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RECOVERY OF STRONTIUM FROM STORED PUREX WASTE
BY LEAD SULFATE CARRIER PRECIPITATION
- PILOT PLANT STUDIES

JANUARY 15, 1965

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RECOVERY OF STRONTIUM FROM STORED PUREX WASTE BY LEAD SULFATE
CARRIER PRECIPITATION - PILOT PLANT STUDIES

By

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I. INTRODUCTION

The Hanford Waste Management Program, as presently scoped, requires the removal of the long-lived fission products, including Sr-90, from Purex and Redox Plant wastes prior to in-tank solidification.⁽¹⁾ The Sr-90 will be removed from current Purex waste by solvent extraction; however a combination of large volumes and gross contamination with iron and aluminum seriously limits the feasibility of solvent extraction for removing strontium from stored Purex and Redox wastes. Accordingly, Bray has proposed a lead sulfate scavenging process for isolating a strontium crude fraction from these wastes.⁽²⁾ The process is similar to the one developed by Bray and Van Tuyl⁽³⁾ now being used in the Purex Plant to prepare a strontium crude for the Strontium Semiworks.⁽⁴⁾

The strontium in the stored, alkaline wastes is contained in a sludge layer which will be dissolved in water and dilute nitric acid. Bray's process involves adding sulfate ion to the acidified, dissolved sludge to 0.7 to 1 M, adjusting the pH to 1 to 2 with sodium carbonate, digesting the mixture at 80C for 15 min., adding lead nitrate to 0.02 M, and centrifuging the resulting slurry. The lead sulfate precipitate, containing over 95% of the strontium, is metathesized with a sodium hydroxide-sodium carbonate mixture and dissolved in dilute nitric acid.

The pilot plant runs described in this report were designed to test and optimize Bray's flowsheet on a 100 to 700-liter scale and to evaluate alternate methods of separating the precipitate from the supernatant liquid. The tests were restricted to Purex-type wastes, but the results should be approximately the same for Redox wastes.

II. SUMMARY

Strontium losses of 5% or less were demonstrated in the pilot plant using Bray's process as outlined above. High iron concentration (0.35M) in one series of runs was believed to have contributed to high strontium losses (ranging from 6 to 28%) through sulfate depletion by complexing and ferric sulfate precipitation.

The precipitate, after digestion, proved to be quite insoluble and could be washed with cold water or very dilute nitric acid (pH > 1) with no significant solubility losses for either strontium or cerium.

The precipitate was satisfactorily metathesized to the acid-soluble carbonate by using a mixture of sodium hydroxide and carbonate as the metathesis solution. Best results were obtained when the hydroxide/lead mole ratio was 15 or above; under these conditions, a sizable fraction of the lead dissolved as the plumbite. As little as 0.2 M carbonate was sufficient to prevent strontium solubility losses. The overall success of the metathesis procedure depended on the efficiency of washing the sulfate freed from the precipitate during metathesis.

Overall product decontamination factors for some of the feed constituents were obtained. Under optimum washing conditions, the DF's ranged from 30 to 460 for iron, aluminum, calcium, magnesium, manganese, and nickel. Lead decontamination factors of 3 and 8 were obtained using hydroxide/lead mole ratios of 15 and 17, respectively, in the metathesis solutions.

Centrifugation, continuous decantation, and batch settling and decantation proved to be feasible methods for removing the supernate from the precipitate. The latter method, with the centrifuge used as backup, is recommended for the following reasons:

- It eliminates the centrifuge solids capacity as a bottleneck.
- It permits the accumulation of precipitate from several batches of feed in the precipitation tank before metathesis and dissolution must be carried out.
- It provides lead economy by utilizing the excess strontium-carrying capacity of the accumulated lead. (As little as 0.01 M added lead was required when the feed was digested in the presence of lead sulfate from previous strikes.)

The settling rates for both sulfate and carbonate precipitates were generally in excess of 2 in./min. and were greater in hot solutions than in cold.

III. FEED PREPARATION

Pilot plant feeds, simulating both acidified stored waste and current Purex waste, were prepared in two ways. The first method followed Bray's recommended procedure: sodium sulfate was added to the acidic waste and the pH adjusted to 1 ± 0.3 with 2 M sodium carbonate. The desired pH was easily obtained because of the strong buffering action of sulfate ion at that pH range (about 0.5 moles of hydrogen ion are held per mole of sulfate at pH 1). Little or no foaming was observed due to acidification of the carbonate. The second method involved recycle of the supernate from preceding runs after a simple chemical adjustment to replace strontium, cerium, and other ions as necessary. Strontium-85 tracer was added to all feeds to facilitate analyses; the final feed also contained Ce-144.

The feeds were digested for 20 to 60 min. at $85 \pm 5^\circ\text{C}$, usually before lead addition. (In the last run, however, the lead was added to the feed as soon as it reached 80°C .) The lead nitrate solution was added in several ways: to the feed tank with and without agitation, to the feed line just before entering the centrifuge, and to the centrifuge itself.

The feeds for all but the last four runs were prepared in a 1000-liter tank equipped with a slow-speed paddle agitator located 5 inches above the bottom (about 160 liters of liquid heel below the agitator). As a result, about 20 to 30% of the precipitate from each run remained in the tank for the next run. The precipitate heel was periodically flushed out of the tank.

Detailed compositions of the adjusted feeds are presented in Table I. Unless otherwise noted, the compositions are based on initial inputs and, except for strontium, rare earths, lead, and sulfate, do not reflect losses to the precipitate. Spot checks of supernate and precipitate compositions showed that losses of aluminum, manganese, nickel, magnesium, and perhaps calcium were negligible. Iron solubility was apparently limited to about 0.2 M, and appreciable losses occurred with concentrations much greater than this. The main disadvantage of using recycled supernate as feed proved to be the uncertainty of maintaining the desired iron and sulfate concentrations.

IV. RESULTS

A. Centrifuge Studies

A 26-in.-diameter solid-bowl centrifuge was used in the centrifuge studies. The bowl was four inches deep, with a horizontal baffle two inches above the bottom, and held 18 liters when spinning. It was suspended from a vertical shaft and could be operated at either 930 or 1860 rpm (320 and 1280 gravities at the bowl wall). The high speed was used unless otherwise noted.

Supernate samples were collected in 4 oz. bottles from the overflow line. The entire sample was counted on either a single-channel or a 400-channel gamma analyzer and compared with a similar-sized sample of unprecipitated feed. The samples in all runs were placed beside the detector probe rather than on top of it to minimize bias from entrained precipitate.

Detailed results are described in the following sections.

1. Runs 1 and 2. These runs investigated the capability and reproducibility of the precipitation process, using the supernate from Run 1 as the feed for Run 2 after suitable adjustment of the strontium and cerium concentrations. Both feeds were digested one hour at 80 to 90C. The lead was added to 0.02 M instantaneously with the agitator off (but with tank contents still swirling). The agitator was started again after 2 min., and the feed was pumped to the centrifuge after 7 min. The feed temperature was held at 80C, and the feed rate averaged 3.6 liters/min., giving an average centrifuge holdup time of 5 min. The strontium losses to the supernate were the same in both runs, averaging 3% of the feed concentration.

