



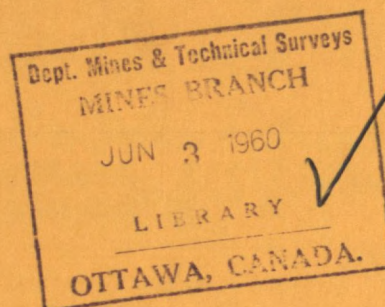
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**THE RECOVERY OF METAL GRADE THORIUM
CONCENTRATE FROM URANIUM PLANT ION EXCHANGE
EFFLUENTS BY AMINE SOLVENT EXTRACTION**

by

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EXTRACTION METALLURGY DIVISION

FEBRUARY 22, 1960

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FROM URANIUM PLANT ION EXCHANGE EFFLUENTS BY
AMINE SOLVENT EXTRACTION

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SYNOPSIS

Ion exchange waste solutions were treated on a pilot plant scale for the recovery of thorium concentrates by solvent extraction with 5% di-tridecyl amine in kerosene, the extract being stripped with either sodium carbonate or sodium chloride. Recovery of thorium from solutions containing from 0.15 to 0.25 g ThO_2/l was 95% or better. Extract loadings ranged from 2.0 to 2.5 g ThO_2/l .

Final products analysing 98% ThO_2 or better were obtained, which were found acceptable for the production of alloying grade thorium metal by the calcium reduction process.

Reagent costs, including solvent losses, varied from 39 cents per lb ThO_2 for the chloride strip procedure to 47 cents per lb ThO_2 for the carbonate strip procedure.

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Direction des mines

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RÉCUPÉRATION DE CONCENTRÉS DE THORIUM POUR FIN
D'ALLIAGE EN PARTANT DES EFFLUENTS DES ATELIERS
DE LESSIVAGE DE L'URANIUM AU MOYEN DE L'EXTRACTION
PAR UN SOLVANT AMINÉ

par

R. Simard *

RÉSUMÉ

La récupération du thorium des solutions de rejet des échangeurs ioniques a été faite à l'échelle pilote au moyen d'extraction par l'amine di-tridecyl à 5% dans la kérosine. L'extrait a été dénudé soit par le carbonate de sodium ou le chlorure de sodium. En partant de solutions d'une teneur de 0.15 à 0.25 g ThO_2 /l, on a récupéré 95% ou plus à une concentration de 2.0 à 2.5 g ThO_2 /l dans le solvant.

Le produit final, un oxyde à 98% ThO_2 ou plus, a été jugé acceptable pour la fabrication du métal devant servir à l'alliage magnésium-thorium.

Le coût des réactifs, y inclus les pertes de solvant, varient de 39 cents à 47 cents par livre de ThO_2 , selon qu'on emploie le dénuelement par le chlorure ou par le carbonate de sodium.

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INTRODUCTION

In the uranium mills of the Bancroft area of Ontario, a considerable amount of thorium, present in the ion exchange effluent, is now going to waste. It has been known for some time that much of this thorium is recoverable. Studies on the recovery of soluble thorium from sulphate solutions by amine solvent extraction were carried out successfully at Oak Ridge,⁽¹⁾ and laboratory investigations at the Mines Branch have also shown encouraging results. The data from continuous countercurrent tests were accumulated for various amine extractants: di-tridecyl amine,* Armeen 2-12,** Primene JM,*** and LA-1.*** On the basis of these findings and in view of the interest shown at that time in the thorium oxide product as a source of metal for the preparation of magnesium-thorium alloys, it was felt that the process should be tested further on a pilot plant scale. The larger quantities of product could then be submitted to the prospective users for evaluation as a source of alloying-grade metal or for further refining for nuclear energy purposes. Consequently, Faraday Uranium Mines Ltd., Bancroft, Ontario, agreed to build a small pilot plant to treat 10-15 tons of solution per day (1.5 - 2.0 gpm) within their own mill, in cooperation with the Mines Branch staff.

The equipment was installed by February 1958 and the plant

* Supplied by Carbide Chemicals Co., Division of Union Carbide Canada.

** Supplied by Armour Chemicals Division.

*** Supplied by Rohm and Haas Co.

operated intermittently till July 1958. During the first six weeks, the author and two technicians from the Mines Branch assisted the mill staff in the operation. After this initial period the mill staff continued some further studies on variations of the process. This report is an account of results obtained during the whole period of operation.

The choice of the flowsheet and the design of the plant were largely based on experience obtained in the Mines Branch laboratories. Since the main objects of this study were to confirm laboratory data with respect to the current mill solutions, and produce sufficient quantities of thorium oxide so that the product could be evaluated, no provision was made to test more than one solvent, viz. di-tridecyl amine, which had shown good selectivity and capacity for thorium in laboratory tests.

