs.

PLANT AND EQUIPMENT PERFORMANCE

The Hot Semiworks was operated by a crew of six engineers and nine technologists on a five day week shift coverage. Two to four people were used per shift commensurate with the work load. Runs were made on a program basis with preparations, product handling, flushing, maintenance, etc. being conducted between programs.

From the maintenance standpoint, the plant was operable about 70% of the time during the five month operating period; however, during that period it was only necessary to operate the columns 15 to 20% of the time for processing. The instantaneous capacity of the plant for strontium recovery was about 80 kilocuries per day during the program; the actual experience, factoring in recycle, maintenance, experimentation, and between run operations was about 240 kilocuries per month. However, these figures do not lend themselves to future extrapolation because of the short operating basis and the unpredictable nature of a contact operated facility.

SOLVENT EXTRACTION COLUMNS

On a typical flowsheet such as the one cycle Sr-6, the general operating ranges for the pulse amplitude and frequency of the columns were about 0.8 inches and 60-70 cycles/minute for the A Column and 1.0 inch and 60-70 cycles/minute for the B Column. Flooding could generally be expected at about 70 cycles/minute for the A Column and 75 cycles/minute for the B Column. A typical volume velocity, sum of both phases, was 1000 gal/hr-ft^2 for the A Column at an A/O of 4.0. For the B Column the volume velocity was about 300 gal/hr ft^2 at an A/O of 0.25. Detailed operating conditions are indicated in Tables 5.3 through 5.6 (in Appendix).

ION EXCHANGE

A total of about 34 hours was required to complete the ion exchange loading and elution cycle. Loading of 200 kilocuries of Sr^{90} onto the column after the resin was converted to the sodium form took about 12 hours; scrubbing, 8 hours; and eluting, about 6 hours. Cleanup washing of the resin required about 8 hours.

WASTE HANDLING

During the operations, about 16,000 gallons of crude were processed through the plant. From this a total of about 50,000 gallons of dilute wastes, including the decontamination flushes, were discharged to tank farm storage. This averaged about 40 gallons per kilocurie or nearly 10,000 gallons per month. Condensates to cribs averaged 100 gallons per kilocurie for a total of 111,000 gallons. The disposal of organic to specific retention cribs at the end of the program was about 2000 gallons.

PULSERS

Remotely driven, long shaft piston pulse generators (Figure 5.11) were used in the strontium program to eliminate leakage and seal problems experienced with conventional piston or bellows pulsers. Basically, the pulser consisted of a standard cam-vari-speed power unit connected to the drive rod through a rocker arm adjustable to provide variable amplitude settings. The drive rod penetrated the roof of the cell through a liquid seal and extended to the graphite piston, located near the bottom of the column to avoid cavitation. A hydraulic balance, maintained between the pulse leg and the column, was monitored through a common flush-and-weight-factor line.

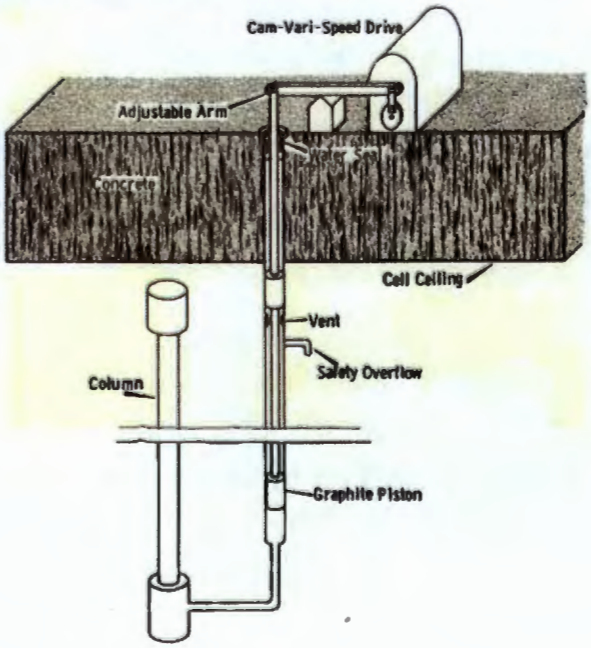

FIGURE 5.11

Hot Semiworks Long Vertical Shaft Piston Pulser

No pulser problems were encountered throughout the processing program. The radiation directly over the rod was less than 6 mr/hr, and if it had been necessary, the piston and drive rod could have been removed through the roof without entry into the cell. The pulsing mechanism was fully accessible.

PUMPS

All pumping was performed by modified canned-rotor, process-lubricated pumps (Figure 5.12). The modifications included the addition of hydroclones on the bearing coolant-lubricant line to eliminate solids and the installation of tapered bearings on the critical feed pumps. The two aqueous feed pumps were installed in a typical Hanford remote fashion to permit removal without decontamination (the only equipment so installed at the Hot Semiworks). The piping to the pumps was duplicated to permit use of either pump as the principal feed pump.

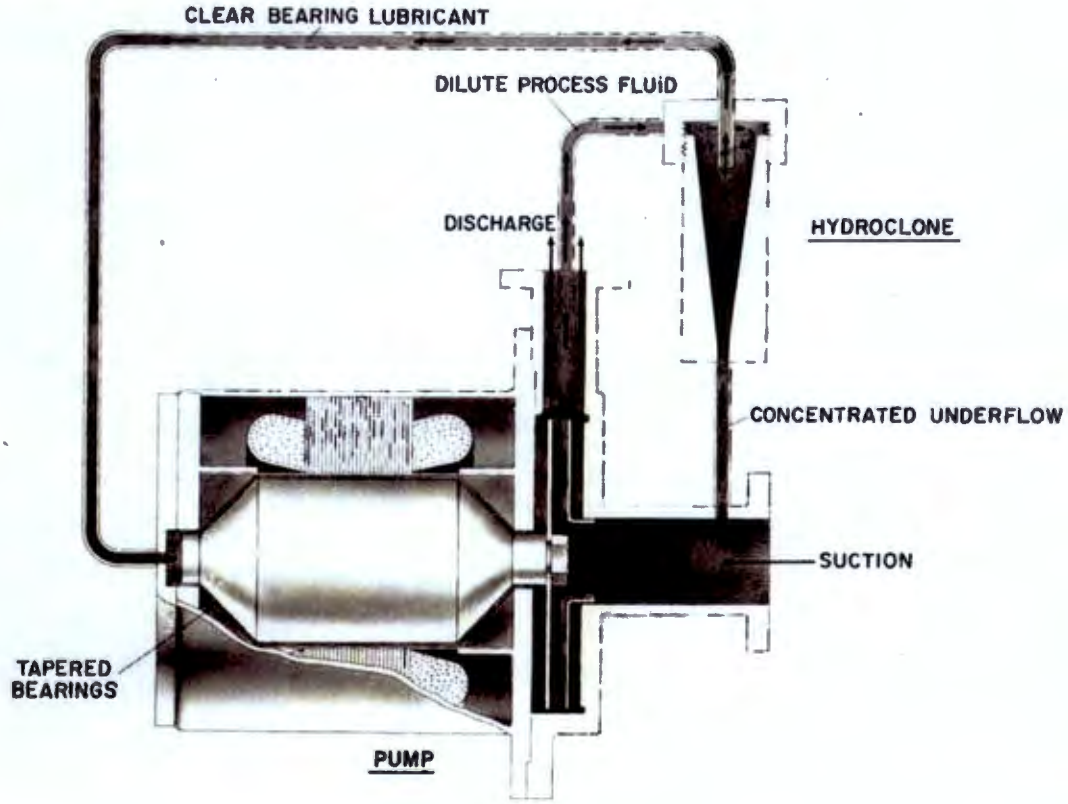

FIGURE 5.12
Hydroclone Canned Motor Pump

The first two feed pumps failed in the early runs by vibrational loosening of the bearings. The next set of pumps was corrected and reinstalled with thermocouples attached to the pump and recirculation lines to detect any recirculation difficulties or pump overheating before it became critical. The reinstalled pumps operated through the remainder of the program (some 350 hours) without difficulty. Although some bearing cooling restrictions developed, flushes and cyclic heating seemed to alleviate any critical problems.

The solvent pumps, with straight bearings, gave excellent service for the short term program.

INSTRUMENTS

Reliable service was generally received from instrumentation and flow control systems. However, valve and rotometers became restricted to the extent that decontamination of the column area was necessary to manually remove the restrictions. Other flow schemes, such as continuous air lift transfer from boiling waste concentrators, were very satisfactory.