Although the feed tank was emptied completely for each run, the feed slurry cleared rapidly as soon as the level fell below the agitator. An estimated 20 to 30% of the precipitate remained in the feed tank for these and the remaining centrifuge runs. This precipitate carryover did not appear to affect centrifuge results, but studies to be described later have indicated that feed digestion in the presence of a lead sulfate heel can lower strontium losses.

The precipitate was deposited in the lower half of the baffled centrifuge bowl. It had a pasty, clay-like consistency and was very difficult to slurry and wash properly in the pilot-plant centrifuge. Consequently, it was eventually

TABLE I
PILOT PLANT FEED COMPOSITIONS

Run No.	Moles/Liter ^(a)													NO ₃ ⁻	SO ₄ ⁼	PO ₄ ⁼	Hydroxy-Acetate	pH	Feed Sources
	Na	Fe	Al	Cr	Mn	Ni	Ca	Mg	Sr ^(b)	Ce ^(b)	La ^(b)	Pb ^(b)							
1	2.5	0.05	0.14	0.01	0.01	0.01	0.007	0.002	0.0004	0.002	0	0.02	1.4	1.1	0	0	0.8	Fresh	
2	2.5	0.05	0.14	0.01	0.01	0.01	0.01	0.002	0.0004	0.002	0	0.02	1.5	(1.0)	0	0	0.7	Recycle from Run 1	
3	2.5	0.05	0.14	0.01	0.01	0.01	0.01	0.002	0.001	0.005	0	0.022	1.5	(0.98)	0	0.43	1.0	Recycle from Run 2	
4	2.0	0.25	0.10	0.007	0.007	0.007	0.008	0.0014	0.001	0.0053	0	0.02	2.1	0.66	0	0.31	1.0	Recycle from Run 3	
5	2.0	0.25	0.10	0.007	0.007	0.007	0.008	0.0014	0.00057	0.0029	0	0-0.02 ^(d)	2.1	0.53	0	0.31	0.9	Recycle from Run 4	
6	2.0	0.25	0.10	0.007	0.007	0.007	0.008	0.0014	(e)	(e)	0	0.0093 ^(d)	2.1	(0.52)	0	0.31	0.9	Recycle from Run 5	
7	2.0	0.25	0.10	0.007	0.007	0.007	0.008	0.0014	(e)	(e)	0	0.01 ^(d)	2.1	(0.50)	0	0.31	1.0	Recycle from Run 6	
8	2.6	0.054	0.15	0.011	0.011	0.011	0.0075	0.0021	0.00043	0.0021	0	0.017-0.026 ^(d)	1.5	1.0	0	0	1.2	Fresh	
9	2.6	0.054	0.15	↓	↓	↓	0.011	↓	0.00043	0.0021	0	0.017-0.028 ^(d)	↓	(0.93)	0	0	1.3	Recycle from Run 8	
10	2.6	0.054	0.15	↓	↓	↓	↓	↓	0.00043	0.0021	0	0.02	↓	(0.86)	0	0	1.3	Recycle from Run 9	
11	2.6	0.054	0.15	↓	↓	↓	↓	↓	0.00043	0.0021	0	0.02	↓	(0.79)	0	0	1.3	Recycle from Run 10	
12	2.6	0.054	0.15	↓	↓	↓	↓	↓	0.00043	0.0021	0	0.02	↓	0.71	0	0	1.4	Recycle from Run 11	
13	2.6	0.054	0.15	↓	↓	↓	↓	↓	0.00043	(e)	0.0021	0.02	↓	(0.64)	0	0	1.1	Recycle from Run 12	
14	2.6	0.054	0.15	↓	↓	↓	↓	↓	(e)	(e)	(e)	(e)(f)	↓	(0.64)	0	0	1.2	Recycle from Run 13	
15	2.6	0.054	0.15	↓	↓	↓	↓	↓	(e)	(e)	(e)	(e)(f)	↓	(0.64)	0	0	1.1	Recycle from Runs 12,13,14 ^(h)	
16	2.6	0.054	0.15	↓	↓	↓	↓	↓	(e)	(e)	(e)	(e)(f)	↓	(0.64)	0	0	1.4	Recycle from Run 15 ^(h)	
17	2.4	0.35	0.11	0.008	0.008	0.008	0.008	0.0016	0.0004	(e)	(e)	0.02	2.1	(0.68)	0.01	0	0.5-0.8	Recycle from Run 16	
18	2.6	0.35	0.11	0.008	0.008	0.008	0.008	0.0016	0.00013	(e)	(e)	0.02	2.1	(0.61)	0.01	0	1.0	Recycle from Run 17	
19	1.5	0.35	0.10	0.007	0.007	0.007	0.0049	0.0014	0.0004	0.0014	0	0.02	1.4	0.93	0.01	0	1.3	Fresh	
20	1.5	0.35	0.10	0.007	0.007	0.007	0.0049	0.0014	0.0004	0.0014	0	0.02	1.4	0.93	0.01	0	1.3	Fresh	
21	1.5	0.16 ^(f)	0.10	0.007	0.007	0.007	0.0049	0.0014	0.0004	0.0014	0	0.02	1.4	0.58 ^(f)	0.01	0	1.1	Recycle from Runs 19,20	
22	1.5	0.16 ^(f)	0.10	0.007	0.007	0.007	0.0049	0.0014	0.0004	0.002	0	0.02	1.4	1.0	0.01	0	1.2	Recycle from Run 22	
23	1.5	0.16 ^(f)	0.10	0.007	0.007	0.007	0.0049	0.0014	0.0004	0.002	0	(g)	1.4	1.0	0.01	0	1.2	Recycle from Run 22	
24	1.5	0.21 ^(f)	0.12 ^(f)	0.007	0.007	0.007	0.021 ^(f)	0.0015 ^(f)	0.0004	0.002	0	(g)	1.4	1.4 ^(f)	0.01	0	1.2	Recycle from Run 22	
25	1.5	0.21 ^(f)	0.12 ^(f)	0.007	0.007	0.007	0.021 ^(f)	0.0015 ^(f)	0.0004	0.002	0	(g)	1.4	1.4 ^(f)	0.01	0	1.2	Recycle from Run 22	

(a) Unless otherwise noted, those values assume no losses due to precipitation except for strontium, cerium, lanthanum, lead, and sulfate.

(b) Based on amount added only - does not include precipitate heels left in tank from preceding runs.

(c) Values in parenthesis are estimated concentrations.

(d) Lead blended with feed after it left feed tank.

(e) Recycled supernate from preceding run without adding this constituent.

(f) Found by analysis of supernate (after lead sulfate precipitation).

(g) Variable. See text.

(h) The precipitate from Runs 12 and 13 were also recycled in Runs 15 and 16.

scraped loose and washed into a 55-gal. drum for dissolution. (The results of metathesis and dissolution studies for these and other runs are described in Section IV-D.) The cake volume averaged about 500 ml per mole of lead, estimated by slurring the precipitate and redepositing it as a cake with a uniform thickness.

