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Mines Branch Investigation Report IR 58-129

PRODUCTION OF METAL GRADE THORIUM CONCENTRATE
BY SOLVENT EXTRACTION FROM ION EXCHANGE EFFLUENTS
FROM FARADAY URANIUM MINES LTD., BANCROFT, ONTARIO

by

R. Simard
Radioactivity Division

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SUMMARY OF RESULTS

Ion exchange waste solutions were successfully treated, on a pilot plant scale, for the recovery of metal grade thorium concentrates by solvent extraction using di-tridecyl amine as the extractant and either sodium carbonate or sodium chloride to strip the loaded extract.

Recovery of thorium from solutions containing from 0.15 to 0.25g ThO₂/l, was 95% or better, with extractant loadings of 2.0 to 2.5 g/l.

Final products were 98% ThO₂ or better and were acceptable as raw material for the production of thorium metal by calcium metal reduction.

Reagent costs were 47¢ per lb ThO₂ for the carbonate strip method and 39¢ per lb ThO₂ for the chloride strip procedure.

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(13 tables, 4 illus.)

INTRODUCTION

In the uranium mills in the Bancroft area of Ontario, a considerable amount of thorium, present in the ion exchange effluent, is now going to waste. During the latter part of 1957, studies done at the Radioactivity Division to investigate the possibility of recovering the thorium by solvent extraction, produced encouraging results⁽¹⁾. To test the process further, it was necessary that a larger scale pilot plant be built. Consequently, Faraday Uranium Mines Ltd., Bancroft, Ontario, agreed to install a plant, capable of treating 10-15 tons of solution per day, in their mill at their expense. It was further agreed that the pilot plant investigation would be carried out by the Faraday mill staff and the Radioactivity Division on a cooperative basis.

The equipment was installed by February 1958 and the plant was operated till July 1958. During the first six weeks, the author and two technicians from the Radioactivity Division assisted the mill staff in the plant's operation. After this initial period, the mill staff continued to run the plant to make further studies on some variations of the process. This report is an account of results obtained during the whole period during which the plant was operated.

GENERAL SUMMARY

The circuit, consisting mainly of four mixer-settlers, could treat a maximum of 2 gal/min of effluent countercurrently to a kerosene solution of 5% v/v di-tridecyl amine as supplied by Canadian Carbide

(1) References are shown at end of this report (pages 29-30).

Chemicals. From a series of forty runs on solutions containing 0.15 to 0.25 g ThO_2 /l, recoveries of 95% or better were possible with extract loadings of 2 to 2.5 g ThO_2 /l. The thorium was stripped with 10% sodium carbonate and precipitated with caustic to produce the oxycarbonate assaying 75-78% ThO_2 . A series of nine runs was also completed with sodium chloride as stripping agent, followed by direct oxalic acid precipitation. Acceptable metallurgical grade oxide of 99⁺% purity was produced by retreating the oxycarbonate in HCl and precipitating the oxalate. Chloride stripping with oxalate precipitation produced slightly lower grade oxide (98% ThO_2), but acceptable for calcium metal reduction. Overall reagent costs, including solvent losses, varied from 39¢ per lb ThO_2 for the chloride-strip procedure to 47¢ per lb ThO_2 for the carbonate-strip procedure.

Two other possible amine extractants, Primene J M and di-dodecyl 9D-178 from Rohm and Haas Co., were also tested in the pilot plant. Results indicated that Primene could be used effectively, but in view of the ease of stripping of di-tridecyl amine with salt, and its lower solvent losses and greater selectivity, it would be favoured in the present application.

DESCRIPTION OF CIRCUIT

The pilot plant was scaled up from an existing laboratory unit already described in Mines Branch Investigation Reports IR 58-4⁽³⁾ and IR 58-30⁽¹⁾. The four-stage pump-mix settler was assembled

from 3/8 in. Plexiglas by the Hickey Plastics Co. of Montreal. Some details of construction are shown in Figure 1. Each stage was made to provide a mixing time of 1.5 min. and a settling area of 1.5 sq ft per gal per min. when operating at a throughput of 2 gal of feed solution per min.

Details of the scrubber and strippers are given in Figure 2, and the pilot plant assembly in Figure 3. The circuit comprised three head tanks to supply the 5% H_2SO_4 scrub, the feed, and the stripping solution. These solutions were fed through flowmeters, while the solvent was metered with a Milton Roy adjustable-stroke pump rated at 1 gal/min maximum. The pump-mix action in the mixer-settlers was obtained by Pneumix air-motored agitators as supplied by the Eclipse Air Brush Co., Newark, N. J. The stripping section consisted of two co-current 6-in. D. mixing tanks in series with a final settler box. The 6 in. D tanks were later changed to 12 in. D to increase retention time. Mixing was provided by laboratory Welch electric mixers. The stripped solvent overflowed to two 10-gal plastic carboys used as surge tanks ahead of the metering pump. All rigid piping was 1/2 in. and 1 in. Vancor pipe connected with Tygon tubing.

Precipitation of the alkaline strip was done in 20-gal steel drums and the settled product filtered on large Buckners. Where chloride stripping was used, rubber-lined tanks were employed for handling and precipitation.

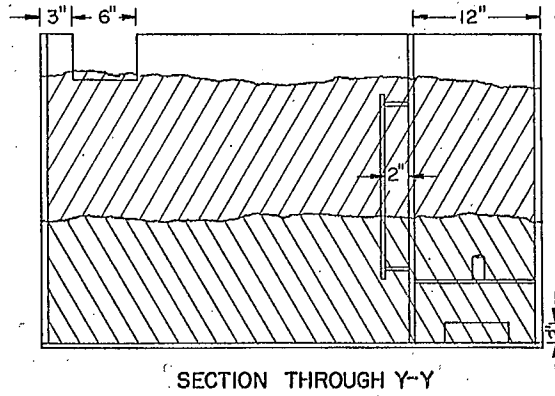
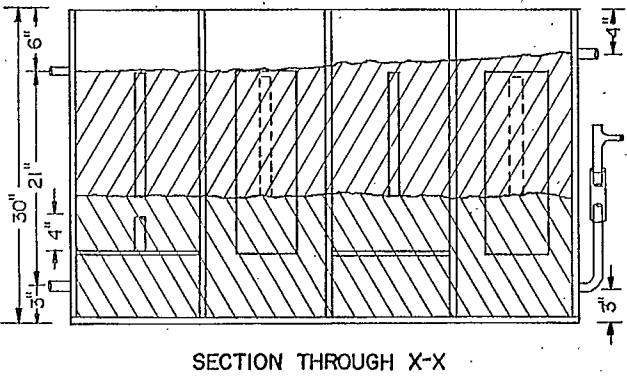
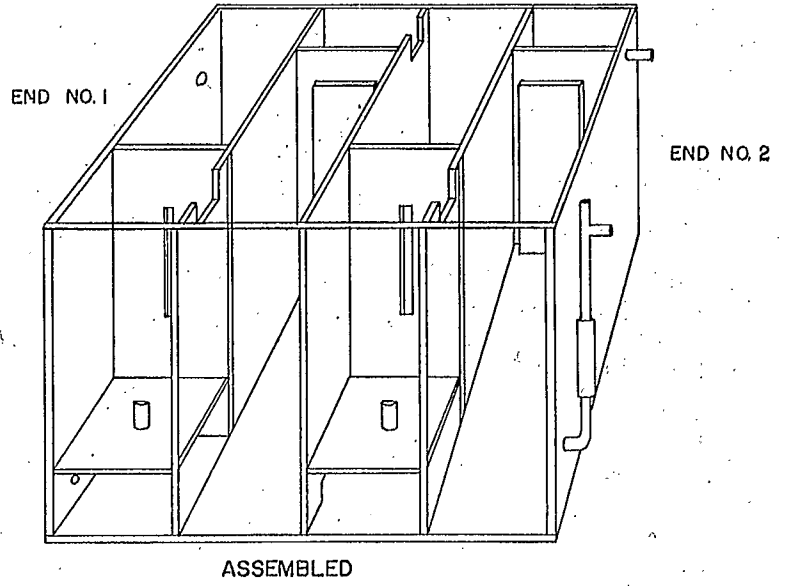
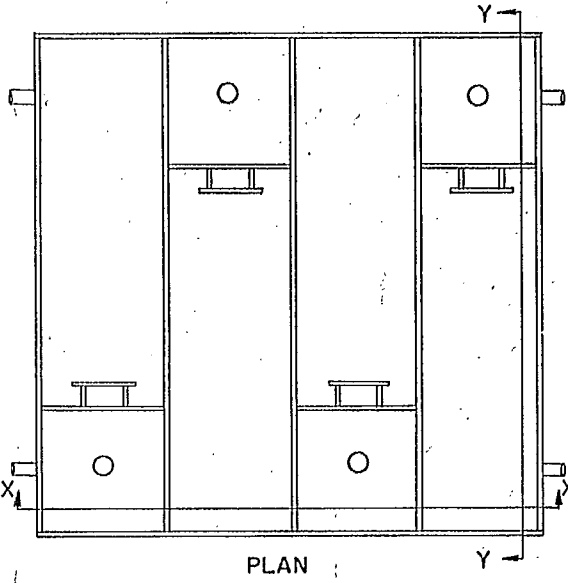