Since the process was pH sensitive, commercial pH cells in-line with the recirculating samplers were used to monitor pH. Considerable difficulty was experienced in maintaining the pH units in an operable condition. The reason for the repetitive probe failures was not determined.

TANK AGITATORS

The tank agitators, many of them originally installed in 1952, gave good service. The only agitator that failed was installed in the waste concentrator just before the strontium program. Although the cause of failure has not been determined, it is postulated that vapors or liquid must have moved through the air purge seal and into the bearing housing to cause a seizure.

VENTILATION

Ventilation and off gas handling in the Hot Semiworks was a serious problem because of the high Sr^{90} concentrations. The process

vessel off-gas system from A Cell (product and waste handling) was routed through a de-entraining tower, a condenser, knockout pot, preheater, a multilayered fiber glass bed, and finally through an absolute CWS filter to a vacuum jet which maintained all of the tank pressures negative relative to the cell atmosphere. Particulate separation with this system was quite adequate. However, the other process vent systems in B and C Cells were designed for atmospheric discharge directly to the main ventilation tunnel. From there, the ventilation air from the cells passed through a large multilayered fiberglass filter and was then routed through a bank of CWS absolute filters. Some Sr^{90} emission was evident through this system during the operating periods, but further testing is needed to define the entire problem.

RADIATION LEVELS AND DECONTAMINATION

Radiation within the cells during processing varied from 6 r/hour in the solvent handling cell to 100 r/hour in the feed and product cell. The level in the column cell was reduced to a general 100 mr/hour during maintenance work by using repetitive heated flushes of 6% sodium hydroxide with 1.5% sodium tartrate, 5% oxalic acid, and 5 to 30% nitric acid. Although no definite leaks could be found within the cell, the external beta activity was severe and external washing of the equipment with similar flushes was also required. The field readings were then reduced with localized shielding of plywood, lucite or lead sheets. Because of precautionary measures, external radiation exposure was not a controlling restriction on operations. The average cumulative individual exposure for the entire 5 month program was about 1 rem, including 325 mr. The maximum cumulative individual exposure was only 1.4 rem, including 500 mr.

PRODUCT LOADOUT

The product loadout cell was 7 by 10 by 9 feet deep, located below ground level and adjacent to the precipitation tank in A Cell. The filter cask was placed inside of the stainless-steel-lined cell and connected to lines from A Cell. Vacuum was used to transfer the solution through the filter cask and back into a collection tank in A Cell. Provision was also included

for venting, back flushing, or slurry and dissolution of the filter cask contents. Other auxiliary services included temperature monitoring, air sampling, ventilation to A Cell, jets, and ball valves,

Only one loadout was made during the program. It involved the precipitation of the desired quantity of strontium solution (Sr-4 product) with potassium bicarbonate and digestion at 80 C for at least 2 hours to promote crystal growth and excess carbonate removal. The cooled and agitated slurry was then vacuum transferred through the cask filter and the filtrate was collected for sampling. Subsequently, to remove sodium, the material was slurried back into the precipitation tank, water washed, and then refiltered again into the cask. The agitator did not reach to the bottom of the precipitation tank; consequently, only about 75% of the material in any one strike was capable of being loaded onto the filter. The potassium bicarbonate strike was quite effective in producing a filterable product without the use of filter aids. Filtration and washing through the stainless steel screen, rated to retain particles greater than 10 μ, resulted in a loss of only 5% of the product to the combined filtrate and washes.

A 10 hour drying period was then used with electrical and steam heat applied to the cask to remove traces of moisture. This proved adequate to prevent pressure buildup after the cask was sealed. Shipment proceeded uneventfully.

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APPENDIX

TABLE 2.1

TENTATIVE EQUILIBRIUM CONSTANTS

Solvent: 0.37M D2EHPA - 0.2M TBP - Shell E-2342 Diluent

Temperature: 25 ± 1 C

Ion	K_1 (a)	K_2 (b)
Na^+	1.1×10^{-4}	4×10^{-10}
Sr^{++}	2.5×10^{-4}	---
Ca^{++}	4.6×10^{-2}	---
Mn^{++}	6.0×10^{-3}	---
Ce^{+++}	0.7	---
Pm^{+++}	2	---

(a) For extraction according to Equation (2).

(b) For extraction of sodium according to Equation (11).

TABLE 2. 2

D2EHPA EQUILIBRIUM DATA

10 minute contact at 25 C, A/O = 1. Shell E-2342 used as diluent. Na^{22} and Sr^{85} tracers added; nitrate anions except where replaced by indicated ligands.

I. Sodium Equilibrium Data

Initial Compositions					
Aqueous Phase		Organic Phase		Equilibrium	
pH	M Na^+	M D2EHPA	M TBP	pH	Na K_d
--	0.1	0.368	0.2	3.1	0.0235
--	0.2	0.368	0.2	2.9	0.0158
--	0.2	0.368	0.2	5.05	0.909
11.5	1.2	0.368	0	3.12	0.0214
11.8	1.2	0.368	0	4.05	0.0768
11.95	1.2	0.368	0	4.65	0.168
2.1	1.2	0.368	0.2	2.1	0.00204
5.45	1.2	0.368	0.2	2.42	0.00474
5.45	1.2	0.368	0.2	2.48	0.00497
11.5	1.2	0.368	0.2	3.15	0.0192
11.5	1.2	0.368	0.2	3.10	0.0201
11.6	1.2	0.368	0.2	3.55	0.0314
11.6	1.2	0.368	0.2	3.50	0.0324
--	1.2	0.368	0.2	4.0	0.0642
11.8	1.2	0.368	0.2	4.15	0.0642
11.8	1.2	0.368	0.2	3.90	0.0614
11.95	1.2	0.368	0.2	4.50	0.168
11.95	1.2	0.368	0.2	4.60	0.166
11.95	1.2	0.368	0.2	5.98	0.380
11.95	1.2	0.368	0.2	6.00	0.407
11.95	1.2	0.368	0.2	12.2	0.405
11.95	1.2	0.368	0.2	12.1	0.420
11.6	1.2	0.736	0.2	2.68	0.0192
11.8	1.2	0.736	0.2	3.92	0.176
--	1.2	0.736	0.2	4.0	0.177
11.95	1.2	0.736	0.2	4.6	0.395
--	1.2	1.104	0.2	4.1	0.405

TABLE 2.2 (contd.)