2. Runs 3 and 4. The losses obtained in the first two runs were 2 to 4-fold lower than normally obtained in the Purex Plant, so the feed composition and digestion procedure were modified to more nearly correspond with the current Purex process. In particular, the strontium and cerium concentrations were increased 2.5-fold, hydroxyacetic acid was added to about 0.4 M, and the iron concentration was increased from 0.05 M in Run 3 to 0.25 M in Run 4. In addition, the pre-digestion period was shortened to 30 min., lead was added over a 15 min. period with the agitator on, and the slurry was digested for 30 min. more at 80-90C before pumping to the centrifuge. The feed rate was the same as in the previous runs. The results, shown below, indicate little or no adverse effect of the changes in feed and operating procedures:

Run	Centrifuge Holdup Time, Min.	M Iron	M Hydroxyacetic Acid	% Sr in Supernate
1 & 2	5	0.05	0	2.9 - 3.2
3	5	0.05	0.43	1.5
4	6	0.25	0.31	3.6

As part of the above test, the feed temperature was decreased from 80 to 40C during Run 4. The strontium loss increased slightly to 4.4%.

3. Runs 5 through 9. Bray obtained low strontium losses after only one minute of digestion after lead addition.⁽²⁾ Runs 5 and 8 were designed to see if low losses could be obtained by adding the lead nitrate directly to the centrifuge. The feed for Run 5 was prepared from Run 4 supernate while Run 8 used the original feed solution. Both feeds were digested for one hour at 80 to 90C before centrifuging. Runs 6 and 7 were attempts to scavenge residual strontium left in the Run 5 supernate. Run 6 used the supernate without further additions or treatment (except for lead addition); Run 7 used the supernate from Run 6 after digestion for one hour at 80C. The primary variables were centrifuge holdup time and lead addition rate. Results are shown in the following table:

Run	Source of Feed	Feed Temp, C	Centrifuge Holdup Time, Min	M Pb in Feed (a)	% Sr in Supernate
5	Prepared from Run 4 supernate	80	5	0	32
5	Prepared from Run 4 supernate	80	5	0.01	13
5	Prepared from Run 4 supernate	80	5	0.02	5.5
5	Prepared from Run 4 supernate	80	14	0.05	3.9
6	Combined Run 5 supernate	25	5	0.009	6.8(b)
6	Combined Run 5 supernate	25	5	0.014	5.1(b)
6	Combined Run 5 supernate	25	5	0.021	5.3(b)
7	Run 6 supernate	80	5.5	0.01	4.5(b)
8	Fresh feed	80	5	0.017	18
8	Fresh feed	80	5	0.026	4.7

(a) Based on a stoichiometric mixture of feed and lead streams.

(b) Based on Run 5 feed composition.

The results showed that low losses could indeed be obtained with short lead contact times but that perhaps as much as 30% more lead was required to give results comparable to the conventional lead addition method. The failure to scavenge more strontium from the Run 5 supernate probably indicates that the loss was solubility limited.

Run 9 used a modification of the above procedure in which the lead nitrate stream was blended with the feed in a small mixing chamber just before the feed entered the centrifuge. The strontium losses ranged from 15 to 22% at centrifuge holdup times of 5 to 7 min. and lead concentrations of 0.017 to 0.028 M. The cause of the high loss was not determined. The feed was prepared from the supernate of Run 8 and was digested for one hour at 80C. The supernate from Run 9 was used in turn to prepare the feed for Run 10 (see below) without adverse effect.

4. Runs 10 and 11. Run 10 was made to confirm the reproducibility of the standard digestion and lead addition procedure and to determine the effect of centrifuge holdup time on strontium losses. Lead addition to the feed tank to 0.02 M was followed by a 30 min. digestion period at 80C. The following results were obtained:

<u>Average Centrifuge Holdup Time, Min.</u>	<u>% Strontium in Supernate</u>
3.8	5.3
5.1	4.7
5.7	3.6
7.1	3.2

Run 11 tested the effect of feed cooling and settling on losses. The first part of the run was made under standard conditions with a centrifuge holdup time of 5 min; the feed for the second part of the run was allowed to cool to 40C. Both parts had strontium losses of 3.5%. The feed tank agitator was shut off for the final part of the run. After settling for one hour, the supernate as pumped from the tank contained 4.2% of the feed strontium and the centrifugate loss was 2.3%. The liquid level in the feed tank was 8 in. at this time.

B. Continuous Settling and Decantation

Because of the favorable results of Run 11, settling and decantation methods for precipitate separation were more extensively investigated. A continuous decantation procedure was studied first. An open-topped 55-gal. drum was inserted between the feed tank and the centrifuge. The pump from the feed tank discharged into this decant drum 11 inches above the bottom and 20 inches below the overflow line into the centrifuge. The holdup volume above the feed inlet was 128 liters. Supernate samples representative of the drum overflow were dipped from the liquid surface and counted as before.

1. Run 12. This was the first and most successful test of the continuous decantation process. The feed was prepared from the supernates of Run 11 by the conventional digestion and lead addition procedure. It was pumped from the agitated feed tank into the settling drum at 3.9 liters/min. to give an average 33 min. holdup time in the drum (above the feed point). Midway during the run, the feed was stopped for cooling and started again at 46C. The centrifuge in this second half was slowed to half speed (320 G's). Toward the end of this period, the settling drum was gently air-sparged to test the effectiveness of the centrifuge at the slower speed. The following strontium losses were obtained:

<u>Feed Temp., °C</u>	<u>Centrifuge Speed, RPM</u>	<u>% Sr</u>	
		<u>Drum Overflow</u>	<u>Centrifugate</u>
80	1860	4.4	1.9
46	930	2.9	2.2
46	930	18*	2.4

* Decant drum air-sparged.

The low strontium content of the drum supernate indicated a strontium settling rate in excess of 0.6 in/min., the average upward flow rate of the solution.

2. Runs 13 through 16. Run 13 was designed to test the effect on the decanter of cooling the feed to 50C after lead addition and of allowing it to settle for an hour before pumping to the decanter. The feed rate was 7.9 liters/min., and the centrifuge was operated at top speed. Identical losses of 11% were found in the supernate leaving the feed tank, the decanter, and the centrifuge. The cause of the high loss was not determined, but it may have been related to the rapid cooling of the feed after lead addition, the high feed rate, or the substitution of lanthanum as the stand-in for rare earths.

The remaining runs in this series tested the performance of the decant drum with both the supernate and precipitate recycled from Run 13. No lead or other feed constituents were added. The feed tank was agitated throughout the series and the centrifuge was operated at top speed. Runs 15 and 16 differed from Run 14 in that the precipitate from Run 12 was also added to the feed to give a heavier precipitate load, and the feeds were digested at 80C for one hour before running to try to lower the strontium loss to the centrifuge. The following results were obtained:

<u>Run</u>	<u>Feed Temp, C</u>	<u>Holdup Time in Drum, Min.</u>	<u>Upward liquid Flow Rate, In./Min.</u>	<u>% Sr^(a)</u>		
				<u>At Pump</u>	<u>Drum Overflow</u>	<u>Centrifugate</u>
13	37	16	1.2	11	12	10
14	35	11	1.7	92	11	9
15	25	13	1.6	65(b)	10	7
16	64	47	0.4	148(b)	12	9
16	20	38	0.5	--	6	8

(a) Based on the feed to Run 13.