It will not be necessary in this report to review the chemistry involved in the process. It will be sufficient to say that it involves the transfer of a thorium sulphate anion complex from an aqueous to an organic phase in multi-stage countercurrent mixer-settlers. The loaded organic phase is then stripped of the thorium complex by an aqueous solution containing an anion such as nitrate, or chloride, or by the irreversible action of a carbonate. The high-grade thorium strip solution is then precipitated with an alkali or an oxalate to give a thorium hydroxide, oxycarbonate, or oxalate product which can be calcined to yield the oxide.

The choice of stripping agent in the present case was

influenced principally by the requirement that the product be a low-iron thorium oxide. The pilot plant work demonstrated that sodium carbonate solution was adequate in this respect. However, some filtering problems were encountered in the treatment of the sodium carbonate strip, so that stripping work in sodium chloride solution was also investigated, even though no prior laboratory data had been obtained on its use.

Although this investigation was limited to the use of di-tridecyl amine as solvent, it should not be forgotten that organic solvents with cationic exchange properties, mainly mono and di-alkyl phosphates, are potential extractants of thorium from sulphate solutions. While these solvents have a lower selectivity for thorium in the presence of ferric iron and require a solution reduction step they have the advantage that they are not affected by the presence of nitrate in the feed solution. This last factor is of no importance in treating the ion exchange effluents from mills in the Bancroft area, since these mills use sodium chloride elution. It would, however, be of importance in the Elliot Lake mills, since nitrate elution is practiced there. However, when nitrate elution is followed by a sulphuric acid flush on the resin column, most of the nitrate is removed and does not appear in the subsequent barren effluent. In this case, amines could be used for thorium recovery from such effluents.

GENERAL SUMMARY

From a series of forty runs on solutions containing 0.15 to 0.25 g ThO_2/l , recoveries of 95% or better were obtained 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 . Acceptable metallurgical grade oxide of 99⁺% purity was produced by treating the oxycarbonate in HCl and precipitating the oxalate. A series of nine runs was also completed with sodium chloride as stripping agent, followed by oxalic acid precipitation. This produced a slightly lower grade oxide (98% ThO_2), but acceptable for calcium metal reduction. Overall reagent costs, including solvent losses, were 39¢ per lb ThO_2 for the chloride-strip procedure and 47¢ per lb ThO_2 for the carbonate-strip procedure.

Two other possible amine extractants, Primene JM and didodecyl 9D-178 from Rohm and Haas Co., were also briefly 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 this application.

DESCRIPTION OF THE PILOT PLANT CIRCUIT

The pilot plant was scaled up from an existing laboratory unit already in use at the Mines Branch. 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 of the pilot plant assembly in Figure 3. The circuit included 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 supplied by the Eclipse Air Brush Co., Newark, N.J. The stripping section consisted of two co-current 6-in. dia. mixing tanks in series with a final settler box. The 6 in. dia. tanks were later changed to 12 in. dia. 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 by Tygon tubing.

