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LABORATORY DEVELOPMENT OF A CARRIER - PRECIPITATION PROCESS
FOR THE RECOVERY OF STRONTIUM FROM PUREX WASTES

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FOR THE RECOVERY OF STRONTIUM FROM PUREX WASTES

by

L. A. Bray and H. H. Van Tuyl

Chemical Research
Chemical Research and Development
Hanford Laboratories Operation

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HANFORD ATOMIC PRODUCTS OPERATION
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I. INTRODUCTION

The acidic waste stream (1WW) from the Purex Chemical Separations Plant at Hanford is this nation's greatest source of fission products. As the technology develops for the use of radioactive isotopes, the recovery of these elements to supply industrial needs will become increasingly important. A research and development program to devise processes for the recovery of the potentially valuable long-lived fission products from the Purex waste stream has been under way for several years. One of these long-lived fission products, strontium-90, is a beta emitter and as such has the properties required especially for the heat source in a thermoelectric generator.⁽¹⁾ When strontium flow sheets were first being developed, the concentrated Purex waste was believed to be primarily a nitric acid solution (6 to 10 M HNO_3) containing fission products and relatively small concentrations of iron, sulfate, and other corrosion products. Early strontium development by G. B. Barton and R. E. Ewing investigated "basic-side" flow sheets in which the pH of the solution was step-wise adjusted to precipitate first the iron and then the desired fission products.⁽²⁾⁽³⁾ Since this early work, including that by T. R. McKenzie,⁽⁴⁾⁽⁵⁾ plant operations have been extensively modified. The plant waste is now more concentrated and is a high salt solution with nitric acid actually a minor constituent. Also, realistic flowsheets were not fully developed until the actual

compositions of several Purex 1WW samples were determined.⁽⁶⁾ Iron and sulfate concentrations in excess of 0.5 molar changed the complexity of the recovery of strontium. The exact composition of the Purex 1WW waste is variable; however, Table I indicates typical concentrations of the major constituents.

Table I

APPROXIMATE COMPOSITION OF PUREX 1WW (CONCENTRATED
FISSION PRODUCT WASTE)

<u>Constituent</u>	<u>Molar Concentration</u>
Na ⁺	0.6
H ⁺	4
Fe (III)	0.5
Al (III)	0.1
Cr (III)	0.01
Ni (II)	0.01
UO ₂ ⁺⁺	0.01
PO ₄ ⁼	0.01
SO ₄ ⁼	1
NO ₃ ⁻	4.5

Because of the availability of the idle Bismuth Phosphate canyons for potential large-scale production and the availability of the Purex head-end centrifuges for pilot plant and interim production use, Hanford has continued to favor precipitation processes, for the initial separation of crude cut concentrates of individual desired fission

products from the salt waste. Final purification would then be completed by additional cycles of precipitation, solvent extraction,⁽⁷⁾ or ion-exchange.⁽⁸⁾

II. OBJECTIVE

The objective of the work described in this report was twofold. The initial work was to determine the flowsheet conditions by which strontium could be removed from the Purex waste with a minimum of contamination from corrosion products or from other fission products. The flowsheets were to be compatible with flowsheets for the recovery of other fission products such as cerium and rare earths. The second purpose of the investigations reported here was to develop a process applicable to the available equipment in the head-end of the Purex plant and, therefore, some of the decisions were based more on equipment limitations in the plant rather than on technical considerations. For example, solvent extraction, ion-exchange, and addition of solid reagents were not considered for use in the Purex equipment.

A workable flowsheet was urgently required for use in recovering a megacurie of strontium-90 for use in the SNAP program prototypes.⁽¹⁾

III. SUMMARY

Strontium recovery from Purex LWW was investigated on a laboratory scale with simulated feeds and tracer activities. Initial experiments demonstrated recovery of over 70 per cent of the strontium by sulfate precipitation from partially neutralized LWW by either increasing the sulfate concentration to about 3 M or by adding carriers such as lead. Precipitation of iron was avoided by addition of one or more moles of tartrate per two moles of iron. Precipitation at elevated temperatures and addition of lead after pH adjustment were shown to be beneficial.

Strontium recoveries of over 95 per cent were achieved by precipitation at about 80 C at pH values of 0.4 to 4.0 with sulfate concentrations of 0.67 to 3 M and over 0.02 M lead carrier added. High sulfate concentrations were required at low pH, but the sulfate concentration is not critical above pH 1. Some separation of strontium from cerium was observed at pH 2 to 4, with the degree of separation being dependent on both tartrate concentration and pH.

Recovery of strontium from the sulfate precipitate by leaching with nitric acid, sodium acetate, or oxalic acid was unsatisfactory because of the large volumes required. Metathesis with sodium hydroxide removed most of the lead as plumbite and converted the precipitate to an acid-soluble form, but resulted in excessive strontium losses. Metathesis with carbonate - hydroxide mixtures retained the benefits of hydroxide metathesis, and resulted in only very low strontium losses. Selective leaching of rare earths from the sulfate or carbonate precipitates using various complexing agents was generally unsuccessful. Recovery of strontium from the carbonate precipitate by washing with mixtures of nitric and oxalic acids, or by dissolution in nitric acid followed by oxalate precipitation was demonstrated.

The techniques developed were successfully applied in the Purex plant in meeting Hanford's megacurie commitment of strontium-90 for the SNAP program prototypes, and strontium production is continuing, using this technology.

IV. EXPERIMENTAL

Preliminary scouting studies and the experiments to determine the effects of various chemical variables were performed using synthetic Purex plant waste containing various radioactive tracers. Analyses

were performed by beta or gamma counting preceded, when necessary, by standard radiochemical separations. Following tracer level experiments, the defined flowsheets were tested in both the High Level Radiochemical Facility and in the actual test plant, the Purex head-end centrifuges. The preliminary scouting studies were performed by L. A. Bray. After the start of the Purex pilot plant, H. H. Van Tuyl completed additional studies to simplify and improve the technology of the process and to correct certain difficulties encountered due to the ~~limitations~~ of the Purex head-end equipment and to the pressing need to reduce time cycles and increase plant capacity.

