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SUMMARY TECHNICAL REPORT

For The Period

October 1, 1965 to December 31, 1965

AEC RESEARCH AND DEVELOPMENT REPORT

FEED MATERIALS PRODUCTION CENTER
NATIONAL LEAD COMPANY OF OHIO

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SUMMARY TECHNICAL REPORT FOR THE PERIOD OCTOBER 1, 1965 TO DECEMBER 31, 1965

S. MARSHALL, Director
Technical Division

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Technical Editor

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1. DEVELOPMENT OF A THORIUM PURIFICATION SYSTEM

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Abstract

Thorium distribution coefficients were determined in the laboratory for the tributyl phosphate (TBP)-thorium nitrate and the diamyl amyl phosphonate (DAAP)-thorium nitrate systems. The data developed in these tests were used in pilot-scale (2-inch-diameter perforated-plate pulse columns) development tests of a liquid-liquid extraction process for the purification of thorium. This process was subsequently implemented in semiworks extraction equipment. DAAP was found to be the superior extractant.

Two additional solvent extraction systems were studied for the separation of thorium and uranium and/or rare earth elements to supplement the DAAP extraction system. Both of these extractants, di-secondary butyl phenyl phosphonate (DSBPP) and TBP, were evaluated in pulse column tests for the production of a thorium nitrate solution which contained less than 5 ppm uranium on a thorium basis.

Introduction

Late in 1963, the Atomic Energy Commission expressed a need for a quantity of extremely pure thorium nitrate for the production of dense thorium dioxide. A literature search revealed that a great deal of thorium distribution data had been obtained at the Oak Ridge National Laboratory for various organic extractants. A comprehensive study of the alkyl phosphonates indicated that these extractants have a much greater affinity for uranium and thorium than does the conventional tributyl phosphate extractant that had been used in the past for uranium and thorium extraction purification processes. Consequently, a conceptual thorium

extraction flowsheet employing two of the alkyl phosphonates, diamyl amyl phosphonate (DAAP) and di-secondary butyl phenyl phosphonate (DSBPP), was submitted to the AEC for consideration and was subsequently approved. The development of this alkyl phosphonate thorium purification process is the subject of this report.

In addition to the need for extremely pure thorium dioxide, the AEC wished to reduce a large inventory of uranium-contaminated, thorium-bearing residues which had been accumulated during an earlier thorium operation and which had been in storage since 1955. This inventory consisted mainly of very impure sintered thorium oxide and a quantity of fairly pure thorium nitrate tetrahydrate (TNT). The latter material, which contained only a minor quantity of uranium, did not meet other purity requirements of the dense thorium dioxide program. Therefore, these materials together with other miscellaneous residue materials such as thorium sump cakes, thorium tetrafluoride, and floor sweepings were to be the feed materials for the new purification process.

Work on the new flowsheet was in progress when the need for a large quantity of purified thorium nitrate became critical. At this point, the first extraction cycle (DAAP) had been sufficiently developed for the general purification of the relatively pure TNT inventory. Therefore, the DAAP flowsheet was implemented in existing Pilot Plant equipment. The purified TNT was shipped to Mallinckrodt Chemical Works for oxide production. The second extraction cycle for uranium and rare earth decontamination, using DSBPP as the extractant, was also implemented even though it had not been fully studied at that time. This second cycle proved to be unnecessary, however, for the

TNT feed material, and its development continued for the uranium and rare earth decontamination of less pure feed materials.

Objectives

The primary objectives of this work were three-fold:

1. To determine the suitability of alkyl phosphonate extractants for thorium purification.
2. To develop laboratory data necessary for the design of a thorium purification process.
3. To test the designed thorium purification process in pilot-scale perforated-plate pulse column equipment.

After a critical need for purified thorium dioxide arose, the prime objective and emphasis of the work changed. The design and implementation of an extraction cycle to purify the existing TNT inventory became primary, and the startup and operation of such a flowsheet received first priority.

Summary of Results

Laboratory tests showed that a 30 vol % DAAP extractant is superior to a 30 vol % TBP extractant for thorium purification in regard to the production rate attainable in a given piece of equipment and the free nitric acid required for the extraction. The DAAP solvent was shown to be stable when in contact with HNO_3 and thorium.

Thorium distribution curves were developed which facilitated the design of a process for thorium purification. The process was subsequently tested in pilot-scale pulse column equipment and shown capable of purifying an existing inventory of TNT to produce a feed material for thorium dioxide production.

Testing of DSBPP and TBP extractants indicated that greater uranium-thorium separation factors could be obtained with DSBPP extractants. However, when DSBPP proved to be difficult to obtain, pulse column conditions were developed to

reduce the uranium content of purified thorium nitrate solutions from 6000 and 12,000 ppm to less than 5 ppm (thorium basis) using TBP-kerosene solvent.

The results of the 30 vol % DAAP development studies were utilized to design a semiworks process for the purification of the existing TNT inventory. Startup difficulties of this unit were overcome, and the extraction system is currently producing about 1 ton per day of thorium as a purified thorium nitrate solution.

LABORATORY DEVELOPMENT

1. Introduction

The objectives of this laboratory study were to determine distribution data for a possible thorium extraction system that could be used in a pulse column system, to evaluate the solvent for stability, and to obtain distribution data for thorium and uranium separation suitable to a pulse column system.

2. Thorium Distribution Studies

Relative thorium distribution coefficients were determined for 30 vol % DAAP - 70 vol % Solvesso 100 and 30 vol % TBP - 70 vol % Solvesso 100 extractants by equilibrating them with aqueous thorium nitrate solutions containing various quantities of nitric acid. The equilibrium tests, which were conducted at $76 \pm 2^\circ\text{F}$, were designed to produce distribution curves for three aqueous-phase free acid (HNO_3) concentrations after equilibration (0.5M HNO_3 , 1.7M HNO_3 , and 6.0M HNO_3). The thorium distribution for these systems is presented in Tables I and II.

A comparison of the DAAP and TBP systems is presented in Figure 1 for equilibrated aqueous feed solutions containing 0.5M HNO_3 . Figure 1 shows clearly the greater thorium extraction capabilities of the DAAP solvent system at identical operating conditions. The other distribution coefficient data

TABLE I Thorium Distribution Between DAAP and Thorium Tetranitrate

0.5M HNO ₃			1.7M HNO ₃			6.0M HNO ₃		
Aqueous Phase Th(g/l)	Distribution Coefficient (DC_A^O)	Organic Phase Th(g/l)	Aqueous Phase Th(g/l)	Distribution Coefficient (DC_A^O)	Organic Phase Th(g/l)	Aqueous Phase Th(g/l)	Distribution Coefficient (DC_A^O)	Organic Phase Th(g/l)
<0.01	>155	1.55	<0.01	>93	0.93	0.003	396	1.19
<0.01	>260	2.60	<0.01	>197	1.97	0.007	323	2.26
0.10	50	4.97	<0.01	>474	4.47	0.061	77	4.67
0.71	13	9.3	0.17	56	9.60	0.33	29	9.58
3.91	5.3	20.9	1.13	20	22.7	2.10	11	22.4
13.5	2.7	36.4	6.70	6.3	42.5	11.0	3.6	39.3
45.5	1.2	52.6	40.0	1.5	58.9	50.5	1.1	53.1
38.4	0.72	63.4	85.5	0.76	64.6	97.7	0.62	61.0
138	0.49	68.1	136	0.50	67.7	149	0.44	66.0
338	0.23	77.0	331	0.24	79.1	352	0.24	84.6

A/O = 1/1

Aqueous Phase: TNT Solution containing 0.5, 1.7, and 6.0M HNO₃ after equilibration.

Organic Phase: 30 vol % DAAP - 70 vol % Solvesso 100.

Temperature: 76° ± 2° F

TABLE II Thorium Distribution Between TBP and Thorium Tetranitrate

0.5M HNO ₃			1.7M HNO ₃			6.0M HNO ₃		
Aqueous Phase Th(g/l)	Distribution Coefficient (DC_A^O)	Organic Phase Th(g/l)	Aqueous Phase Th(g/l)	Distribution Coefficient (DC_A^O)	Organic Phase Th(g/l)	Aqueous Phase Th(g/l)	Distribution Coefficient (DC_A^O)	Organic Phase Th(g/l)
0.76	0.26	0.20	0.45	0.96	0.43	0.28	2.4	0.66
1.63	0.21	0.35	1.08	0.88	0.95	0.58	2.4	1.39
4.25	0.19	0.80	1.79	0.85	1.52	1.48	2.2	3.31
8.49	0.20	1.68	5.45	0.82	4.46	3.33	2.0	6.78
19.9	0.19	3.69	14.3	0.75	10.7	9.93	1.5	14.9
39.8	0.26	10.2	29.4	0.69	20.2	26.5	0.96	25.5
73.5	0.36	26.6	62.9	0.57	35.6	67.7	0.56	38.2
110	0.38	42.4	108	0.44	47.6	116	0.39	45.8
149	0.35	52.7	149	0.36	54.1	169	0.31	51.7
351	0.21	72.5	353	0.20	69.7	366	0.19	69.0

A/O = 1/1

Aqueous Phase: TNT Solution containing 0.5, 1.7, and 6.0M HNO₃ after equilibration.

Organic Phase: 30 vol % TBP - 70 vol % Solvesso 100.

Temperature: 76° ± 2° F

FIGURE 1 Distribution of Thorium Between 30 vol % DAAP, 30 vol % TBP and TNT Solutions

indicate that the DAAP solvent would require less HNO_3 for a thorium extraction circuit and, consequently, would be more economical than TBP for large-scale operation.

The phase disengagement characteristics of the two solvents were about equal; however, higher acid concentration aided the distribution coefficient (DC_A^0) for the TBP system while it showed very little effect with the DAAP system.

The data presented in Tables I and II were graphically analyzed by the McCabe-Thiele method to determine the number of theoretical stages required to achieve a given thorium extraction. Each of these analyses was based upon the following parameters:

1. Aqueous feed concentration: 400 g/l Th
2. Aqueous raffinate concentration: 0.2 g/l Th
3. Organic extract concentration: 80% of saturation
4. Saturation: 30 vol % TBP - 74 g/l Th
30 vol % DAAP - 78 g/l Th

The results of the graphical analyses are presented in Table III.

TABLE III McCabe-Thiele Theoretical Stages for Thorium Extraction

HNO_3 Acid Concentration of Thorium Feed Solution (M)	30 vol % TBP Extraction Stages Required	30 vol % DAAP Extraction Stages Required
0.5	17	2.7
1.7	5	2.0
6.0	4	2.6
Ratio (A/O)	1/6.8	1/6.3

Past experience with uranium extraction indicated that the primary extraction section of the Refinery mixer-settler system at the National Lead Company of Ohio would yield 5 theoretical stages in countercurrent operation while the 25-foot primary extraction pulse column would yield 3 theoretical stages. Consequently, it appeared that the DAAP thorium extraction could be accomplished at low-acid concentrations in either piece of equipment, while an extraction with the TBP solvent would have to be conducted in the mixer-settler system with a high free-acid feed solution.

Thorium re-extraction distribution data were obtained for hot water and the TBP and DAAP extractants. These equilibrium data, which are presented in Table IV were obtained by equilibrating thorium-saturated organic solutions with hot water five successive times. This re-extraction testing indicated that hot water would be satisfactory as a stripping agent for the thorium-loaded TBP extractant, but that complete thorium removal from the DAAP extractant would be difficult with hot water alone. Subsequent solvent testing showed that the DAAP re-extraction difficulties stemmed from impurities, primarily diamyl hydrogen phosphite, contained in the original DAAP sample. However, when this impurity was removed from new DAAP by a NaOH treatment the thorium could be satisfactorily removed from the DAAP by hot water stripping. The data presented in the "Treated DAAP" column of Table IV indicate that nearly complete thorium re-extraction can be achieved with hot water.

TABLE IV Re-Extraction* of Thorium from TBP and DAAP Solvents

Contact 1/1 A/O	30 vol % TBP-Solvensso 100			Standard 30 vol % DAAP-Solvensso 100			Treated** 30 vol % DAAP-Solvensso 100	
	Thorium (g/l)		pH Aqueous Phase	Thorium (g/l)		pH Aqueous Phase	Thorium (g/l)	
	Aqueous Phase	Organic Phase		Aqueous Phase	Organic Phase		Aqueous Phase	Organic Phase
1	59.7	12.3	0.8	42.4	37.8	2.3	42.0	28.9
2	11.9	0.30	2.5	22.9	16.9	2.4	21.3	8.2
3	0.23	0.07	6.2	9.88	5.6	2.5	7.6	0.37
4	0.003	0.002	6.5	1.66	3.3	2.6	0.50	0.20
5	<0.001	0.001	6.6	0.86	2.7	2.8	<0.001	0.04

* Hot water (150°F) was the stripping agent.

** Initial solvent treatment with NaOH.

Pilot-scale thorium extraction tests indicated that when sulfate ions were present in the aqueous feed solution to be extracted a loss in the column's thorium extraction efficiency resulted. Further tests showed that the thorium distribution coefficient (DC_A^O) was adversely affected by the sulfate ion. In addition to the loss of extraction efficiency, sulfate contamination of the product resulted from the extraction of feed containing significant quantities of SO_4 (>1000 ppm thorium basis). Consequently, a series of three-stage countercurrent extraction tests was made in the laboratory with a feed solution containing about 10,000 ppm SO_4 (thorium basis) to determine if excess nitric acid would improve the thorium distribution coefficient for feeds containing large quantities of sulfate. The results of these tests are presented in Table V.

TABLE V Laboratory Batch Countercurrent Extraction* for Thorium

Aqueous Feed In		Organic and Aqueous End Streams**	
Th (g/l)	HNO ₃ (M)	Organic Phase Th (g/l)	Aqueous Phase Th (g/l)
342	1	53.4	9.40
292	3	47.8	0.25

* 30 vol % DAAP - 70 vol % Solvensso 100.

** Three-stage countercurrent contacts at steady-state.

These results indicate that increasing the acid concentration of the feed can prevent high thorium raffinate losses and thus improve thorium distribution to the organic phase. How the acid increase allows for complete extraction and what role various sulfate concentrations play in the extraction circuit are currently being studied more thoroughly in the laboratory.

3. Initial DAAP Solvent Treatment

DAAP re-extraction tests (final aqueous pH values) indicated that organic acids dissolved in the DAAP were probably hindering the re-extraction of thorium.

On the basis of a pH titration test it was determined that DAAP solvent contained phosphoric acids. Addition of any base stronger than water during re-extraction would shift the hydrolysis and lead to a thorium acid precipitation. The pH titration test procedure was as follows:

1. Pipette 25 ml of DAAP solvent into a 250 ml beaker.
2. Add 20 ml of ethanol and 5 ml of distilled water to the beaker.
3. Titrate the solution in the beaker with 0.1M NaOH to a pH of 10.5.

Infrared spectral analyses of DAAP revealed that two foreign organic components were present, 0.5% triamyl phosphite, an initial reactant in the

preparation of DAAP, and 4.5% diamyl hydrogen phosphite (DAHP). The latter, an acid which is a side-product of the DAAP production reaction was removed in laboratory tests by treating the solvent with caustic. Thorium re-extraction tests with treated solvent samples indicated that once the DAHP was removed the thorium retention capabilities of the solvent decreased significantly. The treatment procedure developed for the DAAP solvent involved contacting the solvent with an equal volume of 10% NaOH. After phase separation the basic solvent is then washed with water (A/O = 10/1) and centrifuged to obtain final phase separation.