FIGURE 1

FOUR-STAGE MIXER-SETTLER

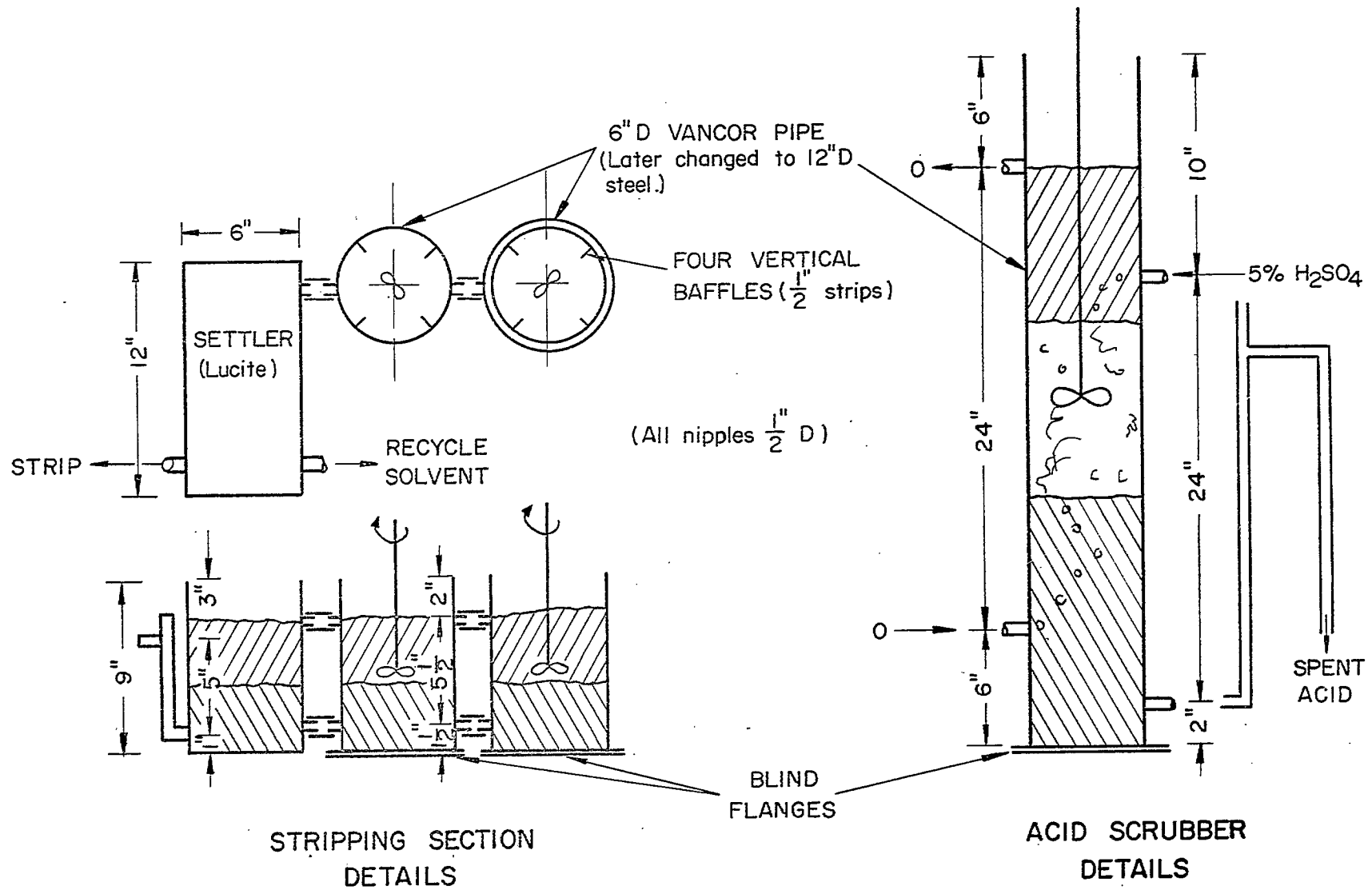


FIGURE 2

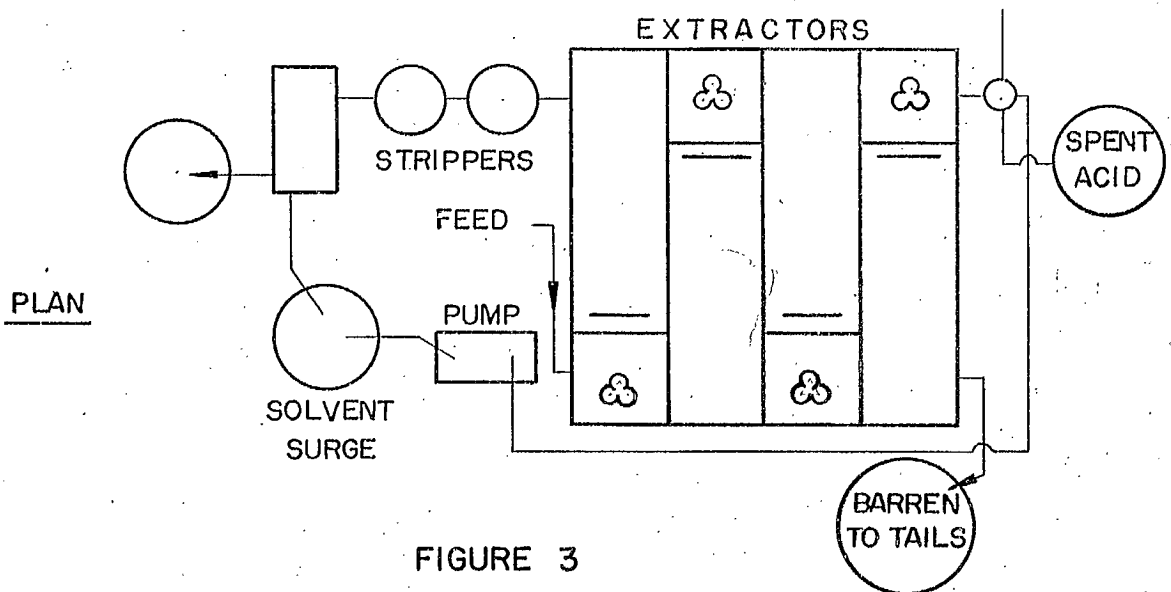
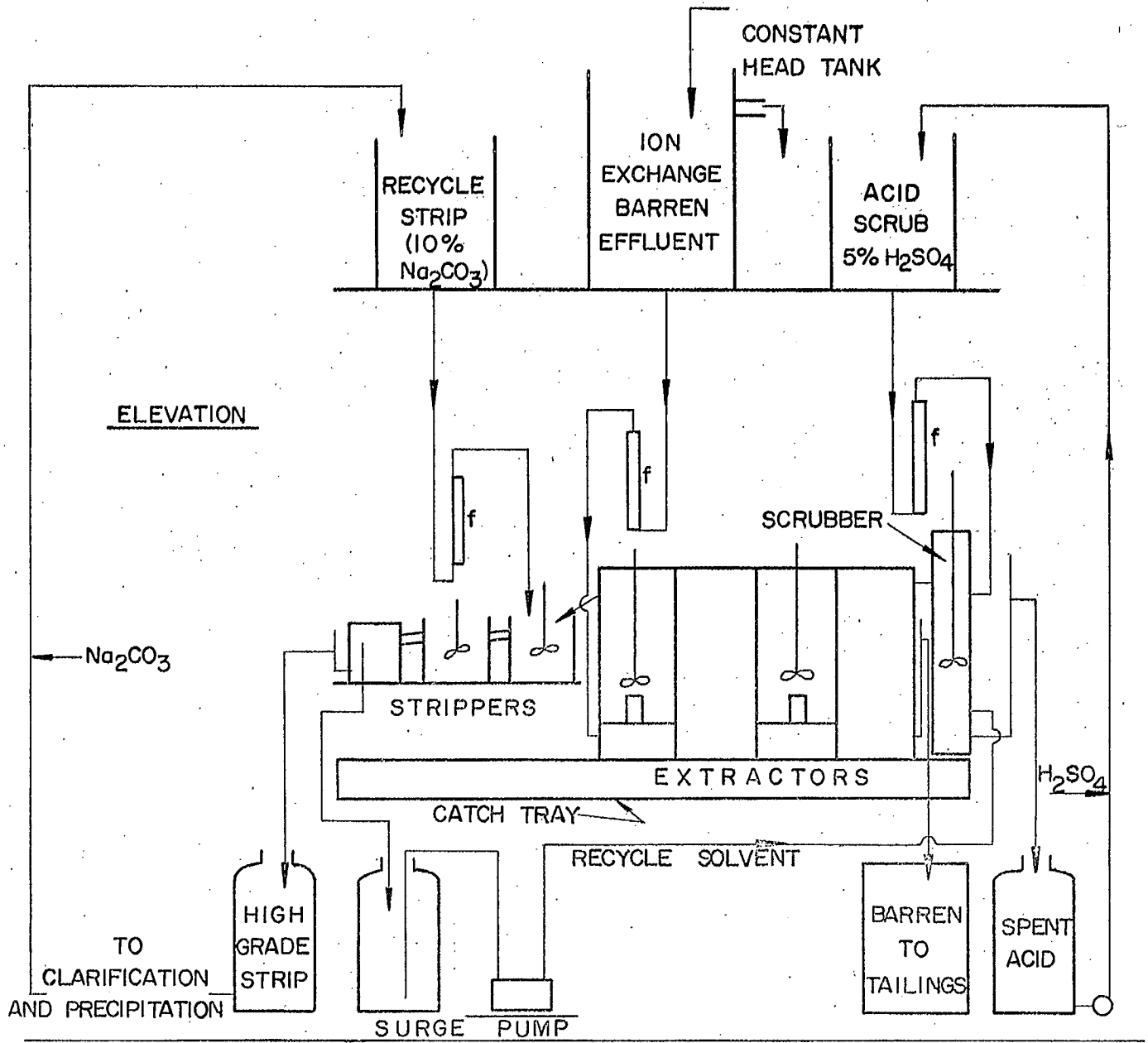


FIGURE 3

FARADAY PILOT PLANT FLOWSHEET

OPERATING PROCEDURE

The circuit was first filled on the 12th February with approximately 100 gallons of solvent made up from Imperial Oil kerosene (Montreal East Refinery), containing 5% di-tridecyl amine as supplied by Canadian Carbide Chemicals. No alcohol was used as a modifier, although batch tests indicated some improvement of settling rate when 2% of mixed decyl alcohols was used. The whole of the solvent was put through the acid scrubber during filling to avoid high pH in the extractors on start-up, and consequent emulsification due to ferric hydroxide precipitation. The scrubber provided the necessary contact to sulphate the amine before entering the last stage of extraction. The spent acid was collected and made up to strength before being pumped back to the head tank. Any possible solvent entrainment was thus maintained in a closed circuit.

The four-stage extractor, as shown in Figure 1, was operated with the interface at 12 in. from the settler bottom and 6 in. from the mixer bottom to provide a mixing ratio, organic to aqueous, of 2/1. To maintain this level throughout the four stages, it was necessary to have sufficient pumping head at the impeller to counteract friction losses and the existing solvent gradient of 1 in. per stage. The initial length of the draught-pipe beneath the impeller was 3 in. This length was found inadequate for this purpose and it was increased to 6 in. The same effect could be achieved by lowering the impeller, but this would tend to produce a discontinuous organic phase as found by experience. The impeller was a 3-in. diameter, three blade, marine type, set at two to

three inches above the interface. Under these conditions it was possible to handle up to 1.8-2.0 gal/min of feed solution without any backing-up effect. The raffinate overflow leg on the final stage could be adjusted also to control the interface level, which tended to rise with increasing throughput. The leg was made of flexible Tygon so that this adjustment could be made easily.

The original two strippers were found to be undersize and were changed after the 12th run. Incomplete stripping was also due to the lower temperature encountered (16° - 17° C) as compared with that of previous tests carried out at the Mines Branch. A steam coil was therefore included in the larger (12 in. D) tanks to maintain a temperature of 25° - 30° C. Before heating was incorporated, sodium sulphate crystals, forming on the walls and in