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

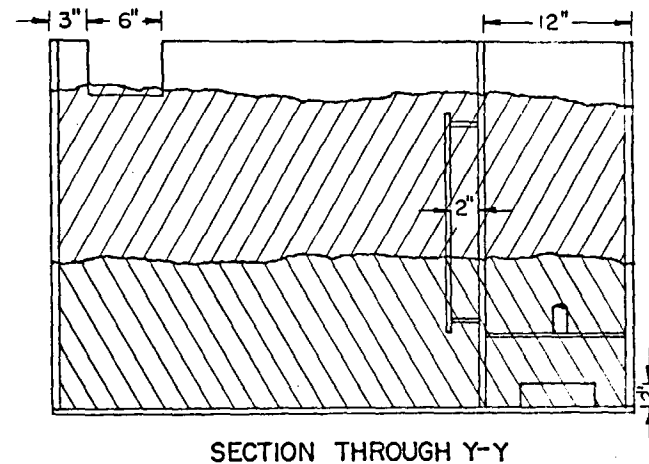
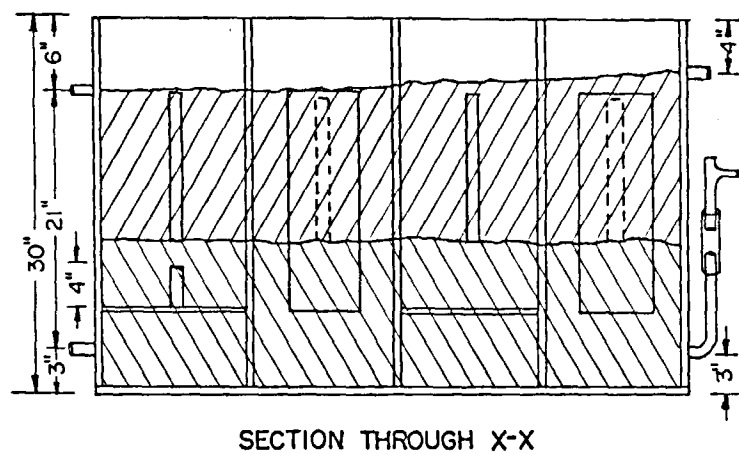
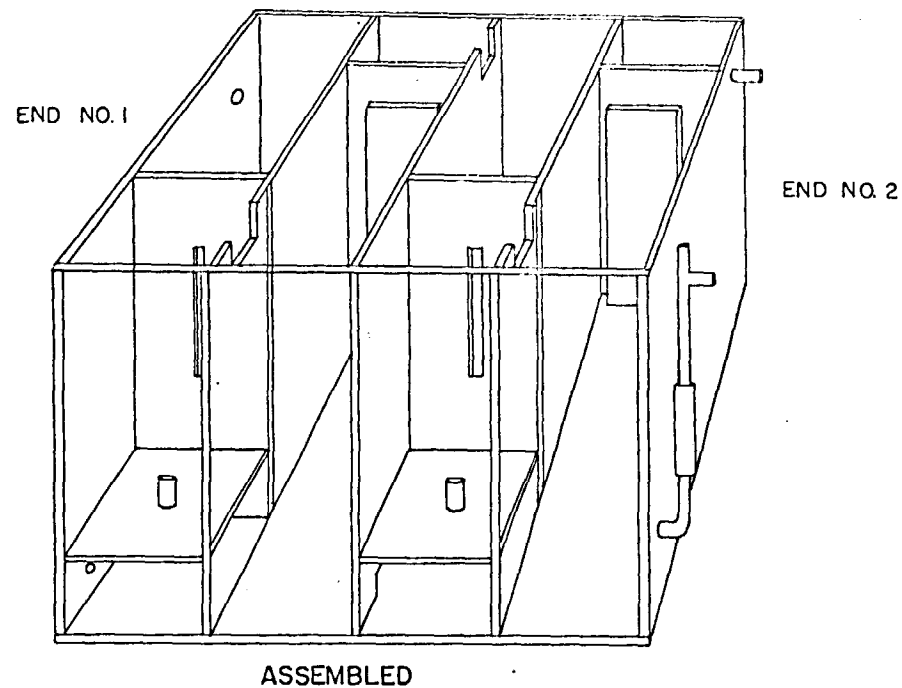
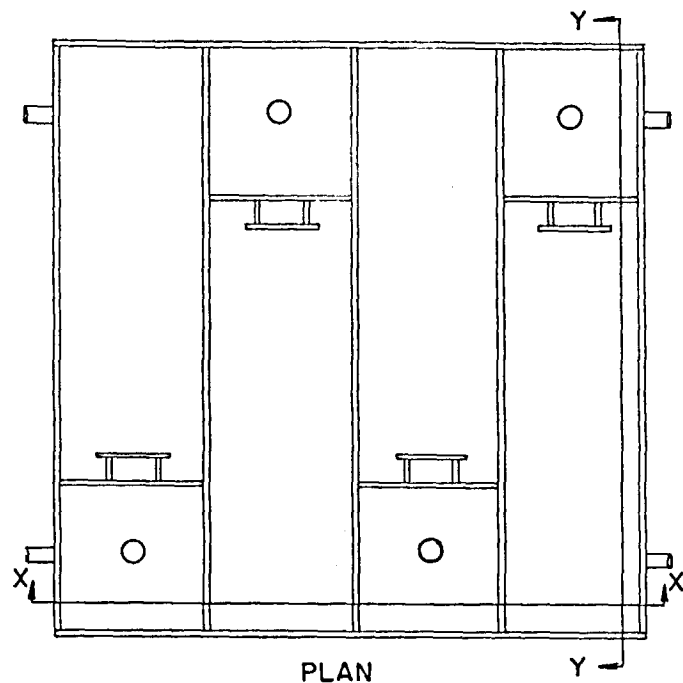


