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SEMIWORKS EVALUATION OF THE MANGANESE DIOXIDE HEAD-END STEP IN THE THOREX PROCESS

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SEMIWORKS EVALUATION OF THE MANGANESE DIOXIDE HEAD-END STEP IN THE THOREX PROCESS

by

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ABSTRACT

The standard Savannah River Plant procedure for precipitating MnO_2 as a head-end step in the Purex process is satisfactory for sorption of protactinium in the dilute Thorex process at rates of ~4000 lb Th/day with the following modifications: (1) sulfamic acid is added to the dissolver solution to decompose nitrous acid, which would otherwise dissolve some of the MnO_2, (2) residual liquid skimmed from the centrifuge is recycled, and (3) the volume of dilute acid used in each of the five washes of the MnO_2 precipitate is doubled to 50 gallons.

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INTRODUCTION

A dilute Thorex process has been developed at the Savannah River Laboratory for separating and purifying ^{233}U from residual thorium, fission products, and protactinium. This process will be operated in the chemical separations plant that is normally used for processing enriched uranium. A head-end step involving the sorption of ^{233}Pa and some of the fission products on a manganese dioxide slurry is used to separate the major fraction of protactinium from the ^{233}U and thorium. The slurry is dissolved with sodium nitrite in acid solution, and is then concentrated and stored to permit essentially complete conversion of the ^{233}Pa to ^{233}U of very high isotopic purity (<0.5 ppm ^{232}U). Removal of ^{233}Pa prior to solvent extraction is necessary to prevent excessive radiation damage to the solvent.

Laboratory tests demonstrated adequate sorption of ^{233}Pa by MnO_2 at the levels of radioactivity expected in the plant process solutions. In addition, tests of the Thorex head-end step in plant prototype equipment were necessary to demonstrate that the standard plant procedure(1) for precipitating MnO_2 and clarifying the resulting solution is satisfactory, and to define the processing rate of the plant equipment. The results of these tests are presented in this report.

SUMMARY

Semiworks tests of the head-end step for the MnO_2 sorption of ^{233}Pa from Thorex process feed solutions showed that:

- Approximately 4000 lb thorium per day can be processed through the head-end cycle in the enriched uranium plant.

- Addition of sulfamic acid to the solution prior to precipitation of MnO_2 is required to decompose nitrous acid; otherwise, a fraction of the MnO_2 would be dissolved by nitrous acid that is generated radiolytically in the nitric acid solution. One mole of sulfamic acid per mole of nitrous acid is required.

- The supernatant liquid skimmed from the centrifuge must be recycled, because it contains a significant amount of flocculent MnO_2.

- 50 gallons of dilute acid should be used in each of five washes of the MnO_2 precipitate — the maximum possible for the size of the bowl. The washes remove thorium and ^{232}U which would otherwise contaminate the high purity ^{233}U that is extracted after decay of ^{233}Pa.

With slight changes to include these conditions, the standard Purex plant procedure for precipitating MnO_2 and clarifying the feed solution is satisfactory for the dilute Thorex process.

DISCUSSION

Equipment

The semiworks installation, Figure 1, consists of a prototype plant centrifuge and associated tankage to simulate plant conditions. The centrifuge, Figure 2, manufactured by the Bird Machine Company, includes a four-compartment solid bowl that is 40 inches in diameter (60 gallons dynamic volume). The 5-5/8-inch-high compartments are formed by three perforated baffles that extend 6 inches inward from the wall. The casing of the bowl collects the liquor overflow; the precipitate remains in the compartments. A 40-hp electric motor drives the bowl at speeds up to 1750 rpm.

The centrifuge feed jet piping, slurry-removal jet piping, and high pressure spray piping simulate the plant arrangements. A Z-6 plant-rate jet was used for feeding the centrifuge, and a 25-S_1 plant transfer jet was used for removing the slurry from the centrifuge bowl.

A positive displacement pump capable of delivering at 600 psig was used to remove the MnO_2 precipitate from the walls of the centrifuge.