II. Strontium Equilibrium Data

In all cases initial organic phase was 0.368M D2EHPA - 0.2M TBP - Shell E-2342

Initial Aqueous Phase Composition									Equilibrium			Calculated
pH	M Sr^{++}	M Ca^{++}	M Na^{+}	M Acetate	M Citrate	M HEDTA	M EDTA	M DTPA	pH	Sr E_a^o	Na K_d	M Free D2EHP*
2.98	0.05	0	1.20	0.50	0	0	0	0	2.22	0.19	0.0026	0.336
3.5	0.05	0	1.20	0.50	0	0	0	0	2.62	0.68	0.0070	0.287
4.05	0.05	0	1.20	0.50	0	0	0	0	3.5	6.22	0.0164	0.196
4.5	0.05	0	1.20	0.50	0	0	0	0	4.1	20.5	0.0320	0.177
5.0	0.05	0	1.20	0.50	0	0	0	0	4.5	30.4	0.0543	0.174
5.5	0.05	0	1.20	0.50	0	0	0	0	4.7	32.7	0.0909	0.174
4.0	0.033	0.0071	1.29	0	0.95	0	0	0	4.1	2.41	--	0.247
4.25	0.033	0.0070	1.46	0	0.94	0	0	0	4.25	2.16	--	0.251
4.5	0.033	0.0070	1.63	0	0.93	0	0	0	4.55	1.19	--	0.270
5.0	0.032	0.0068	2.04	0	0.91	0	0	0	4.85	0.382	--	0.307
2.5	0.05	0	1.20	0.50	0	0.05	0	0	2.15	0.207	0.0034	0.334
3.0	0.05	0	1.20	0.50	0	0.05	0	0	2.35	0.417	0.0044	0.309
3.5	0.05	0	1.20	0.50	0	0.05	0	0	2.7	1.09	0.0093	0.264
4.0	0.05	0	1.20	0.50	0	0.05	0	0	3.4	5.22	0.0156	0.200
4.5	0.05	0	1.20	0.50	0	0.05	0	0	4.05	15.9	0.0297	0.180
5.0	0.05	0	1.20	0.50	0	0.05	0	0	4.50	21.3	0.0566	0.177
5.5	0.05	0	1.20	0.50	0	0.05	0	0	4.75	16.2	0.0838	0.180
2.5	0.05	0	1.20	0.50	0	0.10	0	0	2.3	0.306	0.0044	0.321
3.0	0.05	0	1.20	0.50	0	0.10	0	0	2.5	0.540	0.0051	0.298
3.5	0.05	0	1.20	0.50	0	0.10	0	0	2.9	1.44	0.0097	0.250
4.0	0.05	0	1.20	0.50	0	0.10	0	0	3.5	5.29	0.0153	0.200
4.5	0.05	0	1.20	0.50	0	0.10	0	0	4.2	15.3	0.0330	0.180
5.0	0.05	0	1.20	0.50	0	0.10	0	0	4.6	16.4	0.0625	0.180
5.5	0.05	0	1.20	0.50	0	0.10	0	0	4.82	9.98	0.0988	0.186
--	0.0014	0.0284	1.21	0.40	0	0	0.0293	0	4.1	37.3	--	0.249
--	0.0014	0.0284	1.21	0.40	0	0	0.0293	0	4.3	45.5	--	0.249
--	0.0014	0.0284	1.21	0.40	0	0	0.0293	0	4.8	26.5	--	0.249
3.4	0.05	0	1.20	0.50	0	0	0.05	0	2.75	1.01	0.0084	0.267
4.0	0.05	0	1.20	0.50	0	0	0.05	0	3.4	4.18	0.0143	0.207
4.48	0.05	0	1.20	0.50	0	0	0.05	0	4.0	12.9	0.0289	0.182
5.0	0.05	0	1.20	0.50	0	0	0.05	0	4.5	17.2	0.0601	0.179
5.42	0.05	0	1.20	0.50	0	0	0.05	0	4.85	10.0	0.0886	0.186
3.5	0.05	0	1.20	0.50	0	0	0.10	0	2.95	1.36	0.0108	0.253
4.08	0.05	0	1.20	0.50	0	0	0.10	0	3.52	4.66	0.0206	0.203
4.38	0.05	0	1.20	0.50	0	0	0.10	0	4.05	10.9	0.0307	0.185
4.8	0.05	0	1.20	0.50	0	0	0.10	0	4.55	11.0	0.0573	0.185
5.55	0.05	0	1.20	0.50	0	0	0.10	0	4.9	5.7	0.116	0.198
--	0.0014	0.0293	1.21	0.40	0	0	0	0.0293	4.0	42.0	--	0.245
--	0.0014	0.0293	1.21	0.40	0	0	0	0.0293	4.3	54.7	--	0.245
--	0.0014	0.0293	1.21	0.40	0	0	0	0.0293	4.7	45.1	--	0.245

*Fee D2EHP = 0.368 - 4(M Sr)$_o$ - 4(M Ca)$_o$

48C-48 RICHLAND, WASH.

TABLE 2.3

SELECTED ACID DISSOCIATION AND STABILITY CONSTANTS

(Log Stability Constants, 20-30 C)

	Hydroxyacetate	Acetate[2]	Citrate[2]	HEDTA[12, 27]	EDTA[2, 13]	DTPA[11,13,19]
pK_1	3.82	4.64	3.057	2.64	1.99	1.79
pK_2		--	4.759	5.33	2.67	2.56
pK_3		--	6.400	9.73	6.16	4.42
pK_4		--	--	--	10.26	8.76
pK_5		--	--	--	--	10.42
Fe^{+3}		--	11.85	--	25.1	28.6
Ni^{+2}		0.74	--	17.0	18.62	20.2
Y^{+3}		--	--	14.49	18.09	22.40
Pb^{+2}		2.52	6.50	--	18.04	--
Al^{+3}		--	--	--	16.13	--
Eu^{+3}		--	--	15.21	17.35	22.91
Ce^{+3}		1.68	--	14.08	16.0	20.24
La^{+3}		--	--	13.22	15.5	19.96
Mn^{+2}		--	--	10.7	14.04	15.1
Ca^{+2}		0.53	4.85	8.0	10.70	10.74
Sr^{+2}		0.43	2.85	--	8.63	9.68
Ba^{+2}		0.39	2.84	--	7.76	8.63

TABLE 2.4

SAMPLE CALCULATION OF STRONTIUM E_a^o

1A COLUMN FEED POINT CONDITIONS

See Figure 4.1, Section 4, for flowsheet description.

1. Initial Aqueous Phase Composition:

	Feed	Scrub	Combined Feed and Scrub
M Sr	0.0016	0	0.0015
M Ca	0.004	0	0.0038
M Na	1.1	0.3	1.06*
M Fe + Pb	0.033	0	0.031
M Acetate	0.46	0	0.435
M EDTA	0.09	0	0.085
M Citrate	0	0.6	0.033
pH	4.7	2.9	(4.7)*
Volume	130	7.5	137.5

*Assumed equilibrium values

2. Solvent Composition: 0.4M D2EHPA, 0.2M TBP; Volume = 30

3. Free D2EHP: (Assume only strontium and calcium extract and that their extraction is quantitative.)

$$M\ (Sr + Ca)_a = 0.0053$$

$$M\ (Sr + Ca)_o = \frac{(0.0053)(137.5)}{30} = 0.0243$$

$$M \text{ free D2EHP} = 0.4 - 4(0.0243) = 0.303$$

4. Ideal Strontium K_d:

From Figure 2.3, using $Na^+ = 1.06$ and pH = 4.7,

$$Sr\ K_d/(\text{free D2EHP})^2 = 2000$$

$$(\text{Free D2EHP})^2 = (0.303)^2 = 0.0918$$

$$\therefore Sr K_d = (2000)(0.0918) = 184$$

5. "Free" Ligand Concentration, (L_n):

(Assume all iron and lead are complexed by EDTA)

Free EDTA = 0.085 - 0.031 = 0.054M

Free Citrate = 0.033M = total citrate

Free Acetate = 0.435M = total acetate

6. Correction Factor for Ligand Complexing:

From Figure 2.5, using the feed pH of 4.7,

$K'_{EDTA} = 60$ and $(K'L)_{EDTA} = (60)(0.054) = 3.2$

$K'_{Citrate} = 100$ and $(K'L)_{Citrate} = (100)(0.033) = 3.3$

$K'_{Acetate} = 1.5$ and $(K'L)_{Acetate} = (1.5)(0.435) = 0.7$

$\therefore\ 1 + \Sigma(K'L) = 8.2$

7. Corrected Strontium E_a^o

$$Sr\ E_a^o = \frac{Sr\ K_d}{1 + \Sigma(K'L)}$$

$$= \frac{184}{8.2} = 22.$$

This should represent the minimum Sr E_a^o in the extraction section. (Note: because the free D2EHP concentration in the above calculation was nearly double the free D2EHP concentration used to derive the correlation, a more conservative (and probably more nearly correct) value for the Sr E_a^o would be about 13, or 60% of the calculated value.)

TABLE 4.1

PULSE COLUMN CARTRIDGE DESCRIPTION

A. 1A Column (All nozzle-plate cartridges)

Cartridge No.:	1	2	3	4	5	6
Run No.:	1 through 19	20 through 37	38 through 64	65 and 66	67*	68 through 76*
Scrub Section						
Height, ft	6	6	6	12	12	9
Plate Spacing, in.	3	3	4	4	4	4
Hole Diam., in.	3/16	3/16	3/16	3/16	3/16	1/8
% Free Area	23	23	23	23	23	10
Nozzles Point	Down	Up	Up	Up	Down	Down
Extraction Section						
Height, ft	12	12	12	6	6	9
Plate Spacing, in.	2	2	4	4	4	4
Hole Diam., in.	3/16	3/16	3/16	3/16	3/16	3/16
% Free Area	23	23	23	23	23	23
Nozzles Point	Down	Up	Up	Up	Down	Down

*22% free area louver plates inserted at 2 ft intervals in scrub section

B. 1B Column

Cartridge No.:	1	2
Run No.:	1 through 6c	Remaining
Height, ft.	10	10
Plate Spacing, in.	4	4
Hole Diam., in.	3/16	1/8
% Free Area	33	10
Type of Plate	SS Sieve	Nozzle
Nozzles Point	--	Up

