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**SUMMARY TECHNICAL REPORT FOR THE PERIOD OCTOBER 1, 1959  
TO DECEMBER, 1959 - (USED AS A REFERENCE IN OU1 RI)**

12/31/59

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NLCO-800

Technology - Feed Materials

(M-3679, 23rd Ed.)

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SUMMARY TECHNICAL REPORT  
FOR THE PERIOD  
OCTOBER 1, 1959 TO DECEMBER 31, 1959

Official Classification of this Report is  
UNCLASSIFIED

Although the Original Classification may  
not have been removed from all pages.

F. L. CUTHBERT, DIRECTOR  
C. E. CROMPTON, ASSOCIATE DIRECTOR  
TECHNICAL DIVISION

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TECHNICAL PROJECT SUPERVISION

NATURE OF ACTIVITY (Projects)	PERFORMED UNDER SUPERVISION OF
<u>Chemical</u> Projects Relating to Feed Evaluation, Refining and Chemical Processing.	M. A. DeSesa, Head, Chemical Department.
<u>Metallurgical</u> Projects Relating to Fabrication, Foundry Technology and Physical Metallurgy.	C. E. Polson, Head, Metallurgical Department.
<u>Pilot Plant</u> Metals Development, Pilot Production, Process Engineering and Refinery Operations.	J. O. Davis, Head, Pilot Plant.
<u>Analytical Chemistry</u> Investigations in Wet Chemical and Instrumental Analysis.	J. W. Robinson, Head, Analytical Department.
<u>Statistical Studies and Technical Illustration Services.</u>	P. N. McCreery, Head, Accountability - Quality Control Department.

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SUMMARY

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Edgemont, Gunnison, Lucky Mc, and Uravan concentrates were approved for Refinery processing, while Homestake - New Mexico and Texas Zinc concentrates were not. . . . . 11

A low acid-metal nitrate Refinery flowsheet has been investigated in the Pilot Plant.

Feed materials that have high  $Ca \times SO_4$  numbers or high concentrations of thorium can be processed by use of this flowsheet by blending with other feed materials. . . . . 19

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A valve has been developed that allows more efficient charging of magnesium-UF<sub>4</sub> briquettes into a heated graphite reactor. Two production-size ingots were cast, one partly and one completely from metal produced by the semicontinuous process. Reactor-grade ingots can be made from uranium produced by this process. . . . . 73

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As-cast uranium was found to give shorter tool life during machining than did beta heat treated uranium.

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## 1. FEED MATERIALS EVALUATION

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**Abstract**

Complete feed material evaluations are reported for six uranium concentrates. Partial evaluations are reported for six others.

**Introduction**

The digestion and extraction characteristics of new feed materials must be evaluated prior to their processing in the solvent extraction pulse column system in the Refinery. Also, the chemical analyses of the concentrates must be compared with National Lead Company of Ohio impurity tolerance limits for feed materials, as blending may be necessary to obtain acceptable processing operations with respect to column scale, corrosion, etc., and to obtain acceptable product purity in the final product, uranyl nitrate solution.

Feed material evaluations of twelve feed materials were either initiated, continued and/or completed during this quarter. They are: Durango, Edgemont, Gunnison, Homestake-New Mexico, Homestake-Sapin, Kermac, Lucky Mc, Moab, Phillips Petroleum, Texas Zinc, Uravan, and Vitro uranium concentrates.

**Prior Work on Project**

The feed materials evaluation program has been in existence since January, 1957. It was previously reported<sup>1</sup> that feed material evaluations of 24 feed materials had been completed, while the evaluation of twelve Colorado feed materials was yet to be initiated or was partially completed.

**Objective for This Quarter**

To complete the feed material evaluations for Edgemont, Gunnison, Homestake-New Mexico, Lucky Mc, Texas Zinc, and Uravan uranium concentrates and to initiate or continue the feed material evaluations of Durango, Homestake-Sapin, Kermac, Moab, Phillips Petroleum, and Vitro uranium concentrates.

**Summary of Results**

Feed material evaluations were completed for Edgemont, Gunnison, Homestake-New Mexico, Lucky Mc, Texas Zinc, and Uravan uranium concentrates. Edgemont, Gunnison, Lucky Mc, and Uravan concentrates were approved for Refinery processing. Homestake-New Mexico and Texas Zinc uranium concentrates were not approved for Refinery processing because (1) Homestake-New Mexico contains excessive nitric acid-insoluble uranium and has undesirable extraction characteristics, and (2) Texas Zinc contains an excessive amount of organic compounds, which also results in undesirable extraction characteristics.

**Chemical Analyses of the Concentrates**

A sample of each concentrate investigated is submitted to the Analytical Department at this site for (1) complete spectrochemical analyses and (2) chemical analyses of constituents for which feed materials impurity tolerance limits<sup>2</sup> exist. Wet chemical and complete spectrochemical analyses of nine feed materials are presented in Tables 1.1 and 1.2, respectively.

The analyses of the feed materials show that:

1. Durango, Edgemont, Gunnison, Homestake-Sapin, Phillips Petroleum, Uravan, and Vitro concentrates meet all tolerance limits.
2. Homestake-New Mexico exceeds the tolerance limits for chloride and total organic.
3. Lucky Mc exceeds the tolerance limit for chloride.

Before being used as a feed to the Refinery, Homestake-New Mexico and Lucky Mc would have to be blended to satisfy those impurity tolerance limits which they exceed.

**Laboratory Digestion Tests**

Standard digestion tests<sup>3</sup> consist of (1) laboratory digestion of the concentrates in dilute nitric

TABLE 1.1 Wet Chemical Analyses of Concentrates

Results are given in per cent on a sample basis.

Constituent	Durango Lot 606	Edgemont Lot 116	Gunnison Lot 66	Homestake- New Mexico Lot 64	Homestake- Sapin Lot 42	Lucky Mc Lot 92	Phillips Petroleum Lot 44	Uravan Lot 796	Vitro Lot 168
Uranium (U)	72.70	66.26	69.03	60.02	58.55	62.58	63.38	68.48	73.19
Ammonia (NH <sub>3</sub> )	0.004	0.007	None	None	0.006	0.006	None	0.02	None
Calcium (Ca)	0.26	<0.10	<0.10	0.69	0.51	0.61	0.23	0.64	<0.10
Carbonate (CO <sub>3</sub> <sup>-2</sup> )	0.37	<0.10	<0.10	3.56	2.05	<0.10	1.01	<0.10	<0.10
Chloride (Cl <sup>-</sup> )	<0.010	0.039	<0.010	0.079	0.028	0.10	0.042	0.043	<0.010
Fluoride (F <sup>-</sup> )	0.014	0.037	0.021	0.013	0.013	0.059	<0.010	0.012	0.011
Iron (Fe)	0.33	0.08	0.31	0.13	0.61	0.11	0.12	3.29	0.33
Magnesium (Mg)	<0.50	0.78	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
Molybdenum (Mo)	<0.03	0.07	0.56	0.07	<0.03	0.11	0.05	0.77	0.09
Phosphate (PO <sub>4</sub> <sup>-3</sup> )	0.15	<0.10	<0.10	0.19	0.13	0.31	0.24	3.48	0.39
Silicon Dioxide (SiO <sub>2</sub> )	2.17	0.06	0.04	3.79	3.39	1.54	3.68	0.30	0.14
Sodium (Na)	2.70	3.60	8.70	9.90	7.60	5.50	9.50	0.98	2.30
Sulfate (SO <sub>4</sub> <sup>-2</sup> )	0.78	3.63	4.47	0.90	<0.10	4.67	1.38	2.43	8.62
Thorium (Th)	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Total Organic Material	0.017	0.017	<0.01	0.088	0.065	<0.01	0.027	0.02	<0.01
Vanadium (V)	0.46	<0.10	<0.10	2.42	2.59	<0.10	1.42	0.06	2.30

TABLE 1.2 Complete Spectrochemical Analyses of Concentrates

Results are given in parts per million on a uranium basis.

Constituent	Durango Lot 606	Edgemont Lot 116	Gunnison Lot 66	Homestake- New Mexico Lot 64	Homestake- Sapin Lot 42	Lucky Mc Lot 92	Phillips Petroleum Lot 44	Uravan Lot 796	Vitro Lot 168
Aluminum (Al)	4,000	<400	<400	2,000	6,000	<400	2,000	450	<400
Antimony (Sb)	<20	<70	<20	20	40	<20	<20	<70	<20
Arsenic (As)	<100	<100	<100	100	<100	200	100	3,500	<100
Boron (B)	<2	3	4	8	4	10	3	80	15
Bismuth (Bi)	<20	<20	<20	<20	<20	<20	<20	<20	<20
Cadmium (Cd)	<200	<200	<200	<200	<200	<200	<200	<200	<200
Chromium (Cr)	<100	<100	<100	<100	<100	<100	<100	<200	<100
Cobalt (Co)	<100	<100	<100	<100	<100	<100	<100	<100	<100
Copper (Cu)	100	<100	<100	400	<100	<100	<100	<100	<100
Dysprosium (Dy)	<4	<4	<100	14	13	<4	100	<4	<4
Erbium (Er)	<4	<4	<4	16	14	<4	36	<4	<4
Europium (Eu)	<4	<4	<4	<4	<4	<4	15	<4	<4
Gadolinium (Gd)	<4	<4	<4	8	7	<4	50	<4	<4
Holmium (Ho)	<4	<4	<4	12	10	<4	44	<4	<4
Lead (Pb)	150	120	100	300	200	40	300	60	60
Lutetium (Lu)	<4	<4	<4	<4	<4	<4	15	<4	<4
Manganese (Mn)	1,250	<40	400	<40	40	40	150	120	60
Nickel (Ni)	<20	20	<20	<20	20	20	<20	<20	40
Samarium (Sm)	<4	<4	<4	8	5	<4	50	<4	<4
Terbium (Tb)	<4	<4	<4	<4	<5	<4	23	<4	<4
Thulium (Tm)	<4	<4	<4	<4	<4	<4	19	<4	<4
Tin (Sn)	<10	<10	<10	1,250	<10	<10	<10	<10	<10
Yttrium (Y)	17	10	11	120	128	6	600	13	14
Ytterbium (Yb)	<4	<4	<4	19	20	<4	68	<4	<4
Zinc (Zn)	2,000	<200	<200	<200	<200	<200	<200	<200	<200

acid, and (2) determination of the following data from a feed slurry containing  $250 \pm 10$  g/l uranium and having a nitric acid concentration of  $3.0 \pm 0.2N$ :

1.  $HNO_3$  consumption.
2. Volume change factor.
3. Digestion efficiency
4. Solids content of slurry.
5. Any unusual behavior.

Digestion data for ten feed materials are tabulated in Table 1.3. The results indicate that:

1. Durango, Edgemont, Gunnison, Lucky Mc, Texas Zinc (calcined at  $550^\circ C$ ), Uravan, and Vitro have good digestion characteristics.
2. Homestake-New Mexico and Homestake-Sapin contain considerable insoluble uranium.
3. Homestake-New Mexico, Homestake-Sapin, and Phillips Petroleum form very gelatinous slurries.

It appears that Texas Zinc concentrate is not dried at a high enough temperature to completely remove the solvent used in the milling process. When Texas Zinc was dried at  $550^\circ C$  (compared

with the  $140^\circ C$  used at the mill), it exhibited excellent digestion characteristics.

#### Uranium Distribution Curves

Uranium distribution curves<sup>4</sup> for Durango, Edgemont, Gunnison, Homestake-New Mexico, Lucky Mc, and Uravan uranium concentrates were made from data collected from laboratory extraction tests (in which aqueous feed slurries of varying uranium concentrations are equilibrated with equal volumes of 33.5 per cent TBP in kerosene). These curves (represented by one curve) and the distribution curve for pure uranyl nitrate hexahydrate solution are shown in Figure 1.1. The distribution data are listed in Table 1.4.

The uranium distribution curves for all six concentrates compare favorably with the uranium distribution curve for UNH solutions. Severe emulsions were encountered when aqueous solutions of Homestake-New Mexico were equilibrated with 33 per cent TBP in kerosene. No serious emulsification tendencies were noted with the other five concentrates.

TABLE 1.3 Digestion of Concentrates

Concentrate	Acid Consumption*	Volume Change Factor**	Digestion Efficiency† (%)	Digestion Insolubles†† (%)	Digestion Reaction
Durango	0.0077	0.997	>99.99	1.93	Mild
Edgemont	0.0070	0.981	>99.99	0.12	Mild
Gunnison	0.0078	0.985	>99.99	0.34	Mild
Homestake-New Mexico	0.0086	0.980	99.50	3.05	Mild
Homestake-Sapin	0.0090	0.971	99.88	2.17	Moderate
Lucky Mc	0.0066	0.986	>99.99	<0.10	Mild
Phillips Petroleum	0.0082	0.953	>99.99	1.59	Mild
Texas Zinc†	0.0088	0.978	>99.99	1.24	Mild
Uravan	0.0080	0.989	>99.99	0.99	Mild
Vitro	0.0057	0.965	>99.99	0.80	Mild

\* Acid consumption given as gram equivalents of  $HNO_3$  consumed in digesting to 250 g/l U and 0.0N  $HNO_3$  per gram of concentrate.

\*\* Volume Change Factor = Initial Volume of Dilute Acid/Final Volume of Slurry.

† Digestion Efficiency =  $100 (\text{Soluble U}/\text{Total U})$ .

†† Per cent by weight of insolubles in the concentrate.

‡ Texas Zinc concentrate calcined for two hours at  $550^\circ C$ .

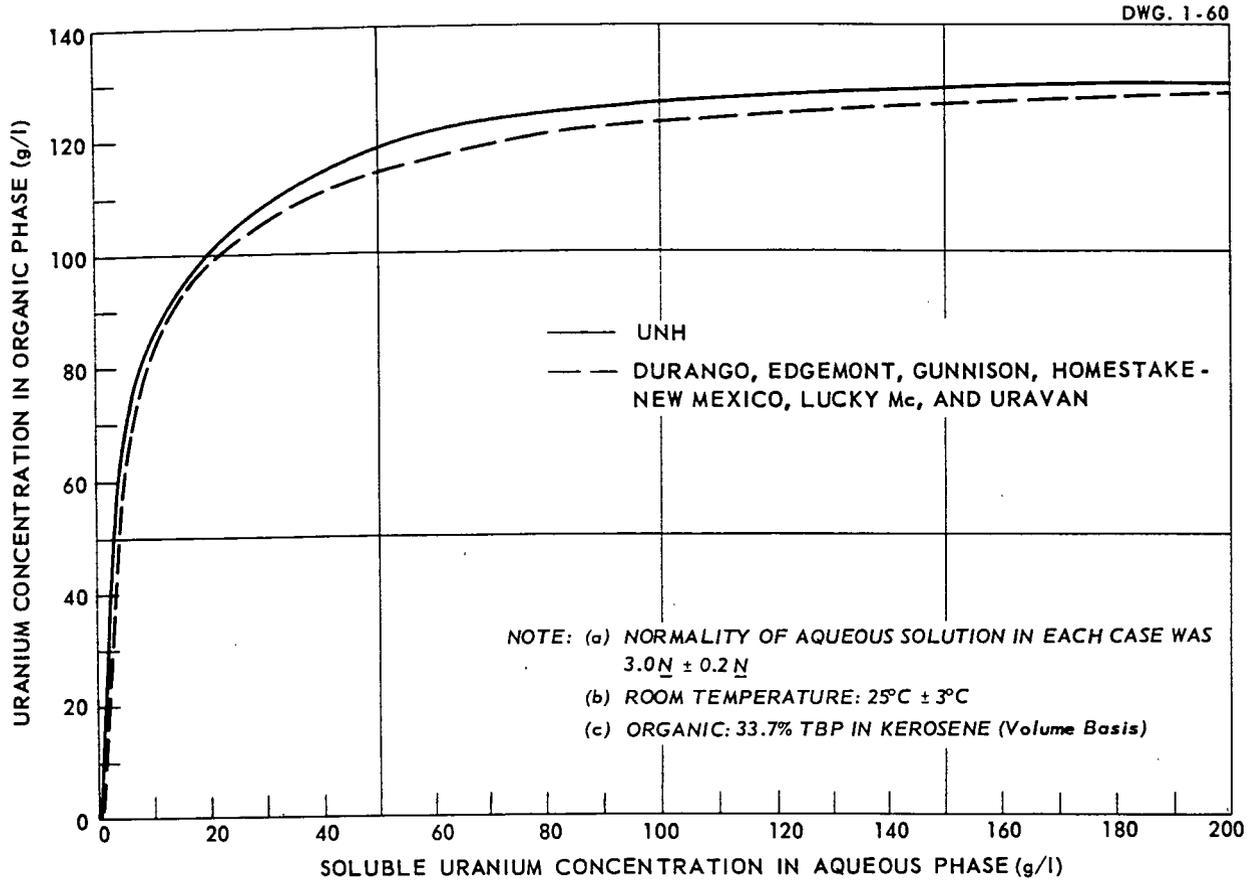


FIGURE 1.1 Laboratory Distribution Curves

TABLE 1.4 Uranium Distribution, As Determined in Laboratory Extraction Tests

The solvent used was 33.2 per cent TBP in kerosene (volume basis).  
 Results are in grams of uranium per liter.  
 The nitric acid concentration of the aqueous phase after each equilibration was 3.0N ± 0.2N.

UNH		Durango		Edgemont		Gunnison		Homestake-New Mexico		Lucky Mc		Uravan	
Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.
200	129.0	200	127	199	128	179	126	162	128	203	128	197	127
129.6	127.8	154	126	167	126	119	125	99.2	124	171	127	164	126
79.4	123.5	102	123	111	123	74.0	119	55.7	119	116	123	107	123
39.0	113.7	64.5	118	77.5	120	42.7	112	32.9	111	81.2	119	66.0	117
16.6	96.5	29.4	110	37.5	111	17.2	95.5	12.8	90.7	40.1	110	30.0	109
5.9	71.5	5.9	75.3	8.7	81.2	5.4	64.4	4.7	57.7	9.2	82.7	6.2	77.1
—	—	2.5	50.1	2.9	56.1	2.5	40.8	2.5	38.3	3.1	56.1	2.6	51.3

Extraction Tests in the Pilot Plant Two-Inch Pulse Column

Pilot Plant two-inch pulse column extraction tests<sup>5</sup> were performed, using feed slurries prepared

from Durango, Edgemont, Gunnison, Homestake-New Mexico, Lucky Mc, and Uravan uranium concentrates. The test conditions and procedures are listed in Table 1.5. A summary of the results of these tests is presented in Table 1.6, while the

TABLE 1.5 Operating Conditions for Pilot Plant Tests

Streams	Aqueous Feed* (AF) 250 ± 10 g/l U; 3.0 ± 0.2N HNO <sub>3</sub> ; 90° to 110°F.	
	Organic Extractant (AX)	33.5% TBP in kerosene, non-acidified, at ambient temperature.
	Scrub Water (BS)	Deionized water at ambient temperature.
Desired AP Density	0.997 ± 0.003 at 60°F	
Desired Flowrates	AF = 5.40 gph AX = 13.50 gph BR = 1.50 gph	
Desired Flow Ratios	AX/AF = 2.5/1 AX/BR = 9/1 AX/AF/BR = 9/3.6/1	
Desired Total Column Throughput	A-Column = 1,000 gsfh B-Column = 740 gsfh	
Continuous Phase	A-Column = Organic B-Column = Aqueous	
Pulse Conditions	A-Column	Frequency = 65 cpm; Amplitude = 0.75 inch
	B-Column	Frequency = 35 cpm; Amplitude = 0.60 inch

\* Note: After concentrate addition to the proper quantity of nitric acid, each digestion batch is heated to 180° to 190°F for approximately one hour.

TABLE 1.6 Summary of Pilot Plant Pulse Column Test Results

Durango Concentrate – Lot 606

The extraction column performance of a feed slurry prepared from Durango concentrate was not satisfactory. The feed slurry contained very dense nitric acid insolubles which persistently plugged the aqueous feed (AF) pump and/or piping. Steady-state conditions were never achieved. Another pulse column test is scheduled in which a different aqueous feed pump will be used.

Edgemont Concentrate – Lot 116

The extraction column performance of a feed slurry prepared from Edgemont concentrate was satisfactory. With normal uranium saturation of the organic product (AP), aqueous raffinate (AR) losses were within specification (0.2 g/l uranium). The A-column flooding capacity was greater than 1500 gsfh for this concentrate.

Gunnison Concentrate – Lot 66

The extraction column performance of a feed slurry prepared from Gunnison concentrate was satisfactory. With normal uranium saturation of organic product (AP), aqueous raffinate (AR) losses were within specification. The A-column flooding capacity was greater than 1500 gsfh for this concentrate. It was necessary to increase the A-column pulse amplitude to 1 inch to achieve good column operation.

Homestake-New Mexico Concentrate – Lot 64

The extraction column performance of a feed slurry prepared from Homestake-New Mexico concentrate was not satisfactory. With normal uranium saturation of the organic product, loss of soluble uranium in the aqueous raffinate was 1.1 g/l. The aqueous raffinate also contained 1.5 g/l nitric acid insoluble uranium. It was necessary to increase the A-column pulse amplitude to 1 inch to achieve good column operation. The A-column flooding capacity was greater than 1,000 but less than 1,250 gsfh for this concentrate.

Lucky Mc Concentrate – Lot 92

The extraction column performance of a feed slurry prepared from Lucky Mc concentrate was satisfactory. With normal saturation of the organic product, aqueous raffinate losses were well within specification. The A-column flooding capacity was greater than 1,500 gsfh for this concentrate.

Uravan Concentrate – Lot 796

The extraction column performance of a feed slurry prepared from Uravan concentrate was satisfactory. With normal uranium saturation of the organic product, soluble uranium losses were well within specification, while total uranium losses were the same as the specification (0.2 g/l uranium). The A-column flooding capacity was greater than 1,500 gsfh for this concentrate.

results of each test are tabulated in Tables 1.7 and 1.8.

The results of these tests indicate that Edgemont, Gunnison, Lucky Mc, and Uravan concentrates will not present any processing difficulties with respect to extraction column performance and process product purity control limits.

Operational difficulties were encountered with Durango concentrate. The material contains nitric

acid insolubles which are very dense and cause persistent plugging in the aqueous feed (AF) pump and/or piping. Further testing of Durango concentrate will be necessary.

Insufficient uranium extraction and excessive insoluble uranium losses were found in the Homestake-New Mexico test. It is recommended that Homestake-New Mexico concentrate not be considered as a Refinery feed material.

TABLE 1.7 Pilot Plant Pulse Column Test Results

Feed Composition	Test 52 Durango Lot 606	Test 54 Edgemont Lot 116	Test 45 Gunnison Lot 66	Test 46 Homestake- New Mexico Lot 64	Test 53 Lucky Mc Lot 92	Test 43 Uravan Lot 796
A - Column Throughput (gsfh)		973	1,015	942	963	978
<u>Aqueous Feed (AF)</u>						
Flowrate (gph)		5.32	6.58	4.94	5.27	5.52
U (g/l)		255	230	292	253	253
HNO <sub>3</sub> (N)		2.8	2.9	3.2	3.2	3.1
<u>Organic Extractant (AX)</u>						
Flowrate (gph)		13.08	12.93	13.02	13.09	13.10
U (g/l)		0.13	0.13	0.13	0.23	0.13
TBP (%)		34.3	33.0	33.6	35.3	35.0
<u>Organic Product (AP)</u>						
Flowrate (gph)		13.70	13.36	13.63	13.65	13.63
Density at 60°F		0.995	0.994	0.997	0.996	0.996
U (g/l)		103	104	106	104	106
HNO <sub>3</sub> (N)		0.30	0.28	0.29	0.37	0.32
<u>Aqueous Raffinate</u>						
Flowrate (gph)		6.20	7.07	5.62	6.09	6.60
Soluble U (g/l)		0.017	0.015	1.1	0.010	0.022
Total U (g/l)		—	0.04	2.6	—	0.20
HNO <sub>3</sub> (N)		2.3	2.6	2.7	2.7	2.6
B - Column Throughput (gsfh)		723	703	717	714	720
<u>Scrub Aqueous Raffinate (BR)</u>						
Flowrate (gph)		1.46	1.27	1.28	1.31	1.37
U (g/l)		31.9	30.0	34.9	18.1	41.9
HNO <sub>3</sub> (N)		2.3	3.2	3.1	3.1	2.6
<u>Scrubbed Organic Product (BP)</u>						
Flowrate (gph)		13.61	13.20	13.57	13.57	13.58
U (g/l)		100	100	103	100	101
HNO <sub>3</sub> (N)		0.041	0.060	0.042	0.07	0.061
Length of Test (hr)		13	13	12.5	12	13
Hour Samples Were Taken		9,10,11	9,10,11	9,10,11	10,10.5,11	9,10,11
A-Column Flooding Capacity (gsfh)		>1,500	>1,500	>1,000 >1,250	>1,500	>1,500

TABLE 1.8 Spectrochemical Analyses (ppm)  
of Organic Product (BP) Produced  
in Pilot Plant Tests\*

The accuracy of these results is  
estimated to be  $\pm 50$  per cent.

Element	Test 54 Edgemont	Test 45 Gunnison	Test 46 Homestake - New Mexico	Test 53 Lucky Mc	Test 43 Uravan
Al	<6	<6	<6	12	<6
B	>2	>2	>20	>2	>2
Bi	<1	<1	<1	--	2
Cd	<0.2	<0.2	<0.2	<0.2	<0.2
Cr	<10	<10	<10	<10	<10
Cu	2	<1	<1	2	<1
Fe	<10	<10	<10	13	<10
Mg	<4	<4	<1	<4	<4
Mn	<4	<4	<4	<4	<4
Mo	<6	<6	<6	<6	<6
Ni	<10	<10	<10	<10	<10
P	200	<20	<20	<20	<20
Pb	<1	<1	<1	<1	<1
SiO <sub>2</sub>	<10	<20	<10	<10	<20
Sn	<1	<1	<1	<1	<1
V	<40	<40	<40	<40	<40
Zn	<20	<20	<20	<20	<20

\* The contamination level of the scrubbed organic product (BP) will normally be equivalent to the contamination level of a final aqueous uranyl nitrate product (CP) produced by stripping the scrubbed organic with deionized water.

#### Future Work

Evaluations of Durango, Homestake-Sapin, Kermac, Moab, Phillips Petroleum and Vitro uranium concentrates will be completed. Complete evaluations will be initiated for any other new uranium concentrates which may become available at this site.

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## 2. SELECTIVE DIGESTION

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## Abstract

UAP\* cannot be used as a feed material for the low acid-metal nitrate flowsheet.

Calcium sulfate scaling and thorium contamination can be controlled by blending the feed materials.

## Introduction

The background for this project, the initial laboratory investigations, the preliminary Pilot Plant tests, and the preliminary cost evaluations of the proposed system have been discussed previously.<sup>1</sup> The preliminary work showed that from both an operational and an economical standpoint, the low acid-metal nitrate aqueous feed system is feasible for uranium extraction from normal uranium concentrates. However, some problems which arose during the preliminary studies required further investigation. They involve (1) the solubility of UAP, (2) the solubility of  $\text{CaSO}_4$ , and (3) the decontamination factors for thorium in the proposed system, which provides for no phosphate being present. This report deals with these problems and the refinement of the low acid-metal nitrate flow sheet.

## Previous Work on Project

Uranium distribution curves obtained in the laboratory have demonstrated that uranium distribution into a TBP-kerosene solvent varies significantly as the amount of nitric acid and/or metal nitrates in the aqueous phase varies. Use of an aqueous system containing 0.5N  $\text{HNO}_3$  and 2.5N  $\text{NaNO}_3$  results in more favorable distribution toward the solvent phase than does a system containing 3N  $\text{HNO}_3$ .

\* A chemical precipitate, uranyl ammonium phosphate, is calcined at approximately 1500 F to produce a uranium concentrate which is mostly uranyl phosphate and is commonly called UAP.

Pilot Plant 2-inch-column tests in which the UNH feed solutions were low in acid and contained sodium nitrate have demonstrated good column operation and uranium extraction. Similar tests in which uranium concentrates were used resulted in several problems, which are topics of this report.

## Objectives for This Quarter

The objectives for this period were:

1. Laboratory determination of the solubility of UAP in a feed slurry containing 400 g/l uranium, 0.5N  $\text{HNO}_3$ , and 0.5M metal nitrate.
2. Laboratory determination of the solubility of  $\text{CaSO}_4$  in a low acid-metal nitrate feed slurry; Pilot Plant determination of the maximum quantity of  $\text{CaSO}_4$  that can be maintained in the low acid-metal nitrate feed slurry without column scaling.
3. Pilot Plant determination of thorium decontamination factors, using the low acid-metal nitrate flowsheet with no phosphate present (1) at a normal uranium concentration (approximately 105 g/l) in the organic product (AP) and (2) at a high uranium concentration (approximately 125 g/l) in the organic product (AP).

## Summary of Results Obtained This Quarter

1. Laboratory studies clearly show that UAP is only partially soluble in 0.5N  $\text{HNO}_3$  solutions and consequently can not be used as a feed material in the low acid-metal nitrate flowsheet.
2. The solubility of  $\text{CaSO}_4$  in a  $\text{HNO}_3$ - $\text{NH}_4\text{NO}_3$  system was determined in the laboratory. The solubility of  $\text{CaSO}_4$  for the proposed low acid-metal nitrate flowsheet (0.5N  $\text{HNO}_3$  0.5M  $\text{NH}_4\text{NO}_3$ ) is 14.3 g/l or a  $\text{Ca} \times \text{SO}_4$  number<sup>†</sup> of 2.66. The level of  $\text{CaSO}_4$  (expressed as the  $\text{Ca} \times \text{SO}_4$  number) that can be tolerated in the low acid-metal nitrate

<sup>†</sup>  $\text{Ca} \times \text{SO}_4$  number is a value used to define the levels of calcium and sulfate in a given feed slurry. It is calculated as follows: (% Ca, uranium basis)  $\times$  (%  $\text{SO}_4$ , uranium basis).

feed slurry without column scaling was determined in the Pilot Plant to be approximately 7.5.

3. Thorium decontamination factors have been established at normal and high uranium concentrations in the organic product (AP). The results of these tests indicate that the product purity specification for thorium can be met by selectively blending the feed materials and/or by adjusting the uranium concentration in the organic product.

#### Laboratory Studies: UAP Solubility

A series of feed slurries were prepared having various nitric acid and/or phosphate concentrations. The range of nitric acid concentrations was 0.6 to 3.0N. The range of phosphate concentrations was 5 g/l to 85 g/l. Sodium nitrate was used as the metal nitrate at a concentration of 0.5M. (Ammonium nitrate could not be used as the metal nitrate, since in its presence uranyl ammonium phosphate precipitates - even in slurries that are

up to 3 to 4N in HNO<sub>3</sub>.) It was found in studies conducted at ambient temperature that uranium phosphate precipitation was quite erratic; however, in the 0.5 to 1.0N HNO<sub>3</sub> range, appreciable precipitation occurred in every case. It could only be concluded that UAP can not possibly be processed in the low acid-metal nitrate flowsheet.

#### Laboratory Studies: CaSO<sub>4</sub> Solubility

In a solution 0.0N in HNO<sub>3</sub> and 0.5M in NaNO<sub>3</sub> and in a solution 0.0N in HNO<sub>3</sub> and 0.5M in NH<sub>4</sub>NO<sub>3</sub>, the solubilities of CaSO<sub>4</sub> are 4.50 g/l and 5.10 g/l, respectively, according to data found in Seidell's<sup>2</sup> solubility tables. Since the solubility in the 0.0N HNO<sub>3</sub> - 0.5M NH<sub>4</sub>NO<sub>3</sub> solution is slightly greater, it was decided to further investigate (in the laboratory) the solubility of CaSO<sub>4</sub> in a HNO<sub>3</sub> - NH<sub>4</sub>NO<sub>3</sub> system.

A series of twelve solutions were prepared containing various concentrations of HNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub>.

TABLE 2.1 Solubility of CaSO<sub>4</sub> in HNO<sub>3</sub> - NH<sub>4</sub>NO<sub>3</sub> Solutions

Chemicals: Distilled H<sub>2</sub>O  
CaSO<sub>4</sub> · 2H<sub>2</sub>O C. P.  
NH<sub>4</sub>NO<sub>3</sub> R. G.  
HNO<sub>3</sub> R. G. (15.8N)

HNO <sub>3</sub> (N) NH <sub>4</sub> NO <sub>3</sub>	0N (0 ml)		0.5N (15.8 ml)		1.0N (31.6 ml)		1.5N (47.4 ml)	
	1	2	3	4	5	6	7	8
0.5N (20 g)	4.6 g/l SO <sub>4</sub> <sup>-2</sup> 1.92 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 0.552	10.1 g/l SO <sub>4</sub> <sup>-2</sup> 4.21 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 2.658	14.1 g/l SO <sub>4</sub> <sup>-2</sup> 5.87 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 5.173	17.0 g/l SO <sub>4</sub> <sup>-2</sup> 7.08 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 7.522	5	6	7	8
1.0N (40 g)	5.2 g/l SO <sub>4</sub> <sup>-2</sup> 2.17 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 0.705	12.0 g/l SO <sub>4</sub> <sup>-2</sup> 5.00 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 3.750	15.3 g/l SO <sub>4</sub> <sup>-2</sup> 6.37 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 6.091	17.8 g/l SO <sub>4</sub> <sup>-2</sup> 7.42 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 8.255	9	10	11	12
1.5N (60 g)	6.0 g/l SO <sub>4</sub> <sup>-2</sup> 2.50 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 0.938	12.3 g/l SO <sub>4</sub> <sup>-2</sup> 5.13 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 3.945	15.9 g/l SO <sub>4</sub> <sup>-2</sup> 6.62 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 6.579	18.4 g/l SO <sub>4</sub> <sup>-2</sup> 7.67 g/l Ca <sup>+2</sup> Ca × SO <sub>4</sub> = 8.821				

NOTES: 1. Approximately 10 g CaSO<sub>4</sub> was added to each 100 ml of test solution.

2. Ca × SO<sub>4</sub> = %Ca × %SO<sub>4</sub>, uranium basis, assuming 400 g/l uranium in aqueous test solution although the solution was in fact uranium-free.

To each sample was added an excess of  $\text{CaSO}_4$ . The samples were placed in a constant-temperature room ( $25^\circ\text{C}$ ) for one week and were agitated several times each day. At the end of one week, the samples were filtered and the filtrate was analyzed for calcium and sulfate.

The results of these tests are tabulated in Table 2.1, and a graphical representation is presented in Figure 2.1. The results show that the  $\text{Ca} \times \text{SO}_4$  number for the system being studied (400 g/l uranium, 0.5N  $\text{HNO}_3$  and 0.5M  $\text{NH}_4\text{NO}_3$ ) is 2.66. This is very low, considering that the average  $\text{Ca} \times \text{SO}_4$  number for slurries prepared from normal Refinery feed materials is approximately 4 to 6 in the same system. However, it was thought that this value (2.66) should be substantiated in the Pilot Plant.

#### Pilot Plant Extraction Tests – $\text{CaSO}_4$ Scaling

A Pilot Plant pulse column extraction test was made, using  $\text{NH}_4\text{NO}_3$  as a "salting agent" instead of the  $\text{NaNO}_3$  which was used in all previous Pilot Plant tests. The purpose of the test was to see what effect  $\text{NH}_4\text{NO}_3$  had on  $\text{CaSO}_4$  scaling in a pulse column and also to see if  $\text{NH}_4\text{NO}_3$  was as effective as  $\text{NaNO}_3$  in enhancing uranium extraction. The results of this test, along with the results of a similar previous test which used  $\text{NaNO}_3$  as a "salting agent," are presented as Tests 1 and 2, respectively, in Table 2.2.

The results indicate that  $\text{NH}_4\text{NO}_3$  is effective in reducing  $\text{CaSO}_4$  scaling in the extraction column. One explanation for  $\text{CaSO}_4$  not scaling, even though the solubility of  $\text{CaSO}_4$  had been exceeded, is the effect of electrostatic forces<sup>3,4</sup> between the solid particles and the walls of the container or containers. The results of Test 1 also show that  $\text{NH}_4\text{NO}_3$  is as effective as  $\text{NaNO}_3$  as a "salting agent."