Purex Test Plant Equipment Limitations

The available Purex head-end equipment, as shown in Figure 1, consists of a 5000 gallon feed make-up tank with facilities for reagent addition, heating, cooling and agitation (but when less than 1000 gallons is in the tank, the solution does not reach the agitator blade). The adjusted feed solution may be sent through either or both of two 90 gallon solid bowl centrifuges with the overflow going to another 5000 gallon tank. Skimmers in the centrifuges reduce the heel to about 15 gallons. The cakes remaining in the centrifuges can be washed with a high pressure spray system feed from a 90 gallon tank and the cake slurry can be transferred via a 1700 gallon tank either to waste or back to the feed tank for further processing. Removal of product from the system is accomplished only from the 1700 gallon tank. Reagent addition to the feed tank is accomplished from 700 gallon aqueous make-up tanks through a system of piping with

FISSION PRODUCT RECOVERY-PUREX PLANT

FIGURE 1

about 100 gallons total volume. Therefore, careful control of reagent addition or adjustment to vary narrow pH limits is either difficult or impossible. All process solution transfers are performed by steam jet, and if the solution temperature exceeds about 60 C, the solution is evaporated by the jet and does not transfer as desired. Heels left in the process tanks are about 24 gallons for transfers to the centrifuges or between tanks. However, since the agitators do not reach the bottom of the tanks, a greater fraction of any precipitate is left in the tank than would be indicated by the 24 gallon heel. Tank clean-out is therefore laborious and frequently incomplete.

All of the processing equipment is stainless steel, which permits operations with nitric acid systems, but not with halides. Since the process solutions are eventually neutralized and transferred to underground storage tanks which concentrate by self-boiling, the addition of acids or inorganic salts should be minimized. Because of the hazards associated with ruthenium volatilization, strong oxidizing agents are not acceptable. Organic reagents, which are decomposed by radiolysis, must be sufficiently stable to accomplish the desired end, and must not produce objectionable radiolysis products.

An ideal flowsheet would yield an adequately pure and recoverable strontium precipitate in the centrifuge after a single precipitation step and the necessary washes or leaches. With such a process it would be possible to use each tank for a single purpose instead of having to clean the tanks carefully between cycles.

V. DISCUSSION

A. Recovery of Strontium as a Function of Sulfate Concentration

It was found by T. R. McKenzie that sulfate would quantitatively precipitate cerium and also about 30 per cent of the strontium, yttrium, and trivalent rare earths from a partially neutralized (pH 1.0) Purex LWW waste stream.⁽⁴⁾⁽⁵⁾ E. J. Wheelwright⁽⁸⁾ further developed this approach by demonstrating that cerium-144 and promethium-147 (accompanied by the other rare earths) could be removed from the Purex waste stream in greater than 90 per cent yield as an insoluble crystalline sodium rare earth double sulfate. The precipitation was initiated by adjusting the sulfate concentration to one molar and the pH to between 0.5 and 1.5. The precipitate was then equilibrated at 90 C for several hours and centrifuged at 90 C to take advantage of the lower solubility of the double sulfate at higher temperatures. Under these conditions strontium recoveries of from 30 to 50 per cent were obtained.

It was found⁽⁹⁾ that increased strontium recovery may be obtained by increasing the sulfate concentration from 1 to 3 molar prior to adjustment of the pH to between 0.5 and 1. Figure 2 shows the recovery of strontium from synthetic LWW as a function of the sulfate concentration. A maximum recovery of 80 per cent of the strontium accompanied by a quantitative precipitation of cerium and rare earths as the sodium double sulfate was obtained from the synthetic Purex LWW waste upon the addition of sulfate to a concentration of 3 molar at pH of 0.5 to 1.

FIGURE 2
Recovery of Strontium from Synthetic Purex Waste as a Function of the Sulfate Concentration

B. Tartaric Acid as a Complexing Agent to Prevent Iron Precipitation

When strontium is precipitated as a sulfate from a solution containing in excess of 1 molar sulfate at a pH of 1, it was noted that copious amounts of iron (LWW contains 0.3 to 0.6 mole of iron per liter) as well as cerium and rare earths would also be found in the precipitate. Upon the addition of 0.25 to 0.5 mole of tartaric acid to complex 0.5 mole of iron, the 3 molar sulfate procedure for the recovery of 80 per cent of the strontium from the Purex waste stream continued to allow recoveries as indicated in Figure 2.

To determine the temperature stability of tartaric acid, a synthetic LWW solution was adjusted to contain 3 molar sulfate, 0.5 molar iron and 0.25 molar tartaric acid. The solution was adjusted with NaOH to a pH of 1 and refluxed at 100-110 C. From 4 to 6 hours were required to visually note iron precipitation. A second test with 0.5 molar tartaric acid and all other conditions held constant indicated no visual iron precipitation after 24 hours of boiling at 100-110 C.

To determine the radiation stability of tartaric acid, a solution of tartaric acid was placed in the cobalt irradiation facility in the 325 Building, 300 Area. After receiving a radiation dose of 10^8 R, 73 per cent of the original complexing strength was still available. Tartaric acid when placed in an actual Purex waste solution would receive a radiation dose of about 4×10^6 R per hour. These two experiments demonstrate that the stability of tartaric acid to heat and radiation is adequate.

Actual Purex plant tests have verified the value of tartaric acid and show an extreme improvement in the iron decontamination factor in comparison to former plant tests without the addition of a complexing agent. In a plant test ⁽¹⁰⁾ using tartaric acid, a 1213 gallon volume of Purex LWV was adjusted to 0.17 molar in tartaric acid, the sulfate content was increased to 1.5 molar, and the solution was neutralized to a pH of 1. The solution was equilibrated at 90 C for 1 hour and centrifuged. The precipitate was leached with nitric acid and the decontamination factors were then determined: iron 70, zirconium 10, niobium 20 and ruthenium 35. In previous sulfate precipitation tests without tartaric acid, iron contamination of the sulfate product was serious and the fission product decontamination was low: zirconium and niobium 1 and ruthenium 33.⁽¹¹⁾

C. Effect of Carriers on Strontium Precipitation

The possibility of using a carrier to increase the strontium yield rather than high concentrations of sulfate was next considered. Without the use of sulfuric acid, it is difficult to increase the Purex waste stream to 3 molar sulfate. There is also objection to the high salt content of the resulting waste. It was determined, using synthetic LWV at 1 molar sulfate and a pH of 0.4, that 0.02 molar lead, barium, cerium, rare earths, lanthanum (and probably other related elements) would carry approximately 80 per cent of the strontium. Without the addition of carriers, only 36 per cent of the strontium precipitated as the sulfate. (Figure 3). In other experiments, in which the concentration of strontium was varied over a wide range, it was shown that the

FIGURE 3

Recovery of Strontium from Synthetic Purex Waste as a Function of the Carrier Concentration

precipitation of strontium with these carriers is an adsorption or carrier type reaction, and not simply a solubility product type precipitation of strontium sulfate. The fraction of the strontium precipitated decreased with increasing ^{strontium}/concentration, implying saturation of specific adsorption sites.