Process Description and Chemistry

In the normal plant procedure for precipitating MnO_2 and clarifying Purex feed, approximately 60-pound-batches of manganese dioxide precipitate are formed by adding manganous nitrate solution to the dissolver solution at 70°C, and then adding a stoichiometrically deficient amount of potassium permanganate solution at a slow rate. The reaction between the manganous nitrate and potassium permanganate can be represented as follows:

$$3Mn(NO_3)_2 + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + 2KNO_3 + 4HNO_3$$

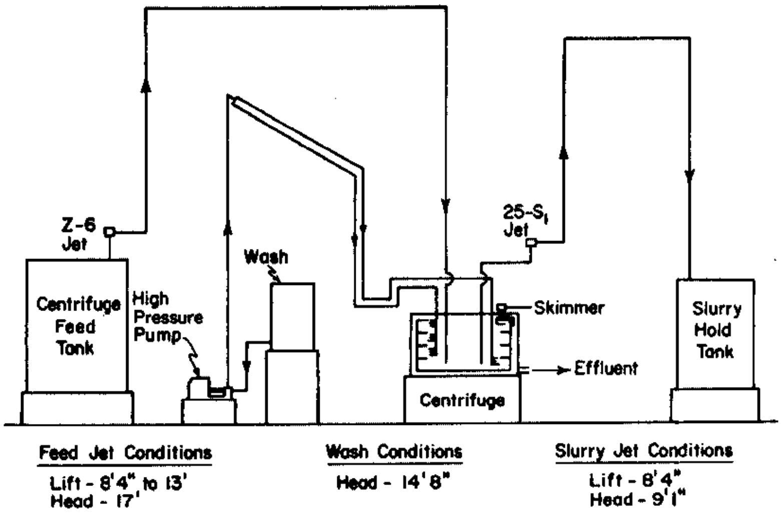

FIG. 1 SEMIWORKS HEAD-END SYSTEM

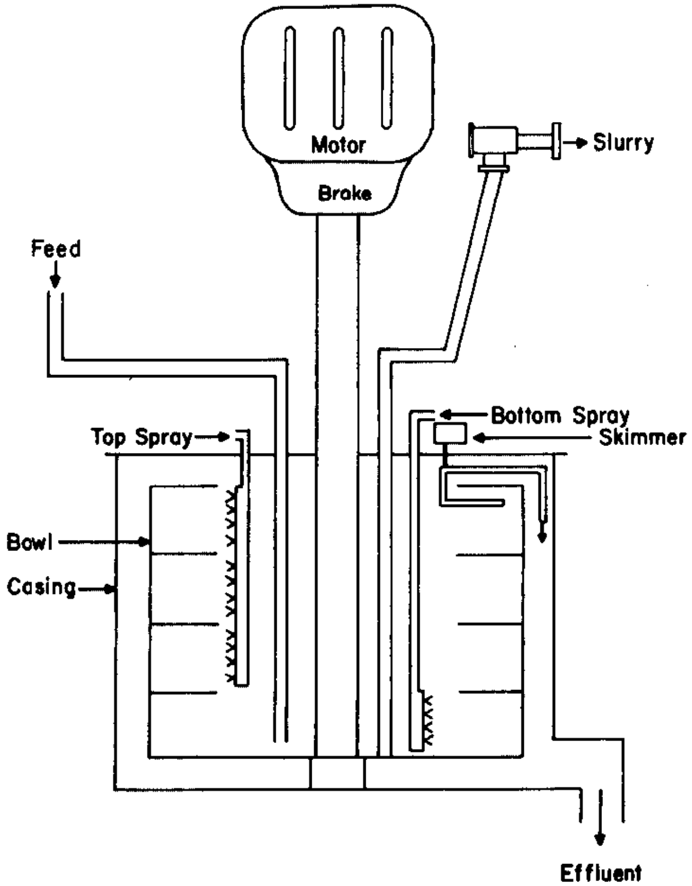

FIG. 2 SEMIWORKS CENTRIFUGE

The quantity of permanganate is sufficient to oxidize only about 85% of the manganous ion in order to avoid a strongly oxidizing environment that releases ruthenium. The resulting manganese dioxide slurry, which constitutes one full load of the centrifuge, is digested at 70°C, cooled to 40°C, and transferred to the centrifuge at a maximum rate of 12 gal/min with a steam jet pump. The final volume of supernate retained in the centrifuge is reduced by decreasing the centrifuge speed from 1740 to 870 rpm and skimming the liquid to the effluent catch tank. The clarified solution is then ready for solvent extraction.

The MnO_2 precipitate is subjected to five successive washes as follows:

The cake is slurried off the bowl wall by spraying 20 to 25 gallons of 0.1M HNO_3 into the four horizontal compartments of the bowl at approximately 600 psig. The slurry is agitated five times by alternately rotating and suddenly stopping the bowl. After recentrifuging the MnO_2, each wash solution is skimmed from the bowl. After the final wash, the cake is slurried from the bowl in four flushes and jetted to the slurry hold tank.