TABLE 4.2

1A COLUMN FEED AND SCRUB COMPOSITIONS

Concentration in Gram-Moles/Liter

Feed No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Strontium	0.005	0.020	0.021	0.020	0.020	0.019	0.020	0.019	0.019	0.018	0.022	0.021	0.002
Calcium	0.022	0.088	0.086	0.079	0.096	0.091	0.090	0.090	0.090	0.12	0.098	0.080	0.013
Iron	0.016	0.063	0.065	0.051	0.064	0.063	0.036	0.033	0	0.060	0.064	0.057	0.006
Lead	0.002	0.026	0.027	0.023	0.0015	0.001	0.001	0.001	0	0.001	0	0.001	0.0001
Zirconium	0	0	0	0	0.005	0.005	0.003	0.002	0	0.004	0	0.004	0.0005
Total Rare Earths	0	0	0	0	0	0	0.003	0.003	0	0.003	0	0.003	0.0005
Barium	0.003	0.003	0.003	0.003	0.002	0.002	0.002	0.002	0	0.002	0	0.002	0.0002
Sodium	1.0	2.0	0.7	1.8	0.8	0.9	0.5	0.5	0.7	1.3	1.0	1.5	1.0
Acetate	0.9	0.9	0.45	0.75	0.8	0.9	0.45	0	0.5	0.8	0.5	0.8	0.6
Tartrate	0.18	0	0	0	0	0	0	0	0	0	0	0	0
Citrate	0	0	0	0	0	0	0	0.43	0	0	0	0	0
HEDTA	0	0	0	0	0.14	0	0	0	0	0.16	0.125	0.14	0.012
EDTA	0	0	0	0	0	0	0	0	0	0	0	0	0
Free HEDTA or EDTA	0	0	0	0	0.066	0	0	0	0	0.094	0.061	0.074	0.005
Runs	1-3	4-13	14-16	17-19	21	20	22	23	24-26	27-30	31-32	33	34-38

Feed No.	14	15	16	17	18	19	20	21	22	23	24	25**
Strontium	0.002	0.002	0.002	0.002	0.002	0.002	0.039	0.010	0.004	0.004	0.001	0
Calcium	0.012	0.012	0.012	0.026	0.002	0.004	0	0	0.004	0.004	0.0007	0
Iron	0.021	0.021	0.023	0.019	0.079	0.020	0	0.03*	0.10	0.10	0.06	0
Lead	0.004	0.004	0.004	0.004	0.003	0.003	0	0	0	0.015	0.04	0
Zirconium	0.002	0.002	0.001	0.002	0.0008	0.	0	0	0	0	0	0
Total Rare Earths	0.002	0.002	0.002	0.002	0.002	0.002	0	0	0	0	0.008	0.005-0.007
Barium	0	0	0	0	0	0	0	0	0	0	0	0
Sodium	1.6	1.4-1.5	1.6	1.6	1.1-1.3	1.2	1.5	1.5	1.4	1.4	1.0	0
Acetate	0.5	0.5	0.4	0.5	0.3-0.4	0.4	1.0	0.5	0.45	0.45	0	0
Tartrate	0	0	0	0	0	0	0	0	0	0	0	0
Citrate	0	0	0	0	0	0	0	0	0	0	0.3	0
HEDTA	0	0.13	0	0.019	0	0	0	0	0	0	0	0
EDTA	0.15	0	0.12	0.028	0.14-0.17	0.070	0	0.09	0.16	0.16	0.15	0
Free HEDTA or EDTA	0.12	0.11	0.09	0.019	0.05-0.09	0.045	0	0.06	0.06	0.04	0.05	0
Sulfate	0	0	0	0	0	0	0	0	0	0.012	0	0
Runs	39-40	41-42	43-46	47-49	50-53	54-56	57-59	60-63	64-68	69-70	71-73	74-76

* Aged ferric hydroxide added with the iron

** Special cerium feeds containing 1M HNO_3 and various oxidizing agents at 0.01 to 0.1M concentrations

Scrub No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Sodium	0	0.16	0.04	1.0	1.0	0.5	0.6	0	0	0.05	0.15	0.4	0
Acetate	0.1	0.2	0.20	0.20	0	0	0	0	1.0	1.0	0	0	0
Nitrate	0	0	0	1.0	1.0	0.5	0.5	0.28	0.2	0	0	0	0.5
Citrate	0	0	0	0	0	0	0	0	0	0.2	0.6	0.3	0
EDTA	0	0	0	0	0	0	0.02	0	0	0	0	0	0
pH	2.7	5.0	4.0	4.0	4.7	4.5	4.0	0.55	0.7	2.5	2.3 r	4.1	0.3
Runs	1-15 22, 23	16-19	20, 21 24-30	31-33	34-41	41-49, 57	50-55	56, 58, 59	60, 61	62, 63	64-70	71-73	74-76