the pipe connections, caused frequent blockage. No such trouble occurred at the higher temperature. The Welch motor stirrers were also found inadequate in the larger tanks and two of these were required per tank, for good mixing. The final settler box operated satisfactorily. Some ferric iron precipitates did build up over a period of a run and was skimmed out from the interface, filtered, and discarded; the solvent was returned to the surge tank.

The 20-gal capacity surge was adequate for most of the fluctuations in the interface level of the extractor. This would allow a volume change of 10% of the inventory in the extractor. In practice a larger surge would be advisable to assure greater flexibility. The Milton Roy pump was very satisfactory for close flow control and provided a compact

solvent circuit without flowmeter or head tank. It was also useful in solvent transfer during filling or make-up.

The records and sampling procedure for each run included hourly readings of flows, and sampling of the various streams. To obtain complete equilibrium in the four stages of extraction, one complete solvent change is required or some 10-12 hours at the solvent flowrate used. It was therefore necessary to operate for two shifts per day to allow for time lost in start-up and shut-down. Whenever shorter runs were made, they could not be used to establish maximum loadings and recovery, but served to determine long term solvent losses. Solvent normality was checked at intervals of a few days to establish soluble loss. Entrainment of solvent in the barren raffinate was made by a direct determination of the kerosene by the infra-red analysis of a carbon tetrachloride extract of the raffinate. No effort was made to check this by a close inventory, due to unaccounted spills and samples taken.

The precipitation of the high-grade carbonate strip was a batch process. The loaded strip solution was first heated to 50-60°C, clarified to remove the insolubles, and the filtrate precipitated by gradual addition of flake caustic to pH 12-12.2. The slurry could be settled to 20% of the volume with Jaguar added as a 1% solution (1 litre/100 litres of strip). The clear decant and filtrate were pumped over to the cooling tank to crystallize out excess sodium sulphate. The product was filtered and washed twice on a Buckner filter to give 1 to 2

volumes of displacement. The wet cake, after weighing, was stored in steel drums.

The chloride strip was also precipitated in batches in rubber-lined drums by the addition of warm 10% oxalic acid. The filtered cake was repulped in water and washed until only traces of sulphate could be detected in the filtrate.