Lead was picked as the carrier of choice because of ease of subsequent removal.

D. Effects of Sulfate and Lead Carrier on Strontium Precipitation

The use of sulfate, tartaric acid to complex iron, and/or a carrier such as lead to remove strontium from the Purex IWW waste stream appeared to be most feasible for the Purex plant operation. Three tests were performed (using synthetic IWW) incorporating the above findings and were designed to demonstrate the simultaneous recovery of strontium and cerium. The results are shown in Table II. They again indicate that 0.15 to 0.25 molar tartaric acid and 3 molar sulfate will permit a strontium recovery of 70 to 80 per cent; and that 0.25 molar tartaric acid, 1.5 molar sulfate and 0.02 molar lead will give a strontium recovery of 95 to 100 per cent. This demonstrates that a combination of sulfate only slightly in excess of 1 molar and a carrier such as lead will allow a near quantitative recovery of strontium. (9)

A series of tests was initiated to determine the recovery of strontium as a function of the molarity of lead carrier and total sulfate. Table III and Figure 4 show the results using synthetic IWW and strontium-85 tracer. It is evident from these results that at a pH of 0.4 the sulfate precipitation of strontium will permit near quantitative recoveries upon the addition of 0.01 to 0.03 molar lead nitrate at 1 to 2 molar sulfate.

Table II
STRONTIUM RECOVERY AS A FUNCTION
OF LEAD CARRIER AND SULFATE

Conditions: Reagents were added to synthetic LWV spiked with strontium-85 and cerium-144 tracers as indicated: carrier lead as the nitrate, sulfate added as sulfuric acid.50 per cent sodium hydroxide to a pH of 0.4, and the resulting solution was stirred at 85 C for 1 hour before centrifugation.

LWV (Milliliters)	Carrier <u>M</u>	Tartaric		Sulfate		Per Cent Strontium		Per Cent Cerium	
		Acid <u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>	Filtrate	Precipitate	Filtrate	Precipitate
500	None	0.16		3.0		20	80	1	99
200	None	0.25		3.0		26	74	4	96
200	0.02(Pb)	0.25		1.5		3	97	4	96

Table III

EFFECT OF SULFATE AND LEAD CARRIER ON
STRONTIUM AND CERIUM PRECIPITATION

Conditions: Reagents were added to synthetic LWW spiked with strontium-85 and cerium-144 tracers as indicated; carrier lead as the nitrate, tartrate to 0.5M, 50 per cent sodium hydroxide to a pH of 0.4, sulfate as sodium sulfate, and the resulting solution was stirred at 65 to 85 C for 1 hour before centrifugation.

<u>Lead</u> <u>M</u>	<u>Sulfate</u> <u>M</u>	<u>Per Cent Strontium</u>		<u>Per Cent Cerium</u>	
		<u>Filtrate</u>	<u>Ppt.</u>	<u>Filtrate</u>	<u>Ppt.</u>
---	3	25	79	2	94
---	2	27	74	1	101
0.005	2	9	85	2	92
0.01	2	4	96	2	98
0.03	2	3	103	3	98
---	1.5	33	67	1	101
0.01	1.5	8	88	2	95
0.02	1.5	5	100	3	101
0.03	1.5	8	94	4	96
---	1	45	54	4	101
0.01	1	10	85	3	95
0.02	1	6	94	2	99
0.03	1	4	--	3	--
---	0.5	65	36	20	84
0.005	0.5	47	54	37	66
0.01	0.5	22	78	14	84
0.02	0.5	22	77	30	68
0.03	0.5	19	81	30	82

FIGURE 4

Recovery of Strontium as a Function of the Lead Carrier and Sulfate Concentration

E. Precipitation of Strontium at Lower Acid Concentrations

The experiments described in the previous sections were carried out at pH's ≤ 1 , and gave satisfactory results. In the course of plant testing, it became of interest to extend the investigation to higher pH's and to investigate the effects of variables in more detail. The results are described in the following sections.

It was observed that an adequate strontium sulfate-lead carrier precipitation can be achieved with the pH as high as 4.5. Tracer level experiments on the recovery of strontium were performed with LWW containing 0.004 M $\text{Ca}(\text{NO}_3)_2$, 0.002 M $\text{Ba}(\text{NO}_3)_2$, and the other fission products and trace impurities. The initial procedure was to add cerium-144 and strontium-85 tracers, 2 M Na_2SO_4 , 5 M $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, 1 M $\text{Pb}(\text{NO}_3)_2$, and 50 per cent NaOH to the LWW to adjust it for strontium precipitation. The mixture was then heated for one hour at 80 to 90 C and filtered. The supernate was analyzed by gamma spectrometry and the precipitate was further treated as described later.

Experiments summarized in Table IV demonstrate that a pH of 3.0 is less satisfactory than somewhat higher pH values and that adequate strontium precipitation can be achieved with the pH as high as 4.5. Only a slight dependence on the amount of lead added was observed with from 0.01 to 0.05 mole of lead per liter of LWW, but unfavorable recoveries were obtained when no lead was added. The addition of up to 2.5 moles of Na_2SO_4 per liter of LWW had little or no effect on the recovery of strontium at these higher pH values.

Table IV

EFFECTS OF pH, LEAD AND SULFATE ON
STRONTIUM PRECIPITATION

Conditions: Reagents were added as indicated to 1 liter of synthetic lww, spiked with strontium-85 and cerium-144, and the resulting solution was stirred at 80 to 90 C for 1 hour and filtered.

pH	Moles Added Per Liter Of lww*			Total Volume After Reagent Addition (liters)	Strontium Loss To Supernate, Per Cent
	$\text{Pb}(\text{NO}_3)_2$	Na_2SO_4	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$		
0.3	0.05	2.5	1.0	2.4	27
1.0	0.05	2.0	0.85	2.4	2.4
1.0	0.03	---	0.85	1.5	6.0
1.0	----	2.0	0.85	2.3	16
1.5	0.03	---	0.85	1.5	3.9
1.5	0.025	2.0	0.85	2.3	4.2
1.5	0.015	2.0	0.85	2.3	5.0
1.5	0.01	---	0.85	1.5	8.2
1.5	0.01	2.0	0.85	2.3	6.4
1.5	----	2.0	0.85	2.3	12
2.0	0.05	2.5	1.0	2.4	2.6
2.0	0.05	2.0	0.85	2.3	3.4
2.0	0.04	1.2	1.0	1.8	2.4
2.0	0.03	---	0.85	1.5	3.0
2.0	0.025	2.5	1.0	2.4	5.5
2.0	0.015	2.5	1.0	2.4	5.4
2.0	----	2.0	0.85	2.3	16
3.0	0.04	2.0	0.85	2.3	3.4
3.0	0.03	---	0.85	1.5	2.4
3.0	0.02	2.0	0.85	2.3	7.7
3.0	0.01	---	0.85	1.5	9.1
3.0	---	2.0	0.85	2.3	18
3.5	0.02	2.0	0.85	2.3	7.8
4.0	0.02	2.0	0.85	2.3	4.7
4.0	0.02	1.0	1.0	1.7	9.1
4.0	0.01	---	0.85	1.5	9.1
4.5	0.02	2.0	0.85	2.3	7.7

*Note that the original lww contains 1 M Na_2SO_4 . Thus the total amount of sulfate is one mole greater than that shown. The molarity of lead, sulfate, or tartrate at the time of precipitation is given by the total number of moles divided by the total indicated volume of solution.

