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**CONTINUOUS SOLVENT EXTRACTION
FEED ADJUSTMENT FOR
HTGR FUEL REPROCESSING**

INTERIM DEVELOPMENT REPORT

**by
L. J. OLGUIN**

**Prepared under
Contract EY-76-C-03-0167
Project Agreement No. 53
for the San Francisco Operations Office
Department of Energy**

DATE PUBLISHED: JUNE 1978

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ABSTRACT

The two-cycle Acid-Thorex solvent extraction process requires that the feed stream to each thorium cycle be processed to reduce its nitric acid concentration (feed adjustment). This interim development report presents the results of bench-scale and pilot-plant-scale feed adjustment experiments using a continuous mode of operation. An examination of formic acid denitration and fluoride ion volatilization is also included.

CONTENTS

ABSTRACT	iii
1. SUMMARY	1-1
2. INTRODUCTION	2-1
References	2-3
3. REQUIREMENTS	3-1
3.1. Flowsheet	3-1
3.2. Objectives	3-1
Reference	3-4
4. APPARATUS	4-1
5. EXPERIMENTAL	5-1
6. RESULTS	6-1
7. DISCUSSION	7-1
7.1. Bench-Scale Investigation	7-1
7.1.1. Continuous Feed Adjustment	7-1
7.1.2. Formic Acid Denitration	7-4
7.2. Pilot Plant Studies	7-5
7.2.1. Equipment Shakedown	7-5
7.2.2. Continuous Mode Operation	7-7
7.2.3. Formic Acid Denitration	7-9
7.2.4. Fluoride Volatility	7-11
References	7-12
8. CONCLUSIONS	8-1
9. RECOMMENDATIONS	9-1
References	9-2
10. ACKNOWLEDGMENTS	10-1

FIGURES

3-1.	Acid-Thorex flowsheet schematic	3-2
4-1.	Pilot plant continuous mode feed adjustment system	4-2
4-2.	Air/steam jet for product removal	4-4
6-1.	Continuous first cycle feed adjustment - Run 26	6-4
6-2.	Continuous intercycle feed adjustment - Run 34	6-5
6-3.	Continuous intercycle feed adjustment with formic acid treatment - Run 35	6-6
6-4.	Continuous first cycle feed adjustment with formic acid treatment - Run 38	6-7
7-1.	Bench-scale continuous feed adjustment apparatus using steam stripping	7-2
7-2.	Bench-scale continuous feed adjustment apparatus using a water strip	7-3
7-3.	Bench-scale feed adjustment apparatus with formic acid addition	7-6

TABLES

3-1.	Feed adjustment stream compositions	3-3
5-1.	Outline of feed adjustment runs	5-1
5-2.	Continuous feed adjustment operating parameters	5-2
6-1.	Analytical results for stream compositions	6-2
7-1.	Fluoride volatility during feed adjustment	7-11

1. SUMMARY

The HTGR Reference Recycle Facility (HRRF) flowsheet for reprocessing of High-Temperature Gas-Cooled Reactor (HTGR) fuel incorporates feed adjustment steps to reduce the nitric acid content of feed streams to the first and second thorium cycles of the Acid-Thorex solvent extraction process. The denitration of nitric acid is essential for the efficient separation of uranium and thorium from fission products. This report examines the results of solvent extraction feed preparation development studies conducted in the General Atomic Company (GA) pilot plant facilities during the period from February 1, 1976, to December 16, 1977.

An existing batch mode feed preparation unit was redesigned to be a continuous mode system and then was modified as necessary. The new continuous mode feed adjustment pilot plant system is capable of processing feed solution for either the first or second thorium cycle at a rate of about 7 l/hr. Possible advantages of operating under a continuous mode would be a totally continuous solvent extraction system, which would have reduced operating costs and fewer process vessels and would also facilitate the downstream operation of waste treatment. For safeguards purposes, accountability techniques used for continuous solvent extraction processes are also applicable to continuous feed adjustment.

Initial startup of the continuous process involves charging the evaporator/stripper with feed and concentrating the solution by evaporation. When the operating concentration is reached as indicated by the boiling point, continuous addition of feed solution and stripping water is begun. The amount of liquid in the evaporator/stripper is maintained at a near constant volume by semicontinuously removing product solution to a receiver tank where the product is diluted with water to prevent crystallization upon cooling.

The following conclusions are based on the results of continuous mode feed adjustment studies performed at GA:

1. The feasibility of a continuous mode feed adjustment step for the first solvent extraction cycle has been successfully demonstrated using a 135°C operating temperature.
2. The HRRF Acid-Thorex flowsheet proposes a two-stage intercycle concentration and denitration step. Pilot plant experiments, however, have shown that it is possible to perform the intercycle feed adjustment step as a single-vessel continuous mode process.
3. Continuous addition of formic acid to the evaporator/stripper vessel during feed adjustment enables the denitration of nitric acid to be performed at lower temperatures, thus reducing corrosion of equipment and the solution freezing point. Continuous mode denitration with formic acid can be performed for both the first and second solvent extraction cycles.
4. There is no apparent difference in the range of fluoride ion volatilized (from 1% to 3%) during continuous mode feed adjustment and during batch mode feed adjustment. Values from bench-scale studies are also within the same range.
5. Formic acid addition has no effect on the degree of fluoride ion volatilization.

Future development work is required to demonstrate a feasible method for tributyl phosphate (TBP) removal from a single-stage intercycle feed preparation process. In addition, iodine and ruthenium volatility studies must be examined on a pilot plant scale.