RESULTS AND DISCUSSION

Feed Solution: (Ion Exchange Barren Effluent)

The plant produces approximately 250 gal/min of waste barren effluent which runs to a 16 ft D tank before lime neutralization and disposal. Weekly composites of the solution taken during January and February showed the following analysis:

TABLE 1

Analysis of
Ion Exchange Barren Effluent
Jan. - Feb. 1958.

pH	Assays, g/l					
	U ₃ O ₈	ThO ₂	SO ₄	Fe ³⁺	Fe ²⁺	Cl
1.7-1.85	0.002	0.15-0.25	10-15	0.4-0.5	0.8-1.0	0.6-0.9

At the time of the pilot plant operation in February and March, some cloudiness was apparent in the barren effluent, due to the formation of gypsum caused by aeration in the surge tank. This could materially affect solvent entrainment. Clarity is reportedly improved during the

warmer season. The chloride content, as shown, is an average and may be much higher at the start of a loading cycle in the ion exchange columns, since the Faraday plant uses sodium chloride-sulphuric acid elution. The capacity of the surge tank can be used advantageously to even out these fluctuations. The effect of high chloride ($>2.0 \text{ g Cl/l}$) will materially affect distribution coefficients, as noted in previous investigations⁽⁴⁾.

Kerosene Diluent and Amine

After some preliminary evaluation of various kerosene samples from Montreal East refineries, Imperial Oil kerosene was used as diluent. The choice was made on a basis of flash point and phase separation. A summary of these tests is given in table 2.

TABLE 2

Properties of Various Kerosene Diluents

for Solvent Extraction

Type: →	B. A. Jet Fuel (Edmonton)	Imp. Oil Kerosene (Montreal)	Shell Kerosene (Montreal)	B. A. Kerosene (Montreal)
Flash Point, °F (Tag, closed cup)	130°	120°	113°	85°
Viscosity 100°F Centistoke	1.39	1.27	1.25	1.16
Phase Separation, sec (no modifier)	110	110	125	125
(+ 2% mixed decyl alc.)	80	70	-	-

The procedure and results of phase separation tests are shown in figure 4. The Imperial kerosene compared favourably with the Jet Fuel used previously in laboratory work. The effect of a modifier on

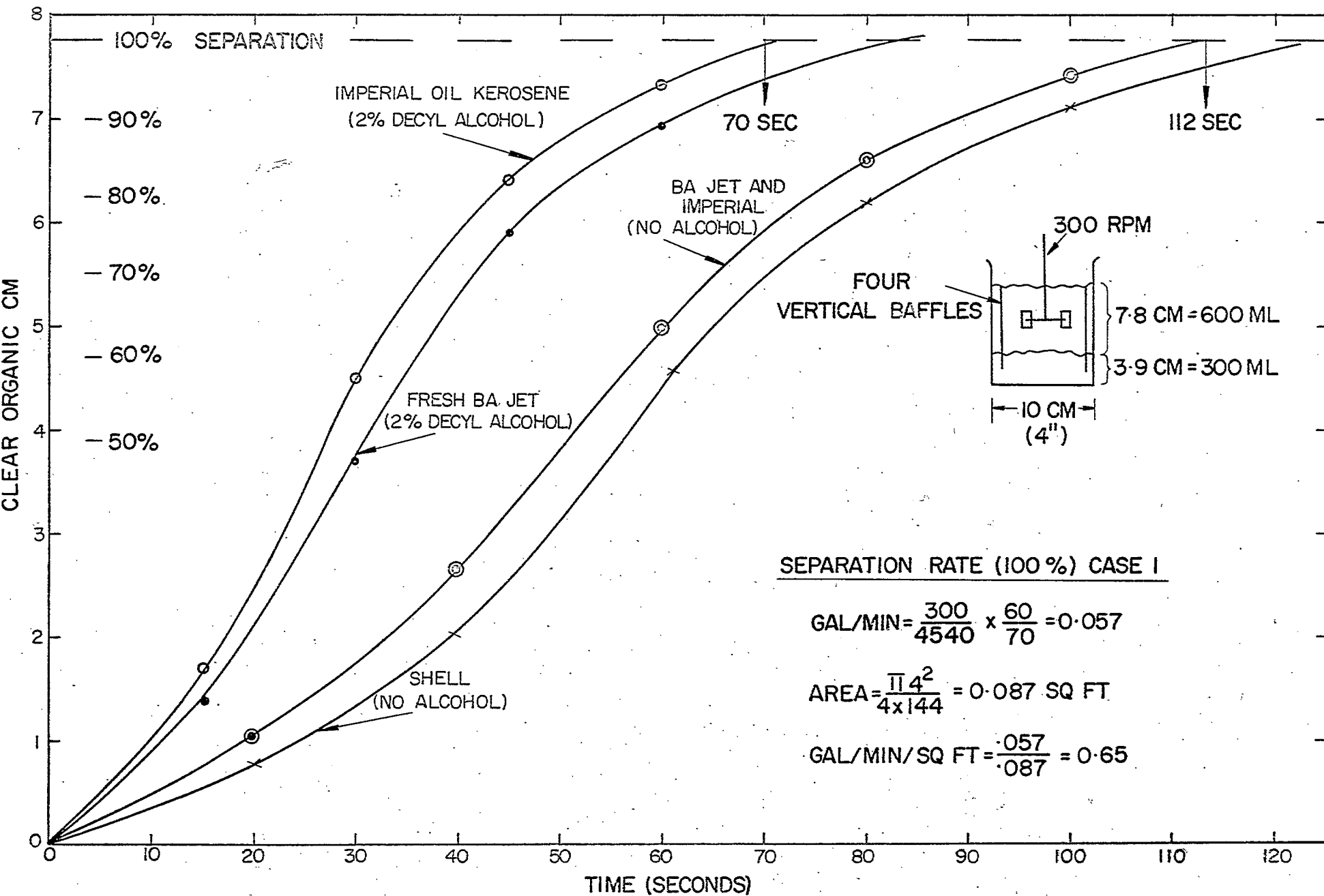


FIGURE 4

RATE OF PHASE SEPARATION OF 5% DI-TRIDECYL AMINE AND THORIUM FEED SOLUTION

separation is quite evident, but delivery of the alcohol was too late to carry out some further tests in the pilot plant.

The amine was supplied in four 4-gal drums, from a limited supply in the U. S. A., by the Canadian Carbide Chemicals Co.

Continuous Extraction with Sodium Carbonate Stripping

A series of forty runs was completed under the conditions mentioned above and a summary of data is presented in Table 3. Flow-rates were held relatively constant at near-maximum throughput.

Variations in the thorium content of the feed were such that it was not possible to operate at maximum loading and recovery. The flow ratio of feed to solvent was set to give a loading of 2.5 g ThO₂ per litre of solvent from a feed of 0.20 g ThO₂/l.

Efficiency of the stripping section was poor for the first twelve runs, for reasons discussed in the section on operating procedure. When retention time was increased from 4 to 12 minutes, and the temperature raised to 25°C, improved results were obtained as shown by the recycle solvent assays of runs 17 to 30. Slowing of the Welch motors in the later runs, due to overheating, also gave high recycle in some runs.