(b) Includes the strontium precipitate from Run 12 as well as Run 13.

The strontium concentrations in the drum and centrifuge supernates were essentially the same in all runs and showed no significant variation with flow rate or feed temperature. The indicated settling velocity in the decant drum was in excess of 1.7 in./min.

3. Runs 17 through 20. This series of runs had the dual objectives of determining the effects of high iron concentration and off-standard digestion procedures. The feed for the first two runs was prepared from Run 16 supernate; that for Runs 19 and 20 was freshly prepared. The feed nominally contained 0.35 M iron and 0.93 M sulfate. A review of the Run 16 supernate composition, however, revealed that the true sulfate concentration in Runs 17 and 18 was probably 0.6 to 0.7 M.

The feeds for Runs 18 and 19 were digested normally. The feed for Run 17 was first digested for 4 hours at 90C, pH 0.5 (lead absent) to simulate the effect of a potential pre-concentration step. The feed was cooled and held for two days. It was then heated to 80C, lead was added to 0.02 M, and the slurry was digested for an additional 30 min. before running. The feed for Run 20 was treated somewhat similarly; it was digested for 2.5 hours at 90C, pH 0.5 with only 0.7 M sulfate present. It was cooled overnight, then adjusted to 0.93 M sulfate, pH 1.3, heated to 80C and digested for one hour (with lead added to 0.02 M after 30 min.). The feeds were agitated throughout all of the runs; feed rates were 4 to 5 liters/min. (0.6 to 0.8 in./min. upflow rate in the decant drum). The following results were obtained:

Run	Digestion Procedure	Estimated <u>M</u> Sulfate ^(a)	% Sr	
			Drum Overflow	Centrifuge
17	See text	0.7	29	28
18	Normal	0.6	17	16
19	Normal	0.93	9.5	6.7
20	See text	0.93	--	6.1

(a) Nominal concentration before precipitation.

The similarity of the results of Runs 17 and 18 and of 19 and 20 shows that prior digestion of the feed in the presence of sulfate and at low acid concentrations had little, if any, effect on strontium losses. The high losses in Runs 17 and 18 were attributed to the high iron and low sulfate concentrations. The stable concentration of iron in feeds containing 0.6 to 1 M sulfate was later found to be only 0.16 to 0.21 M. Analysis of the supernate from Run 21 (which used feed derived from the supernate of Runs 19 and 20) showed that the iron concentration had decreased from 0.35 M to 0.16 M and that about 2 moles of sulfate were removed per mole of iron. Thus actual sulfate concentrations in the digested feeds may have been as low as 0.3 M in runs 17 and 18 and 0.6 M in Runs 19 and 20.

4. Run 21. The results of previous runs showed that digested lead sulfate could be cooled and recycled without losing the co-precipitated strontium. This run tested the concept of making successive lead sulfate strikes without removing the accumulated precipitate from the feed tank. The run was made in

three parts with feeds prepared from the supernates of Runs 19 and 20 and from recycle of the supernate from the first two parts of the run itself. Each feed was adjusted to 0.0004 M Sr , 0.0014 M Ce and digested for 20 min. at 80°C . Lead was then added to 0.02 M and the feed digested an additional 15 min. After settling 15 min., the supernate was pumped to the decant drum-centrifuge system at 3.9 liters/min. Nearly all of the precipitate from each strike remained in the feed tank where it was digested with the succeeding feed. The following results were obtained:

Lead Sulfate Strike No.	% Sr ^(a)			Cumulative % Sr In Centrifugate ^(b)
	At Pump	Drum Overflow	Centrifugate	
1	9	9	10	10
2	13	11	10	4.4
3	8	9	9	4.0

(a) Based on input strontium to each feed.

(b) Based on total strontium in system.

The consistent strontium losses showed no adverse effects of redigesting the precipitate in the presence of fresh feed. The losses for each strike were higher than normal but were consistent with the low sulfate hypothesis discussed in the preceding section.

C. Batch Settling and Decantation

The runs described in this section were designed to explore more fully the potential of making the primary precipitate separation by simple settling and decantation. All tests were carried out in 55 gal. open-top drums. The feeds for each run were prepared from a stock solution derived from Run 21 supernate. The initial iron and sulfate concentrations were 0.16 and 1 M , respectively; concentrations were 30 to 40% higher in the last runs because of evaporation.

Each run simulated the effect of making six consecutive lead sulfate strikes in the digestion tank without removal of the precipitate between strikes. For simplicity, the feed for each strike was prepared by cooling the supernate from the preceding strike (without decantation) to 40°C or less and adding enough concentrated strontium-cerium solution to give nominal concentrations of 0.0004 M Sr and 0.002 M Ce . The feed was then reheated to 80°C before lead addition. After the sixth strike, the supernate was decanted and the precipitate was washed and metathesized in the same drum. (Results of these tests are presented in Section IV-D.)

The supernate samples were withdrawn from the liquid surface after settling 5 to 10 min. The samples were essentially free of precipitate, and the entire sample was counted without further separation. The feed for the last run contained Ce-144 in addition to Sr-85. Counting rates for both tracers were high enough to avoid mutual interference when these samples were counted on the 400-channel analyzer.

1. Run 22. This run extended the results of Run 21, the prototype for this precipitate accumulation procedure, to six consecutive lead sulfate strikes. Lead nitrate solution was added to 0.02 M while agitating, and the slurry was digested 15 min. and settled 10 min. at 80C before sampling the supernate. The supernate was also sampled after cooling to 30C. The following results were obtained:

<u>Strike No.</u>	% Sr ^(a)		
	<u>In Feed^(b)</u>	<u>In Hot Supernate</u>	<u>In Cooled Supernate</u>
1	104	5.7	5.9
2	22	1.5	2.1
3	60	2.0	2.7 ^(c)
4	35	3.5	3.2
5	19	1.3	1.2
6	24	2.4	2.1
Overall Avg ^(d)	32	2.7	2.8

(a) Based on input strontium to each strike.

(b) After heating the reconstituted feed to 80C and before lead addition. The feed was not agitated during sampling.

(c) Cooled overnight.

(d) Last 5 studies.

The results showed that lower losses were obtained when the feed was digested in the presence of lead sulfate from previous strikes; about two-thirds of the feed strontium was removed from the feed by the old precipitate before the fresh lead sulfate strike was made. Cooling was again demonstrated to have no effect on solubility losses.

The volume of settled precipitate was estimated to be about 700 ml per mole of lead.

2. Run 23. The concept of achieving lead economy by lead sulfate accumulation in the precipitation tank was more fully investigated in this run. Two types of experiments were performed. The first investigated the effect of digestion time on the ability of "old" lead sulfate from earlier strikes to remove strontium from fresh feed. The second procedure used incremental lead nitrate addition to determine the minimum "fresh" lead requirements to achieve strontium losses of 5% or less in the presence of old lead sulfate.