2. INTRODUCTION

The spent fuel elements from an HTGR are reprocessed to recover reusable uranium and thorium from the fission product wastes. In the head-end process of the HRRF reprocessing flowsheet (Ref. 2-1), the fuel element is crushed, burned, and leached to produce a nitrate solution containing uranium, thorium, fission products, and other contaminants. An Acid-Thorex solvent extraction process is used to selectively separate the uranium and thorium from the leacher product solution. Finally, the uranium and thorium are partitioned and further processed in separate solvent extraction cycles. Feed adjustment is the method used to reduce the nitric acid concentration of certain flowstreams to suitable operating levels. Development of a continuous mode feed adjustment process has been carried out by GA on a pilot plant scale, and the findings of this development work are presented in this report.

The original Thorex solvent extraction process (Ref. 2-2) utilizes an aluminum salting agent to shift the equilibrium of thorium and uranium from the aqueous phase to the organic phase. Oak Ridge National Laboratory (ORNL) found that a significant tenfold reduction in aqueous waste volume can be obtained by using a nitric acid salting agent instead of aluminum. This nitric-acid-salted process is known as the Acid-Thorex process (Refs. 2-3, 2-4). The Acid-Thorex process gives better decontamination factors with an acid deficient feed. Acid deficiency implies that the ratio of nitrate ions to thorium ions is less than the stoichiometric ratio of 4 to 1. The dissolution of ThO_2 requires a high initial nitric acid concentration ($13\bar{M}$), which reduces to about $9\bar{M}$ after a $1\bar{M}$ thorium concentration is obtained. The method used for feed adjustment differs in the original Thorex and Acid-Thorex processes. The original Thorex process simply evaporated the dissolver solution to acid deficiency by boiling at a temperature of 155°C . The Acid-Thorex process, however, evaporated the dissolver solution to 135°C and then stripped the residual

acid by steam sparging. The concentrated product from both processes had to be diluted with water to prevent solidification upon cooling.

In the Federal Republic of Germany, Kchler et al. (Refs. 2-5, 2-6) observed that a modified Acid-Thorex process must be applied to fuel with high burnup of 100,000 MWd/t since fission product zirconium precipitates during feed adjustment to acid deficiency. The modified Acid-Thorex process uses a two-cycle solvent extraction approach. Thorium and uranium are co-extracted using an acid feed in the first cycle to avoid zirconium precipitation, and then final decontamination occurs in the second cycle using an acid deficient feed. Preparation of a low-acid feed (0.7M to 1.1M HNO₃) for the first cycle was accomplished by evaporating the dissolver solution to 135°C. To achieve acid deficiency for the second solvent extraction cycle, the feed preparation step required steam stripping of residual acid after the solution was evaporated to 135°C. Feed preparation development studies performed in the GA pilot plant (Ref. 2-7) have confirmed that a batch concentration and steam stripping process can be used for the first solvent extraction cycle. The first cycle feed adjustment step must produce a 0.7M to 1.1M nitric acid concentration. Acid deficient conditions (-0.15 ± 0.05 molar H^+/Th^{+4} ratio) were obtained during the second cycle feed preparation step by evaporating the dissolver solution to 135°C followed by steam stripping.

The two-cycle Acid-Thorex process is a fundamentally continuous process. Therefore, it would be advantageous for the overall solvent extraction operation if a continuous mode feed preparation process could be developed. In addition, the feed adjustment condensed overheads would have uniform composition and flow rates, which would simplify the operation of the waste processing system receiving the condensate. Accountability of Special Nuclear Materials (SNM) throughout the solvent extraction process is very important for safeguards reasons. Los Alamos Scientific Laboratory (Ref. 2-8) has defined a model for real-time accountability of SNM for a fuel reprocessing plant. A similar technique would be acceptable for a continuous feed adjustment process.

The purpose of this development work is to demonstrate the feasibility of a continuous mode feed preparation process for both solvent extraction cycles. Results from the present study can be used in designing commercial-scale equipment and in modifying the HRRF flowsheet.

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3. REQUIREMENTS

3.1. FLOWSHEET

Feed adjustment of the leacher product solution is necessary to give adequate heavy metal/fission product solvent extraction separation. The HRRF Acid-Thorex flowsheet schematic shown in Fig. 3-1 identifies the 1A denitrator for the first cycle feed adjustment step. In the first solvent extraction cycle, the uranium and thorium are co-extracted in the 1A column and then separated from each other in the 1BX and 1BS columns.

The partitioned thorium stream (1BT) from the 1BS column contains thorium, nitric acid, and residual uranium, TBP, and fission products, including zirconium. It is necessary to decontaminate the 1BT stream in a second solvent extraction cycle, but first the 1BT stream must be made acid deficient in a two-stage concentration and denitration step. The 1BT concentrator and 2D denitrator are shown in Fig. 3-1. The TBP is steam stripped from the 1BT stream in the 1BT concentrator while the thorium concentration is increased. The product 1TC stream is then fed to the 2D denitrator, where the nitric acid concentration is reduced to an acid deficient level. The composition of the feed preparation streams for both solvent extraction cycles is given in Table 3-1.

Accountability plays an important role in the safeguarding of SNM throughout the solvent extraction process. Therefore, the feed adjustment process must not have a negative impact on SNM control and accounting.