No effort was made to establish extraction distribution points for each individual stage, due to fluctuations in the feed and recycle solvent which would disturb such equilibrium. The indicated possible loadings were 2 to 2.5 g ThO₂/l in the extract, for a feed varying from 0.15 to 2.5 g/l. The strip loading of 12 to 14 g ThO₂/l could not be

TABLE 3
Pilot Plant Operating Data and Results

Date (February and March) Run No	14 1	15 2	16 3	17 4	18 5	19 6	20 7	21 8	22 9	23 10	25 11	26 12	27 13	28 14	1 15	2 16	3 17	4 18	5 19	6 20
Operating time, hr	7.5	7.5	7.5	15	15.2	12.5	11	12	11.5	14.25	13.5	10.5	15.5	6.5	7.75	4	4	7	11	10
Flowrates, gal/min																				
Feed (I.X. Barron Effluent)	0.71	1.73	1.76	1.68	1.65	1.82	1.82	1.84	1.84	1.84	1.84	1.84	1.84	1.79	1.76	1.79	1.80	1.84	1.84	1.84
Solvent (5% DTDA)	0.12	0.12	0.128	0.125	0.128	0.126	0.128	0.128	0.131	0.130	0.120	0.12	0.123	0.130	0.128	0.143	0.138	0.115	0.125	0.126
Strip (10% Na ₂ CO ₃)	0.026	0.027	0.027	0.016	0.012	0.029	0.030	0.032	0.031	0.030	0.030	0.027	0.035	0.036	0.034	0.036	0.035	0.031	0.035	0.036
Scrub (5% H ₂ SO ₄)	0.018	0.023	0.025	0.032	0.023	0.025	0.023	0.020	0.027	0.020	0.025	0.020	0.025	0.013	0.025	0.012	0.020	0.015	0.015	0.019
Assays, ThO ₂ g/l																				
Feed	-	0.161	0.161	0.213	0.22	0.195	0.154	0.211	0.177	0.136	0.194	0.183	-	0.193	0.069	0.206	0.158	0.22	0.166	0.186
Barron (Stage 4)	0.083	0.083	0.096	0.132	0.074	0.024	0.061	0.009	0.007	0.071	0.009	0.036	-	0.001	0.001	0.001	0.0016	0.002	0.002	0.011
Extract	1.10	1.64	1.70	3.0	2.09	2.45	2.18	2.20	2.05	1.76	2.83	1.52	-	0.53	1.09	1.61	2.64	1.97	2.21	
Recycle Solvent	-	-	-	1.66	0.31	0.60	0.34	0.24	1.24	0.79	0.02	-0.75	-	-	-	-	0.004	0.32	0.018	0.027
Strip	12.5	12.1	12.2	12.3	12.3	12.2	13.3	12.4	14.0	14.0	12.7	-	12.4	12.3	12.3	13.3	13.3	13.8	13.8	14.0
Precipitation																				
Vol of strip, gal	12.4	9.5	9.5	13.2	10.3	22.3	17.0	18.1	17.7	19.5	18.9	20.7	21.5	14.7	15.2	6.8	7.5	9.5	18.8	18.0
pH of strip	9.6	9.4	9.4	9.7	9.5	9.5	8.8	9.3	9.5	9.2	9.4	9.4	9.3	9.1	9.3	8.8	9.3	9.2	9.5	9.1
NaOH added, lb	1.82	2.60	-	3.41	1.54	2.20	3.56	3.36	3.08	4.84	2.95	4.05	7.26	4.4	3.74	3.80	1.54	4.06	3.55	3.55
NaOH added, lb/lb ThO ₂ (1)	1.10	2.26	-	1.76	1.21	0.80	1.58	1.50	1.24	1.77	1.21	1.47	2.70	2.42	2.06	4.15	1.54	3.10	1.37	1.41
Barron Strip Assays, g/l																				
Na ₂ CO ₃	-	-	-	-	-	-	84	80	80	79	78	77	76	74	70	68	68	63	61	62
Na ₂ SO ₄	-	-	-	-	-	-	93	90	90	90	90	70	80	90	100	110	110	110	115	115
Precipitate Wet Wt, lb		26.5(2)		10	5.8	13.4	15.5	14.2	11.7	10.5	9.6	16	-	10.2	9.8	6.55(3)	7.2	13.9	14.1	
Normality of Amine	0.095	-	-	-	0.095	-	0.093	-	-	0.094	-	0.0935	-	-	-	-	-	-	0.0925	-

TABLE 3 (Continued)

Pilot Plant Operating Data and Results

Date (March) Run No	7 21	8 22	9 23	10 24	11 25	12 26	13 27	14 28	15 29	16 30	17 31	18 32	19 33	20 34	21 35	22 36	23 37	24 38	25 39	26 40
Operating time, hr	8	8	5	16	15	15	12	12	12.5	10.0	12.2	13.8	5.0	8.75	13	12	13.2	13.2	12.7	12.2
Flowrates, gal/min																				
Feed (I.X. Barron Effluent)	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84	1.84
Solvent (5% DTDA)	0.125	0.127	0.126	0.136	0.129	0.135	0.133	0.138	0.139	0.138	0.137	0.133	0.136	0.140	0.138	0.135	0.135	0.134	0.135	0.135
Strip (10% Na ₂ CO ₃)	0.036	0.037	0.037	0.030	0.031	0.035	0.036	0.034	0.033	0.0305	0.029	0.0295	0.031	0.032	0.031	0.035	0.033	0.035	0.032	0.033
Scrub (5% H ₂ SO ₄)	0.02	0.02	0.02	0.02	0.02	0.027	0.022	0.024	0.026	0.022	0.023	0.026	nil	0.016	0.024	0.020	0.025	0.024	0.025	0.024
Assays, ThO ₂ g/l																				
Feed	0.192	0.157	0.184	0.197	0.173	0.177	0.171	0.191	0.160	0.190	0.20	0.218	0.228	0.189	0.195	0.195	0.142	0.153	0.200	0.14
Barron (Stage 4)	0.005	0.008	0.009	0.006	0.005	0.005	0.003	0.003	0.003	0.004	0.004	0.017	0.013	0.029	0.040	0.014	0.020	0.003	0.017	0.030
Extract	2.19	2.56	2.34	2.50	2.05	2.17	2.17	1.55	1.90	1.83	2.07	1.88	2.46	2.83	1.85	2.14	2.09	2.32	1.26	1.78
Recycle Solvent	0.005	0.044	0.03	0.052	0.05	0.09	0.05	0.14	0.04	0.03	0.18	0.10	0.05	0.15	0.38	0.32	0.20	0.20	0.04	0.09
Strip	13.4	13.0	13.3	13.8	12.0	13.0	13.6	13.6	13.5	12.8	13.7	10.8	15.0	12.6	13.6	12.0	13.7	10.7	11.5	12.1
Precipitation																				
Vol of strip, gal	15.0	12.0	8.9	20.8	20.5	25	20.8	22.0	20.1	17.7	22.5	19.3	9.1	14.1	22.3	21.3	22.0	21.1	21.0	21.2
pH of strip	9.4	9.2	9.2	9.4	9.3	9.7	9.7	9.6	9.6	9.4	9.7	9.5	1.4	9.44	9.35	9.35	9.4	9.2	9.3	9.5
NaOH added, lb	2.70	1.55	1.76	4.50	5.12	5.0	6.09	6.00	6.75	5.31	6.30	4.09	-	2.68	5.40	4.50	4.80	5.24	4.96	5.18
NaOH added, lb/lb ThO ₂ (1)	1.13	1.00	1.48	1.57	1.37	1.6	2.14	1.85	2.49	2.33	2.05	2.00	-	1.50	1.78	1.77	1.58	2.32	2.05	2.05
Barron Strip Assays, g/l																				
Na ₂ CO ₃	61	60	58	96	85	96	75	97	95	89	86	82	88	84	93	-	-	-	85	85
Na ₂ SO ₄	125	130	45	64	75	75	100	92	70	82	88	80	82	80	70	-	-	-	-	-
Precipitate Wet Wt, lb	12.2	7.35	5.8	14.9	17.4	27.6	19.5	23.3	14.7	14.5	18.0	-	-	14.4	13.9	13.4	15.4	17.2	17.4	14.0
Normality of Amine	0.092	-	-	-	0.092	-	-	-	-	-	-	0.0955	-	-	0.0955	-	-	-	-	0.096

(1) Calculated from strip assay and volume.
 (2) Combined precipitate from tests 1, 2 and 3.
 (3) Combined precipitate from tests 16 and 17.

increased much more, due to the tendency for hydrolysis below pH 9.0.

A thorium balance on the forty runs, based on feed, barren and strip assays is presented in Table 4. An overall recovery of 94.5% was obtained from feed and barren assays. Improved results are possible when operating at a good stripping efficiency, and barrens of 0.005 g ThO₂/l are indicated.