Data obtained from pH titration and thorium retention tests for untreated and treated 30 vol % DAAP-Solvesso 100 are presented in Table VI. The results of these tests indicate that the treated solvent had been thoroughly cleaned of the deleterious organic materials and that the two tests (pH titration and thorium retention) could be used to determine extraction system operability of the DAAP-Solvesso 100 solvent.

Sodium carbonate, Na_2CO_3 , a weaker base could be used for the initial DAAP solvent treatment to replace the strong caustic (NaOH); however, three passes or contacts would be required to completely eliminate the DAHP from the solvent.

TABLE VI Solvent Evaluation of DAAP

	NaOH Treated DAAP-Solvesso	Untreated DAAP-Solvesso
pH Titration Test*	< 0.05 ml of 0.2M NaOH	16 ml of 0.2M NaOH
Thorium Retention Test**	< 0.05 g/1 Th	< 2.4 g/1 Th

* The procedure for the test was outlined previously.

** Five hot water contacts at 150°F, A/O = 1/1.

4. Solvent Stability

Factors which normally influence degradation and instability of solvents, such as heat and acid concentration, were studied in the laboratory. Four samples of 30 vol % DAAP-Solvesso 100 were contacted with thorium and/or nitric acid for a period of 9 days. The results of these tests indicated that after a period of 9 days neither acid nor temperature had an adverse effect on the thorium retention properties of the solvent. However, prolonged heating at 150°F in the presence of 0.5M HNO_3 caused the solvent to become dark yellow, but no adverse effect upon the solvent's properties was detected. It was therefore concluded that the DAAP-Solvesso extractant would be fairly stable under normal process extraction conditions of temperature and nitric acid concentrations.

Initial pilot-scale testing of a DAAP thorium extraction flowsheet indicated that after the solvent had been in use for a short time re-extraction difficulties were encountered in the thorium-depleted section of the stripping column. The samples from the above test program were re-evaluated in re-extraction tests which are reported in Table VII.

These results show that solvents that have been in contact with thorium will emulsify during a re-extraction operation and that the emulsion is probably due to the precipitation that occurs. Further testing with other DAAP solvent samples showed that the precipitation and emulsification encountered in these batch stripping tests are caused by a thorium precipitate (probably thorium hydroxide) that forms when the thorium content of the organic solution is low and in the absence of acid from the thorium nitrate hydrolysis reaction and/or free HNO_3 in the organic phase. It was also shown that the precipitate can be redissolved with small quantities of HNO_3 .

5. Thorium - Uranium Separation

Uranium and thorium distribution data which had been previously obtained at ORNL¹ indicated that

TABLE VII Test of Degraded DAAP-Solvesso Extractants*

Degradation Conditions	Degraded Solvent Color	Solvent Re-Extraction Results
New Solvent	Water White	No emulsion or precipitation.
9 day contact with 400 g/l Th solution Temperature: Ambient	Yellow tinge	Precipitation occurred and phases completely emulsified in the last batch stripping contact.
9 day contact with 400 g/l Th 3M HNO ₃ solution Temperature: Ambient	Straw Yellow	
9 day contact with 400 g/l Th solution Temperature: 150°F	Yellow	
9 day contact with 400 g/l Th - 3M HNO ₃ solution Temperature: 150°F	Deep Yellow	

* 30 vol % DAAP-Solvesso 100.

the thorium-uranium separation factor for the DAAP solvent were very low. The data also indicated that equivalent separation factors for TBP and a newer solvent di(sec-butyl) phenyl phosphonate (DSBPP) were considerably higher. Consequently, these solvents were chosen for development of a second extraction cycle to remove all uranium from the purified thorium nitrate stream (extraction product from a DAAP purification process).

Approximately 0.02 grams per liter uranium could be anticipated in the thorium nitrate product from a DAAP purification process, based upon anticipated feed materials. Therefore, equilibrium tests were conducted to determine the concentrations of DSBPP and TBP that would be required in a second-pass separation system. The results of these tests are presented in Table VIII.

It is apparent from the results presented in Table VIII that 15 vol % TBP or 15 vol % DSBPP would extract 0.02 g/l uranium from a thorium solution containing 40 g/l thorium; however, 1.7 and 0.20 g/l thorium would also be extracted by the TBP and DSBPP, respectively. It is desirable to prevent thorium extraction in this second separation to preclude the need of a subsequent thorium recovery process. The data indicate that DSBPP would be a more satisfactory solvent for this intended use since its thorium capacity is lower.

TABLE VIII Thorium and Uranium Equilibrium of TBP and DSBPP Extractants in Solvesso 100

Solvent (vol %)	Th (g/l)	U (g/l)
1.5 TBP	<0.05	0.0003
1.5 DSBPP	<0.05	0.0004
3.0 TBP	<0.05	0.0013
3.0 DSBPP	<0.05	0.0015
15 TBP	1.7	0.035
15 DSBPP	0.20	0.038

NOTE: The organic solvent in each test was contacted four times (1/1 ratio A/O) with fresh aqueous feed containing 40 g/l thorium, 0.02 g/l uranium (500 ppm, thorium basis) and 0.2M HNO₃ acid.

Laboratory batch countercurrent extraction tests were conducted to determine the separation efficiency for uranium from thorium nitrate solutions. Two different concentrations of DSBPP and TBP were used in the tests, and the results of the steady-state end streams are summarized in Table IX.

The countercurrent tests confirmed that the optimum separation of uranium and thorium is obtained with the DSBPP solvent. Further, that the DSBPP extractant can be used in a three-stage countercurrent extraction system to reduce the uranium contamination of a thorium nitrate solution from 500 to <10 ppm (thorium basis). Consequently, the DSBPP solvent was used in early pilot-scale testing of the thorium purification

TABLE IX Laboratory Batch Countercurrent* Operation for Uranium Separation from Thorium Nitrate Solutions

Solvent in Solvesso 100 (vol %)	Aqueous Feed In			Organic and Aqueous End Streams**				
	Th (g/l)	HNO ₃ (M)	U (ppm, Th Basis)	Organic Phase		Aqueous Phase		
				Th (g/l)	U (g/l)	Th (g/l)	U (ppm, Th Basis)	HNO ₃ (M)
8 DSBPP	40.0	0.2	500	<0.05	0.021	40.8	74	0.2
8 DSBPP	39.6	0.19	150	0.06	0.005	39.8	23	0.2
15 DSBPP	40.0	0.2	500	0.24	0.024	40.6	8	0.2
8 TBP	40.5	0.2	444	0.29	0.011	40.5	195	0.2
15 TBP	40.5	0.2	444	1.85	0.012	39.5	23	0.2
15 TBP	41.0	0.1	293	1.41	0.013	39.8	32	0.1

* Three-Stage countercurrent operation.

** End stream samples represent five volume changes.

flowsheet. However, difficulty in obtaining a supply of DSBPP solvent prompted further tests with TBP extractant, and the latter solvent was therefore evaluated for a separation flowsheet capable of handling thorium nitrate feeds containing even larger amounts of uranium.

Uranium distribution was determined between thorium nitrate solutions and a 12.5 vol % TBP - 70 vol % kerosene - 17.5 vol % Solvesso 100 solvent. The purpose of this test was to determine how many ideal extraction column stages would be required to lower the uranium concentration of an aqueous TNT solution from approximately 6000 ppm to less than 10 ppm. Distribution data obtained from the test are presented in Table X and in

TABLE X Uranium Distribution Between 12.5 vol % TBP-Kerosene and TNT Solutions

Uranium (g/l)		Uranium Distribution Coefficient ($D_{C_A}^{O_A}$)	HNO ₃ (M)	
Aqueous Phase	Organic Phase		Aqueous Phase	Organic Phase
0.095	0.36	3.8	0.55	0.04
0.048	0.16	3.3	0.55	0.05
0.024	0.073	3.0	0.55	0.04
0.007	0.017	2.4	0.55	0.04
0.003	0.008	2.7	0.55	0.05
0.00010	0.00017	3.0	0.55	0.05
0.00005	0.00016	2.0	0.55	0.05

A/O = 1/1

Figure 2. The number of theoretical stages was determined by a McCabe-Thiele analysis as illustrated in Figure 2. For a solution containing approximately 6000 ppm uranium (thorium basis) $6\frac{1}{2}$ theoretical column stages would be required to lower the uranium content to less than 10 ppm. Past pulse column experience would indicate that two perforated pulse columns operating in series would be required to achieve this degree of uranium decontamination in a countercurrent extraction process.

FIGURE 2 Uranium Distribution Between 12.5 vol % TBP and TNT Solutions

PILOT-SCALE DEVELOPMENT

1. Introduction

Solvent extraction tests were initiated in the Pilot Plant 2-inch column system² as a result of the favorable thorium extraction characteristics shown by DAAP in the laboratory testing program just described. The primary purpose of this testing program was to develop operable flowsheets for purifying both high-grade thorium nitrate tetrahydrate, containing only small quantities of uranium and rare earth elements, and low-grade thorium-bearing residues, containing large quantities of uranium and rare earth elements.

This report covers the development effort, plant startup, and some of the subsequent assistance activities associated with the pilot-scale thorium program.

2. Development of a DAAP Extraction System

The high-grade thorium nitrate material available for purification contained generally <20 ppm uranium (thorium basis) and <25 ppm total rare earth elements (thorium basis) which, at the time this work began, met the required purity specifications for the product. Consequently, no uranium-thorium separation process was required for this material. Since the laboratory distribution work indicated that the DAAP had a high affinity for thorium, five thorium extraction tests were conducted to evaluate this solvent in a countercurrent extraction operation. The aqueous feed solution for these tests was prepared from the stockpile of thorium nitrate tetrahydrate (TNT); the solvent for the tests was a 30 vol % DAAP (caustic treated) - Solvesso 100 mixture. Two 2-inch-diameter by 25-foot-long perforated-plate pulse columns were used for the extraction testing.

The purpose of Tests 1 and 2 was to determine the thorium extraction efficiency at column throughputs of 800 gsfh in the primary extraction (AX) column and 1200 gsfh in the stripping (CX) column.

Tests 3 and 4 were conducted to determine the flooding velocity in the AX column. Test 5 was conducted to (1) determine the product purity that could be achieved in a DAAP extraction process and (2) evaluate the extraction operation in an extended test at flowsheet conditions designed for the production of 1 ton per day of thorium in an existing but unused 6-inch pulse column system.

A schematic diagram of the column arrangement for the system used in the tests is shown in Figure 3a. The primary extraction column of this system can be operated as a compound extraction and scrub column as illustrated or as a primary extraction column alone when the aqueous feed (AFX) is introduced at the top of the column. The primary extraction column was used as a compound column to permit scrubbing the organic extract in Test 5. Test conditions and steady-state analyses are summarized in Tables XI and XII, respectively. Product purity data from Test 5 are presented in Table XIII.

Phase disengagement in the AX column at the throughputs employed was excellent. Some wall effects were observed during Test 1 as the aqueous phase adhered to the column wall. Dispersed droplets of aqueous phase did not coalesce readily following a pulse but remained generally discrete as they passed through the perforated plates. Poor extraction efficiency is indicated for Test 1 by the somewhat high thorium concentration of 1.23 g/l in the aqueous raffinate (ARX).

In Test 2, an increased pulse frequency apparently led to better efficiency than in the first test. Since a stable AX column operation was maintained in Test 2 at the higher pulse conditions, the flow rates were increased in stepwise intervals until an eventual throughput of 1707 gsfh was reached in the AX column during Test 4. Aqueous phase dispersion was observed to improve with increasing throughput. Droplets of aqueous phase were smaller and coalesced before the succeeding pulse, and wall effects were less significant than in the previous tests. Phase disengagement was

FIGURE 3 Column Arrangements

good at all throughputs although flooding was incipient at 1707 gsfh. Some aqueous entrainment was observed in the organic extract at this high throughput. Comparable extraction efficiencies are indicated by the low raffinate values for throughputs of 1178 and 1707 gsfh. These tests showed that a production rate of 1 ton per day of thorium could easily be achieved in a DAAP extraction process using an aqueous feed containing 400 g/l Th and operating at a throughput of approximately 1200 gsfh in a 25-foot-long 6-inch-diameter pulse column.

During the first test, the stripping (CS) column was operated with the organic phase as the continuous phase. At a throughput of 1219 gsfh, the column operation was at an incipient flooding condition. Consequently, sufficient water was not added to the column to produce a thorium-free organic raffinate (CRX). The aqueous phase was made continuous in the CX column during the second test and both phase disengagement and re-extraction efficiency improved greatly. The column operated well in this test at a high throughput (1252 gsfh), and the thorium content of the CRX was lowered to an acceptable value. A steady-state stripping column operation was not achieved in either Tests 3 or 4 because of emulsification problems probably caused by $\text{Th}(\text{OH})_4$ precipitation in the upper three sections of the column. Column conditions were those employed in the successful stripping operation of Test 2. In both Tests 3 and 4, the operation became unstable shortly after startup. Since the density difference at the top of the column (between loaded APX and water) is the smallest of any place in the column, emulsification in that section would be more likely than elsewhere. Consequently, the strip column startup procedure was modified in Test 5 to permit the establishment of an aqueous phase thorium concentration profile. Good operation was maintained for about 4 hours after which emulsification again occurred in the top section of the column. Even though the emulsion was present, an interface was maintained as the phases disengaged in the enlarged section at

TABLE XI Pilot Plant 2-Inch Column Test Conditions
(Development of High Grade Feed Flowsheet)

	Test 1	Test 2	Test 3	Test 4	Test 5
<u>A. Feed Material</u>					
1. Aqueous Feed* (AFX)	374 g/l Th 0.50M HNO ₃	384 g/l Th 0.58M HNO ₃	385 g/l Th 0.90M HNO ₃	392 g/l Th 0.94M HNO ₃	366 g/l Th 1.34M HNO ₃
2. Organic Feed** (AXX)	30 vol % DAAP	30 vol % DAAP	30 vol % DAAP	30 vol % DAAP	30 vol % DAAP
3. Scrub Water (ASX)	None	None	None	None	Deionized Water, 70°F
4. Strip Water (CSX)	Deionized Water, 150°F	Deionized Water, 150°F	None	None	Deionized Water, 150°F
<u>B. Test Flow Ratios (O/A)</u>					
1. AXX/AFX	6.78/1	6.79/1	7.25/1	6.69/1	6.83/1
2. APX/ASX	—	—	—	—	19.6/1
3. APX or APX/CSX	1.42/1	1.17/1	—	—	1.19/1
<u>C. Test Flow Rates (gph)</u>					
1. AFX	2.14	2.12	2.92	4.54	2.84
2. AXX	14.50	14.40	21.16	30.36	19.39
3. ARX	1.82	1.90	2.48	3.81	3.30
4. APX-1	14.90	14.83	21.58	30.97	19.84†
5. ASX	—	—	—	—	1.01
6. APX-2††	—	14.08	—	—	9.73
7. CSX	10.50	11.99	—	—	8.20
8. CPX	10.93	13.20	—	—	8.40
9. CRX	14.50	13.66	—	—	9.44
<u>D. Column Throughputs (gsfh)</u>					
1. AX Column	814	808	1178	1707	1088
2. CX Column	1219	1252	—	—	861
<u>E. Continuous Phase</u>					
1. AX Column	Organic	Organic	Organic	Organic	Organic
2. CX Column	Organic	Aqueous	—	—	Aqueous
<u>F. Pulse Conditions</u>					
1. AX Column					
Frequency (cpm)	51	59	59	59	60
Amplitude (in.)	0.8	0.8	0.8	0.8	0.8
2. CX Column					
Frequency (cpm)	41	42	—	—	42
Amplitude (in.)	1.05	1.05	—	—	1.05
<u>G. Length of Test (hr)</u>					
1. AX Column	7.75	5.50	7.00	5.50	12.50
2. CX Column	7.75	5.50	—	—	10.75

* Prepared from high-grade thorium nitrate tetrahydrate.