3.2. OBJECTIVES

The feed adjustment process is an integral part of the Acid-Thorex solvent extraction process and therefore needs to be developed on a pilot plant scale to establish suitable operating conditions and equipment design

Fig. 3-1. Acid-Thorex flowsheet schematic

TABLE 3-1
FEED ADJUSTMENT STREAM COMPOSITIONS

Flowstream	Composition				
	Th ⁺⁴	HNO ₃	F ⁻	Al ⁺³	Total NO ₃ ⁻
Leacher product	1.0	8.7	0.05	0.10	13.5
1AF	1.5	1.0	0.08	0.15	8.13
1BT	0.17	0.37	0.01	--	1.04
1TC	1.43	3.5		--	
2DF	1.0	-0.10	0.03		3.90

for a large-scale remote facility. Previous development work at GA (Ref. 3-1) was conducted to confirm the applicability of the batch concentration and steam stripping process to solvent extraction feed preparation. The objectives of the present feed adjustment study are as follows:

1. Demonstration of a continuous feed adjustment operating mode for the first and second thorium solvent extraction cycles and the determination of optimum operating parameters.
2. Demonstration of a continuous feed adjustment operating mode for the first and second thorium solvent extraction cycles using formic acid treatment as an aid in denitration. Also, the determination of optimum operating parameters.
3. Determination of the degree of fluoride volatility during feed adjustment, with and without formic acid addition, for both solvent extraction cycles.
4. Preparation of 1AF and 2DF feedstock for use in pilot plant solvent extraction development studies.

REFERENCE

- 3-1. Brown, C. A., "Solvent Extraction Feed Preparation for HTGR Fuel Reprocessing — Interim Development Report," ERDA Report GA-A13858, General Atomic Company, April 19, 1976.

4. APPARATUS

The pilot-plant-scale solvent extraction feed preparation system installed in the GA reprocessing pilot plant was originally designed for batch mode operation. The system was redesigned and upgraded to perform continuous mode operation and after several tests was modified to its present condition. A schematic of the feed adjustment unit is shown in Fig. 4-1.

The evaporator/stripper vessel is fabricated from a 1.5-m (5-ft) length of 203-mm (8-in.) diameter Type 304L stainless steel pipe. It has an end cap on the bottom and a 150-lb flange at the top. The base is equipped with a 50-mm (2-in.) drain port that is 76 mm (3 in.) in length. The deentrainment tower was enlarged from 102 mm (4 in.) to 203 mm (8 in.) to reduce the pressure drop when adding formic acid and thereby prevent pressurization of the unit. The tower is fabricated from a 1.0-m (3.3-ft) length of Type 304L stainless steel pipe with 150-lb flanges at each end. Two 6.4-mm (1/4-in.) thick support plates were drilled with 6.4-mm holes to give 50% free area and were placed at each end of the tower to allow containment of the tower packing.

A spool piece located between the vessel and the deentrainment tower is used for most penetrations into the vessel. The spool piece consists of a 150-mm (6-in.) length of 102-mm (4-in.) inside diameter Type 304L stainless steel pipe. It has a 150-lb flange on the top end and a 6.4-mm (1/4-in.) thick flat plate attached to the bottom.

The tower was originally void of packing material, but after preliminary tests using formic acid addition the tower was packed to reduce entrainment. Several types of tower packing were tested including 12.7-mm (1/2-in.) ceramic Intalox saddles and 15.9-mm (5/8-in.) stainless steel Pall rings, but both types of packing exhibited excessive pressure drop. A third type of packing, 25.4-mm (1-in.) stainless steel Pall rings, was

Fig. 4-1. Pilot plant continuous mode feed adjustment system

found to be efficient in reducing entrainment and also in preventing pressurization of the system. The evaporator/stripper vessel is insulated to reduce heat losses.

The overhead condenser is a tube-in-shell unit from the American Standard Company (Model 03036). The unit is constructed of Type 316 stainless steel and contains about 1.0 m^2 (10.8 ft^2) of heat transfer area.

The evaporator/stripper vessel is supplied internally with two steam heating coils in parallel, a steam/air jet with a product removal suction tube, two air-purged dip tubes for liquid level and specific gravity measurement, and a type K thermocouple. The heating coils are made from continuous lengths of 12.7-mm (1/2-in.) outside diameter Type 304L stainless steel tubing. The feed and stripping agent supply and steam/air jet product removal tubes are 12.7-mm (1/2-in.) outside diameter Type 304L stainless steel tubes. The formic acid addition line is a 6.4-mm (1/4-in.) outside diameter Type 304L stainless steel tube.

Flowrates for the steam heating coil, feed addition, and steam stripping were measured with Brooks Model 3623-5522D rotameters. Wallace and Tiernan purgemeters were used to measure flowrates of the strip water and of the gas supply to the air jet and the nitrogen purge. The air jet, shown in Fig. 4-2, was custom built by Penberthy-Houdaille Company. All flowrates were controlled manually, either with hand valves or with manual control of Model P78S Research Control Valves. Liquid levels and specific gravities were monitored in all tanks using 6.4-mm (1/4-in.) outside diameter, Type 304L stainless steel, nitrogen-purged dip tubes; Barton differential pressure cells; and Barton pen recorders. Meriam manometers were also connected to the nitrogen-purged dip tubes. In-line measurement of overhead nitric acid conductance was obtained with a Beckman Solubridge conductivity indicator (Model RIC5), a Beckman conductivity cell (Model CEL-TFH50), and a Beckman automatic temperature compensator (Model T/C KQX9-S). The temperature of the concentrate in the evaporator/stripper vessel was recorded with a Barton pen recorder.