In the digestion-time tests, a heel of lead sulfate precipitate was prepared by making the first of the six strikes with 0.06 M lead. The strontium loss was 1%. The second feed was digested for a total of 85 min. (including heating time). The loss was 3.2% with no fresh lead addition. The third feed was also digested without lead addition and had an equilibrium loss of 20%. The results for both tests are tabulated below and presented in Figure 1 as a function of digestion time.

Digestion Time, Min.	% Sr in Supernate ^(a)	
	First Test ^(b)	Second Test ^(c)
25 ^(d)	21	41
45	6.3	25
65	3.8	21
85	3.2	20
105	---	20

(a) Based on strontium in the fresh feed.

(b) Second strike. Cumulative Pb/Sr mole ratio = 73.

(c) Third strike. Cumulative Pb/Sr mole ratio = 49.

(d) Time required to heat feed from 40 to 80C.

The incremental lead addition test was started with the supernate from the second test, above. The lead was added at 80C in 0.0006 to 0.005 M increments with 15 to 20 min. digestion and 5 min. of settling between additions. As soon as strontium losses were lowered to about 5%, the supernate was cooled to 40C and reconstituted as feed. It was then digested 15 min. at 80C and the incremental lead addition-digestion was repeated. The results are tabulated below and plotted in Figure 2.

Feed No.	M Pb Added ^(a)	Cumulative Pb/Sr Mole Ratio ^(b)	% Strontium in Supernate ^(c)
3	0	49	20
3	0.0025	51	2.8
4	0	38	28
4	0.000625	39	16
4	0.00125	39	12
4	0.0025	40	8.6
4	0.005	41	4.1
5	0	33	41
5	0.0025	34	19
5	0.005	36	6.7
6	0	29	28
6	0.005	31	6.5
6	0.010	33	2.1

(a) Cumulative fresh lead added to each strike.

(b) Based on total lead and strontium in tank.

(c) Based on fresh strontium.

These tests demonstrated that overall lead requirements could be cut nearly in half by digesting the feed in the presence of accumulated lead sulfate from previous strikes. Equilibrium strontium scavenging by old precipitate was reached within 60 to 80 min. of digestion (within 40 min., neglecting heat-up time).

Figure 1

BNWL-4

Figure 2

3. Run 24. The incremental lead addition procedure of Run 23 was repeated to determine minimum lead requirements for the entire series of six strikes. Standard digestion and settling times were 20 and 10 min., respectively.

<u>Strike No.</u>	<u>M Pb Added (a)</u>	<u>Cumulative Pb/Sr Mole Ratio (b)</u>	<u>% Sr in Supernate (c)</u>
1	0.005	12	18
	0.0075	18	9.7
	0.01	24	8.7
2	0	12	36
	0.005	18	10
	0.0075	21	5.2
	0.010	24	4.4
3	0	16	36
	0.005	20	13
	0.0075	22	5.3
	0.010	24	4.9
	0.0125	26	3.2
4	0	20	29
	0.0075	24	6.3
	0.010	26	5.9
5	0	20	37
	0	20	19(d)
	0.010	25	4.4
6	0	21	31
	0.010	25	9.7
	0.0125	26	4.8

(a) Cumulative fresh lead added to each strike.

(b) Based on total lead and strontium in system.

(c) Based on fresh strontium.

(d) After settling overnight at 90C.

After the initial strike, the results indicated that about 0.01 M added lead was sufficient to lower strontium losses to 6% or less and that twenty minutes of simple digestion without lead addition consistently lowered the strontium concentration by about threefold. The ultimate lead requirement of 25 moles per mole of strontium is close to the amount used in the Purex Plant process, which has about twofold higher strontium and rare earth concentrations.

4. Run 25. The final run was a demonstration of the recommended process evolved from the results of the preceding runs. A graduated lead addition was used, and Ce-144 was added to compare its behavior with that of strontium. In all cases, the lead nitrate was added to the feed as soon as the feed temperature reached 80C. Thirty minute digestion and ten minute settling times were used.

Settling-rate tests were also made to permit estimation of settling time requirements for the actual case in which supernate is decanted between strikes. The latter tests were made by withdrawing samples while agitating and observing the time required for the solids-supernate interface to settle 4 and 8 inches in a tall, graduated cylinder. The effect of temperature was also investigated in these settling studies. Results are shown below:

Strike No.	M Pb Added	Cumulative Pb/Sr Mole Ratio	Temp, C	% in Supernate		Settling Rate, In./Min.	
				Sr	Ce	4 In.	8 In.
1	0.019	48	80	6.7	9.1	1.8	----
2	0.014	42	80	5.5	13	3.1	----
			50*	3.8	11	1.7	----
			30**	3.1	9.7	1.1	----
			80*	5.5	10	2.9	3.1
3	0.0093	36	80	5.1	12	2.4	3.8
4	0.0093	33	80	3.6	8.1	2.3	2.3
5	0.0093	31	80	5.5	9.3	2.0	1.9
6	0.0093	29	80	8.7	8.5	1.7	----
			40**	2.4	4.8	0.9	0.7
			80*	4.4	4.5	1.6	1.3

* Agitated and allowed to settle before sampling.

** Cooled overnight.

The strontium losses generally confirmed the results of Run 24. Average cerium losses were twofold greater than the strontium losses but showed a decreasing tendency with precipitate accumulation. Neither strontium nor cerium losses were affected by temperature, even when the precipitate was allowed to cool overnight, although the solubility of the double salt of the sodium-cerium sulfate is reported to have an inverse temperature dependency.⁽⁵⁾

Temperature did have an important effect on the precipitate settling rates. The average settling rate at 80C was 2.3 in./min., while that at 30 to 40C was only 0.9 in./min. The higher temperature appeared to favor coagulation of the precipitate into large, flocculent particles, which, incidentally, were effective scavengers for extremely fine particles (the suspension was actually milker-looking at the top after a few seconds of settling than at the bottom).

D. Metathesis and Cake Dissolution Studies

The precipitate from Run 1 was washed and metathesized in the centrifuge by a procedure similar to that used in the Purex Plant. The precipitate (7 to 10 moles of PbSO_4 in about 5 liters of cake) was washed three times with 3 liters each of 1 M sodium sulfate at pH 1, then contacted a total of 5 times with 4 to 8 liters of 2 M sodium carbonate. All washes were at about 40C, and strontium

losses to the washes totaled 0.7%. The precipitate was then treated with a total of 61 moles of nitric acid, but only 56% of the input strontium was found in the resulting supernate. Similar results were obtained in Run 2. The poor strontium recoveries were attributed to inability to slurry and wash the cake properly in the pilot plant centrifuge.

A total dissolution approach without metathesis was next tried. A total of 24 liters of 1.3 M Na_4EDTA (the sodium salt of ethylenediaminetetra-acetic acid) was added to dissolve the cake from Run 3. The mixture was combined with the acid supernate and undissolved cake from Runs 1 and 2. The total mole ratio of EDTA to lead was about 1.2, and about 80% of the input strontium to the first three runs was recovered.