A series of five Pilot Plant tests (Tests 3 through 7) were made (using UNH as feed material) to establish the maximum level of  $\text{CaSO}_4$  that can be tolerated in the feed slurry without scaling occur-

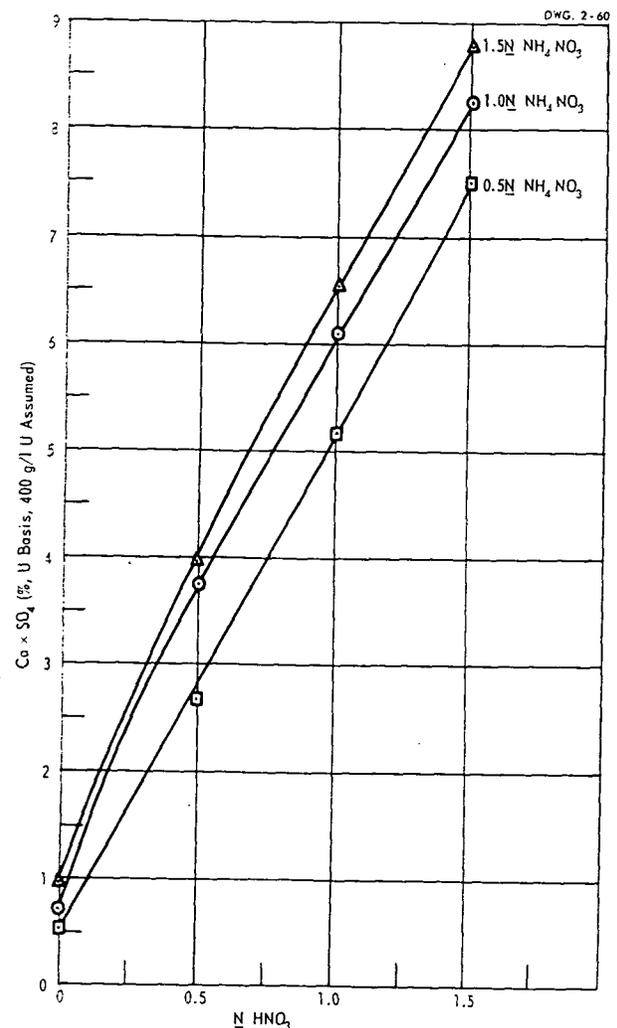


FIGURE 2.1 Nitric Acid Normality vs  $\text{Ca} \times \text{SO}_4$  Number.

ring in the extraction column. The five tests utilized the extraction column only and were short in length (4 to 5 hours). The data from these tests indicate that no scaling occurs at a  $\text{CaSO}_4$  number of 7.5, but that scaling does occur at a number of 9.0. Based on these results, two more Pilot Plant tests (Tests 8 and 9) were made – the first with a UNH feed having a  $\text{CaSO}_4$  number of 7.5 and the second with a South African feed having a  $\text{CaSO}_4$  number of 7.5. The duration of both tests was approximately 13 hours. No significant  $\text{CaSO}_4$  scaling occurred in either test.

TABLE 2.2 Tests in Pilot Plant 2-Inch Extraction Columns – Limits of CaSO<sub>4</sub> Scaling

	Test No.									
	1	2	3	4	5	6	7	8	9	
Aqueous Feed (AF)	So. African	So. African	UNH	UNH	UNH	UNH	UNH	UNH	So. African	
	418 g/l U	393 g/l U	346 g/l U	358 g/l U	366 g/l U	378 g/l U	378 g/l U	290 g/l U	376 g/l U	
	0.51N H <sup>+</sup>	0.4N H <sup>+</sup>	0.72N H <sup>+</sup>	0.75N H <sup>+</sup>	0.78N H <sup>+</sup>	0.82N H <sup>+</sup>	0.82N H <sup>+</sup>	0.54N H <sup>+</sup>	0.42N H <sup>+</sup>	
	1.0M NH <sub>4</sub> NO <sub>3</sub>	1M NaNO <sub>3</sub>	0.5M NH <sub>4</sub> NO <sub>3</sub>	0.5M NH <sub>4</sub> NO <sub>3</sub>	0.5M NH <sub>4</sub> NO <sub>3</sub>	0.5M NH <sub>4</sub> NO <sub>3</sub>	0.5M NH <sub>4</sub> NO <sub>3</sub>	0.5M NH <sub>4</sub> NO <sub>3</sub>	0.5M NH <sub>4</sub> NO <sub>3</sub>	
	Ca×SO <sub>4</sub> = 4.6	Ca×SO <sub>4</sub> = 4.6	Ca×SO <sub>4</sub> = 20	Ca×SO <sub>4</sub> = 10	Ca×SO <sub>4</sub> = 5	Ca×SO <sub>4</sub> = 7.5	Ca×SO <sub>4</sub> = 9.0	Ca×SO <sub>4</sub> = 7.5	Ca×SO <sub>4</sub> = 7.5	
Organic Extractant (AX)	0.065 g/l U	0.15 g/l U	0.08 g/l U	0.92 g/l U	0.62 g/l U	0.91 g/l U	0.91 g/l U	0.30 g/l U	0.05 g/l U	
	34.4% TBP	34% TBP	33.6% TBP	33.4% TBP	34.0% TBP	34.0% TBP	34.0% TBP	34.1% TBP	33.5% TBP	
Aqueous Raffinate (AR)	0.014 g/l U	0.36 g/l U	0.063 g/l U	0.074 g/l U	0.12 g/l U	0.24 g/l U	0.11 g/l U	0.10 g/l U	0.15 g/l U	
	0.47N H <sup>+</sup>	0.22N H <sup>+</sup>	0.29N H <sup>+</sup>	0.29N H <sup>+</sup>	0.34N H <sup>+</sup>	0.28N H <sup>+</sup>	0.29N H <sup>+</sup>	0.32N H <sup>+</sup>	0.30N H <sup>+</sup>	
Organic Product (AP)	108 g/l U	118 g/l U	111 g/l U	114 g/l U	115 g/l U	109 g/l U	111 g/l U	103 g/l U	110 g/l U	
	0.14N H <sup>+</sup>	0.075N H <sup>+</sup>	0.13N H <sup>+</sup>	0.13N H <sup>+</sup>	0.15N H <sup>+</sup>	0.15N H <sup>+</sup>	0.15N H <sup>+</sup>	0.11N H <sup>+</sup>	0.084N H <sup>+</sup>	
Aqueous Scrub Recycle (BR)	89.7 g/l U	85 g/l U	Tests 3 through 7 did not utilize the Scrub ("B") Column					48.2 g/l U	77.1 g/l U	
	0.92N H <sup>+</sup>	0.75N H <sup>+</sup>						1.38N H <sup>+</sup>	0.87N H <sup>+</sup>	
Scrubbed Organic Prod. (BP)	106 g/l U	105 g/l U						98 g/l U	104 g/l U	
	0.07N H <sup>+</sup>	0.035N H <sup>+</sup>						0.04N H <sup>+</sup>	0.03N H <sup>+</sup>	
Flowrates										
AF	3.26 gph	3.91 gph	4.24 gph	4.21 gph	4.01 gph	3.85 gph	3.87 gph	4.68 gph	3.77 gph	
AX	13.20 gph	13.10 gph	12.70 gph	13.10 gph	13.09 gph	13.05 gph	13.09 gph	13.12 gph	13.05 gph	
AR	3.83 gph	3.51 gph	3.65 gph	3.64 gph	3.47 gph	3.33 gph	3.37 gph	5.02 gph	4.28 gph	
AP	13.79 gph	13.62 gph	13.56 gph	13.67 gph	13.71 gph	13.69 gph	13.73 gph	13.94 gph	13.59 gph	
BR	0.94 gph	0.81 gph	–	–	–	–	–	0.89 gph	1.27 gph	
BP	13.66 gph	13.48 gph	–	–	–	–	–	13.81 gph	13.48 gph	
Column Throughput										
"A"	842 gsfh	872 gsfh	829 gsfh	848 gsfh	837 gsfh	827 gsfh	832 gsfh	914 gsfh	937 gsfh	
"B"	716 gsfh	690 gsfh	–	–	–	–	–	712 gsfh	713 gsfh	
Material Balance										
"A"	U	+5.71%	-1.61%	+2.86%	+3.52%	+7.49	+2.61%	+3.28%	+2.64%	-1.25%
	H <sup>+</sup>	+30.9%	-16.4%	-4.29%	-9.81%	+3.53%	-3.80%	-4.10%	-16.50%	-10.02%
"B"	U	-0.73%	-3.43%	–	–	–	–	–	-2.74%	+0.54%
	H <sup>+</sup>	-10.7%	+7.84%	–	–	–	–	–	+16.35%	+23.62%
Overall	U	+5.35%	-5.20%	–	–	–	–	–	-0.07%	-0.79%
	H <sup>+</sup>	+32.4%	-17.8%	–	–	–	–	–	-3.01%	-4.43%
Scrub Ratio AX/BR	~18/1	~18/1	–	–	–	–	–	~15/1	~11/1	
CaSO <sub>4</sub> Scaling	None	Very Serious After 1½ hr	Very Serious After ½ hr	Very Serious After 1 hr	None	None	Serious After 3 hr	None	Almost Negligible	

Pilot Plant Extraction Tests – Thorium Decontamination

Two Pilot Plant pulse-column extraction tests were made, using feed materials containing relatively high concentrations of thorium. In the first test, in which Dyno concentrate was used as a feed material, steady-state conditions for thorium were not reached because of insufficient operational time. The second test, using Stanleigh concentrate, was in essence two tests, each 24 hours in

length. An organic product (AP) uranium concentration of 106 g/l was maintained during the first phase of the test and a concentration of 128 g/l during the second phase of the test. Samples were taken at the end of each phase of the test. The results of these tests are presented in Table 2.3.

The results show that in both phases of Test No. 2, the specification for thorium in the aqueous product (CP) was satisfied (the specification being 1500 ppm, uranium basis, compared with 939 ppm,

TABLE 2.3 Tests in Pilot Plant 2-Inch Extraction Columns - Thorium Decontamination

	Test No. 1	Test No. 2, Phase 1	Test No. 2, Phase 2	
Aqueous Feed (AF)	Dyno Concentrate 418 g/l U 0.51N H <sup>+</sup> 0.5M NH <sub>4</sub> NO <sub>3</sub> 4.90 g/l Th	Stanleigh Concentrate 403 g/l U 0.51N H <sup>+</sup> 0.5M NH <sub>4</sub> NO <sub>3</sub> 3.19 g/l Th	Stanleigh Concentrate 411 g/l U 0.48N H <sup>+</sup> 0.5M NH <sub>4</sub> NO <sub>3</sub> 3.34 g/l Th	
Organic Extractant (AX)	0.035 g/l U 34.0% TBP	0.075 g/l U 33.9% TBP	0.070 g/l U 33.9% TBP	
Aqueous Raffinate (AR)	0.013 g/l U 0.0N H <sup>+</sup> 0.011 g/l Th	0.12 g/l U 0.037N H <sup>+</sup> 1.31 g/l Th	0.14 g/l U 0.29N H <sup>+</sup> 2.59 g/l Th	
Organic Product (AP)	106 g/l U 0.20N H <sup>+</sup> 2.72 g/l Th	106 g/l U 0.12N H <sup>+</sup> 1.23 g/l Th	128 g/l U 0.09N H <sup>+</sup> 0.64 g/l Th	
Aqueous Scrub Recycle (BR)	52.3 g/l U 1.57N H <sup>+</sup> 22.7 g/l Th	61.8 g/l U 1.2N H <sup>+</sup> 17.3 g/l Th	214 g/l U 0.69N H <sup>+</sup> 19.5 g/l Th	
Scrubbed Organic Product (BP)	103 g/l U 0.07N H <sup>+</sup> 0.25 g/l Th	99 g/l U 0.04N H <sup>+</sup> 0.093 g/l Th	123 g/l U 0.05N H <sup>+</sup> 0.012 g/l Th	
<u>Flowrates</u>				
AF	3.26	3.48	3.95	
AX	13.20	13.11	13.41	
AR	3.83	4.01	4.24	
AP	13.79	13.73	13.77	
BR	0.94	1.05	0.46	
BP	13.66	13.59	13.63	
<u>Column Throughput</u>				
"A"	850	863	873	
"B"	707	710	684	
<u>Material Balance</u>				
"A"	U	+4.05%	-0.61%	+3.30%
	H <sup>+</sup>	-12.66%	+2.96%	+11.24%
	Th	+0.69%	-24.27%	-15.28%
"B"	U	-1.37%	-3.36%	+0.97%
	H <sup>+</sup>	-15.61%	+1.69%	-16.89%
	Th	-33.75%	+76.50%	+3.98%
Overall	U	+2.65%	-4.20%	+3.38%
	H <sup>+</sup>	-50.07%	+11.91%	+1.60%
	Th	-78.44%	-40.63%	-15.42%
<u>Scrub Ratio</u>				
AX/BR	Approximately 14/1	Approximately 13/1	Approximately 29/1	
<u>Thorium Decontamination</u>				
AP to BP	-	13.4 to 1	55 to 1	
AF to BP	-	8.8 to 1	823 to 1	

uranium basis, for Phase 1 and 98 ppm, uranium basis, for Phase 2). It is thought that with selective blending of the feed materials, thorium contamination of the final product is no problem.

It appears from the material balances for thorium

that steady-state conditions had not been reached in either phase of the test, but hourly sample analyses indicate that Phase 1 came very close to steady-state conditions and that Phase 2 reached steady-state conditions. The large error in the material balances for thorium is mainly attributed

to the cumulative error imposed by the thorium analyses.

Conclusions

1. UAP cannot be solubilized and thereby processed in the Refinery in an 0.5N acid system.

2. CaSO<sub>4</sub> scaling in an 0.5N acid 0.5M NH<sub>4</sub>NO<sub>3</sub> system will be negligible for most feed materials presently received. With selective blending of the feed materials, CaSO<sub>4</sub> scaling can be adequately controlled.

3. Thorium contamination of the final product (CP) can be kept within the specification limits with no phosphate present. Minor blending may be required.

4. The low acid-ammonium nitrate flowsheet has been developed sufficiently to be tested in the Refinery.

References

<sup>1</sup>R. K. Klopfenstein, C. T. Hicks, and J. R. Nelli. "Selective Digestion," Summary Tech. Rpt., USAEC report NLCO-790, pp. 17-26. July 20, 1959 (Classified).

<sup>2</sup>A. Seidell. Solubilities of Inorganic and Metal Organic Compounds, 3rd ed., pp. 337, 340. New York: Van Nostrand, 1940.

<sup>3</sup>W. J. Moore. Physical Chemistry, 2nd ed., p. 521. New York: Prentice Hall, 1955.

<sup>4</sup>B. Levy and A. R. Fritsch. "Zeta Potentials of ThO<sub>2</sub> and of Stainless Steel as Related to Aggregation and Caking," Nucl. Sci. Eng., 5:143. 1959.

3. BONDING IN THE TBP-H<sub>2</sub>O-U-ACID SYSTEM

R. K. Klopfenstein      D. A. Stock      T. J. Collopy

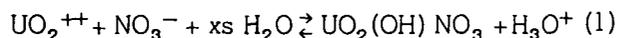
**Abstract**

Laboratory evaporation tests of uranyl nitrate solutions, with ammonium hydroxide added either before or after concentration of the uranium, have established a relationship for uranic acid precipitation from such a solution in terms of uranium concentration and the ammonium to uranium mole ratio.

**Introduction**

During the past few months, laboratory studies of the TBP-H<sub>2</sub>O-U-acid system (which is employed at the National Lead Company of Ohio to purify uranium) have been directed toward investigations of the re-extraction of uranium from the tri-n-butyl phosphate (TBP) - kerosene solvent with water and/or dilute ammonium hydroxide.<sup>1</sup> Currently, the pulse column re-extraction operation utilizes water at 150°F; dilute ammonium hydroxide is added to the aqueous uranyl nitrate product solution<sup>2</sup> to enhance the "reactivity" of the orange oxide (UO<sub>3</sub>) product from the subsequent evaporation, boildown, and denitration operations.

Laboratory investigations are intended to ultimately elucidate the possible benefits to be derived from introduction of the dilute ammonium hydroxide near the bottom (high uranium concentration end) of the re-extraction columns, rather than after uranium re-extraction is completed. Water, which must be considered a base relative to the acidic uranyl ion, is effective in re-extracting uranium from the TBP-kerosene solvent by shifting the equilibrium in Equation 1 to the right. Thus, the addition of an even stronger base, such as ammonium hydroxide, should cause an even greater equilibrium shift, resulting in enhanced uranium re-extraction.



Such an enhancement in uranium re-extraction provides two immediately useful benefits - i.e., either

increased uranium concentration in the re-extraction product, resulting in reduced boildown ratios, and/or a decreased aqueous to organic ratio during re-extraction, resulting in reduced volume throughputs in the pulse columns for the same uranium throughputs.

From a laboratory point of view, ammonium hydroxide re-extractions and subsequent boildown tests of the product solution should contribute to present knowledge of the formation, stability, and character of the soluble basic nitrate complex [UO<sub>2</sub>(OH)NO<sub>3</sub>] and the insoluble uranic acid [H<sub>2</sub>UO<sub>4</sub>] intermediates which have been postulated to occur during the conversion of an aqueous solution of uranyl nitrate to UO<sub>3</sub>.<sup>3</sup>

**Previous Work on This Project**

A number of ten-stage laboratory batch counter-current re-extraction tests were conducted, using water in the second through the tenth stages and either water or dilute ammonium hydroxide in the first stage.<sup>4</sup> Initial evaluation of these tests showed that up to an ammonium hydroxide concentration of 0.35M, the uranium distribution coefficient [DC =  $\frac{U_{aq}}{U_{org}}$ ] shifted toward the aqueous phase

as successively higher concentrations of ammonium hydroxide were used. At 0.35M ammonium hydroxide, uranic acid precipitated from the aqueous product solution upon standing. A more thorough evaluation of the results revealed a number of difficulties:

1. Generally poor material balances due to inaccurate analyses and/or nonattainment of equilibrium in the individual stages and the over-all system.

2. Poor correlation between results obtained from fresh solvent and those obtained from used Refinery solvent.

As a result, many of these tests were repeated, with more accurate colorimetric and volumetric

TABLE 3.1 Laboratory Evaporation of UNH Solutions Containing NH<sub>4</sub>OH

All tests conducted at 80° to 90° C with constant agitation

Initial U (g/l)	Initial NH <sub>4</sub> OH (M)	Initial U (M)	Initial Vol. (ml)	Final Vol. (ml)	Final U (M)	Final NH <sub>4</sub> OH (M)	$\frac{[OH^-]}{[U]}$
101.8*	0.10	0.428	1200	100	5.132	1.20	0.234
110.9*	0.15	0.466	1200	110	5.078	1.64	0.323
101.3	0.15	0.426	1200	110	4.643	1.64	0.353
111.8	0.18	0.470	1200	120	4.697	1.80	0.383
101.4	0.18	0.426	1200	125	4.091	1.73	0.423
111.6	0.20	0.469	1200	125	4.501	1.92	0.427
101.8	0.20	0.428	1200	170	3.019	1.41	0.468
116.7	0.25	0.490	800	115	3.411	1.74	0.511
101.1	0.25	0.425	400	60	2.832	1.67	0.590
101.5	0.30	0.427	400	150	1.137	0.80	0.704
Approx. Error	±1	±0.01		±0.5%	±2 to 5%	±2 to 5%	

\* No precipitation of uranic acid occurred.

TABLE 3.2 Laboratory Test of NH<sub>4</sub>OH Addition to Concentrated UNH Solutions

All tests conducted at 80° to 90° C with constant agitation

Initial U (g/l)	Initial Vol (ml)	NH <sub>4</sub> OH Added		Final Vol (ml)	Final U (g/l)	Final U (M)	Final NH <sub>4</sub> OH (M)	$\frac{[OH^-]}{[U]}$
		(ml)	(M)					
403.3	25	3.16	7.6	28.16	358	1.507	0.85	0.565
668.6	25	4.38	7.6	29.38	569	2.390	1.13	0.473
891.4	25	2.65	15.2	27.65	806	3.386	1.47	0.434
999.6	25	2.98	15.2	27.98	893	3.752	1.62	0.432
1102.5	25	3.50	15.2	28.50	967	4.063	1.87	0.460
Approx. Error	±2%	±2%	±5%			±5%	±5%	

added before evaporation and Curve B represents tests in which ammonium hydroxide was added after evaporation. Curves A and B were established by use of the method of least squares. The equations for these curves are:

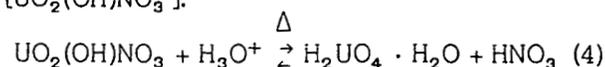
$$\text{Curve A: } [U] = -10.005 \frac{[NH_4OH]}{[U]} + 8.387 \quad (2)$$

$$\text{Curve B: } [U] = -16.687 \frac{[NH_4OH]}{[U]} + 10.909 \quad (3)$$

Curve C represents an average of the two sets of results.

### Discussion

In general, these evaporation tests indicate, as was expected, a systematic relationship between the NH<sub>4</sub>OH/U mole ratio and the precipitation of uranic acid (as the dimeric monohydrate, [H<sub>2</sub>UO<sub>4</sub> · H<sub>2</sub>O]<sub>2</sub>). Such a precipitation must be a function of an equilibrium shift in Equation 4 due to increasing temperature after increasing UO<sub>2</sub><sup>++</sup> first shifts the equilibrium in Equation 1 toward increasing concentrations of the basic uranyl nitrate, [UO<sub>2</sub>(OH)NO<sub>3</sub>].



Of the results of these evaporation tests, the most immediately useful finding was that Refinery re-extraction, evaporation, and boil-down operations could be completed without uranic acid precipitation only if ammonium hydroxide addition during re-extraction was 0.15M or less (assuming an aqueous uranyl nitrate product of 100 to 110 g/l U).

#### Future Work

Additional laboratory batch countercurrent re-extraction tests now in progress involve more than two volume changes. An attempt is being made to determine any overall benefit to uranium re-extraction from the use of 0.15M ammonium hydroxide in the first stage of re-extraction. Other similar tests are planned involving ammonium hydroxide addition to the second or third stages instead of the first.

A program of Pilot Plant 2-inch-column re-extraction tests will be initiated to allow evaluation of ammonium hydroxide addition under Refinery re-extraction conditions (i.e., use of a pulse column contactor, hot water, and warm organic phase).

#### References

<sup>1</sup>T. J. Collopy, W. S. Miller, and D. A. Stock. "Bonding in the TBP-H<sub>2</sub>O-U-Acid System," Summary Tech. Rpt., USAEC Report NLCO-795, pp. 15-18. October 20, 1959 (Classified); and preceding quarterly reports.

<sup>2</sup>C. W. Huntington, J. F. Blum, M. G. Mendel, K. J. Notz, and J. H. Krekeler. "Ammonia Activation of Orange Oxide," Summary Tech. Rpt., USAEC Report NLCO-690, pp. 49-51. October 21, 1957 (Classified); and preceding quarterly reports.

<sup>3</sup>P. S. Gentile, L. H. Talley, and T. J. Collopy, "The Chemistry of Uranyl Nitrate - Hydroxide - Urea Systems," J. Inorg. Nuclear Chem., 10: 110. 1959.

<sup>4</sup>T. J. Collopy, W. S. Miller, and D. A. Stock. *op. cit.*, pp. 15-18.

#### 4. LABORATORY INVESTIGATION OF SOLVENT EXTRACTION DECONTAMINATION FACTORS FOR MOLYBDENUM, VANADIUM, AND SEVERAL MINOR CONSTITUENTS IN URANIUM CONCENTRATES

R. K. Klopfenstein      J. H. Krekeler      J. R. Nelli

##### Abstract

Laboratory tests and analyses to determine concentrations and decontamination factors for minor constituents of uranium concentrates have shown that niobium, ruthenium, and tantalum are essentially insoluble in the Refinery nitric acid digestion medium. Antimony, titanium, and tungsten, although slightly soluble in the digestion medium, are virtually nonextractable into a TBP-kerosene solvent.

Molybdenum and vanadium are each soluble in the digestion medium and extractable in the solvent. Decontamination factors (uranium basis) during uranium extraction and scrubbing are:  $\sim 800/1$  and  $\sim 12/1$  for molybdenum, and  $> 350/1$  and  $\sim 5/1$  for vanadium.

##### Introduction

In recent months, an interest has been shown in establishing specifications for eight constituents in orange oxide ( $UO_3$ ) and green salt ( $UF_4$ ). The elements of interest are molybdenum, vanadium, niobium, ruthenium, antimony, tantalum, titanium, and tungsten. With the exception of the first two (molybdenum and vanadium) little or nothing was known regarding: their concentrations in incoming National Lead Company of Ohio Refinery<sup>1</sup> feed materials, their solubilities in the Refinery nitric acid digestion medium, or their extractability into the Refinery tri-*n*-butyl phosphate (TBP) - kerosene solvent.

To partially alleviate this lack of information, a threefold laboratory investigation was undertaken to provide a cursory evaluation of each of the eight elements of interest in terms of the three criteria mentioned above (i.e., concentration in the feed, solubility in the digestion medium, and extractability into the solvent, or decontamination).

##### Objective for This Quarter

The laboratory tests and analyses conducted during the present quarter were designed to answer the following questions:

1. What is the maximum concentration of each of the eight elements in the current Refinery feed materials?
2. How soluble are these elements (at their maximum anticipated concentration in the uranium concentrate) in the Refinery  $3N$   $HNO_3$  digestion medium?
3. What are the decontamination factors for these elements during the uranium extraction and scrubbing operations, using a TBP-kerosene solvent?

##### Summary of Results Obtained This Quarter

Laboratory equilibration tests and analyses have demonstrated the virtual insolubility of niobium, ruthenium, and tantalum in a nitric acid feed slurry medium. Further, although slightly soluble in the nitric acid medium, antimony, titanium, and tungsten have been shown to be essentially nonextractable into a TBP-kerosene solvent.

Finally, both molybdenum and vanadium are soluble in the nitric acid medium, and both are extracted by the solvent. Decontamination factors (uranium basis) for molybdenum during the extraction and scrubbing operations were calculated to be  $\sim 800/1$  and  $\sim 12/1$ , respectively. Similar factors for vanadium are  $> 350$  and  $\sim 5/1$ .

##### Laboratory Work and Results

The initial step in the investigation of the behavior of the eight elements of interest involved a spectrochemical analysis of each current Refinery uranium concentrate feed material for molybdenum, vanadium, ruthenium, tantalum, niobium, antimony,

titanium, and tungsten. A total of 31 feed materials were analyzed in this manner, and the results are presented in Table 4.1. (Ruthenium analyses were incomplete, since an independent procedure was required for this single element.) It will be noted from Table 4.1 that the apparent maximum concentrations (uranium basis) for the various elements are as follows:

Mo 3,500 ppm Ru <17 ppm Ta 57 ppm  
 V >17,100 ppm Nb 28 ppm Sb 58 ppm  
 Ti 2,940 ppm W 77 ppm

These concentrations, with some changes (either in the interests of simplicity or in the light of other

analyses) were used in the laboratory batch shake-out tests described below.

To evaluate the solubility and extractability of these eight elements in Refinery operations, separate standard uranyl nitrate solutions were prepared (3N excess HNO<sub>3</sub>, 225 g/l uranium). The elements were added, individually, at the following concentrations (uranium basis):

Mo 10,000 ppm Ru 20 ppm Ta 50 ppm  
 V 100,000 ppm Nb 30 ppm Sb 60 ppm  
 Ti 3,200 ppm W 80 ppm

Preparation of these solutions was complicated by difficulties in solubilizing the various elements.

TABLE 4.1 Spectrochemical Analyses of Uranium Concentrates For Mo, V, and Other Minor Constituents

Concentrate	Lot No.	Official Assay	Metal Constituents (ppm, U basis)							
			Mo	Nb	Ru	Sb	Ta	Ti	V	W
Algom	849	68.3	44	<15	—	<30	<15	1,460	38	<30
Anaconda Acid	1,604	66.0	1,520	<15	—	<30	<15	15	61	<30
Aust. Radium Hill	63	60.2	<34	<17	—	<34	17	17	585	<34
Aust. Rum Jungle	101	60.1	<42	<17	—	<34	17	17	<34	<34
Bicroft	104	57.8	<34	<17	—	<34	17	695	<34	<34
Blockson	3	39.6	63	<25	—	<50	<50	455	2,530	<50
Can-Met	315	58.2	43	<17	—	<34	17	346	<34	<34
Dennison	994	65.0	<30	<15	—	<30	<15	310	<30	<30
Durango	606	75.7	66	<13	—	<26	<13	530	990	<26
Dyno	25	68.4	<30	<15	—	<30	30	730	37	<30
Faraday	90	67.9	<30	<15	—	<30	<15	59	44	<30
Gunnison	66	69.0	725	<15	—	<30	<15	29	<30	<30
Homestake New Mex.	64	60.0	84	<17	—	<34	<17	25	>16,700	<84
Homestake Sapin	42	58.6	1,710	<17	<17	56	<17	17	>17,100	<34
Kerr-Mc	13	69.7	72	<15	<15	58	<15	15	>14,400	<30
Lorado	134	52.2	77	<19	—	<38	<19	19	<38	77
Lucky-Mc	92	62.6	400	<16	—	<32	<16	16	48	<32
Milliken	164	66.3	<30	<15	<15	<30	<15	15	38	<30
Mines Development	116	66.3	300	<15	—	<30	<15	30	600	<30
Moab	580	69.4	720	<15	—	<30	<15	15	2,160	<30
Northspan	433	67.3	<30	<15	—	<30	<15	300	38	<30
Phillips Petroleum	44	63.4	79	<16	—	32	<16	16	3,160	<32
Pronto	361	53.1	<38	<19	—	<38	57	570	<38	<38
Rayrock	42	62.6	32	<16	—	<32	48	160	<32	<32
Rifle	68	71.2	3,500	28	<14	28	<140	1,410	14,100	<28
South African	815	75.3	<28	<14	—	<28	40	53	40	28
Stanleigh	146	68.3	<30	<15	<15	<30	45	2,940	<30	<30
Starrock	100	69.1	58	<15	—	<30	30	290	29	<30
Texas Zinc	104	66.0	1,520	<15	—	<30	<15	8	61	<30
Uravan	796	68.5	585	<15	<15	<30	<150	29	14,600	<30
Vitro	168	73.2	343	<14	—	<28	14	14	<28	<28
Maximum Level	—	—	3,500	28	<17	58	57	2,940	>17,100	77

## UNCLASSIFIED

TABLE 4.2 Decontamination of Minor Constituents in Synthetic Feed Solutions  
Laboratory Digestion and Equilibration Tests

Impurity	Intended Impurity Addition (ppm, U basis)	Standard U-HNO <sub>3</sub> Solution Analyses			Equilibration Tests						Decontamination Factor, U Basis
		Impurity Dissolved (ppm, U basis)	U (g/l)	H <sup>+</sup> (N)	Aqueous Phase			Organic Phase			
					U (g/l)	H <sup>+</sup> (N)	Metal (ppm, U basis)	U (g/l)	H <sup>+</sup> (N)	Metal (ppm, U basis)	
Mo - as (NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	9,000	8,874	222	3.1	21.2	2.83	93,400	93.8	0.47	11	800/1
Nb - as Nb metal	31	2	228	3.3	44.6	2.98	*	89.2	0.49	*	-
Ru - as Ru metal	21	<1	229	3.6	23.5	3.22	*	99.0	0.42	*	-
Sb - as Sb metal	60	10	227	3.3	38.9	2.87	<20	91.6	0.46	<2	-
Ta - as Ta <sub>2</sub> O <sub>5</sub>	53	<1	226	3.2	24.1	2.94	*	96.6	0.42	*	-
Ti - as TiO <sub>2</sub>	3,200	10	233	3.3	34.2	2.94	59	97.8	0.43	<1	-
V - as NH <sub>4</sub> VO <sub>3</sub>	100,000	66,800	259	3.5	149	3.05	108,800	56.6	0.25	190	350/1
W - as Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	79	20	228	3.5	21.1	3.16	>190	99.0	0.24	<1	-

\* Not analyzed due to essential insolubility in the original solution.

Thus, none of the solutions contained the desired concentrations, despite the use of small amounts of hot, concentrated H<sub>2</sub>SO<sub>4</sub> (in the cases of niobium, antimony, tantalum, and vanadium), hot aqua regia (in the case of ruthenium), or hot NaOH (in the case of tungsten).

Analyses of these solutions are included in Table 4.2 under the heading, Standard U-HNO<sub>3</sub> Solution Analyses.

Once the eight UNH-HNO<sub>3</sub> aqueous solutions had been prepared, each was equilibrated once at room temperature with fresh 33 per cent TBP-67 per cent kerosene solvent at an organic to aqueous ratio of 20/11. This equilibration should produce a uranium-laden organic phase containing 90 to 100 g/l uranium and 0.3 to 0.4N HNO<sub>3</sub> and closely resembling a Refinery AP solution. Further, the equilibrated aqueous phase should resemble a Refinery AR (uranium-depleted aqueous raffinate), at least insofar as minor constituents are concerned. Analysis of first the original aqueous

phases and then the aqueous and organic phases\* after equilibration allowed the determination of decontamination factors across the primary extraction ("A") column. These results are included in Table 4.2.

At the time of these tests, samples of AP\*\* and BP\*\*\* taken during Refinery tests of the processing of molybdenum and vanadium-bearing uranium concentrates were available for laboratory use. Four pairs of AP and BP samples were selected for analyses, two representing the processing of a blend of concentrates containing 16 weight per cent (uranium basis) Colorado concentrate (~1,000

\* All spectrochemical analyses were conducted with aqueous solutions. Thus, organic phases to be analyzed were stripped of uranium (and, most probably, of minor constituents) by seven successive equal-volume water washes. The water washes were then concentrated by boiling down prior to analysis.

\*\* The uranium-laden organic product from the primary extraction column of the Refinery.

\*\*\* Scrubbed organic product.

TABLE 4.3 Molybdenum and Vanadium Decontamination of Plant Test Samples

Per Cent Colorado Concentrate in Blend	Analyses				Scrub Column Decontamination Factors (U basis)		
	Sample Source and Number	U (g/l)	Mo (ppm, U basis)	V (ppm, U basis)	Sample Pair	Mo	V
16*	AP-1	104	9	1.5	1	>15	>2.5
	AP-2	104	8	1.5	2	13	1.7
	BP-1	99	<0.6	<0.6			
	BP-2	100	0.6	0.9			
33**	AP-3	102	9.5	4	3	14	>6.7
	AP-4	102	9.5	6	4	7	6.7
	BP-3	99	0.7	<0.6			
	BP-4	98	1.5	0.9			

\* Approximately 1,000 ppm Mo and 3,000 ppm V, uranium basis, in the feed slurry.

\*\* Approximately 2,000 ppm Mo and 6,000 ppm V, uranium basis, in the feed slurry.

ppm molybdenum, ~3,000 ppm vanadium, uranium basis) and two representing the processing of a blend containing 33 per cent (uranium basis) Colorado concentrates (~2,000 ppm molybdenum and ~6,000 ppm vanadium, uranium basis). Each of the samples was analyzed\* for molybdenum and vanadium, and the results are presented in Table 4.3.

#### Discussion and Conclusions

From the results in Table 4.2, it is apparent that niobium, ruthenium, and tantalum (having concentrations of 2 ppm or less, uranium basis, in the aqueous phase) are essentially insoluble in the Refinery feed digestion medium. It is also apparent that, although slightly soluble in the digestion medium, titanium, antimony, and tungsten (having concentrations of less than 2 ppm in the organic phase) must be considered nonextractable in the TBP-kerosene solvent. Thus, it is concluded on the basis of this laboratory testing that the presence of more than 1 ppm (uranium basis) of niobium, ruthenium, tantalum, titanium, antimony or tungsten in Refinery product uranyl nitrate solution (and subsequently in  $UO_3$  or  $UF_4$ ) is virtually impossible.

On the other hand, molybdenum and vanadium are each soluble and extractable. Based on current

tests, molybdenum decontamination across the "A" column (Table 4.2) and "B" column (Table 4.3) is calculated to be ~800/1 and ~12/1 (uranium basis), assuming normal Refinery operations.

Calculation of similar factors for vanadium is hindered by the abnormally low uranium content of the AP from the batch shakeout test (Table 4.2) and the undoubtedly high vanadium content resulting therefrom. The poor results noted may be due to a combination of two factors: reduced uranium extraction because of a high  $H_2SO_4$  content in the aqueous phase, and reduced uranium extraction because of the formation of a vanadate complex. Despite these complications, decontamination factors were calculated for both the "A" and "B" columns. They were ~350/1 and ~5/1 (uranium basis), respectively. The factor for the "A" column is assumed to be low.

Use of the molybdenum and vanadium decontamination factors calculated above allows determination of maximum feed slurry contents compatible with a UNH product containing less than 1 ppm (uranium basis) of molybdenum and vanadium. For molybdenum, the maximum level permissible in feed slurries was calculated to be 10,000 ppm, uranium basis. For vanadium, a similar level (apparently low, as explained above) was 1,750 ppm (uranium basis). The Refinery tests mentioned

earlier (Table 4.3) demonstrated the production of uranyl nitrate containing less than 1 ppm (uranium basis) of molybdenum and vanadium, while processing feed slurries containing up to 2,000 ppm (uranium basis) of molybdenum (well below the level calculated as feasible) and 6,000 ppm (uranium basis) of vanadium (well above the level calculated as feasible).

One last important point must be mentioned regarding the calculated decontamination factors. In all cases, they apply only to de-entrained organic phases (free of solids and aqueous phases). Entrainment is a well-known problem which could markedly reduce the decontamination factors calculated here; however, its evaluation in the laboratory is virtually impossible.

#### Future Work

The National Lead Company of Ohio Analytical Department is currently conducting studies of molybdenum extraction into, re-extraction from, and/or retention by TBP-kerosene solvents in varying states of degradation, using a radioactive molybdenum tracer. These studies will be reported in the future.

#### Reference

<sup>1</sup>B. G. Ryle, T. C. Runion, and W. J. Stratman. "The Extraction Process; Fernald Refinery," Current Commission Methods for Producing UO<sub>2</sub>, UF<sub>4</sub>, and UF<sub>6</sub>, USAEC Report TID-5295, pp. 73-141. January, 1956 (Classified).



## 5. SOLVENT DEGRADATION AND TREATMENT STUDIES

R. K. Klopfenstein      S. A. Sauerland      J. R. Nelli

**Abstract**

Continued use of a program of routine evaluation of "in-use" TBP-kerosene solvents has provided long-term confirmation of the correlations between (1) solvent condition, as indicated by solvent analyses for uranium retention, coalescence time, and diluent degradation products and (2) Refinery operations. Results of these evaluations have provided strong evidence of the beneficial results to be obtained by the addition of centrifuges to the solvent treatment systems.