** Acidified prior to use. Solvesso-100 is the diluent.

† APX generated in A column.

†† APX used in C column.

TABLE XII Pilot Plant 2-Inch Column Test End Stream Analyses
(Development of High Grade Feed Flowsheet)

	Th (g/l)	HNO ₃ (M)	Th (g/l)	HNO ₃ (M)	Th (g/l)	HNO ₃ (M)	Th (g/l)	HNO ₃ (M)	Th (g/l)	HNO ₃ (M)
A. A Column Streams	Test 1		Test 2		Test 3		Test 4		Test 5	
1. Aqueous Feed (AFX)	374	0.50	384	0.58	385	0.90	392	0.94	366	1.34
2. Organic Feed (AXX)	—	—	—	—	0.070	0.036	0.22	0.026	0.47	<0.01
3. Organic Product (APX)	55.1	0.09	54.6	0.07	49.0	0.12	54.9	0.13	51.4	0.12
4. Aqueous Raffinate (ARX)	1.23	0.33	0.41	0.25	0.061	0.26	0.084	0.22	3.61	0.29
B. C Column Streams										
1. Aqueous Product (CPX)	63.2	0.12	54.7	0.081	—	—	—	—	56.4	0.18
2. Organic Raffinate (CRX)	6.04	<0.01	0.51	<0.02	—	—	—	—	0.32	<0.01
C. Material Balances (%)										
1. AX Column	+3.38	—	-5.47	—	-6.05	-4.57	-4.80	-3.82	-1.61	-12.3
2. CX Column	-5.41	-4.62	-5.18	+2.53	—	—	—	—	-4.67	+22.8

the top of the column. The strip water rate was then reduced to 85% of the organic feed rate (O/A = 1.19/1), which resulted in the breaking of the emulsion. The organic raffinate (CRX) was found to contain 0.32 g/l thorium at this condition of reduced strip water and was considered satisfactory for flowsheet purposes.

Following the sampling of the end streams at steady-state, the strip water rate was increased to give an O/A ratio of 0.83/1 which resulted in column emulsification. Upon reducing the strip water rate to 75% of the organic feed rate (O/A ratio = 1.33/1), the emulsion cleared and operation was maintained for approximately 1 hour. The organic raffinate (CRX) was sampled and found to contain 0.48 g/l Th. Although the final sample was probably not a steady-state sample, the low thorium concentration indicates that the CX column could be efficiently operated at an O/A ratio of 1.33/1 while reducing the chance of encountering an emulsion.

The capacity of the CX column seems to be about 1250 gsfh with an aqueous continuous phase. A throughput of 861 gsfh was maintained in a stable operation during Test 5 and would be sufficient for the 1 ton per day production rate in the one 9-inch column of the Pilot Plant's 6-inch pulse column system.

A prime objective of Test 5 was to determine product purity for an operation in which the organic product (APX) was countercurrently contacted with water to remove entrained and/or extracted impurities. The O/A ratio used in the scrubbing operation was approximately 20/1. Good impurity decontamination is indicated (Table XIII) for the alkali and alkaline earth metals, as well as for boron,

TABLE XIII Two-Inch Column Product Purity Analyses (Development of High Grade Feed Flowsheet, Test 5)

Impurity	Impurity Concentration (ppm - Th Basis)	
	Aqueous Feed (AFX)	Aqueous Product (CPX)
Cation Impurities: B	9	<0.2
Ca	71	<4
Fe	30	<4
K	15	<4
Mg	33	<4
Na	430	4
Pb	1	<1
U	33	14
Rare Earths: DY	1.6	<0.1
Eu	<0.15	<0.15
Sm	>0.7	0.24
Gd	>2.0	0.35
Anion Impurities: F ⁻	0.032	0.007
Cl ⁻	0.014	0.0005
SO ₄ ⁼	0.120	<0.002

iron, and lead. Insufficient amounts of other metallic impurities were present in the feed to permit a full evaluation of decontamination capabilities of the DAAP system. Uranium was removed to some degree as were rare earth metals and anionic impurities; however, a more comprehensive study of the DAAP system will be required to ascertain accurately the uranium and rare earth decontamination.

The results of these tests were encouraging, and it was apparent that the TNT stockpile could be purified at the rate of about 1 ton per day of thorium in the existing 6-inch pulse column equipment with a 30 vol % DAAP - Solvesso 100 extractant. Consequently, this pulse column system was reactivated and altered to accommodate the DAAP flowsheet.

3. Development of a Flowsheet for Thorium - Uranium Separation

During the first phases of processing thorium nitrate at this site, the process specification limit for uranium was 20 ppm (thorium basis). Later this specification was lowered to 5 ppm uranium (thorium basis) at the request of the reactor sites using the thorium as fuel. It therefore became necessary to employ a second extraction system for thorium-uranium separation to meet the new specification. This second extraction would also be essential if the low-grade feed materials were to be processed, since these materials contain sizeable amounts of uranium and rare earth elements. Consequently, tests were conducted to evaluate the uranium decontamination achieved by extraction in both a first pass, DAAP-Solvesso system, and a second pass, TBP-kerosene system. The DSBPP extractant was not evaluated in this testing program because it had proven difficult to obtain commercially.

DAAP-Solvesso Extraction System

Two tests were conducted for the purpose of evaluating column efficiencies and determining the path of materials for the DAAP-Solvesso extrac-

tion of thorium from residue feed liquor. Feed solutions of 1.2M and 2.0M HNO_3 were tested. The sulfate concentration of both feed liquors was approximately 3600 ppm (thorium basis).

The aqueous feed was prepared from a low-grade feed blend of thorium oxide, floor sweepings, and dry sump cake in a gross weight proportion of 1.0 : 1.0 : 0.6. Alumina-treated DAAP-Solvesso from the Pilot Plant 6-inch column operation was used as the solvent.

Test conditions are summarized in Table XIV. The flow rates employed were chosen to give column throughputs of approximately 1200 gsfh in the extraction column and 900 gsfh in the stripping column, which is equivalent to a thorium production rate of 1 ton per day in the Pilot Plant 6-inch system. Column arrangements were as shown in Figure 3a. Scrubbing was employed in these tests using deionized water at an O/A of 20/1.

Satisfactory column operation was achieved in both columns in each test. Steady-state analyses are presented in Table XV. The high aqueous raffinate (ARX) value of 2.63 g/l thorium in Test 8 is attributed primarily to the short length of column (5 feet) used as the scrub section, even though the organic feed (AXX) concentration was very high. An earlier test (Test 5) conducted under similar conditions, but with a low thorium concentration in the AXX stream, yielded approximately the same raffinate concentration. The higher acidity of the feed used in Test 9 produced a considerably lower raffinate concentration. These results indicate that a 2.0M HNO_3 feed would be necessary for processing in the 6-inch Pilot Plant system because of the limited number of stages in primary extraction.

The stripping column was operated using an O/A ratio of 1.24/1 which produced an aqueous thorium product (CPX) of approximately 60 g/l thorium. Although the organic raffinate values are somewhat high, a concentration of less than 1.0 g/l thorium is tolerable. However, some difficulty might be encountered if a Na_2CO_3 solvent treat-

TABLE XIV Thorium-Uranium Separation
Using DAAP Extractant; 2-Inch Column
Test Conditions

	Test 8	Test 9
<u>Feed Material</u>		
1. Aqueous Feed (AFX)	229 g/l Th 1.24M HNO ₃	199 g/l Th 1.93M HNO ₃
2. Organic Extractant (AXX)	30 vol % DAAP-Solvesso 5.75 g/l Th	30 vol % DAAP-Solvesso 0.37 g/l Th
3. Scrub Water (ASX)	Deionized water, ambient temp.	Deionized water, ambient temp.
4. Strip Water (CSX)	Deionized water, 150°F	Deionized water, 150°F
<u>Test Flow Ratios</u>		
1. AXX/AFX	4.27/1	4.03/1
2. APX/ASX	20.0/1	19.9/1
3. APX/CSX	1.23/1	1.24/1
<u>Test Flow Rates (gph)</u>		
1. AFX	4.45	4.74
2. AXX	19.0	19.1
3. APX* (calc)	19.8	19.9
4. ARX (calc)	5.26	5.52
5. ASX	0.99	1.00
6. CSX	8.15	8.16
7. APX**	10.0	10.1
8. CRX (calc)	9.6	9.71
9. CPX (calc)	8.47	8.48
<u>Column Throughputs (gsfh)</u>		
1. AX Column	1195	1215
2. CX Column	886	892
<u>Continuous Phase</u>		
1. AX Column	Organic	Organic
2. CX Column	Aqueous	Aqueous
<u>Pulse Conditions</u>		
1. AX Column:		
Frequency	60 cpm	60 cpm
Amplitude	0.8 in.	0.8 in.
2. CX Column:		
Frequency	40 cpm	40 cpm
Amplitude	1.0 in.	1.0 in.
<u>Length of Test (hours)</u>		
1. AX Column	5.75	4.75
2. CX Column	5.50	4.75

* APX generated in AX Column.

** APX used in CX Column.

ment system were operated with an organic raffinate of this thorium concentration.

Material balance closures for Th, HNO₃, U, and F are shown in Table XV. Poor uranium and fluoride balances over the C column were observed in both tests. Also, the A column uranium balance in Test 9 was poor.

Purity data of the DAAP extraction product are presented in Table XVI. Zirconium, calcium, iron, and fluoride concentrations are higher than expected. Some uranium decontamination was realized in the DAAP extraction operation even though the final concentrations were far from specification.

The distribution of materials during DAAP extraction is shown in Figure 4 from the data obtained in Test 8. The thorium recovery efficiency was 97.2%. This can be improved for a given extrac-

FIGURE 4 Distribution of Materials in Test 8

tion column length by increasing the acidity of the feed liquor as was demonstrated in Test 9. Almost half of the nitric acid that enters the AX column is extracted into the APX stream and is completely stripped in the subsequent re-extraction operation. Approximately 40% of the uranium entering the system leaves with the aqueous product. Consequently, the importance of maintaining a Na_2CO_3 solvent treatment operation in conjunction with the DAAP extraction system is emphasized since approximately 60% of the uranium entering would be recycled to the AX column in the CRX stream. Failure to remove the uranium would result in a gradual increase in the uranium concentration of the aqueous product (CPX) stream, thereby increasing the load on a second cycle extraction system. An inspection of the fluoride path indicates that approximately 12% of the fluoride is carried through with the product. A sizeable fluoride decontamination is accomplished in primary extraction as is indicated by the 83% leaving in the aqueous raffinate.

The physical operation of the first extraction system on low-grade thorium residue feeds is comparable with an operation using high-grade thorium nitrate feed. Thorium recovery efficiency and column operational stability are similar for both feed liquors. However, complete decontamination of calcium, iron, fluoride, chloride, and zirconium

was not achieved, and revised scrubbing conditions will be necessary to achieve the necessary product purity with the low-grade feed materials.

TABLE XVI DAAP Extraction Product Purity (ppm, Th Basis)

Element	Test 8	Test 9
U	166	250
Zr	445	445
Na	4	20
Ca	1400	890
Mg	15	< 4
Fe	121	152
F	1485	2100
Cl	61	83

TBP-Kerosene Extraction System

Five tests were conducted in the 2-inch pulse column system to determine the uranium decontamination capabilities of 15 vol % TBP in kerosene. The columns were arranged as shown in Figures 3b and 3c. Low uranium feeds were tested in a single extraction column with subsequent uranium stripping in the DY column. Both columns were used in series as a single primary extraction (BY) column for testing feeds containing a high uranium concentration.

TABLE XV Thorium-Uranium Separation Using DAAP Extractant; Steady-State End Stream Analyses

	Test 8				Test 9			
	Th (g/l)	HNO_3 (M)	U (g/l)	F (g/l)	Th (g/l)	HNO_3 (M)	U (g/l)	F (g/l)
A. AX Column Streams								
1. Aqueous Feed (AFX)	229	1.24	0.31	1.55	199	1.93	0.67	1.29
2. Organic Feed (AXX)	5.75	0.012	0.002	—	0.37	< 0.01	0.08	—
3. Organic Product (APX)	55.2	0.18	0.082	0.17	48.0	0.28	0.15	0.043
4. Aqueous Raffinate (ARX)	2.63	0.45	0.0002	1.06	0.61	0.74	0.0006	1.11
B. CX Column Streams								
1. Aqueous Feed (CSX)	—	0.05	—	—	—	0.05	—	—
2. Aqueous Product (CPX)	66.3	0.28	0.011	0.098	57.4	0.35	0.014	0.12
3. Organic Raffinate (CRX)	0.94	< 0.01	0.015	0.038	0.67	< 0.01	0.25	0.01
C. Material Balance Closures (%)								
1. AX Column	+1.9	+3.9	+12.7	+14.8	+0.86	+5.1	-37	+12.4
2. CX Column	+3.3	+7.1	-71	-30	+1.7	-5.3	+40	+61

The product from the Pilot Plant's 6-inch extraction columns was spiked with uranium and used as the aqueous feed in these tests. Thorium and acid concentrations were adjusted to the desired values. The organic solvent was batch stripped three times with water, treated with caustic, washed with water, and acidified prior to use in the test series.

Test conditions are presented in Table XVII. BY column throughputs were approximately 600 gsfh in each test and the column gave no indication of flooding nor emulsification in any of the tests. However, emulsification was encountered in the middle section of the DY column during Test 11 which caused the stripping operation to be terminated. The stripping conditions employed were

TABLE XVII Thorium-Uranium Separation Using TBP Extractant; 2-Inch Column Testing Conditions

	Test 7	Test 10	Test 11	Test 13	Test 14
A. Feed Material					
1. Aqueous Feed (BFY)	67.8 g/l Th 0.57M HNO ₃ 12,500 ppm U*	50.6 g/l Th 0.34M HNO ₃ 187 ppm U*	70.6 g/l Th 0.54M HNO ₃ 115 ppm U*	74.0 g/l Th 0.57M HNO ₃ 4800 ppm U*	69.3 g/l Th 0.55M HNO ₃ 11,140 ppm U*
2. Organic Feed (BYY)	15 vol % TBP-Kerosene	15 vol % TBP-Kerosene	15 vol % TBP-Kerosene	15 vol % TBP-Kerosene	15 vol % TBP-Kerosene
3. Strip Water (DSY)	Process Water, 150°F	Deionized Water, 150°F	None	None	None
B. Test Flow Ratios (O/A)					
1. BY or B ₁ Y Column	1.00/1	0.95/1	1.03/1	1.00/1	1.00/1
2. DY or B ₂ Y Column	1.96/1	0.95/1	—	1.00/1	1.00/1
C. Flow Rates (gph)					
1. BFY	6.17	6.16	6.07	6.12	6.14
2. BYY	6.17	5.88	6.20	5.98	6.06
3. BIPY	—	—	—	6.12	6.14
4. BIRY	—	—	—	6.10	6.18
5. BPY	6.11	6.10	6.01	6.06	6.08
6. BRY-1**	6.23	5.94	6.26	6.10	6.18
7. DSY	3.06	6.01	—	—	—
8. BRY-2†	6.23	5.77	—	—	—
9. DRY	6.17	5.71	—	—	—
10. DWY	3.09	6.07	—	—	—
D. Column Throughput (gsfh)					
1. BY or B ₁ Y Column	600	589	600	592	597
2. DY or B ₂ Y Column	443	565	—	586	591
E. Continuous Phase					
1. BY or B ₁ Y Column	Organic	Organic	Organic	Organic	Organic
2. DY or B ₂ Y Column	Aqueous	Aqueous	—	Organic	Organic
F. Pulse Conditions					
1. BY or B ₁ Y Column					
Frequency (cpm)	80	80	80	80	80
Amplitude (in.)	0.8	0.8	0.8	0.8	0.8
2. DY or B ₂ Y Column					
Frequency (cpm)	40	40	—	80	80
Amplitude (in.)	1.0	1.0	—	0.8	0.8
G. Length of Test (hr)					
1. BY or B ₁ Y Column	6.5	5.5	4.0	14.7	11.8
2. DY or B ₂ Y Column	6.5	4.5	—	14.7	11.8

* Th basis.