F. Effect of Tartrate on Strontium Precipitation

Experiments were performed, as shown in Table V, to determine the effect of variations in the amount of tartrate added. Again only a slight dependence of strontium recovery on the amount of lead added was observed, with large amounts of lead giving increasing strontium recoveries. Cerium precipitation was virtually independent of lead additions. Dependence on the amount of tartrate added was quite pronounced for both elements, with higher tartrate concentrations yielding poorer recoveries of each element, but also effecting a reasonable separation of strontium from cerium at pH of 3 under proper conditions. At a pH of 2 both elements are precipitated almost quantitatively, but at a pH of 4 both elements remain predominantly in the supernate.

Table V

EFFECT OF TARTRATE ON STRONTIUM PRECIPITATION

Conditions: Reagents were added as indicated to synthetic 1WW spiked with strontium-85 and cerium-144, and the resulting solution was stirred at 80 to 90 C for 1 hour and filtered.

Moles Added Per Liter of 1WW		Per Cent Remaining in Supernate					
		pH 2		pH 3		pH 4	
<u>Pb(NO₃)₂</u>	<u>H₂C₄H₄O₆</u>	<u>Ce</u>	<u>Sr</u>	<u>Ce</u>	<u>Sr</u>	<u>Ce</u>	<u>Sr</u>
0.01	1.5			98	48		
0.02	0.75	<5	5.4	<4	3.6	45	55
0.02	1.0			16	7.2		
0.02	1.25			74	14		
0.03	0.75	2.2	3.5	<4	2.4	14	4.4
0.03	1.0			24	5.6		
0.03	1.25	5.1	3.2	78	13	90	41
0.03	1.5			84	18		
0.03	1.75	19	5.6	88	12	99	75
0.04	0.75			3.7	2.6		
0.04	1.0			37	4.5		
0.04	1.25			59	12		
0.06	0.75	<4	2.1	<4	2.0	20	2.5
0.06	1.0			61	2.6	80	33
0.06	1.25			62	4.0	92	54
0.06	1.5			71	6.7	95	77

G. Effect of Temperature on Strontium Precipitation

Because of the difficulty encountered in the plant in processing solutions at temperatures above about 60 C, the effect of digestion at lower temperatures was investigated in the higher pH range of interest, as shown in Table VI. In each case, 0.03 mole of lead and 1.25 moles of tartaric acid were added per liter of lww and the solution was digested for 1 hour. At each of the three pH values investigated, the maximum precipitation of each element was obtained at elevated temperature and recovery at ambient temperatures was inadequate, even at a pH of 2. The best separation of strontium from cerium was obtained at a pH of 3 with elevated temperatures and the best precipitation of both elements simultaneously was obtained at a pH of 2 with elevated temperatures.

Table VI

EFFECTS OF TEMPERATURE ON STRONTIUM PRECIPITATION

Conditions: To 1 liter of synthetic lww, spiked with strontium-85 and cerium-144, 0.03 mole of lead and 1.25 moles of tartaric acid were added. The solution was digested at the temperature shown for 1 hour and filtered.

<u>Temperature, C</u>	<u>Per Cent Remaining in Supernate</u>					
	<u>pH 2</u>		<u>pH 3</u>		<u>pH 4</u>	
	<u>Ce</u>	<u>Sr</u>	<u>Ce</u>	<u>Sr</u>	<u>Ce</u>	<u>Sr</u>
20	81	28	85	62	100	96
40	69	21	82	58	95	81
60	37	9.7	79	26	99	86
80	6.2	4.0	78	13	98	84

H. Effect of Order of Reagent Addition on Strontium Precipitation

An experiment was performed to determine the optimum order of reagent addition. The results, summarized in Table VII, show that addition of lead after pH adjustment results in substantially better strontium recovery. The two experiments with over 60 per cent of the strontium remaining in the supernate are possibly erroneous because of improper pH adjustment, but this was not investigated further. Similar experiments using citric acid instead of tartaric acid resulted in precipitation of both strontium and cerium regardless of the order of reagent addition.

Table VII

EFFECT OF ORDER OF REAGENT ADDITION ON STRONTIUM PRECIPITATION

Conditions: To 1 liter of synthetic 1WW, spiked with strontium-85 and cerium-144, 0.03 mole of lead and 1.25 moles of tartaric acid were added. The solution was adjusted to a pH of 3, digested at 80 to 90 C for 1 hour and filtered.

<u>Order of Addition</u>	<u>Per Cent in Supernate</u>	
	<u>Ce</u>	<u>Sr</u>
Pb, Tartrate, NaOH	78	13
Tartrate, Pb, NaOH	97	68
Tartrate, NaOH, Pb	85	8
Pb, Wait 30 min., Tartrate, NaOH	98	61
Tartrate, Pb, Wait 30 min., NaOH	84	13
Tartrate, NaOH, Heat to 80°, Pb	81	7
Tartrate, NaOH, Heat 30 min., Pb	79	6

I. Effect of pH on Strontium and Cerium Precipitation

A set of experiments was performed to evaluate the strong dependence of both cerium and strontium precipitation on pH when excess tartaric acid is added. The results, shown in Table VIII, demonstrate a decontamination factor of four or more from cerium

in the strontium precipitation when the pH was above 2.5, and excessive strontium losses when the pH was above about 3.2. While the separation between cerium and strontium is adequate in this range, the control of pH in the plant is usually not accurate enough to assure being in this range unless very careful adjustment of the pH is made.

Table VIII

EFFECT OF pH ON STRONTIUM AND CERIUM PRECIPITATION FROM PUREX 1WW

Conditions: To 1 liter of synthetic 1WW, spiked with strontium-85 and cerium-144, 1.25 moles of tartaric acid and 0.03 mole of lead were added. The solution pH was adjusted with sodium hydroxide and the slurry was digested for 1 hour at 60 C and filtered.