**Introduction**

As a result of a rather long and varied investigation into the behavior of the tri-*n*-butyl phosphate (TBP)-kerosene solvent during uranium refining operations,<sup>1</sup> a program of routine evaluation of the solvents in the National Lead Company of Ohio Refinery was instituted. This program included:

1. Determination of how much uranium is retained by the solvents during re-extraction due to the presence of (1) di-*n*-butyl phosphate (DBP) and/or (2) unknown uranium complexing agents (probably organic acid degradation products of the kerosene diluent).

2. Determination of the coalescence time of the solvent after agitation with a standard synthetic aqueous uranium-nitric acid solution.

3. Determination, by the use of infrared spectroscopy, of the concentrations of organic acids, organic nitrates, and organic nitro compounds in the solvent as a result of diluent degradation.

This program was initiated in November, 1958; evaluations based on experience up to February 3,

1959, were reported earlier. The present report includes all evaluations for the 52 weeks beginning November 11, 1958, and ending November 9, 1959.

**Objectives for This Quarter**

The objective of this report is the presentation and discussion of the results of weekly solvent evaluations conducted during the last year (November, 1958, to November, 1959).

**Summary of Results Obtained This Quarter**

Weekly solvent evaluations, conducted over a twelve-month period, have demonstrated adequate correlations between Refinery operations and TBP-kerosene solvent condition as reflected by uranium retention, coalescence time, and infrared spectral analyses for diluent degradation products. The addition of centrifuges to the mixer-settler solvent treatment systems for each of the two extraction systems has been shown to be very beneficial in improving solvent condition and, thereby, Refinery operations.

**Routine Refinery Solvent Evaluations**

Solvent samples were obtained on a once-a-week basis from (1) the Refinery pulse column extraction system<sup>2</sup> (33.5 volume per cent TBP) and (2) the Refinery mixer-settler extraction system (22.5 volume per cent TBP). The evaluation procedures used in establishing solvent uranium retention, coalescence time, and infrared spectral analyses for diluent degradation products were described in a previous report.<sup>1</sup> The results of 52 consecutive solvent evaluations for the column system solvent (Table 5.1 and Fig. 5.1) and the mixer-settler system solvent (Table 5.2 and Fig. 5.2) are presented.

TABLE 5.1 Evaluations of Refinery Column System Solvent

Date of Sample	TBP (vol %)	U Retention (g/l)			Coales. Time (sec)		Infrared Analyses (Absorbance) <sup>††</sup>		
		Total	U/DBP*	U/UCA**	Fresh Solvent <sup>†</sup>	Current Solvent	Acids	Nitrates	Nitro Compounds
Nov. 11, 1958	33.1	0.18	0.05	0.11	85	160	0.157	0.376	0.350
Nov. 16, 1958	32.7	0.27	0.10	0.17	84	143	0.210	0.491	0.469
Nov. 25, 1958	34.3	0.28	0.08	0.20	91	160	0.229	0.597	0.686
Dec. 2, 1958	34.1	0.19	0.04	0.15	90	193	0.216	0.615	0.686
Dec. 9, 1958	33.6	0.38	0.10	0.26	87	205	0.266	0.722	0.820
Dec. 16, 1958	33.1	0.38	0.06	0.32	85	225	0.219	0.715	0.905
Dec. 23, 1958	33.0	0.51	0.14	0.47	84	225	0.276	0.711	0.880
Dec. 30, 1958	33.5	0.32	0.04	0.28	87	300	0.290	0.737	0.910
Jan. 6, 1959	33.4	0.48	0.06	0.40	87	270	0.265	0.701	0.962
Jan. 13, 1959	34.4	0.40	0.05	0.35	93	360	0.325	0.838	1.31
Jan. 20, 1959	32.4	0.43	0.05	0.38	82	240	0.320 0.064 <sup>‡</sup>	0.820 0.166 <sup>‡</sup>	1.10 0.241 <sup>‡</sup>
Jan. 27, 1959	36.0	3.40	1.24	2.16	104	>1000	0.792 0.152 <sup>‡</sup>	1.00 0.202 <sup>‡</sup>	∞ 0.534 <sup>‡</sup>
Feb. 3, 1959	32.5	0.60	0.42	0.18	82	275	0.544 0.111 <sup>‡</sup>	0.900 0.179 <sup>‡</sup>	∞ 0.418 <sup>‡</sup>
Feb. 10, 1959	32.8	0.50	0.06	0.44	84	205	0.396 0.072 <sup>‡</sup>	0.87 0.162	∞ 0.308
Feb. 17, 1959	32.7	0.48	0.12	0.34	83	265	0.394 0.072 <sup>‡</sup>	0.91 0.173 <sup>‡</sup>	1.6 0.299 <sup>‡</sup>
Feb. 24, 1959	32.5	0.48	0.06	0.42	82	155	0.328 0.057 <sup>‡</sup>	1.0 0.176 <sup>‡</sup>	1.7 0.281 <sup>‡</sup>
March 3, 1959	32.3	0.31	0.02	0.29	81	190	0.255	0.85	1.11
March 10, 1959	33.5	0.37	0.10	0.27	88	155	0.297	0.83	1.10
March 17, 1959	32.6	0.39	0.07	0.32	83	190	0.272	0.775	1.1
March 24, 1959	31.5	0.25	0.06	0.20	78	150	0.167	0.570	0.733
March 31, 1959	32.3	0.21	0.02	0.19	82	155	0.149	0.573	0.702
April 7, 1959	32.5	0.30	0.03	0.27	83	160	0.188	0.659	0.722
April 14, 1959	32.9	0.24	0.03	0.21	84	205	0.223	0.670	0.729
April 21, 1959	33.7	0.35	0.07	0.28	89	225	0.270	0.76	0.90
April 28, 1959	34.0	0.40	0.07	0.33	90	375	0.310	0.76	0.733
May 5, 1959	33.1	0.35	0.07	0.28	84	290	0.303	0.77	0.79
May 12, 1959	33.4	0.35	0.06	0.29	90	205	0.255	0.77	0.77
May 19, 1959	33.8	0.42	0.06	0.36	90	350	0.262	0.83	0.78
May 26, 1959	33.8	0.42	0.06	0.36	90	265	0.281	0.87	0.82
June 2, 1959	33.4	0.37	0.07	0.30	87	250	0.279	0.89	0.89
June 9, 1959	33.3	0.60	0.06	0.54	87	475	0.308	0.94	0.89
June 16, 1959	33.2	0.35	0.07	0.28	86	350	0.301	0.93	0.89
June 23, 1959	32.9	0.48	0.09	0.37	85	>600	0.334	1.00	0.91
June 30, 1959	33.7	0.53	0.12	0.41	89	>600	0.326	0.95	0.89
July 7, 1959	33.7	0.39	0.06	0.33	89	475	0.305	0.92	0.87
July 14, 1959	32.8	0.43	0.10	0.33	84	430	0.328	0.86	0.85
July 21, 1959	33.5	0.01	Nil	0.01	87	285	0.265	0.81	0.758
July 28, 1959	34.0	0.33	0.01	0.32	90	190	0.303	0.80	0.729
Aug. 4, 1959	33.2	0.40	0.01	0.39	86	176	0.290	0.80	0.80
Aug. 11, 1959	33.3	0.32	0.02	0.30	87	191	0.312	0.92	0.87
Aug. 18, 1959	33.6	0.37	0.02	0.35	88	228	0.294	0.89	0.89
Aug. 25, 1959	33.1	0.36	0.04	0.34	85	260	0.362	1.0	0.91
Sept. 1, 1959	34.4	0.18	0.05	0.13	93	340	0.389	0.90	1.0
Sept. 8, 1959	34.1	0.55	0.07	0.48	91	180	0.294	0.80	0.85
Sept. 15, 1959	34.4	0.43	0.01	0.42	93	135	0.340	0.85	0.87
Sept. 22, 1959	32.9	0.29	0.01	0.28	85	115	0.248	0.68	0.67
Sept. 29, 1959	33.7	0.31	0.05	0.26	89	128	0.241	0.67	0.66
Oct. 6, 1959	32.9	0.24	Nil	0.24	84	34	0.236	0.64	0.60
Oct. 13, 1959	33.5	0.27	0.01	0.26	87	104	0.220	0.65	0.58
Oct. 20, 1959	33.5	0.28	0.01	0.27	87	138	0.220	0.64	0.56
Oct. 27, 1959	34.2	0.35	0.01	0.34	92	169	0.272	0.72	0.66
Nov. 3, 1959	33.8	0.31	0.01	0.30	90	191	0.281	0.77	0.62

\* U/DBP is the uranium retention in re-extracted solvent due to the presence of DBP.

\*\* U/UCA is the uranium retention in re-extracted solvent due to the presence of unknown complexing agents.

† From standard curve of coalescence time versus fresh solvent.

†† In the infrared analyses, carboxylic acids absorb at 5.78 $\mu$ , organic nitrates at 6.14 $\mu$ , and organic nitro compounds at 6.44 $\mu$ .

‡ The lesser number represents analysis conducted with a shorter path length cell.

TABLE 5.2 Evaluations of Refinery Mixer-Settler System Solvent

Date of Sample	TBP (vol %)	U Retention (g/l)			Coales. Time (sec)		Infrared Analyses (Absorbance) <sup>††</sup>		
		Total	U/DBP*	U/UCA**	Fresh Solvent <sup>†</sup>	Current Solvent	Acids	Nitrates	Nitro Compounds
Nov. 11, 1958	22.7	2.17	0.80	1.37	52	160	0.486	0.984	1.00
Nov. 18, 1958	24.2	0.95	0.32	0.63	55	138	0.330	0.637	0.686
Nov. 25, 1958	24.4	0.13	0.03	0.10	55	95	0.313	0.630	0.537
Dec. 2, 1958	23.9	0.34	0.05	0.29	54	142	0.263	0.659	0.576
Dec. 9, 1958	21.8	0.39	0.15	0.24	50	95	0.171	0.451	0.385
Dec. 16, 1958	22.2	0.43	0.10	0.33	51	135	0.176	0.464	0.415
Dec. 23, 1958	22.5	0.57	0.16	0.41	51	110	0.176	0.468	0.377
Dec. 30, 1958	21.0	0.37	0.13	0.24	49	103	0.161	0.453	0.329
Jan. 6, 1959	21.0	0.39	0.14	0.25	49	112	0.183	0.508	0.368
Jan. 13, 1959	20.9	0.25	0.08	0.17	49	110	0.110	0.372	0.249
Jan. 20, 1959	20.2	0.09	0.03	0.06	48	59	0.029	0.109	0.143
Jan. 27, 1959	22.4	1.55	0.12	1.43	52	102	0.176	0.505	0.398
Feb. 3, 1959	20.8	0.86	0.25	0.61	49	100	0.236	0.580	0.598
Feb. 10, 1959	22.6	0.72	0.25	0.47	52	103	0.262	0.613	0.740
Feb. 17, 1959	21.3	0.52	0.26	0.26	50	120	0.255	0.627	0.585
Feb. 24, 1959	21.0	0.63	0.20	0.43	49	115	0.207	0.519	0.502
Mar. 3, 1959	21.0	0.19	0.02	0.17	49	102	0.152	0.546	0.468
Mar. 10, 1959	21.6	0.21	0.05	0.16	50	63	0.130	0.470	0.420
Mar. 17, 1959	22.4	0.27	0.08	0.19	51	100	0.161	0.555	0.444
Mar. 24, 1959	22.5	0.035	0.02	0.015	51	73	0.072	0.472	0.348
Mar. 31, 1959	23.7	0.043	0.03	0.013	54	75	0.079	0.486	0.332
Apr. 7, 1959	22.3	0.023	0.006	0.017	51	67	0.053	0.350	0.243
Apr. 14, 1959	23.6	0.033	0.01	0.023	53	72	0.053	0.358	0.299
Apr. 21, 1959	22.7	0.30	0.04	0.26	52	130	0.176	0.581	0.535
Apr. 28, 1959	23.8	0.12	0.01	0.11	54	77	0.185	0.644	0.574
May 5, 1959	23.8	0.085	0.03	0.055	54	42	0.158	0.619	0.554
May 12, 1959	24.0	0.095	0.03	0.065	55	62	0.146	0.596	0.553
May 19, 1959	22.5	0.14	0.02	0.12	51	46	0.152	0.627	0.554
May 26, 1959	23.4	0.13	0.03	0.10	53	80	0.161	0.740	0.606
June 2, 1959	21.7	0.17	0.02	0.15	50	85	0.176	0.821	0.656
June 9, 1959	21.3	0.12	0.02	0.10	49	92	0.167	0.77	0.59
June 16, 1959	23.2	0.15	0.08	0.07	54	80	0.140	0.675	0.538
June 23, 1959	22.9	0.14	0.11	0.03	52	83	0.140	0.736	0.559
June 30, 1959	22.4	0.11	0.05	0.06	51	84	0.149	0.665	0.581
July 7, 1959	23.8	0.15	Nil	0.15	54	68	0.164	0.706	0.610
July 14, 1959	23.3	0.09	0.01	0.08	53	80	0.152	0.659	0.553
July 21, 1959	23.6	0.12	Nil	0.12	53	100	0.164	0.634	0.594
July 28, 1959	23.4	0.14	Nil	0.14	53	90	0.170	0.682	0.581
Aug. 4, 1959	22.7	0.19	0.01	0.18	52	107	0.173	0.649	0.581
Aug. 11, 1959	22.3	0.012	Nil	0.01	49	90	0.176	0.66	0.59
Aug. 18, 1959	23.5	0.18	0.03	0.15	53	107	0.210	0.765	0.619
Aug. 25, 1959	22.6	0.21	0.02	0.19	49	98	0.182	0.719	0.602
Sept. 1, 1959	23.0	0.13	0.02	0.11	52	90	0.250	0.86	0.600
Sept. 8, 1959	23.4	0.24	0.03	0.21	53	88	0.170	0.698	0.556
Sept. 15, 1959	22.3	0.16	0.006	0.154	49	70	0.193	0.797	0.602
Sept. 22, 1959	23.6	0.17	0.01	0.16	53	62	0.243	0.87	0.66
Sept. 29, 1959	23.0	0.19	0.02	0.17	52	62	0.182	0.76	0.56
Oct. 6, 1959	22.8	0.095	0.005	0.09	52	70	0.127	0.525	0.425
Oct. 13, 1959	22.6	0.080	0.007	0.073	51	59	0.130	0.620	0.417
Oct. 20, 1959	22.8	0.078	0.01	0.068	51	60	0.100	0.491	0.354
Oct. 27, 1959	23.8	0.079	0.007	0.072	55	59	0.143	0.609	0.435
Nov. 3, 1959	23.9	0.051	Nil	0.051	54	61	0.179	0.793	0.476

\* U/DBP is the uranium retention in re-extracted solvent due to the presence of DBP.

\*\* U/UCA is the uranium retention in re-extracted solvent due to the presence of unknown complexing agents.

† From standard curve of coalescence time versus fresh solvent.

†† In the infrared analyses, carboxylic acids absorb at 5.78 $\mu$ , organic nitrates at 6.14 $\mu$ , and organic nitro compounds at 6.44 $\mu$ .

Discussion of Pulse Column System Solvent Evaluations

Reference to Figure 5.1 reveals that the column system solvent has shown rather wide variations in condition during the past year. Of first interest is the fact that the entire column system solvent inventory was replaced with fresh TBP and kerosene on October 27, 1958, shortly before evaluations were begun. The solvent showed a continual loss of condition from November 11, 1958, through January 20, 1959. This change was due simply to (1) TBP hydrolysis and kerosene degradation resulting from continued use and (2) relatively inefficient mixer-settler solvent treatment equipment.

The large and exceedingly detrimental loss of condition between January 20, 1959, and February 3, 1959, was a result of the accidental recycling of a large volume of solvent to the Refinery digestion area, where excessive heat and nitric acid caused

rapid and serious solvent degradation. The very poor condition of the solvent was reflected in increased Refinery operating problems.

By the end of February, the solvent had returned to fair condition. It remained so until about April 14, when a definite trend toward poor condition again became apparent. In this case, the loss of condition was due to systematic additions of partially, but not completely, rehabilitated solvent. This solvent had been discarded earlier. Subsequently, it was batch treated until it was thought that its re-entry into the extraction system would not seriously upset operations. Such would probably have been the case had it not been for other factors whose effect became most apparent during June. Among the factors involved were upsets in Refinery operations due to feed slurry difficulties, comparatively high carbon contents in the feed slurry, and a second accidental recycling of a significant volume of solvent to the digestion area.

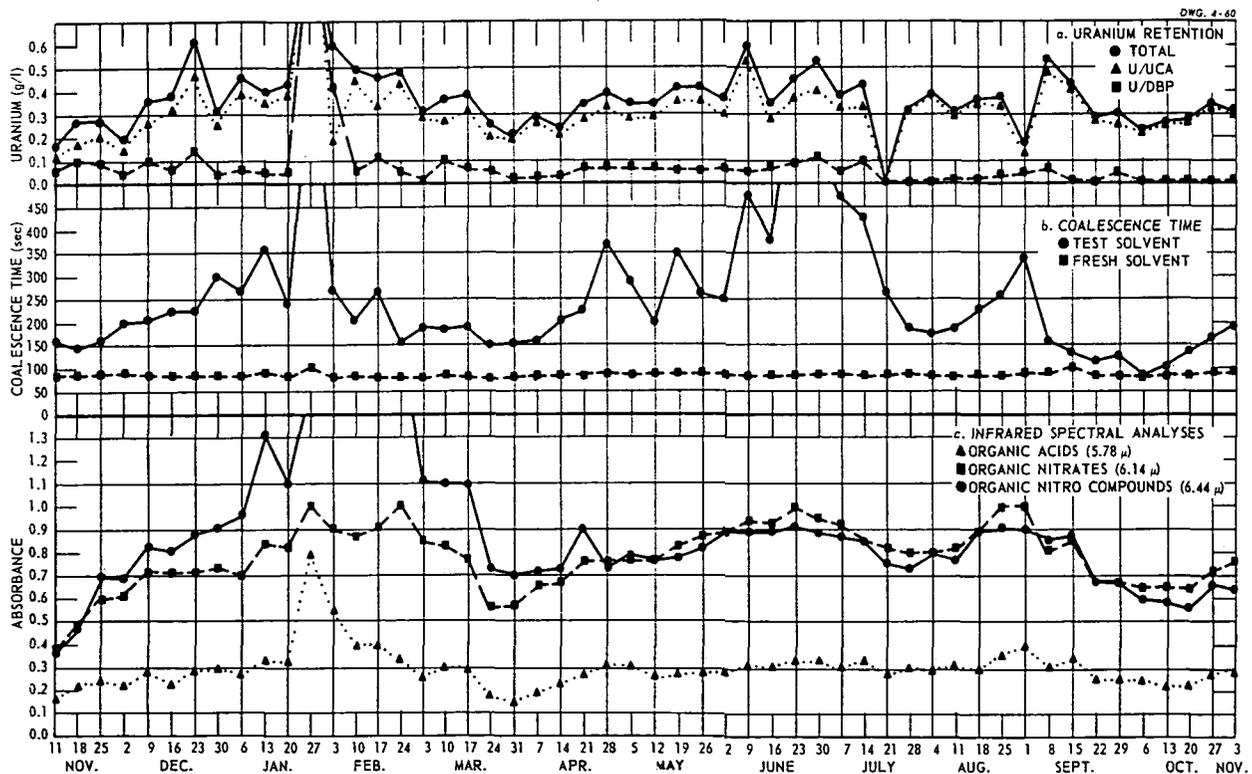


FIGURE 5.1 Weekly Evaluations of Refinery Column System Solvent (~33.5 vol % TBP)

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Recovery of solvent condition after this last phase of deterioration was greatly enhanced by the installation and use of centrifuges in the solvent treatment system, following the sodium carbonate wash stage. This took place near the beginning of July, and solvent improvement was immediately obvious. Since July, the solvent has retained good to fair condition. The rise noted near September 1 was again due to difficulties in the feed slurries (high-carbon poor-quality concentrates). The slight loss of condition after October 6th was due to small additions ( $\sim 1,000$  gallons per week) from a second volume of batch-treated solvent which had previously been discarded.

#### Discussion of Mixer-Settler System Solvent Evaluations

It is apparent from Figure 5.2 that the mixer-settler solvent was in temporarily poor condition at the beginning of November, 1958. Improvement

was rapid but temporary. A new peak of deterioration appeared in February, 1959. There was no immediately obvious explanation for this abrupt, but brief, loss of condition except the possibility of a bad sample.

In the case of the mixer-settler system, a centrifuge was added to the solvent treatment operation during March, 1959, with obvious and seemingly permanent beneficial results. Since that time, the mixer-settler system solvent has been in good condition. The slight condition loss noted on April 21 was due to the addition of 3,000 gallons of the partially rehabilitated solvent previously mentioned. In recent months, column system solvent has been used as make-up material in the mixer-settler system; evaluations indicate no serious or permanent effects from this practice. One fact which continually benefits mixer-settler solvent condition is the systematic addition of fresh kerosene to

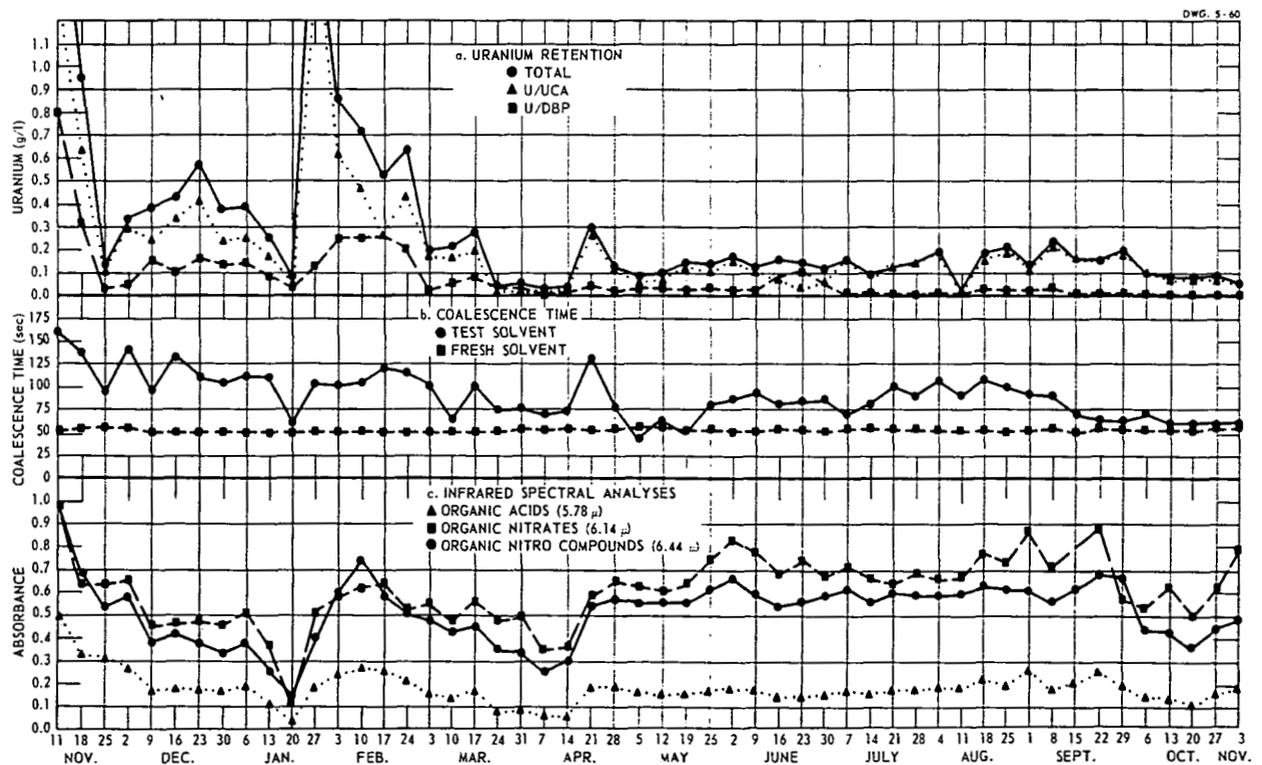


FIGURE 5.2 Weekly Evaluations of Refinery Mixer-Settler System Solvent ( $\sim 22.5$  vol % TBP)

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replace that lost by evaporation from the open, warm settler tanks.

#### General Discussion and Conclusions

These evaluations, conducted over the past 12 months, have provided graphic evidence of the effects to be expected from:

1. Recycling good solvent to the digestion area (where degradation is excessive).
2. Processing of feed slurries having high carbon contents.
3. Inefficient solvent treatment operations.
4. Use of centrifuges to increase solvent treatment efficiency.
5. Addition of partially rehabilitated used solvents to the normal inventories.

Consideration of the results presented here verifies the correlation between the condition of the solvent in use and the laboratory evaluation criteria (i.e., uranium retention, coalescence time, and infrared spectral analyses for degradation products). Although the three criteria do not always vary in the same direction at the same time to the

same magnitude, variations taken over several weeks are usually very consistent in their trends. These three criteria have aptly indicated the direct relationship between solvent condition and ease of Refinery operation.

#### Future Work

The routine solvent evaluation procedure will continue in use; however, future results will serve only as internal information, since the developmental aspects of the procedure have been completed.

#### References

<sup>1</sup>R. K. Klopfenstein. "Solvent Degradation and Treatment Studies," Summary Tech. Rpt., USAEC report NLCO-785, p. 29 April 15, 1959 (Classified); and preceding summary technical reports.

<sup>2</sup>B. G. Ryle, T. C. Runion, and W. J. Strattman. "The Extraction Process; Fernald Refinery," Current Commission Methods for Producing UO<sub>2</sub>, UF<sub>4</sub>, and UF<sub>6</sub>, USAEC Report TID-5295, pp. 73-141. January, 1956 (Classified).

## 6. EVALUATION OF COALESCER - DE-ENTRAINER UNITS

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### Abstract

Recent coalescer - de-entrainer pilot unit tests resulted in the design, installation, and testing of a plant-scale unit in the Refinery. Water, solids and cation decontamination of the primary extract stream from one of the Refinery extraction systems has been achieved by this plant-scale unit. Purity of the Refinery product stream also has been improved by its use.

### Introduction

Testing of a pilot coalescer - de-entrainer unit (installed in the Refinery) began in April, 1957. This unit had as its design basis, laboratory work which was performed at the Hanford Atomic Products Operation.<sup>1,2</sup> The objective of these tests was to remove, from the primary extract stream (AP), entrained solids and water which were known to contain cation impurities (i.e., sodium and iron). Sodium and iron are contaminants in the Refinery product stream (CP liquor).

In this application, a coalescer - de-entrainer functions as follows:

The water wets steel wool in the coalescer - de-entrainer, then coalesces and is removed from the bottom of the unit. The filtering action of the steel wool partially removes solids.

The results of this work indicated that the unit was achieving iron and solids decontamination of the extraction process primary extract stream (AP).<sup>3</sup> Since sodium and water analyses of samples obtained from the testing of this unit were inconsistent and nonreproducible, testing and operation of the coalescer was discontinued September, 1957. Testing was to be resumed when better methods for measuring these constituents had been developed.

Periodic sodium and iron contamination of the Refinery product stream continued to present a serious production problem, and testing of the

coalescer unit was resumed in January, 1959. During the interim, improved procedures had been developed for analyzing for water, solids, sodium, and iron in the organic stream. The pilot coalescer unit had also been modified to permit automatic operation for test runs of long time durations.

The pilot unit tests that were conducted during January, 1959, are described in this report. So successful were they that a plant unit was designed in February and installed in April. The satisfactory initial operation of the plant unit was marred only by difficulties in cleaning the unit. A study (reported here) was initiated to evaluate the coalescer and to develop an operable cleaning procedure for the unit.

### Prior Work on Project

In the coalescer - de-entrainer pilot unit previously referred to, iron and solids decontamination of the Refinery primary extract stream (AP) was achieved at a 200-gsfh throughput.<sup>3</sup> Evaluation of the unit indicated that it would be adaptable to the Refinery extraction process.

### Objectives

The objectives of the pilot coalescer - de-entrainer tests were (1) to determine the efficiency with which entrained solids, water, and cation impurities could be removed by this technique, (2) to determine operating characteristics of the unit, and (3) to obtain data for design of a plant-scale unit.

The objectives of the plant-scale test program were (1) to confirm the pilot-scale decontamination results, (2) to evaluate the effect of the coalescer on Refinery product (CP) purity, and (3) to develop an operable cleaning procedure for the plant unit.

Summary of Results

Additional testing of the pilot coalescer - de-entrainer unit indicated that a large-scale plant unit would effectively improve the quality of the Refinery's extraction system product. The objectives of the pilot-scale tests were attained as follows:

1. The average removal of solids, water, sodium, and iron from the primary extract stream for these tests (i.e., for the tests conducted at a 200-gsfh throughput) was:

Solids	—	68%
Water	—	58%
Sodium	—	65%
Iron	—	57%

2. It was found that the decontamination efficiencies for water and solids were affected by the inlet concentrations of the impurities, as well as by the unit pressure drop of the coalescer - de-entrainer unit. A unit pressure drop of 2 to 3 psi at startup was desired. This requirement was satisfied by use of a cleaning cycle that included a water backwash and a kerosene backwash of the pilot unit. The rate of increase for the pilot unit pressure drop was 0.04903 psi/hr during a test of 114 hours' duration.

3. The scale-up of the coalescer test unit presented no special problems.

The objectives of the plant-scale test program were attained as follows:

a. Water decontamination of the primary extract stream achieved by the plant-scale unit was improved (in comparison with the pilot unit) by increasing the packed height of the plant unit and by designing for a slightly lower operating throughput.

b. Purity of the Refinery extraction system product has been improved by use of the coalescer unit. Generally, more than 50 per cent of the entrained impurities (iron, sodium, etc.) in the primary extract stream have been removed by use of this relatively inexpensive de-entrainment equipment.

c. The cleaning procedure utilized for the pilot unit was not effective for the plant unit, and a new cleaning cycle has been developed. The average operating time between cleaning periods has been approximately 65 hours for the plant unit. The basis for this time factor is an operating range of from 3 to 9 psi and an average rate of pressure drop rise of 0.0923 psi/hr for the plant coalescer unit.

Equipment

A. Pilot Coalescer - De-entrainer Unit

The pilot unit coalescer - de-entrainer<sup>3</sup> used for the 1957 tests (4-inch-diameter glass column, 24 inches long, and packed with 10 pounds of stainless steel wool per cubic foot) was modified for continuous operation in the 1959 tests as illustrated in Figure 6.1. The major modification was

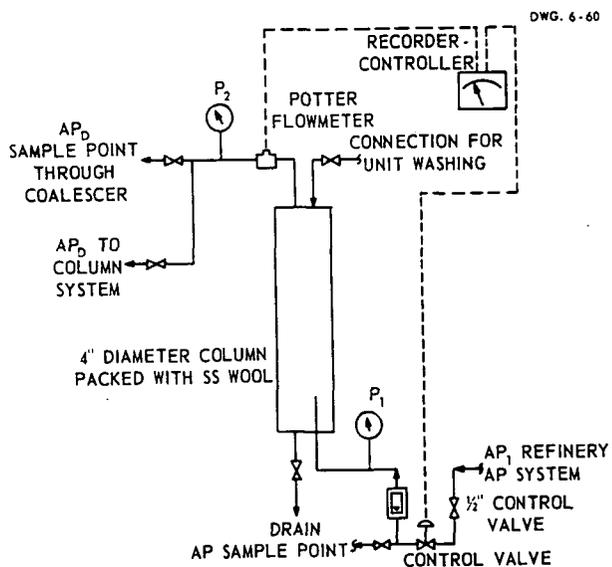


FIGURE 6.1 Pilot Unit: Coalescer - De-entrainer (as modified for 1959 tests)

KEY

- AP - Feed from the Refinery extraction columns.
- AP<sub>1</sub> - Feed from the two extraction columns on the "cold" side of the Refinery.
- AP<sub>D</sub> - Refinery AP stream after it has passed through the coalescer-de-entrainer system.
- P<sub>1</sub> and P<sub>2</sub> - Pressure gauges.

addition of automatic flow control instrumentation, which consisted of a diaphragm control valve, operated by a Potter Flowmeter through a recorder-controller. This modification permitted continuous testing of the unit over long periods of time by removing the need for constant operator attention. This change also eliminated large variations in flow and pressure which had previously caused periodic self-cleaning of the steel wool bed and thus undesired re-entrainment of the water and solids to the extract stream.

### B. Plant Coalescer - De-entrainer Unit

The plant (i.e., the Refinery) has a radioactively "cold" extraction system and a "hot" extraction

system. Each extraction system includes two primary extraction columns (A columns), one scrub column (B column), and two re-extraction columns (C columns). Each system is identical (i.e., auxiliary equipment, control loops, equipment size, etc.) with the exception that the coalescer - de-entrainer unit operates between the A and B columns of the "cold side" extraction system only.

The plant unit was designed to process the entire product stream (AP) from two primary extraction columns, as shown in Figure 6.2. Characteristics of the plant unit are similar to those of the pilot unit; however, a stainless steel tank rather than a glass column is utilized for the unit. A greater

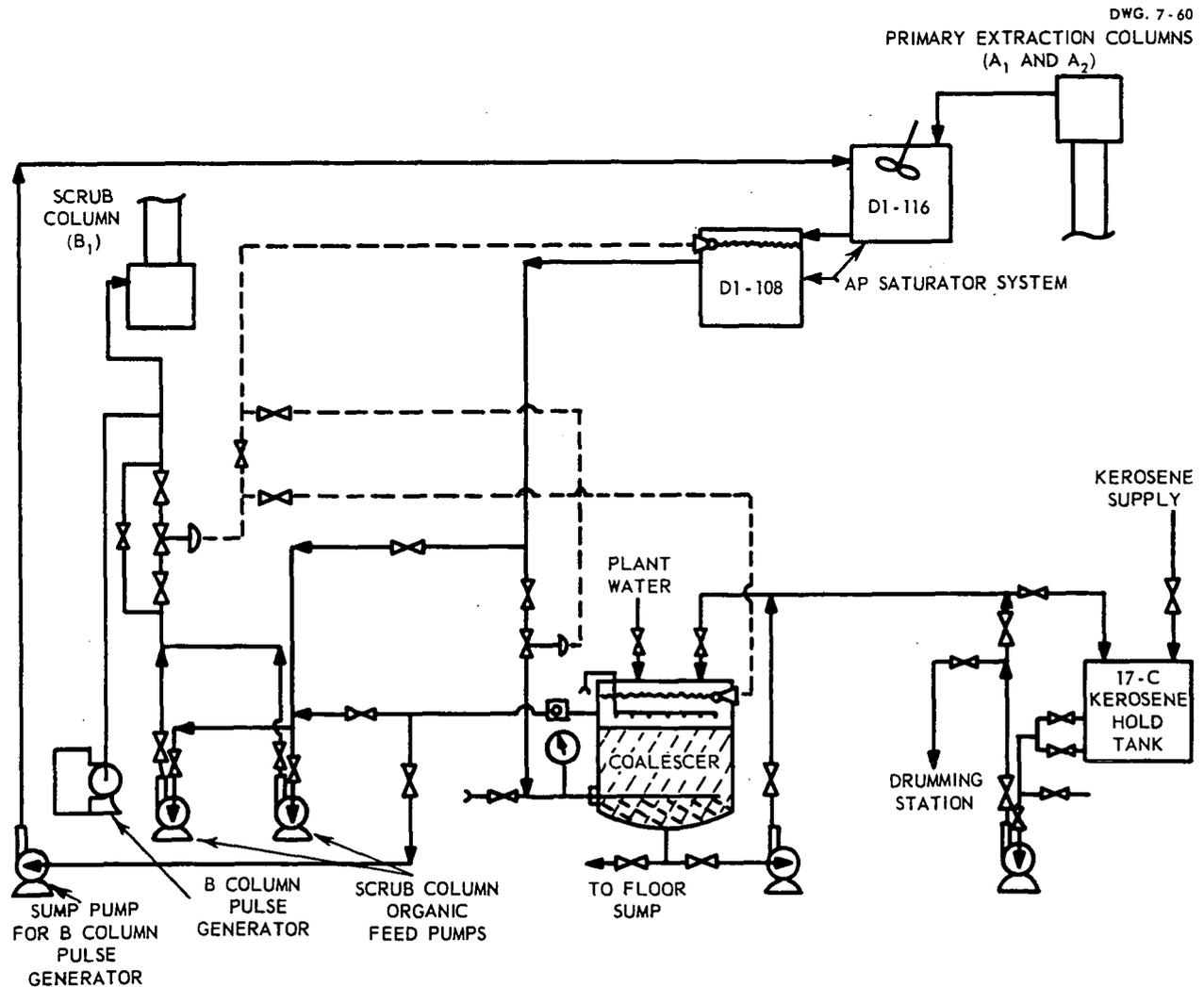


FIGURE 6.2 Refinery Unit: Coalescer - De-entrainer

addition of automatic flow control instrumentation, which consisted of a diaphragm control valve, operated by a Potter Flowmeter through a recorder-controller. This modification permitted continuous testing of the unit over long periods of time by removing the need for constant operator attention. This change also eliminated large variations in flow and pressure which had previously caused periodic self-cleaning of the steel wool bed and thus undesired re-entrainment of the water and solids to the extract stream.

system. Each extraction system includes primary extraction columns (A columns), scrub column (B column), and two re-extractive (C columns). Each system is identical to the other (except for auxiliary equipment, control loops, equipment, etc.) with the exception that the coalescer-entrainer unit operates between the A columns of the "cold side" extraction system

The plant unit was designed to process a product stream (AP) from two primary columns, as shown in Figure 6.2. Characteristics of the plant unit are similar to those of the refinery unit; however, a stainless steel tank rather than a glass column is utilized for the unit.