A similar procedure (after partial metathesis to reduce the sulfate concentration) was followed in Runs 4, 5, and 8 through 11 to provide feed for solvent extraction studies.⁽⁶⁾ Tartaric acid was also added to improve dissolution of iron. The final composite product solution from Runs 1 through 5 and 8 through 11 was analyzed by "cold" methods and found to contain essentially all of the strontium, cerium, and lead in the feeds to those runs. Total mole ratios of EDTA and tartrate to lead were 1.1 and 0.8, respectively (the tartrate-to-iron ratio was 2.2).

Simplified metathesis procedures were investigated in the last six runs. The tests were based on observations by Boldt⁽⁷⁾ that both the lead sulfate and carbonate precipitates were quite insoluble in water and that strontium recovery efficiency was limited chiefly by inadequate sulfate removal from the metathesized precipitate. The results of Boldt's pilot plant test (using precipitate from Run 20) and of the remaining runs are individually summarized in the following sections. The precipitates were derived from the corresponding precipitation runs previously described.

1. Run 20. The 10 moles of lead sulfate precipitate accumulated in the decant drum from Run 20 were successively contacted at 30C with the following solutions:

- 25 liters of 2 M Na_2SO_4 , pH 1
- 30 liters of water
- 30 liters of 1M NaOH , 1 M Na_2CO_3
- 30 liters of water.

Each wash was routed first to the centrifuge and then to the decant drum where it was agitated with the precipitate for 3 to 5 min. After settling, the wash solution was decanted to the centrifuge via a jet leg located about 1/2 in. from the bottom of the drum. Wash samples from the centrifuge contained a total of 2% of the feed strontium; the product solution after acidification contained 84% of the strontium in the drum. The relatively low strontium recovery was later attributed to inadequate washing after metathesis. A sample of the carbonate slurry was water-washed in the laboratory and dissolved completely when then acidified.

2. Run 21. The precipitate from Run 21 was accumulated and washed in the 1000-liter feed tank. The initial 100-liter volumes of wash and metathesis solutions did not reach the agitator, so mixing was attempted by use of an inefficient air sparger. Only 17% of the strontium was recovered on acidification. The procedure was repeated twice more with 200-liter portions (just sufficient to reach the tank agitator blade). The cumulative strontium recovery was only 71%. The run is of interest only in demonstrating the necessity of good agitation for effective strontium recovery.

3. Run 22. The decant drum was used to metathesize the 20 moles of lead sulfate from Run 22. Each wash solution was digested with the precipitate for 15 to 30 min. at 50 to 80C. The air-sparged slurries were then settled and decanted to the centrifuge. The acidified product from the first metathesis test contained only 46% of the input strontium, so a second metathesis was made. Test conditions and results are summarized in the table below:

<u>Wash No.</u>	<u>Solution Composition</u>	<u>Liters</u>	<u>Cumulative NaOH/Pb Mole Ratio</u>	<u>Sr in Supernate, % of Input</u>
1	0.1 M HNO ₃	50	---	0.6 ^(a)
2	0.1 M HNO ₃	50	---	2.2
3	0.33 M NaOH, 0.43 M Na ₂ CO ₃	50	0.83	0.14
4	Water	50	---	1.5
5	1.6 M HNO ₃	50	---	46 ^(b)
6	1.9 M NaOH, 0.43 M Na ₂ CO ₃	30	3.7	0.47
7	0.11 M Na ₂ CO ₃	30	---	0.23
8	1.6 M HNO ₃	50	---	22 ^(b)
9	13 M NaOH	5	6.9	6.3
10	Water flush	20	---	<u>2.6</u>

Total = 82%

(a) 0.9% after settling overnight before decanting.

(b) Product samples.

Again, inadequate agitation during washing was the suspected cause of the poor recovery, although the extensive digestion procedure employed during the precipitation may have contributed to the refractoriness of the precipitate. The final 13 M NaOH wash was intended to convert the remaining lead precipitate to the soluble plumbite, and it apparently removed nearly all of the precipitate left in the drum. The 18% strontium unaccounted for was presumably either left in the centrifuge or entrained with the acidified products, which were not decanted through the centrifuge.

4. Run 23. The metathesis procedure used in this run was similar to that used in Run 22. The precipitate contained 13 moles of lead sulfate. Digestion temperatures of 40C were used for all but the first two NaOH-Na₂CO₃ contacts, which were at 80C. Typical agitation (digestion) times, using an improved air sparger, were 20 to 40 min. The metathesis procedure was repeated to improve strontium recovery. The wash supernates were decanted to the centrifuge, partly via hydroclone as part of the hydroclone studies described in Section IV-E. No attempt was made to recover the strontium routed to the centrifuge during hydroclone testing. Wash compositions and results are shown below:

<u>Wash No.</u>	<u>Solution Composition</u>	<u>Liters</u>	<u>Cumulative NaOH/Pb Mole Ratio</u>	<u>% Sr in Supernate</u>
1	0.05M HNO ₃	20	---	0.3
2	0.05M HNO ₃	20	---	0.5
3	0.05M HNO ₃	20	---	0.5
4	1M NaOH, 0.5M Na ₂ CO ₃	40	2.3	0.8
5	1M NaOH, 0.5M Na ₂ CO ₃	40	4.6	0.4
6	0.1M Na ₂ CO ₃	30	---	1.3
7	2.2M HNO ₃	30	---	26
8	2M NaOH, 0.5M Na ₂ CO ₃	30	9.1	0.7
9	0.1M Na ₂ CO ₃	10	---	0.2
10	2.2M HNO ₃	30	---	11
11	Water	30	---	1.2
12	3M NaOH, 0.2M tartrate	50	21	3.8
13	2M HNO ₃	30	---	0.3
Total =				47%

The results are difficult to interpret because of the poor material balance caused by the hydroclone test. Evidently there was no improvement over the results of Run 22, despite attempts to improve agitation during digestion.

5. Run 24. Considerably more care was used in this run to assure that all of the precipitate was properly digested and washed. The decant drum-centrifuge system was used as before with the various wash solutions used to flush the centrifuge contents back to the digestion drum. The precipitate nominally contained 10.9 moles of lead, 2 moles of cerium, and 0.4 moles of strontium. The procedure this time was highly effective; the material balance, in fact, indicated recovery of precipitate from previous runs. The metathesis solution was digested for 30 min. at 80C; other washes were made at 25 to 80C. The following results were obtained:

Wash No.	Solution Composition	Liters	Digestion Temp., C	Cumulative NaOH/Pb Mole Ratio	% Sr in Supernate
1	0.05M HNO ₃	30	50	---	0.4
2	0.05M HNO ₃	30	50	---	1.9
3	0.05M HNO ₃	80	80	---	0.7
4	2M NaOH, 0.5M Na ₂ CO ₃	80	80	15	0.8
5	0.1M Na ₂ CO ₃	30	25	---	0.6
6	0.1M Na ₂ CO ₃	30	80	---	0.2
7	HNO ₃ product	(a)	25	---	121
Total =					126%

(a) Combined acid flushes of drum and centrifuge contained 87 moles of HNO₃ in 100 liters total.