FIGURE 1
FOUR-STAGE MIXER-SETTLER

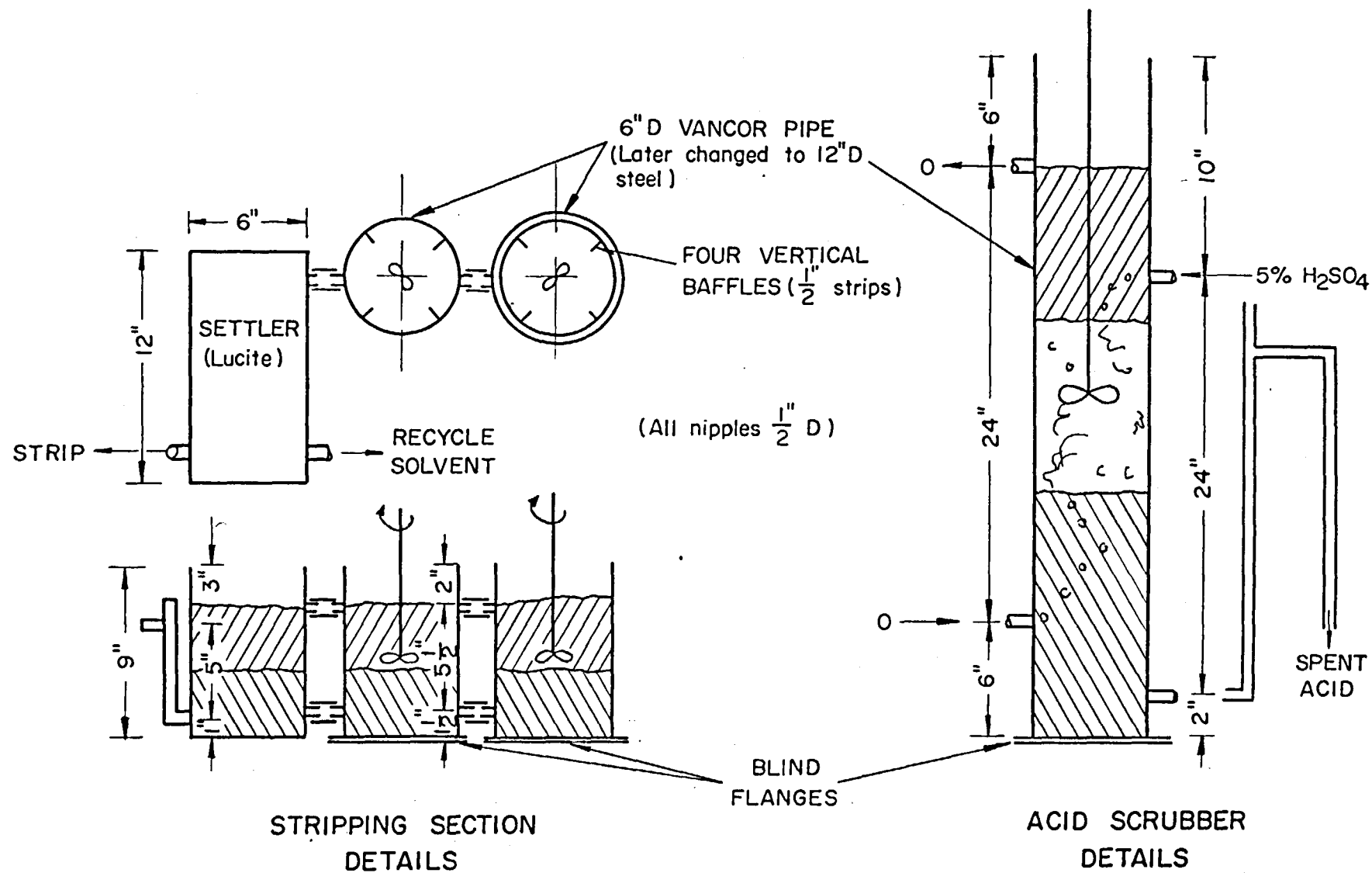
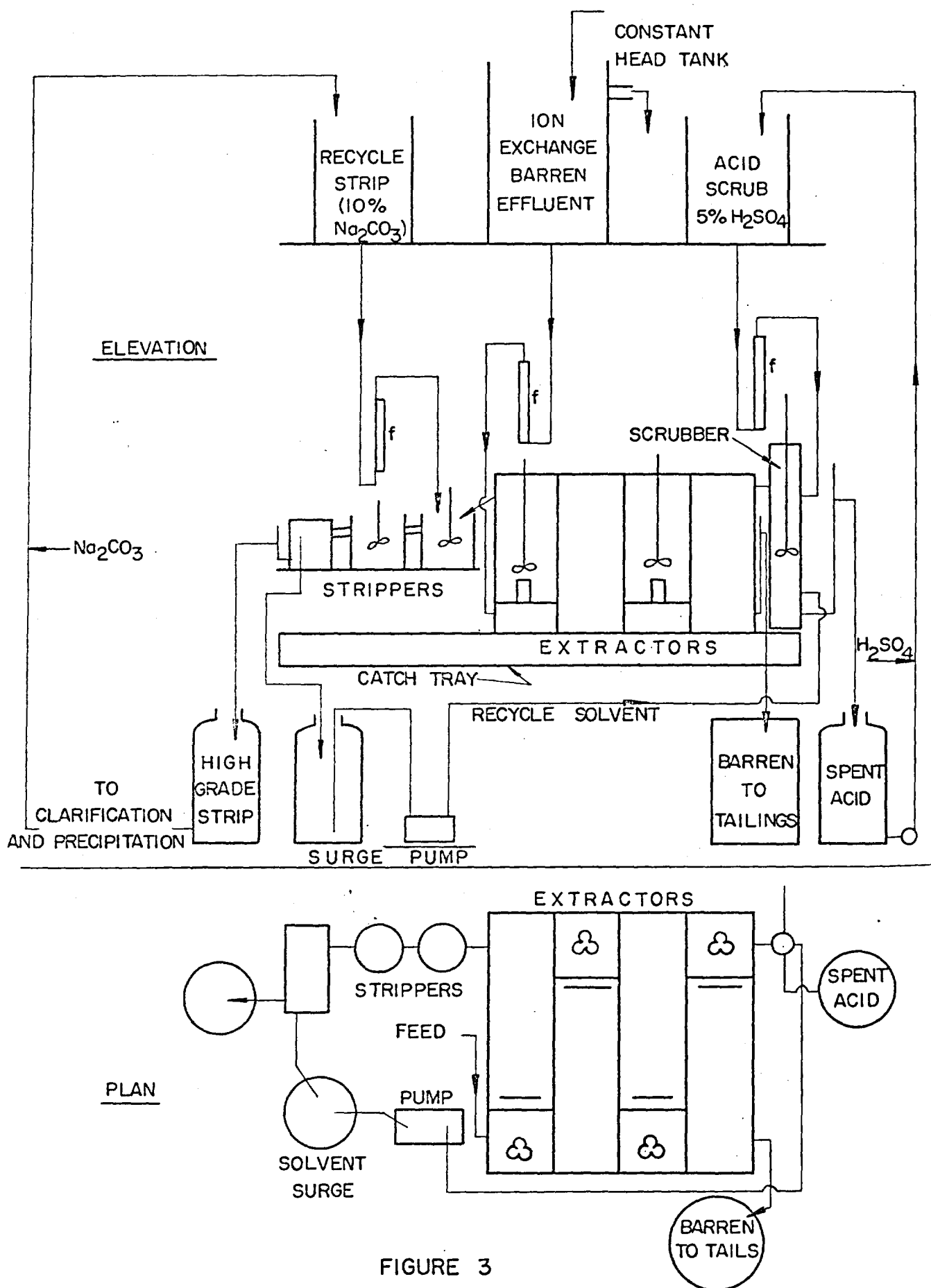