B. Plant Coalescer - De-entrainer Unit

The plant (i.e., the Refinery) has a radioactively labeled "cold" extraction system and a "hot" extraction

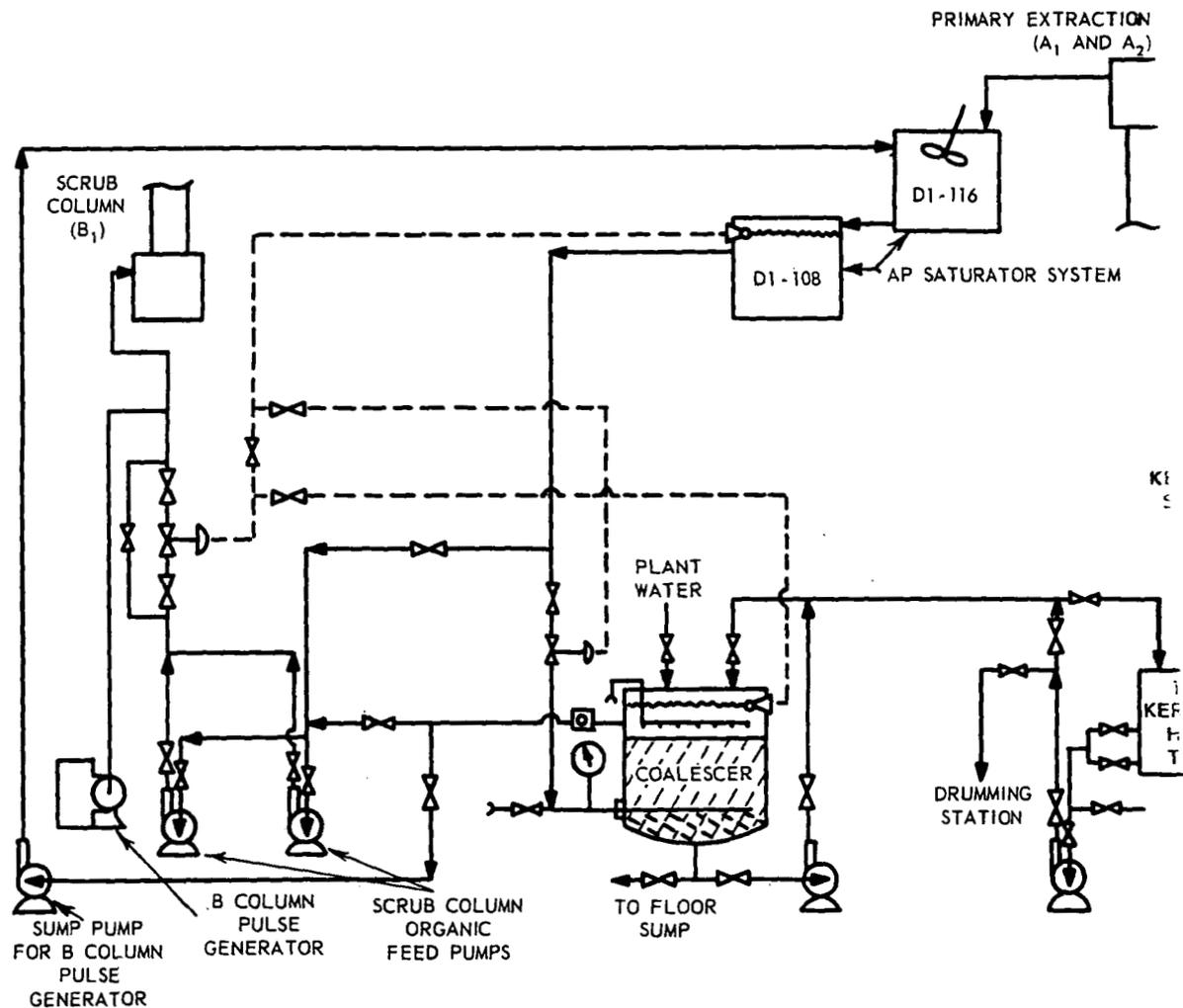


FIGURE 6.2 Refinery Unit: Coalescer - De-entrainer

water decontamination than had been achieved in the pilot unit was desirable; therefore, the plant unit was designed for operation at a lower throughput (150 gsfh for the plant unit vs 200 gsfh for the pilot unit), and the height of the stainless steel wool bed was increased from 2 feet to 3 feet.

An extract distributor was required in the plant unit coalescer because of its larger diameter. The distributor consists of a crossbar assembly (1-inch-diameter stainless pipes placed perpendicular to each other) which contains forty  $\frac{1}{8}$ -inch-diameter holes drilled uniformly across the lengths of the pipes. The distributor is placed in the coalescer tank so that a dead zone of approximately 150 gallons remain at the bottom of the unit for collection of the coalesced aqueous phase. This dead zone is packed with Berl saddles. The main bed packing is placed directly on top of the saddles and is fastened in place at the top of the bed by crossbars bracketed to the sides of the tank. The bed consists of 24 pie-shaped 6-inch-thick stainless steel wool pads (4 pie-shaped pads per layer; 6 layers high). The packing density of each pad is 10 lb/cu ft. The wire diameter varies from 0.002 to 0.0035 inch.

The plant unit is equipped with a spray ring for the backwash cleaning cycle. The ring consists of a circular piece of  $\frac{1}{2}$ -inch-diameter pipe with one crossbar ( $\frac{1}{2}$ -inch-diameter pipe) that is connected at each end to the inner periphery of the ring. The diameter of the ring is approximately one foot less than the diameter of the coalescer unit. One hundred and fifty  $\frac{1}{16}$ -inch-diameter holes are drilled in the spray ring and cross piece, at equal intervals (staggered on each side of the lower portion of the pipe at a  $30^\circ$  angle with the vertical axis).

The plant unit is integrated into the operation of the "cold side" extraction system, as illustrated in Figure 6.2. AP from the primary extraction columns is fed by gravity to the AP saturator system (D1-116 and D1-108). A level is maintained in the settler of this system (D1-108) by use of a

level control and a diaphragm valve on the settler discharge line. (This line serves also as the inlet line of the coalescer.) The line and valve were designed so that a pressure of at least 7 psi is available at the inlet to the coalescer unit.

Gravity flow is employed to remove the de-entrained organic ( $AP_D$ ) from the coalescer to the scrub column ( $B_1$ ) organic feed pump. A level control in the coalescer tank activates a diaphragm control valve on the discharge side of this pump.

The instrumentation and piping of the coalescer system is arranged so that the coalescer is bypassed during the cleaning cycle. During the cleaning cycle, the de-entrained organic in the coalescer unit is displaced with water and flows first to the sump pump for the B column pulse generation and subsequently back into the system at the AP saturator (D1-116).

#### Sampling Procedures and Analyses

The sampling procedure and schedule for pilot unit tests were based upon an assumption that there was no backmixing in the unit. Samples were taken on a time schedule of one volume change. That is, for 200 gallons per square foot per hour (gsfh) tests, the inlet sample (AP) was taken 4.7 minutes before the outlet sample ( $AP_D$ ) was taken.

Automatic samplers were not incorporated into the design of the plant unit, and it was thought that an assumption of no backmixing in this unit would be completely invalid due to the size and configuration of the equipment. Therefore, the sampling procedure utilized for pilot unit tests (time between inlet and outlet sampling equals time for one volume change in the unit) was not used in the plant unit. Inlet and outlet samples were taken at approximately the same time. Average efficiencies were calculated from the plant operational data, and no attempts were made to statistically evaluate the data.

Water and solid entrainment determinations were made by high-speed centrifugation of 10-ml ali-

quots of the AP and AP<sub>D</sub> samples. These determinations were made in a De Laval gyro test unit.

Sodium determinations were made with a Beckman flame photometer, while iron was determined by a colorimetric method utilizing orthophenanthroline as the chromogenic reagent. The procedure for preparing the aqueous samples used in sodium and iron determinations is designed to ensure that the samples are representative of the AP and AP<sub>D</sub>. The entire sample is stripped three times with equal volumes of a 1N HCl solution after the sample bottles have been washed with the first volume of HCl stripping solution. The precision of both the sodium and iron analyses in the lower gamma-per-milliliter range is approximately  $\pm 0.3$   $\gamma$ /ml (LE<sub>x</sub> for 95 per cent confidence limit).

(after coalescer treatment) by a high-speed batch centrifugation (Table 6.1).

It had been reported previously<sup>3</sup> that at 200 to 300 gsfh throughput, good iron removal from the AP stream had been achieved in the pilot coalescer unit. After alteration of the pilot unit in January, 1959, these results were confirmed in four pilot unit tests. A summary of the iron and sodium decontamination achieved in these tests is presented in Table 6.2. Particularly impressive are the results of pilot test No. 27. This test, which was conducted successfully over a period of 114 hours, yielded an average sodium decontamination of 70 per cent. Since the iron content of the AP stream was less than 0.5  $\gamma$ /ml during this test, no effort was made to determine a decontamination factor for this element.

#### Decontamination -- Pilot Unit

##### A. Sodium and Iron

Previous investigations indicated that sodium and iron contamination of the Refinery product stream was directly attributable to the aqueous phase and solids entrained in the primary extract (AP) and scrubbed extract (BP) streams. Confirmatory results were observed in recent tests which showed that physical de-entrainment in a coalescer unit removes sodium and iron from the AP stream. For all practical purposes, the sodium and iron can be removed from the organic phase

##### B. Solids and Water

Solids and water decontamination of the AP stream was achieved in all pilot unit tests, No. 24 through No. 27 (Table 6.2). Individual sample analyses for test No. 27 are presented in Table 6.3. During the test, the decontamination efficiency for each constituent varied over wide ranges.

It was reported<sup>3</sup> that decontamination efficiency of water and solids seemed to be affected by (1) the unit pressure drop ( $\Delta P$ ), and (2) the concentrations of these impurities in the feed stream. Therefore, the data presented in Table 6.3 were subjected to statistical analysis. A technique

TABLE 6.1 Removal of Sodium and Iron From the Primary Extract Stream

Sample No.	AP, Primary Extract Stream		AP <sub>D</sub> , Primary Extract Stream After Passing Through Coalescer De-entrainer Unit (Plant Unit)		Primary Extract From the Coalescer De-entrainer Unit After Batch Centrifugation	
	Na ( $\gamma$ /ml)	Fe ( $\gamma$ /ml)	Na ( $\gamma$ /ml)	Fe ( $\gamma$ /ml)	Na ( $\gamma$ /ml)	Fe ( $\gamma$ /ml)
1	1.90	1.75	0.48	0.74	<0.1	<0.1
2	1.72	1.67	0.58	0.74	<0.1	<0.1
3	1.60	1.59	0.46	0.97	<0.1	0.13
4	1.70	1.70	0.46	0.55	<0.1	0.14

TABLE 6.2 Pilot Coalescer Tests (1959 Tests)

Test No.	Date	Coalescer Throughput (19sfh)	Sample Sets Represented	Avg. Water Decontamination* (%)	Avg. Solids Decontamination* (%)	Avg. Sodium Decontamination* (%)	Avg. Iron Decontamination* (%)	Test Duration (hr)
24	Jan. 23, 1959	200	20	70	70	60	50	6
25	Jan. 25, 1959	400	20	50	70	70	30	6
26	Feb. 4, 1959	200	10	70	90	50	70	2
27	Feb. 19-23, 1959	200	45	50	60	70	**	114
Average of all Samples from 200-gsfh Tests				58	68	65	57	

$$* \% \text{ Decontamination} = \frac{\text{Conc. (In)} - \text{Conc. (Out)}}{\text{Conc. (In)}} \times 100$$

\*\* Inlet sample concentration only slightly greater than the analytical detection value.

of multiple regression<sup>4</sup> was utilized to reduce the data to equations of the form:

$$E = b_0 + b_1 \Delta P + b_2 C + b_3 C$$

where E = Decontamination Efficiency

$\Delta P$  = Pressure Drop

C = Concentration of Solids (or Water)

b = Constants

The multiple regression analyses of the data from test No. 27 substantiated the observations that pressure drop and the concentration of these impurities affect decontamination efficiency. The solids decontamination data reduced to an equation:

$$E_S = 0.920 - 0.090 \Delta P + 1.094 C_S$$

where  $E_S$  = Solids Decontamination Efficiency

$$= \frac{C(\text{In}) - C(\text{Out})}{C(\text{In})}$$

$C_S$  = Concentration of Solids (vol %)

$\Delta P$  = Coalescer Unit Pressure Drop (psi)

On the basis of this equation, 50.7 per cent of the variation in the solids decontamination efficiency could be explained ( $LE_x$ , 95 per cent confidence limits). The variable,  $\Delta P$ , represents 44.7 per cent of the variation, while the solids concentration of the feed represents 6.0 per cent of the

variation explained. The negative and positive signs of the equation indicate that decontamination efficiency is decreased with an increase in the unit pressure drop, while the efficiency increased with an increased solids concentration in the feed. The 49.3 per cent variation in  $E_S$  unexplained by the equation is probably due largely to sample scheduling and procedure, together with other unmeasured variables (i.e., temperature and slight changes in the total flowrate).

Water decontamination data (Table 6.3) reduced to an equation:

$$E_W = 0.328 - 0.034 \Delta P + 1.199 C_W$$

where  $E_W$  = Water Decontamination Efficiency

$$= \frac{C(\text{In}) - C(\text{Out})}{C(\text{In})}$$

$C_W$  = Concentration of Water (vol %)

$\Delta P$  = Coalescer Unit Pressure Drop (psi)

By this equation, 31.8 per cent of the variation in the water decontamination efficiency could be explained. Again, efficiency decreased with an increased  $\Delta P$ , but increased with increases in the water content of the feed; however, the effect of initial water concentration was large (25 per cent)

TABLE 6.3 Pilot Unit - Coalescer - De-entrainer Test No. 27

Test Duration (hr)	Date	Hour of Test	Coalescer $\Delta P^*$ (psi)	Entrainment				Total	
				Solids (vol %)		Water (vol %)		Total (vol %)	
				AP	AP <sub>D</sub>	AP	AP <sub>D</sub>	AP	AP <sub>D</sub>
6	2/19/59	0	1.2	-	-	-	-	-	-
6		1	1.1	0.10	0.01	0.30	0.08	0.40	0.09
2		2	1.3	0.12	0.02	0.23	0.08	0.35	0.10
114		3	1.4	0.20	0.06	0.40	0.34	0.60	0.40
		4	1.5	0.05	0.02	0.15	0.06	0.20	0.08
		5	1.5	0.08	0.02	0.12	0.06	0.20	0.08
		6	1.7	0.08	0.005	0.12	0.04	0.20	0.05
		7	-	-	-	-	-	-	-
		8	1.8	0.07	0.01	0.13	0.08	0.20	0.09
		9	2.0	0.08	0.02	0.12	0.07	0.20	0.09
	10	2.2	0.08	0.02	0.10	0.07	0.18	0.09	
2/20/59	11	2.3	0.08	0.02	0.10	0.07	0.18	0.09	
	12	2.2	0.09	0.02	0.11	0.07	0.20	0.09	
	13	2.1	0.03	0.005	0.07	0.05	0.10	0.06	
	14	2.2	0.08	0.02	0.10	0.08	0.18	0.10	
	15	2.2	0.07	0.02	0.08	0.07	0.15	0.09	
	16	2.3	0.07	0.02	0.08	0.08	0.15	0.10	
	17	2.1	0.05	0.01	0.07	0.05	0.12	0.06	
	18	2.1	0.05	0.02	0.15	0.06	0.20	0.08	
	19	2.5	0.02	0.005	0.06	0.05	0.08	0.06	
	20	2.7	0.05	0.02	0.15	0.06	0.20	0.08	
	21	2.8	0.07	0.02	0.13	0.07	0.20	0.09	
	22	-	-	-	-	-	-	-	
	23	3.0	0.04	0.01	0.16	0.08	0.20	0.09	
	24	3.1	0.05	0.01	0.10	0.04	0.15	0.05	
2/21/59	27	3.2	0.08	0.05	0.12	0.07	0.20	0.13	
	30	3.2	0.10	0.04	0.30	0.08	0.40	0.12	
	34	3.7	0.07	0.05	0.23	0.10	0.30	0.15	
	38	4.0	0.05	0.02	0.15	0.09	0.20	0.11	
	42	4.6	0.04	0.03	0.16	0.09	0.20	0.12	
	46	4.9	0.15	0.02	0.25	0.08	0.40	0.10	
	50	3.7	0.10	0.05	0.15	0.10	0.25	0.15	
	54	4.0	0.15	0.05	0.30	0.09	0.45	0.14	
	58	4.3	0.05	0.01	0.15	0.09	0.20	0.10	
	62	4.6	0.05	0.04	0.15	0.10	0.20	0.14	
2/22/59	66	4.3	0.05	0.03	0.10	0.10	0.15	0.13	
	70	4.5	0.10	0.06	0.20	0.11	0.30	0.17	
	74	4.8	0.07	0.04	0.15	0.10	0.22	0.14	
	78	5.2	0.10	0.05	0.30	0.10	0.40	0.15	
	82	5.5	0.04	0.04	0.12	0.11	0.16	0.15	
	86	5.6	0.10	0.04	0.30	0.11	0.40	0.15	
2/23/59	90	6.0	0.10	0.05	0.20	0.10	0.30	0.15	
	94	5.8	0.10	0.06	0.30	0.14	0.40	0.20	
	98	6.3	0.35	0.05	0.65	0.15	1.00	0.20	
	102	6.6	0.04	0.04	0.16	0.16	0.20	0.20	
	106	6.6	0.08	0.04	0.32	0.16	0.40	0.20	
2/24/59	110	6.6	0.09	0.04	0.28	0.16	0.37	0.20	
	114	7.1	0.15	0.08	0.30	0.22	0.45	0.20	
Average				0.09	0.03	0.19	0.10		
Decontamination Efficiency (Avg)				70%		50%			

\* Coalescer  $\Delta P$  is the pressure drop through the coalescer - de-entrainer unit.

as compared to the effect of unit pressure drop (only 6.8 per cent of the explained variation). An equation ( $E_w = 0.316 + 0.334C_w - 0.024\Delta P + 1.88C_s$ ) was written for water decontamination efficiency to include the variable,  $C_s$ . It was found that this variable would explain a 5.6 per cent variation in  $E_w$  at a 94 per cent confidence limit, suggesting that water is probably associated to some extent with the solids contained by the AP stream.

Decontamination – Plant Unit

A. Primary Extract Decontamination

The scale-up factors used for the plant unit design were predicated upon two main objectives.

TABLE 6.4 Plant-Scale Coalescer – De-entrainer: Solids and Water Removal\*

Hour of Test	$\Delta P$ in Coalescer (psi)	AP Solids (vol %)	AP <sub>D</sub> Solids (vol %)	AP Water (vol %)	AP <sub>D</sub> Water (vol %)
4	3.1	0.02	0.03	0.18	0.04
8	3.6	0.01	0.03	0.19	0.10
12	3.9	0.04	0.02	0.36	0.07
16	4.1	—	—	—	—
20	5.0	0.01	0.01	0.19	0.18
24	4.8	0.02	0.01	0.10	0.01
28	4.5	0.04	0.01	0.14	0.02
32	4.3	0.03	0.01	0.18	0.02
36	4.6	0.03	0.02	0.17	0.01
40	5.0	0.02	<0.01	0.09	0.04
44	5.1	0.02	<0.01	0.18	0.05
48	5.2	0.01	<0.01	0.19	0.04
52	6.0	0.04	0.01	0.20	0.09
56	5.8	0.04	<0.01	0.36	0.05
60	6.2	0.03	0.03	0.32	0.15
64	4.2	0.02	0.01	0.11	0.06
68	5.0	0.02	<0.01	0.15	0.05
72	5.4	0.02	0.01	0.06	0.06
76	5.2	0.01	0.01	0.10	0.04
80	6.9	0.01	0.02	0.16	0.03
84	6.2	0.05	0.02	0.36	0.04
88	6.3	0.02	<0.01	0.20	0.05
92	6.8	0.01	0.01	0.06	0.08
Average		0.02	0.01	0.18	0.06
Avg Decontamination Efficiency		50%		70%	

\* Coalescer Throughput = 150 gsfh

The first objective was to increase the over-all water decontamination through the unit. The second objective was to increase solids decontamination at larger unit pressure drops. To achieve these objectives, the final design of the plant unit incorporated a lower unit throughput (150 gsfh) and an extra foot of packed bed height. Table 6.4 illustrates the solids and water decontamination achieved in the plant-scale coalescer – de-entrainer operation. A comparison of water decontamination achieved in the pilot unit (Table 6.3) and the plant unit (Table 6.4) reveals that over a similar  $\Delta P$  range and with identical concentrations of water in the AP stream, average water decontamination achieved in the plant unit is significantly higher than that achieved in the pilot unit – 70 per cent vs 50 per cent.

Solids decontamination in the plant coalescer unit has been good (Tables 6.4 and 6.5). Soon after installation of this unit in the extraction system, other changes in the Refinery extraction system effected a significant reduction in the solids content of the AP stream. Therefore, com-

TABLE 6.5 Start-Up of Plant Coalescer – De-entrainer System\*

Date	Time	Entrainment					
		Solids (vol %)		Water (vol %)		Total (vol %)	
		AP	AP <sub>D</sub>	AP	AP <sub>D</sub>	AP	AP <sub>D</sub>
6/5/59	12:30 pm	0.08	0.10	0.10	0.01	0.18	0.11
	1:30 pm	0.09	0.10	0.11	0.02	0.20	0.12
6/8/58	10:00 am	0.06	0.01	0.34	0.06	0.40	0.07
	2:00 pm	0.08	0.05	0.37	0.10	0.45	0.15
	6:00 pm	0.02	0.03	0.08	0.03	0.12	0.06
6/9/59	4:00 am	0.08	0.04	0.12	0.06	0.20	0.10
	7:00 am	0.02	0.03	0.08	0.03	0.10	0.06
	8:00 am	0.03	0.03	0.15	0.06	0.18	0.09
	10:00 am	0.05	0.01	0.10	0.08	0.15	0.09
6/10/59	2:00 pm	0.10	0.03	0.10	0.08	0.20	0.11
	10:00 am	0.14	0.02	0.36	0.08	0.50	0.10
	6:00 pm	0.05	0.05	0.20	0.05	0.25	0.10
Average		0.07	0.04	0.18	0.06		
Decontamination Efficiency (Avg)		40%		70%			

\* Coalescer throughput = 150 gsfh

parison of the plant coalescer and pilot coalescer, as far as solids removal is concerned, has been impractical.

The removal of cation impurities from the AP stream by use of the coalescer unit has been very satisfactory. Entrained impurities (sodium, iron, potassium, aluminum, magnesium, and lead) have been largely removed from the AP stream (Table 6.6). Decontamination efficiencies for these elements seemingly have depended largely upon the inlet (AP) concentration of the element. Outlet (AP<sub>D</sub>) concentrations of iron and sodium, for example, remained relatively constant throughout the entire test period, as indicated in Table 6.6.

**B. Effect Upon Product Purity**

The effect of the coalescer - de-entrainer upon the purity of Refinery product has been difficult

to ascertain since normal daily changes in operation and variables also have effects. With the coalescer unit in operation, sodium contamination of the product stream (CP) has decreased after a coalescer cleaning cycle has been completed. This effect of the coalescer unit on the "cold side" product stream (CP<sub>1</sub>) is clearly indicated in Table 6.7. The sodium value of the CP<sub>1</sub> stream presented in this table is a calculated value based upon the sodium results obtained from analyses of the product stream (CP<sub>5</sub>) from another extraction system and the analyses for the combined CP<sub>5</sub> and CP<sub>1</sub> streams. Actual CP<sub>1</sub> and CP<sub>5</sub> flowrates were utilized for these calculations.

Operation of the "cold" extraction system and the "hot" extraction system on July 7, 1959, can be compared in Table 6.8. On July 7, 1959, both

**TABLE 6.6 Plant - Scale Coalescer - De-entrainer Operation**

Hours of Operation After Start-Up	Coalescer ΔP (psi)	Total Entr. In AP (vol %)	Total Entr. In AP <sub>D</sub> (vol %)	Na*		Fe*		Spectrochemical Analyses (ppm)*											
				(y/ml)		(y/ml)		K		Al		Mg		Mo		Pb		V	
				AP	AP <sub>D</sub>	AP	AP <sub>D</sub>	AP	AP <sub>D</sub>	AP	AP <sub>D</sub>	AP	AP <sub>D</sub>	AP	AP <sub>D</sub>	AP	AP <sub>D</sub>	AP	AP <sub>D</sub>
0	3.0	-	-	-	-	-	-												
4	3.1	0.20	0.07	5.1	2.1	4.0	1.6												
8	3.6	0.20	0.13					10	7	25	10	>100	75	2	10	10	10	2	2
12	3.9	0.40	0.09	8.5	3.2	5.2	2.1												
16	4.1																		
20	5.0	0.20	0.19	4.5	3.7	2.9	2.5												
24	4.8	0.12	0.02					8	3	15	<6	100	60	2	2	9	4	3	1
28	4.5	0.18	0.03	6.4	1.8	4.4	1.4												
32	4.3	0.21	0.03					9	3	25	<6	75	15	6	10	8	4	4	2
36	4.6	0.20	0.03	7.1	1.9	5.0	1.3												
40	5.0	0.11	0.04					9	5	15	<6	100	15	10	10	8	4	4	1
44	5.1	0.20	0.05	6.0	2.0	3.9	1.3												
48	5.2	0.20	0.04	5.2	2.6	3.3	2.1												
52	6.0	0.24	0.10					9	8	40	<6	>100	25	10	10	13	5	6	3
56	5.8	0.40	0.05					10	4	50	<6	>100	25	10	5	15	5	8	2
60	6.2	0.35	0.18	12.9	2.7	10.2	2.4												
64	4.2	0.13	0.07					10	5	25	10	100	25	10	8	10	3	5	3
68	5.0	0.17	0.05					10	4	15	10	75	20	4	10	10	3	3	2
72	5.4	0.08	0.07	4.4	1.9	3.2	1.8												
76	5.2	0.11	0.05					18	6	25	6	100	25	2	10	10	4	2	2
80	6.9	0.17	0.05					6	8	10	6	75	75	4	2	8	5	5	5
84	6.2	0.41	0.06	13.5	2.0	12.2	1.5												
88	6.3	0.22	0.05					9	9	25	6	100	50	4	2	9	4	7	3
92	6.8	0.07	0.09					5	10	12	40	75	>100	8	2	6	10	6	3
Average		0.21	0.07																

\* Sodium and iron analyses LE<sub>x</sub> ± 0.3 y/ml

\*\* All spectrochemical analyses LE<sub>x</sub> ± 50%

systems were being fed feed stock (AF) from the same feed hold tank and organic solvent (AX) from the same source. On this day the operating conditions (i.e., flowrates, primary extract saturation, flowratios) were identical in both extraction systems; however, the coalescer - de-entrainer was operating in the "cold" extraction system. On the "cold side" of the Refinery, entrainment in the

primary extract was substantially lower than on the "hot side", as was the sodium contamination of the AP<sub>D</sub> when compared to that of AP<sub>2</sub>. The lower sodium content of the "cold side" AP resulted in a lower sodium profile for the "cold side" scrub column (exit streams, BP<sub>1</sub> and BR<sub>1</sub>), which in turn indicates a better product purity for the "cold side" extraction process.

TABLE 6.7 Effect of Coalescer - De-entrainer Upon Product Sodium Contamination

Date	Time	Coalescer ΔP (psi)	Sodium in CP <sub>1</sub> * (ppm)	
9/16/59	12 Midnight	Off Stream during Cleaning of Coalescer	24	
	2 am		24	
	4		21	
	6		21	
	8		24	
	10		-	
	12 Noon		33	
	2 pm		37	
	4		2.8	28
	6		3.2	15
9/17/59	8	3.6	8	
	10	5.2	10	
	12 Midnight	7.8	8	
	2 am	7.0	6	
	4	7.3	6	
	6	7.5	6	
	8	7.6	8	
	10	8.2	8	
	12 Noon	7.7	8	
	2 pm	7.6	10	
9/18/59	4	7.7	8	
	6	8.0	8	
	8	8.8	10	
	10	9.0	13	
	12 Midnight	8.8	8	
	2 am	Off Stream during Cleaning of Coalescer	6	
	4		10	
	6		15	
	8		12	
	10		15	
12 Noon	10			
2 pm	6			
4	19			
6	22			
8	19			

\* Values calculated from the sodium levels in the combined CP<sub>1</sub> (the "cold side" product stream) and CP<sub>5</sub> (the product stream from another extraction stream) where the uncombined CP<sub>5</sub> value was known (ppm, U basis).

Plant Unit; Mechanical Operation and Cleaning Cycle

Since it was undesirable to subject the AP stream to harsh pump mixing (which would produce a more finely dispersed aqueous phase) prior to the coalescing treatment, the plant coalescer unit was designed to operate with gravity flow from the primary extraction columns. A minimum head of 7 psig was required at the coalescer inlet. Tests have indicated (Table 6.9) that a maximum of approximately 9.5 psig is available for the plant unit.

From the pressure drop data obtained in the pilot unit (test No. 27), it was predicted that the operational time between cleaning cycles (based upon an initial pressure drop of 3 psi and a final

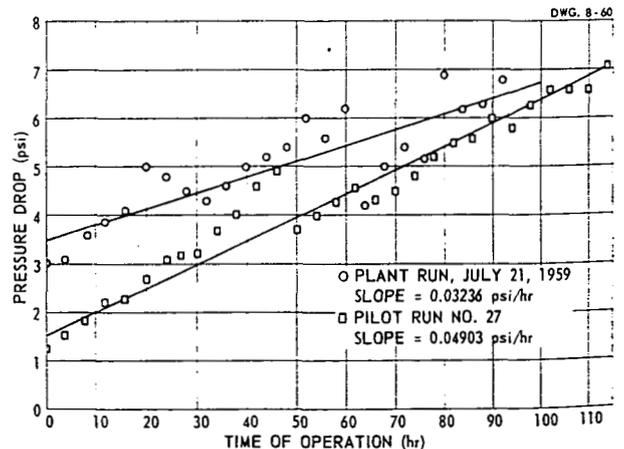


FIGURE 6.3 Coalescer - De-entrainer Pressure Rise Data. Pressure Drop Across the Coalescer (psi) vs Time of Coalescer Operation (hr). Straight lines are lines of least squares.

TABLE 6.8 Refinery Operational Data - July 7, 1959

Time	Column Entrainment (vol %)												Sodium Contamination (y/ml)					
	Primary Extraction Columns						Scrub Columns						Primary Extract Streams		Scrubbed Extract Streams		Scrub Raffinate Streams	
	AP <sub>D</sub> "Cold Side"			AP <sub>2</sub> "Hot Side"			BP <sub>1</sub> "Cold Side"			BP <sub>3</sub> "Hot Side"			AP <sub>D</sub> "Cold"	AP <sub>2</sub> "Hot"	BP <sub>1</sub> "Cold"	BP <sub>3</sub> "Hot"	BR <sub>1</sub> "Cold"	BR <sub>3</sub> "Hot"
	Total	Solid	Water	Total	Solid	Water	Total	Solid	Water	Total	Solid	Water						
11:00 am	0.15	0.14	0.01	0.20	0.19	0.01	-	-	-	-	-	-	2.7	3.3	-	-	20	32
3:00 pm	0.15	0.11	0.04	0.20	0.20	0.00	-	-	-	-	-	-	1.7	2.9	-	-	23	54
7:00 pm	0.06	0.06	0.00	0.20	0.16	0.04	0.15	0.05	0.10	0.15	0.01	0.14	1.7	4.7	0.9	1.6	20	40
11:00 pm	0.07	0.07	0.00	0.18	0.15	0.03	0.20	0.02	0.18	0.15	0.02	0.13	1.2	3.5	0.7	1.1	22	31
3:00 am	0.07	0.07	0.00	0.20	0.19	0.01	0.15	0.01	0.14	0.20	0.01	0.19	1.0	2.2	0.6	1.2	18	34
7:00 am	0.07	0.01	0.06	0.35	0.33	0.02	-	-	-	0.30	0.02	0.28	1.4	2.2	1.2	2.1	22	44

AP<sub>D</sub>: Primary Extract from the "Cold" Extraction Process  
 AP<sub>2</sub>: Primary Extract from the "Hot" Extraction Process  
 BP<sub>1</sub>: Scrubbed Extract from the "Cold" Extraction Process  
 BP<sub>3</sub>: Scrubbed Extract from the "Hot" Extraction Process  
 BR<sub>1</sub>: Scrub Raffinate from the "Cold" Extraction Process  
 BR<sub>3</sub>: Scrub Raffinate from the "Hot" Extraction Process

TABLE 6.9 Plant Coalescer - Cleaning Studies

Date Cleaned	Date On Stream	Time On Stream	ΔP at Start-up (psi)	Date Off Stream	Time Off Stream	Final ΔP (psi)	Time On Stream (hr)	Avg Pressure Rise (psi/hr)
9/4/59	9/9/59	12 Noon	1.6	9/10/59	5 am	7.4	63*	0.092
9/16/59	9/16/59	4 pm	2.8	9/18/59	3 am	9.2	35	0.183
9/21/59	9/22/59	10 am	3.0	9/23/59	6 pm	7.8	32	0.150
10/2/59	10/2/59	2 pm	2.9	10/5/59	10 pm	7.8	28*	0.175
10/7/59	10/8/59	2 am	4.5	10/9/59	8 pm	8.7	42	0.100
10/12/59	10/12/59	3 pm	3.2	10/16/59	5 am	8.0	86	0.056

\* Weekend shut-down periods not included.

\*\* Insufficient steam pressure available to properly clean unit.

pressure drop of 7 psi) would be approximately 82 hours. This was calculated by finding the line of least squares for the pressure drop data of test No. 27 (Fig. 6.3) and by dividing the slope of the line (psi/hr) into the expected pressure drop operation range (i.e., 4 psi). Although plant operation has at times closely approximated this prediction (e.g., the data for plant operation of July 21, 1959, Fig. 6.3), the average pressure rise per hour has been greater than anticipated and has averaged 0.0923 psi/hr for all plant operations to date (10 operating cycles). With this average pressure rise and an operational range of from 3 to 9 psi, the calculated time between cleaning cycles is now 65

hours. The frequency of cleaning cycles has been a direct function of the concentration of solids entrained in the AP stream.

The simple gravity-flow cleaning cycle (water backwash, followed by a kerosene backwash) that had been successfully utilized for cleaning the pilot unit was not effective for cleaning the plant unit coalescer. A spray ring for unit backwashing was incorporated into the design of the plant unit, and a new cleaning cycle was developed. The new cycle includes water backwashing, a steaming period (the unit is filled first with water), and a kerosene recycle period. The new cleaning proce-

ture (time requirement: approximately 3½ hours) has been used successfully eight times during recent weeks to achieve the desired initial pressure drop range of 2 to 3 psi. In Table 6.9 are the pressure drops obtained before and after six of these cleaning cycles.

Conclusions

It is concluded that the plant coalescer - de-entrainer unit removes greater than 50 per cent of the cation impurities entrained in the AP stream. The unit is especially effective for removing entrained water from the AP stream. While this unit removes significant quantities of solid material from the AP stream, removal of solids is largely dependent upon the unit pressure drop and the absence of large flow fluctuations which "clean" the bed and return the solids to the AP stream. Best operation of this unit is realized when the AP

stream contains large quantities of entrained solids; however, this necessitates more frequent cleaning of the unit. The coalescer - de-entrainer has become an integral part of the "cold side" extraction system and is an effective tool for the improvement of product purity.

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7. CONTINUOUS POT-DENITRATION

C. W. Huntington      A. E. Abbott      D. C. Bonfer      D. J. Loudin  
M. G. Mendel      K. J. Notz      E. J. Walter

Abstract

Continuous pot-denitration was investigated in a plant-scale test. Operation of the process in a plant denitration pot equipped with dual uranyl nitrate feed tubes and a central gulping tube showed that the productivity was at least as great as that of the batch process and that the severity of the thermal treatment imposed on the reactor shell is very much reduced. Difficulties in withdrawing the product by vacuum have motivated consideration of overflow product-discharge facilities for future tests.

The dense, spherical oxide produced was relatively unreactive in reduction and hydrofluorination tests; however, it is believed that through additional development of operating techniques, product reactivity can be appreciably improved.

Introduction

The production of orange oxide (UO<sub>3</sub>) at this site is currently accomplished by batchwise calcination of uranyl nitrate in agitated denitration pots. This process has several disadvantages, chief of which is the high level of maintenance required to keep the pots in operating condition. In addition, the variation in product quality which occurs as a consequence of batchwise operation often adversely affects the subsequent production of green salt (UF<sub>4</sub>).