The nitric acid was added incrementally at first as a rough titration of the carbonate. The pH was lowered to 1.2 after addition of 24 moles of HNO₃ in 30 liters of solution, and 90% of the strontium was found in the supernate at this time. Most of the remaining strontium was recovered by flushing the centrifuge with 4M HNO₃.

6. Run 25. The centrifuge was replaced by a second open-topped 55-gal. drum for the final run. Both drums were equipped with high-speed agitators. The precipitate in the first drum was digested 10 to 30 min. at the indicated temperatures. The washed precipitate was allowed to settle, and the supernate was pumped (from the bottom) to the second drum where it was agitated about 5 min., allowed to settle, and pumped to waste (again from the bottom). The accumulated precipitate in the second drum was slurried back to the first drum before metathesis and again before acidification. Supernate analyses are based on settled supernates before decanting. A total of 12 moles of lead, 2 moles of cerium, and 0.4 moles of strontium were present at the start.

Wash No.	Solution Composition	Liters	Digestion Temp., C	Settling Time, Min (a)		% Sr		% Ce	
				Drum 1	Drum 2	Drum 1	Drum 2	Drum 1	Drum 2
0	Supernate(b)	160	70	30	20	0.9	1.1	0.9	1.2
1	0.1M HNO ₃	105	80	10	10	6.5	5.0	4.9	3.3
2	0.1M HNO ₃	105	80	15	45	12	13	57	60
3	2M NaOH, (c) 0.2M Na ₂ CO ₃	100	80	60	1000	1.2	1.5	0.2	0.4
4	0.1M Na ₂ CO ₃	100	80	75	60	4.8	1.5	0.8	0.3
5	0.33M HNO ₃	37	40	--	--	73	----	29	----
6	1.8M HNO ₃ (d)	40(d)	80	--	--	75(d)	----	36(d)	----
7	1.1M HNO ₃ (d)	90(d)	90	--	--	76(d)	----	37(d)	----

Overall Material Balance: Product = 76% Sr 37% Ce
Discarded Washes = 22% 65%
Total 98% 102%

- (a) Average liquid depth in the drums was 15 in.
- (b) Final supernate from precipitation study.
- (c) 16.7 moles of NaOH/mole lead
- (d) Cumulative value; the product was not decanted between acid additions. Most of the cake was dissolved after the first addition of 12.2 moles of HNO_3 . The resulting pH was 1.2

The excellent material balance was achieved despite the fact that the supernate samples on which losses were based would not include precipitate entrained in the wastes discarded from the second drum.

Settling rate studies were made during washing and metathesis by the procedure described in Section IV-C-4. The results are summarized below:

<u>Wash Solution</u>	<u>Temp., C</u>	<u>Settling Rate, In./Min.</u>	
		<u>4 In.</u>	<u>8 In.</u>
0.1M HNO_3	80	5.3	---
0.1M HNO_3	80	6.0	---
2M NaOH, 0.2M Na_2CO_3	80	2.8	2.3
	50	1.0	1.1
	20	0.5	---
0.1M Na_2CO_3	24	1.3	---
	80	6.0	5.6

The effect of temperature on settling is strikingly illustrated by these results. The settling rate was increased four- to fivefold by increasing the temperature from ambient to 80C.

E. Hydroclone Studies

Hydroclone tests included in Runs 20, 23, and other special tests showed that hydroclones were ineffective for separating lead sulfate and carbonate precipitates from their respective supernates. Two hydroclones were tested: one 0.6-in. and the other 1.5-in. in diameter (measured at the feed inlet). Pump pressure up to about 110 psi were used. Visually, little or no separation occurred with either hydroclone at 50 psi, but some clearing of the overflow stream was observed at 90 to 110 psi with the smaller hydroclone. The results of the scouting studies did not appear to warrant further development studies.

F. Decontamination Performance

Metathesized products from several of the runs were analyzed to determine the decontamination performance. The analytical precision is not known but may be no better than $\pm 50\%$ for some of the components because of the complexity of the solutions. The results are shown below:

Run No:	Impurity/Sr Mole Ratio in Product				Decontamination Factor ^(a)			
	<u>1-5,8-11^(b)</u>	<u>12-16^(b)</u>	<u>24</u>	<u>25</u>	<u>1-5,8-11</u>	<u>12-16</u>	<u>24</u>	<u>25</u>
Fe	9.9	7.2	4.5	1.2	18	17	120	460
Al	---	---	1.6	3.3	---	---	190	90
Mn	0.05	0.052	---	---	370	500	---	---
Ni	0.31	0.28	---	---	55	91	---	---
Ca	1.9	1.7	0.95	1.1	7	15	57	48
Mg	0.12	0.039	0.035	0.14	28	125	110	28
Pb	33	38	9.1	3.9	1.1	1.2	2.9	7.7

(a) Defined as the average impurity/Sr mole ratio in the feed to that in the product.

(b) Prepared as feed for CSREX pilot plant runs.⁽⁶⁾

V. DISCUSSION

A. Precipitation

Strontium losses of 5% or less were obtained in the pilot plant runs described above by adhering to the following procedure:

1. Add sodium sulfate to the dissolved, acidified sludge to at least 0.7M sulfate in the final supernate solution.
2. Adjust the pH to 1 ± 0.3 by adding sodium carbonate. (The pH can be adjusted with sodium hydroxide if hydroxyacetic acid is first added to complex the iron. Higher pH's can probably be used but were not tested.)
3. Heat the feed solution to 80C and digest for 15 to 30 minutes.
4. During the digestion period, add lead nitrate to give 0.02M lead in the resulting slurry.

Iron concentrations above 0.25M were found to interfere with strontium recovery, probably through sulfate depletion by ferric sulfate complexing and precipitation. The maximum stable concentration of iron in the pilot plant feeds was about 0.2M in the absence of hydroxyacetic acid or other iron complexing agents. Iron should not be a problem in the actual sludge waste, however, since the feed adjustment steps, using approximately 2M solutions of sodium sulfate and carbonate, will dilute the acidified sludge by at least twofold.

The lead sulfate precipitate proved to be quite insoluble after the prescribed digestion period. Little or no strontium was leached from the precipitate, either by cooling the slurry or by water-washing the precipitate. Similar behavior was observed for cerium in the final run. As a result, the digested slurry can safely be cooled before separating the precipitate, and the precipitate can be washed free of mother liquor with water or a suitable low-salt solution.

The stability of the precipitate also permits accumulation of precipitate from several batches of feed. Digestion of new feed in the presence of accumulated lead sulfate from previous strikes actually proved beneficial. Up to twofold lead economy was achieved by this technique. Maximum scavenging was obtained by about 40 min. of digestion at 80C.

The digestion and lead addition steps proved generally to be less sensitive than indicated by Bray.⁽²⁾ Pilot plant losses were not affected by the rate of lead addition, by the degree of agitation during addition, or by the time of addition after reaching the digestion temperature, provided that at least 15 min. of digestion were provided. Strontium scavenging by old precipitate was improved by longer digestion times, as described above.