** BRY generated in the BY Column.

† BRY consumed in the DY Column.

identical to those used for Test 10 in which good operation was maintained without difficulty. Process water was used in Test 11 instead of Pilot Plant deionized water, which may have been slightly acidic because it contained some water from the product evaporation process. Laboratory scoping tests have indicated that the stripping operation at low-thorium, low-acid concentration is susceptible to emulsification. Additional testing in the 2-inch system is being conducted to determine the influence of thorium and acid concentration conditions on the performance of the stripping operation. Re-extraction may have to be accomplished at a low pH (1.0 to 2.0) in this extraction cycle.

Steady-state analyses for these tests are summarized in Table XVIII. Uranium extraction from low-concentration uranium feeds is essentially complete in one column as indicated by the aqueous product (BPY) uranium values in Test 10 and 11. Although the product uranium concentration was greater than the recently imposed specification of 5 ppm in Test 7 (Table XVIII), acceptable product was obtained from a feed containing 11,000 ppm uranium (thorium basis) in Test 14 when two columns were operated in series. An acceptable product was also produced from a feed containing 6000 ppm uranium in Test 13 using a series BY column. The uranium content of the stripped organic product (DRY) from Test 11 indicates that uranium removal in the DY column is sufficiently effective to permit continuous recycling of the solvent.

Thorium extraction by the organic in the BY column was higher than anticipated. The average thorium loss to the organic (BRY) in these tests was 13% giving a thorium recovery efficiency of 87%. Acid losses to the BRY averaged about 7%. A comparison of BRY and BIRY raffinate values in Tests 13 and 14 indicates that thorium loading was complete in the B₁Y column at approximately 11 g/l, and no additional thorium loading occurred in the B₂Y column. This is substantiated by the

thorium concentration of the BIPY stream being nearly the same as the feed concentration and shows that thorium equilibrium was nearly reached in 25 feet of extraction length. If a very high thorium feed (approximately 400 g/l) were used in this operation, a significant production rate increase would be achieved for the same column throughputs, and the thorium recovery efficiency would improve. Material balance closures are excellent in each test for thorium and acid; however, the uranium balances are generally poor and probably are caused by the small quantity of uranium involved in the testing program.

The number of ideal stages for the uranium separation in each test was determined by a McCabe-Thiele analysis. The results are presented in Figure 5 as the number of ideal stages required for the uranium separation from 12,500 ppm uranium (0.85 g/l) to 1 ppm uranium. Almost 11 stages would be required to reach 1 ppm, while 8 stages would be required to make current specification product. In either case, the use of two 25-foot columns operating in series as a single extraction column would be necessary. It is estimated that feeds containing less than 0.01 g/l U could be decontaminated in a single column to meet the 5 ppm specification.

4. Pilot Plant 6-Inch Column Startup Operations

The Pilot Plant 6-inch column facility for thorium extraction went on-stream on January 25, 1965. This facility, Figure 6, employed a double extraction system. The first extraction cycle (X) utilized a 30 vol % DAAP - 70 vol % Solvesso 100 solvent to achieve cationic and anionic decontamination. Heavy metal impurities, such as uranium and rare earth elements, not decontaminated in the DAAP system were to be removed in the second system (Y) which utilized an 8 vol % DSBPP - Solvesso 100 solvent. The second cycle solvent was later changed to a 15 vol % TBP - 85 vol % kerosene when additional DSBPP could not be obtained.

**TABLE XVIII Thorium-Uranium Separation Using TBP Extractant;
2-Inch Column Steady-State Analyses**

	Th (g/l)	HNO ₃ (M)	U (g/l)	Th (g/l)	HNO ₃ (M)	U (g/l)	Th (g/l)	HNO ₃ (M)	U (g/l)
	Test 7			Test 10			Test 11		
<u>A. BY Column Streams</u>									
1. Aqueous Feed (BFY)	67.8	0.57	0.85	50.6	0.34	0.0095	70.6	0.54	0.0082
2. Organic Feed (BYY)	0.0	0.01	0.01	0.0033	0.01	0.0023	0.075	0.013	0.002
3. Aqueous Produce (BPY)	62.6	0.57	(81)*	46.2	0.34	(<1)*	62.7	0.53	(<1)*
4. Organic Raffinate (BRY)	8.1	0.04	1.02	12.9	0.02	0.010	9.93	0.04	0.0043
<u>B. DY Column Streams</u>									
1. Aqueous Feed (DSY)	0.0	0.0	0.0	0.0	0.0	0.0	—	—	—
2. Aqueous Waste (DWY)	14.6	0.04	1.93	12.0	0.02	0.004	—	—	—
3. Organic Product (DRY)	0.002	<0.01	<0.0005	<0.001	<0.01	0.0005	—	—	—
<u>C. B₂Y Column Streams</u>									
1. Aqueous Feed (BFY)	—	—	—	—	—	—	—	—	—
2. Organic Feed (BIRY)	—	—	—	—	—	—	—	—	—
3. Aqueous Product (BIPY)	—	—	—	—	—	—	—	—	—
4. Organic Raffinate (BRY)	—	—	—	—	—	—	—	—	—
<u>D. B₁Y Column Streams</u>									
1. Organic Feed (BYY)	—	—	—	—	—	—	—	—	—
2. Aqueous Product (BPY)	—	—	—	—	—	—	—	—	—
<u>E. Material Balance Closures (%)</u>									
1. BY or B ₁ Y Column	+3.4	-4.0	+17.0	+13.0	+1.82	-17.5	+2.27	+2.21	-55
2. DY or B ₂ Y Column	-10.6	-25.0	-6.1	-2.1	+4.94	-53.0	—	—	—
	Test 13			Test 14					
<u>A. BY Column Streams</u>									
1. Aqueous Feed (BFY)	—	—	—	—	—	—			
2. Organic Feed (BYY)	—	—	—	—	—	—			
3. Aqueous Product (BPY)	—	—	—	—	—	—			
4. Organic Raffinate (BRY)	—	—	—	—	—	—			
<u>B. DY Column Streams</u>									
1. Aqueous Feed (DSY)	—	—	—	—	—	—			
2. Aqueous Waste (DWY)	—	—	—	—	—	—			
3. Organic Product (DRY)	—	—	—	—	—	—			
<u>C. B₂Y Column Streams</u>									
1. Aqueous Feed (BFY)	74.0	0.57	0.36	69.3	0.55	0.77			
2. Organic Feed (BIRY)	11.7	0.04	0.0005	10.9	0.04	<0.0005			
3. Aqueous Product (BIPY)	73.8	0.58	0.004	69.5	0.54	0.0007			
4. Organic Raffinate (BRY)	12.0	0.04	0.26	11.0	0.04	0.48			
<u>D. B₁Y Column Streams</u>									
1. Organic Feed (BYY)	0.003	<0.01	0.005	0.06	0.03	<0.0005			
2. Aqueous Product (BPY)	63.7	0.54	(<1)*	60.4	0.51	(<1)*			
<u>E. Material Balance Closures (%)</u>									
1. BY or B ₁ Y Column	+1.25	+0.11	-94	-1.73	-3.98	-8.64			
2. DY or B ₂ Y Column	+0.11	+1.14	-26	+0.37	-2.73	-39.0			

* ppm U (Th basis).

FIGURE 5 Ideal Stage Requirement for Uranium Decontamination of DAAP Extraction Product

Some difficulties were encountered upon startup of the relatively old, 6-inch column equipment, but these were corrected as encountered. Control of the DAAP stripping column thorium profile and/or pH was critical in order to prevent emulsions. The original strip water control system proved to be inadequate to provide the precise control required, and that system was modified. In some instances, pumps were operating at the extreme ends of their operating ranges, thus causing control difficulties. These situations were corrected by pump switching and replacement where necessary.

Two major difficulties were encountered in this operation which required modifications of the existing extraction system. The extraction efficiencies obtained in the DAAP extraction column were not as good as those obtained in the 2-inch column system. It was found that hot organic raffinate (CRX) from the stripping column returning to the primary extraction column contributed to the poorer extraction efficiency since it raised the column operating temperature above 100°F. The solvent treatment centrifuge was used temporarily to cool the solvent leaving the strip column until a solvent cooler could be installed.

The poorer efficiency of the DAAP primary extraction system also necessitated that the portion of the column designed for scrubbing the organic extract be used for thorium extraction until the column was lengthened by 5 feet. Although this scrubbing operation was not essential for product purity with the high-grade thorium nitrate feed, it was necessary to reduce the nitric acid content of the DAAP product (CPX). Even though these changes were made the primary extraction column raffinate continued to contain a higher concentration of thorium than had been predicted by the 2-inch column testing. The high raffinate values were found to be partially due to the processing of high sulfate feeds, and this problem was overcome by increasing the free acid content of the feed solutions from 1.0 to 3.0M HNO₃. However, raffinate values still ranged from 1.0 to 5.0 g/l thorium. Consequently, the concentration of the feed was decreased from 300 to 200 g/l thorium. Concurrently, the feed rate was increased to give about 50 g/l thorium loading in the APX in order to maintain the 1.1 ton per day production rate. This increased the AX column throughput from approximately 1200 to 1300 gsfh and reduced the raffinates to consistently less than 0.3 g/l thorium. The improvement is attributed to better dispersion of the aqueous phase at the higher throughput, and as a result, the extraction efficiency has been improved by about a half stage.

The purity of the first product was generally good with two notable exceptions (see Table XIX). Iron contamination exceeded the specification and greatly exceeded that in the product from the 2-inch column testing. It became apparent from monitoring the product streams that the iron contaminant was introduced in the boildown operation even though the product was neutralized to a pH of 2 with ammonia prior to boildown. Similar experiences suggested that a black iron component in the boildown system was responsible for the high iron contamination of the product. This hypothesis was eventually confirmed.

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FIGURE 6 Pilot Plant Thorium Extraction System

TABLE XIX Product Analyses for Thorium Extraction System*

Impurity or Element	First Product From 6-Inch Columns**	Target Specification	Test 5 2-Inch Column System
Th (g/l)	415	>300	56.4 †
U	13	<30	—
B	0.2	<2	<0.2
Total Rare Earths	<25	<25	<25
Gd	<0.4	<5	0.36
Sm	0.68	<5	0.24
Dy	<0.2	<2	<0.1
Na	17	<100	4
K	<6	<50	<6
Ca	6	<100	<4
Mg	6	<50	<4
Al	<10	<25	<10
Be	<1	<100	<1
Cr	4	<25	<4
Cu	5	<25	<1
Fe	84	<50	<4
Mn	1	<25	<1
Ni	2	<25	<4
Pb	<1	<25	<1
Si	10	<100	<10
Zn	<20	<25	<20
Zr	<10	<100	<10
C	—	<100	—
Cl	<25	<100	8
F	<25	<100	—
P	<100	<100	—
SO ₃	116 ††	<100	<35.5 ††
Organic (%)	<0.005	—	—

* ppm, thorium basis, unless otherwise specified.

** Concentrated Th(NO₃)₄ solution prepared for shipment to MCW.

† Prior to boildown.

†† SO₄ analyses transposed to SO₃ to correspond to specification designation.

The other contaminant to exceed specification was the sulfate ion. However, when the free acid concentration of the feed slurries was increased from 1.0 to 3.0M HNO₃, as previously discussed, the SO₄ content of the product fell to 30.5 ppm (thorium basis) with the same quantity of SO₄ in the feed solutions (approximately 16,000 ppm SO₄, thorium basis).

After several truckloads of thorium nitrate solution had been shipped to Mallinckrodt Chemical Works for the production of ThO₂, a request was received to reduce the existing uranium specification from 20 to 5 ppm (thorium basis). This necessitated reprocessing approximately 3000 gallons of thorium nitrate product which contained about 20 ppm uranium (thorium basis). Approximately, 3000 gallons of uranium-contaminated (about 200 ppm uranium, thorium basis) product from extraction testing of low-grade residue feeds were also available for reprocessing. A special flowsheet was designed for this operation from data obtained in the 2-inch column testing of the TBP-kerosene flowsheet. This extraction system is illustrated in Figure 7.

The high thorium content (about 380 g/l) of the feed solution caused solvent splitting during start-up operations. Solvesso 100 diluent was added to the 15 vol % TBP — 85 vol % kerosene solvent until the solvent contained 20 vol % Solvesso 100. This stabilized the solvent solution, and no other operational problems were experienced with the flowsheet. Approximately 18,200 pounds of thorium were processed in this special operation at a production rate of 2.65 tons per day. The final product from this operation contained <5 ppm uranium (thorium basis).

Future Work

Although the DAAP-Solvesso 100 extractant has proved to be fairly stable to thorium and nitric acid, some difficulties have been encountered with the solvent during the continuous extraction operation. It is believed that "tramp organic materials," which are soluble in the solvent, may be responsible, as both alumina and charcoal adsorption treatments have been successfully used to rehabilitate solvent samples. Solvent treatment tests are continuing, and the final results of this work will be reported at a future date.

Additional impurity studies will be conducted for both the DAAP-Solvesso 100 and TBP-kero-

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FIGURE 7 Special Extraction System, 6-Inch Columns

sene-Solvesso 100 extractants. Rare earth elements, fluoride, calcium, and zirconium are of special interest, and decontamination data will be obtained for these elements. Additional work will be done to determine if various low-grade thorium-bearing residues from the existing AEC stockpile can be processed in the dual extraction process.

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2. EFFECT OF FURNACE HEATING ELEMENT ARRANGEMENT ON URANIUM METAL QUALITY

E. W. Mautz

D. C. Bonfer

Abstract

The quality of uranium reguli (derbies) was improved in production operations by use of reduction furnaces operating with three resistance heating elements instead of only two elements. Some improvement was also noted at the higher of two magnesium excesses studied.

Introduction

The optimum production conditions for the preparation of uranium derby metal by the reduction of UF_4 with magnesium metal¹ are functions of many variables. These include UF_4 quality and method of production, reduction furnace heating arrangement, and the excess of magnesium used in the reduction of the UF_4 (over that required by stoichiometry). A recent production-scale evaluation of the last two variables has led to appreciable improvement in the quality of the uranium derby metal.

Summary of Results

A production-scale study showed that uranium derby quality was improved by operation of the reduction furnaces in a three-element arrangement instead of a two-element arrangement (with the third heating element inoperative). Some improvement was observed for derbies produced at the higher of two magnesium excesses studied.

The primary derby improvement resulted from a reduction in the incidence of inclusion-laden caps that formed on top of the derbies or from a reduction in the band of inclusions of the $U(C,N,O)$ type in the upper portion of the derby metal. These improvements are readily detected through measurement of the derby density by Archimedes' principle.