FIGURE 2



OPERATING PROCEDURE

The circuit was first filled on February 12th with approximately 100 gallons of solvent made up from Imperial Oil kerosene (Montreal East Refinery), containing 5% di-tridecyl amine supplied by Carbide Chemicals Co., Division of Union Carbide Canada Ltd. No alcohol was used as a modifier, although batch tests indicated some improvement of settling rate when the solvent contained 2% mixed decyl alcohols. The whole of the solvent was put through the acid scrubber, during filling, to sulphate the amine and so avoid high pH in the extractors on start-up, with 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 counter-act 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 tended to produce a discontinuous organic phase. 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 barren 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 easily made.

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 ($16^{\circ} - 17^{\circ}\text{C}$) as compared with that of previous tests carried out at the Mines Branch. A steam coil was therefore included in the larger (12 in. dia.) tanks to maintain a temperature of $25^{\circ} - 30^{\circ}\text{C}$. 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 precipitate did build up over a period of a run and was removed from the interface, filtered, and discarded; the solvent was returned to the surge tank.

The 20-gal capacity solvent surge tank 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 tank 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 for transferring solvent 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 they aided in determining long-term solvent losses. Solvent normality was checked at intervals of a few days to establish soluble loss. Entrainment of solvent in the barren was measured by extracting a raffinate sample with carbon tetrachloride and determining the extracted kerosene by infra-red analysis of the extract. No effort was made to check this by a close inventory, due to unaccounted spills and to samples taken.

The precipitation of the 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 a cooling tank to crystallize out excess sodium sulphate. The product was filtered and washed twice on a Buchner 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

Materials and Reagents

Feed Solution - Uranium plant ion exchange effluent:

The uranium plant produced approximately 250 gal/min of ion exchange barren effluent which was run to a 16 ft dia. tank before neutralization with lime and disposal. Weekly composites of the solution taken during January and February showed the following average analysis:

TABLE 1

Analysis of Uranium Plant Ion Exchange Effluent

Jan. - Feb. 1958

pH	Analyses, 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. This could materially affect solvent entrainment. However, precipitation of gypsum was much less during the later months.

The chloride content shown in Table 1 is an average over one operating cycle of the ion exchange columns, and could be higher at the start of loading on the columns. A surge tank could be used advantageously to even out this possible fluctuation. A previous investigation⁽²⁾ has shown that chloride concentration higher than 2.0 g Cl/l can materially affect the thorium distribution coefficient.

Kerosene Diluent, and Amine:

After some preliminary evaluation of various commercial kerosene samples from Montreal East refineries, Imperial Oil kerosene was adopted as diluent. The choice was made on the basis of a higher flash point and better phase separation. The effect of adding n-decyl alcohol as a modifier (2% by volume) was also considered. This reduced phase separation time for a continuous-organic phase system of 600 ml organic and 300 ml aqueous from 110 to 70 seconds. Unfortunately, delivery of the alcohol was not made in time to be tested in the pilot plant.