Bray indicates that the specified 15 min. digestion period is required to prevent interference from rare earths, which precipitate slowly as the double sodium sulfate salts under the test conditions. Most of the pilot plant tests used cerium as a stand-in for the other rare earths. A higher-than-normal strontium loss was obtained in Run 13 in which lanthanum was substituted for cerium, though other off-standard conditions may have been the cause. The use of other rare earths with different solubilities in the sulfate system could conceivably give less favorable results than those reported.

B. Metathesis and Cake Dissolution

The hydroxide-carbonate metathesis procedure proposed by Bray and Van Tuyl⁽³⁾ and further refined by Boldt⁽⁷⁾ proved to be the most satisfactory method of treating the pilot plant lead sulfate cakes. The following procedure is recommended from the combined results of the laboratory and pilot plant studies:

1. Wash the precipitate with water at 40 to 80C to remove residual supernate solution. Dilute HNO_3 , up to 0.05M, can also be used to minimize hydrolysis of iron.
2. Metathesize with 2M NaOH - 0.2M Na_2CO_3 at 60 to 80C. Use sufficient solution to provide 15 to 20 moles of NaOH per mole of lead sulfate.
3. Wash the metathesized precipitate with 0.1M Na_2CO_3 at 60 to 80C to remove sulfate ion.
4. Dissolve the precipitate by adding dilute HNO_3 to a final pH of less than 1 (0.1 to 1M free acid).

The wash volumes required in the above procedure and the number of washes depend on the washing method and the decantation efficiency. One or two washes of about 10 times the cake volume (about 10 liters per mole of lead sulfate) should eliminate over 95% of the entrained mother liquor. Boldt has used both 2M Na_2SO_4 and water for this step without having appreciable strontium losses. The pilot plant work also demonstrated low losses with 0.05M HNO_3 ; however both strontium and cerium losses were excessive with two successive washes with 0.1M HNO_3 .

The final wash is used to remove sulfate ion released by the metathesis and to lower the basicity. Water has been used successfully in laboratory studies, but a dilute carbonate solution may be preferred to assure low strontium solubility losses. Volume requirements are similar to the first wash.

The optimum concentrations of NaOH and Na_2CO_3 in the metathesis solution was not determined. It would depend somewhat on the desired objective: low volume, high lead decontamination, low strontium loss, etc. Boldt has shown that the metathesis is more efficient with hydroxide present and that the carbonate concentration could be as low as 0.1M without increasing the strontium loss. (Complete absence of carbonate could increase strontium loss because of the solubility of strontium hydroxide.)

Lead decontamination is improved by high concentrations or large volumes of NaOH. Lead sulfate is converted to hydrated lead oxide by the addition of hydroxide. An excess of reagent converts the oxide to the plumbite: Na_2PbO_2 . The solubility of lead oxide in sodium hydroxide is dependent on the crystalline form of the oxide, the temperature, and the amount of excess hydroxide. Typical solubilities are shown in Fig. 3, as given by Applebey and Powell.⁽⁸⁾ The results of a laboratory study in which NaOH solutions were titrated with 1M lead nitrate until a stable precipitate formed are also include in this figure. The method of plotting illustrates the total NaOH required per mole of lead oxide to be dissolved as a function of NaOH concentration. The titration study gave somewhat higher solubilities than the literature values; however, actual metathesis solutions obtained in Runs 24 and 25, after 30 min. digestion at 70 to 80C, contained hydroxide-to-lead mole ratios of about 18 in the presence of undissolved lead. This ratio is higher than would be predicted by either the published or laboratory data and may reflect an effect due to carbonate ion.

The degree of agitation during washing and metathesis was found to be extremely important. Quantitative strontium recovery was obtained only by the use of a high-speed agitator or a highly-efficient air sparger. Although the lead sulfate did not settle to a cake, it was fairly difficult to re-suspend once settled.

C. Precipitate-Supernate Separation

Three methods of decanting the supernate were successfully tested: centrifugation, continuous overflow from a settling tank in which the slurry was introduced at a low rate near the bottom, and batch settling and decantation. The latter two methods would also route the decanted supernate to a centrifuge for final cleanup. They offer an improvement over simple centrifugation in that the centrifuge load should be less than 5% of the total precipitate. Hydroclones (both 0.6 and 1.5-in. diameter) were also tested but were found to give unsatisfactory separation.

Figure 3

Lead Oxide Solubility In Sodium Hydroxide

The performance of the various decantation methods can be compared as a function of the particle diameter. Figs. 4, 5, and 6 show the settling rates and separation efficiency that might be expected for simple settling⁽⁹⁾, centrifugation⁽¹⁰⁾, and hydroclones⁽¹¹⁾. For example, a lead carbonate precipitate was examined by microscope and found to have particle diameters in the range of 0.4 to 1 microns. The graphs show that centrifugation should readily remove particles of this size but that hydroclones would be relatively ineffective unless extremely small (<0.5-in. diameter) and operated at high pressures (>100 psi).

From Fig. 4, the indicated settling velocity for 1 micron spherical particles is about 0.01 in./min. This low velocity would apparently rule out simple settling as a satisfactory operating procedure; however, actual settling rates of lead sulfate and carbonate slurries were generally greater than 2 in./min. at 80C. This rate would indicate that the sub-micron particles had agglomerated into much larger particles; and, indeed, the visual appearance of such precipitates confirms this, particularly at elevated temperatures. Particle agglomeration may also improve centrifuge performance, but the high shear forces and low holdup time evidently prohibit any such benefit for the hydroclones.

D. Recommended Procedure

The most satisfactory operating procedure tested, and one that should be readily adaptable to the Waste Management Program, was that used in Run 25. Briefly, this incorporates the following steps:

1. Successively precipitate several batches of feed by the procedure outlined in Section V-A. Follow each strike by simple settling and decantation to waste via centrifuge. The estimated time required for each feed batch is about 6 hours.
2. Following accumulation of the desired amount of precipitate, flush the centrifuge back to the precipitation tank and prepare for metathesis.
3. Wash and metathesize the precipitate by the procedure of Section V-B. This can be done either in the precipitation tank or the precipitate can be transferred to a smaller tank so that precipitation of a fresh batch of feed can proceed concurrently with metathesis. All washes and metathesis solutions would be decanted through the centrifuge after settling. Losses should be small in the centrifugates, but some strontium and lead economy might be achieved by recycling them to succeeding feeds. Estimated time required for cake washing and metathesis is about 10 hours.
4. Dissolve the metathesized precipitate in a minimum of acid (0.1 to 1M hydrogen ion in the final solution).

The over-all time cycle for this process, assuming accumulation of five feed strikes before cake dissolution, would be about 40 hours.

Figure 4

Terminal Settling Velocities of Spherical Particles in Water

Source of Data: Reference 9, Fig. 5-74

Figure 5

Centrifuge Performance As A Function Of Particle Size

Source of Data: Reference 10, Equations 19-28 and 19-30

Figure 6

Hydroclone Performance As A Function Of Particle Size

Source of Data: Reference 11, Equation 1

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