An investigation was recently begun to determine whether these problems can be alleviated by operating the denitration pots continuously-i.e., by continuous introduction of uranyl nitrate and simultaneous withdrawal of orange oxide. Continuous operation of the denitration process would eliminate the severe thermal cycling which is the major cause of pot failures and would produce a more nearly uniform product. The feasibility of

this approach as a denitration process improvement was demonstrated in a series of tests performed in laboratory-scale equipment.<sup>1</sup> Because the small size of this equipment greatly limited its usefulness in the study of continuous pot-denitration, arrangements were made to investigate the process further in one of the plant reactors.

Objective of Work Completed This Quarter

To determine the feasibility of continuous pot-denitration in a plant reactor system equipped with uranyl nitrate feed tubes and vacuum product-withdrawal facilities.

Summary of Results Obtained This Quarter

The feasibility of operating the plant denitration pots on a continuous basis has been established. Production rates equal to those obtained by batchwise operation were attained without difficulty, at reactor temperatures much lower than those required in the batch process. Difficulty with the vacuum gulping system pointed to the desirability of incorporating overflow product-discharge facilities in this process.

The oxide produced was dense, spherical, and exhibited a low surface area and low reduction and hydrofluorination activities. It is believed that product quality can be materially improved as techniques for operating the continuous process are developed.

Equipment

The denitration pots at the National Lead Company of Ohio Refinery are cylindrical vessels, 5½ feet in diameter and 3½ feet in height, with dish-shaped bottoms. Each has a flooded capacity of 430 gallons. Agitation is provided by anchor-type agitators. For each batch operation, a 275-gallon charge of molten uranyl nitrate [with a specific

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gravity of 2.5, corresponding to a concentration of 80 per cent  $UO_2(NO_3)_2$ ] is fed to the pot by gravity flow from a 6,000-gallon storage tank.

The denitration pots are each heated by 108 radiant gas-fired burners arranged in three concentric rings below the pot bottom. The heat input is controlled on the basis of flue gas temperature. For most pots, a maximum flue gas temperature of 1150°F is observed, at which point the flame is reduced until the flue gas temperature reaches 950°F. With this type of temperature control, the maximum reactor skin temperature may vary appreciably, depending upon the amount of scale formation on the inside surface. Temperatures in excess of 1600°F have been observed. After the process material reaches the "dough" stage, the temperature of the powder remains rather constant at about 450°F. Upon completion of the cycle (approximately 7 to 8 hours), the orange oxide powder is manually gulped from the pot by means of a flexible vacuum hose.

Relatively few modifications to the reactor itself were required for the initiation of continuous denitration tests. Most of the preparative effort involved the fabrication of two steam-cooled feed tubes and a gulping tube for oxide withdrawal. The main features of the experimental system, which is represented in Figure 7.1, were as follows:

1. Molten uranyl nitrate ["boildown product," approximately 80 per cent  $UO_2(NO_3)_2$ ] may be fed to the pot by either or both of two steam-cooled feed tubes. Details of the feed tube design (which was adapted from that used in the Hanford continuous trough process)<sup>2</sup> are given in Figure 7.2.
2. The uranyl nitrate flow may be maintained either by gravity or by means of a centrifugal pump.
3. The flow of uranyl nitrate through each feed tube is controlled by means of a rotameter.
4. Uranyl nitrate is introduced beneath the surface of a resident bed of orange oxide.
5. The heating rate is controlled on the basis of temperature measurements taken in the oxide bed; the temperatures of the pot bottom and of the flue

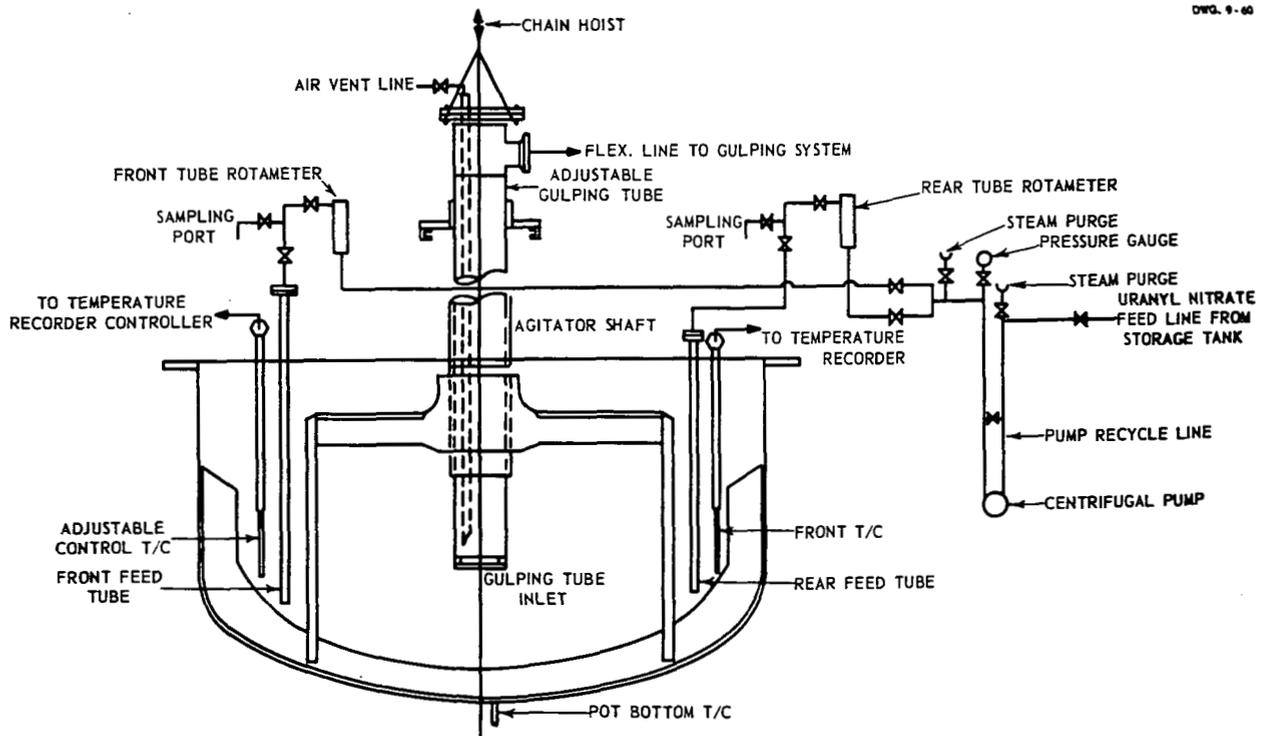


FIGURE 7.1 Continuous Pot-Denitration Feed and Gulping System



ture was therefore lowered to 500°F, which ultimately proved to be a satisfactory level.

After the gravity flow of feed had been instituted and the bed temperature had been lowered, a 48-hour period of uninterrupted operation ensued, during which time the feed rate through one feed tube was slowly increased to the 0.6 gal/min target level. This feed rate was maintained without difficulty for 38 hours. The second feed tube was then placed in service, and the target feed level was again easily attained. As the feed rate was increased, the oxide particles gradually assumed the dense spherical form characteristic of continuous agitated-bed denitration processes. When the bed completely converted to production of this form of particle, it possessed a high degree of fluidity, and very little dusting occurred.

For simplicity, nonsulfated uranyl nitrate was used for startup operations. After the workability and productivity of the system had been established, arrangements were made to add sulfuric acid to the uranyl nitrate storage tanks to give a concentration of 1,500 ppm SO<sub>4</sub> on a uranium basis.

After the higher production rates were achieved and loss of material via the off-gas line was greatly reduced, the gulping system became the limiting feature of the process. This was largely due to the fact that, even with spherical particles

being produced, it was not possible to gulp from beneath the surface of the bed; thus, as the oxide was removed from the surface, a large amount of the gaseous decomposition products was concurrently educted. Condensation of the off-gas vapors throughout the gulping system resulted in the plugging of lines, corrosion of parts of the blower system, and frequent blinding and rupture of the wool felt bags in the dust collector system. As the test progressed, these difficulties caused an increasing amount of downtime and necessitated frequent reductions in the feed rate to minimum levels to permit repairs to the system. When it became evident that continued operation under these conditions would not yield significant information on either reactor performance or product quality, the denitration pot was returned to regular production service, and attention was directed toward the design of overflow product-discharge facilities which would eliminate the difficulties associated with vacuum withdrawal of the product.

#### Data and Discussion

A summary of typical process data from the most nearly stable periods of operation is given in Table 7.1.

The target production rate for the test was 420 pounds UO<sub>3</sub>/hr, which is approximately equal to

TABLE 7.1 Typical Process Data From Plant Test of Continuous Pot-Denitration With Vacuum Removal of Product

Time Interval (hr)	Uranyl Nitrate Feed Rate (gpm)		Production Rate (lb UO <sub>3</sub> /hr)	Average Bed Temperature (°F)	Maximum Pot Bottom Temperature (°F)	Maximum Flue-Gas Temperature (°F)
	Front Feed Tube	Rear Feed Tube				
11.0	0.175	—	129	625	1300	1050
6.6	0.285	—	210	570	1280	1060
3.2	0.385	—	282	495	1440	1280
2.0	0.455	—	330	500	1400	1250
37.8	0.575	—	420	495	1200	1130
2.3	0.880	—	525	490	1400	1280
2.4	—	0.330	240	505	1230	1080
4.1	0.295	0.250	357	490	1400	1260
5.0	0.300	0.300	432	490	1380	1270
1.0	0.330	0.385	522	480	1350	1230

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the rate obtained by batchwise operation in which a 275-gallon charge of uranyl nitrate with a specific gravity of 2.5 is processed in a 7-hour cycle. As can be seen in Table 7.1, the process was operated for approximately 38 hours at the target rate, and at a rate of 520 to 525 pounds  $UO_3$ /hr, for two short intervals. There were no indications at any time during these periods that scale was forming on the inside surface of the pot or that the maximum throughput with respect to heat transfer limitations had been approached. Thus, the productivity of the continuous pot process was shown to be at least equal to, and probably greater than, that of the batchwise operation.

In continuous operation, the reactor shell is subjected to a much less severe thermal treatment than is imposed in the batch process; therefore, pot life should be greatly prolonged. As shown in Table 7.1, it is possible to operate at the target production level of 420 pounds  $UO_3$ /hr with a maximum pot bottom temperature of 1200°F. With the type of temperature control used during this test, the bottom temperature cycled between 800°F and 1200°F over 20-minute intervals at this production level. This variation is much less than occurs during a regular denitration cycle; with additional experience, it should be possible to improve the temperature control so that the cycling is reduced even further.

Because of the difficulties encountered with the gulping system, it very often was necessary to reduce the feed rate considerably, or to shut down completely for short periods. As a result, it was difficult to maintain control of process temperatures, and the oxide was subjected to much longer retention times and higher temperatures than would have otherwise prevailed. Because of these difficulties, the oxide incurred a certain degree of thermal damage, and is therefore not considered entirely typical of the oxide which can be produced by the continuous pot process.

The physical and chemical properties of a representative sample of continuous pot orange oxide

originating from this test are given in Table 7.2. As the data show, the oxide was dense, rather coarse, low-surface-area material. The reduction and hydrofluorination activities were both relatively low and were not as favorable as those exhibited

TABLE 7.2 Properties of Orange Oxide Produced By Continuous Pot-Denitration in a Plant Reactor With Vacuum Product-Discharge Facilities

U (%)	82.66
$NO_3$ (%)	0.38
$H_2O$ (%)	0.30
$U_3O_8$ (%)	0.79
$SO_4$ (ppm, U basis)	1434
Tap Density (g/cc)	4.5
Bulk Density (g/cc)	4.3
Surface Area (sq m/g)	
As produced	0.62
Calcined at 932°F	0.54
Calcined at 1000°F	0.48
Calcined at 1100°F	0.44
Calcined at 1200°F	0.33
$UO_2$ , reduced at 1000°F	3.4
$UO_2$ , reduced at 1100°F	3.1
$UO_2$ , reduced at 1200°F	2.3
Particle Size Distribution (%)*	
Retained on 40 mesh screen	5
Retained on 80 mesh screen	12
Retained on 100 mesh screen	7
Retained on 150 mesh screen	12
Retained on 200 mesh screen	20
Retained on 325 mesh screen	26
Passed through 325 mesh screen	18
Reduction Time (sec)**	
At 932°F	2900
At 1000°F	1410
At 1100°F	560
Hydrofluorination Conversion at 120 min (% $UF_4$ )***	
Reduction at 1000°F; hydrofluorination at 1000°F	90.5
Reduction at 1000°F; hydrofluorination at 1100°F	87.7
Reduction at 1000°F; hydrofluorination at 1200°F	80.2
Reduction at 1100°F; hydrofluorination at 1000°F	91.7
Reduction at 1100°F; hydrofluorination at 1100°F	89.8
Reduction at 1100°F; hydrofluorination at 1200°F	80.0

\* Wet Screen Analysis

\*\* Time required for 97% conversion to  $UO_2$  (a pulverized specimen)

\*\*\* Pulverized samples used

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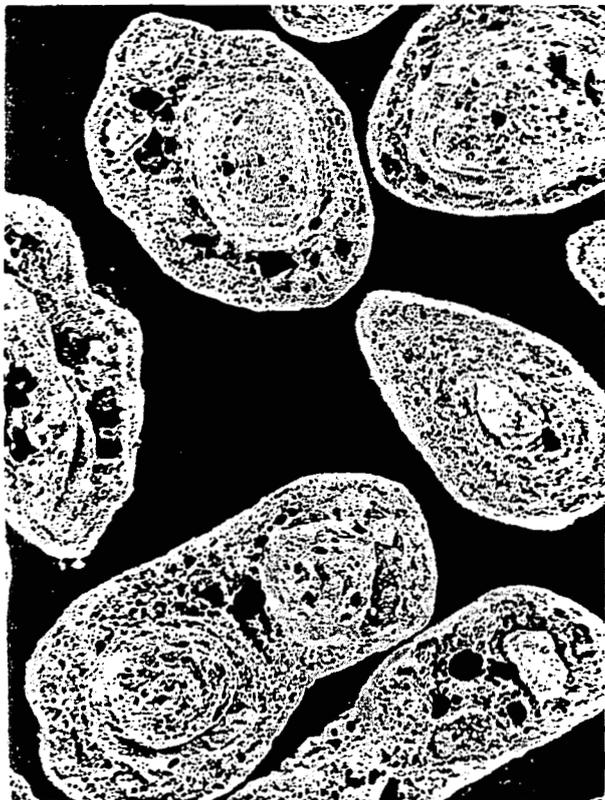


FIGURE 7.3 Laboratory Continuous Pot-Denitrated  $UO_3$ . +100 Mesh Particles Were Prepared in Section. All Dark Areas Represent Depressions. Reflected Light, 60X, B. F.

by oxide produced in the laboratory continuous pot unit;<sup>7</sup> it is believed that these responses can be greatly improved by improved reactor operation.

A microscopic examination of laboratory and plant specimens of continuous pot orange oxide revealed several differences in internal structure between the two samples (Fig. 7.3 and 7.4). The plant sample was definitely spherical and exhibited concentric growth around a single nucleus. The laboratory material was more irregular in shape, with many particles containing two or more nuclei. In addition, the laboratory sample contained a greater percentage of voids. These differences are the result of the slower rate of particle growth in the plant-scale system. Improvement of the plant process to permit truly continuous operation, with consequent reduction in retention time and

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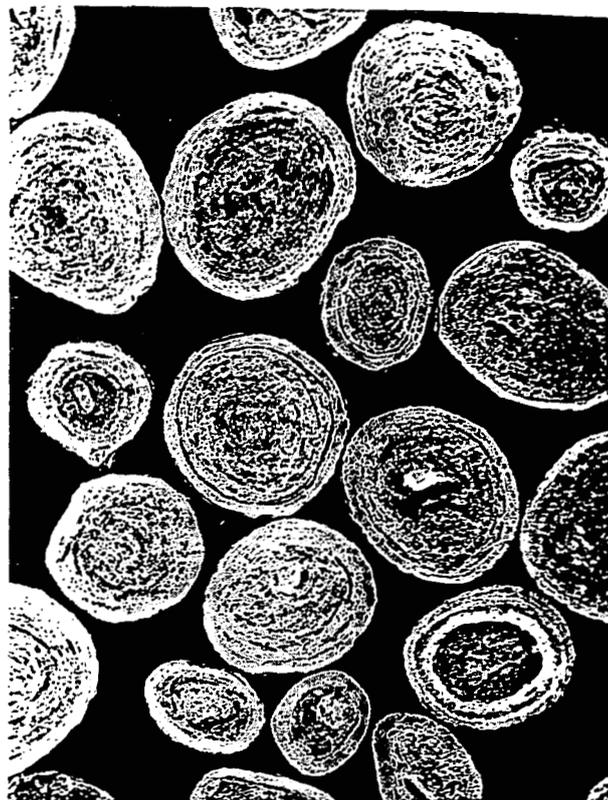


FIGURE 7.4 Plant Continuous Pot-Denitrated  $UO_3$ . +100 Mesh Particles Were Prepared in Section. All Dark Areas Represent Depressions. Reflected Light, 60X, B. F.

improved temperature control, should therefore produce an oxide which is more amenable to gas-solid reaction than the plant specimens obtained to date have been.

#### Future Work

A plant denitration reactor will be equipped with overflow product-discharge facilities, and investigation of continuous pot-denitration will be resumed.

#### Acknowledgment

F. J. Podlizec and J. Snook, of the Production Engineering Department, contributed to the development and installation of the reactor system.

Microscopic examinations were made by W. W. Brock of the Metallurgical Department.

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<sup>2</sup>M. J. Szulinski. "Development of an Agitated-Trough Continuous Calciner," Chem. Eng. Progr., 53:586. 1957.



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## 8. THE CORRELATION OF "AMMONIUM DIURANATE" PROPERTIES WITH PRECIPITATION VARIABLES

G. M. Reinhart

D. J. Loudin

### Abstract

Precipitation temperature, precipitation pH, uranium concentration, and ammonium hydroxide concentration were studied as to their effects upon particle size and tap density of the product of ADU precipitation.

### Introduction

In previous studies<sup>1,2</sup> of the continuous precipitation of ADU from ammonium hydroxide solution and uranyl nitrate, the effect of variables has been uncertain because of lack of control and precision. Reliable correlations of the effect of the variables on product properties would clarify the relations and facilitate process design. These correlations can best be obtained by statistical design and analysis.

### Objectives for This Quarter

Through operation of a fully automated laboratory precipitation unit, it was planned to obtain data which would permit prediction of how changes in precipitation conditions will affect ADU product properties.

### Summary of Results Obtained This Quarter

The pH of precipitation exerts the principal effect on product characteristics. Precipitation temperature and uranyl nitrate concentration have strong secondary effects, particularly in combination with each other and with pH. Whether ammonium hydroxide concentration is 4 or 7 per cent is relatively unimportant.

### Experimental Design

Consideration of earlier work has established the importance and the experimental levels of the

variables listed below.

Slurry pH	5.0 5.7 6.5
Ammonium Hydroxide (% NH <sub>3</sub> )	4 7
Uranyl Nitrate Solution (g U/l)	80 250
Slurry Temperature (°F)	80 160
Agitation	A constant (thorough)
Mean Retention Time in the Reactor (min)	A constant (60 minutes)
Reagent Addition Points	A constant (approx. 180° apart)

The values chosen for the experimental conditions cover the range within which the process is expected to operate. The upper levels of the NH<sub>3</sub> range (up to 28 per cent) were eliminated (1) because high vapor pressures at these concentrations would result in storage and handling problems and (2) because of previous negative results at these concentrations.<sup>3</sup>

Twenty-four runs permitted the use of a factorial experiment design with complete replication. The experimental order was randomized by use of a random number table. Analysis of the data by four-factor analysis of variance disclosed the direct and interacting effects of changes in variables.

Virtually unattended operation was possible with the equipment shown in Figure 8.1. Elevated stainless steel storage tanks held enough uranyl nitrate solution and ammonium hydroxide for the usual 10 to 20-hour run. The reactants flowed by gravity from the storage tanks through rotameters to control valves. A manually operated needle valve held the ammonium hydroxide flow constant at a level calculated to maintain a uniform total volumetric flow throughout the series of runs. An automatic valve controlling the uranyl nitrate flow in response to signals from a recorder-controller maintained a constant pH in the precipitated slurry.

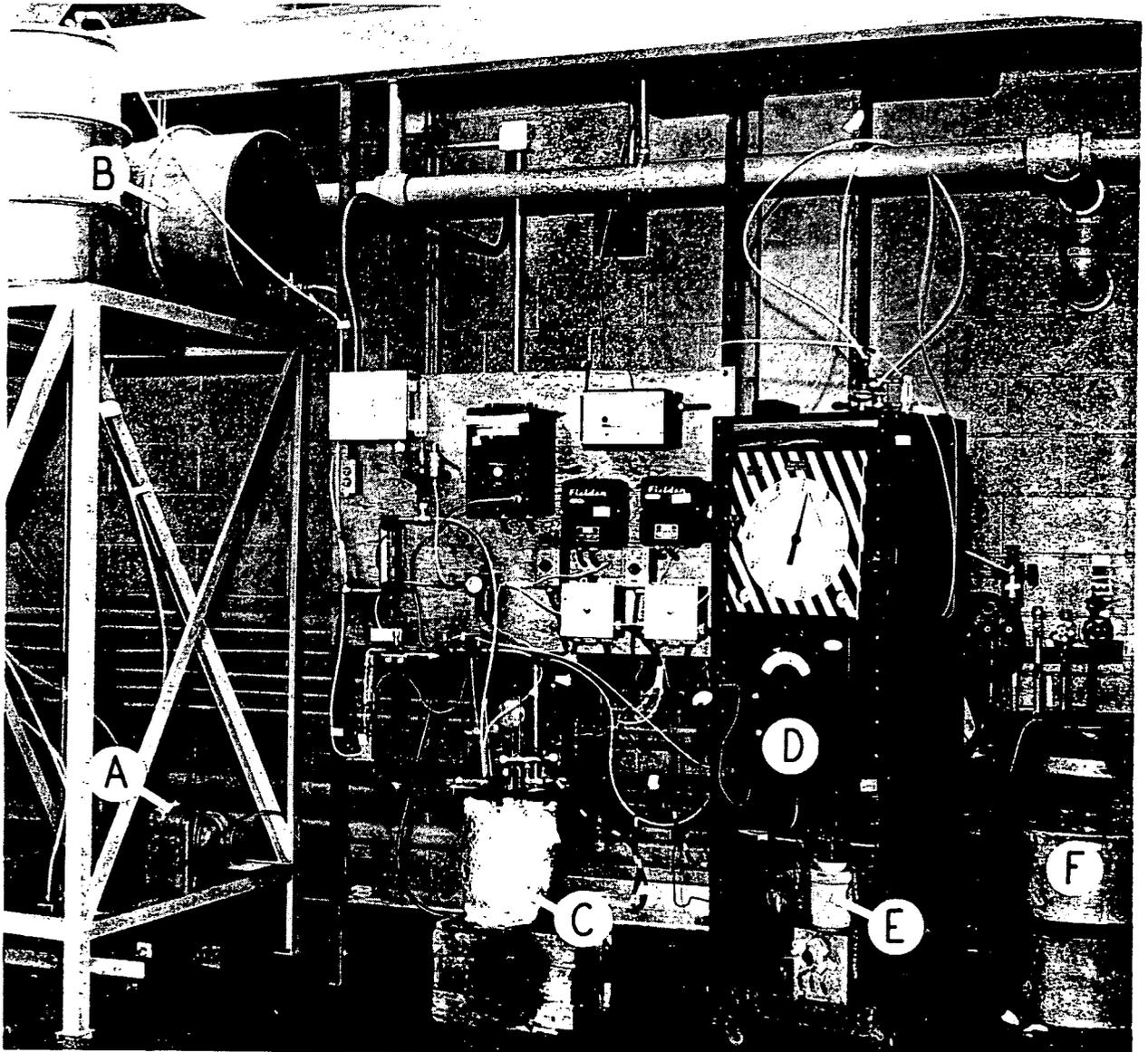


FIGURE 8.1 Equipment Arrangement. A. Storage Tank Filling Pumps. B. Storage Tanks (for Uranyl Nitrate Solution and Ammonium Hydroxide). C. Reaction Tank. D. pH Control. E. Level Control. F. Product Storage Drum.

The reactants then flowed to the 2-gallon heated reaction tank (precipitation tank). The resultant slurry of ADU solids and  $\text{NH}_4\text{NO}_3$  solution was agitated by a 2-inch, 3-bladed marine propellor aided by four 1-inch-wide baffles. The pair of pH electrodes were in an almost diametrically opposed

position to the pair of reactant inlet tubes in order to avoid control upsets caused by local high ammonia concentrations on the surface of the slurry. A positive-displacement (peristaltic) pump was used to withdraw ADU slurry continuously at a rate controlled by a pneumatic level control.<sup>2</sup>

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Safety circuits automatically provided control of the precipitation operation. Coils which sensed movement of the rotameter floats, resistance-actuated level controls, and alarm contacts on the temperature indicator could detect deviations from set operating conditions and stop the operation by shutting off the reaction tank heaters and all motors, and stopping reactant flow. A timer-actuated valve permitted sampling of the ADU slurry during unattended periods.

### Operating Procedure

A single sample of uranyl nitrate solution from the Refinery evaporators was diluted from 390 g U/l to the desired concentrations with distilled water. Analytical grade ammonium hydroxide was diluted with filtrate (from previous laboratory precipitation runs) which contained about 5 per cent  $\text{NH}_4\text{NO}_3$  and a trace of ADU solids. Factors (other than the variables under study) known to produce variations in ADU product properties were held constant. Before each run, pH electrodes were cleaned and buffered to maintain accuracy and sensitivity, and the reaction tank was cleaned to avoid seeding by residual product from the previous test. Agitator speed, the relative position of pH electrodes and reagent inlet tubes, and start-up procedures were also carefully standardized.

In a series of preliminary tests, the changes in physical properties with time were investigated. The conditions used (4 per cent  $\text{NH}_3$ , 80 g U/l, pH 5.7, 80°F) were those expected to give the slowest approach to equilibrium. It was found that within 6 to 7 hours after reagents began to flow into the reaction tank, product physical properties had reached values which remained unchanged for an additional 22 hours of run. From this evidence, it was concluded that equilibrium of physical properties had been attained in 6 to 7 hours. A standard run time of 8 hours from beginning of reagent flow to sampling of product allowed a margin of safety.

Individual samples of the ADU product slurry (equivalent to 1.5 minutes of run time) were aspirated from the reaction tank discharge line, filtered on paper, rinsed with 5 milliliters of distilled water, dried 24 hours at 212°F, brushed through a 100-mesh screen, and calcined in air in a quartz tube furnace for 0.5 hour at 930°F. Particle size was determined with a Sharples Corporation Micromerograph, viscosity by a Brookfield Viscosimeter, and tap density by measuring the weight of 1 milliliter of sample in a graduated cylinder after tapping to a minimum value. Colorimetric determination of uranium, titration of ammonia, and determination of surface area by nitrogen absorption (Brunauer, Emmett, and Teller)<sup>4</sup> were other methods used.

### The Effect of Precipitation Variables

Experimental conditions for the 24-run series are shown in Table 8.1. Results, as evaluated by a multifactor analysis of variances, are shown in Tables 8.2 and 8.3. The pH, alone or in combination, has the major effect. Temperature, which has been found to have an effect on pH,<sup>5</sup> shows an even more positive relationship with particle size, particularly at low uranium concentration and at pH 5.0. Ammonium hydroxide concentration (shown to have a major effect at higher concentrations)<sup>3</sup> has no significant influence at the concentrations used in this test. However, uranium concentration displays a major effect on particle size, which parallels that of ammonia concentration over the full 4 to 28 per cent  $\text{NH}_3$  range.

In general, the results show that at pH 5.7 and ambient temperature, a stable condition exists in which product properties are relatively insensitive to reagent concentration changes. The portion of the experiment run at the lower uranyl nitrate concentration (80 g U/l) shows more sensitivity to changes and contains both upper and lower extremes of density and particle size.

Some of the data could not be correlated, chiefly the viscosities listed in Table 8.1.

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TABLE 8.1 Factorial Experiment of ADU: Precipitation Variables and Precipitate Characteristics

Reynold's Number of Agitated Slurry  $10,500 \pm 3,700$   
 Agitator Power Consumption ( $\text{HP} \times 10^{-3}$ )  $1.5 \pm 0.4$   
 Heat of Reaction ( $\text{kg cal/g mole U}$ )  $13 \pm 3$

Run No.	Slurry Temp (°F)	Slurry pH		Concentration of $\text{NH}_3$ in Feed (wt %)	Concentration of U in Uranyl Nitrate Solution (g/l)	Viscosity (cp)		Agitator Speed (rpm)	Precipitate Characteristics				
		at Slurry Temp	at 86°F			at Slurry Temp	at 86°F		Dried Product		Calcined Product		
		Color	Lump Hardness						Tap Density (g/cc)	% of Particles Less Than $10\mu$	Color		
1	97	5.3	5.4	4.2	78	5.3	6.5	1250	Orange	Soft	2.41	23	Black
2	101	5.0	5.1	4.1	247	7.6	8.5	1225	Orange	Soft	2.11	56	Black
3	94	4.8	4.9	6.4	82	7.9	8.0	1275	Orange	Soft	2.42	24	Black
4	103	5.2	5.2	6.6	250	5.2	6.5	1250	Yellow-Orange	Soft	1.92	72	Brown
5	93	5.7	5.8	4.2	85	6.3	6.4	1250	Orange	Soft	2.20	74	Black
6	101	5.7	5.8	4.0	250	6.4	7.4	1250	Orange	Soft	2.15	83	Brown-Black
7	97	5.7	5.7	7.0	83	5.8	6.3	1175	Orange	—	2.13	40	Black
8	108	5.6	5.6	7.2	247	6.2	7.6	1300	Orange-Yellow	Medium	2.11	80	Black
9	95	6.6	6.6	3.4	80	5.4	5.8	1200	Orange	Soft	1.71	100	Black
10	98	6.5	6.6	3.6	250	5.7	6.2	1250	Yellow	Hard	1.55	98	Yellow-Brown
11	92	6.5	6.6	7.0	83	5.4	5.3	1225	Yellow-Orange	Soft	1.79	91	Green-Brown-Black
12	99	6.6	6.7	7.0	247	7.0	7.8	1225	Yellow	Hard	1.61	100	Yellow-Brown
13	157	5.0	6.0	4.6	83	5.3	9.4	1200	Yellow-Orange	Very Soft	1.74	36	Green-Black
14	159	5.0	6.0	3.6	247	5.4	9.6	1300	Yellow-Orange	Soft	1.87	59	Green-Black
15	164	5.0	6.0	7.0	88	5.4	9.5	1200	Yellow-Orange	Soft	1.96	66	Green-Black
16	158	5.1	6.1	7.1	247	5.6	9.6	1200	Orange	Soft	1.93	53	Black
17	158	5.8	6.6	4.1	80	5.3	9.3	1225	Orange	Soft	1.74	78	Black
18	162	5.6	6.6	4.2	252	5.0	9.1	1200	Yellow	—	1.87	59	Green-Brown-Black
19	163	5.6	6.2	7.0	88	6.3	10.4	1250	Yellow-Orange	Soft	1.54	85	Green-Brown-Black
20	164	5.8	6.9	7.2	247	7.0	11.1	1250	Yellow	Hard	1.51	98	Yellow-Brown
21	161	6.5	7.5	4.0	80	5.3	9.4	1275	Yellow	Hard	0.89	100	Yellow-Brown
22	160	6.5	7.7	3.9	245	6.2	10.2	1225	Yellow	Hard	1.48	100	Yellow-Brown
23	161	6.5	7.4	7.0	88	5.8	8.9	1200	Yellow	Hard	0.99	94	Green-Brown
24	161	6.5	7.7	7.0	245	6.7	10.7	1200	Yellow	—	1.25	100	Yellow-Brown

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TABLE 8.2 Rank of Precipitation Variables As To Effect Upon Tap Density

Classification of Effect	Variable or Combination of Variables	Averaged Effect on Tap Density* (g/ml)
Major	P	-0.64 ± 0.03
	T	-0.46 ± 0.02
	TP	-0.38 ± 0.04
	TUP	-0.30 ± 0.06
	TNP	-0.27 ± 0.06
Moderate	TU	-0.24 ± 0.03
	NP	-0.20 ± 0.04
	UP	-0.19 ± 0.04
	TNU	-0.18 ± 0.05
	PNU	-0.14 ± 0.06
Small	NU	-0.05 ± 0.03
	N	-0.04 ± 0.02
	U	-0.03 ± 0.02
	TN	Not Significant

## SYMBOLS

P - pH of precipitation  
 T - Temperature of slurry  
 U - Uranium concentration of uranyl nitrate solution  
 N - Ammonia concentration of ammonia solution

\* Changes of tap density noted are for increasing values of the variables listed.

## Future Work

No further laboratory work is currently contemplated on the ADU project. A topical report summarizing the work done on this project is being prepared.

## References

<sup>1</sup>G. M. Reinhart and C. W. Huntington. "Pilot Plant Precipitation of Ammonium Diuranate", Summary Tech. Rpt., USAEC Report NLCO-750, p. 64. July 18, 1958 (Classified).

<sup>2</sup>G. M. Reinhart. Continuous Ammonium Precipitation of Uranium from Pure Uranyl Nitrate Solution, USAEC Report NLCO-757. August 11, 1958 (Classified).

TABLE 8.3 Rank of Precipitation Variables As To Effect Upon Particle Size (% Less Than 10 $\mu$ )

Classification of Effect	Variable or Combination of Variables	Averaged Effect* on Particle Size (%)
Major	P	+49 ± 4
	UP	20 ± 6
Moderate	TP	18 ± 6
	TUP	18 ± 8
	U	15 ± 3
	NP	15 ± 6
	NUP	14 ± 8
	TU	12 ± 5
	TNP	12 ± 8
	T	10 ± 3
Small	TNU	8 ± 6
	TN	5 ± 5
	N	N.S.
	NU	N.S.

## SYMBOLS

P - pH of precipitation  
 T - Temperature of slurry  
 U - Uranium concentration of uranyl nitrate solution  
 N - Ammonia concentration of ammonia solution  
 N.S. - Not Significant

\* Changes in the per cent of particles less than 10 $\mu$  are for increasing values of the variables listed.

<sup>3</sup>G. M. Reinhart, D. J. Loudin, and T. A. Hehemann. "Pilot Plant Studies of Precipitation", Summary Tech. Rpt., USAEC Report NLCO-775, pp. 50-51. January 22, 1959 (Classified).

<sup>4</sup>S. Brunauer, P. H. Emmett, and E. Teller. "Adsorption of Gases in Multimolecular Layers", J. Amer. Chem. Soc., 60:309. 1938.

<sup>5</sup>G. M. Reinhart and C. W. Huntington. op. cit., p. 65.

Editor's Note - The following topical report was issued during the report period:

NLCO-786 Engineering Evaluation of Semi-Works ADU Production. Donald J. Loudin. March 13, 1959.



## 9. THE EFFECTS OF MAGNESIUM METAL CHARACTERISTICS ON THE BOMB REDUCTION OF $UF_4$ TO METAL

O. R. Magoteaux

J. H. Trapp

### Abstract

The effects of the physical characteristics of regular production magnesium metal on crude yield and preheat time in bomb reduction were evaluated. No significant difference in crude yield was found, but the size and surface area of the magnesium particles had an effect upon preheat time.

In one series of reductions, the reaction locus and preheat time were controlled by the use of a blend of  $UF_4$  and fine magnesium concentrated in one location in the charge.

### Introduction

In the bomb reduction of green salt by magnesium metal, it has long been believed that the particle size and surface area of magnesium metal used for production affect crude yield and preheat time. In particular, the effect of a small amount of -50 mesh magnesium was believed to be important. No quantitative data describing these effects were available. It was therefore decided to perform controlled bomb reductions to obtain these data.

### Objectives for This Quarter

The objective of this study was to determine the effects of magnesium metal physical characteristics (primarily particle size and surface area) on crude derby yield and preheat time.

### Summary of Results Obtained This Quarter

1. Variation of the magnesium particle size from fractions containing up to 3 per cent -120 mesh particles to fractions containing all +14 mesh particles did not produce significant differences in crude derby yields, or slag metal separation but did produce significant differences in preheat times.

2. The reaction locus and the preheat time were altered by using a blend of green salt and magnesium fines (-50 mesh magnesium) concentrated at the bottom of the bomb charge.

### Materials and Procedures

Photomicrographs of the regular production magnesium granules (obtained from Metals Selling Corp.) are shown in Figures 9.1 and 9.2. Samples of these magnesium granules were screened, a Ro-Tap being used to obtain all of the desired particle sizes except those less than 120 mesh. The latter were obtained by using a Selectro vibrating screen (Model 3AS-4-18). The magnesium particle distributions obtained are shown in Table 9.1.

Surface areas of the different magnesium sizes were measured by the Brunauer-Emmet-Teller (BET) method, using krypton as the adsorbing gas.<sup>1,2</sup> Surface area data are shown in Table 9.2.

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FIGURE 9.1 MSC Magnesium, Unetched. Reflected Light. 8.7X.

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FIGURE 9.2 MSC Magnesium, Nital Etch. Reflected Light. 540X.

The green salt used in the reductions performed was obtained from regular production, contained 97.7 per cent  $UF_4$ , 0.91 per cent  $UO_2F_2$ , and 0.25 per cent AOI (ammonium oxalate insolubles), and had been made by the hydrofluorination of uranium dioxide.

Two investigations were made: One measured the effects of different sizes of magnesium particles having different surface areas, and the other measured the effects of small amounts of -50 mesh magnesium located throughout and at the bottom of the charge.