The amine was obtained in 4-gal drums from the Carbide Chemicals Co., Division of Union Carbide Canada Ltd.

Continuous Countercurrent Extraction with Sodium Carbonate Stripping

A series of forty runs was completed under the conditions mentioned earlier. A summary of the data obtained is presented in Table 2. Flow rates were held relatively constant at near-maximum throughput. The flow ratio of aqueous to organic was set to give loadings of 2.5 g ThO_2 /l solvent from a feed of 0.20 g ThO_2 /l.

Efficiency of the stripping was poor for the first twelve runs, since the original 6 in. dia. strippers were undersize and the feed solution temperature was too low. In runs 17 to 30, by increasing the retention time from 4 to 12 minutes and the temperature from 15° to 25°C, improved results were obtained as shown by the lowered ThO_2 content of the recycle solvent. Slowing down of the stirrers in the later runs, due to overheating, led to some high ThO_2 contents in the recycle solvent as shown.

No effort was made to plot thorium equilibrium data for individual stages, since fluctuations in the thorium content of the feed and recycle solvent prevented equilibrium from being attained. The indicated possible solvent loadings were 2-2.5 g ThO_2 /l with a recovery of 95% or better. Maximum strip solution loadings were 14 g ThO_2 /l, beyond which thorium begins to precipitate out.

A thorium balance made on the total forty runs showed that 88.69 lb ThO_2 had been recovered from a calculated feed of 93.33 lb ThO_2 . This represents a thorium recovery of approximately 95%.

TABLE 2

Continuous Pilot Plant Extraction with Sodium Carbonate Stripping

Conditions:

Feed: Uranium plant ion exchange effluent
 Solvent: 5% V/V Di-tridecyl amine in kerosene
 Strip: Recycled Na_2CO_3 solution (60-90 g $\text{Na}_2\text{CO}_3/\text{l}$)
 Scrub: Recycled H_2SO_4 solution (50 g $\text{H}_2\text{SO}_4/\text{l}$)

Results:

Date (February and March/58)	14	15	16	17	18	19	20	21	22	23	25	26	27	28	1	2	3	4	5	6
Run No	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	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	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	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	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	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	0.012	0.025	0.012	0.020	0.015	0.015	0.019
Analyses, 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
Barren (Stage 4)	0.083	0.083	0.006	0.132	0.074	0.024	0.061	0.009	0.007	0.071	0.009	0.036	-	0.001	0.001	0.001	0.001	0.001	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	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	13.3	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 $\text{ThO}_2^{(1)}$	1.18	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
Barren Strip Analyses, g/l																				
Na_2CO_3	-	-	-	-	-	-	84	80	80	79	78	77	76	74	70	68	68	63	61	62
Na_2SO_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	-	0.093	-	-	-	-	-	-	0.0925	-

TABLE 2 (Continued)

Date (March/58)	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Run No	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	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	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	0.125	0.127	0.126	0.136	0.129	0.135	0.131	0.138	0.130	0.139	0.137	0.133	0.136	0.140	0.138	0.135	0.135	0.134	0.135	0.135
Strip	0.036	0.037	0.037	0.030	0.031	0.035	0.036	0.034	0.033	0.0305	0.029	0.029	0.031	0.032	0.031	0.035	0.033	0.035	0.032	0.033
Scrub	0.02	0.02	0.02	0.02	0.02	0.027	0.022	0.021	0.026	0.022	0.023	0.026	nil	0.016	0.024	0.020	0.025	0.024	0.025	0.024
Analyses, 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	0.229	0.189	0.195	0.195	0.142	0.153	0.200	0.14
Barren (Stage 4)	0.005	0.008	0.009	0.006	0.005	0.004	0.003	0.003	0.004	0.004	0.017	0.013	0.013	0.014	0.013	0.013	0.013	0.013	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	0.04	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	20.3	28.5	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 $\text{ThO}_2^{(1)}$	1.13	1.00	1.48	1.57	1.37	1.6	2.14	1.85	2.49	2.35	2.05	2.00	-	1.50	1.78	1.77	1.58	2.32	2.05	2.05
Barren Strip Analyses, g/l																				
Na_2CO_3	61	60	58	96	85	96	75	97	95	89	86	82	-	88	84	93	-	-	85	-
Na_2SO_4	125	130	45	64	75	75	100	92	70	82	88	95	-	82	80	70	-	-	85	-
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	0.095	-	-	-	0.092	-	-	-	-	-	-	0.095	-	-	0.095	-	-	-	-	0.096

(1) Calculated from strip analyses and volume.

(2) Combined precipitate from tests 1, 2 and 3.

(3) Combined precipitate from tests 16 and 17.

Improved results were possible when operating at higher stripping efficiency, and barrens of 0.005 g ThO_2/l were obtained, for a thorium recovery of 98%.