Fig. 4-2. Air/steam jet for product removal

The auxiliary process vessels include two feed tanks, a product storage tank, an overhead distillate tank, and a formic acid feed tank. The two feed tanks and the product storage tank are fabricated from a 1.5-m (5-ft) length of 203-mm (8-in.) diameter Type 304L stainless steel pipe with a 150-lb flange on the top and an end cap on the bottom. Each base has a 38-mm (1.5-in.) drain port that is 76 mm (3 in.) in length.

The overhead distillate tank is made from a 1.2-m (4-ft) length of 0.5-m (1.5-ft) diameter Type 304L stainless steel pipe. The bottom end cap has a 38-mm (1.5-in.) drain port that is 76 mm (3 in.) in length. A 115-mm (4.5-in.) diameter Type 304L stainless steel pipe sleeve, 127 mm (5 in.) long, is welded to the top plate of the vessel.

The formic acid feed tank is fabricated from a 0.4-m (1.4-ft) length of 165-mm (6-in.) diameter Type 304L stainless steel pipe. The top has a 150-lb flange, and the bottom end cap has a 38-mm (1.5-in.) drain port that is 76 mm (3 in.) long.

5. EXPERIMENTAL

Fifteen solvent extraction feed adjustment runs were performed during the interim report period using a continuous mode of operation. Table 5-1 outlines the type and order of runs made. The operating parameters for Runs 22 through 38 are given in Table 5-2.

TABLE 5-1
OUTLINE OF FEED ADJUSTMENT RUNS

Feed Adjustment Run No.	Operating Mode	Solvent Extraction Cycle	Formic Acid Denitration	Fluoride Volatility Test
22	Continuous (shakedown)	Intercycle		
23	Continuous (shakedown)	Intercycle		
25	Continuous	Intercycle		
26	Continuous	First cycle		✓
27	Continuous	Intercycle		
28	Continuous	First cycle	✓	
29	Continuous	First cycle	✓	
30	Continuous	First cycle	✓	
31	Continuous	Intercycle		
32	Continuous	Intercycle		
33	Continuous	Intercycle		
34	Continuous	Intercycle		✓
35	Continuous	Intercycle	✓	✓
36	Continuous	First cycle	✓	
38	Continuous	First cycle	✓	✓

TABLE 5-2
CONTINUOUS FEED ADJUSTMENT OPERATING PARAMETERS

Run No.	Solvent Extraction Cycle	Sparge Rate (scfh)	Feed Rate (1/hr)	Water Strip Rate (1/hr)	Formic Acid Rate (1/hr)	Initial Charge (1)	Operating Temperature (°C)
22	Intercycle	4	4.8	14.3	--	27.2	135
23	Intercycle	4	17.3	--	--	19.8	135
25	Intercycle	12	30.0	--	--	32.0	135
26	First cycle	8	12.5	7.9	--	26.9	135
27	Intercycle	12	36.6	--	--	42.3	130
28	First cycle	6	20.2	--	0.81	15.9	120
29	First cycle	6	22.0	12.0	--	27.1	130
30	First cycle	6	18.0	21.8	0.30	40.7	125
31	Intercycle	6	10.7	19.0	--	48.2	120
32	Intercycle	6	12.0	28.5	--	25.2	120
33	Intercycle	4	25.2	12.6	--	27.7	125
34	Intercycle	6	16.2	13.8	--	19.1	135
35	Intercycle	6	9.7	14.4	0.34	32.6	120
36	First cycle	7	5.4	17.4	0.60	18.2	125
38	First cycle	6	5.4	10.8	0.78	21.0	125

An example of the pilot plant procedure used in a typical continuous mode feed adjustment process is given below:

1. The evaporator/stripper vessel was charged with 20 to 25 l of dissolver solution or 1BT feed.
2. The feed tanks were filled with 1BT or dissolver solution. If 23M formic acid was to be added, then the formic acid tank was also filled.
3. To begin the run, the steam to the coil was turned on and the solution was evaporated to a given temperature.
4. When the operating temperature was reached, continuous addition of the feed and stripping water was started. If formic acid was to be continuously added, the addition was started five degrees below the final temperature.
5. A near-constant liquid level was maintained in the evaporator/stripper vessel by drawing off product semicontinuously using the air jet.
6. Dilution water was added to the product tank to prevent the product from solidifying upon cooling. The specific gravity of the dilute product was around 1.60.
7. A constant operating temperature was maintained by adjusting the steam flow to the heating coil and/or by adjusting the feed, stripping water, and formic acid addition flowrates.
8. Samples were taken from the evaporator/stripper vessel and the overhead distillate stream every hour throughout the run. The samples from the evaporator/stripper vessel were immediately diluted with a premeasured amount of water to prevent solidification.

9. The run was terminated when all the feedstock solution had been added to the evaporator/stripper vessel.
10. The run samples were submitted to the Analytical Chemistry Department and analyzed for nitric acid, thorium, aluminum, and fluoride concentrations and for specific gravity.

6. RESULTS

Table 6-1 shows representative compositions of the initial evaporator/stripper charge and the feed, product, and overheads distillate streams. The stream compositions for Runs 28, 29, and 31 are not given because of operational upsets which prevented the collection of sufficient data.

Runs 26 and 34 were successful demonstrations of continuous mode feed adjustment for the first cycle and intercycle solvent extraction feed adjustment, respectively. The first cycle and intercycle feed adjustment steps using formic acid treatment were successfully demonstrated in Runs 38 and 35, respectively. The mole ratio of hydrogen ion to thorium ion in the evaporator/stripper product, as a function of operating time, is shown in Figs. 6-1, 6-2, 6-3, and 6-4, respectively, for Runs 26, 34, 35, and 38.