<u>pH</u>	<u>Per Cent Remaining in Supernate</u>	
	<u>Cerium</u>	<u>Strontium</u>
2.0	26	3.7
2.2	68	5.6
2.4	70	6.4
2.6	81	8.6
2.8	84	10.0
3.0	88	13.6
3.2	88	17
3.4	95	34
3.6	97	65
3.8	98	68
4.0	98	82

J. Nitric Acid Leaching of the Lead Sulfate Precipitate

The studies to obtain efficient recoveries of strontium from the Purex 1WW waste stream terminated with two general approaches: adjustment of the starting waste material to contain a sulfate concentration beyond that required for rare earth precipitation, or use of a carrier such as lead. Both methods require the use of a complexing agent such as tartaric acid to prevent the copious precipitation of iron. Because of objections to the high salt content

of the resulting sulfate waste, the lead carrier precipitation method was chosen for further study. Lead was chosen over other carriers on the basis of several considerations including cost of chemical reagents and ease of subsequent processing. The process adopted is shown in Figure 5.

After completion of the initial sulfate precipitation step the objective then is to dissolve the sulfate precipitate and separate the strontium away from the lead, cerium and rare earths. Nitric acid was first investigated for the leaching of the sulfate cake from the Purex centrifuge. A synthetic LWW solution was precipitated as indicated in Figure 5. The laboratory results are computed on the basis of a Purex plant scale equivalent of 2000 gallons of LWW (containing 0.04 mole of lead per liter). The precipitate was batch contacted with the equivalent of 80 gallons of 6 molar nitric acid at 80 to 100 C for 15 minutes. Twenty-eight leaches were required to completely dissolve the sulfate precipitate. Figure 6 presents the rate of dissolution of strontium and cerium by leaching the lead sulfate precipitate with 6 molar nitric acid. The results indicate that 99 per cent of the cerium was removed at the end of six leaches while the strontium and lead were dissolved uniformly at approximately 4 per cent per leach. Because of these excessive volumes, the acid dissolution for the removal of a lead sulfate precipitate from the centrifuge is not feasible for the Purex plant.

K. Sodium Acetate Leaching of the Lead Sulfate Precipitate

The recovery of strontium and cerium by leaching a lead sulfate precipitate with sodium acetate was next considered. A

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A LEAD SULFATE CARRIER PRECIPITATION CYCLE

<u>PUREX 1WW</u>			
HNO ₃	4.0 M	Ce	100%
Al	0.1	R.E.	100%
Fe	0.5	Sr	100%
Cr	0.01	Cs	100%
Ni	0.01	Zr-Nb	100%
SO ₄	1.0		

Vol. 100

1.0M Pb(NO₃)₂ to 0.02M, Vol. 42.0M Na₂SO₄ to 1.5M, Vol. 50

5.0M Tartaric Acid to 0.5M, Vol. 20

NaOH to pH 0.5 to 2.5

Total Vol. 100

Digest at 90 C - 1 Hour

Wash, 1.5M Na₂SO₄, pH 1

Centrifuge

Sulfate Precipitate

Sr	90%
RE	97%
Ce	97%
Fe	0.5%
Zr-Nb	0.5%
Cs	1%
Pb	99%
Vol.	2

Sulfate Supernate

Sr	10%
RE	3%
Ce	3%
Fe	99.5%
Zr-Nb	99.5%
Cs	99%
Pb	1%
Vol.	200

FIGURE 5

FIGURE 6

Recovery of Strontium and Cerium by Leaching a Lead Sulfate Precipitate
 with 6 M Nitric Acid

synthetic LWW solution was treated as indicated in Figure 5. The experiment was again equivalent to 2000 gallons of LWW and contained 0.04 mole of lead per liter of LWW. The precipitate was batch contacted repetitiously with the equivalent of 80 gallons of 4 molar sodium acetate at 80 to 100 C for 15 minutes. The first four leaches recovered 99 per cent of the cerium and only 2 per cent of the strontium. The next three sodium acetate leaches and a final 6 molar nitric acid leach recovered 1 per cent of the cerium and 97 per cent of the strontium. Figure 7 presents the rate of dissolution of strontium and cerium by leaching a sulfate precipitate with 4 molar sodium acetate.

The dissolution of the sulfate cake from the Purex centrifuge when lead is added as a carrier appears from these experiments to be most difficult, as contrasted to ease of dissolution of the simple double sulfate. For these experiments, the precipitate was placed in a beaker and continuously stirred during the dissolution. Removal from a Purex centrifuge would be even more difficult. Further work to convert the sulfate precipitate by metathesis with carbonate, hydroxide, or oxalate was clearly indicated.

L. Selective Leaching of Cerium from the Lead Sulfate Precipitate

Selective removal of cerium from the sulfate cake (without removing strontium) by leaching with complexing agents was also attempted. A sulfate precipitate was prepared, using a pH of 2 and adding 0.03 mole of lead per liter of LWW. About 20 per cent of the cerium and 4.5 per cent of the strontium were lost to the supernate. The precipitate was leached four times with 100

FIGURE 7

Recovery of Strontium and Cerium by Leaching a Lead Sulfate Precipitate
 with Sodium Acetate

milliliters of solution per liter of original lww, with 10 minutes contacting and 60 C leaching temperature.

Citrate, tartrate, and N-hydroxyethylethylenediaminetriacetic acid (HEDTA) were observed to be quite similar, but ethylenediaminetetraacetic acid (EDTA) was found to exhibit practically no selectivity for cerium. The dependence on pH of the wash solution is only slight, with less removal of each element at lower pH values. The addition of sulfate to the leach solution reduces the amounts of both cerium and strontium that are removed and significantly improves the ratio of cerium to strontium removed. Optimum conditions are about 0.25 molar complexant and 0.5 molar sulfate. However, with the best conditions tested only about half of the cerium is removed when strontium losses are below 10 per cent. Therefore, this approach does not appear very promising for plant application.

M. Metathesis of the Lead Sulfate Precipitate to the Hydroxide

After completion of the initial sulfate precipitation (Figure 5) the objectives remaining were to convert or dissolve the lead sulfate precipitate and to separate the strontium from the lead, cerium and rare earths. The separation of strontium from rare earths by an oxalate precipitation leaving the strontium in the supernate had already been suggested by G. B. Barton⁽²⁾ and appeared suitable for this portion of the separation. The main objective then was to obtain a suitable solution for the strontium oxalate separation of the rare earths and cerium. From the work reported in the previous sections, it was concluded that a nitric acid dissolution was not practical and that other methods of direct dissolution also appeared impractical. Metathesis of

the sulfate precipitate to the carbonate, hydroxide or oxalate was next considered.