The above procedure was followed during the plant-scale tests of the procedure for MnO_2 sorption of ^{233}Pa from dissolved thoria containing ^{233}U. In these tests unirradiated thoria was used, no ^{233}Pa was present, and ^{238}U was substituted for ^{233}U.

RESULTS

Test Conditions

Laboratory data showed that, for effective sorption of ^{233}Pa by MnO_2, the concentration of the dissolver solution should not exceed 0.4M Th - 0.7M Al - 0.8M HNO_3. Two semiworks tests were made with plant-scale equipment and simulated dissolver solution at the maximum thorium and aluminum concentrations, but with varied acid concentrations. A small amount of mercuric nitrate was also used in the second test because the aluminum cladding of the thoria target elements is dissolved with mercury as a catalyst. The data from the two tests are summarized in the following table:

MnO_2 Preparation and Centrifugation Tests

Simulated plant agitation during precipitation

	Test I	Test II
Test solution (2700 gal at 70°C)		
$Th(NO_3)_4$, M	0.37	0.41
HNO_3, M	0.39	0.77
$Al(NO_3)_3$, M	0.66	0.81
U, g/liter	0.21	0.85
NO_2^-, M	0.0074	0.0087
$Hg(NO_3)_2$, M	-	0.0025
Specific gravity	1.2805	1.3162
NO_2^- after addition of 1 mole sulfamic acid per mole NO_2^-, M	10^{-6}	10^{-6}
MnO_2 formed, lb	62	58
MnO_2/Th,(a) mole ratio	0.086	0.073
Feed rate to plant prototype centrifuge, gpm	11-15	13
MnO_2 in first 100 gallons of centrifuge effluent,(b) % of total	0.12	0.21
MnO_2 in remainder of centrifuge effluent, % of total	0	0
MnO_2 in skimmed supernatant liquid, % of total	0.11	0.22
MnO_2 in washes,(b) % of total	1.9	1.8
Volume of MnO_2 in centrifuge,(c) gal	33	26
MnO_2 removed from centrifuge,(d) % of total	93.0	97.7
Dilute acid in each of five washes, gal	25	50
Product washed from precipitate, % of total in feed		
Uranium	1.3	1.3
Thorium	0.9	1.4
Residual product in washed precipitate, % of total in feed		
Uranium(e)	0.71	0.038
Thorium	0.13	0.007

(a) Normal ratio in plant = 0.053 (60 lb MnO_2 per 4000 gal solution). Semiworks tank limited to 2700 gal.

(b) Normally recycled to later batch.

(c) This volume reduces to about 10 gal during the acid washes.

(d) Material balance within accuracy of MnO_2 analysis.

(e) This uranium will be extracted after the ^{233}Pa decays to ^{233}U.

Removal of Nitrous Acid

Any nitrous acid that is generated radiolytically in the dissolver solution will interfere with ^{233}Pa recovery either by reacting with the $KMnO_4$ or by dissolving the MnO_2 precipitate after formation. Data for the removal of nitrous acid from the dissolver solution are summarized in Figure 3. The concentration of nitrous acid in the dissolver was not changed by heating to 70°C during normal plant agitation. Sparging with air at 10 scfm removed the nitrous acid, but only at a very slow rate that was not improved by increasing the sparge to 14.5 scfm. Addition of sulfamic acid completely destroyed the nitrous acid; at least 1 mole of sulfamic acid per mole of NO_2^- is needed to ensure removal of the nitrous acid.

Centrifugation of MnO_2 Precipitate

The MnO_2 prepared at the semiworks was very similar to that prepared in the laboratory. MnO_2 formed in the presence of aluminum and thorium is more flocculent than that formed when the analogous procedure is used in the Purex process. Although the higher acidity of the second feed solution apparently decreased the bulk volume of the ~60-lb precipitate from 33 to 26 gallons (Purex volume ranges from 13 to 20 gallons), little difference was seen in the centrifuging characteristics. The volume of the precipitate reduces to ~10 gallons during washing, the same volume as in the Purex process. The slurry was fed to the centrifuge at 11 to 15 gpm with no breakthrough to the effluent except in the first 100 gallons, which is recycled. However, a significant amount of flocculent MnO_2 is unavoidably skimmed with the final supernatant solution, which must be recycled. The wash solution also contained a significant amount of precipitate and was recycled.