TABLE 6-1
ANALYTICAL RESULTS FOR STREAM COMPOSITIONS

Run-Stream	$[H^+]/[Th^{+4}]$	$H^+(\bar{M})$	$Th^{+4}(\bar{M})$	$Al^{+3}(\bar{M})$	$F^-(\bar{M})$	Density at 22°C (g/ml)
22-Initial charge	-0.24	-0.54	2.25	0.19	0.13	1.88
Feed	9.24	1.59	0.17	0.02	0.01	1.12
Product	-0.24	-0.28	1.16	0.11	0.07	1.52
Distillate (a)	--	0.40	2.6×10^{-5}	<1 ppm	1.1×10^{-3}	1.02
23-Initial charge	-0.08	-0.28	3.27	0.14	0.14	1.95
Feed	1.37	0.28	0.21	0.02	0.02	1.10
Product	-0.22	-0.29	1.35	0.12	0.09	1.56
Distillate	--	0.36	2.2×10^{-5}	<1 ppm	1.3×10^{-3}	1.02
25-Initial charge	-0.33	-0.03	1.02	0.07	0.05	1.30
Feed	2.50	0.40	0.16	0.02	0.01	1.05
Product	-0.09	-0.23	2.70	0.22	0.02	1.84
Distillate	--	0.44	15.8×10^{-5}	1 ppm	0.2×10^{-3}	1.02
26-Initial charge	-0.09	-0.23	2.70	0.22	0.02	1.82
Feed	9.74	7.69	0.79	0.10	0.08	1.53
Product	0.34	0.47	1.38	0.15	0.10	1.60
Distillate	--	2.77	20.0×10^{-5}	<1 ppm	0.5×10^{-3}	1.11
27-Initial charge	2.50	0.50	0.20	0.02	0.02	1.09
Feed	2.70	0.54	0.20	0.03	0.02	1.10
Product	0.08	0.12	1.47	0.15	0.08	1.55
Distillate	--	0.60	2.0×10^{-5}	<1 ppm	0.1×10^{-3}	1.02
30-Initial charge	4.66	4.99	1.07	0.13	4.2×10^{-4}	1.57
Feed	5.00	5.00	1.00	0.15	4.0×10^{-4}	1.57
Product	0.50	0.80	1.80	0.25	5.7×10^{-4}	1.75
Distillate	--	3.00	2.6×10^{-5}	1.6×10^{-4}	1.4×10^{-4}	1.09
32-Initial charge	2.71	0.57	0.21	0.03	9.6×10^{-4}	1.11
Feed	2.64	0.58	0.22	0.03	3×10^{-3}	1.15
Product	0.43	0.61	1.42	0.19	0.07	1.60
Distillate	--	0.15	9.3×10^{-4}	<1 ppm	1.2×10^{-3}	1.01
33-Initial charge	0.40	0.78	1.96	0.23	0.07	1.79
Feed	2.73	0.60	0.22	0.02	0.01	1.11
Product	0.26	0.42	1.63	0.18	0.03	1.66
Distillate	--	0.46	1.3×10^{-3}	<1 ppm	8.0×10^{-5}	1.01

(a) Average of samples taken during steady state operation.

TABLE 6-1 (Continued)

Run-Stream	$[H^+]/[Th^{+4}]$	$H^+(\bar{M})$	$Th^{+4}(\bar{M})$	$Al^{+3}(\bar{M})$	$F^-(\bar{M})$	Density at 22°C (g/ml)
34-Initial charge	2.61	0.60	0.23	0.02	0.01	1.11
Feed	2.64	0.58	0.22	0.02	0.01	1.11
Product	-0.15	-0.33	2.17	0.25	0.03	1.82
Distillate	--	0.34	<1 ppm	<1 ppm	1.5×10^{-4}	1.01
35-Initial charge	2.48	0.57	0.23	0.03	0.08	1.12
Feed	2.50	0.60	0.24	0.03	0.01	1.12
Product	-0.25	-0.38	1.52	0.20	0.04	1.65
Distillate	--	0.28	--	<1 ppm	1.4×10^{-4}	1.00
36-Initial charge	9.30	8.09	0.87	0.07	0.05	1.57
Feed	8.90	8.00	0.90	0.07	0.05	1.58
Product	1.20	1.63	1.33	0.13	0.06	1.59
Distillate	--	2.00	--	<1 ppm	2.0×10^{-4}	1.07
38-Initial charge	8.73	8.03	0.92	0.06	0.02	1.57
Feed	9.54	8.40	0.88	0.06	0.02	1.57
Product	0.59	0.83	1.41	0.08	0.04	1.59
Distillate	--	2.90	--	<1 ppm	2.1×10^{-4}	1.08

Fig. 6-1. Continuous first cycle feed adjustment - Run 26, $[H^+]/[Th^{+4}]$ ratio versus denitration time

Fig. 6-2. Continuous intercycle feed adjustment - Run 34, $[H^+]/[Th^{+4}]$ ratio versus denitration time

Fig. 6-3. Continuous intercycle feed adjustment with formic acid treatment - Run 35, $[H^+]/[Th^{+4}]$ ratio versus denitration time

Fig. 6-4. Continuous first cycle feed adjustment with formic acid treatment - Run 38, $[H^+]/[Th^{+4}]$ ratio versus denitration time

7. DISCUSSION

7.1. BENCH-SCALE INVESTIGATIONS

The purpose of the bench-scale continuous feed adjustment experiments was to identify operating features unique to the process and to establish optimum operating conditions as part of the initial flowsheet development work. The results of the bench-scale investigations were applied as a basis for further development studies performed in the pilot plant feed adjustment unit.