Process Description and Problem Discussion

The blended UF_4 -Mg charge is reduced in a sealed, refractory-lined steel furnace pot. The reaction is initiated by heating the pot in an electric resistance-type furnace (Figure 1) until auto-ignition² occurs. After the reaction takes place, the furnace pot is air-cooled to below red heat, water-cooled to room temperature, then opened for removal of the slag and the uranium regulus, or derby. Separation of the derby from the slag mass generally requires the use of a hand-operated pneumatic hammer. Final cleaning is effected, as required, in a shot-blasting unit employing centrifugally-accelerated uranium shot.³

The plant reduction furnaces (Fig. 1) are built with three ribbon-type electric resistance elements mounted on the inner refractory wall, one above the other, encircling the furnace pot. The top and center elements are connected in series and have a power input of 30 kva (15 kva each). Power to the bottom element can be varied, in increments of 2 kva, to 10 kva. When used, it normally operates at 8 kva.

Until recently, it was standard practice not to use the bottom heating element except for reduction charges containing UF_4 produced by the hydrogen-reduction of uranium hexafluoride (UF_6). With this exception, satisfactory derby results had been obtained without using the bottom heating element. (The two-element technique reduced maintenance costs because the bottom element was quite vulnerable to mechanical damage and even destruction if the furnace pot failed during reaction, as happened occasionally.)

For reasons which are not known, many recent derbies were found to have a cap as thick as $\frac{1}{2}$ -

FIGURE 1 Electrical Resistance Furnace. (1) Lid; (2) Furnace Pot Support Ring; (3) Top Element; (4) Thermocouple (Spring Loaded); (5) Center Element; (6) Bottom Element; (7) Furnace Pot; (8) Refractory.

FIGURE 2 Uranium Derby Section Showing an Extreme Case of Inclusion-Laden Cap; Upper Portion of Composite Was Polished and Etched. (Approx. $\frac{3}{4}X$)

inch adhering to their tops. Most of these caps appeared to consist of sound metal but, upon closer examination, were found to include substantial dispersed quantities of mixed oxides and fluorides. An extreme example of such a cap is shown in Figure 2. A subsequent study revealed a band of similar composition in the upper portion of the derby proper. The material in the derby cap, as well as that in the band at the top of the derby, was not removed by shot-cleaning. This foreign material was found to be associated with an increased incidence of cracked graphite crucibles in the subsequent ingot casting operation and an undesirable trend to inclusions of the U(C,N,O) type in the finished uranium fuel cores.

Discussion of Experimental Results

Several production furnaces were tested with all three elements operating to determine the general effect of this change on derby quality. Observation of derbies from the three-element furnaces showed a substantial reduction in the incidence of derby caps and a visible improvement in the top surfaces of the derbies.

A formal evaluation of derby quality was instituted in conjunction with the study of electrolytic

magnesium, discussed in Section 3 of this report, with furnace element arrangement (2 or 3 elements) and magnesium excess being subsidiary variables.

The reduction data obtained for cut-crown magnesium (the regular type now used on a production basis) are given in Table I. (Similar results were observed for electrolytic magnesium reductions.)

The data in Table I, representing 104 derbies, show the improvement in derby density and derby grade for the three-element furnaces compared with the two-element furnaces. A similar improvement can be seen in the percentage of derbies having the cap containing objectionable impurities. The data also show that the higher magnesium excess was effective in lowering the percentage of derbies having caps but the derby density remained essentially unchanged. It was observed that the higher magnesium excess permitted separation of the cap and the derby when extra effort was applied with the pneumatic hammer.

Figures 3 and 4 show the basic difference in the band of inclusions in the upper portion of the derby metal from the two-element and three-element furnaces.

TABLE I Reduction Data for Two- and Three-Element Furnaces and Two Magnesium Excesses

Magnesium Excess (%)	Furnace Elements (No.)	Firing Time (min)	Derby* Density (g/cm ³)	Derby** Yield (%)	Derby Grade (%) [†]		Derby Caps (%)
					1	2	
2.8	2	241	17.7	96.6	55.6	44.4	100
2.8	3	246	18.5	97.7	88.9	11.1	11
4.2	2	251	17.5	97.3	33.3	66.7	22
4.2	3	246	18.4	96.6	66.7	33.3	0
2.8	Both	244	18.1	97.2	72.2	27.8	56
4.2	Both	249	17.9	97.0	50.0	50.0	11
Both	2	246	17.6	97.0	44.4	55.6	61
Both	3	246	18.5	97.2	77.8	22.2	6

*Derby density determined by Archimedes' principle (weight in water compared with weight in air).

**Derby yield adjusted for derby density.

[†]Grade 2 derbies require shot-cleaning prior to remelting and casting into ingots; Grade 1 derbies are satisfactory for use as-reduced for most fuel core product streams.

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FIGURE 3 Uranium Derby Section Showing the Inclusion-Laden Upper Band Typical of Two-Element Furnace Product; Upper Portion of Composite Was Polished and Etched. (Approx. $\frac{3}{4}X$)

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FIGURE 4 Uranium Derby Section Showing Relatively Inclusion-Free Upper Band Typical of Three-Element Furnace Product; Upper Portion of Composite Was Polished and Etched. (Portions of the Upper Band, Left, Show Grain Structure, Not Inclusions.) (Approx. $\frac{3}{4}X$)

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3. COMPARISON OF ELECTROLYTIC AND FERROSILICON-PROCESS MAGNESIUMS FOR URANIUM PRODUCTION

E. W. Mautz

D. C. Bonfer

Abstract

Electrolytic magnesium (Dow Grade 6) has been shown to produce uranium metal of satisfactory yields and of quality comparable with that resulting from the use of ferrosilicon process (Nelco cut-crown) magnesium.

Introduction

Ferrosilicon process cut-crown magnesium is the type now regularly used at the National Lead Company of Ohio for the reduction of uranium tetrafluoride (UF_4) to produce uranium metal. This type of magnesium was described in a previous report.¹ Employment of ferrosilicon (Pidgeon) process² magnesium in the form of cut-up (about -4, +50 mesh) condensate crowns lowers uranium production costs, compared with the chipped ingot magnesium previously used, because the crown remelting and ingot casting steps are eliminated.

In reviewing the quality of commercial electrolytic magnesium,³ it appeared that this material might be an alternate and potentially cheaper type of magnesium metal for uranium production. Hence a quantity of electrolytic magnesium was purchased and tested as a reductant for UF_4 . This report contains the results of the production-scale⁴ tests. The test data are compared with similar data from cut-crown magnesium.

Summary of Results

Electrolytic magnesium (Dow Grade 6) was found to be equivalent to ferrosilicon process magnesium (Nelco cut-crown) for uranium production operations. Uranium derby and ingot yields, as well as ingot analyses, showed equivalent results between the two magnesium types. A specification range

for iron in magnesium of 250 to 350 ppm is indicated to meet the present uranium specifications.

The tendency of Dow Grade 5 electrolytic magnesium to expel magnesium vapor and molten slag from the reduction container (observed in a previous test) was not encountered with the Dow Grade 6 material.

Preliminary Reduction Study of Magnesium and Uranium Impurities

The electrolytic magnesium was obtained from Dow Chemical Company as commercial Grade 6 material. The cut-crown magnesium was withdrawn from regular on-site stock supplied by Nelco Metals, Inc., a subsidiary of Charles Pfizer and Company. The two types of magnesium were procured to meet the chemical and physical specifications shown in Table I. Samples of the two materials are shown in Figure 1.

To determine the general reduction characteristics of the electrolytic magnesium and the level of impurities in the uranium metal, production-size reductions were made with both electrolytic and cut-crown magnesium types (four of each type). The same blended lot of UF_4 was used in the reductions, and each 330-pound uranium regulus (derby) was drill-sampled for analysis of the uranium turnings. The average analysis for uranium, related to each magnesium type, is shown in Table II.

These analytical data show the lower aluminum, magnesium, silicon, and lead levels in the uranium derby metal produced using electrolytic magnesium. The values for copper, iron, and manganese are higher in the uranium derby metal produced using electrolytic magnesium.

TABLE I Chemical and Physical Specifications for Magnesium

Chemical		
Impurity Limits (ppm except Mg)	Magnesium Type	
	Electrolytic	Cut - Crown
Magnesium, Percent min	99.8	99.8
Aluminum, max	300	300
Boron, max	0.3	0.3
Cadmium, max	1.0	0.5
Chromium, max	50	—
Copper, max	200	—
Iron, range	250 min, 500 max	225 max
Manganese, max	75	75
Nitrogen, max	200	500
Nickel, max	50	—
Silica (SiO ₂), max	250	250
Zinc, max	300	300
Zirconium, max	100	—
Others (each), max*	100	—
Physical		
U.S. Standard Sieve No. (Mesh)	Electrolytic (Chipped Ingot) (wt %)	Cut - Crown (wt %)
Retained on 4	—	0
Retained on 8	—	10-26
Retained on 10	2 max	—
Retained on 12	—	22-30
Retained on 16	—	19-25
Retained on 20	50-66	12-19
Retained on 30	26-40	7-11
Retained on 40	3-10	—
Retained on 50	1-3	5-11
Retained on 120	2.5	0.5-3.0
Through 120	0.2 max	0.2 max

* Except oxygen, which shall be included in the total impurity content at a maximum of 0.2% in order to maintain the 99.8% minimum magnesium content.

The impurity of primary interest in this work was iron. On a uranium basis, the UF₄ contained 65 ppm iron while the magnesium contained 66 ppm and 2 ppm, respectively, for the electrolytic and cut-crown types. These values indicate that approximately 30 ppm of the iron content is being contributed by the by-product magnesium fluoride slag used as a refractory liner to protect the steel reduction vessel.

TABLE II Uranium Derby Analytical Results

Impurity	Magnesium Type	
	Electrolytic (ppm)	Cut - Crown (ppm)
Aluminum	< 6	41
Boron	< 0.15	< 0.15
Beryllium	< 1	< 1
Bismuth	< 1	< 1
Cadmium	< 0.2	< 0.2
Chromium	20	20
Copper	37	31
Iron	165	98
Magnesium	12	> 22
Manganese	20	9
Molybdenum	< 6	< 6
Nickel	64	64
Lead	3	11
Silicon	< 10	13
Tin	4	4
Vanadium	< 5	< 5

The reductions involving the electrolytic magnesium showed no tendency to expel magnesium vapor or molten slag from the reduction vessel during the reaction. This behavior was in contrast to earlier, unreported reduction studies with Dow Grade 5 electrolytic magnesium. (This material had a lower iron content, meeting the cut-crown magnesium specification.) The Grade 5 magnesium showed a marked tendency to expel magnesium vapor and molten slag as the magnesium excess was increased above the stoichiometric requirement, and, in addition, showed a reluctance to begin reacting at furnace temperature settings which are satisfactory for ferrosilicon process crown or ingot magnesium.

Expanded Production - Scale Evaluation

After the scoping reduction study above indicated that acceptable quality uranium metal could be obtained from electrolytic magnesium, a 2-ton quantity of Dow Grade 6 electrolytic magnesium was obtained for a plant test. Derbies were produced and cast into ingots for each of three major fuel core production streams. The products of

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ELECTROLYTIC

CUT-CROWN

FIGURE 1 Electrolytic and Cut-Crown Magnesium Types

these three streams, which will be designated A, B, and C, have iron specifications as follows:

	Allowable Iron Content (ppm)
Product A	125 to 225
Product B	115 to 200
Product C	100 to 200

The data obtained in the reduction and ingot steps for Product A are representative of results obtained for the other two product streams; hence they are used (in Table III) to illustrate the results obtained between the electrolytic and cut-crown magnesium types.

The data in Table III show the similarity in reduction and ingot results between the two magnesium types. (The firing time difference is fortuitous and is not considered to have any significant effect on the other responses.)

The uranium ingot analytical data in Table IV show the similarity for most impurities between electrolytic and cut-crown magnesium types. The iron values were of particular interest in this evaluation and indicate that the specification range (125 to 225 ppm) was readily met with the uranium ingots related to electrolytic magnesium (175 ± 21 ppm at the 95% confidence level). The 207 ppm iron value of the uranium ingots related to cut-crown magnesium was obtained by adding elemental iron to the crucible charge.

Conclusions

This evaluation demonstrated the satisfactory characteristics of electrolytic (Dow Grade 6) magnesium for uranium production operations. The ingot analyses for iron indicate that a specification range of 250 ppm to 350 ppm iron in the magnesium would be satisfactory for meeting the specification range for this element in the uranium product.

TABLE III Reduction and Ingot Results - Product A

Mg Type*	Reduction Phase			Ingot Phase		
	Firing Time (min)	Derby Yield (%)**	Derby Density (g/cm ³)†	Charge Composition (%)		Finished Ingot Yield (%)
				Derby Metal	Nonvirgin Metal	
Cut-Crown	280	98.3	18.5	67.9	32.1	92.0
Electrolytic	253	98.3	18.7	67.9	32.1	92.2

* Optimum reduction results were found at magnesium weights of 4.1% and 2.5% above stoichiometric requirements for cut-crown and electrolytic magnesium types, respectively.

** Derby yield adjusted for derby density.

† Derby density determined by Archimedes' principle (weight of derby in air compared with weight immersed in water).

TABLE IV Comparison of Uranium Ingot Analyses of Electrolytic and Cut-Crown Magnesium

Impurity	Electrolytic (ppm)	Cut-Crown (ppm)
Aluminum	< 7	23
Beryllium	< 1	< 1
Boron	< 0.15	< 0.15
Cadmium	< 0.2	< 0.2
Carbon	412	388
Chromium	23	24
Copper	11	9
Hydrogen	1.0	1.0
Iron	175	207
Magnesium	< 4	< 4
Manganese	12	10
Nickel	39	39
Nitrogen	13	18
Silicon	187	187
Zirconium	< 5	< 6
Density	18.95 g/cm ³	18.94 g/cm ³

Acknowledgements

The assistance of J. L. Gindlesperger, W. A. Schrader, and H. L. Smay in supervision of the operational steps is gratefully acknowledged.

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4. CONTROLLING FURNACE CYCLE WITH INFRARED PYROMETERS IN THE CASTING OF LARGE URANIUM INGOTS

G. Brodi

A. E. Abbott

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Abstract

Two-thousand-pound ingots were cast in a plant test to determine the feasibility of controlling the melting cycle of NPR furnaces with infrared radiation pyrometers sighted on the crucible pour plug. The ingots cast were compared in a statistical test with control ingots cast by the conventional time-power cycle.

Introduction

Many methods have been used in the past to control the remelt operation. The method presently in use, control of the remelt pour temperature by regulating the furnace power on a time cycle, cannot eliminate variations in melt temperature caused by differences in the thermal efficiency of the individual furnaces. An immersion thermocouple was developed to measure bath temperatures, but its use is not practical in the present production furnaces.

Encouraging results were obtained by sighting an infrared radiation pyrometer through a port in the furnace shell onto the graphite pour plug of the crucible during the melting cycle. After the pour plug is sheared, the pour stream is also viewed by the sensing device. The pyrometer readings of the pour plug and the pour stream can then be converted into temperatures, provided their emissivities are known.

Previous Work on the Project

Early work in the Pilot Plant on this project established the general feasibility of the concept of using infrared pyrometers to control the remelt pouring temperature.¹ A later Pilot Plant test confirmed the earlier test results and demonstrated

close control of temperature over 11 heats.² A large-scale test in the Metals Production Plant showed that reproducible results could be attained over a 4-week period using pyrometers of the same model on more than one furnace.³

Objectives for this Quarter

The principal objective for this quarter was to determine if the same infrared pyrometers used for controlling the remelt cycle of the Metals Production Plant furnaces, in which 1400-pound ingots are produced, could also be used for controlling the remelt cycle of the larger NPR furnaces, in which 2000-pound ingots are produced. A secondary objective was to perform a statistical analysis on the test data.