AEC-GE RICHLAND, WASH

TABLE 4.3

1A COLUMN RUN SUMMARY

Run No.	Date	Ampl., Inch	Freq., Cycles/Min. Normal Operating	Freq., Cycles/Min. Instab. Thresh.	Volume Velocity GPH/ft² Extr.	Volume Velocity GPH/ft² Scrub	A/O Extr.	A/O Scrub	Interface	Cartridge No.	Feed No.	Scrub No.	Feed Point pH	Product Composition (1AP)[a] % Sr	% Ca	% Fe	% Pb	% Zr	M Freq D2EHP[b]	Waste Composition (1AW)[a] % Sr	% Ca	% Fe	% Pb	% Zr
2	9-1-60	1.0	60	80	700	300	3.3	0.85	Top	1	1	1	2.5	--	86	<0.5	--	--	0.28	(320)	81	94	85	--
3	9-2-60	1.0	--	--	890	290	2.6	0.88	Top	1	1	1	2.5	--	47	--	--	--	0.28	117	71	98	95	--
4	9-7-60	1.0	--	95±5	350	210	1.0	0.22	Top	1	2	1	2.5											
5	9-8-60	1.0	--	90±5	380	250	1.0	0.35	Top	1	2	1	2.5											
6	9-8-60	1.0	--	75±5	820	560	1.1	0.42	Top	1	2	1	2.5											
7	9-9-60	1.0	--	65±5	380	240	0.94	0.25	Bottom	1	2	1	2.5											
8	9-9-60	1.0	--	(60)	780	520	1.0	0.33	Bottom	1	2	1	2.5											
9	9-9-60	0.5	--	125±5	400	260	1.1	0.38	Bottom	1	2	1	2.5											
10	9-9-60	0.5	--	77±7	760	540	0.88	0.32	Bottom	1	2	1	2.5											
11	9-10-60	0.5	--	>125	380	250	1.0	0.34	Top	1	2	1	2.5											
12a	9-10-60	0.5	--	90±10	870	610	1.1	0.45	Top	1	2	1	2.5											
12b	9-12-60	0.5	--	≥119	830	560	1.1	0.44	Top	1	2	1	2.5											
13	9-12-60	0.5	--	95±5	950	620	0.86	0.28	Top	1	2	1	2.5											
14	9-15-60	0.5	80	--	790	520	1.0	0.35	Top	1	3	1	2.6	<0.8	23	69	--	--	0.20	86	57	8.6	81	--
15	9-16-60	0.5	72	--	790	520	1.0	0.35	Bottom	1	3	1	(2.5)	<0.8	17	86	--	--	0.16	98	74	27	85	--
16	9-16-60	0.5	80	--	790	520	1.0	0.36	Bottom	1	3	2	(2.5)	2.5	41	77	--	--	0.12	100	88	24	81	--
17	9-22-60	0.5	80	--	540	410	0.55	0.18	Top	1	4	2	3.7	110	136	69	114	--	0.13[c]	<0.9	3.4	40	<0.03	--
18	9-22-60	0.5	80	80	550	410	0.56	0.18	Top	1	4	2	4.8	92	96	75	106	--	0.16[c]	<0.8	3.1	27	0.32	--
19	9-23-60	0.5	80	90	550	430	0.54	0.20	Top	1	4	2	3.5	97	111	(195)	109	--	(0.06)[c]	<0.9	3.2	37	0.07	--
21	10-3-60	0.5	70	--	730	520	0.58	0.11	Top	2	5	3	3.4	98	114	3.6	<6.9	<4.5	0.08[c]	1.3	16	93	82	75
20	10-4-60	0.5	70	--	700	480	0.61	0.12	Top	2	6	3	3.8	102	105	89	(184)	108	(0.01)[c]	0.6	16	55	13	15
22	10-10-60	0.5	70	--	780	570	0.53	0.12	Top	2	7	1	2.3	4.5	(183)	53	13	112	0.14	103	(72)	45	80	<5
23	10-11-60	0.5	70	--	720	520	0.57	0.12	Top	2	8	1	1.8	<1.3	41	11	13	8	0.23	100	51	80	(168)	98
24	10-18-60	0.5	80	--	710	490	0.62	0.12	Top	2	8	3	3.7	44	115	--	--	--	0.08[c]	12	14	--	--	--
25	10-19-60	0.5	80	--	440	310	0.65	0.14	Top	2	9	3	3.8	80	119	--	--	--	0.07[c]	17	13	--	--	--
26	10-19-60	0.5	100	--	420	290	0.65	0.14	Top	2	9	3	3.8	(126)	(147)	--	--	--	(0.03)[c]	11	14	--	--	--
27	10-21-60	0.5	50	~80	810	610	0.48	0.12	Top	2	10	3	5.4	87	53	<0.8	1.5	<7.5	0.25[c]	3.3	19	77	73	51
28	10-21-60	0.5	55	--	680	490	0.61	0.18	Top	2	10	3	5.4	106	102	<0.7	3.0	<5.9	0.11[c]	1.6	4.9	87	86	58
29	10-24-60	0.5	50	--	760	570	0.50	0.13	Top	2	10	3[d]	5.2	89	72	<0.8	3.7	<7.2	0.20[c]	2.2	23	77	79	65
30	10-27-60	0.5	40	50	700	520	0.64	0.15	Top	2	10	2	5.1	89	90	0.7	22	6.5	0.16	1.0	17	92	104	87
31	10-29-60	0.5	49	--	720	530	0.57	0.14	Top	2	11	4	5.3	78	90	<0.7	--	--	0.19[e]	11	23	86	--	--
32	10-31-60	0.5	49	--	730	530	0.56	0.14	Top	2	11	4	4.0	86	87	<0.7	--	--	0.22	12	8.9	101	--	--
33	11-1-60	0.5	62	--	650	450	0.67	0.16	Top	2	12	4	4.4	88	118	--	--	--	0.14	<0.8	18	--	--	--
34	11-2-60	0.5	82	--	840	180	4.1	0.10	Top	2	13	5	4.7	102	86	--	--	--	0.17	<7	(67)	--	--	--
35	11-3-60	0.5	91	--	920	200	3.6	0.11	Top	2	13	5	4.7	101	83	--	--	--	0.20	<7	28	--	--	--
35a	11-4-60	0.5	--	65±5	820	190	3.8	0.12	Top	2	13	5	4.9											
35b	11-4-60	0.5	--	75±5	1000	220	4.1	0.11	Top	2	13	5	4.9											
35c	11-7-60	0.5	--	65±5	1300	290	3.8	0.09	Top	2	13	5	4.9											
36d	11-10-60	0.5	--	70±5	830	190	3.9	0.15	Bottom	2	13	5	4.9											
36e	11-10-60	0.5	--	65±5	1020	240	3.9	0.12	Bottom	2	13	5	4.9											
37	11-11-60	0.5	60	--	820	190	3.9	0.12	Bottom	2	13	5	4.8	97	(148)	--	--	--	(0.03)	<5	(35)	--	--	--
38	11-15-60	0.5	60	70	810	190	3.9	0.13	Bottom	3	13	5	4.6	106	112	--	--	--	0.08	<5	(22)	--	--	--
39	11-22-60	0.5	80	--	820	180	3.8	0.09	Bottom	3	14	5	4.9	88	80	0.9	<0.3	<2	0.17	5.1	(61)	106	100	88
40	11-23-60	0.5	--	40	1240	280	3.7	0.07	Bottom	3	14	5	4.9											
41	11-29-60	0.5	80	--	800	180	3.8	0.09	Bottom	3	15	5	4.8	95	118	--	--	--	0.12	<5	(220)	98	100	81
42	11-28-60	0.5	80	--	800	180	3.9	0.09	Bottom	3	15	6	4.7	83	(134)	--	--	--	(0.08)	<5	(260)	99	98	80
43	11-29-60	0.5	80	--	810	180	4.0	0.08	Bottom	3	16	6	4.8	75	111	--	--	--	0.13	40	--	--	--	--
44	11-29-60	0.5	80	--	770	140	5.1	0.11	Bottom	3	16	6	4.8	47	90	--	--	--	0.12	55	--	--	--	--
45	11-30-60	0.5	80	--	730	120	6.2	0.14	Bottom	3	16	6	4.9	30	99	--	--	--	0.09	75	--	--	--	--
46	11-30-60	0.5	80	--	700	90	9.0	0.16	Bottom	3	16	6	4.9	16	67	--	--	--	0.07	82	--	--	--	--
47	12-1-60	0.5	80	--	820	180	3.9	0.08	Bottom	3	17	6	4.6	98	86	--	--	--	(0.01)	<5	0.2	98	86	83
48	12-1-60	0.5	80	--	830	190	4.1	0.08	Bottom	3	17[e]	6	4.7	83	87	--	--	--	(0.01)	<5	8.8	104	102	98
49	12-2-60	0.5	--	115±5	820	180	4.0	0.07	Bottom	3	17[e]	5	4.7											
50	12-12-60	0.5	80	--	770	140	5.4	0.14	Bottom	3	18	7	4.8	90	(130)	--	--	--	0.29	9.1	--	--	--	--

Notes:
a. Percent based on composition of the 1AP
b. Total M D2EHPA = 4M (Sr + Ca + Fe + Pb + Zr)
c. The solvent entered in the sodium form in these runs
d. 0.08M HEDTA added
e. Feed heated to 60 C (column temperatures ca 45 C)

TABLE 4.3 (contd.)

Run No.	Date	Ampl., Inch	Freq. Cycles/Min. Normal Operating	Freq. Cycles/Min. Instab. Thres.	Volume Velocity GPH/ft^2 Extr.	Volume Velocity GPH/ft^2 Scrub	A/O Extr.	A/O Scrub	Interface	Cartridge No.	Feed No.	Scrub No.	Feed Point pH	Product Composition (1AP)[a] % Sr	Product Composition (1AP)[a] % Ca	Product Composition (1AP)[a] M Na	Product Composition (1AP)[a] M "Free" D2EHPA	Waste Composition (1AW)[a] % Sr	Na DF in Scrub Section
51	12-12-60	0.5	80	--	780	140	5.1	0.12	Bottom	3	18	7	4.3	105	(140)	0.092	0.28	<6	--
52	12-12-60	0.5	80	--	780	140	5.3	0.15	Bottom	3	18	7	3.8	99	94	0.061	0.30	<5	--
53	12-13-60	0.5	80	--	850	240	3.0	0.09	Bottom	3	18	7	4.8	93	(190)	0.19	0.32	<6	--
54a	12-16-60	0.8	70	70	780	150	5.2	0.19	Bottom	3	19	7	4.1	97	(52)	0.064	0.31	<6	--
54b	12-16-60	0.8	60	--	790	150	5.2	0.19	Bottom	3	19	7	4.9	96	(45)	0.11	0.31	<6	--
54c	12-17-60	0.8	--	70±10	400	70	8.5	0.58	Bottom	3	19	7	4.9						
54d	12-17-60	0.8	60	65	660	160	4.0	0.19	Bottom	3	19	7	4.9	99	(41)	0.14	0.33	<6	--
55	12-20-60	0.8	50	60	1020	210	4.3	0.09	Bottom	3	19	7	4.8	95	89	--	0.29	<6	--
56	12-21-60	0.8	50	--	1050	230	4.2	0.15	Bottom	3	19	8	4.9	98	--	0.16	0.29	<6	1.52
57	1-3-61	0.8	76	--	870	610	0.69	0.20	Bottom	3	20	6	4.5	93	--	0.14	0.31	<0.4	--
58	1-4-61	0.8	76	--	860	610	0.69	0.20	Bottom	3	20	8	4.7	100	--	0.095	0.31	<0.4	--
59	1-4-61	0.8	76	--	880	630	0.66	0.19	Bottom	3	20	8	4.0	103	--	0.046	0.31	<0.4	--
60	1-11-61	0.8	50	--	1060	440	2.3	0.37	Bottom	3	21	9	4.8	95	--	0.096	0.32	<1.4	--
61	1-11-61	0.8	39	39	1080	430	2.4	0.35	Bottom	3	21	9	3.8	97	--	0.061	0.32	<1.5	--
62	1-13-61	0.8	39	39	1000	380	2.6	0.37	Bottom	3	21	10	3.8	81	--	0.075	0.33	<1.5	0.9
63	1-13-61	0.8	39	--	1060	440	2.1	0.30	Bottom	3	21	10	4.8	98	--	0.13	0.32	<1.4	1.5
64	1-17-61	0.8	65	--	780	180	4.0	0.15	Bottom	3	22	11	4.6	98	97	0.10	0.27	<3	2.5
65	1-17-63	0.8	71	--	780	180	4.0	0.15	Bottom	4	22	11	4.6	100	113	0.058	0.26	<3	3.3
66	1-18-61	0.8	70	--	830	220	4.3	0.40	Bottom	4	22	11	3.7	65	117	0.006	0.29	21	6.5
67	1-20-61	0.8	62	70	810	190	4.2	0.24	Bottom	5	22	11	4.6	99	108	0.054	0.27	≤3	3.2
68	1-25-61	0.8	49	≥49	800	190	4.1	0.24	Bottom	6	22	11	4.6	101	126	0.043	0.26	≤3	2.8
69	1-27-61	0.8	49	≥49	810	190	4.2	0.25	Bottom	6	23	11	4.6	96	120	0.036	0.27	<3	3.3
70	2-1-61	0.8	70	≥80	800	190	4.1	0.25	Bottom	6	23	11	3.8	101	96	≤0.006	0.27	<3	≥7.9