7.1.1. Continuous Feed Adjustment

Bench-scale tests have shown that a continuous mode feed adjustment step is feasible for both the first cycle and intercycle solvent extraction processes. For the first cycle continuous feed adjustment experiment, 100 ml of leacher product solution was initially charged to the apparatus shown in Fig. 7-1. By evaporating the leacher solution to 135°C, followed by steam stripping and continuous feed addition, it was possible to lower the free acid concentration from 9.0M to 0.5M or less (Ref. 7-1). A low acid product of 1.0M HNO₃ is required for the first cycle solvent extraction process.

The apparatus shown in Fig. 7-2 was used for bench-scale testing of continuous mode intercycle feed adjustment. This setup differs from that used for first cycle feed adjustment tests in that water replaces steam as the stripping medium. Continuous intercycle feed adjustment experiments indicated that acid deficiency was attainable with 1BT feed stock, at 135°C, when equal volumes of stripping water and 1BT feed were metered into the reaction flask (Ref. 7-2).

Fig. 7-1. Bench-scale continuous feed adjustment apparatus using steam stripping

Fig. 7-2. Bench-scale continuous feed adjustment apparatus using a water strip

The experimental procedure used for the continuous intercycle feed adjustment tests involved batch evaporation and stripping to produce an initial acid deficient boiler pot solution. Continuous addition of water strip and 1BT feed stock was begun upon completion of the batch evaporation step. Boiler pot and distillate samples were collected routinely throughout each run.

7.1.2. Formic Acid Denitration

Formic acid has been used successfully to promote the denitration of nitric acid beyond the capabilities of water stripping alone at temperatures below 135°C. Consideration was given to the use of alternate denitration agents such as sugar and formaldehyde, but each had certain disadvantages which made them less favorable than formic acid. For instance, sugar contains carbon-carbon bonds which upon reaction might form intermediate thorium oxalate complexes that would precipitate. Formaldehyde, on the other hand, is highly volatile and would create process control problems. Some advantages of formic acid denitration are:

1. Fast reaction rate.
2. Comparatively low volatility.
3. No precipitate formation.

The following general equations are given for the reaction of formic acid with molten thorium nitrate:

The reaction product probably has the following general formula:

Formic acid denitration was tested for the first cycle and intercycle feed adjustment steps on a continuous basis. The experimental procedure consisted of placing a measured volume of feed solution into a 300-ml reaction flask and evaporating to 30% of the original volume. Figure 7-3 shows the apparatus used for the formic acid denitration experiments. Continuous denitration was performed by adding either $1\bar{M}$ thorium-Thorex feed or 1BT feed and formic acid during steam stripping. The first cycle and intercycle feed adjustment steps were conducted at 135°C and 125°C , respectively.

Results of the first cycle feed adjustment tests show that a low acid product ($1\bar{M}$ HNO_3) was attainable (Ref. 7-3) using formic acid to aid in denitration. Also, by using formic acid addition during continuous mode intercycle feed adjustment tests, it was possible to produce an acid deficient product (Ref. 7-2).

7.2. PILOT PLANT STUDIES

7.2.1. Equipment Shakedown

The pilot plant feed adjustment unit was converted from a batch mode to a continuous mode system. Two shakedown runs, using continuous mode operation, were made to check out the initial system modifications. Later runs involving the addition of formic acid revealed equipment deficiencies which led to further modifications of the system.

The feed adjustment system was modified to include a product storage tank, a formic acid supply tank, a larger condensate tank, and a submerged jet for product removal. The product removal system was considered the most important equipment aspect to be defined. To prevent solidification of concentrated solution (between $2.5\bar{M}$ and $3.5\bar{M}$ thorium and 1.7 and 2.0 g/cc specific gravity) in the steam jet suction leg, the jet itself was submerged to the bottom of the evaporator/stripper, thereby eliminating the need for a long suction leg. The product removal line, between the evaporator/stripper and the bottoms product tank, was steam jacketed to

Fig. 7-3. Bench-scale feed adjustment apparatus with formic acid addition

prevent in-line cooling and solidification of the solution. Either nitrogen or 620-kPa (90-psig) steam is supplied to the jet so that it may operate as an air or steam jet.

The shakedown runs demonstrated the feasibility of a continuous feed preparation process. The new system checked out rather well throughout the entire operation of both runs, including startup, continuous operation, sampling, and shutdown.

7.2.2. Continuous Mode Operation

7.2.2.1. First Cycle Feed Adjustment. Run 26 was the first successful attempt to continuously adjust the leacher product feed to the desired nitric acid and thorium concentrations of $1\bar{M}$ and $1.5\bar{M}$, respectively. An operating temperature of 135°C was maintained throughout the run while continuously adding the feed and stripping water. It was found that water stripping is equally as effective as steam stripping in removing nitric acid, and water stripping was selected for use because it has better flow control capabilities (Ref. 7-4). Product was continuously removed and diluted with water to prevent solidification upon cooling. The required final mole ratio of nitric acid to thorium is 0.67 or less, and feed adjustment Run 26 was successful in achieving a nitric acid to thorium mole ratio of 0.34 for the concentrated product. Therefore, it is feasible to use a continuous mode feed adjustment step for the first solvent extraction cycle.