Precipitation of Thorium Oxycarbonate:

Individual batches of strip solution collected from each run were heated to 60°C and clarified to remove the insolubles, mainly iron hydroxide, amounting to approximately 2% by weight of the thorium produced. (In practice this iron hydroxide precipitate would be re-dissolved at the head of solvent extraction circuit.) The addition of flake caustic soda to the clarified solution produced a precipitate of thorium oxycarbonate, which, however, was very finely divided and filtered poorly. Additions of Jaguar were found to be helpful in settling and filtering the precipitate. In filtering it was found that the cake cracked, and that washing on the filter was not effective, so washing by repulping was used.

Typical analyses of a composite precipitate from runs 15 to 30 are shown in Table 3, with and without the repulping step.

TABLE 3

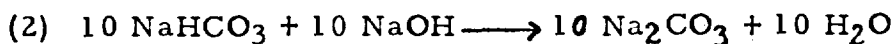
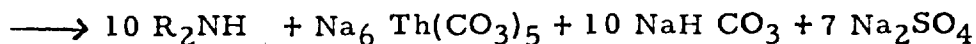
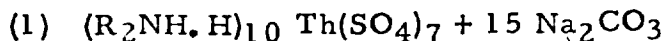
Analyses of Thorium Oxycarbonate Precipitate Composite of Runs 15 to 30

Sample	% Dry Basis					
	ThO_2	Na	SO_4	CO_2	Fe	U_3O_8
No repulping	52.4	14.8	10.9	12.8	0.18	0.57
With repulping	76.8	3.8	0.13	9.1	0.30	0.45

More care in the clarification of the strip before precipitation would probably have reduced the iron in the thorium oxycarbonate. Uranium, although quite low in the feed solution, follows the thorium through the extraction process and builds up in the recycled sodium carbonate until it reaches a high enough concentration to precipitate with the thorium product.

Sodium Hydroxide-Sodium Carbonate Consumption:

The caustic soda consumptions shown in Table 2 are based on actual weights added to individual batches and on the thorium analyses of the solutions. These results vary over a wide range, due to the difficulty of accurate pH control of the strip solutions in the range of pH 12.0 in the course of precipitation of the thorium. An average consumption, based on runs 15 to 30, during which the precipitate was collected as one composite lot and analyzed, gives a value of 2.5 lb NaOH/lb ThO₂. This figure is in agreement with that obtained in previous laboratory studies. On the basis of the ThO₂ and SO₄ analyses of the extract, the theoretical consumption is 12 mols NaOH per mol ThO₂ or 1.82 lb NaOH/lb ThO₂ as may be seen from the following equations:



The higher consumption actually obtained in the pilot plant is considered to be due mainly to the presence of bisulphate in the extract.

The equations given above also show that the theoretical consumption of sodium carbonate is 1 mol per mol ThO_2 or 0.4 lb/lb ThO_2 . However, due to entrainment losses in the sodium sulphate crystallization, the actual consumption as found by make-up requirements is closer to 0.5 lb/lb ThO_2 .

Solvent Losses:

Losses to the barren are twofold: (1) soluble amine, (2) entrained amine and kerosene. The first item was determined by the drop in amine concentration of the solvent from runs 1 to 25, during which time there was no fresh make-up of amine. The loss amounted to 0.034 lb amine/lb ThO_2 . Entrained solvent was calculated from a kerosene determination on the barren composite of runs 1 to 25 and amounted to 0.20 lb kerosene/lb ThO_2 and by calculation to 0.008 lb amine/lb ThO_2 . Total amine loss was therefore 0.042 lb/lb ThO_2 .

Treatment of the Thorium Oxycarbonate Precipitate:

Two methods were tested to refine the thorium oxycarbonate to an acceptable grade.

1. Direct calcination at 1000°C was not successful in driving out all the carbonate due to the formation of fused carbonates. The calcine assayed 95% ThO_2 .

2. Redissolution of various lots of the wet precipitate in HCl to a 10% ThO_2 solution and subsequent addition of 1 lb oxalic acid per lb ThO_2 resulted in the formation of filterable product. This was repulped, washed, and calcined at 800°C . The oxide assayed 99% ThO_2 with 0.01% Fe and $<0.01\%$ Al.

Continuous Extraction Tests with Sodium Chloride Stripping

In view of the filtering problem encountered in the stripping with sodium carbonate, a series of runs was made with acidified sodium chloride as the stripping agent. Preliminary batch stripping tests had shown high strip-to-organic thorium distribution coefficients (<200) with 1N NaCl. In addition, recycling of the amine in the chloride form was found to have no noticeable depressing effect on the extraction efficiency.

To simplify the operation, the stripping unit was not changed from a cocurrent to countercurrent system, although this would have improved the stripping efficiency since chloride stripping is a reversible process. Nevertheless, by limiting the concentration in the strip solution to 10 g ThO_2 /l it was possible to obtain relatively efficient thorium removal. Results of these tests are summarized in Table 4.