The necessity of using a carrier such as lead to promote a quantitative strontium precipitate also introduced an additional separations problem in that lead will interfere with the separation of the rare earths from cerium.⁽¹³⁾ Therefore, a hydroxide metathesis of the sulfate precipitate prior to the strontium oxalate separation would accomplish two steps: 1) conversion of the sulfate precipitate to the hydroxide, and 2) conversion of the lead to the soluble lead plumbite.

Lead sulfate forms hydrated lead oxide with sodium hydroxide and is soluble in an excess of the reagent forming the plumbite:

Several tests indicated that it would be possible to metathesize the sulfate to the hydroxide while the precipitate was contained in the Purex centrifuge. The resulting hydroxide precipitate from such a metathesis contained all the cerium, rare earths, 5 to 15 per cent of the lead, but only 50 to 78 per cent of the strontium originally in the sulfate precipitate. It was concluded that the solubility of strontium hydroxide would not permit complete strontium recovery by metathesis from the sulfate with sodium hydroxide alone.

N. Metathesis of the Sulfate Precipitate with Sodium Carbonate - Sodium Hydroxide

As pointed out in the preceding section, leaches with sodium hydroxide alone dissolved much of the lead and rendered the

residual precipitate much more soluble in acid, but strontium losses to the leach supernate were excessive. Leaches with 0.5 to 1.5 molar sodium carbonate removed less than 1 per cent of the strontium and rendered the residual precipitate readily soluble in dilute nitric acid. The most granular precipitates were obtained when 1 molar sodium carbonate was used and the metathesis was performed at elevated temperatures. The precipitate quality was still very good with either 0.5 or 1.5 molar carbonate reagent.

Because of the success with carbonate, a mixture of carbonate and hydroxide was tried, as shown in Table IX, to simultaneously remove the lead and sulfate. The sulfate precipitate was formed as previously described except that varying amounts of lead were added and lead addition preceded the pH adjustment. The resulting precipitate was then washed twice with 80 milliliters of 1 molar sodium sulfate to remove iron and tartrate before the alkaline metathesis. The leaches were performed at 60°C with 10 minute contacting periods. From these results it is concluded that the removal of lead is dependent both on the amount of lead added to the Purex 1WW and also on the volume of the leach solution. The volume per leach appears less important than the total volume used, but there is some benefit to making several washes with small volumes. About 300 milliliters of leach solution per liter of 1WW appears adequate for removing most of the lead when 0.03 mole or less of lead is initially added, but additional washes are required if more lead is present.

Table IX

METATHESIS OF THE SULFATE - LEAD PRECIPITATEWITH CARBONATE - HYDROXIDE MIXTURES

Conditions: To 1 liter of synthetic lww, spiked with strontium-85 and cerium-144, 1 mole of tartaric acid and the indicated amount of lead nitrate were added. The solution was adjusted to a pH of 2 with sodium hydroxide and the slurry was digested for 1 hour at 60 C and filtered. The precipitate was washed twice with 80 milliliters of 1 molar sodium sulfate. The leaches were then performed at 60 C with 10 minute contacting periods.

Moles Pb Per liter of lww	Leach Volumes per Liter of lww			Molar Concentrations		Per Cent Removed		
	No. of Leaches	Vol. Per Leach, ml.	Total Vol. ml.	Na_2CO_3	NaOH	Pb	Ce	Sr
0.03	2	40	80	1	5	41	<0.4	2.2
0.03	1	100	100	0.5	5	37	6.1 ^a	4.3 ^a
0.03	3	40	120	1	5	63	<1 ^a	11 ^a
0.01	3	80	240	1	5	81		0.7
0.04	3	80	240	1	2	70		1.2
0.06	3	80	240	1	5	33	<0.3	1.0
0.03	4	80	320	1	5	95	<1	1.3
0.06	6	80	480	1	5	57	<0.5	<1

^aNot washed with Na_2SO_4 before caustic metathesis.

0. Metathesis of the Lead Sulfate Precipitate with Carbonate-Hydroxide-Tartrate Solutions

The addition of tartrate to the alkaline metathesis solution was investigated as shown in Table X. The procedure used was similar to that used for the carbonate-hydroxide metathesis, except that all leach volumes were 100 milliliters per liter of lww and initial lead was constant at 0.03 mole per liter of lww. The pH of the sulfate precipitation was varied to obtain sulfate cakes with different amounts of cerium precipitated.

Table X

METATHESIS OF THE SULFATE - LEAD PRECIPITATEWITH CARBONATE-HYDROXIDE-TARTRATE SOLUTIONS

Conditions: To 1 liter of synthetic LWV, spiked with strontium-85 and cerium-144, 1 mole of tartaric acid and 0.03 mole of lead nitrate were added. The solutions were adjusted to various pH values with sodium hydroxide and the slurry was digested for 1 hour at 60 C and filtered. The precipitate was washed twice with 80 milliliters of 1 molar sodium sulfate. All leach volumes were 100 milliliters per liter of LWV and were performed at various temperatures with 10 minute contacting periods.

No. of Washes	Temp., C	Leach Composition, M			Per Cent Removed				
		Tartrate	Na ₂ CO ₃	NaOH	Previously		By Washes		
					Ce	Sr	Pb	Ce	Sr
2	25	0.001	0.5	5	87	11	~90	11	40
2	25	0.01	0.5	5	90	20	92	8.2	48
2	60	0.0001	0.5	5	84	11	99	5.8	8.4
1	60	0.001	0.5	5	88	15	83	5.7	5.2
2	60	0.001	0.5	5	87	17	99	7.4	11
3	60	0.001	0.5	5	18	4.1	~75	9.0	7.9
1	60	0.01	0.5	5	91	30	93	6.4	7.5
2	60	0.01	0.5	1	87	17	~50	4.9	4.3
2	60	0.01	0.5	2	85	9	84	10	16
2	60	0.01	0.5	5	88	17	99	8.2	18
2	60	0.01	1	5	88	16	>90	8.4	23
2	60	0.01	0.5	8	88	16	~100	8.7	34
3	60	0.01	0.5	5	18	4.0	~90	22	12
1	60	0.05	0.5	5	90	21	90	7.0	23
2	60	0.1	0.5	5	91	22	>90	7.6	42
2	80	0.01	0.5	5	85	13	90	10	11

Two washes with 0.001 M or one wash with 0.01 M tartrate are adequate to remove over 90 percent of the lead from the precipitate if most of the rare earths have been previously removed. Otherwise either more washes or higher tartrate concentrations or both are required for equal lead removal. Lower wash temperatures

reduce lead removal, and increase strontium losses. Little selectivity in cerium removal was found under any conditions tested. Optimum conditions for lead removal are 0.001 M tartrate, 5 M or more sodium hydroxide, 0.5 M sodium carbonate, and 60 C or over. One wash is sufficient if rare earths have been previously removed (e.g., in the sulfate precipitation step), while three washes are required if the rare earths are present during the leaches.