Washing of MnO_2 Precipitate

About 1 to 2% of the uranium and thorium in the dissolver solution remained in the centrifuge with the precipitate after the final supernatant solution was removed by skimming. The volume of 0.1M HNO_3 for each wash was doubled (to 50 gallons) to remove this residual uranium and thorium with the normal five washes, as shown in Figure 4. With this procedure, ^{233}U essentially free from ^{232}U can be obtained from the MnO_2 after the ^{233}Pa has decayed. The increase in volume of each wash (rather than in the number of washes) has no marked effect on the time cycle. A wash volume greater than 50 gallons added to the 10 gallons of MnO_2 would overflow the bowl, which has a dynamic holdup of 60 gallons.

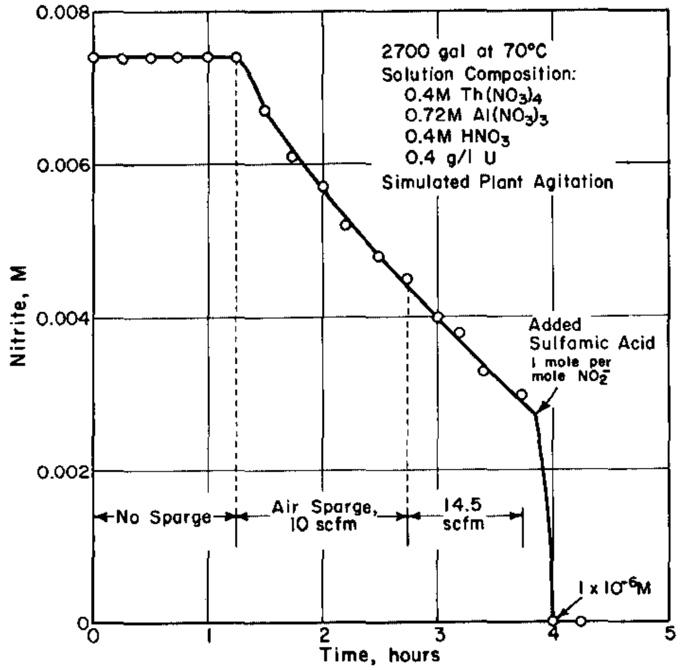

FIG. 3 REMOVAL OF NITRITE FROM DISSOLVER SOLUTION

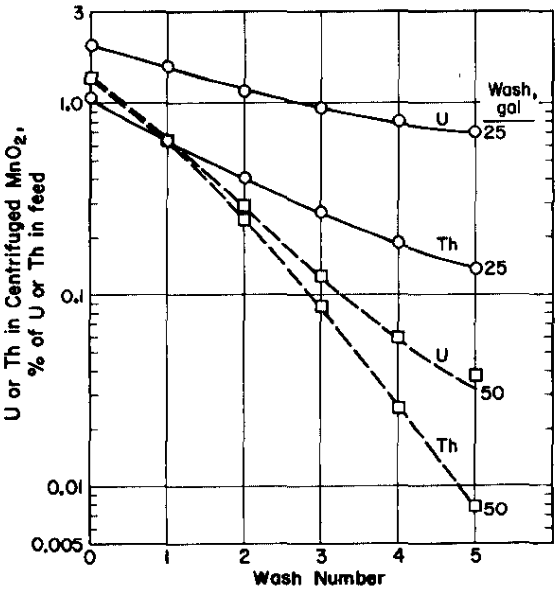

FIG. 4 WASHING OF CENTRIFUGED MnO_2

Plant Processing Rate

The plant head-end cycle for the dilute Thorex process will require a total of 18 hours to process ~3000 lb of thorium. Therefore, the plant head-end processing rate will be ~4000 lb Th/day. The detailed schedule is shown in the following table.

Head-End Time Cycle

Based on 4000 gallons of 0.4M Th per batch (~3000 lb Th)

			Time Required, minutes
1.	Jet 4000 gal of raw metal solution to head-end strike tank and destroy nitrous acid with sulfamic acid		90
2.	Add 340 lb of a 25% solution of $Mn(NO_3)_2$ and heat to 70°C		30
3.	Add 1420 lb of a 3% solution of $KMnO_4$ at approximately 10 lb/min		142
4.	Simmer at 70°C for 2 hours		120
5.	Jet slurry to centrifuge at 12 to 15 gal/min		370
6.	Skim mother liquor		10
7.	Wash cake		
	a. Spray	3	
	b. Slurry 5 times	10	
	c. Reset cake at 1800 rpm	19	
	d. Skim wash solution	10	
	Time per wash cycle	42 min	
	Time for 5 wash cycles		210
8.	Jet slurry and two rinses to cake slurry hold tank		45
		Total time	1017 (18 hrs)

Plant capacity: $3000 \times \frac{24}{18} = 4000$ lb (Th)/day

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