Methods and pilot-scale equipment described previously<sup>3</sup> were used for these reductions. A magnesium excess of 4 per cent and a furnace control temperature of 1250°F were used. This equipment produces a 5.8-inch-diameter derby weighing approximately 29.9 pounds (100 per cent yield)

TABLE 9.1 Sieve Analyses of (1) Regular Production Magnesium\* and (2) Magnesium Retained by Each Sieve (Weight Per Cent Retained)

Particle Size	Regular Production Magnesium	Fraction Retained On							
		Pan	120 Mesh	50 Mesh	40 Mesh	30 Mesh	20 Mesh	16 Mesh	14 Mesh
+10	0.3			0.3	0.3	0.2	0.3	1.0	3.8
-10, +14	6.0			6.1	6.5	5.6	9.1	30.5	96.2
-14, +16	13.1			13.3	14.3	13.5	20.4	68.5	
+20			0.3						
-16, +20	40.7			41.4	44.3	41.0	70.2		
-20, +30	32.2			0.6	32.7	30.1	39.7		
-30, +40	4.3			0.4	4.4	4.5			
-40, +50	1.7			0.3	1.7				
-50, +60				0.7					
-50, +80	1.0								
-60, +80				43.7					
-80, +100				24.7					
-80, +120	0.3								
-100, +120		1.8							
-120, +140		26.7							
-120	0.3								
-140, +150			18.3						
-150, +200			33.4	7.0					
-200, +325			19.7						
-325			18.5	4.0					

\* Note: The +50 mesh fraction of regular production magnesium is referred to in the text as the coarse fraction; the -50 mesh fraction is referred to as the fines.

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TABLE 9.2 Reductions Made With Various Size Magnesium Particles  
Blended Throughout Charge

No. of Reductions	Mg Size (mesh)	Surface Area (sq m/g)	Avg. Preheat Time (min)	Magnitude of Preheat Time Effect With 95% Confidence Limits	Avg. Crude Yield (%)	Magnitude of Crude Yield Effect With 95% Confidence Limits
3	Regular	0.018	104.3	—	97.8	—
3	1% -120*	**	107.3	3.3 ± 6.9	96.8	-0.9 ± 3.1
4	2% -120*	**	106.0	1.7 ± 8.8	97.1	-0.6 ± 3.5
3	3% -120*	**	100.7	-3.6 ± 2.9	93.6	-4.2 ± 10.4
3	+50	0.021	112.3	8.0 ± 3.2	97.6	-0.2 ± 2.4
3	+40	0.023	111.7	7.4 ± 5.2	92.5	-5.3 ± 7.5
3	+30	0.018	110.7	6.4 ± 6.7	97.6	-0.2 ± 1.1
3	+20	0.019	116.3	12.0 ± 2.9	97.4	-0.4 ± 3.7
3	+16	0.018	111.3	7.0 ± 7.4	94.6	-3.1 ± 4.1
3	+14	0.020	132.0	27.7 ± 4.7	95.5	-2.3 ± 5.0

\* The remainder of the charge was +50 mesh regular magnesium.

\*\* The surface area of the -120 mesh magnesium was 0.140 sq m/g.

from a charge consisting of 6.34 pounds of magnesium and 39.38 pounds of UF<sub>4</sub>.

#### Magnesium Particles of Specified Size (Blended Throughout Charge)

It was found that in comparison with the controls, crude yields did not differ significantly for reductions made with the various magnesium particle sizes and the different surface areas (Table 9.2). Furthermore, there was no appreciable difference of slag-metal separation between the derbies produced (Figure 9.3).

Major differences in the average preheat time occurred only when magnesium particles of +14 mesh were used or when 1, 2, or 3 weight per cent -120 mesh magnesium was added to +50 mesh magnesium particles. The first significant difference in average preheat time occurred with the magnesium containing 3 per cent fines (Table 9.2). The preheat time was 3.5 per cent less than that for the control. As the magnesium particle size was increased from +50 mesh through +14 mesh, there was no major change in average preheat time until the +14 mesh magnesium gave a 26.6 per cent increase. The data showing the relationship of preheat time and magnesium size are plotted in Figure 9.4.

#### Blend; With Fine Magnesium Located Preferentially in Charge

In Table 9.3 are shown the results of reductions performed to determine if the reaction locus could be controlled by appropriate use of fine magnesium.

One reduction was made using a blend of green salt and magnesium composed of 50 wt % +50 mesh and 50 wt % -50 mesh magnesium. The preheat time was 71 minutes, or 68.1 per cent of the average preheat time of the controls.

TABLE 9.3 Reductions Made With Magnesium  
Fines Located Preferentially in Charge

No. of Reductions	Mg Size (mesh)*	Crude Yield (%)	Preheat Time (min)
1	50 wt % fines & 50 wt % +50	90.7	71
1	2½ wt % fines, remainder +50; fines in bottom center	97.0	92
1	2½ wt % fines, remainder +50; fines in bottom center	100.0	87
3	Regular Production	97.8	104.3

\*Fines are regular magnesium from which +50 mesh fraction has been removed.

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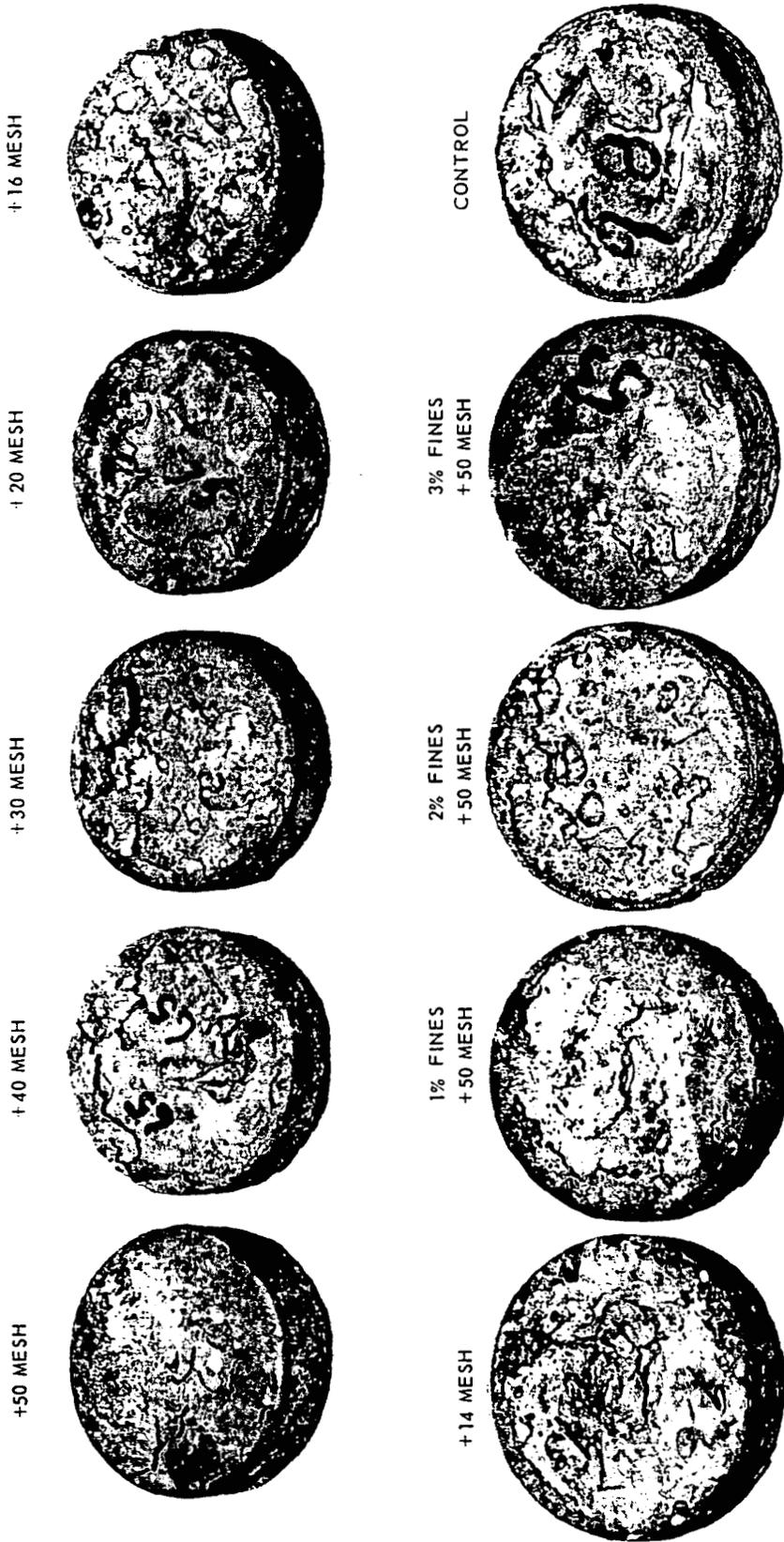


FIGURE 9.3 Typical 5.8 - Inch - Diameter Derbies Made With Different Sizes of Magnesium Particles and Different Proportions of Fines in the Charge.

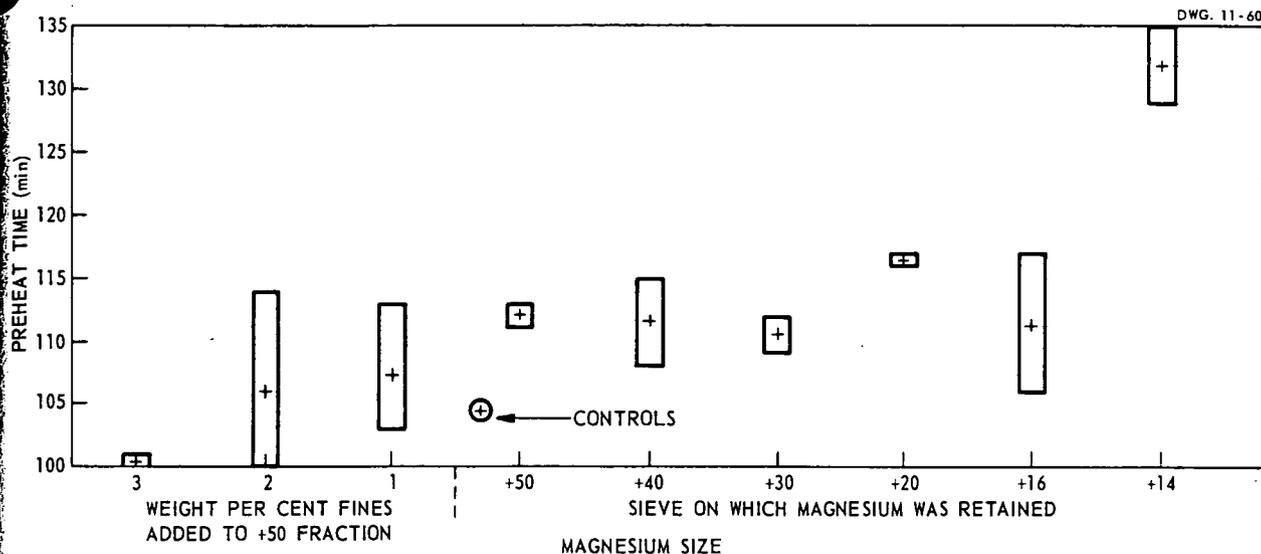


FIGURE 9.4 Relationship of Preheat Time and Magnesium Size. NOTE: The + sign represents the average and the rectangle represents the range.

Two reductions were then performed in which +50 mesh magnesium was used for most of the charge, the remainder (2½ wt %) being -50 mesh. The fines were mixed with green salt and were packed as a 2½ -inch diameter by 2-inch core (or "fuse") just above the bottom liner. The remainder of the charge, containing +50 mesh magnesium, was then placed around this core. Preheat times for these two reductions were 92 minutes and 87 minutes, compared with 104.3 minutes for the controls. As it had been demonstrated that a high percentage (50 wt %) of fines shortened the preheat time by 31.9 per cent, the shorter preheat times for the "fused" bombs are attributed to the presence of the -50 mesh magnesium. If this is true, then the preheat time and reaction initiation site can be controlled by preferential placement of a charge containing magnesium-green salt "fuses."

#### Future Work

It is planned to perform reductions using higher than 3 w/o magnesium fines to determine more

precisely their effects upon the crude yields and preheat time.

#### References

- <sup>1</sup>R. A. Beebe, J. B. Beckwith, and J. M. Honig. "The Determination of Small Surface Areas By Krypton Adsorption At Low Temperature," *J. Am. Chem. Soc.* 67: 1554. 1945.
- <sup>2</sup>Oak Ridge National Laboratory. *ORNL Master Analytical Manual*, Method No. 900602. January 15, 1958.
- <sup>3</sup>O. R. Magotiaux and C. C. Smitherman. "The Effect of Process Changes and Operating Conditions on Bomb Reduction Efficiency and Metal Quality," *Summary Tech. Rpt.*, USAEC Report NLCO-785, pp. 73-80. April 15, 1959 (Classified).

Editor's Note: The following topical report was issued during the report period:

- NLCO-794. *Factors Affecting Yield and Metal Quality in the Reduction of UF<sub>4</sub> to Metal*. O. R. Magotiaux and C. C. Smitherman. February 18, 1959.

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## 10. SEMICONTINUOUS REDUCTION OF URANIUM TETRAFLUORIDE TO URANIUM METAL WITH MAGNESIUM

O. R. Magoteaux

C. A. Neu

G. Brodi

### Abstract

A semicontinuous process for producing uranium by the reduction of uranium tetrafluoride ( $UF_4$ ) with magnesium inside a reactor is being developed on a pilot scale. Equipment of improved efficiency for charging the  $UF_4$ -Mg into the reactor was developed. Uranium produced by this process was vacuum melted and cast into two production-size reactor-grade ingots.

### Introduction

A batch bomb reduction process is presently used in the Metals Production Plant to convert uranium tetrafluoride to uranium with magnesium for subsequent vacuum casting into reactor-grade ingot uranium.

A lower-cost semicontinuous process is being developed in which the reduction of uranium tetrafluoride (green salt) with magnesium takes place inside an induction-heated graphite reactor. In this process, the green salt is blended with magnesium and is formed into briquettes on a rotary press. The briquettes are presently charged from a belt conveyor, through an open tube, into the heated graphite reactor where the reaction occurs. The molten products of the reduction (uranium and magnesium fluoride slag) are then alternately tilt-poured into separate graphite molds. The uranium formed is called "as-reduced."

In regular production practice, bomb-reduced uranium is vacuum melted with solid scrap and cast into an ingot mold. The resulting ingots are then fabricated into slugs (bare fuel cores) by rolling and machining. It is intended that the uranium produced by the semicontinuous process be utilized in the same manner.

### Previous Work on Project

Previous work<sup>1</sup> included: (1) testing of initial material handling equipment and reduction facilities, (2) the preparation of green salt-magnesium briquettes on a rotary press, (3) reduction tests to determine the green salt-magnesium ratio which would provide the highest reduction efficiency, (4) studies to evaluate the effect of green salt quality on reduction efficiency, (5) the evaluation of various methods of removing the molten products from the reactor, (6) the demonstration of a two-way tilt, lip-pour, induction furnace for reduction-pouring, (7) the development of more efficient material-handling equipment, (8) the establishment of the most efficient reactor temperature, and (9) the evaluation on a small-scale of magnesia-alumina as the reactor material.<sup>2</sup>

### Objectives for This Period

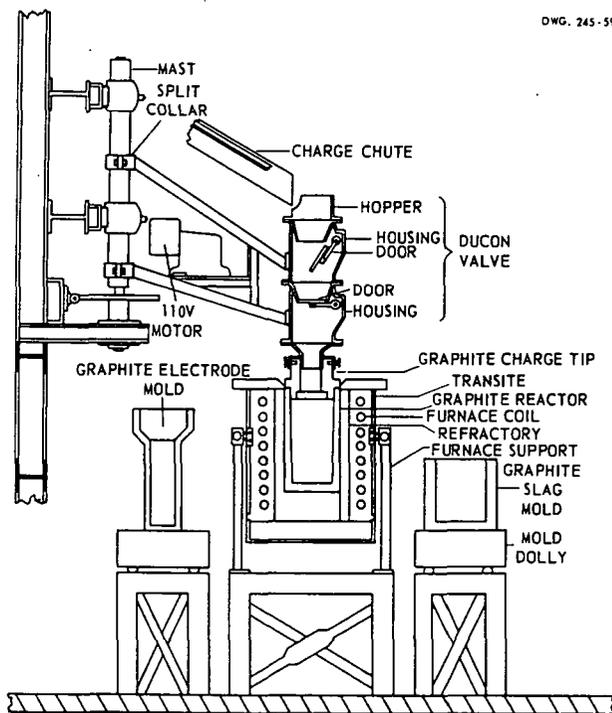
The objectives for this period were (1) the development of an improved charging device for the briquettes, and (2) the preparation and metal quality evaluation of vacuum-cast ingot uranium.

### Summary of Results Obtained This Period

A two-door, cast iron valve was developed for efficiently charging the briquettes into the reactor. Reactor-grade ingots were made from charges consisting entirely of "as-reduced" uranium and charges consisting of 50 per cent "as-reduced" and 50 per cent solid scrap uranium. The vacuum melting and casting procedures used were similar to those used in production practice.

### Description and Operation of the Valve

A two-door, motor-operated discharge valve (Type C), purchased from the Ducon Company, In-



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FIGURE 10.1 Schematic View of Semicontinuous Reduction Equipment

corporated, was modified by relocating the gear-motor and replacing the bronze bearings with cast iron bearings to allow operation at higher temperatures (Fig. 10.1 and 10.2). Lines for purging with helium were placed to the middle chamber (2, Fig. 10.2) and the lower chamber (5, Fig. 10.2) of the valve. A graphite tip was attached to the valve to seal the top of the reactor. The valve was mounted on a steel framework and mast so that it could be lifted and rotated horizontally to and from the reactor. Chromel-alumel thermocouples (1 to 8, Fig. 10.2), which were fastened to various positions of the valve and the graphite tip, were used to measure temperatures during operation.

Briquettes of green salt-magnesium were fed into the top of the valve. The two doors of the valve were opened alternately every three seconds by a gear-motor drive. This permitted the briquettes in the bottom chamber to drop into the reactor while the door from the top chamber was

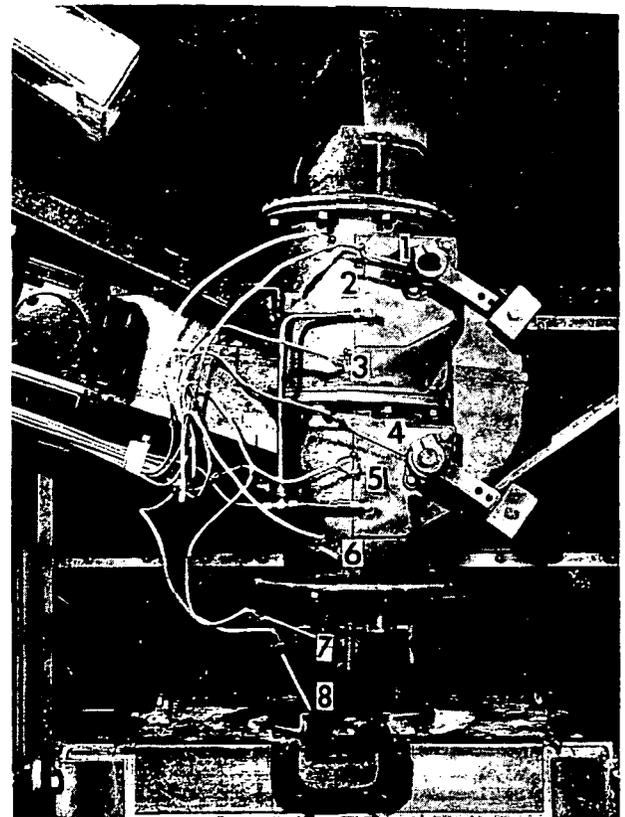


FIGURE 10.2 Two-Door Valve in Position for Charging the Reactor With Briquettes. The Numbers Show Where Thermocouples Are Located.

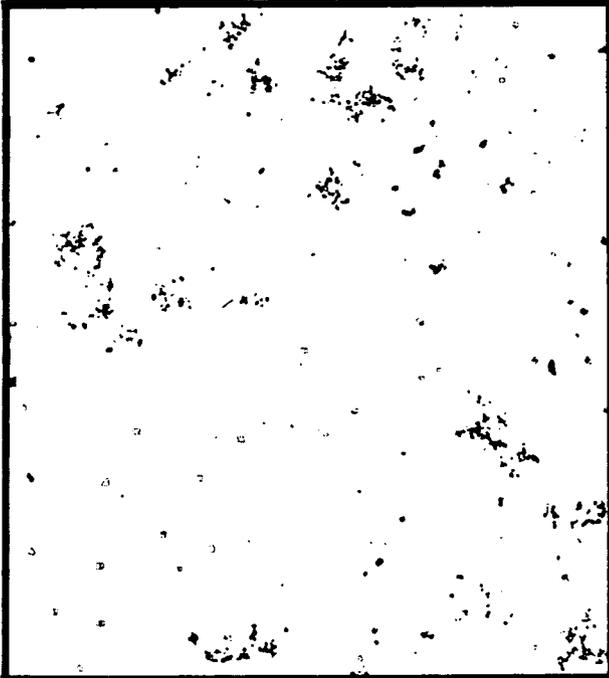
closed. In this manner, not only was entrance of air prevented, but also a slightly positive pressure of magnesium vapor and an inert gas atmosphere were maintained inside the reactor during reduction. Although parts of the discharge valve reached 1260°F during charging, no major operating difficulties were experienced.

### Preparation of Ingots

Two production-size (7-inch-diam. by 46-inch-long) ingots were produced in the Pilot Plant by vacuum melting and casting. The vacuum remelt furnace in the Pilot Plant was utilized, and the standard operating procedures for melting and for casting ingots were used. The melting cycle was

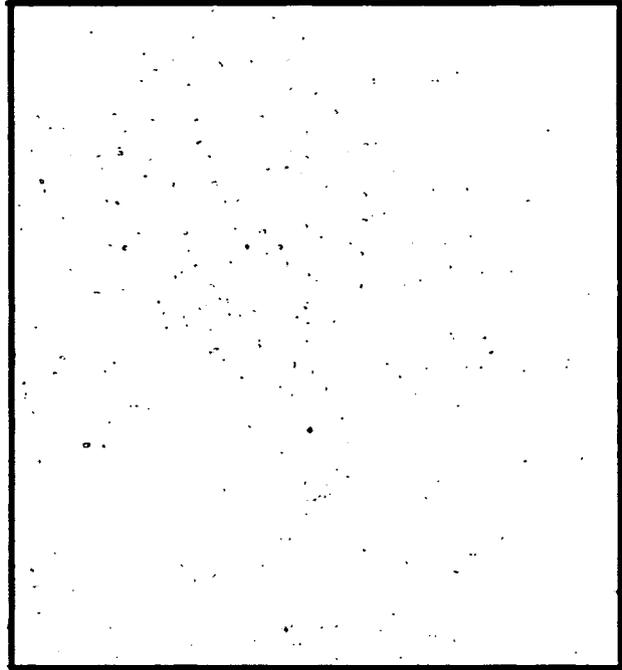
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270 - 1



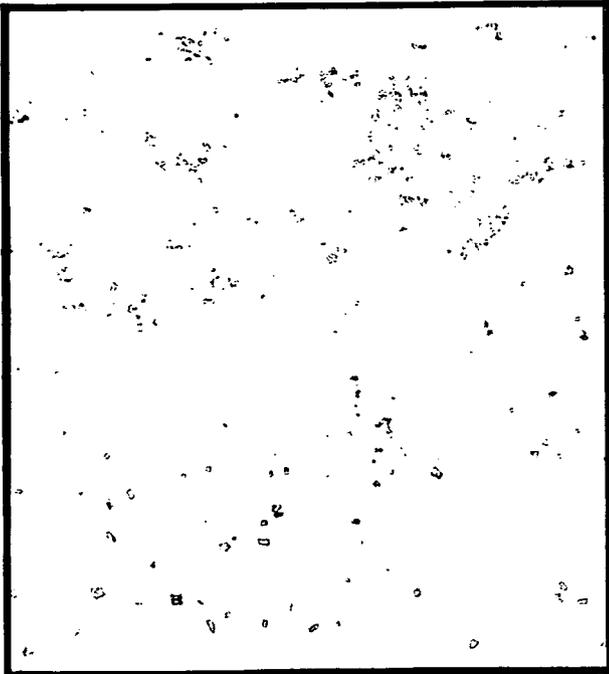
"AS-REDUCED" METAL

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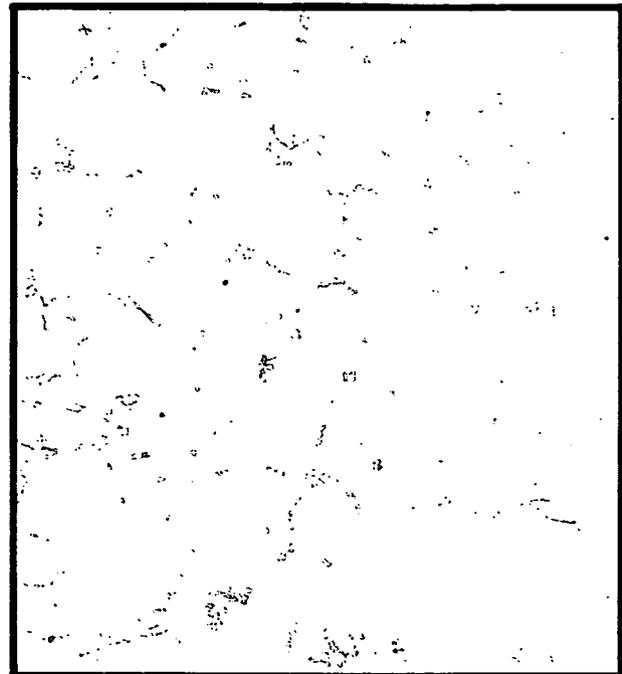
INGOT 1. MADE WITH ALL  
"AS-REDUCED" METAL

338 - 1



INGOT 2. MADE WITH 50% "AS-REDUCED"  
METAL AND 50% SOLID SCRAP

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PRODUCTION INGOT

FIGURE 10.3 Inclusions in "As-Reduced" Experimental Ingots and a Production Ingot (100X)

165 kw for 55 minutes, followed by 100 kw until a temperature of 2550°F was reached (measured with an optical pyrometer). The power was then turned off for 5 minutes and the melt was cast.

The charge for one ingot (No. 1) consisted of 100 per cent "as-reduced" uranium, while the charge for the other ingot (No. 2) consisted of 50 per cent "as-reduced" and 50 per cent solid scrap (reject slugs, rod ends). The "as-reduced" uranium used in the first ingot was cast into a cold mold, while the "as-reduced" uranium for the second ingot was cast into a mold heated to 1000°F.

Chemical analyses and metallographic examinations were made of samples cut from the "as-reduced" metal and the ingot metal.

### Results and Discussion

Chemical analyses of the uranium before and after casting are shown in Table 10.1. The inclusion content of ingot No. 1 was similar to that of production ingots, except that the inclusions were smaller and more widely dispersed (Fig. 10.3). In ingot No. 2, the amount and distribution of inclusions were similar to that of production ingots (Fig. 10.3). The crude yield for ingot No. 1 was 84.9 per cent, and the yield for ingot No. 2 was 96.6 per cent.

### Future Work

Future work will include:

1. An 8 to 24-hour demonstration of the reduction-pouring process, and an evaluation of the

TABLE 10.1 Analyses of "As-Reduced" Uranium and Ingot Uranium

	"As-Reduced" Metal	Ingot 1	"As-Reduced" Metal	Ingot 2
<b>Chemical</b>				
C (ppm)	340	390	409	512
H <sub>2</sub> (ppm)	5.23 to 9.87	1.09	—	1.59
N <sub>2</sub> (ppm)	15 to 100	28	28 to 73	36
O <sub>2</sub> (ppm)	—	—	15 to 111	22
Density (g/cc)	—	18.93	18.93	18.93
<b>Spectrochemical</b>				
Fe (ppm)	130*	139*	71	73
Ni (ppm)	350*	375*	20	21
Si (ppm)	14	19	14	25

\*High iron and nickel are from "off specification" green salt used for reduction.

ingots made with the uranium produced.

2. The evaluation on a pilot-scale of magnesia-alumina (MgO·Al<sub>2</sub>O<sub>3</sub>) spinel reactors.

### References

<sup>1</sup>O. R. Magoteaux, C. A. Neu, D. L. Elston, and G. Brodi. "Semi-Continuous Reduction of Uranium Tetrafluoride to Uranium Metal with Magnesium," Summary Tech. Rpt., USAEC Report NLCO-775, pp. 91-94. January 22, 1959 (Classified); and preceding quarterly reports.

<sup>2</sup>D. L. Elston, O. R. Magoteaux, and W. W. Brock. "Evaluation of Small-Scale Magnesia-Alumina Crucibles for the Semicontinuous Reduction of Uranium Tetrafluoride with Magnesium," Summary Tech. Rpt., USAEC Report NLCO-795, pp. 33-38. October 15, 1959 (Classified).

## 11. MATERIAL BALANCE VARIATIONS IN THERMAL-SHOCKING OF URANIUM DERBIES\*

A. J. Klee

### Abstract

The effect of thermal-shocking on production uranium derbies has been investigated with respect to material balance considerations. A random sample of 103 uranium derbies, as well as historical data for 13 months, has indicated that the thermal-shocking process must be considered as both a slag-removing process and a uranium-removing process. Average removal figures have been developed; in addition, variations in these figures have been explained in terms of variations in the proportion of Grade II derbies thermal-shocked.

### Introduction

Derbies produced in the Metals Production Plant are characterized, by visual means, into three different grades. The system is such that Grade I derbies are those containing little or no slag (slag is generated in the reduction of  $UF_4$  to metal); Grade II derbies are those with only a moderate amount of slag; and Grade III derbies are those with a considerable amount of adhering slag.

The thermal-shock treatment of Metals Production Plant derbies, which is undertaken by the Pilot Plant, has for its purpose removing excessive amounts of adhering slag. The derbies to be shocked are loaded into basket-type containers and are heated for a specified time and temperature in a Rockwell furnace. After cooling, the derbies are chipped in a breakout station before returning to the Metals Production Plant. For Accountability purposes, the derbies are considered to be Grade II after shock treatment.

This report summarizes the findings obtained after investigation of:

- a. One hundred and three Metals Production Plant derbies, and

- b. Thirteen months' historical data pertaining to Accountability records of Pilot Plant thermal-shocking.

The 103 derbies were examined prior to and after thermal-shocking, with respect to the weight of each derby and the amount of adhering slag contained thereupon.

### Objective for This Quarter

In order to provide a sound basis for an economic evaluation of the thermal-shocking process, it was desired to obtain statements of material balance together with proper confidence limits. Specifically, it was desired to determine:

1. Average over-all weight loss/derby in thermal-shocking.
2. Average uranium loss/derby in thermal-shocking.
3. Factors which influence variations in the above averages.

### Summary of Results

1. The average weight loss in thermal-shocking was  $21.7 \pm 3.8$  pounds per derby (for 103 derbies).
2. The true uranium loss in thermal-shocking during a recent 13-month period was 8.3 per cent. The results for 103 derbies indicate that perfectly clean derbies would lose 6.2 pounds of metal (2 per cent) during thermal-shocking, due to oxidation reactions. Thus, the thermal-shocking process must be considered not only a slag-removing process, but a uranium-removing process as well.
3. Most of the variations in over-all weight loss and uranium loss can be attributed to variations in the proportion of Grade II derbies shocked.

*Work performed by A. J. Klee and J. E. Vath*

**Effect of Thermal-Shocking on 103 Observed Derbies**

The changes that occurred upon thermal-shock treatment of 103 Metals Production Plant derbies (which included 89.3 per cent Grade III derbies) are summarized in Table 11.1.

**TABLE 11.1 Average Weight Change for 103 Derbies**

Item	Weight Change* (%)	Weight Change* (lb)
Over-all Weight	-6.7 ± 1.2	-21.7 ± 3.8
Slag Weight	-72.9 ± 15.8	-7.4 ± 1.6
Metal Weight	-4.5 ± 1.7	-14.2 ± 5.4

\* With 95 per cent confidence limits.

To determine the extent to which the initial amount of slag adhering to the derby affects ultimate losses in thermal-shocking, a simple regression correlation between the over-all weight loss and the initial slag volume was made. A significant correlation was obtained as follows:

$$y = 6.2 + 0.17x$$

where y is the over-all weight loss of a derby (in pounds) and x is the cubic inches of initial adhering slag. Such a correlation yields a correlation coefficient of 0.41, indicating that correlation with slag volume explains 17 per cent of the variation in over-all weight loss. It also follows from an extrapolation of the equation that for the 103 derbies studied, 6.2 pounds of metal (2 per cent) would be lost if an absolutely clean derby were thermal-shocked.

By the use of average slag volume figures,<sup>1</sup> uranium weight losses for Grade II and Grade III derbies could be extrapolated (Table 11.2).

**TABLE 11.2 Calculated Metal Loss by Derby Grade for 103 Derbies**

Derby Grade	Over-all Metal Loss (lb)	Over-all Metal Loss (%)
II	8.3	2.6
III	20.0	6.2

It was known that on the basis of Accountability Department records, these loss figures were suspiciously low. At this point, it was decided to examine these records.

**Accountability Records**

The results of a tabulation of Accountability records are shown in Table 11.3. It may be noted that over-all weight losses and uranium losses varied greatly from month to month.

**TABLE 11.3 Uranium Losses as a Result of Thermal-Shocking, July, 1958, through July, 1959**

Date	No. of Grade III Derbies Produced	No. of Derbies Shocked	Over-all Weight Loss (%)	Uranium Loss (%)	Corrected Uranium Loss (%)
1958					
July	444	255	18.8	17.3	17.3
Aug.	521	913	10.5	8.8	10.6
Sept.	84	194	9.7	8.5	9.0
Oct.	185	616	12.4	10.8	11.9
Nov.	686	912	10.4	8.8	9.2
Dec.	1209	1278	9.9	8.2	8.3
1959					
Jan.	780	1093	10.7	9.0	9.5
Feb.	1052	1153	8.6	7.0	7.1
Mar.	735	1076	5.2	4.5	4.7
Apr.	885	1408	8.1	6.4	7.0
May	637	782	8.6	6.9	7.2
June	827	733	10.2	8.6	8.6
July	909	1078	8.8	7.1	7.4

Columns 4 and 5 for March confirm the suspicion that the 103 derby sample (which was taken in March) happened to coincide with a period of low-loss derbies.

The Accountability figures in Table 11.3 are based upon assumptions as follows:

1. Thermal-shocking in the Pilot Plant produces all Grade II derbies.
2. The uranium assay of Metals Production Plant derbies received for thermal-shocking is 97.402 per cent.
3. The uranium assay of thermal-shocked derbies is 99.189 per cent.

These assumptions were checked, and the following facts were obtained:

1. Thermal-shocking in the Pilot Plant does produce a Grade II derby (though a Grade II derby that is slightly heavy with slag).

2. Grade III derbies have an average uranium assay of 97.365 per cent.

3. Grade II derbies have an average uranium assay of 99.581 per cent.

It was concluded that the Accountability assumptions would be valid if all derbies received for the thermal-shocking were Grade III. However, use of the 97.402 per cent factor for all derbies sent to the Pilot Plant for thermal-shocking cannot be defended. Columns 2 and 3 of Table 11.3 show that in some months, a large number of Grade II derbies are thermal-shocked. The Accountability uranium loss figures are therefore too low, on the average. These figures have been corrected and are shown in Column 6 of Table 11.3.

The average (weighted) uncorrected uranium loss for July, 1958, to July, 1959, was 7.86 per cent. After correction for Grade II derbies among the derbies thermal-shocked, this figure was 8.32, an increase of 0.5 per cent.

#### Comparison of Values from Accountability Records with Values from 103-Derby Samples

The March, 1959, sample checks out with Accountability data, as shown in Table 11.4.

In accordance with Pilot Plant historical data, a correction of approximately 0.2 per cent for uranium loss for burnouts was made.

After corrections, the findings of Accountability for March, 1959, agreed completely with those for the 103-derby study. The agreement is not quite as good for over-all weight loss, because the 103-derby sample contained a smaller proportion of Grade II derbies than did the month's Pilot Plant operation.

TABLE 11.4 Uranium Loss for Derbies Thermal-Shocked

Source	U Loss (%)	Over-all Weight Loss (%)
103-Derby Sample	4.5	6.7 (The sample contained 10.7% Grade II Derbies)
103-Derby Sample (corrected for burn-outs)*	4.7	
March, 1959, Accountability Records	4.5	6.2 (The derbies included 31.7% Grade II Derbies - mostly slaggy Grade II Derbies)
March, 1959 Accountability Records (corrected for Grade II)	4.7	

\* A burnout is a derby which undergoes complete and uncontrollable oxidation. This is an infrequent occurrence.