P. Direct Metathesis of the Lead Sulfate Precipitate to the Oxalate

If a sulfate cake containing fission products and lead (0.04 mole per liter of LWV) were slurried from the Purex centrifuge with high pressure water into a precipitation tank, a separation of the strontium from cerium, lead and rare earths by use of a direct oxalate metathesis is then possible and attractive because of the reduction of time cycles. The strontium content of the oxalate filtrate was found to vary with the ratio of the volume of the slurried LWV sulfate, the molarity of the oxalate used for precipitation of the lead, cerium and rare earths, and with the amount of lead carrier. Table XI contains two sets of data showing first that the recovery of strontium in the supernate is dependent upon the moles of lead per liter of LWV at a constant oxalate concentration, and second, the recovery of strontium in the supernate is dependent upon the molarity of the oxalic acid at a constant lead concentration. Table XI shows that if it were possible to slurry the sulfate precipitate containing strontium, lead, and rare earths from the Purex centrifuge, it would then be possible to metathesize the sulfate directly to the oxalate, converting the cerium, rare earths, and lead to an insoluble oxalate precipitate, leaving the strontium and iron in the supernate.

Table XI

SEPARATION OF STRONTIUM FROM CERIUM, RARE EARTHS AND LEAD AS OXALATES

Conditions: To 1 liter of synthetic lww, spiked with strontium-85 and cerium-144, 1 mole of tartaric acid, sodium sulfate to 1.5 molar, and lead nitrate were added. The solutions were adjusted to a pH of 0.4 with sodium hydroxide and the resulting slurry was digested for 1 hour at 85 C and filtered. The sulfate precipitate was then slurried with water and nitric acid added to a pH of 0.7 at the volumes indicated. Oxalic acid (0.5 molar) was added to adjust the solution to the final indicated molarity. The resulting solution was heated at 80 to 100 C for 30 minutes and centrifuged.

Starting Material (lww) <u>Liters</u>	Concentration of Lead Carrier <u>Moles/Liter lww</u>	Volume of Slurried Sulfate (pH 0.7) <u>Liters</u>	Oxalic Acid <u>Molarity</u>	<u>Per Cent Recovery</u>					
				<u>Oxalate Filtrate</u>			<u>Oxalate Precipitate</u>		
				<u>Ce</u>	<u>Sr</u>	<u>Pb</u>	<u>Ce</u>	<u>Sr</u>	<u>Pb</u>
1	0.02	1	0.21	98			2		
1	0.04	1	0.21	49			51		
1	0.06	1	0.21	34			66		
1	0.04	0.5	0.225	3	82	3	97	18	97
1	0.04	0.5	0.300	3	92	1	97	8	99
1	0.04	0.5	0.375	4	97	1	96	3	99

The selective removal of strontium from both sulfate and carbonate precipitates by leaching with oxalic acid was also investigated. These experiments were performed on cakes prepared while investigating the sulfate precipitation step and, therefore, the cakes differ somewhat in lead content. All cakes were prepared at pH 2 or less, so that the rare earths were precipitated in the cake. Some experiments were run directly on a sulfate cake, while for others the cake was metathesized with 0.5 molar sodium carbonate and 5 molar sodium hydroxide to remove the sulfate and about 75 per cent of the lead. Oxalate leaches

were performed at 60 C with 10 minute contacts, using 80 milliliters of leach per liter of 1WW.

Table XII shows that the removal of strontium is inadequate when the sulfate cake is leached directly, when lead carrier is used. Removal of strontium from the carbonate cake is almost quantitative when 0.5 molar or more nitric acid is used. The oxalate concentration has little effect on the strontium removal, but about 0.5 molar oxalic acid is required to prevent excessive cerium leaching.

Table XII

METATHESIS OF CARBONATE AND SULFATE PRECIPITATES
WITH OXALIC ACID SOLUTIONS

Conditions: Sulfate and carbonate precipitates containing tracer strontium-85 and cerium-144 were prepared during previous experiments. The oxalate leaches were performed at 60 C with 10 minute contacting periods, using 80 milliliters of leach per liter of 1WW.

<u>Moles Pb per</u> <u>Liter of 1WW</u>	<u>Cake</u> <u>Type</u>	<u>No. Of</u> <u>Leaches</u>	<u>HNO₃</u>	<u>H₂C₂O₄</u>	<u>Per Cent Removed*</u>	
					<u>Ce</u>	<u>Sr</u>
0	SO ₄ ²⁻	3	0.3	0.1		51
0	SO ₄ ²⁻	3	0.3	0.25		45
0	SO ₄ ²⁻	6 ^a	0.3	0.25		95
0	SO ₄ ²⁻	3	0.5	0.25		79
0.01	SO ₄ ²⁻	3	0.5	0.25		55
0.03	SO ₄ ²⁻	3	0.5	0.25		18
0.04	CO ₃ ²⁻	3 ^a	0.3	0.25		69
0.03	CO ₃ ²⁻	3	0.3	0.25		74
0.015	CO ₃ ²⁻	3 ^a	0.3	0.5		64
0.025	CO ₃ ²⁻	3 ^a	0.3	0.5		58
0.05	CO ₃ ²⁻	3 ^a	0.3	1		54
0.01	CO ₃ ²⁻	3	0.5	0.25		99
0.03	CO ₃ ²⁻	2	0.5	0.25		99
0.03	CO ₃ ²⁻	3	0.5	0.25		99
0.06	CO ₃ ²⁻	4	1	0.5	24	95
0.06	CO ₃ ²⁻	4	1	0.5	< 0.2	90
0.06	CO ₃ ²⁻	4	1	0.25	4.2	98

*Percent of amount in precipitate rather than of initial amount.

^aWash volume only 40 ml. each.

*Cerium analyzed in three experiments only.