Sodium Hydroxide Consumption

Sodium hydroxide consumption as shown in Table 3 is based on strip assays and total caustic added, and is somewhat erratic. Another estimate, based on total thorium produced from runs 15 to 30 versus total caustic added in that period, shows the following:

Total wet weight of product runs 15 to 30, lb	= 192.7
ThO ₂ assay, wet basis, %	= 13.75
ThO ₂ content, lb	= 26.5
Total NaOH consumed, runs 15-30, lb	= 64.5
NaOH consumption, lb/lb ThO ₂	= 2.5

This confirms previous results under similar conditions as reported in Investigation Report IR 58-30⁽¹⁾. Due to some sodium carbonate retained in the wet cake and some lost in sodium sulphate crystallisation, sodium carbonate make-up will amount to approximately 0.5 lb/lb ThO₂.

Theoretically, nearly all the sodium carbonate would be made up as caustic according to the following composite reactions:

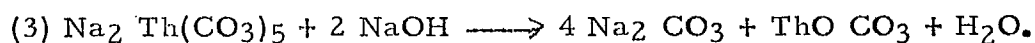
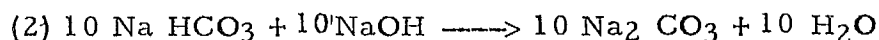
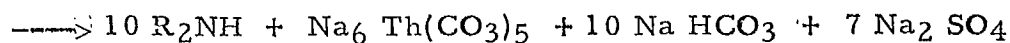
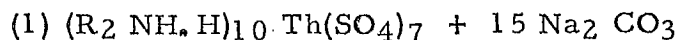


TABLE 4

Thorium Balance for Runs 1 to 40

Date	Run No.	Tons of Feed		Pounds of ThO ₂				
		Daily	Cum.	Heads	Barren		Strip	
				Daily	Daily	Cum.	Daily	Cum.
Feb. 14	1	3.92		1.49	0.10	0.10	1.55	1.55
15	2	3.97		1.27	0.10	0.20	1.15	2.70
16	3	4.04		1.30	0.05	0.25	1.16	3.86
17	4	7.71		3.28	0.10	0.35	1.93	5.79
18	5	7.70		3.39	0.10	0.45	1.27	7.06
19	6	7.24		2.82	0.10	0.55	2.73	9.79
20	7	6.13		1.89	0.10	0.65	2.26	12.05
21	8	6.16		2.85	0.13	0.78	2.25	14.30
22	9	6.33		2.24	0.09	0.87	2.47	16.77
23	10	8.02	61.22	2.18	0.11	0.98	2.73	19.50
25	11	7.51		2.91	0.14	1.12	2.40	21.90
26	12	5.82		2.13	0.10	1.22	2.75	24.65
27	13	8.63		2.83	0.10	1.32	2.67	27.32
28	14	3.42		1.32	0.01	1.33	1.81	29.13
Mar. 1	15	4.17		0.58	0.01	1.34	1.87	31.00
2	16	2.19		0.90	0.00	1.34	0.91	31.91
3	17	2.29		0.72	0.01	1.35	1.00	32.91
4	18	3.89		1.71	0.01	1.36	1.31	34.21
5	19	6.43	106.17	2.13	0.10	1.46	2.60	36.81
6	20	5.54		2.06	0.12	1.58	2.51	39.39
7	21	4.41		1.75	0.04	1.62	2.01	41.40
8	22	4.46		1.40	0.07	1.69	1.55	42.95
9	23	2.86		1.05	0.05	1.74	1.18	44.13
10	24	6.62		2.61	0.09	1.83	2.86	47.09
11	25	8.44	138.50	2.92	0.08	1.91	3.73	50.82
12	26	8.40		2.97	0.09	2.00	2.73	53.55
13	27	6.66		2.28	0.05	2.05	2.84	56.39
14	28	6.85		2.62	0.04	2.09	3.24	59.63
15	29	7.08		2.55	0.05	2.14	2.71	62.34
16	30	5.68		2.16	0.04	2.18	2.27	62.34
17	31	7.46	180.63	2.98	0.06	2.24	3.09	67.70
18	32	7.69		3.35	0.26	2.50	2.04	69.74
19	33	4.25		1.94	0.11	2.61	1.37	71.11
20	34	4.93		1.86	0.29	2.90	1.78	72.89
21	35	7.37		2.87	0.56	3.46	3.02	75.91
22	36	6.94		2.71	0.19	3.65	2.54	78.45
23	37	7.46		2.12	0.30	3.95	3.02	81.47
24	38	7.41		2.27	0.04	3.99	2.25	83.72
25	39	7.13		2.85	0.24	4.23	2.41	86.13
26	40	6.90	240.71	1.93	0.41	4.64	2.56	88.69

The above reactions indicate a theoretical sodium hydroxide consumption of 12 mols per mol ThO_2 or 1.82 lb/lb ThO_2 . Since the compound of equation(1) is the empirical expression of the thorium-to-sulphate ratio found in the extract by analysis, the formula could also be expressed with some bisulphate ions present which would then account for a higher caustic consumption, as found.

Solvent Loss

Solvent losses, as entrained and soluble amine in the barren raffinate, were quite low. The normality drop from runs 1 to 25, during which time no fresh solvent was added for make-up, indicates the following soluble loss:

Normality drop, runs 1-25	=	0.003
Total solvent in circuit (5% Amine), l. gal	=	120
Amine loss, lb = $120 \times \frac{5}{100} \times \frac{0.003}{0.095} \times 0.9$	=	1.71
Total thorium treated; runs 1-25, lb ThO_2	=	50
Soluble loss, lb amine./lb ThO_2	=	0.034

Entrainment loss from a kerosene determination on a composite barren for runs 1 to 25 is as follows:

Kerosene in raffinate, g/l	=	0.033
Equivalent amine (5%), g/l	=	0.0016
Thorium in feed solution (av), g/l	=	0.20
Entrainment loss, lb amine/lb ThO_2	=	<u>0.008</u>
Total amine loss, lb amine/lb ThO_2	=	<u>0.042</u>

Precipitate Characteristics

Before precipitation, the collected strip from each run was clarified prior to caustic addition. The insolubles, mainly iron hydroxide, did not represent a significant weight (2% of thorium product), but in

practice this product would be redissolved at the head of the circuit. The addition of flake caustic to the clear filtrate produced a fine product that filtered slowly and cracked readily. Jaguar was very helpful in giving a clear decant, which could be sent directly to the cooling tank. A composite precipitate of runs 15 to 30 was repulped in water to remove the soluble salts. Tests were also done to reduce other impurities, mainly iron and uranium. The latter, although quite low in the feed solution, was effectively extracted, resulting in a build-up of uranium in the carbonate strip. Eventually the uranium precipitated out with the thorium product. Results of the repulping tests are given in Table 5.

TABLE 5

Analysis of the Thorium Oxycarbonate Precipitate (ThOCO₃)
Composite of Runs 15 to 30

(a) Chemical Assays:

Sample	Treatment	Assays, % (dry basis)					
		ThO ₂	Na	SO ₄	CO ₂	Fe	U ₃ O ₈
A.	no repulp	52.4	14.8	10.9	12.8	0.18	0.57
B.	repulp in water	76.8	3.8	0.13	9.1	0.30	0.45
C.	" in 1% Versene	76.2	-	-	-	0.33	0.31
D.	" in 1% H ₂ O ₂	76.5	-	-	-	0.33	0.29

(b) Spectrographic Assays... semi-quantitative (%)

Sample	Th	Na	Fe	Mg	Si	Ca	Al	Ti
A.	P. C.	20	0.6	0.2	0.10	0.1	0.08	0.06
B.	P. C.	5	0.7	0.5	0.10	0.1	0.09	0.09
C.	P. C.	5	0.6	0.4	0.10	0.2	0.10	0.07
D.	P. C.	5	0.7	0.4	0.10	0.2	0.08	0.07

P. C. - principal constituent.

The removal of sodium sulphate and sodium carbonate was almost complete. All other impurities, as shown by analysis, are not materially removed by these treatments. More care in the clarification of the strip before precipitation will reduce the iron content of the carbonate product. Subsequent repulping and washing of the precipitate, to completely hydrolyse any possible thorium sulphate complex, will remove the sulphate and break down some of the oxycarbonate to the hydroxide. The effect of calcining the oxycarbonate precipitate at 1000°C is shown in Table 6.