Summary of Results

The infrared pyrometric equipment that had been used in the Metals Production Plant test was installed on two NPR furnaces in the Special Products Plant. For 4 weeks, half of the ingots produced were cast by controlling the melting cycle according to predetermined infrared pyrometer readings of the crucible pour plug. The remaining ingots were produced by the standard power-time cycle.

The results of this test demonstrated that the melting cycle could be controlled by infrared pyrometers when melting 2000-pound charges. The ingots produced were poured within a narrow temperature range. Reproducible results were obtained over an extended period of time with different pyrometers of the same model used on the two furnaces.

Results of the statistical analysis may be summarized as follows:

1. When the remelt cycle was controlled by pyrometer, there were no significant differences in the pour stream temperature 20 seconds after the start of pouring either between furnaces or at any time during the test. However, the time necessary to reach the pouring temperature did increase as the test proceeded.

2. When the remelt cycle was controlled by the standard power-time cycle, the pour stream temperature 20 seconds after the start of pouring varied as much as $125 \pm 43^\circ\text{F}$ during the 4-week test period, the temperatures decreasing as the test proceeded.

3. The carbon contents of both the test and control ingots decreased steadily as the test proceeded (510 to 419 ± 34 ppm, average).

Test Equipment and Procedure

The equipment used in this test was the same as that used in the work previously reported.^{1,2,3} The infrared radiation pyrometers used were Thermot Model TD-6B's. Two NPR furnaces were modified by cutting openings in the furnace shell and refractory so that the pyrometer could be sighted directly on the graphite pour plug in the bottom of the crucible and on the uranium pour stream after the plug was sheared. The commercial-grade fused-quartz sight port was protected by a remotely controlled shutter.

To convert infrared pyrometer readings to temperatures, it is first necessary to know the emissivity of the radiation source. The emissivity of the graphite crucible pour plug was determined in this test by a method similar to that previously reported.³ A strip of silver was cemented to the pour plug, and the pyrometer was sighted on an area of the graphite plug immediately adjacent to the strip. At the instant the silver melted (1760°F), a pyrometer reading was taken. In this manner the apparent emissivity of the pour plug was found to be 0.95. These silver strips were cemented to the pour plugs at the beginning of each week so that the reproducibility of the pyrometer readings could be checked.

An apparent emissivity of 0.47 for the uranium pour stream was derived by correlating immersion thermocouple temperature measurements with pyrometer readings of the pour stream 20 seconds after start.

Experimental work performed in the Special Products Plant prior to the start of the reported test program revealed that a pour plug pyrometer reading of 2085°F resulted in a uranium pour stream temperature of 2750°F and produced ingots of good metal quality.

The power cycles for the test and control ingots were as follows:

Crucible Coil (kw)	Cycle 2 (2 to 3 Derby Charge)		Cycle 3 (3 to 4 Derby Charge)	
	Test	Control	Test	Control
170	69 min	69 min	73 min	73 min
140	2085°F on Pyrometer or 70 min	60 min	2085°F on Pyrometer or 70 min	60 min
0	5 min	5 min	5 min	5 min

— POUR —

After 32 hours of operation in the test period, the power cycle for three-derby charges was changed from cycle 3 to cycle 2 because the pour temperature of the control ingots was consistently higher than the pour temperature of the test ingots as determined by the pyrometer readings.

During some preliminary experimental work prior to the test run, a condition developed that had not been present during the pyrometer evaluation in the Metals Production Plant. Immediately after the plug was sheared a condensate formed on the sight port which altered the pyrometer reading of the pour stream. The cause of the condensate was not immediately determined. This problem was circumvented by closing the solenoid-activated shutter just prior to pouring and keeping it closed for 3 seconds after shearing the plug. By that means, the vapor was prevented from condens-

ing on the sight port. The few seconds that the shutter was closed did not hamper the operation.

All ingots cast were analyzed individually for carbon content to obtain data for the statistical analysis.

Statistical Test

Test Design

The statistical investigation of the variables is based on analysis-of-variance⁴ of a balanced block design. In a block experiment, the major variables likely to be affected by uncontrollable or random variables associated with time are considered. A balanced experiment means that an equal amount of data is studied for each variable within each block. Consequently, out of all the ingots cast during the 4-week period, only matched data were used in setting up nine balanced blocks. A block consisted of 12 ingots cast within a 3-day period. The casting conditions by block were as follows:

Casting Sequence	Furnace No.	Casting Conditions
1	1	Test
2	2	Control
3	1	Test
4	2	Control
5	1	Test
6	2	Control
7	1	Control
8	2	Test
9	1	Control
10	2	Test
11	1	Control
12	2	Test

Confidence limits throughout the statistical analysis were held at 95%.

The variables examined were (1) the time necessary to reach 2085°F on the pour plug by pyrometer, (2) pyrometer readings at power off, start of pour, and 20 seconds after the start of pour, and (3) the individual ingot carbon analyses.

Test Results and Discussion

1. Time Needed to Reach 2085°F on the Graphite Pour Plug

The variations in the time required to reach 2085°F on the pyrometer are depicted graphically in Figure 1 by block. The test ingots produced during the first 2 days (block 1) by pyrometer control were poured in a significantly shorter time than during any other day of the test. During this 2-day run, the first step of the power cycle was reduced from 73 to 69 minutes because of the obvious high pour temperatures achieved. However, the ingots produced during the time period represented by the last two blocks were poured in a significantly longer time than the ingots produced in the time periods of blocks 1, 2, and 6; therefore, there are definite factors that influence the pour temperature by time.

With the test ingots, there was a statistically significant difference between the two furnaces in the average time required to reach the same pour temperature. It required 2.6 ± 1.5 minutes longer to reach the pour temperature in furnace 1 than furnace 2. The difference is not great and

FIGURE 1 Minutes of Power On at 140 kw, Test Ingots

probably is due to the difference in the ages of the refractories in the two furnaces.

2. Pyrometer Readings

At Power Off - The differences between the average pour plug temperatures of the test and the control ingots were statistically significant ($10 \pm 7^\circ\text{F}$).

The pour plug temperatures of the control ingots (cast by a power-time cycle) at power off steadily decreased as the test progressed. They varied from a high of $2105 \pm 15^\circ\text{F}$ for the first block to a low of $2045 \pm 15^\circ\text{F}$ during the last block. Figure 2 shows the interaction between these temperatures and the blocks.

Start of Pour - The average temperature at the start of the pour stream for the test ingots (controlled by pyrometer) was $25 \pm 15^\circ\text{F}$ hotter than the temperature at the start of the pour stream for the control ingots. Also, the temperature at the start of the pour stream from furnace 2 was $40 \pm 15^\circ\text{F}$ hotter than the start of the pour stream from furnace 1.

FIGURE 2 Pour Plug Temperatures at Power Off, Control Ingots

With the test ingots, there were some interactions between the temperature at the start of the pour stream and the blocks. The pour streams of block 9 were hotter than those of blocks 1 and 6 by 50 and $40 \pm 30^\circ\text{F}$, respectively. With the control ingots, there were even greater differences noted in the temperatures of the pour streams at start of pour among several of the blocks, as shown in Figure 3. The pour streams of those ingots poured during the first day averaged $80 \pm 30^\circ\text{F}$ hotter than those poured during the last day of the test.

20 Seconds After Start of Pour - The pour stream temperature 20 seconds after the start of pour for **all ingots** cast in furnace 2 averaged $35 \pm 22^\circ\text{F}$ hotter than the pour stream temperature 20 seconds after start of pour for **all ingots** cast in furnace 1.

The average pour stream temperatures of the test ingots differed by no more than $15 \pm 35^\circ\text{F}$ by block and hence, were not significantly different. However, the average pour stream temperatures of the control ingots differed by as much as $125 \pm 43^\circ\text{F}$ by block as shown in Figure 4.

FIGURE 3 Uranium Pour Stream Temperatures at Start of Pour, Control Ingots

FIGURE 4 Pour Stream Temperatures 20 Seconds After Start of Pour, Control Ingots

3. Carbon Analyses

The decrease in pour temperatures as the test progressed was accompanied by lower carbon values toward the end of the test. Figure 5 shows this trend toward lower carbon values for all ingots, test and control combined. This trend in carbon values would be expected for the control ingots produced by the power-time melting cycle at progressively lower temperatures but would not be expected for the test ingots that were produced under pyrometer control and, hence, were cast at a constant temperature. Since the melt cycle became longer toward the end of the test period, more time was available for carbon pickup.

This trend in carbon values, as well as some of the other trends mentioned above that increased or decreased steadily as the test progressed, may be attributable to variations in the crucible charge composition. The slag content of the derbies in the charge was observed to increase as the test proceeded, and this is the only known condition not held constant during the test. This variable will be investigated in future work.

FIGURE 5 Carbon Content of Combined Test and Control Ingots

Conclusions and Recommendations

It is concluded that infrared pyrometers can be used satisfactorily to determine (1) when the melt should be poured, and (2) the temperature of the pour stream in the furnaces used to cast 2000-pound NPR ingots.

It is recommended that infrared pyrometers of the type tested, or their equivalent, be installed on all remelt furnaces.

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5. THERMOELECTRIC COOLING OF CUTTING TOOLS

R. D. McCright

Abstract

The effect of thermoelectric, or Peltier, cooling on the tool life of carbide cutting tips when machining uranium was evaluated. The test results showed no significant improvement in tool life when thermoelectric cooling was used.

Introduction

Cutting tools used to machine uranium rods and tubes to finished fuel cores at the National Lead Company of Ohio are tipped with special grades of carbide. In the continuing effort to optimize machining conditions and reduce production costs, much attention has been focused on tool life, since improvements in this area could yield sizable cost savings.

Cutting tool life is inversely related to the temperature generated at the cutting tool-chip interface. In a previous study, it was shown that cutting speeds in the range used in this test (400-600 sfpm) produced high temperatures (1250 to 1695°F) at the tool-chip interface.¹ Therefore, any condition that reduces the cutting tool temperature should increase tool life. At present, large quantities of cutting fluid flood the work to increase tool life and to cool the pyrophoric chips. It had been reported that thermoelectric, or Peltier, cooling of cutting tools was another technique by which tool temperatures could be reduced and tool life thereby increased.²

According to the Peltier principle, when a direct current is made to flow in a closed loop of two dissimilar conductors, heat is generated at one junction and is absorbed at the other. If this system is arranged so that the cold junction is in thermal contact with the cutting tool, the heat produced

during cutting is conducted through the tool and into the thermoelectric circuit by way of the cold junction.

The Peltier emf, a thermoelectric work function, is determined by the conductor pair constituting the thermoelectric loop. The amount of energy that can be absorbed by the system is the product of the Peltier emf and the direct current in the thermoelectric loop. The thermoelectric circuit materials are usually dipped semiconductors; several circuits are banked in a cascade arrangement to be electrically in series, thermally in parallel.³

The objective of the reported work was to evaluate the effect of thermoelectric, or Peltier, cooling on cutting tool life. Uranium was machined both with and without such cooling under otherwise identical conditions.

Summary of Results

Test results indicated that the thermoelectric equipment used was incapable of absorbing enough heat from the cutting zone to reduce significantly the temperature at the tool-chip interface; consequently, there was no appreciable increase in tool life. Temperature measurements during the test showed that only a very small portion of the heat produced was conducted through the tool and into the thermoelectric circuit; nearly all of the heat produced in cutting was carried away by the chip and the coolant.

Experimental Methods

The Peltier cooling unit was manufactured by Meyers Electro-Cooling Products, Inc., of Manchester, Connecticut. The unit, a Model 201A Electro/Cooler, is about 6 inches wide by 8 inches long by 4¼ inches high and was mounted on the cross slide of a Monarch Model 20 Monomatic lathe.

The Electro/Cooler head, Figure 1, houses the thermoelectric modules. These modules are insulated from the copper housing by thin strips of an electrically insulating, thermally conductive material. All components of the clamp assembly (seats, anvils, shims) are copper plated so that the carbide cutting insert is in thermal contact with the thermoelectric modules. To further facilitate heat transfer, the carbide insert is coated with silicone lubricant to insure good contact of the tool with the copper-plated components. Heat from the "hot" junctions of the modules is removed by circulating water through the head.

The power for the Electro/Cooler head was supplied by converting 115-v, single-phase ac to

10-v, 45-amp dc by means of silicon diode rectifiers. A system of relay switches prevents damage to the modules by de-energizing the dc circuit if insufficient water circulates through the head or if the water is too warm.

Since the manufacturer does not recommend using the Electro/Cooler head as a tool holder without having the Peltier cooling system energized, standard tool holders (Kennametal KTDR-86 and KTDR-86C) were used for the control tests without Peltier cooling.

The carbide cutting tips used in the test were in the form of disposable triangular inserts. These inserts were of WL grade (Model TNG-432 and

1783

FIGURE 1 Electro/Cooler Tool Head

TPG-432) manufactured by Firth Sterling, Inc., Pittsburgh, Pennsylvania. Auxiliary equipment included a hand tachometer for setting the speed, an electric clock to time the machining operation, and a stereoscopic microscope (60X) to measure the land wear.

Procedure

Tool life was defined as the elapsed time from the start of cutting until (1) a 0.015-inch uniform wear land or a 0.030-inch localized wear land formed on the side flank, or (2) the tool fractured. The wear land was observed and measured under the microscope at the end of each pass across the workpiece, or fraction of a pass when failure seemed imminent. When standard conditions were used, machining was resumed immediately after the tool was examined. However, when the Electro/Cooler was used, sufficient time (15 minutes) was allowed between passes to permit the tool to become chilled.

Conditions

Tests were run at 400, 500, and 600 surface feet per minute, with negative and positive tool geometries, and with and without thermoelectric cooling.

All other variables were held constant, as listed below:

Workpiece Material: Normal unalloyed uranium, double beta heat treated before machining; hardness, R_B 84 to 88

Tool Material: WL carbide (73% WC, 21% TaC, 6% Co) triangular inserts.

Depth of Cut: 0.050 inch

Feed: 0.010 inch/revolution

Cutting Fluid: Texaco C water-soluble oil diluted 17:1.

It was necessary to use cutting fluids for all tool-life tests to prevent chips from welding to the cutting tool flank. Furthermore, the pyrophoricity of uranium made it necessary to quench the chips as they were formed.

Results

Tool-Life Tests

Six different machining conditions, three machining speeds and two tool geometries (negative and positive) were evaluated with and without thermoelectric cooling. Three to six individual tool life tests were performed for each condition. Results of the tests using negative geometry tools are tabulated in Table I.

TABLE I Tool Life Tests Using Negative Tool Geometry

Speed (sfpm)	Thermoelectric Cooling	No. Tests	Tool Life* (min)		Type Failure
			Range	Mean	
400	No	6	16.6-36.0	25.9	(4) Fracture (2) Uniform wear land
400	Yes	5	2.7-37.8	18.5	(2) Fracture (3) Uniform wear land
500	No	5	1.7-3.1	2.2	Uniform wear land
500	Yes	5	1.9-5.7	3.5	Uniform wear land
600	No	5	1.8-2.6	2.2	Uniform wear land
600	Yes	5	1.8-2.3	2.0	Uniform wear land

* Tool signature was -5° , -5° , 5° , 5° , 60° , 30° , $\frac{1}{32}$ inch.