7.2.2.2. Intercycle Feed Adjustment. The second thorium solvent extraction cycle, or intercycle, feed adjustment to acid deficient conditions was originally planned as a two-stage concentration and denitration process. A reduction in process equipment could be realized if the two-stage process could be performed in a single feed adjustment step. Run 25 was an initial attempt at continuously denitrating 1BT feed to acid deficiency in a single stage. The evaporator/stripper was charged with 32 l of acid deficient solution to demonstrate continuous denitration during steady-state operating conditions. The run proved successful by reaching the desired acid deficient

product specification. A high initial boiloff rate resulted in entrainment and some carryover of solution from the packed tower. Subsequent runs used a lower initial boiloff rate. The product was semicontinuously removed to maintain a solution volume of 20 l in the evaporator/stripper. The operating temperature was 135°C and a stripping medium was not used.

Run 27 simulated continuous mode denitration of the 1BT stream with an initial charge of 1BT feed to the evaporator/stripper. This run was similar in operation to Run 25 except that a 130°C operating temperature was used. According to Kaiser and Merz (Ref. 7-5), at a temperature of 135°C only 90% to 99% of the free acid is removed during the evaporation step and a stripping medium is required to achieve acid deficiency. As expected, an acid deficient product was not achieved during Run 27 although the desired thorium concentration was obtained.

The next attempts to adjust the 1BT feed to acid deficiency were Runs 31, 32, and 33. These runs were made following modification of the evaporator/stripper to overcome operational difficulties encountered with the formic acid addition tests (see Section 7.2.3.1). Prior to Run 31 the deentrainment tower had been packed with ceramic 13-mm (1/2-in.) Intalox saddles and the off-gas line was enlarged. However, the packed tower pressure drop caused pressurization of the evaporator/stripper during Run 31, and no significant flowsheet performance data were collected. The ceramic packing was replaced with 15.9-mm (5/8-in.) stainless steel Pall rings before Run 32, but again there was pressurization during the run. Run 32 was interrupted while the tower packing was changed to 25.4-mm (1-in.) stainless steel Pall rings. The run was restarted without any further pressurization incidents. The desired acid deficient product was not achieved during operation at a temperature of 120°C with water stripping.

In another attempt (Run 33), a 125°C operating temperature was used with water stripping but acid deficient conditions were still not obtained, although the hydrogen-to-thorium mole ratio was less (0.26) than that in Run 32 (0.43). Acid deficient conditions were finally met in Run 34, which was operated with water stripping at a temperature of 135°C. The product

removal system performed satisfactorily with air as the motive gas. The final product had a hydrogen-to-thorium mole ratio of -0.15. The 1BT feed rate was 0.27 l/min and the stripping water rate was 0.23 l/min. Run 34 demonstrates the feasibility of operating the intercycle feed adjustment step as a single-stage, continuous mode process.

7.2.3. Formic Acid Denitration

Bench-scale investigations (Section 7.1) have shown that the nitric acid concentration of solutions can be reduced through reaction with formic acid. The results of these studies led to the use of formic acid treatment as an aid in feed adjustment. The main advantage of formic acid treatment is the increase in denitration at lower operating temperatures. Decreased corrosion rates and a lower freezing point of the concentrated product are desirable results of lower operating temperatures.

7.2.3.1. First Cycle Feed Adjustment. Various methods of introducing formic acid to the evaporator/stripper were examined during Runs 28, 29, and 30. Formic acid with a concentration of about 23M was used for these tests. In Run 28, formic acid was added through the tower and there was essentially no effect on denitration. The formic acid was vaporized and carried over with the off-gas and therefore could not react with the nitric acid in the bottoms solution. Prior to Run 29, 12.7-mm (1/2-in.) ceramic Intalox saddles were packed into the tower and the formic acid addition point was relocated near the bottom of the evaporator/stripper. This addition method proved unsuccessful due to inadequate hydraulic characteristics which prevented the formic acid from being gravity fed into the vessel. For Run 30, the addition point was raised to the normal interface of the liquid and vapor in the vessel. Also, a small metering pump was installed to allow better flow control. Steady-state operation was maintained for 25 min during Run 30 before pressurization of the vessel occurred. The evolution rate of carbon dioxide and oxides of nitrogen exceeded the off-gas capacity of the system. The results of Runs 28, 29, and 30 indicated that the best introduction point for formic acid is at the liquid-vapor interface and that a different tower packing was needed for future tests.

The tower packing was changed to 25.4 mm (1-in.) stainless steel Pall rings before Run 36 was made. Run 36 simulated continuous mode feed adjustment of leacher product solution. Feed, stripping water, and formic acid were continuously added to the evaporator/stripper while an operating temperature of 125°C was maintained. The formic acid addition rate was equivalent to 0.17 mole per mole of acid in the leacher product feed. The denitrated product had an acid-to-thorium mole ratio of 1.2. This run indicated that additional formic acid or a higher operating temperature would be required to meet the flowsheet conditions of a 0.67 acid-to-thorium mole ratio.

The formic acid addition rate was increased for Run 38 in an attempt to reduce the nitric acid concentration from 9M to 1M while operating at 125°C. Leacher product feed, stripping water, and formic acid were continuously added to the pot at rates of 0.09, 0.18, and 0.013 l/min, respectively. The formic acid addition rate was equivalent to 0.39 mole per mole of acid in the feed. The nitric-acid-to-thorium mole ratio of the product was 0.59, which is acceptable according to the HRRF flowsheet requirements. Run 38 successfully demonstrated that continuous mode feed adjustment for the first solvent extraction cycle can be achieved at 125°C (versus 135°C) with the aid of formic acid treatment. Corrosion rates can therefore be decreased while also lowering the freezing point of the concentrated product.