Q. Precipitation of Oxalates from Dissolved Carbonate Precipitates

The direct oxalate treatment of the sulfate precipitate (slurry) was shown (Table XI) to be inadequate for good strontium recovery unless the volume of the oxalate precipitation solution was increased to more than the LWW volume. Precipitation from the dissolved carbonate cake, prepared by leaching the sulfate cake with 1 molar sodium carbonate, was more successful. Before adding oxalic acid and digesting, the carbonate cake was treated with 200 milliliters of 2 molar nitric acid per liter of LWW and digested for 1 hour at 80 C. Good strontium recovery was obtained with digestion times of 1/2 and 3 hours, at temperatures of from 25 to 90 C, and from a pH of 0.7 to a nitric acid concentration of 1.7 molar.

For further investigations of the precipitation of oxalates from the dissolved carbonate cake, a synthetic carbonate cake solution was prepared to insure uniformity of feed for the oxalate precipitation and to avoid the tedium of preparing many individual precipitations and leaches. The feed solution, which represents about a five-fold concentration of the fission products from LWW, contained 0.08 molar iron, 0.06 molar lead, 0.07 molar rare earths, 0.01 molar strontium and 1 molar nitric acid. Before adding the precipitants, the solution was made 0.014 molar in sodium sulfate to simulate the sulfate carry-over from the preliminary purification step. This was not added to the stock solution since it produced a precipitate and made uniform sampling of the stock solution difficult. Reagents were added as shown in Table XIII, digested for 1 hour at the temperatures shown, filtered, and the supernates and dissolved precipitates were analyzed by gamma spectrometry. Two supernates were also analyzed for lead by coulometry.

Table XIII

PRECIPITATION OF OXALATES FROM SIMULATED CARBONATE CAKE SOLUTION

Conditions: A synthetic carbonate feed solution containing 0.08 molar iron, 0.06 molar lead, 0.07 molar rare earths, 0.01 molar strontium, 1 molar nitric acid, a strontium-85 and a cerium-144 spike was adjusted to 0.014 molar sodium sulfate. Reagents were then added as shown, the slurry digested for 1 hour and filtered.

Moles Added Per Liter of Feed		Temp. °C	Per Cent in Supernate		
$\text{H}_2\text{C}_2\text{O}_4$	NaOH		Pb*	Ce	Sr
0.2	0	25		80	93
0.2	0.5	25		43	96
0.2	0	60		96	96
0.2	0.5	60		72	95
0.3	0	25		16	97
0.4	0	25		10	96
0.4	0.5	25		7.4	98
0.4	0.83	25		<8	97
0.4	0	60		29	89
0.4	0.5	60		22	92
0.4	0.83	60		< 8	96
0.4	0	80	46	64	98
0.6	0	25	3.7	4.8	96
0.6	0.5	25		4.3	98
0.6	0.83	25		<9	88
0.6	0	60		17	97
0.6	0.5	60		11	96
0.6	0.83	60		<9	94
0.6	0	80		30	92
0.8	0	25		5.5	94
0.8	0.5	25		<5	94
0.8	0.83	25		<10	88
0.8	0	60		9	96
0.8	0.5	60		<5	97
0.8	0.83	60		<11	93

*Lead analyzed in two experiments only.

With 0.2 mole of oxalic acid added per liter of feed, most of the oxalate is used to complex the iron present, so practically no precipitate develops at 60 C, or without the addition of sodium hydroxide. Addition of more than 0.4 mole of oxalate per liter does not improve

cerium removal appreciably at 25 C. Practically no strontium is precipitated under any conditions investigated, but cerium precipitation is dependent on both the amount of sodium hydroxide added and on temperature. Lead was precipitated to a greater extent than was cerium in the two cases investigated. Good separation between cerium and strontium is obtained with half of the nitric acid neutralized, 0.4 mole of oxalic acid, and digestion at 25 C. More oxalic acid is required if the digestion is performed at elevated temperatures.

R. Plant Operating Procedure

Various combinations and modifications of the procedures described in this report have been used by the Purex plant to produce over a megacurie of strontium-90 crude for further processing by ion-exchange or solvent extraction. The current plant procedure consists of adding 900 gallons of a mixture of 2 M sodium sulfate and 1.17 M tartaric acid to 1000 gallons of LWV, adding about 300 gallons of 50 per cent sodium hydroxide to adjust the pH to 1.5 to 2.5, adding 90 gallons of 0.5 M lead nitrate, digesting for one hour at 80 C, cooling to 60 C, and centrifuging at 1500 G at a rate of 20 gallons per minute. The feed tank is washed with 300 gallons of 1 M sodium sulfate, and the wash is transferred through the centrifuge to partially wash the cake. The cake is then completely washed with 80 gallons of 1 M sodium sulfate at 60 C via the centrifuge spray system. Losses through these sulfate steps are about 15 per cent of the strontium, which is in reasonable agreement with the laboratory data for 60 C. Higher temperatures cannot be used in the plant because of the problems of jetting very hot solutions.

The sulfate cake is then washed three times with 80 gallons of a mixture of 5 M sodium hydroxide and 1 M sodium carbonate, and one time with 80 gallons of 1 M sodium carbonate alone. This step removes about 70 per cent of the lead, and converts the remaining cake to the carbonate form. The final carbonate-only wash is used to minimize the heat of neutralization on dissolving the cake, thus facilitating removal of the cake from the centrifuge. Losses during this step have not been accurately determined because of the difficulty of representative sampling.

The cake is dissolved in 240 gallons of 2 M nitric acid, and two batches are combined for the oxalate precipitation step. The solution at about pH 0.5 is treated with 400 gallons of 1 M oxalic acid, digested two hours at 30 C, and centrifuged. The feed tank is washed with 100 gallons of 0.25 M oxalic acid in 1 M nitric acid, and the cake is washed via the spray system with 80 gallons of the same solution. The cake, which contains over 90 per cent of the cerium, is discarded. The strontium loss of about 4 per cent agrees with laboratory experiments.

Two batches of oxalate supernate are combined, 155 gallons of 50 per cent sodium hydroxide is added to give a pH of about 10, and 900 gallons of 1 M sodium carbonate is added. The supernate is discarded after centrifugation, and the cake is dissolved in about 50 gallons of 1 M nitric acid. The dissolved cake is the Purex plant strontium product. Loss of strontium in this concentration step is about 4 per cent.

In addition to the measured losses of about 23 per cent mentioned above, some of the strontium is left as a heel in the centrifuge

feed tank after both the sulfate and oxalate precipitations. These mechanical losses account for about 16 per cent of the strontium. Material balances are generally low, with about 5 per cent of the strontium usually remaining unaccounted for. This could be lost to the alkaline washes, or to other heels left in the processing vessels. Thus the overall recovery has averaged about 55 per cent.

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