Note: The tool signature is the listing of the various tool angles and the nose radius, given in this order: back rake angle, side rake angle, end relief angle, side relief angle, end cutting edge angle, side cutting edge angle, and nose radius in inches.⁴

Results of tool life tests using positive geometry tools are tabulated in Table II.

Unfortunately, the data for tests with and without thermoelectric cooling using the positive tool geometry are not directly comparable because of the difference in back rake angle. Increasing the rake angle decreases the included angle of the tool and increases the temperature at the cutting tip.⁵ This difference is small even for large changes in the rake angle. However, it may account for the results in Table II indicating that when thermoelectric cooling was used tool life tended to be slightly lower than when no thermoelectric cooling was used.

Because tool life tests tend not to be easily reproducible, emphasis should be given to the range of values obtained rather than to the mean value when the number of tests is small. Thus, in the case of negative tool geometries, where all other machining conditions are the same, the tool life data with and without thermoelectric cooling cover much the same range of values at a given machining speed.

The tool life data are plotted in Figures 2, 3, 4, and 5 to conform to the Taylor equation $Vt^n = C$ where V is the cutting speed, t is the tool life, n is an exponent, and C is an empirical constant. For sintered carbides n is approximately 0.25.⁶ All but one of the curves approximate this slope.

The increase of wear with machining time is nearly the same for tools used with and without thermoelectric cooling. This is shown in Figure 6.

Temperature Measurements

Temperatures of the carbide tool insert at rest while being cooled by the Electro/Cooler are shown in Figure 7. These temperatures were measured by a chromel-alumel thermocouple embedded in a slot ground into the tool face. Temperature measurements at several points on the tool showed about the same cooling rate. All of these points reached the same minimum temperature, -22°F .

Temperatures of the carbide inserts were measured during cutting also by embedded chromel-alumel thermocouples. The thermocouple locations were as follows: Point A was on the top (rake) surface about 0.15-inch from the nose. Point B was on the bottom surface of the tool immediately below A. Point C was on the top surface about 0.70-inch from the nose. Point D was on the bottom surface immediately below C. Machining was done with and without thermoelectric cooling and with and without cutting fluid. The temperatures measured are listed in Table III.

The temperatures listed in Table III indicate that thermoelectric cooling does not cool the tool sufficiently to make an appreciable difference in tool life.

TABLE II Tool Life Tests Using Positive Tool Geometry

Speed (sfpm)	Thermoelectric Cooling	No. Tests	Tool Life* (min)		Type Failure
			Range	Mean	
400	No	3	12.5-19.1	16.0	Fracture
400	Yes	3	7.1-18.3	13.4	Fracture
500	No	3	5.7-8.1	7.3	Fracture
500	Yes	3	2.5-7.1	4.8	Fracture
600	No	4	2.0-3.1	2.4	(2) Fracture (2) Uniform wear land
600	Yes	3	2.1-3.4	2.9	Fracture

* Tool signature was $0^{\circ}, 5^{\circ}, 5^{\circ}, 5^{\circ}, 60^{\circ}, 30^{\circ}, \frac{1}{32}$ inch for the tests run without thermoelectric cooling and was $5^{\circ}, 5^{\circ}, 5^{\circ}, 5^{\circ}, 60^{\circ}, 30^{\circ}, \frac{1}{32}$ inch for the tests run with thermoelectric cooling. (See footnote to Table I for definition of tool signature.)

FIGURE 2 Tool Life of WL Carbide Without Thermoelectric Cooling; Negative Tool Geometry

FIGURE 4 Tool Life of WL Carbide without Thermoelectric Cooling; Positive Tool Geometry

FIGURE 3 Tool Life of WL Carbide with Thermoelectric Cooling; Negative Tool Geometry

FIGURE 5 Tool Life of WL Carbide with Thermoelectric Cooling; Positive Tool Geometry

FIGURE 6 Wear Pattern of Carbide Cutting Tools With and Without Thermoelectric Cooling

FIGURE 7 Cooling Rate of Carbide Tool Cooled by Thermoelectric Unit

TABLE III Thermocouple Temperature Measurements of Tool Tip (°F)

	Location*			
	A	B	C	D
Without Thermoelectric Cooling:				
Without Cutting Fluid	250	179	114	99
With Cutting Fluid	160	120	85	80
With Thermoelectric Cooling:				
Without Cutting Fluid	205	145	28	22
With Cutting Fluid	155	120	56	34

* See text for locations of thermocouples on tool tips.

Note: The above tests were run at 400 sfpm, with the negative tool geometry. Temperature of the cutting fluid was 75°F. All other conditions were those given in text as applying to all tests.

Temperatures were also measured at the chip-tool interface using a technique, previously reported,⁷ in which the tool and the workpiece form the two elements of a thermocouple. An emf is generated which is proportional to the temperature at the interface. The temperatures given by this method were as follows:

Without thermoelectric cooling

Without cutting fluid — 1310°F

With cutting fluid — 1250°F

With thermoelectric cooling

Without cutting fluid — 1370°F

With cutting fluid — 1310°F

These results show a **lower** temperature at the tool-chip interface when thermoelectric cooling was **not** used. A possible explanation of this rather surprising result is as follows: A temperature differential existed at the point of contact between the copper lead and the carbide tool, the differential being approximately that shown by the temperature differences between points C and D in Table III. Thus another emf may have been introduced into the system at the copper-carbide junction to bias the results above.

A rough estimate of the heat dissipation from the cutting zone by the chip and by conduction through the tool would be that the chip removed 78.5 Btu/min and the tool removed 1.1 Btu/min. These figures are based on calculations of the heat flux through the tool and on the specific heat of uranium.

Conclusions

It is concluded that:

1. Thermoelectric cooling is ineffective in decreasing the temperature of the tool-metal interface during the machining of uranium and therefore does not increase tool life. The very small area of contact between tool and chip permits only a small percentage of the heat produced at medium cutting speeds to be conducted through the tool. The chips remove most of the heat. Therefore, thermoelectric cooling offers no advantage over the present uranium machining method.

2. There was no evidence of catastrophic spalling of the chilled carbide tool during the machining operation. The wear and cratering patterns were similar in tests run with and without thermoelectric cooling, all other machining conditions remaining the same.

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6. INHIBITION OF CORROSION OF TYPE -304L STAINLESS STEEL FROM FLUORIDES IN NITRIC ACID SOLUTIONS

T. R. Kato

Abstract

The inhibiting effects of Fe^{+3} , Al^{+3} , and Th^{+4} ions on the corrosion rate of type -304L stainless steel in nitric acid solutions containing 0.1M HF were investigated over a temperature range of 80 to 190°F. Corrosion data obtained show that all three types of ions are capable of reducing the corrosion rate to a tolerable level, depending upon the cation-fluoride ratio, acid normality, and temperature.

Introduction

The process equipment used at this site for the recovery and purification of uranium and thorium is constructed largely of type -304L stainless steel. Aqueous solutions used in digestion, filtration, extraction, evaporation, and denitration contain nitric acid in varying concentrations, and many of the feed materials contain fluorides which are soluble in nitric acid solution. The corrosion of stainless steel proceeds at a more rapid rate when fluoride ions are present. Fortunately, however, this increase in the corrosion rate can be inhibited by inorganic cations.^{1,2,3,4}

This study was undertaken to determine the conditions for effective control of fluoride corrosion of stainless steel process equipment at the National Lead Company of Ohio. Specifically, the objective was to determine the amounts of Fe^{+3} , Al^{+3} , or Th^{+4} necessary to hold to a tolerable level (25 mils per year) the corrosion rate of type -304L stainless steel in nitric acid solutions ranging from 2N to 12N and containing 0.1M HF. The temperatures studied ranged from 80°F to 190°F.

Summary of Results

The results of the laboratory tests were as follows:

1. The inhibiting effects of the three cations studied on the corrosion rate of type -304L stainless steel in HNO_3 -HF acid solution depend upon the cation-to-fluoride ratio, the acid concentration, and the temperature.
2. Th^{+4} ions have greater inhibiting effect than Al^{+3} ions at lower acidity; but at higher acidity, Al^{+3} ions are more effective in reducing corrosion.
3. Fe^{+3} can reduce the corrosion rate at low HNO_3 concentration and low temperature.

Test Procedure

Laboratory corrosion rates were calculated by the weight-loss method. A total of 400 cc of test solution was used for each 1-inch by 3-inch by $\frac{1}{16}$ -inch specimen of type -304L stainless steel. All tests were performed in the liquid phase in 600-cc polypropylene bottles which were placed in a constant-temperature water bath. The duration of the tests varied from 4 to 72 hours. Calculated amounts of iron, aluminum, or thorium were added as the nitrate.

Discussion

Uniform corrosion occurred on all type -304L specimens over the temperature range of 80°F to 190°F in HNO_3 -HF solutions containing Fe^{+3} , Al^{+3} , or Th^{+4} ions. The fluoride complexes formed were found to be less stable at higher HNO_3 concentrations as the temperature increased.

All three types of ions were capable of reducing corrosion to a tolerable level (25 mils per year) or lower. Specific results were as follows:

Effect of Al^{+3}

Figures 1 and 2 summarize the effect of 0.1M and 0.2M Al^{+3} ion additions to nitric acid solutions containing 0.1M HF. An Al/F molar ratio of 2 is required to reduce the corrosion rate below 20 mils per year in 12N HNO_3 at 190°F.

Effect of Th^{+4}

Figures 3, 4, 5, and 6 show the effect of 0.01M, 0.05M, 0.1M, and 0.2M Th^{+4} additions to nitric acid solutions containing 0.1M HF. Th^{+4} additions have greater inhibiting effects than Al^{+3} below 6N HNO_3 at all temperatures studied, but at 12N HNO_3 , Th^{+4} has less inhibiting effect.

Effect of Fe^{+3}

Figures 7 and 8 summarize the effect of adding 0.1M and 0.2M Fe^{+3} to a nitric acid solution containing 0.1M HF. Iron can be used as an inhibitor at temperatures below 160°F provided the Fe/F molar ratio is at least 2 and the HNO_3 normality is less than 8. Work now in progress indicates that at an Fe/F ratio of 6, higher temperatures can be tolerated.

FIGURE 1 Effect of Aluminum Addition on the Corrosion Rate of Type-304L Stainless Steel (0.1M Al^{+3} , 0.1M HF, Al/F = 1.0)

FIGURE 2 Effect of Aluminum Addition on the Corrosion Rate of Type-304L Stainless Steel (0.2M Al^{+3} , 0.1M HF, Al/F = 2.0)

FIGURE 3 Effect of Thorium Addition on the Corrosion Rate of Type-304L Stainless Steel (0.01M Th^{+4} , 0.1M HF, Th/F = 0.1)

FIGURE 4 Effect of Thorium Addition on the Corrosion Rate of Type-304L Stainless Steel (0.05M Th^{+4} , 0.1M HF, Th/F = 0.5)

FIGURE 6 Effect of Thorium Addition on the Corrosion Rate of Type-304L Stainless Steel (0.2M Th^{+4} , 0.1M HF, Th/F = 2.0)

FIGURE 5 Effect of Thorium Addition on the Corrosion Rate of Type-304L Stainless Steel (0.1M Th^{+4} , 0.1M HF, Th/F = 1.0)

FIGURE 7 Effect of Iron Addition on the Corrosion Rate of Type-304L Stainless Steel (0.1M Fe^{+3} , 0.1M HF, Fe/F = 1.0)

FIGURE 8 Effect of Iron Addition on the Corrosion Rate of Type-304L Stainless Steel (0.2M Fe^{+3} , 0.1M HF, Fe/F = 2.0)

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7. THE DETERMINATION OF U^{235} BY GAMMA-RAY SPECTROSCOPY

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Abstract

A gamma-ray spectrometric method has been developed for the rapid measurement of U^{235} in uranium solution samples. The 184-keV gamma ray of U^{235} is measured after U^{238} decay products have been removed by liquid-liquid extraction. Total analysis time is less than 2 hours, and the precision is better than ± 0.02 wt % U^{235} up to the 5% U^{235} level. Standards need be run only occasionally since the count rate is corrected for drift by means of a special U^{235} standard. Technicians can operate the system with a minimum of training.

Introduction

A program to recover uranium from residues containing up to 5 wt % U^{235} was initiated at this site. The residue materials were blended to produce a final isotopic concentration of 1.25 wt % U^{235} . Rapid isotopic analysis was required at several points in the process stream to maintain process and nuclear safety control. Although a gas-type mass spectrometer was used to measure the U^{235} of the mixing tank solution before and after blending, it could not be used efficiently at other stages because of the large range of U^{235} values encountered. It was therefore decided to see if a suitable analytical procedure for U^{235} could be developed using gamma-ray spectroscopy. Specific requirements were as follows:

1. A time limit for analysis of 2 hours from receipt of sample to the reporting of results. This was made necessary by the limited storage capacity of the hold tanks used in the process.
2. A precision of ± 0.02 wt % U^{235} at the 95% C. L.
3. A trouble-free, reliable system employing techniques simple enough for use by inexperienced technicians.

Summary of Results

A method was developed that met all of the above requirements for the analysis of U^{235} in uranium residues. The 184-keV gamma-ray activities of residue samples are compared with standards of known isotopic levels. Minimal time is consumed in the measurement of these standards owing to the use of a 99.2 wt % U^{235} special standard. The training time required by personnel unfamiliar with the method is less than 1 week. The time required for analysis from receipt of the sample to reporting is less than 2 hours. The precision of analysis is better than ± 0.02 wt % U^{235} at the 95% C. L. A high degree of reliability was obtained by use of a simple, interchangeable, single-channel analyzer system.

Experimental

A gamma spectral measurement, based on the 184-keV gamma ray emitted by U^{235} , was chosen. To obtain high counting precision, a 3×3 NaI(Tl) crystal with a $1\frac{1}{2}$ -inch-diameter well was used as the detector. This allowed large samples to be counted, thus giving a large count in a relatively short time. The detector was coupled to a single-channel analyzer system that utilized analog peak stabilization. A block diagram of the apparatus is shown in Figure 1. This simple system is highly dependable, and replacements are readily available if they should be required.

When decay products of U^{238} are present, as they are in all uranium feed streams, they produce a significant activity in the 184-keV region. This activity is due principally to bremsstrahlung radiation from hard beta particles. If these decay products are at equilibrium in all samples, their effect is constant; but they do seriously affect the statistical precision of counting. When these decay products are not in equilibrium, as is the

FIGURE 1 Block Diagram of Counting System

case in the process streams, at this site, errors as high as 200% can occur. To correct such drastic errors and increase the statistical precision of counting, analytical samples were first subjected to a chemical separation. This separation involved liquid-liquid extractions with ethyl acetate and α -thenoyltrifluoroacetone (TTA). Figure 2 shows the spectrum of an unseparated sample containing 2.0 wt % U^{235} . This spectrum was taken from the oscilloscope of a 400-channel pulse height analyzer. Figure 3 shows the decay product reduction obtained after ethyl acetate and TTA extractions were made on the sample shown in Figure 2. After extraction, the 4-minute count under the 184-kev peak was 65,252 compared with 69,713 for the sample before extraction. This change is equivalent to an error of 0.15 wt % U^{235} . Larger errors would occur if greater decay product concentrations were encountered.

Because of the buildup of decay product activity with time, it is necessary to count all samples and standards soon after separation. This buildup is illustrated in Figure 4.