#### Effect of Number of Derbies Thermal-Shocked Upon Weight Loss

A visual examination of the Accountability data suggested that over-all weight loss upon thermal-shocking had varied with the number of derbies shocked. A simple regression correlation of over-all weight loss vs the number of derbies shocked was made and was found to be significant. The correlation is as follows (Fig. 11.1).

$$y = 14.7 - 0.005x$$

where y is the over-all weight loss (per cent) and

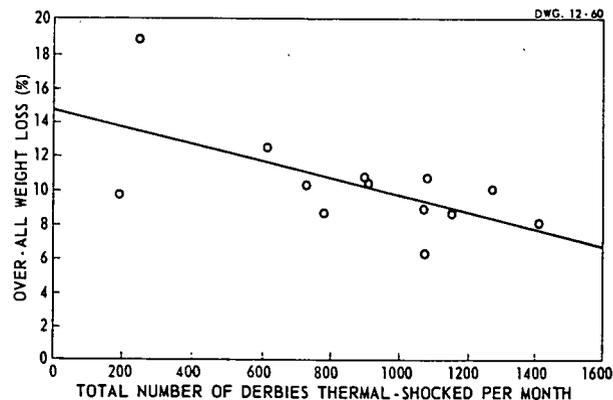


FIGURE 11.1 Over-All Weight Loss vs Number of Derbies Thermal-Shocked.

x is the number of derbies shocked (in any one month).

The correlation coefficient was 0.62, indicating that 38 per cent of the variation in over-all weight loss was explained through correlation with the number of derbies shocked.

At this point, it was suspected that the over-all weight loss variation was really correlated with the number of Grade II derbies that were shocked during any particular month. The following correlation was obtained (Fig. 11.2):

$$y = 13.2 - 0.014x$$

where y = over-all weight loss (per cent) and x = number of Grade II derbies shocked. The correlation coefficient was 0.79, indicating that 62 per cent of the variation in over-all weight loss was

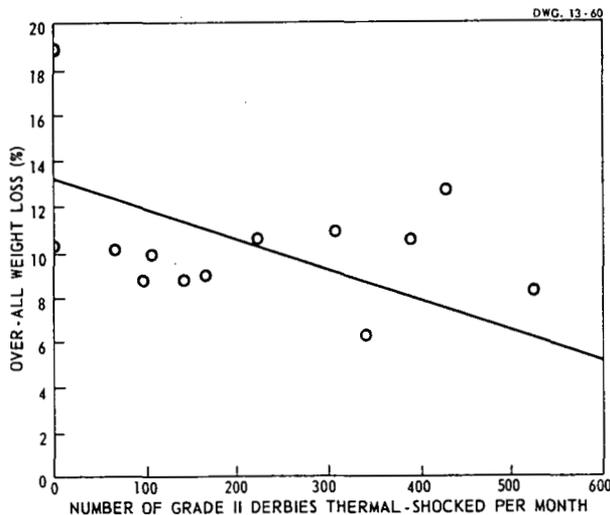


FIGURE 11.2 Over-All Weight Loss vs Number of Grade II Derbies Thermal-Shocked.

explained by correlation with the number of Grade II derbies shocked.

It can be concluded, therefore, that the variation in losses can be traced mostly to variations in the number of Grade II (or Grade I) derbies received by the Pilot Plant for thermal-shocking. It is also apparent that if the number of Grade II derbies thermal-shocked were decreased, the average losses experienced in thermal-shocking would be higher than they now are.

### Conclusions

1. Accountability figures relating to thermal-shocking, when suitably corrected, reliably indicate true losses experienced in the process. The average monthly over-all and uranium weight loss values are lower than the actual losses experienced by Grade III derbies in thermal-shocking. This is due to the fact that Grade III derbies lose more weight than Grade II or Grade I derbies. The value that had been used by Accountability to represent uranium loss during thermal-shocking was corrected by adding 0.5 per cent. This took into account the effect of Grade II derbies.

2. The poorer the grade of derby, the greater the slag and uranium losses during the thermal-shocking.

### Reference

1. A. J. Klee and J. E. Vath. "Analyses of Variations in Visually Determined Derby Grades," Summary Tech. Rpt., USAEC Report NLCO-790, pp. 57-59. July 20, 1959 (Classified).

12. THE RECOVERY OF MAGNESIUM METAL FROM  $MgF_2$  SLAG

E. W. Mautz

**Abstract**

The recovery of magnesium metal by  $CaC_2$  reduction of  $MgF_2$  slag\* was both studied in a laboratory retort and demonstrated in a plant-scale retort at Nelco Metals, Inc., Canaan, Connecticut. Economic studies indicate, however, that the  $CaC_2$ - $MgF_2$  slag process for magnesium recovery, followed by HF recovery from the retort residue ( $CaF_2$  and C) is not competitive with current practice.

**Introduction**

Magnesium metal (used in the reduction of  $UF_4$  to uranium metal) and anhydrous HF (employed in the conversion of  $UO_2$  to  $UF_4$ ) contribute substantial costs to the production of uranium metal. Thus, the recovery of magnesium metal and HF from  $MgF_2$  slag represents a potential means of reducing costs in uranium metal production.

The currently used Pidgeon process for magnesium manufacture involves calcination of dolomite, ball-milling of dolomite and 75 per cent ferrosilicon (individually, then combined with 5 per cent addition of fluorspar), briquetting, and bagging in paper bags for charging to the magnesium production retorts. The retorts are charged at operating temperature ( $2150^\circ F$ ), the head flange is attached, vacuum valves are opened, and the retort is then operated on an 11-hour cycle. A 40-pound magnesium "crown" is obtained in the water-cooled condenser section of the retort, representing a 90 to 95 per cent utilization of silicon in the ferrosilicon reducing agent. The magnesium condensate is removed from the condenser sleeves with a hydraulically operated ram, then remelted under a molten salt consisting mainly of magnesium chloride. The molten magnesium is hand-ladled into molds in an endless conveyor system which automatically drops the 20-pound ingots at the dis-

charge point. The ingots are collected in lots to represent each remelt charge and are shipped to Metal Sellings Company, Putnam, Connecticut for milling to AEC particle-size specifications.

**Previous Work on This Project**

Previous laboratory work on (1) the reduction of  $MgF_2$  slag to magnesium metal with calcium carbide and (2) the recovery of HF has been reported.<sup>1</sup> These tests demonstrated the technical feasibility of the reactions involved.

**Objective for This Quarter**

The reduction of  $MgF_2$  slag with calcium carbide was to be demonstrated in existing magnesium production retort facilities, for comparison with the current ferrosilicon-dolomite process.

**Summary of Results Obtained This Quarter**

Nelco laboratory results on the  $MgF_2$  slag -  $CaC_2$  reaction confirmed prior laboratory work at National Lead Company of Ohio and also served as background information for plant-scale evaluation of the reaction.

Tests of the reaction of  $MgF_2$  slag and  $CaC_2$  in plant-scale retorts have confirmed the technical feasibility of the process for preparation of magnesium metal. The process, however, appears to offer no advantage over the current dolomite-ferrosilicon process. In addition, the over-all costs of magnesium and HF recovery are such as to make the process economically unattractive in comparison with present costs.

**Laboratory Apparatus, Procedure, and Results**

The laboratory retort unit consists of an electrically heated furnace containing a 2-inch-diameter stainless steel retort extending about 12 inches into the furnace and having a 3-inch length out-

\*  $MgF_2$  slag is obtained in the reduction of  $UF_4$  to uranium metal with magnesium.

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side the furnace equipped with coils for cooling water. A split-shell condensing surface for the magnesium fits inside the cooled portion of the retort tube, while the charge material is contained in a 4-inch-long boat located centrally in the heated section. The retort closure is a bolted type flange.

The  $MgF_2$  slag, supplied by National Lead Company of Ohio as representative of by-product from the uranium metal operation, was ground to less than 200 mesh. Except as noted for run 175 (Table 12.1), the calcium carbide was  $\frac{1}{4}$  XD size obtained from Union Carbide Olefins Company. Table 12.1 summarizes the laboratory data obtained. No corrosion of the equipment was observed, and the spent charge showed only slight sintering.

The following general observations may be made, based on the laboratory data:

1. For  $MgF_2$  slag -  $CaC_2$  blends, using a 4-hour residence time, and pressures below 300

microns, temperatures near 2000°F yield 80 per cent magnesium or better.

2. Unblended charges tended to result in lower yields.

3. Higher yields were obtained in the laboratory retort than in the plant retort; also, minor sintering was experienced in the laboratory retort, as contrasted to variable sintering in the plant retort. This indicates, based on similar experience with the dolomite-ferrosilicon reaction (not reported here), that briquetting of the charge would (1) improve heat transfer in the plant retort and (2) minimize solids-handling problems caused by sintering.

#### Plant Equipment, Procedure, and Results

The plant-scale retort used was a standard size, 10-inch-diameter, Pidgeon process retort tube installed in a single oil-fired furnace (independent of the main banks of multiple-retort production furnaces). A separate vacuum system serves the retort employed in these tests. In the experimental

TABLE 12.1 Laboratory Retort Runs:  $MgF_2$  Slag -  $CaC_2$ \*

Nelco Run**	Temp (°F)	Residence Time (hr)	De-gas Step†	Final Pressure ( $\mu$ )	$MgF_2$ (g)	$CaC_2$ (g)	Mg Recovered (g)	Mg Recovery (%)	Comments
162	1900	—		15	69.3	80.0	—	80	Cold retort; unblended charge
163							10.6	83	
164							11.5	90	
165							11.5	90	
166	2000	4	Yes	300	34.5	40.0	12.9	101	Slag on top $CaC_2$ ; unblended charge
167				350			8.6	67	
168	2100	4	Yes	35	34.5	40.0	9.1	71	Slag on top $CaC_2$ ; unblended charge
169	2000	30	10.9	85					
170	1900	15	9.9	77	34.5	40.0	10.5	82	Slag on top $CaC_2$ ; unblended charge
171	250	11.0	86						
172	2000	3	No	300	34.5	40.0	10.8	84	Cold retort
173		2					8.5	66	
174		1					8.8	69	
175††		1					9.8	77	
176		1.5							

\*  $\frac{1}{4}$  XD Union Carbide  $CaC_2$ , except Run 175.

\*\* Unless noted otherwise, a blended charge was inserted into the hot retort.

† The "degassing" step involved arresting the temperature during heat-up at about 850°F for  $\frac{1}{2}$  hour.

††  $\frac{1}{4} \times \frac{1}{12}$   $CaC_2$ .

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runs described below, stainless steel boats were used that are 4 feet long, slightly less than 10 inches in diameter, and approximately semi-circular in end cross-section. T-shaped heat distributor baffles are welded inside the boats at 3-inch intervals.

The charge consisted of minus 200 mesh  $MgF_2$  slag supplied by National Lead Company of Ohio and  $\frac{1}{4}$  XD size  $CaC_2$  obtained from Union Carbide Olefins Company. The charge was weighed (10 per cent excess  $CaC_2$ ), blended in tightly sealed drums (generally 30-gallon size), loaded without briquetting into the boats, and charged into the hot retort tube. The retort was sealed, the vacuum valve was opened, and the runs were completed, using the operating cycles as described below:

#### Run 1

A 4.7-pound quantity of  $MgF_2$  slag was blended with 5.3 pounds of  $CaC_2$  in a 5-gallon drum and was charged to a single boat, forming a pile 4 inches deep and 12 inches long. Before it was opened for charging, the retort was at  $2150^\circ F$  and  $40 \mu$  pressure. The boat was placed midway along the length of the retort. The following data summarize this run:

Time (min)	Temp ( $^\circ F$ )	Pressure ( $\mu$ )
0	2070	2600
3	2070	1300
17	2090	1000
27	2095	800
32	2100	700
42	2110	350
57	2140	300
72	2150	250
157	2150	125

A net weight of 1.1 pounds of magnesium condensate was recovered (65 per cent yield). The metal appeared to be clean and good and did not burn upon discharge. The residue in the boat was hard, but after it cooled overnight, it was very soft and in powder form.

#### Run 2

A 14-pound quantity of slag was mixed in a 30-gallon drum with 16 pounds of  $CaC_2$ , forming a pile 6 inches deep and 15 inches long. A target temperature of  $2150^\circ F$  was again employed and the pressure at discharge was  $50 \mu$ . The total run time was three hours. The amount of magnesium metal recovered from this run represented a 50 per cent yield. The residue, left in the boat overnight, was observed to be harder than that from Run 1, above. The residue consisted of a soft  $\frac{1}{2}$  inch layer on top, a hard center requiring a hammer and chisel for removal, and a soft layer on the bottom.

#### Run 3

A 37.3-pound quantity of slag and 42.7 pounds of  $CaC_2$  were blended as in Run 2. This charge filled the boat about two-thirds full (6 inches by approximately 36 inches). No burning was noted during charging or discharging of materials. A temperature of  $2150^\circ F$  was again used and the final pressure after 21 hours was  $30 \mu$ . The magnesium condensate weighed 14.6 pounds (the theoretical weight being 13.8 pounds).

#### Run 4

A blended charge of 70 pounds of slag and 80 pounds of  $CaC_2$  was prepared. Since 114 pounds of the blend filled the boat to capacity, this was all that was used. At the end of reaction at a temperature of  $2150^\circ F$  for 9 hours, the final pressure was  $35 \mu$ . A 71 per cent yield (i.e., 14 pounds) of magnesium metal was obtained. The residue in the boat was very hard, requiring hammer and chisel for removal.

#### Run 5

Two batches, each consisting of 58 pounds of slag and 67 pounds of  $CaC_2$ , were charged into two new stainless steel boats. The boats were vibrated in order to get all of the charge into the boats. The carbide tended to settle during vibration of the boats. The charge (contained in the two boats)

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was then heated to 2150°F at 30  $\mu$  for 24 hours. A 31-pound magnesium crown was recovered (72 per cent yield). The boat residue was again very hard, requiring hammer and chisel for removal.

## Run 6

Two batches, each consisting of 51.3 pounds of slag and 58.7 pounds of  $\text{CaC}_2$ , were charged into two boats and were heated to 2150°F at 30  $\mu$  for 20 hours. A 29.8-pound crown of magnesium metal was obtained (78 per cent yield). The residue was not as hard as in Run 5.

Corrosion was not indicated to be a problem in these tests.

The results of two additional runs using nominal 90 per cent and 120 per cent stoichiometric  $\text{CaC}_2$  (to examine the effect of this variable on residue sintering and magnesium yield) are not available at this time.

## Discussion

The runs in the plant-size retort unit, together with laboratory observations, indicate that the  $\text{MgF}_2$  slag -  $\text{CaC}_2$  process offers no apparent improvement over the conventional dolomite-ferrosilicon process with respect to operating temperature, pressure, cycle time, and material-handling considerations. Thus, if it is assumed that there are no technological differences in the two processes, the present dolomite-ferrosilicon process is substantially favored on the basis of obvious cost

factors relating to reducing agent, materials shipping, safety considerations relating to  $\text{MgF}_2$  slag dust hazards, and necessary controls in  $\text{CaC}_2$  handling. Any cost deficits accrued in a magnesium production step using  $\text{MgF}_2$  slag as a feed must be deducted from potential cost savings in the proposed subsequent HF recovery.\* As indicated above, cost estimates of the over-all magnesium and HF recovery show that recovery of these values from  $\text{MgF}_2$  slag is not competitive with present procurement practice.

## Future Work

No additional work on this project is planned.

## Acknowledgment

The laboratory and pilot plant data contained in this section were developed at Nelco Metals, Inc., Canaan, Connecticut, by P. Gasperini and R. Gunn under the supervision of W. J. Ash.

## Reference

<sup>1</sup>E. W. Mautz and D. C. Bonfer. "The Recovery of Magnesium Metal from  $\text{MgF}_2$  Slag," Summary Tech. Rpt., USAEC Report NLCO-795, pp. 93-95. October 20, 1959 (Classified) and preceding quarterly reports.

\* It has been proposed that HF be recovered by treating the magnesium retort residue (mainly  $\text{CaF}_2$  and carbon) with sulfuric acid.

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## 13. MACHINING RESEARCH

W. E. Stephens

R. J. Jansen

## Abstract

The machinability of as-cast uranium was compared with that of beta heat treated uranium, and as-cast uranium was found to give shorter tool life.

A Meyer exponent rating was obtained for uranium. (This rating indicates a material's capacity for work-hardening.) Uranium was found to have a high capacity for work-hardening, as compared with most steels.

In a series of tests on tool geometry, it was determined that an increase in the side cutting edge angle of a tool increases its life considerably.

## Introduction

Cost reductions in all phases of fuel core production are continually being sought. One area for which considerable savings are anticipated is the final fabricating step: machining. Over the years, many improvements have been made, but due to a lack of background information on uranium machining, these advancements have been time-consuming and costly. For further benefits to be realized in this field, both basic and complex principles of uranium machinability must be found and understood. Therefore, a machining research program was initiated to study the behavior of the material.

## Previous Work on the Project

More than a year ago, necessary equipment for carrying on a machining research program was acquired and set up.<sup>1</sup> This consisted mainly of a test lathe and a tool dynamometer with amplifiers and recorders for measuring tool forces and tool temperature.

Tool life and tool tip temperature tests were run,<sup>2</sup> and the following results were obtained:

1. When beta heat treated uranium was machined with various grades of carbide tools, tools containing large amounts of tantalum carbide (20 per cent) were found to be superior.

2. During operation at normal speeds (300 to 400 fpm) for uranium machining, the tool tip temperature was found to be above the practical operating limit for carbide tool materials.

3. The determining factor for tool life was found to be failure of the tool's side cutting edge which failure was brought about by a severe cratering action to the top of the tool.

Since large additions of tantalum carbide gave longer tool life, a tool was obtained<sup>3</sup> containing a higher percentage of tantalum carbide than did the tool mentioned in (1) above. A 40 per cent tantalum carbide tool was tested and had a tool life not significantly longer than the tool life of 20 per cent tantalum carbide tools.

In an effort to find the cause of tool failure in the machining of beta heat treated uranium, a study of the chip formation and tool forces was made.<sup>3</sup> These tests indicated that the primary cause of tool cratering and subsequent failure is the heat of primary deformation. Two other significant factors were also reported: the high strain hardening capacity of uranium and the low coefficient of friction between the uranium chip and the tool.

## Objectives for This Period

1. Thus far, the results from the machining research program were obtained by the use of uranium workpieces which were rolled and then double beta heat treated. To see what effect metal structure has upon uranium machinability, a test was set up to learn the machining properties of "as-cast" material by comparing the results obtained when the two metal structures were machined.

2. It had previously been determined that uranium exhibits a high capacity for work-hardening.

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One method of giving a numerical value to a metal's ability to work-harden is the Meyer exponent test. Several samples were selected, and their Meyer exponent was determined, for comparison of uranium with other machinable metals.

3. In the machining of beta heat treated uranium, it had been found that the chip thickness affected the type of chips produced. Factors which determine the calculated chip thickness are feed rate and tool side cutting edge angle. Tool life tests at various feed rates had previously been run. The effect of side cutting edge angle on tool life was investigated at this time.

#### Summary of Results Obtained

1. A comparison of the machinability of beta heat treated and "as-cast" uranium shows that there is no significant difference in tool cutting edge temperature and tool forces but that at low speeds tool life with "as-cast" materials was

considerably shorter than that of beta heat treated uranium. The reason for tool life being shorter is not readily explainable except by the fact that wear and abrasion are slightly greater with the as-cast material.

2. The Meyer exponent for uranium was found to vary from 2.31 to 2.77. The range for common steels is 2.1 to 2.4. Thus, uranium has a greater capacity to work-harden during machining than do most steels.

3. The tool's side cutting edge angle was increased from  $0^{\circ}$  to  $75^{\circ}$ , in increments of  $15^{\circ}$ . As the angle increased, tool life increased. At angles above  $60^{\circ}$ , excessively high radial forces occurred and chatter began.

#### Machinability of "As-Cast" Uranium Compared With Machinability of Beta Heat Treated Uranium

In the comparison of "as-cast" uranium with beta heat treated uranium, a metallographic evaluation of each structure was first made. Figure 13.1

187-2

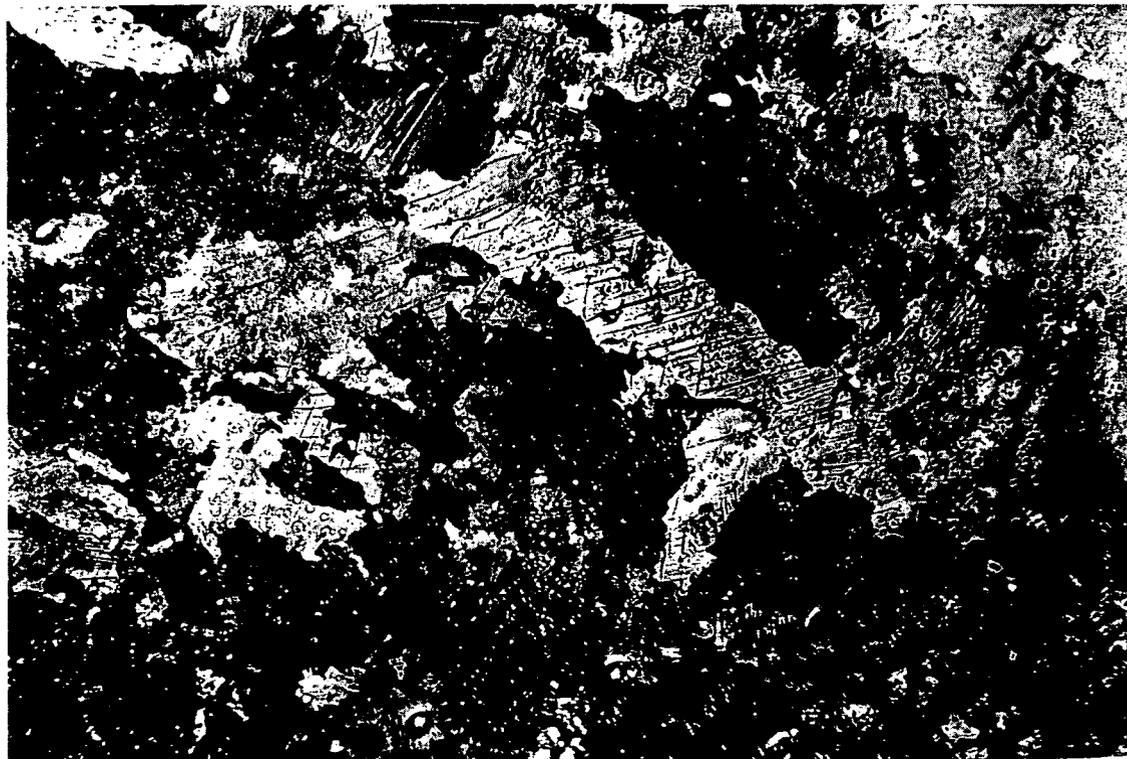


FIGURE 13.1 Sample From Typical Double Beta Heat Treated Uranium Test Billet. Inclusion Concentration: Average; Avg. Grain Size: 0.133 Millimeter; Magnification: 100X.

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shows the grain size and inclusion concentration of the beta structure. The average grain size in the metal shown is 0.133 millimeter. Figure 13.2 shows the grain size and inclusion concentration of the "as-cast" uranium. The "as-cast" grain size ranges from 0.300 to 0.500 millimeter. The only significant differences between the two structures are hardness ("as-cast" being 64.2  $R_A$  and beta being 58  $R_A$ ) and grain size.

Next, the tool life of each material during turning with a single-point tool on a lathe was determined. The cast uranium tool life tests were performed on a 7-inch cast hollow billet; the beta treated uranium used was a 3-inch-OD double beta treated billet. The tool used for each test was a clamped type carbide Kennametal grade E7560 with the following geometry:  $0^\circ$  back and side rake;  $0^\circ$  side cutting edge angle;  $8^\circ$  end cutting edge angle; and  $7^\circ$  side and end relief with  $\frac{1}{32}$  inch nose radius. The depth of cut was 0.050 inch, and

the feed was 0.010 inch per revolution. The coolant used in this test was a 17 to 1 ratio of water to Texaco "C" soluble oil. To get a good comparison of tool life, tests were run at four speeds: 300, 400, 500, and 800 surface feet per minute (S.F.P.M.).

Results showed that tool life was shorter with cast uranium than with beta treated uranium. Table 13.1 is a comparison of the two materials:

TABLE 13.1 Tool Life of As-Cast and Beta Heat Treated Uranium

S.F.P.M.	Tool Life* (min)	
	As-Cast U	Beta Heat Treated U
300	63	215.9
400	27.9	37.5
500	10.3	12.3
800	3.5	3.8

\* Tool life was determined as time to 0.015-inch wear land or fracture of the cutting edge, whichever occurred first.

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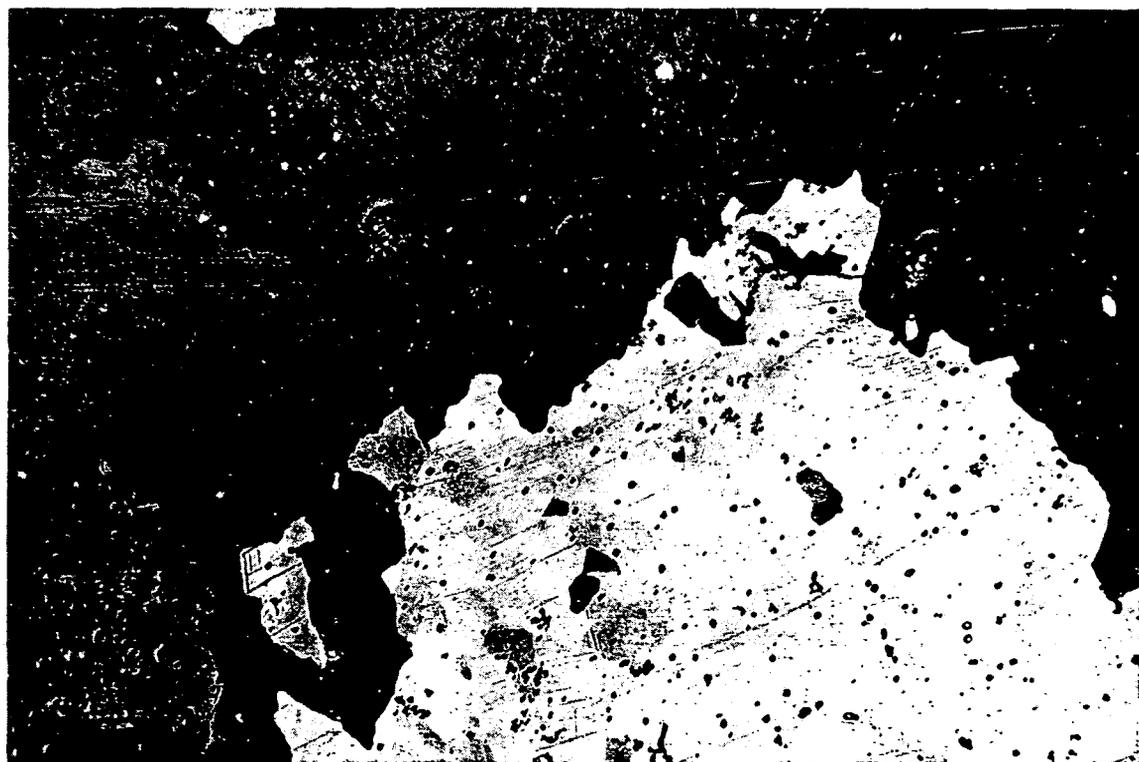


FIGURE 13.2 Sample From Typical As-Cast Uranium Test Billet. Inclusion Concentration: Average; Grain Size: 0.300 to 0.500 Millimeter; Magnification: 100X.

It is apparent in the above comparison that as the speed is increased, the per cent difference in tool life between the materials becomes much less significant. This is due to the high cutting edge temperatures obtained at the greater speeds. At these elevated temperatures (which are above the normal operating range of carbide), the carbide binder breaks down and the tool fails rapidly. Thus, at higher speeds, the abrasiveness of the work material appears to have little effect on tool life, with temperature being the predominant factor.

Cutting edge temperature tests of both uranium structures were performed. The results (Table 13.2) show no appreciable difference between cast uranium and beta treated uranium.

TABLE 13.2 Cutting Edge Temperature

S.F.P.M.	As-Cast U (°F)	Beta Heat Treated U (°F)
300	1185	1210
400	1200	1240
500	1280	1280

Tool force measurements were taken on beta heat treated and "as-cast" uranium, using K4H carbide as the cutting tool. A feed of 0.010 inch per revolution and speeds of 300 and 500 S.F.P.M. were used in these tests. The results are shown in Table 13.3.

The results show no difference in cutting forces between the two materials. Two speeds were used in order to double-check the results obtained. This is valid because speed has no effect on the forces.

TABLE 13.3 Cutting Force and Thrust Force During Machining

Speed (S.F.P.M.)	As-Cast U		Beta Heat Treated U	
	F <sub>C</sub> (lb)	F <sub>T</sub> (lb)	F <sub>C</sub> (lb)	F <sub>T</sub> (lb)
300	317	120	320	120
500	317	120	317	120

F<sub>C</sub> = cutting force

F<sub>T</sub> = thrust force

Meyer Exponent

To provide a better insight into the machinability of uranium, the Meyer exponent (capacity to work-harden) was found. The test was performed on a Brinell hardness-testing machine, using a 10 millimeter ball indenter under loads of 1000, 2000, and 3000 kilograms. After the impression was made, its diameter was measured.

The capacity for work-hardening is found by using the equation  $L = aD^n$  where  $n$  is the Meyer exponent,  $L$  is the load in kilograms,  $D$  is the diameter of the impression in millimeters, and  $a$  is a constant whose value depends on the material being tested. When the exponent,  $n$ , is 2, the metal has no capacity for work-hardening. For common steel, the value of  $n$  varies between 2.1 and 2.4. The Meyer exponent for three different structures of uranium are listed in Table 13.4.

TABLE 13.4 Work Hardening Capacity for Various Uranium Structures

Uranium Sample	Meyer Exponent	Brinell Hardness (3000-kg Load)
Alpha Rolled	2.59	207
Beta Heat Treated*	2.31	197
Annealed** (after beta heat treatment)	2.77	192

\* Sample from 3-inch-OD double beta treated billet.

\*\* The annealed sample was heated to 1175°F and allowed to cool in the furnace.

Most of the uranium processed at this site is in the alpha rolled or beta heat treated condition. In this state, uranium's work-harden-ability is in the high range for a machinable metal. Since work-hardening generally reduces tool life in the machining of a metal, the high capacity of uranium for work-hardening is one of the reasons for the relatively short tool life obtained.

The Effect of Tool Side Cutting Edge Angle

The side cutting edge angle (S.C.E.A.) affects the machining operation as follows: A tool with a

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0° S.C.E.A. has a contact length along the side cutting edge equal to the depth of cut (here, 0.050-inch with a calculated chip thickness of 0.010 inch). As the S.C.E.A. is increased, this contact length also increases. At 75° the contact length becomes about 0.120 inch, and the calculated chip thickness becomes approximately 0.004 inch.

In these tests, samples from 3-inch-OD double beta treated billets were used. The S.C.E.A. was varied from 0° (the standard angle in all previous tests) to 75°. Table 13.5 shows the effect of S.C.E.A. on the tool life obtained.

TABLE 13.5 Effect of Side Cutting Edge Angle Upon Tool Life\*

S.C.E.A.	Tool Life (min)
0°	9.3
15°	8.6
30°	12.1
45°	14.9
60°	18.8
75°	45.8

\*These tests were run at a speed of 500 surface feet per minute and a feed of 0.010 inch per revolution.

These results show that increasing the S.C.E.A. to 75° results in a marked increase in tool life. This is explained by the fact that increasing the S.C.E.A. decreases the effect of the feed while

distributing the load over a greater portion of the cutting edge. As the S.C.E.A. is increased, however, the radial force increases to a point where it becomes a major concern. (Radial force is the force which tends to push the tool away from the workpiece in a direction normal to the axis of the workpiece.) As a result of this excessively high force, a rigid tool-workpiece combination must be maintained or chatter will result.

#### Future Work

Tool geometry and its effect on tool life, cutting forces, and cutting edge temperature will be further investigated.

A series of tests will also be performed in which the effect of several different types of coolant on the machining of uranium will be compared. Related tests will be performed to find the best means of coolant application.

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- <sup>1</sup>R. J. Titmuss and J. F. MacNeill. "Machining Research," Summary Tech. Rpt., USAEC Report NLCO-750, pp. 111-116. July 18, 1958 (Classified).
- <sup>2</sup>R. J. Titmuss and J. F. MacNeill. "Machining Research," Summary Tech. Rpt., USAEC Report NLCO-775, pp. 99-103. January 22, 1959 (Classified).
- <sup>3</sup>R. J. Titmuss, J. F. MacNeill, and W. E. Stephens. "Machining Research," Summary Tech. Rpt., USAEC Report NLCO-785, pp. 101-112. April 15, 1959 (Classified).

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## 14. THE RELATION BETWEEN SURFACE QUALITY, STRINGER CONCENTRATION, AND TYPE OF INCLUSIONS IN PRODUCTION SLUGS

C. V. Lovoy

### Abstract

The surface defects on unclad uranium fuel cores are shown to be related to the subsurface defects (stringers)\*. This relationship provides a useful tool for evaluating production "metal quality" with a reasonable number of samples. Density was found to be related to stringer concentration, and stringer concentration was found to be related to the oxygen content of the metal.

### Introduction

The acceptance of slugs produced by the National Lead Company of Ohio is governed by surface quality. The slugs produced show varying amounts of striations and narrow seams on their surfaces. Several per cent of the slugs are rejected by the Inspection Group because of surface metal quality defects. These can be categorized as follows:

1. *Striations* – Short (less than ¼-inch) hair-like discontinuities, to which no width can be assigned with the naked eye.
2. *Narrow Seams* – Essentially long striations that have a definite but very slight width.
3. *Wide Seams\*\** – Those defects, regardless of length, having both appreciable width and depth.

### Objective

The objective is to determine the causes and chemical composition of striations and narrow seams. It was assumed that striations and narrow seams are equivalent to internal defects known as stringers – that is, that striations and narrow seams are differentiated from stringers only by the former

\* *Stringers*<sup>1</sup> are elongated internal defects formed, during rolling, from inclusions trapped in the cast metal.

\*\* *Wide seams*, 2 inches or longer, were not considered in this study. This type of defect is not believed to be a metal quality defect, but the result of fabrication.

appearing on the slug surface. If that assumption is correct, a precise method of determining metal quality on the basis of either density or the concentration of trace elements might be developed.

It was thus an objective of this study to make a comprehensive analysis of the inclusion species (stringers) contained within the matrix of reactor grade uranium fuel elements. Any relationship of impurities to the surface quality of finished slugs was to be determined.

### Summary of Results

Study of the slugs indicated that:

1. Internal stringers appear on slug surfaces as striations and narrow seams.
2. Stringers are primarily oxides.
3. Density, as expected, was strongly related to the concentration of stringers.
4. Silicides and nitrides are contained in some stringers.

### Uniformity of Stringer Distribution; Relation of Stringer Rating to Surface Quality

In this study:

1. Samples having a wide range of metal quality were used.
2. Samples were carefully selected (i.e., in regard to location in slug, etc.).
3. Straight line regression analyses were made when trends were apparent in accumulated data.

It was of paramount importance to select equivalent defects, externally and internally.

First, uniformity of stringer distribution was studied. Stringer rating was based on the visual stringers on a central plane along the longitudinal axis of a split slug. A macro-stringer rating method which rated the outer ¼ inch of a central plane of slug half-sections showed a good correlation with

slug-to-good-slug yield. Therefore, there should be a relationship between the "outer 1/4 inch" stringers of any central longitudinal interface and the surface metal quality for a slug section. The correlation also indicated that the circumferential surface condition of a slug section is represented internally to a depth of 1/4 inch. Therefore, stringer rating was next compared with surface metal quality.

Fifty-eight 2-inch-long slug sections were split through the central axis. One of the half-sections from each slug was pickled in nitric acid for 30 seconds to reveal the surface defects (Fig.

14.1, B and D). All surface defects (1/16 inch to 2 inches long) on the circumferential surface were measured visually. The sum of all lengths for each slug half-section investigated was divided by the area examined. This gave the average surface defects lineally, in inches per square inch of surface investigated.

The central plane of each half-slug section was etched and "macro-stringer rated"<sup>2</sup> (Fig. 14.1, A and C), and these values were plotted against the corresponding average surface defect sum (Fig. 14.2). A trend was noted, and simple straight line regression analysis\* gave a correlation coefficient of 0.704.

The work can be summarized as follows:

1. A uniform distribution of stringers about the outer 1/4 inch "shell" is indicated for each slug half-section investigated.
2. Surface defects (striations and narrow seams) are associated with internal defects (stringers).