TABLE 6

Effect of Calcining the Oxycarbonate Precipitate

Lot No.	L. O. I.	ThO ₂	SO ₄	CO ₂	Fe	Al	Mn	Si	Ni
1 and 2 before calcining	-	78.5	trace	5.6	0.15	0.20	0.10	0.10	<.005
3 calcined	12.5	94.8	N.D.	-	0.47	0.036	-	-	-
4 calcined	11.6	94.9	N.D.	-	0.13	0.030	<0.10	<0.1	<0.005

Some iron contamination, due to the use of metal trays, in drying is believed to account for the higher iron assays (Tables 6 and 7). High aluminum assays were due to the use of aluminum-base paint on the drums used initially for precipitation. The remainder of the weight in the calcined products will be accounted for by fused carbonate.

Retreatment of the Oxycarbonate Precipitate

Various lots of the wet precipitate were redissolved in a minimum quantity of HCl to make approximately a 10% ThO₂ solution. Commercial oxalic acid was added on the basis of 1 lb per lb ThO₂.

The resulting oxalate precipitate was filtered, repulped, and washed.

The calcined oxalate from these various lots showed the following analyses:

TABLE 7

Analysis of Calcined (800°C) Oxalate Precipitate
(from oxycarbonate retreatment)

Lot No.	Assays, %								
	ThO ₂	SO ₄	CO ₂	Fe	C	Al	Si	Mn	Ca
2	93.5	present	0.05	0.26	0.018	0.7	0.1	<0.1	0.05
5	99.0	N.D.	-	0.01	-	0.006	<0.1	-	0.08
6	99.1	<0.05	-	0.01	-	0.01	-	-	0.03

Ni, Cu, Cr were less than 0.001% in all cases.

Salt-Sulphuric Acid Stripping of Extract

A series of batch tests was conducted to establish the thorium distribution coefficients between 1.0N NaCl, 0.1N H₂SO₄ and 5% di-tridecyl amine. Three stages of cross-current stripping, on 6.5 litres of extract from the circuit, were completed with an organic to strip ratio of 10/1 per stage. Results are tabulated below:

TABLE 8

Batch Cross-Current Stripping of Di-tridecyl Amine
with 1.0N NaCl, 0.1N H₂SO₄
O/S ratio = 10/1

Stage No.	Assays, ThO ₂ g/l		E _s O
	Strip	Solvent	
1	19.15	0.93	20.5
2	8.94	0.04	224.
3	0.44	0.001	440.

Such high coefficients (>200) in stages 2 and 3 cannot be explained. Previous tests on synthetic extracts indicated coefficients of 40 to 50. On the other hand, continuous stripping in the pilot plant confirmed these high values. The combined strips of stages 1, 2, and 3 (1785 ml) were precipitated with 0.9 g oxalic acid per g ThO₂ and gave a barren of 0.15 g ThO₂/1 for a recovery of 98.5%. The filtered precipitate was washed, dried, and calcined at 750°C. Assays are reported in Table 9.

TABLE 9

Calcined Oxalate Product (from Chloride Strip) in Batch Tests

Chemical Assay, %	ThO ₂ 82.2	SO ₄ 0.45	U ₃ O ₈ 0.02	Fe <0.001			
Spectrographic Assay, %	Th P.C.	Na 15	Ca 0.3	Si 0.15	P <0.05	Al 0.02	Fe 0.007

The high sodium shown by spectrographic analysis is probably the product of the following reaction:



which indicates the presence of sodium oxalate in the precipitate in the form of a double sodium-thorium salt. Subsequent washing of the calcine would remove this sodium carbonate.

The effect of recycling the amine in the chloride form was studied and showed no marked depression of the thorium distribution coefficient (E_A^O). Results are summarized in Table 10. The tests were made on 250 ml of 5% DTDA conditioned with 10% Na₂ CO₃ before the first extraction cycle. The solvent was then loaded in 5 stages at an aqueous to organic ratio of 1/1 with a synthetic solution containing 0.87 g ThO₂/1,

1.0 g Fe³/l and 10 g SO₄/l at a pH of 1.45. The loaded extract was stripped in 3 stages with 1N NaCl, 0.1N H₂SO₄. The stripped solvent was then reloaded in a similar manner and stripped a second time.

TABLE 10

Effect of Chloride Stripping on Thorium Distribution Coefficients

Conditions: Aqueous: Synthetic Liquor 0.87g ThO₂/l.
Solvent: 5% Di tridecyl amine in kerosene
Strip: 1.0 N NaCl, 0.1N H₂SO₄

Assays: ThO₂, g/l

<u>1st Cycle</u>	Raffinate	Extract	Strip	Recycle Solvent
Stage 1	<0.001	0.87	20.8	0.80
2	<0.001	1.74	4.33	0.11
3	<0.001	2.61	0.38	0.055
4	0.02	3.46		
5	0.52	3.81		
<u>2nd Cycle</u>				
Stage 1	<0.001	0.92	21.8	0.85
2	<0.001	1.74	4.74	0.10
3	<0.001	2.66	0.28	0.05
4	0.02	3.51		
5	0.54	3.84		

On the basis of these results, it appeared practical to carry out continuous tests in the pilot plant to produce sufficient oxalate product for acceptability tests. This work was done by the mill engineer, Mr. J. Boag. To simplify the operation, the stripping unit was not changed to countercurrent multi-stage to allow a lower strip to organic ratio. Due to the high strip to organic distribution coefficient at a concentration of 8-10 g ThO₂/l strip, it was possible to obtain

relatively efficient stripping at an organic to strip ratio of 4 or 5 to 1, which is possible with the simpler co-current stripping. An account of the results is given in Table 11.

TABLE 11

Continuous Pilot Plant Extraction Run with Chloride Stripping

Conditions:

Feed: I.X. Barren Effluent
 Solvent: 5% V/V DTDA
 Strip : runs 48-54: 1N NaCl, 0.1N H₂SO₄
 runs 61-62: 0.35N NaCl, 0.15N HCl
 Scrub: none

Run No. —————>	48	49	50	51	52	53	54	61	62
Operating Time, hr	7 1/2	8	8	7	8	9	8	7	8
<u>Flowrates, gal/min</u>									
Feed	1.85	1.85	1.85	1.85	1.77	1.80	1.76	1.76	1.76
Solvent	0.13	0.13	0.13	0.13	0.128	0.128	0.127	0.128	0.127
Strip	0.044	0.030	0.028	0.029	0.029	0.028	0.028	0.028	0.030
<u>Assays, ThO₂, g/l</u>									
Feed	0.12	0.27	0.26	0.22	0.24	0.16	0.134	0.22	0.28
Barren	0.074	0.003	0.014	0.013	0.009	0.051	0.004	0.009	0.004
Extract	2.21	3.03	2.63	2.56	2.47	1.81	2.00	2.90	2.05
Recycle Soln	0.12	0.29	0.04	0.05	0.17	0.127	0.039	0.30	0.18
Strip	10.9	9.30	11.9	10.80	10.6	11.0	12.4	11.1	10.30

Since these tests were done mainly to collect sufficient strip solution for precipitation work, no effort was made to operate at maximum loading and recovery. On the other hand, the single-stage stripping unit gave sufficiently low thorium in the recycle for continuous operation. A batch saturation test indicated a maximum strip loading of 19 g ThO_2 /l with 1.0N NaCl, 0.5N H_2SO_4 .

The high-grade solution was precipitated with commercial oxalic acid. The oxalate precipitate, calcined at 800°C , resulted in a product having the composition shown in Table 12.