1819-2

FIGURE 2 Gamma Spectrum of a 2.0 wt % U^{235} Sample as Received

1819-1

FIGURE 3 Gamma Spectrum of Same Sample as in Figure 2 After Purification

Obviously, the requirements for speed and simplicity could not be met if it were necessary to separate and count several standards each time a sample was run. Ideally, standards should be run only occasionally and the sample counts corrected for count rate shifts in the instrumentation. To accomplish this correction, a special standard was made up from 99.2 wt % U^{235} that would have a

FIGURE 4 The Effect of Decay Product Build-up on U^{235} Assay

count rate near that of the samples. This standard obviously contained very little of the U^{238} decay products, and it was at equilibrium with its own decay products. While samples or standards are being extracted, this special standard is counted, thereby adding no additional time to the analysis. The ratio of the special standard count taken when the standards were counted and when the sample was counted is used to correct for any count drift.

Method

Special Standard

An 80-mg sample of U_3O_8 with an isotopic assay of 99.2 wt % U^{235} was dissolved in nitric acid and made up to a total volume of 35 ml in a 4 oz polyethylene counting container. This special standard is used to correct daily count rate variations between the samples and the standards.

Standards

Standards, stored as uranyl nitrate solutions, are prepared and counted in the same manner as

the samples described below, except that five aliquots rather than three are averaged. Each of the six standards used is reanalyzed at 3-week intervals, with a pair of standards being analyzed each week. The levels employed ranged from 0.9 wt % to 5.3 wt % U^{235} .

Sample Preparation

Samples in an acid nitrate media are extracted using ethyl acetate; aluminum nitrate is used as a salting agent. The uranium is back-extracted into water and re-extracted with TTA in xylene at a controlled pH. The uranium, in the aqueous phase, is precipitated using hydrogen peroxide. The precipitation cake is converted to U_3O_8 at $900^\circ C$ in moist air.

Three 1-gram aliquots of the U_3O_8 are dissolved in nitric acid and made up to 25 ml in a volumetric flask. The solutions are transferred to 4-ounce polyethylene bottles for counting; 10 ml of water are used for rinsing.

Sample Counting

While the sample is being prepared the special standard is counted for 20 minutes, giving a total count of approximately 4×10^5 . Each sample aliquot is subsequently counted for 4 minutes, and the counts of the three aliquots are averaged. If any one aliquot count deviates more than 1% from any other, a fourth aliquot is counted and included in the average.

Calculation

The average sample count is adjusted for any counting efficiency changes by multiplying it by the ratio of the special standard counts. This ratio is obtained by dividing the special standard count obtained when the standards were run by the special standard count obtained when the sample aliquots were run. A linear interpolation, to determine the wt % U^{235} , is made between the nearest bracketing standards for the adjusted sample count. The form of calculation is as follows:

$$W_s = W_l + \left(\frac{W_h - W_l}{C_h - C_l} \right) (C_s R - C_l)$$

and

$$R = \frac{\text{counts/20 min (measured with standards)}}{\text{counts/20 min (measured with samples)}}$$

where

R = special standard ratio

W_s = wt % U^{235} of unknown sample

W_l = wt % U^{235} of low bracketing standard

W_h = wt % U^{235} of high bracketing standard

C_s = average counts/4 min of unknown sample

C_l = average counts/4 min of low standard

C_h = average counts/4 min of high standard

The terms W_l , W_h , C_l , C_h , and $\left(\frac{W_h - W_l}{C_h - C_l} \right)$ are all determined in advance (when the standards are analyzed) and their values are posted to simplify calculations. Although the curve of standard ac-

tivity versus wt % U^{235} is not truly linear over the entire range of standards used, it approaches linearity between consecutive standards (Figure 5).

Results

A study was made to determine the precision and estimate the accuracy of the method by comparing results with those obtained using a gas-type mass spectrometer. The standards used for all the determinations were counted during a single day and were not reanalyzed during the program. Table I shows the results. Assuming that the mass spectrometer value represents the best value, a precision of ± 0.015 wt % U^{235} at the 95% C. L. was obtained for the gamma spectrometric method. No significant bias was found in the results.

The time required for analysis is approximately 100 minutes. The total analysis time could be cut in half if samples were received and analyzed on a continuous basis, permitting one set to be counted while another was being separated.

FIGURE 5 Variation of Count Rate with Isotopic Level

TABLE I Precision Data (wt % U^{235})

Date of Gamma Analysis	Gamma Spectrometer		Mass Spec Result	Difference
	Individual Results	Average Result		
8/31/65	1.454, 1.430, 1.422	1.435	1.442	-0.007
9/1/65	1.246, 1.256, 1.254	1.254	1.247	+0.007
9/1/65	1.265, 1.266, 1.240	1.257	1.249	+0.008
9/1/65	1.150, 1.141, 1.132	1.141	1.136	+0.005
9/1/65	1.129, 1.137, 1.135	1.134	1.136	-0.002
9/2/65	1.243, 1.232, 1.236	1.237	1.232	+0.005
9/2/65	1.248, 1.245, 1.245	1.246	1.247	-0.001
9/2/65	1.223, 1.225, 1.231	1.226	1.227	-0.001
9/3/65	1.215, 1.220, 1.220	1.219	1.229	-0.010
9/3/65	2.007, 2.025, 2.015	2.016	2.003	+0.013
9/3/65	1.246, 1.240, 1.245	1.244	1.253	-0.009
9/7/65	1.598, 1.606, 1.603	1.603	1.601	+0.002
9/8/65	1.070, 1.064, 1.074	1.068	1.057	-0.011
9/8/65	1.041, 1.043, 1.038	1.040	1.033	+0.007
9/8/65	2.823, 2.835, 2.861	2.840	2.827	+0.013
9/8/65	1.992, 2.011, 2.001	2.001	2.003	-0.002
9/8/65	2.990, 2.992, 2.976	2.986	2.989	-0.003
9/8/65	1.441, 1.444, 1.454	1.446	1.440	+0.006
9/8/65	4.994, 4.981, 4.990	4.988	4.990	-0.002
9/8/65	3.999, 4.037, 4.040	4.025	4.030	-0.005
9/8/65	1.598, 1.610, 1.616	1.608	1.601	+0.007

Two persons each from the second and third shifts of the spectrochemical laboratory were trained to operate the system in 4 days.

The system has now been in operation for 3 months. In addition to running samples for the original program, it has been successfully used for development programs and to determine the per-

cent U^{235} range when isotopic dilutions are to be made for mass spectrometry.

Conclusions

The system described has proven to be a rapid, dependable, analytical tool for the analysis of U^{235} up to 5 wt %. By use of appropriate standards, the system can be expanded to analyze effectively all isotopic levels of U^{235} .

8. THE DETERMINATION OF BETA ACTIVITIES IN PLANT EFFLUENTS

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Abstract

Two methods were devised for determining the beta activity of plant effluents containing uranium and thorium decay products. The lower detection level was 3 d/m/ml of effluent water. The first method, developed for laboratory use, utilizes a barium coprecipitation at high pH, followed by gross beta counting with an anthracene crystal. The second method, developed for plant use, utilizes a detector head consisting of four Geiger-Müller tubes which are submersed for counting in a known volume of effluent. The count is compared with that of a standardized europium-152, 154 solution.

Introduction

A method was needed to determine the beta activity of various plant effluent water streams. These streams were either recirculated for further processing or were mixed with nonactive streams and pumped into the river. Since the mixing ratio depended on such factors as the river flow, etc., a large safety factor was utilized. Therefore, a measurement precision of $\pm 20\%$ at the 300 d/m/ml level was deemed satisfactory. Since storage tank capacity for these effluents was limited, decisions to pump out or reprocess had to be made within about 1 hour of collection time. Hence it was necessary that the analysis be completed in less than 1 hour from the time of sample receipt. The method needed to be such that inexperienced personnel could be easily trained as operators.

To meet these criteria, two methods were developed. The first, or laboratory method, was developed for immediate needs and to serve as a reference method. The second, or operational method, was designed for use by operators of the

water treatment plant. The development of the operational method gave several advantages. First, the time and personnel required for delivery of samples to the laboratory was saved. Second, the personnel handling the effluent could obtain their own results and thereby have a better "feel" for the system. Third, these analyses would not tie up laboratory equipment and personnel.

Summary of Results

Two simple methods to measure the total beta activity of effluent samples were developed.

The laboratory method utilizes a basic barium precipitation and scintillation counting. This method requires approximately 40 minutes of a laboratory technician's time and has a relative precision of $\pm 6.4\%$, (95% C.L.) at the 300 d/m/ml level.

In operational method, four mounted Geiger-Müller (G-M) tubes are submersed in the effluent water system and a count is made. The time required to analyze a sample is 40 minutes, but only approximately 15 minutes of an operator's time is required. The precision of this system is $\pm 17.5\%$ relative (95% C.L.) at the 300 d/m/ml level.

Experimental

Laboratory Method

With the exception of francium-223, all decay products of uranium and thorium are insoluble in strongly basic media. Basic precipitation using a barium carrier was used as a concentrating means. The precipitation was made from 25 ml of effluent. The filter paper was counted by means of 2 - inch by $\frac{1}{4}$ -inch anthracene crystal with a 0.005-inch aluminum mask. This detector was mounted on a 2-inch photomultiplier tube. The assembly was mounted over a sample slide and surrounded by 2

inches of lead. The signal passed through a RC linear amplifier-discriminator to an electronic scaler. The scaler was controlled by an electronic timer. All of these instruments were of the transistorized, modular type.

Self-Absorption Effects

In low-activity samples there is no appreciable self shielding. Most samples of high activity contain large amounts of "mud". Most of the activity was found to reside in the mud and hence, could not be filtered out prior to separation. Consequently, considerable self-shielding was encountered with these samples. Since the self-shielded count, in each case, was well over the cut-off point for repurification, and this uncorrected count was on the low side, no correction was applied. If a correct count was required, smaller volumes of the effluents would have been taken. This self-shielding effect is shown in Figure 1 where various volumes of a particular sample were taken and the apparent specific activity was calculated from the count.

Separation Efficiency

Five samples were studied to determine the separation efficiency. The activity range was from 5 d/m/ml to 5,000 d/m/ml. In each case an aliquot was evaporated to dryness at approximately 120°C, and counted. A second aliquot was analyzed in the normal manner. The filtrate from this second aliquot was slowly evaporated and counted. The results are shown in Table I. The large difference in sample 5 is attributed to self-shielding effects. It was assumed that the separation efficiency was near 100%.

Counting Efficiency

The efficiency of the counting system, instrumental and geometrical combined, was measured by counting standards at the identical position to that used for samples. The results are shown in Table II. A value of 10% was used for the efficiency.

Gamma Ray Interference

Cobalt-57 and -60 and cesium-137 were used to check the efficiency of gamma ray detection. After shielding for beta particles, the count was compared to that obtained with a standardized NaI(Tl) crystal. The anthracene crystal efficiency was 0.03%. This was deemed negligible.

Count Stabilization and Calculation

During each determination, a bismuth-210 beta standard at an identical position to the sample was counted. This standard count was used to

TABLE I Separation Efficiency Data

Sample No.	Specific Activity (d/m/ml)		
	Total Evaporation Method	Normal Method	Filtrate
1	6	6	N.D.
2	15	16	N.D.
3	120	118	N.D.
4	369	378	N.D.
5*	5,250	4,193	N.D.

* Sample had high "mud" content.

N.D. = None Detected

FIGURE 1 The Variation of Specific Activity Due to Selfabsorption

TABLE II Counting Efficiency

Isotope	Energy	Efficiency
Carbon-14	0.155 Mev	3.8%
Thallium-204	0.764 Mev	10.7%
Bismuth-210	1.155 Mev	10.4%
Protactinium-234	2.31 Mev	10.5%

correct for any count drift. Precipitations were made from 25-ml aliquots of effluent, and the precipitates were counted for 10 minutes. The following calculation was used:

$$A = \frac{\bar{C}_s}{25 \text{ ml} \times 10 \text{ min} \times E} \cdot \frac{C_e}{C_b}$$

where: A = the activity in d/m/ml

$\bar{C}_s$ = the average of two aliquot counts that check within 10%, with background subtracted

C_b = the standard count, background subtracted, taken with the sample

E = the counting efficiency

C_e = the standard count, background subtracted, taken when the efficiency was measured.

Operational Method

A fast simple plant system required that the waste water itself be measured without chemical treatment. To have enough activity at low counting ranges, the detector would have to be of large area and be in intimate contact with the sample. For this purpose, submersible G-M tubes with active lengths of 4 inches and window thicknesses of 3 mg/cm² were used.

Four tubes were wired in parallel to give effectively the same area as one tube with four times the surface area. The four tubes were mounted in a Lucite positioner that would mount over a 800-ml graduated beaker. When so mounted, equal distances between the detectors and between the detectors and the walls were maintained. A water volume of 650 ml was used in the beaker. Magnetic stirring was used to maintain any solids

in uniform suspension. Four inches of lead was used to surround the assembly. The G-M tubes are supplied by a stable high-voltage supply and, in turn, feed an electromechanical scaler. The timer is electromechanically operated.

The system is calibrated daily using a europium-152, -154 standard solution which is made up to near 30 d/m/ml and calibrated by the laboratory method. The equation used is as follows:

$$A = C_s \times f$$

where: A = activity of the water sample in d/m/ml

C_s = background corrected sample count taken for 20 minutes

f = factor obtained from the standard count by dividing the standard activity in d/m/ml by the background corrected standard count taken for 20 minutes.

This operational system has been transferred to the water treatment plant and is being operated by their personnel. The laboratory system is now used to calibrate the europium standard and to run occasional check samples.

Results

After good recovery of total activity was demonstrated (Table I), the precision was evaluated. Samples of various concentrations were made by diluting a stock solution with distilled water. The activities of these samples were determined by each of the two methods. The results are shown in Table III. From these limited data precisions were calculated and are shown in Table IV. Since samples are run in duplicate, the precision of results would be better by a factor of $1/\sqrt{2}$.

To determine the precision in the 0 to 50 d/m/ml range to a higher degree, fifteen aliquots of a single sample were run by each method. The results are shown in Table V. Although the scatter is as great as that shown in Table III, the larger number of determinations has reduced the magnitude of the limit. The precision of 95% C.L. for the laboratory method at 38 d/m/ml was found to be ± 10 for one aliquot or ± 7 for duplicates. For

the operational method, the precision at 95% C.L. was ± 13 for a single determination and ± 9 for duplicates.

TABLE III Comparison of Methods

Sample	Laboratory Results	Operational Results
	(d/m/ml)	(d/m/ml)
Undiluted	325	361
	338	320
	319	318
	322	341
	331	310
Average	327	330
1:1 Dilution	165	190
	172	152
	163	129
	158	158
	159	167
Average	164	159
10:1 Dilution	39	22
	29	35
	37	46
	32	29
	25	35
Average	32	33
100:1 Dilution	5	N.D.*
	2	8
	1	4
	7	8
	3	N.D.*
Average	4	4

* None Detected

TABLE IV Method Precision (95% C.L.)
for Single Determinations

Sample	Laboratory Method		Operational Method	
	Average	Precision	Average	Precision
Undiluted	327	± 21	330	± 58
1:1 Dilution	163	± 16	159	± 62
10:1 Dilution	32	± 16	33	± 25
100:1 Dilution	4	± 7	4	± 11

Note: All dilutions were made with distilled water.

TABLE V Results from 15 Aliquots of
One Sample (d/m/ml)

Trial	Laboratory Method	Operational Method
1	37	35
2	32	48
3	41	50
4	38	37
5	41	39
6	35	42
7	40	29
8	32	38
9	35	35
10	37	32
11	48	41
12	36	39
13	39	44
14	31	31
15	42	40
Average	38	38