a. Percent based on composition of the 1AF

b. Total M D2EHPA - 4M (Sr + Ca + Fe + Pb + Zr)

c. The solvent entered in the sodium form in these runs

d. 0.08M HEDTA added

ACC-GE RICHLAND, WASH

TABLE 4.4

1B COLUMN RUN SUMMARIES*

Run No.[a]	Date	Freq., Cycles/Min. Normal Operating	Freq., Cycles/Min. Dstab. Thresh.	Volume Velocity, GPH/ft²	A/O	Feed No.[b]	IBX Comp. M	Calcium DF[c]	Product Composition (1BP)[d] pH	% SR	%Ca	% Fe	% Pb	M(Sr+Ca)	M Na	Waste Composition (1BW)[d] % Sr	%Ce	% Fe	% Pb	M Free D2EHP[e]
1a	8-24-60	--	--	1710	1.8	1	0.1 HNO_3	~1	--	115	128	1.1	100	0.027		12	3.6	100	1.5	0.34
1b	9-24-60	--	--	1440	0.97	1	0.1 HNO_3	~1	--	114	118	0.12	--	0.030		<2	4.7	77	--	0.36
2a	10-4-60	80	--	1170	1.3	2	0.11 HNO_3	1.6	--	86	55	(32)	112	0.027		3.1	16	86	7.3	0.29
2b	10-5-60	85	--	1180	1.3	2	0.11 HNO_3	1.2	--	98	78	8.2	91	0.036		3.2	22	79	3.3	0.28
3	10-5-60	80	--	1160	1.4	3	0.03 HNO_3	1.0	--	97	97	3.6	88	0.038		2.7	8.3	(200)	6.3	0.27
6a	10-20-60	70	--	700	0.90	4	0.11 HNO_3	1.3	--	84	63	--	--	0.088		13	29	--	--	0.22
6b	10-20-60	70	--	550	0.52	4	0.11 HNO_3	1.7	--	54	31	--	--	0.080		13	49	--	--	0.14
6c	10-20-60	70	--	470	0.31	4	0.11 HNO_3	2.6	--	45	17	--	--	0.082		18	80	--	--	(0.002)
7a	10-27-60	--	75±5	640	0.98	5	0.1 HNO_3		--											
7b	10-27-60	--	75±5	640	0.98	5	0.5 HNO_3		--											
7c	10-28-60	--	85±5	550	0.74	5	0.5 HNO_3		--											
7d	10-28-60	--	75±5	450	0.38	5	0.5 HNO_3		--											
7e	10-28-60	--	65±5	930	0.98	5	0.5 HNO_3		--											
7f	10-28-60	--	60±5	830	0.76	5	0.5 HNO_3		--											
8a	10-31-60	--	85±5	450	0.37	5	2 HNO_3		--											
8b	10-31-60	--	87±2	400	0.20	5	2 HNO_3		--											
1A-33	11-1-60	70	--	480	0.24	6	2.2 HNO_3	~1	--	66	101	--	--	0.196	--	<1.5	≤0.9	--	--	0.36
1A-35	11-3-60	60	--	190	0.09	7	1 $NaNO_3$	~1	--	2.0	2.9	--	--	0.015	1.0	96	86	--	--	0.24
9a	11-9-60	60	65±5	680	1.0	8	1.5 Cit. Acid	2.3	1.9	105	45	--	--	0.031	0.23	≤0.3	24	--	--	0.31
9b	11-9-60	70	--	490	0.44	8	1.5 Cit. Acid	2.8	3.0	83	30	--	--	0.049	0.31	0.3	44	--	--	0.27
10a	11-11-60	60	--	700	1.1	9	1 Tart. Acid	1.2	2.2	90	69	--	--	0.031	--	0.2	27	--	--	0.32
10b	11-11-60	60	--	500	0.51	9	1 Tart. Acid	2.6	2.1	88	34	--	--	0.030	--	0.1	43	--	--	0.30
10c	11-15-60	60	--	420	0.24	9	1 Tart. Acid	5.5	2.8	93	17			0.050	0.37	≤1.4	50	--	--	0.27
10d	11-18-60	60	--	380	0.13	9	1 Tart. Acid	15	2.9	88	8.8	--	--	0.060	0.48	1.3	94	--	--	0.26
11a	12-2-60	60	--	790	0.25	10	1 Cit. Acid	2.7	2.3	90	32	--	--	0.097	0.091	<1.6	88	--	--	0.21
11b	12-2-60	60	--	740	0.17	10	1 Cit. Acid	3.2	2.2	83	25	--	--	0.121	0.067	<1.6	77	--	--	0.19
1A-54a	12-16-60	72	--	150	0.21	11	1 Cit. Acid	36	2.5	69	1.8	--	--	0.036	0.31	7.2	105	--	--	0.30
1A-54b	12-16-60	72	--	150	0.21	11	1 Cit. Acid	11	2.9	84	5.6	--	--	0.030	0.53	24	42	--	--	0.35
1A-54d	12-17-60	72	--	160	0.20	11	1.1 Cit. Acid	38	3.2	46	1.2	--	--	0.018	0.73	71	48	--	--	0.33
1A-55	12-20-60	70	--	230	0.17	11	2 Cit. Acid	43	3.0	52	1.2	--	--	0.027	1.14	11	88	--	--	0.32
1A-57	1-3-61	70	--	650	0.28	12	1.5 Cit. Acid	--	3.7	96	--	--	--	0.067	0.52	1.2	--	--	--	0.39
1A-58	1-4-61	70	--	650	0.27	12	1.3 Cit. Acid	--	3.3	95	--	--	--	0.068	0.34	≤0.6	--	--	--	0.38
1A-59	1-4-61	70	--	670	0.28	12	1.3 Cit. Acid	--	3.1	118	--	--	--	0.078	0.22	<0.5	--	--	--	0.39
1A-60	1-11-61	69	--	380	0.18	13	1 Tart. Acid	--	2.8	84	--	--	--	0.068	0.36	15	--	--	--	0.38
1A-61	1-11-61	69	--	380	0.19	13	1 Tart. Acid	--	2.4	92	--	--	--	0.091	0.15	11	--	--	--	0.38
1A-62	1-13-61	69	--	340	0.21	12	1 Cit. Acid	--	2.8	70	--	--	--	0.068	0.27	22	--	--	--	0.37
1A-63	1-13-61	69	--	400	0.17	12	1 Cit. Acid	--	3.0	36	--	--	--	0.037	0.60	61	--	--	--	0.35
1A-64	1-17-61	68	--	190	0.25	13	1 Cit. Acid	51	2.1	87	1.7	--	--	0.054	0.18	<0.7	91	--	--	0.34
1A-65	1-17-61	66	--	190	0.25	13	1 Cit. Acid	62	2.4	82	1.0	--	--	0.038	0.31	5.1	103	--	--	0.33
1A-66	1-18-61	70	--	190	0.25	13	1 Cit. Acid	19	1.8	58	3.4	--	--	0.037	0.079	>0.7	--	--	--	0.33
1A-67	1-20-61	70	--	190	0.25	13	1 Cit. Acid	44	2.1	80	1.8	--	--	0.050	0.13	1.5	104	--	--	0.33
1A-68	1-25-61	70	--	190	0.25	13	1 Cit. Acid	39	2.1	78	2.0	--	--	0.058	0.18	0.8	114	--	--	0.33
1A-69	1-27-61	70	--	190	0.24	13	1 Cit. Acid	48	2.2	81	1.7	--	--	0.052	0.22	1.7	116	--	--	0.33
1A-70	2-1-61	70	--	190	0.25	13	1 Cit. Acid	30	1.7	97	3.2	--	--	0.058	≤0.014	0.6	89	--	--	0.33

* All runs made with top interface, pulse amplitude = 1 in.