TABLE 4

Continuous Pilot Plant Extraction Tests with Chloride StrippingConditions:

Feed: Uranium plant ion exchange effluent
 Solvent: 5% V/V Di-tridecyl amine in kerosene
 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	0.12
Strip	0.044	0.030	0.028	0.029	0.029	0.028	0.028	0.028	0.03
<u>Analyses, 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	0.00
Extract	2.21	3.03	2.63	2.56	2.47	1.81	2.00	2.90	2.05
Recycle solvent	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

These tests were done mainly to collect sufficient strip solution for precipitation studies; hence, no effort was made to operate at maximum loading or recovery. A batch saturation test gave a maximum concentration of 19 g ThO_2 /l in the strip solution.

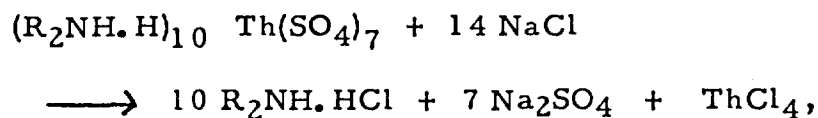
Batch precipitation was done using 1.2-1.3 lb oxalic acid per lb ThO_2 . The thorium oxalate was washed thoroughly to remove sulphate and chloride salts, dried, and calcined at 800°C . Loss of weight on ignition was 51%, and analysis of the calcine is shown in Table 5.

TABLE 5

Analysis of Calcined Oxalate Produced from
Sodium Chloride Strip Solution

ThO_2	Fe	Al	RE_2O_3
98.1	0.03	0.01	0.45 %

In practice, the sodium chloride strip solution would not be recycled for re-use, partly because it would accumulate a content of sodium sulphate, as shown by the following equation:



and partly because it would contain some residual oxalic acid which would precipitate thorium in the stripping circuit. If the sodium chloride solution were not re-used, the equation shows that the sodium chloride consumption would be 3.1 lb NaCl /lb ThO_2 recovered. The equation also shows that a 1 normal NaCl solution may be loaded

to the extent of 18-19 g ThO_2 /l. This was confirmed in laboratory batch stripping tests.

An alternative to oxalic acid precipitation would be to acidify the strip solution to 40% H_2SO_4 which would precipitate thorium sulphate tetrahydrate. The reported solubility⁽³⁾ of this salt in 40% acid is 0.02% as $\text{Th}(\text{SO}_4)_2$. If this procedure were employed, the acid solution, after separation of the thorium sulphate tetrahydrate, could be used in the uranium plant leaching circuit, where it would not raise the chloride level materially.

CONCLUSIONS

The pilot plant operation has confirmed previous findings on the feasibility of an economical process for thorium recovery from this uranium plant ion exchange effluent 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 have to be justified by the demand and the purity requirements. The highest grade will be obtained by a treatment of the oxycarbonate with HCl followed by precipitation with oxalic acid. 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 sodium carbonate stripping or sodium chloride stripping, followed by oxalate precipitation, would be suitable for metal production, giving 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 6. In all cases solvent losses are the same and are based on the present findings.

TABLE 6
Tentative Reagent Costs for Various Methods of
Stripping and Precipitation

0.045 lb amine DTDA/lb ThO_2 (at \$2.00/lb) = 9.0 cents/lb ThO_2
 0.200 lb kerosene/lb ThO_2 (at 2.4 cents/lb) = 0.5 cents/lb ThO_2
 Total 9.5 cents/lb ThO_2

	Product	Reagent Used, lb/lb ThO_2	Cost, cents/lb ThO_2
<u>Case 1</u> Na ₂ CO ₃ stripping NaOH precipitation Strip recycled	ThOCO ₃	NaOH: 2.5 Na ₂ CO ₃ : 0.5 Solvent: Total:	12.5 1.0 9.5 <u>23.0</u>
<u>Case 2</u> Na ₂ CO ₃ stripping, etc., as in Case 1 HCl dissolution Oxalic acid precipitation Calcination	ThO ₂	HCl: 0.9 Oxalic acid: 1.0 Total:	23.0 4.5 20.0 <u>47.5</u>
<u>Case 3</u> NaCl stripping Oxalic acid precipitation Calcination	ThO ₂	NaCl: 3.5 H ₂ SO ₄ : 0.5 Oxalic: 1.2 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) ₂ • 4H ₂ O	NaCl: 3.5 H ₂ SO ₄ : 1.0 Solvent: Total:	4.9 1.2 9.5 <u>15.6</u>

In cases 1 and 2, the filtration and repulping problems should be kept in mind in a complete comparative study.

Direct precipitation of the chloride strip with alkalies was not considered suitable, since the specifications for iron, aluminum and other base metals are low in the thorium product for alloy use. Therefore, it has not been proposed in the present estimate.

ACKNOWLEDGMENTS

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APPENDIX

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 and secondary amine LA-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 to 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.
- (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.

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

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