7.2.3.2. Intercycle Feed Adjustment. During Run 35, feed representative of the 1BT stream was continuously fed to the evaporator/stripper concurrently with stripping water and formic acid, all at fixed rates. The operating temperature was maintained at 120°C by controlling the steam flow rate to the heating coils in the pot. Product was semicontinuously removed. The addition rates for the feed, formic acid, and stripping water were 0.162, 0.006, and 0.24 l/min, respectively. The final product had a nitric-acid-to-thorium molarity ratio of -0.25, which meets the requirements for the HRRF flowsheet.

Run 35 demonstrated that the second thorium solvent extraction cycle feed adjustment process can be successfully performed at a 120°C operating temperature with the aid of formic acid treatment. The intercycle feed adjustment step can also be conducted as a single vessel, continuous mode operation.

7.2.4. Fluoride Volatility

The residual fluoride ions from the Thorex solution become a potentially volatile species during the feed adjustment step. The volatility of fluoride ions leads to increased equipment corrosion, and this is undesirable. Bench-scale tests were conducted at GA (Ref. 7-6) to determine comparative fluoride losses to the overhead distillate stream during batch and continuous mode operations. Results of the bench-scale tests revealed no difference in fluoride ion volatilization due to the type of operating mode for feed adjustment.

The pilot plant continuous mode feed adjustment studies have confirmed the bench-scale work, as shown in Table 7-1. Also, it was found that there was no appreciable effect on fluoride volatilization due to formic acid treatment at lower operating temperatures.

TABLE 7-1
FLUORIDE VOLATILITY DURING FEED ADJUSTMENT

Run No.	Operating Mode	Solv. Extr. Cycle	Wt % F ⁻ Volatilized	Formic Acid Treatment	Operating Temperature (°C)
Bench scale	Batch	First cycle	1	No	135
Bench scale	Continuous	First cycle	1	No	135
26	Continuous	First cycle	1	No	135
34	Continuous	Intercycle	3	No	135
38	Continuous	First cycle	3	Yes	125
35	Continuous	Intercycle	3	Yes	120

REFERENCES

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8. CONCLUSIONS

Feed adjustment development studies at GA are intended to aid in the design and operation of commercial-scale feed adjustment equipment such as in the HRRF. The following conclusions were made from test data obtained during the development of the continuous mode pilot plant feed preparation system:

1. Leacher product solution can be continuously adjusted to meet the solvent extraction feed specifications at a 135°C operating temperature with continuous addition of feed and stripping water and no formic acid addition.
2. With continuous formic acid addition, leacher product solution can be continuously adjusted at an operating temperature of 125°C.
3. The partitioned thorium stream (1BT) can be continuously adjusted to the second thorium solvent extraction cycle feed specifications in a single step at 135°C with continuous addition of feed and stripping water and no formic acid addition.
4. With continuous formic acid addition, the partitioned thorium stream (1BT) can be continuously adjusted in a single step at an operating temperature of 120°C.
5. During continuous feed adjustment, the amount of fluoride ion which is volatilized is in the range of about 1 to 3 wt % of that in the solution. There appears to be no difference between the amount of fluoride volatilization occurring in batch mode and continuous mode feed adjustment. Also, the degree of fluoride volatilization is not influenced by the addition of formic acid.

6. In the design of commercial- or engineering-scale feed adjustment equipment, the deentrainment tower above the evaporator/stripper vessel should be designed to handle increased vaporization when formic acid is added.
7. The modified pilot plant feed adjustment equipment, which includes vessels, process piping, and instrumentation, performed satisfactorily during the course of testing.
8. Continuous mode feed adjustment would appear not to affect the real-time accounting of SNM, thereby complying with safeguards requirements.

9. RECOMMENDATIONS

The pilot plant developmental studies performed during this interim report period have established the feasibility of continuous mode feed adjustment. Other important aspects of the solvent extraction feed preparation process need to be investigated before commercial-scale design can begin. Recommendations for further development work are as follows:

1. Intercycle feed preparation experiments performed in the pilot plant have shown that a single-stage denitration and concentration step is capable of adjusting the 1BT feed to the desired 2DF product. If a single-stage feed adjustment step is selected for use in HRRF, then an additional process must be developed to remove TBP and organic degradation products from the 1BT stream. Steam stripping of TBP from the 1BT stream has been successfully demonstrated in bench-scale experiments (Ref. 9-1) and should be tested in the pilot plant.
2. Investigations have shown (Ref. 9-2) that during the feed adjustment process, formic acid reduces nitric acid to NO_x and water vapor. The water vapor that rises through the stripping section of the evaporator/stripper vessel has the potential to strip out TBP from a down-coming stream of 1BT feed and thereby eliminate the need for an extra piece of process equipment. Further tests should be performed in the pilot plant to test the feasibility of such a process using actual 1BT solution with TBP from the solvent extraction process.
3. Bench-scale experiments at GA (Ref. 9-3) have revealed that radioactive iodine is difficult to volatilize during the dissolution of ThO_2 . As a backup, the degree of iodine volatility during the feed adjustment step should be determined.

4. Hot cell tests at ORNL (Ref. 9-4) determined that ruthenium volatility during feed adjustment is significant. On the other hand, GA bench-scale tests (Ref. 9-5) found that ruthenium losses due to volatilization during feed adjustment are minimal. Pilot plant tests on ruthenium volatility should be conducted to confirm either the ORNL or GA results and to assess the impact on off-gas treatment.

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