TABLE 12

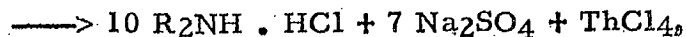
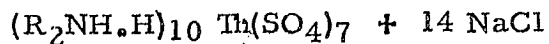
Calcined Oxalate Product from Chloride Strip in Continuous Tests

Assays, %

Lot No.	L.O.I.	ThO_2	SO_4	Fe	Al	RE_2O_3	CaO	MgO
7	40.1	90.6	1.5	0.06	0.015	-	2.2	5.3
9	51.6	98.1	-	0.03	0.21	0.45	-	-

Total oxalic consumption was 1.2-1.3 lb/lb ThO_2 , which is somewhat higher than the theoretical (0.82 lb/lb), due to the presence of other consuming ions, mainly iron and uranium.

It was not proposed to recycle the spent chloride strip, due to the high sulphate build-up and to the presence of excess oxalic acid which would cause precipitation in the strippers. Where maximum use is made of the salt in 2 to 3 stages of countercurrent stripping, the NaCl requirements would be as follows:



or 3.1 lb NaCl per lb ThO₂. The above reaction indicates a possible loading of 18-19 g ThO₂/l in the strip when using 1 N NaCl. The effective use of the salt will be 72% of the original; therefore the spent solution will contain 0.28N NaCl and 0.6-0.7 N Na₂SO₄. From these considerations, recycling of the strip will not be practical because the small amount of chloride saved (0.5 lb/lb ThO₂) probably would not warrant the cost of removing the sulphate from the recycle by crystallization or bleeding. The excess oxalic acid and the iron and uranium build-up would also present further problems.

An alternative to oxalic acid precipitation would be to acidify the strip to 40% H₂SO₄ and recover the sulphate tetrahydrate. The reported solubility (5) in 40-50% H₂SO₄ is 0.02% ThSO₄. The strong acid could then be used in the leaching circuit and would not raise the chloride level materially (0.1 g Cl/l). Were a market for the sulphate to be developed, it could be produced more cheaply than the oxalate. The thorium sulphate could also be digested with caustic to produce the hydroxide at a cost of approximately 1 lb NaOH per lb ThO₂.

CONCLUSIONS

The pilot plant operation has confirmed previous findings on the feasibility of an economical process for thorium recovery from this uranium plant by amine solvent extraction. The thorium can be produced in various forms: the oxycarbonate, the oxalate, the oxide, or possibly the sulphate. In each case the cost of producing these various grades will be justified by the demand and the purity requirements. The highest grade will likely be obtained by a retreatment of the oxycarbonate. Where minor impurities such as iron and sodium salts can be tolerated, other methods would be equally satisfactory. The comments of a prospective buyer of these products show that the oxides produced by either the carbonate strip or chloride strip, followed by oxalate precipitation, would be suitable for metal production with a yield of 85 to 90% in the calcium reduction step.

A tentative list of reagent costs for the various methods of stripping and precipitation is shown in Table 13.

TABLE 13

Reagent Costs

(For the Production of Thorium Concentrates
by Di-tridecyl Amine Solvent Extraction
From the Faraday Plant I.X. Barren Effluents)

Note: In all cases solvent losses will be the same and are based on the present findings.

0.045 lb amine/lb ThO₂ at \$2.00/lb=9.0 cents/lb ThO₂

0.200 lb kerosene/lb ThO₂ at 24¢/lb=0.5 cents/lb ThO₂

Total 9.5 cents/lb ThO₂

	Product	Reagent Used, per lb ThO ₂	Reagent Cost, Cents/lb ThO ₂
<u>Case 1:</u> Na ₂ CO ₃ stripping and NaOH precipitation. Strip recycled.	ThOCO ₃	2.5 lb NaOH 0.5 lb Na ₂ CO ₃ Solvent Total	12.5 1.0 9.5 <u>23.0</u>
<u>Case 2:</u> Na ₂ CO ₃ stripping with oxalate retreatment and calcining.	ThO ₂	as in (1) 1.0 lb oxalic 0.9 lb HCL Total	23.0 20.0 4.5 <u>47.5</u>
<u>Case 3:</u> NaCl stripping, no recycling, oxalate precipitation.	ThO ₂	3.5 lb NaCl 0.5 lb H ₂ SO ₄ 1.2 lb oxalic Solvent Total	4.9 0.6 24.0 9.5 <u>39.0</u>
<u>Case 4:</u> NaCl stripping, H ₂ SO ₄ precipitation, recycle acid to leach.	Th(SO ₄) ₄ H ₂ O	3.5 lb NaCl 1.0 lb H ₂ SO ₄ Solvent Total	4.9 1.2 9.5 <u>15.6</u>

The cost of calcining the oxalate is not included but should not represent a major item of cost. In cases 1 and 2 the filtration and repulping problems would represent major equipment and labour costs and should be emphasized in any comparative study. Since, for direct

calcium reduction, metallurgical grade thorium concentrates must be low in iron, aluminum and other base metals, precipitation of the acid strip with alkalies would not be suitable, and this has not been proposed in the above cost estimate.

ACKNOWLEDGMENTS

The author wishes to acknowledge the full cooperation of the Faraday Mill staff (Messrs. R. Roach, R. Behan and J. Boag, together with the chief chemist, Mr. A. Pittuck), who have carried out the greater part of this investigation. The assistance of Messrs. A. Poulin and R. Warner, technicians from the Radioactivity Division and efficient operators of the pilot plant during the first six weeks of the operation, is also appreciated.

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(Appendices 1 and 2 follow,
on pages 31 and 32.)

APPENDIX I

The Use of Rohm and Haas Primene JM and LA-1 as Substitutes
For Di-Tridecyl Amine

From the favourable results obtained previously with primary amine Primene JM (6) and secondary amine LA-1 (1) from the Rohm and Haas Co., it appeared that some data should be obtained in the pilot plant on the use of these amines as substitutes. The results were not conclusive, due to the lack of countercurrent stripping facilities and subsequent high recycle values when using a chloride strip. The results have nevertheless emphasized the following points:

- 1) Stripping with sodium chloride will require a higher concentration; up to 2N in the case of Primene mainly.
- 2) The thorium-to-iron selectivity is much lower in both cases than that of DTDA.
- 3) The thorium capacity for 5% Primene was equivalent to that of DTDA but lower loadings were obtained with LA-1, in the order of 1 g ThO₂/l.
- 4) Solubility loss of Primene to the barren raffinate was estimated at 0.35 lb/lb ThO₂, which would outweigh the advantage of its lower price.

On the basis of these findings the use of DTDA would be favoured for the present system, using sodium chloride stripping.

APPENDIX 2

Production of Thorium Hydroxide

(Test work done by the Faraday mill staff subsequent to the work detailed in this report)

As the report title states, the work was primarily done to produce thorium concentrates suitable for thorium metal production. However, a limited market exists for thorium as the very high purity nitrate in the manufacture of gas lamp mantles. Since production of thorium nitrates of such purity was beyond the scope of this work, it was decided to produce a readily acid-soluble precipitate, such as the hydroxide, to meet the possible demands of this market.

Sufficient strip solution had accumulated from test runs on several substitute solvents to produce approximately 20 pounds of thoria. These solvents, however, were not as selective for thorium as that on which this work was initiated. A bench scale precipitation of this solution with caustic soda produced a precipitate too high in iron to be of commercial value. The remaining strip solution was treated with powdered aluminum to reduce the iron, filtered, and precipitated with caustic to pH 4.5. This treatment was effective in eliminating iron, but the grade was still too low to be acceptable. Analysis for sulphate indicated that the thorium was precipitating as both the sulphate and hydroxide, containing approximately 35% sulphate. Repulping this precipitate in 0.5 normal hydroxide successfully eliminated all of the sulphate, upgrading the precipitate to an acceptable 70% ThO₂. The use of aluminum in full scale operation would not be necessary, for the original amine rejected nearly all of the iron.

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