Notes: a. Numbers preceded by "1A" refer to runs made in cascade with the 1A column run of the same number.

b. Approximate 1BF feed compositions:

Feed No.	Run No.	M Sr	M Ca	M Fe	M Pb	M Zr
1	1	0.006	0.026	0.012	0.007	--
2	2	0.010	0.046	0.003	0.0007	--
3	3	0.009	0.047	0.004	0.001	$<10^{-6}$
4	6	0.016	0.10	0	0	0
5	7	0.007	0.035	--	--	--
6	1A-33	0.008	0.047	--	--	--
7	1A-35	0.005	0.035	--	--	--
8	9	0.008	0.050	--	--	--
9	10	0.006	0.033	--	--	--
10	11	0.007	0.056	--	--	--
11	1A-54,55	0.01	(0.02)	--	--	--
12	1A-58 to 64	0.018	0	0	0	0
13	1A-64 to 71	0.015	0.013	0	0	0

c. DF's based on actual strontium recovery. Since strontium profile may not be at steady-state in many of these runs, calcium DF's are probably conservative.

d. % based on composition of 1BF (or 1AF on 1A-1B cascade runs)

e. M D2EHPA = 4 (M Sr + M Ca + M Fe + M Pb)

TABLE 4.5

CERIUM EXTRACTION RUNS

Run No.:	71	72	73	74	75	76
Pulse Ampl., in.: 1A	0.8	0.8	0.8	0.8	0.8	0.8
1B	1.0	1.0	1.0	1.0	1.0	1.0
Freq., Cycles min: 1A	70	53	53	82	70	70
1B	70	64	64	64	56	56
Volume Velocity: 1A Extr.	540	930	950	730	730	740
1A Scrub	210	330	350	390	390	380
1B	200	290	300	390	390	390
Flow Ratio, A/O: 1A Extr.	2.5	2.9	2.8	1.3	1.3	1.3
1A Scrub	0.37	0.39	0.41	0.20	0.21	0.19
1B	0.25	0.21	0.20	0.21	0.21	0.22
Interface: 1A	Bottom	Bottom	Bottom	Bottom	Bottom	Bottom
1B	Top	Top	Top	Top	Top	Top
Cartridge No.: 1A	6	6	6	6	6	6
1B	2	2	2	2	2	2
Feed No.	24	24	24	25[a]	25[b]	25[c]
Feed pH	3.1	3.5	3.8	~0	~0	~0
Scrub No.	12	12	12	13	13	13
Strip Composition	1M HNO_3	1M HNO_3	1M HNO_3	1M HNO_3	1M HNO_3	0.5M HNO_3
				0.1M NH_2OH	0.1M NH_2OH	0.15M H_2O_2
1AP[d]: % Cerium	71	69	71	40	48	< 22
% Strontium	100	107	104	--	--	--
1AW[d]: % Cerium	< 15	< 12	< 15	67	79	79
% Strontium	< 10	< 10	< 10	--	--	--
1BP[d]: % Cerium	74	62	62	51	27	3
% Strontium	122	99	110	--	--	--
1BW[d]: % Cerium	0.3	0.2	0.2	0.5	0.9	< 0.1
% Strontium	< 4	< 3	< 3	--	--	--

Notes:
a. 0.012M $KMnO_4$ added to oxidize cerium
b. 0.1M $Na_2Cr_2O_7$ added
c. 0.1M $(NH_4)_2S_2O_8$ added
d. % of 1AF

TABLE 5.1

APPROXIMATE COMPOSITIONS OF PUREX CRUDE AND ADJUSTED HOT SEMIWORKS FEED*

	Run Sr-4		Run Sr-5		Run Sr-6		Run Sr-7	
	Crude	Feed**	Crude	Feed**	Crude	Feed**	Crude	Feed**
Strontium	0.0025	0.0034	0.0023	0.0015	0.0026	0.0033	0.0034	0.008
Calcium	0.005	0.004	0.005	0.0032	0.005	0.0036	(0.017)	(0.015)
Barium	0.0004	0.0003	0.0004	0.0003	0.0004	0.0003	(<0.0002)	(0.003)
Iron	0.024	0.017	0.024	0.015	0.042	0.030	0.019	0.014
Lead	0.019	0.013	0.019	0.012	0.007	0.005	0.005	0.003
Sodium	0.3	1.3	0.3	1.1	0.46	1.4	0.3	1.0
Hydrogen	0.78	pH 4.8	0.86	pH 4.45	0.86	pH 4.7	0.62	pH 4.5
Acetate	0	0.45	0	0.43	0	0.42	0	0.51
EDTA	0	0.088	0	0.085	0	0	0	0.015
DTPA	0	0	0	0	0	0.083	0	0
Citrate	0	0.032	0	0	0	0.037	0	0.080
Sulfate	--	≥0.0007	--	≥0.0007	--	≥0.0007	--	--
Isotope								
Sr^{90}	18	24	17	11	19	23	24	58
Sr^{89}	51	68	40	26	37	45	58	137
Ce^{144}	165	116	256	164	48	34	38	28
$ZrNb^{95}$	43	30	3.4	2.1	0.5	0.3	4.8	3.5
Ru^{106}	≤2	1.4	≤1	<1	<0.1	<0.1	<0.1	<0.1
Pm^{147}	--	--	--	--	--	--	6.9	5.0
Volume, Liters	12,000	17,100	11,200	17,500	20,000	28,300	17,200	25,000

*Isotope concentrations in curies/liter all others in M.

**Typical values, including product backcycle in Runs Sr-4, 6, and 7.

TABLE 5.2

APPROXIMATE INTERCYCLE FEED COMPOSITIONS

	Sr-4	Sr-5			Sr-7			
	1XF	2AF	3AF-1	3AF-2	2AF	3AF	4AF	5AF
M Strontium	0.032	0.022	0.056	0.0008	0.021	0.010	0.013	0.011
M Calcium	0.007	0.002	0.003	--	0.010	(0.04)	--	0.0052
M Barium	<0.0009	0.002	0.0007	--	0.012	--	--	0.0017
M Manganese	0	0	0	0	0	0.078	--	0.0024
M Sodium	~0.2	1.1	0.7	0.8	1.0	0.9	1.4	0.8
M Acetate	0	0	0.36	0.33	0.22	0	0.35	0.38
M EDTA	0	0.10	0	0	0	0	0	0
M DTPA	0	0	0.022	0.039	0.044	0	0.046	0.04-0.05
M Citrate	0.89	0.73	0	0	0.68	0.28	0.17	0
pH	2.7	4.1	4.7	4.5	4.5	2.8	4.6	4.7
Curies/Liter								
Sr^{90}	227	150	400	6	150	74	92	73
Ce^{144}	9	9	<2	--	2	3	21	7
$ZrNb^{95}$	<0.009	<0.1	<1	--	<0.07	<0.1	<0.003	<0.1
Ru^{106}	<0.02	--	<1	--	<0.2	<0.1	<0.005	<0.3
Volume, liter	900	1500	380	2440	2300	1450	2830	3720

TABLE 5.3

Sr-4 DETAILED RUN SUMMARY

Operating Conditions:	1A Extr.	1A Scrub	1B
Volume Velocity, gph/ft^2	960	220	220
Aqueous/Organic Flow Ratio	4.3	0.25	0.25
Pulse Amplitude, in.	0.8		1.0
Typical Pulse Freq., Cycles/min	65		70
Run Length, hr	70		72
Aqueous Effluent, pH	4.65		2.3

Analytical Results:

	1AF	1AP - 1BF	1BP - 1XF	1XP	1XP - Recycle
Sr^{90}, Kilocuries	212	(207)	205	150	32
Curie/Curie Sr^{90}:					
Ce^{144}	9.3	(2.1)	3.8×10^{-2}	$\leq 5 \times 10^{-4}$	--
$ZrNb^{95}$	2.4	($\leq 2 \times 10^{-3}$)	$< 4 \times 10^{-5}$	$\leq 2 \times 10^{-5}$	--
Ru^{106}	<0.1	($\leq 8 \times 10^{-4}$)	$< 8 \times 10^{-5}$	$\leq 5 \times 10^{-5}$	--
Gram/Gram Strontium:					
Calcium	0.9	--	0.1	0.05	--
Barium	~0.3	--	<0.05	<0.01	--
Cumulative DF's:					
Ce^{144}	1	(4.5)	247	$\geq 2 \times 10^4$	--
$ZrNb^{95}$	1	($\geq$1400)	$>6 \times 10^4$	$\geq 1.2 \times 10^5$	--
Ru^{106}	1	($\geq$150)	$>1.5 \times 10^3$	$\geq 2.4 \times 10^5$	--
Calcium	1	--	8.9	17	--
Barium	1	--	>6	>28	--

Strontium Isotopic Composition:

Isotope	Atom Percent
Sr^{90}	56
Sr^{88}	43
Sr^{87}	0.5
Sr^{86}	0.7

$\frac{Ca}{Sr\text{-}90}$ mole ratio ~ 3.62 Ca DF = 8.9 no IX

Used pot. [illegible] Sr recycle

Solvent loading - 30%. Ca+Sr including backcycle

TABLE 5.4

Sr -5 DETAILED RUN SUMMARY

Operating Conditions:	1A Extr.	1A Scrub	1B	2A Extr.	2A Scrub	2B
Volume Velocity, gph/ft^2	1020	230	230	650	220	360
Aqueous/Organic Flow Ratio	4.6	0.24	0.24	1.5	0.18	1.0
Pulse Amplitude, in.	0.8		1.0	0.8		1.0
Typical Pulse Freq., Cycles/min	40		70	60		65
Run Length, hr.	66		68	18		20
Aqueous Effluent, pH	3.9-4.3		--	4.0		1.8-2.4

Analytical Results:	1AF	1AP - 1BF	1BP - 2AF	2AP - 2BF	2BP
Sr^{90}, Kilocuries	223	(231)	(231)	193	193
Curie/Curie Sr^{90}:					
Ce^{144}	13	4	0.056	0.045	0.0064
$ZrNb^{95}$	0.17	<0.0025	$<7 \times 10^{-4}$	$<7 \times 10^{-4}$	2×10^{-5}
Ru^{106}	≤ 0.05	<0.009	$<4 \times 10^{-3}$	$<3 \times 10^{-3}$	$<7 \times 10^{-6}$
Gram/Gram Strontium					
Calcium	0.8	---	0.04	---	0.018
Barium	0.2	---	0.1	---	0.015
Cumulative DF's:					
Ce^{144}	1	3.2	229	290	2000
$ZrNb^{95}$	1	>67	>260	>250	9100
Ru^{106}	1	> 6	> 14	> 19	>6900
Calcium	1	--	19	--	45
Barium	1	--	2	--	16

Strontium Isotopic Composition:

Isotope	Atom Percent
Sr^{90}	57
Sr^{88}	42
Sr^{87}	0.7
Sr^{86}	0.7

Ca mole ratio ~ 3.16
Sr 90

Ca DF = 19
1st cycle only

2 cycles, no recycle
Solvent loading ≈ 1 % Ca + Sr

TABLE 5.5

Sr.-6 DETAILED RUN SUMMARY

Operating Conditions:	1A Extr.	1A Scrub	1B
Volume Velocity, gph/ft^2(max)	1170	320	300
Aqueous/Organic Flow Ratio	3.7	0.24	0.22
Pulse Amplitude	0.8		1.0
Typical Pulse Freq., Cycles/min	65		43
Run Length, Hours	116		118
Aqueous Effluent, pH	4.3-4.5		2.15

Analytical Results:	1AF	1AP - 1BF	1BP
Sr^{90}, Kilocuries	363	(316)	305
Curie/Curie Sr^{90}:			
Ce^{144}	2.7	(0.11)	0.0011
$ZrNb^{95}$	0.063	($<10^{-4}$)	$< 3.5 \times 10^{-5}$
Ru^{106}	<0.007	($< 2 \times 10^{-4}$)	$< 7 \times 10^{-5}$
Gram/Gram Strontium:			
Calcium	0.79	---	0.020
Barium	0.24	---	0.025
Cumulative DF's:			
Ce^{144}	1	(24)	2380
$ZrNb^{95}$	1	(>500)	>1800
Ru^{106}	1	(> 30)	>94
Calcium	1	---	40
Barium	1	---	9.4

Strontium Isotope Composition:

Isotope	Atom Percent
Sr^{90}	56
Sr^{88}	43
Sr^{87}	0.5
Sr^{86}	0.7

$\frac{Ca}{Sr\text{-}90}$ mole ratio = 3.17 Ca DF = 40

recycle mode.

Solvent loading 23% Ca + Sr including backcycle.

TABLE 5.6

Sr-7 DETAILED RUN SUMMARY

Operating Conditions:	1A Extr.	1A Scrub	1B	2A Extr.	2A Scrub	2B	3A Extr.	3A Scrub	3B	4A Extr.	4A Scrub	4B	5A Extr.	5A Scrub	5B
Volume Velocity gph/ft^2	1050	340	370	520	280	310	1030	720	820	1040	550	550	480	240	280
Aqueous/Organic Flow Ratio	2.6	0.16	0.28	1.0	0.10	0.20	0.52	0.06	0.22	1.3	0.20	0.19	1.5	0.23	0.48
Pulse Amplitude, in.	0.8		1.0	0.8		1.0	0.8		1.0	0.8		1.0	0.8		1.0
Typical Pulse Freq., Cycles/Minute	50		35	25		40	67		30	27		43	68		60
Run Length, Hours	125		128	31		33	15		17	17		18	51		53
Aqueous Effluent pH	4.0	4.2	2.5	4.0		--	(2.6)		--	4-4.2		--	4.1		1.9

Analytical Results:	1AF	1AP-1BF	1BP-2AF	2AP-2BF	2BP	Ce-Feed	Ce-Product	Ce-Waste-3AF	3AW	4AF	4AP-4BF	4BP	5AF	5AP-5BF	5BP
Kilocuries															
Sr^{90}	178	(460)	348	344	176	(110)	3	107	68	259	252	107	283	272	251
Ce^{144}	662	(330)	4.7	16	5.4	(315)	308	4.5	--	60	-	16	21	9	0.5
Pm^{147}	119	(60)	--	--	(572)	(24)	(372)	24	2.5	--	--	--	--	--	--
Curie/Curie Sr^{90}:															
Ce^{144}	1.4	--	0.014	0.047	0.031	--	-	0.042	0.029	0.230	--	0.148	0.075	0.034	0.00178
$ZrNb^{95}$	0.17	--	$<4 \times 10^{-4}$	$<3 \times 10^{-4}$	$<5 \times 10^{-4}$	--	-	--	--	$<4 \times 10^{-5}$	--	$<9 \times 10^{-4}$	$<7 \times 10^{-4}$	$<2 \times 10^{-3}$	$<3 \times 10^{-4}$
Ru^{106}	<0.004	--	$<10^{-3}$	$<2 \times 10^{-3}$	$<7 \times 10^{-4}$	--	--	--	--	$<6 \times 10^{-5}$	--	$<2 \times 10^{-3}$	$<10^{-3}$	$<4 \times 10^{-3}$	$<5 \times 10^{-4}$
Gram/Gram Strontium:															
Calcium	2.0	--	0.20	--	0.086	--	--	--	--	--	--	--	0.22	--	0.028
Barium	<0.08	--	0.86	--	0.34	-	--	--	--	--	--	--	0.25	--	0.048
Manganese	--	--	--	--	--	--		4.6	--	--	--	--	0.14	--	0.009

Strontium Isotope Composition (Atom Percent): Sr^{90} = 57.5, Sr^{88} = 41.7, Sr^{87} = 0.3, Sr^{86} = 0.05

In recycle mixed

feed $\frac{Ca}{Sr\text{-}90}$ mole ratio = 7.83 Ca DF = 10 1st cycle only

solvent loading 49% Ca + Sr including recycle

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