#### Stringer Concentration

Portions of 20 established standards<sup>4</sup> (Fig. 14.3) were utilized in developing a stringer rating method based on visual comparison of stringer concentration. A relative value (different for each standard) was obtained for the nonmetallic (stringer) substance removed from the central plane matrix of a uranium slug by etching treatment. From an area heavily contaminated with stringers, a large volume of nonmetallic substance was removed, as opposed to a lesser volume of nonmetallic substance removed from an area (of identical dimensions) that

\* Simple straight line regression analysis fits a straight line to a series of points. The correlation coefficient ( $r$ ) is a measure of the linear relationship between any two variables, and  $r$  must lie between +1.00 and -1.00. A +1.00 correlation coefficient indicates a perfect direct linear relationship, while -1.00 would indicate a perfect inverse linear relationship. A coefficient of 0.00 indicates a complete absence of linear relationship. The square of the correlation coefficient ( $r^2$ ) gives the percentage of total variation explained (fitted) or removed by the regression line.<sup>3</sup>

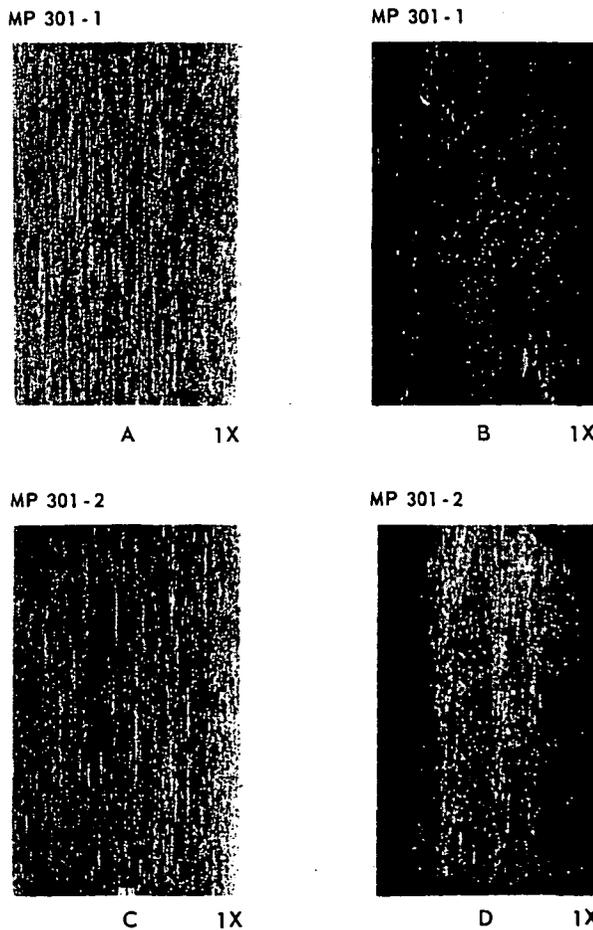


FIGURE 14.1 Two-Inch-Long Half-Sections of Slugs. A and C: The Etched Surface of the Central Plane, Revealing Internal Stringers. B and D: The Corresponding Surface Defects (Striations and Narrow Seams) on the Circumferential Surface.

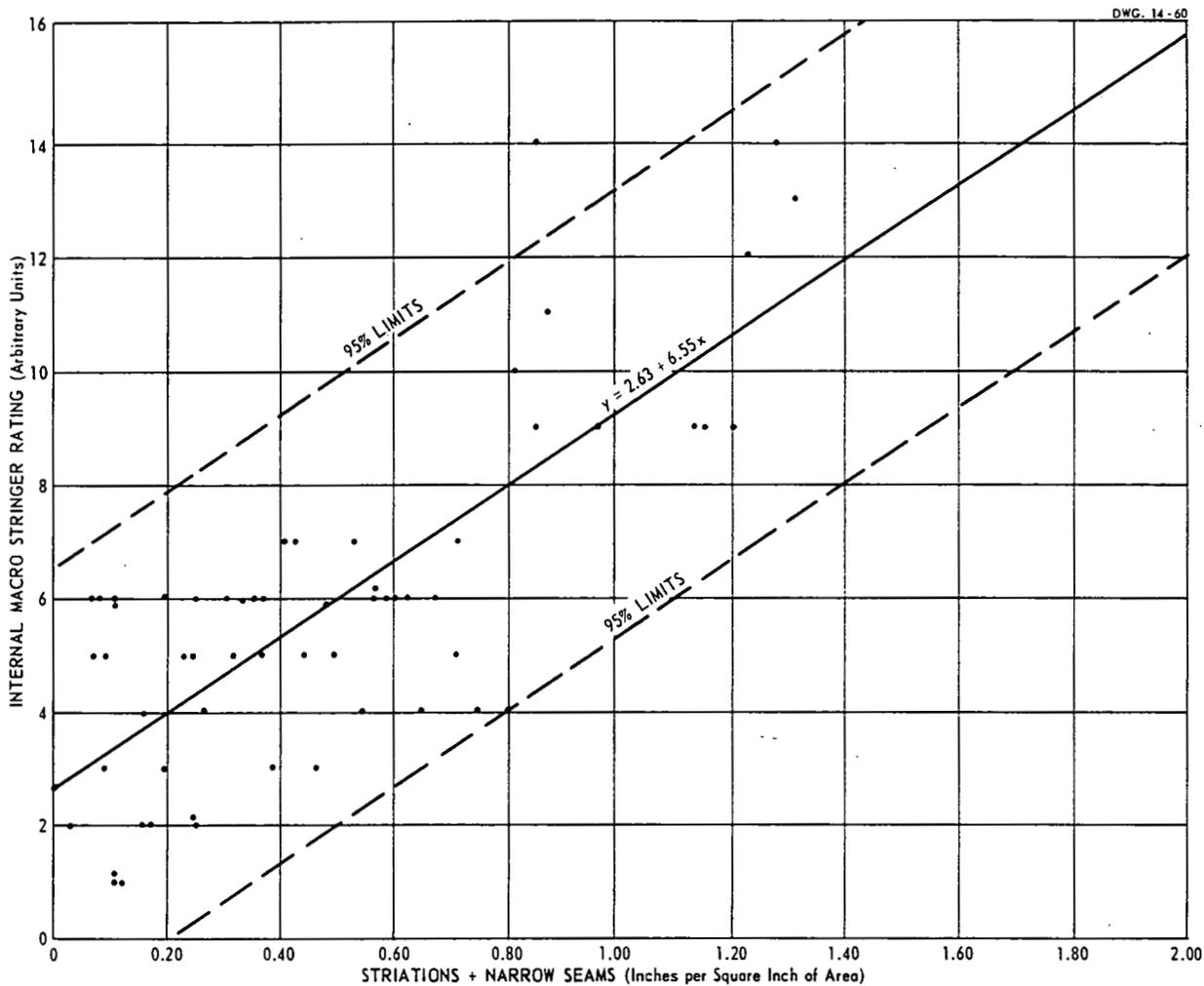


FIGURE 14.2 Internal Macro Stringer Rating vs Measurement of External Narrow Seams and Striations

was not heavily contaminated. These values were considered surface area-volume ratios, since stringers tend to be uniformly distributed about the outer  $\frac{1}{4}$  inch "shell" of a 2-inch half-section.

Ultimately, 9 stringer concentration standards were selected from the 20 stringer rating standards. They were numbered from 1 to 9, increasing in stringer content in order of the stringer rating standard numbers (Fig. 14.4). As in the set of 20 stringer rating standards, the set of 9 stringer concentration standards considered only the outer  $\frac{1}{4}$  inch periphery.

The slugs investigated in this study had an OD of 1 inch. The outer  $\frac{1}{4}$  inch was rated, and then the inner  $\frac{1}{4}$  inch (i.e., the area between the slug axis and the outer  $\frac{1}{4}$  inch). The latter was done because subsequent studies with density and center chemistry required knowledge of center stringer concentration.

#### Metal Sampling

The metal sampling plan (Fig. 14.5) was organized so as to obtain the best possible correlation between metal quality (as evaluated by the stringer

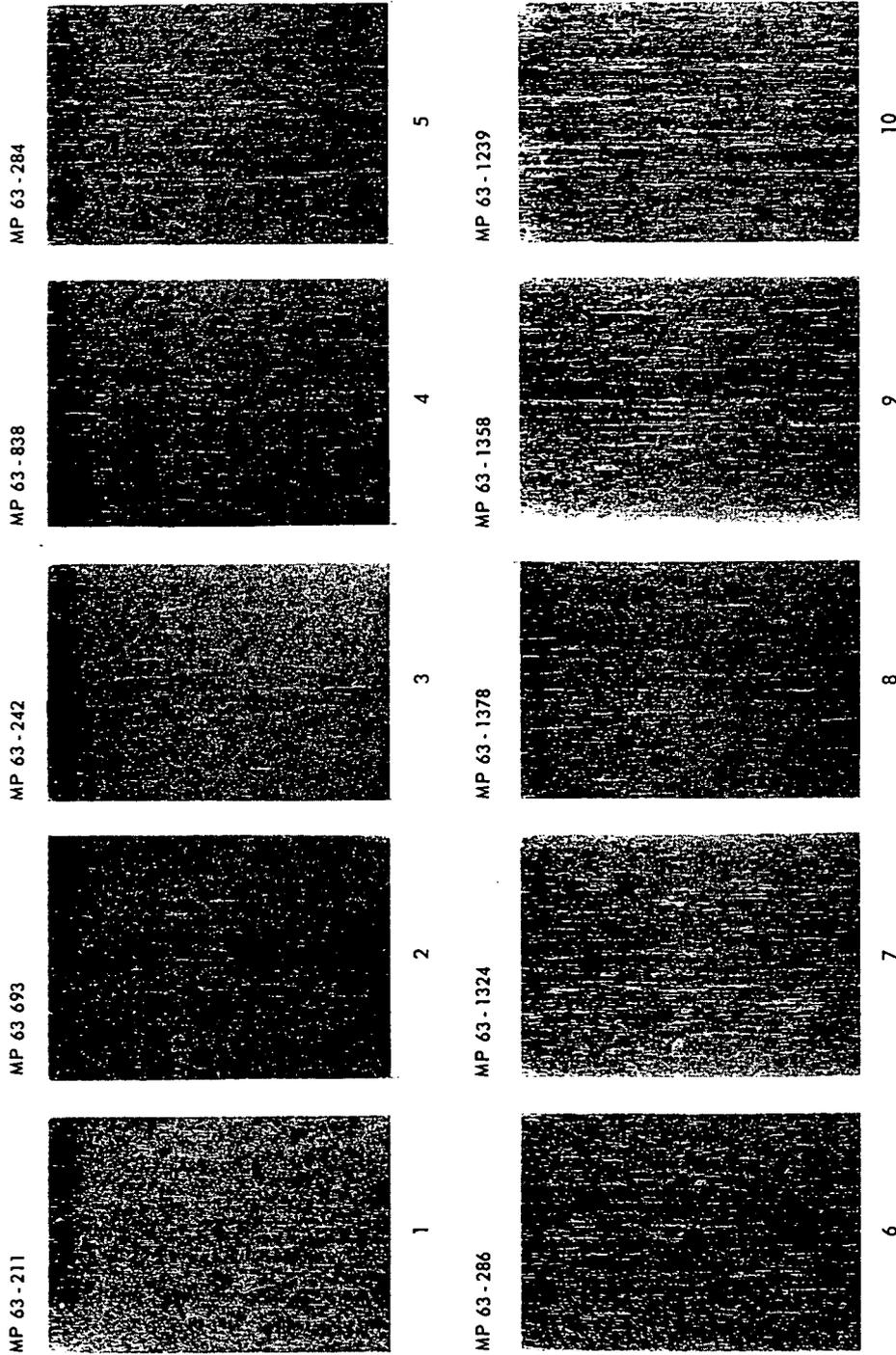
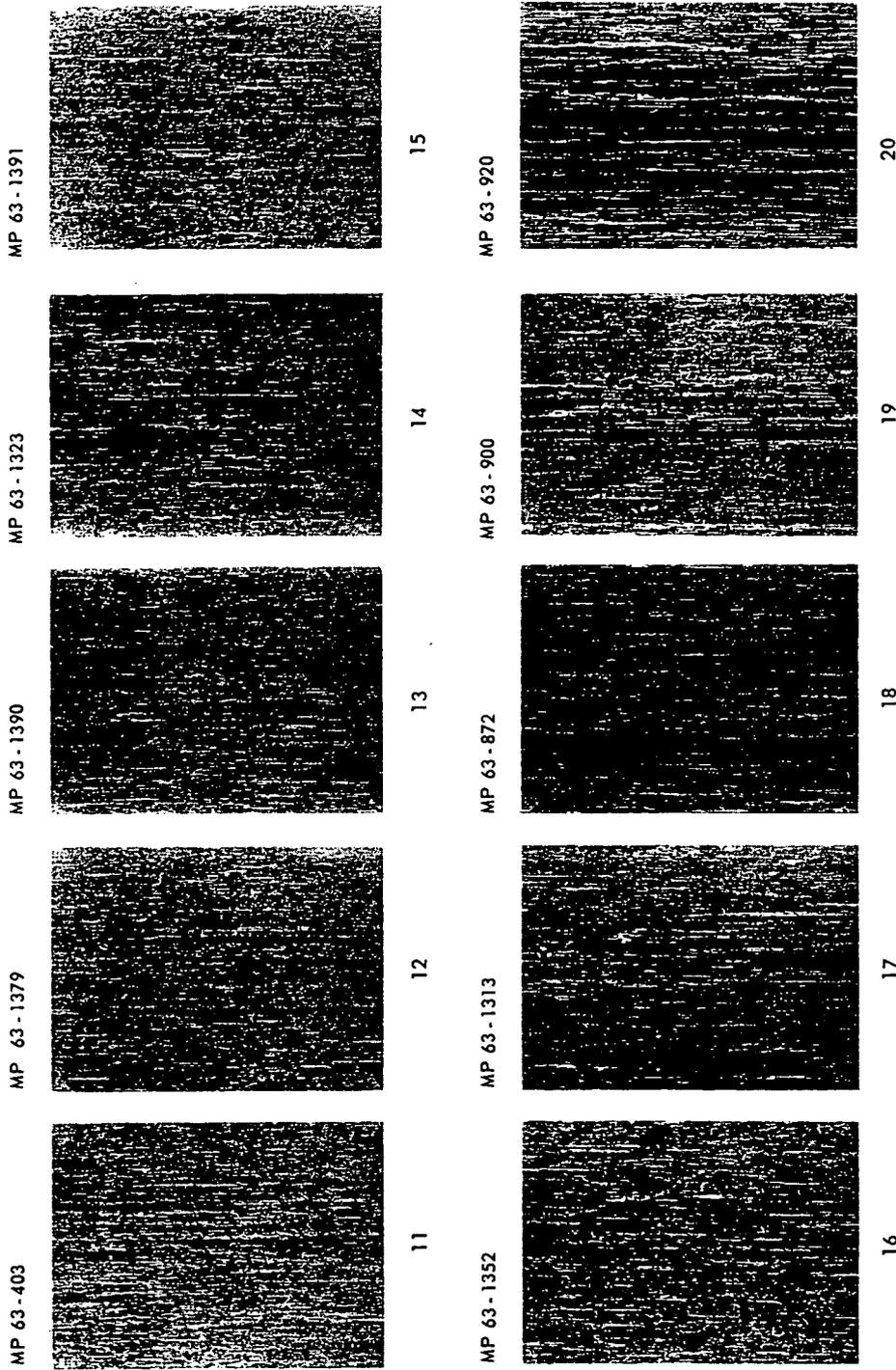


FIGURE 14.3-A Stringer Rating Standards (IX)

NOTE: These photographs show the central plane of split slug sections. The short dimension in each photograph is the diameter of the slug section. Thus, the longitudinal axis of each slug section is at the center line of the long dimension.



**FIGURE 14.3-B** Stringer Rating Standards (1X)

**NOTE:** These photographs show the central plane of split slug sections. The short dimension in each photograph is the diameter of the slug section. Thus, the longitudinal axis of each slug section is at the center line of the long dimension.

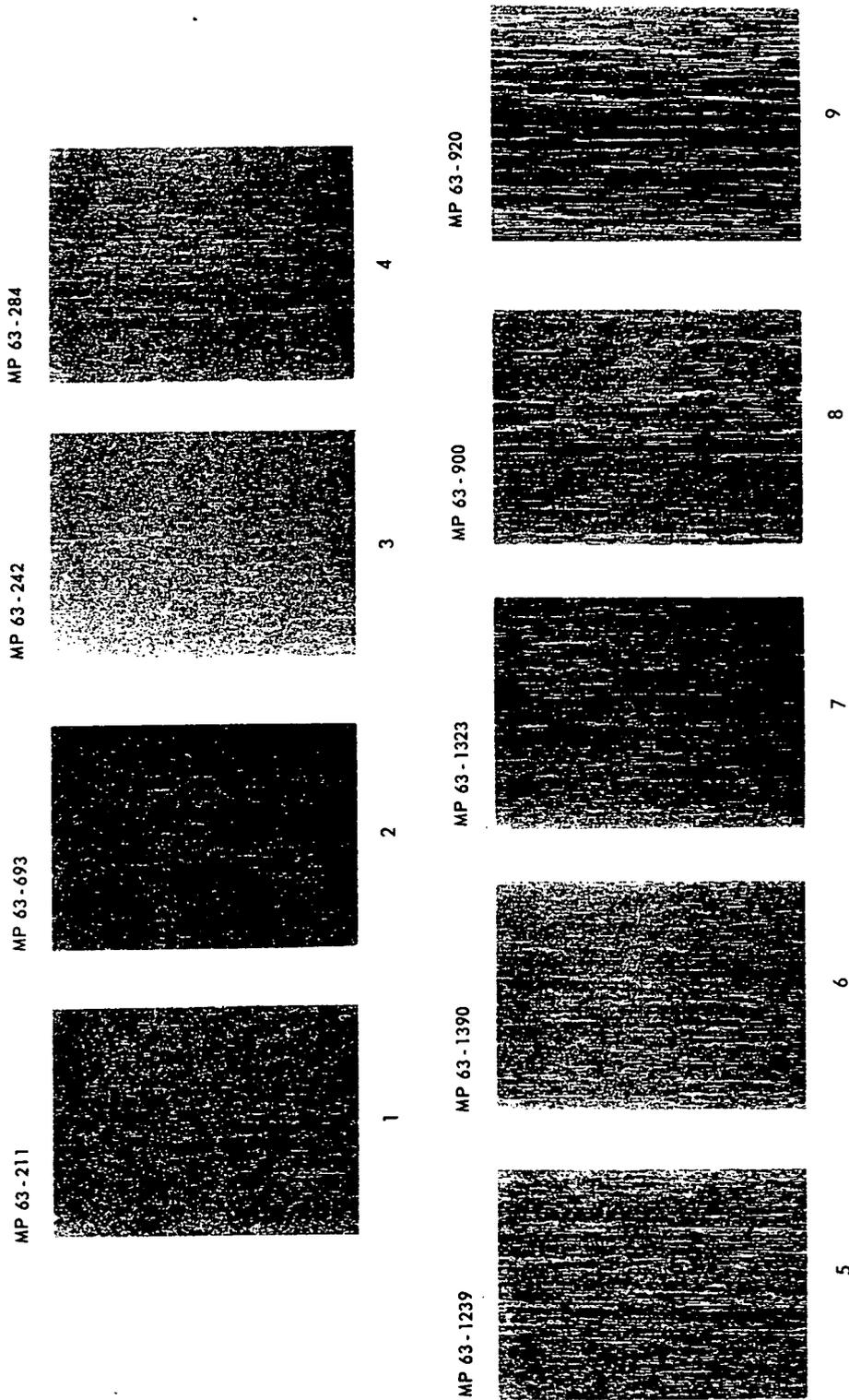


FIGURE 14.4 Stringer Concentration Standards (IX)

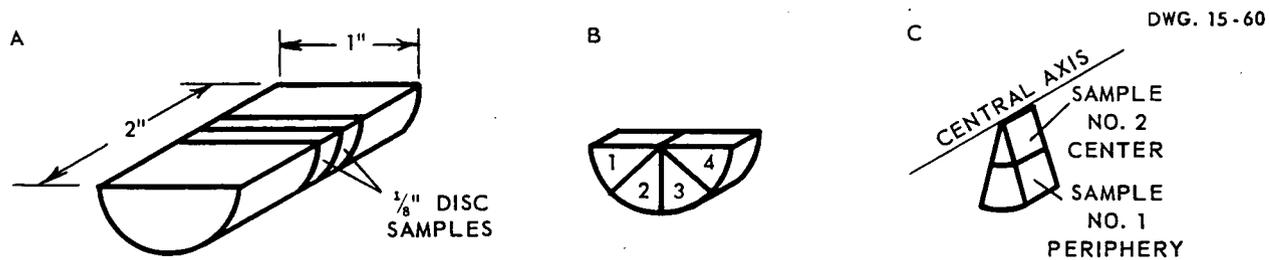


FIGURE 14.5 A. Disc Samples From Slug Half-Section. B. Dividing Disc Into Four Equal Sectors. C. The Two Samples From Each Sector.

rating technique) and chemical composition and density. Two transverse sections approximately  $\frac{1}{8}$  inch thick were cut from each of 40 split sections of typical production slugs (Fig. 14.5-A). One of the two discs was submitted for density determination, and the other was further cut for chemical analysis. The latter disc was split into four equal pie-shaped sections (Fig. 14.5-B). Each section was then cut by bisecting the bounding radius (Fig. 14.5-C). The eight samples, four from the outer  $\frac{1}{4}$  inch and four from the center of the slug, were submitted for chemical analysis.

Figures 14.6, 14.7, and 14.8 show the type of data accumulated for the various samples. Note particularly the direct relationship between stringer content and oxygen content and the inverse relationship between stringer content and density. The number of samples required in this type of evaluation was discussed in the previous quarterly report.<sup>2</sup>

#### Density Versus Stringer Concentration

The stringer concentration (the average for center and outer segments) was plotted against the corresponding density (Fig. 14.9). Simple straight line regression analysis gave a correlation coefficient ( $r$ ) of 0.775 and a square of the correlation ( $r^2$ ) of 0.600. Thus, 60 per cent of the total density variation can be explained by the associated stringer content which diluted the uranium matrix.

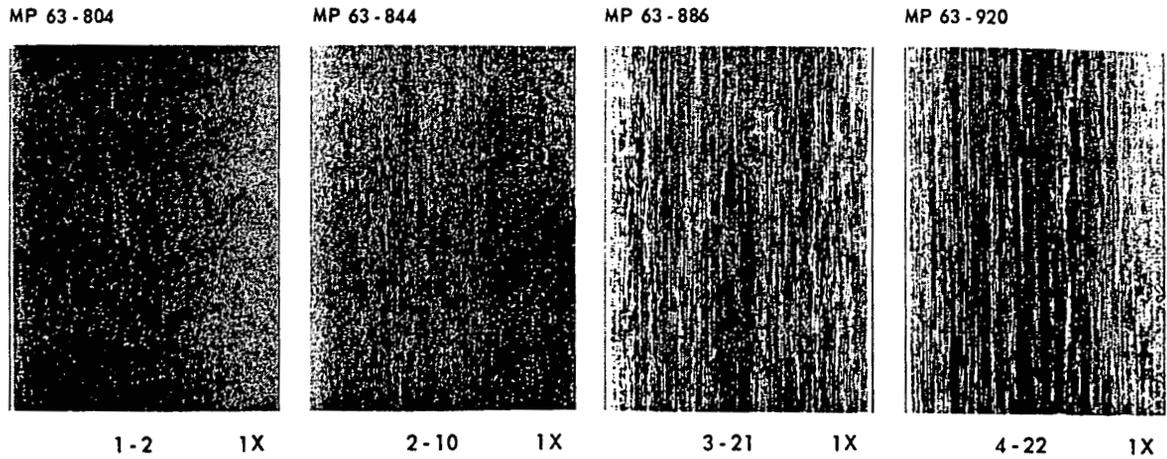
#### Stringer Concentration Versus Chemistry

Magnesium, nitrogen, carbon, iron, silicon, nickel, chromium, and oxygen exhibit noticeable quantitative fluctuations from sample to sample. Carbon showed the greatest variation from ingot to ingot and sometimes within an ingot. Each trace element was plotted against the corresponding stringer concentration. These plots (Fig. 14.10 to 14.13) show the relationships of stringer concentration with four trace elements: silicon, nitrogen, magnesium (slightly), and oxygen (strongly).

Table 14.1 gives (1) the ranges of the determinations and (2) the correlation coefficients. The oxygen content is related to the stringer concentration, with 68.6 per cent of the variation in stringer

TABLE 14.1 Relationship of Stringer Concentration to Chemical Composition

Range of Stringer Concentration (S.C.)	1 to 9	
Range of Oxygen	12 ppm to 252 ppm	
Range of Silicon	<10 ppm to 48 ppm	
Range of Nitrogen	21 ppm to 148 ppm	
Range of Magnesium	<4 ppm to >100 ppm	
Variables	Correlation Coefficient	
	$r$	$r^2$
S.C. - Oxygen	0.828	0.686
S.C. - Silicon	0.545	0.297
S.C. - Nitrogen	0.444	0.197
S.C. - Magnesium	0.412	0.170



**FIGURE 14.6** Correlation Between Chemistry and Stringer Concentrations. Ingot No. 68284. The first number under each photomicrograph corresponds to the rod position in the ingot and the second number to the slug position in that rod. The first value under chemical results is for the peripheral (outer) sample and the second is for the adjacent center sample.

Analyses and Physical Properties	Chemical Results (ppm)			
	1 - 2	2 - 10	3 - 21	4 - 22
Rod and Slug Position	1 - 2	2 - 10	3 - 21	4 - 22
Oxygen	37 - 36	59 - 45	137 - 82	95 - 96
Nitrogen	50 - 54	70 - 68	88 - 70	148 - 61
Carbon	466 - 360	505 - 487	567 - 561	546 - 494
Iron	72 - 74	100 - 104	85 - 72	135 - 71
Magnesium	5 - 4	8 - 5	16 - 10	60 - 12
Silicon	15 - 25	11 - 17	34 - 27	48 - 33
Chromium	14 - 13	16 - 20	18 - 17	25 - 13
Nickel	28 - 32	30 - 34	30 - 28	33 - 32
Density	18.94 g/cc	18.92 g/cc	18.83 g/cc	18.84 g/cc
Peripheral Stringer Concentration	1	4	9	9
Center Stringer Concentration	1	4	8	9
Average Stringer Concentration	1	4	8.5	9

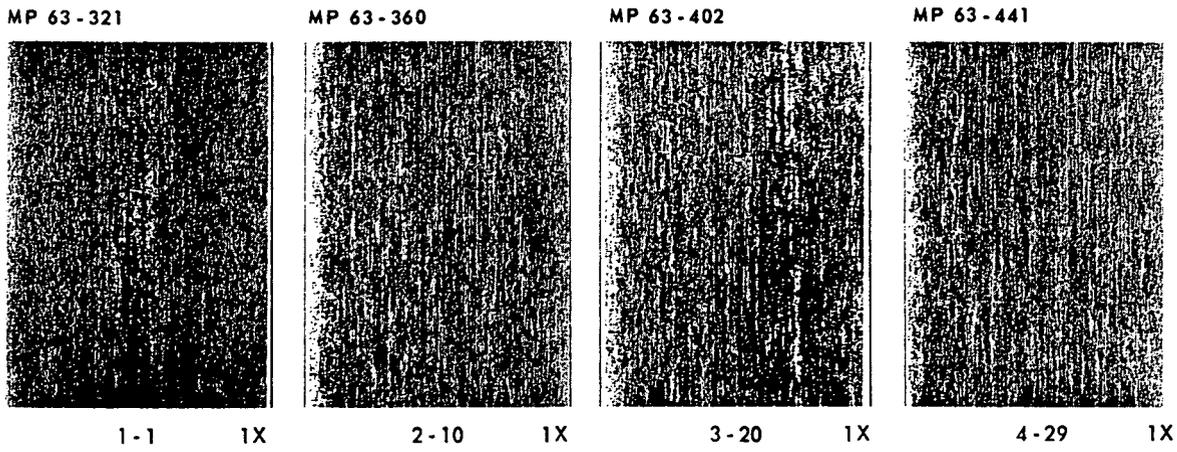
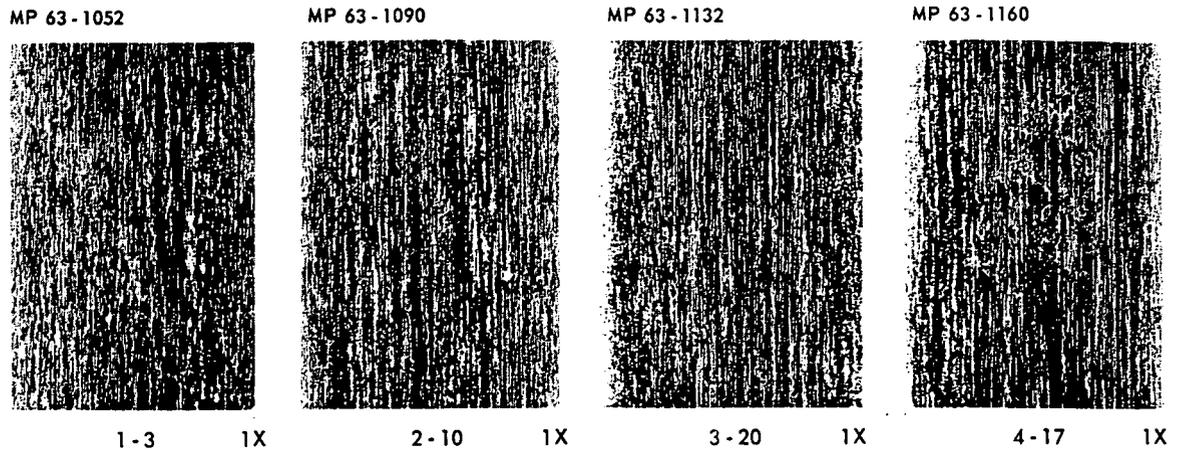


FIGURE 14.7 Correlation Between Chemistry and Stringer Concentrations. Ingot No. 66646. The first number under each photomicrograph corresponds to the rod position in the ingot and the second number to the slug position in that rod. The first value under chemical results is for the peripheral (outer) sample and the second is for the adjacent center sample.

Analyses and Physical Properties	Chemical Results (ppm)			
	1- 1	2- 10	3- 20	4- 29
Rod and Slug Position	1- 1	2- 10	3- 20	4- 29
Oxygen	45- 46	65- 84	81- 72	86- 84
Nitrogen	61- 56	73- 75	74- 81	67- 63
Carbon	465-541	622-580	601-591	586-605
Iron	61- 81	74- 92	74- 85	72- 86
Magnesium	4- 4	6- 4	6- 5	5- <4
Silicon	10- 12	10- 19	10- 13	10- 18
Chromium	12- 15	17- 20	15- 14	15- 18
Nickel	37- 33	42- 35	36- 34	35- 47
Density	18.93 g/cc	18.87 g/cc	18.85 g/cc	18.86 g/cc
Peripheral Stringer Concentration	4	7	7	7
Center Stringer Concentration	4	7	7	7
Average Stringer Concentration	4	7	7	7

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**FIGURE 14.8** Correlation Between Chemistry and Stringer Concentrations. Ingot No. 69277. The first number under each photomicrograph corresponds to the rod position in the ingot and the second number to the slug position in that rod. The first value under chemical results is for the peripheral (outer) sample and the second is for the adjacent center sample.

Analyses and Physical Properties	Chemical Results (ppm)			
	1- 3	2- 10	3- 20	4- 17
Rod and Slug Position	1- 3	2- 10	3- 20	4- 17
Oxygen	159-189	159-159	151-130	141- 91
Nitrogen	99- 92	47-120	85- 77	75- 72
Carbon	363-362	333-370	349-368	305-278
Iron	71- 87	90-102	78- 94	72- 63
Magnesium	18- 39	>100- 20	10- 7	33- 38
Silicon	27- 35	38- 35	20- 23	22- 28
Chromium	14- 13	19- 12	11- 12	12- 13
Nickel	36- 29	21- 24	31- 31	35- 45
Density	18.85 g/cc	18.78 g/cc	18.86 g/cc	18.91 g/cc
Peripheral Stringer Concentration	9	9	9	9
Center Stringer Concentration	9	9	9	9
Average Stringer Concentration	9	9	9	9

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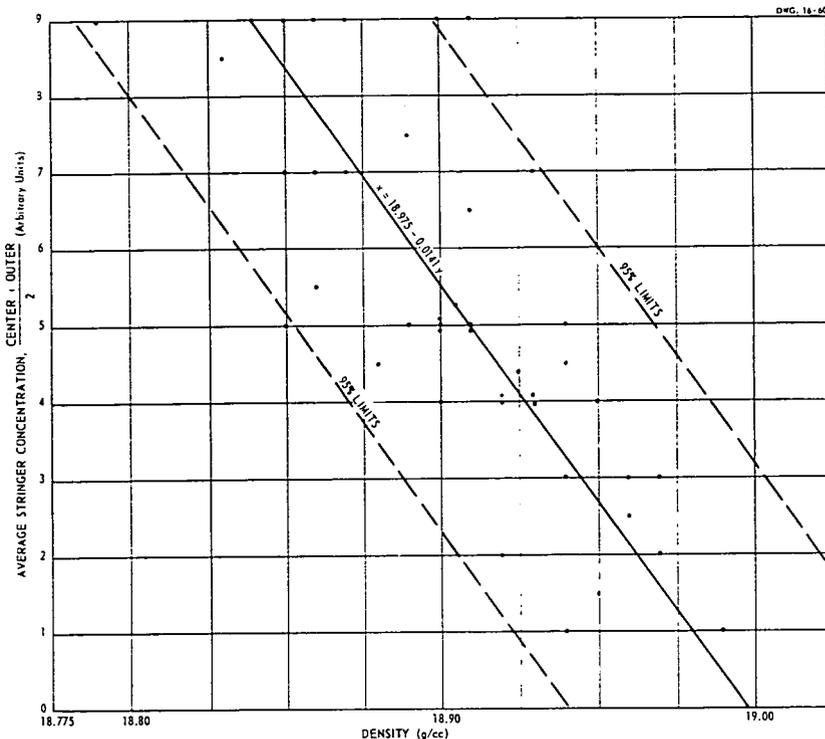


FIGURE 14.9 Stringer Concentration vs Density

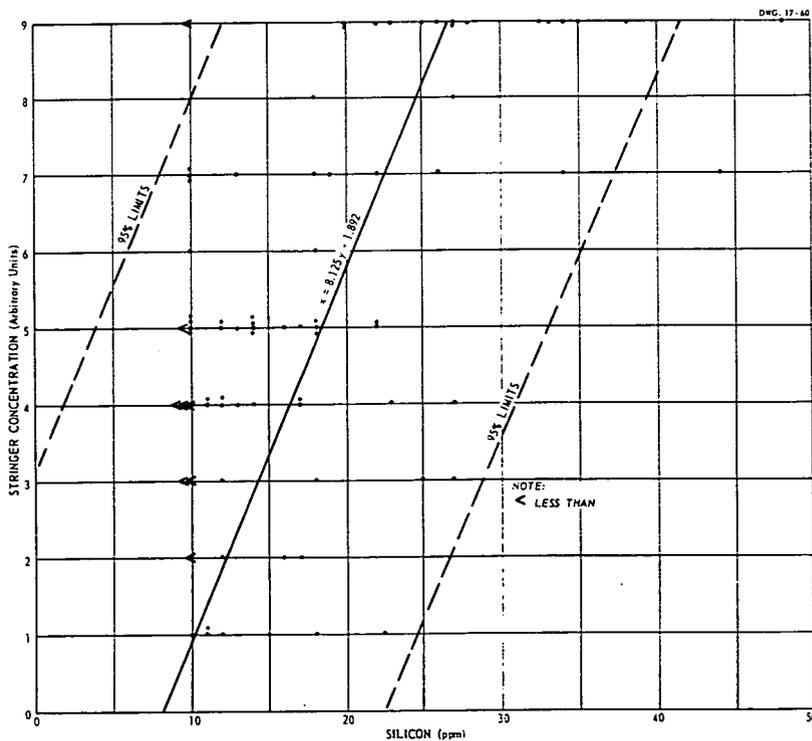


FIGURE 14.10 Stringer Concentration vs Silicon

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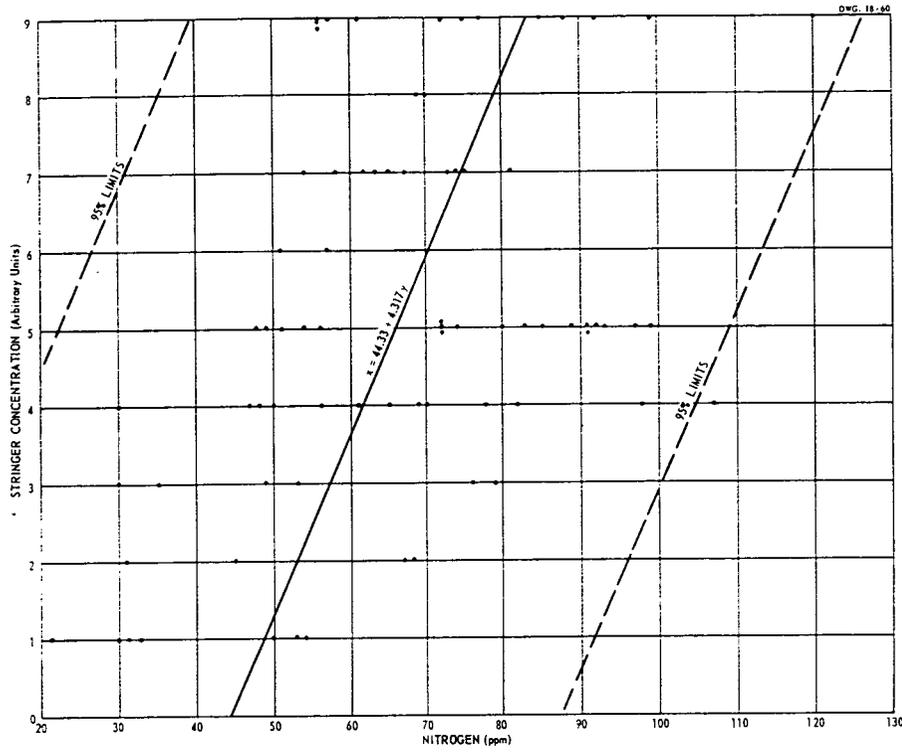


FIGURE 14.11 Stringer Concentration vs Nitrogen

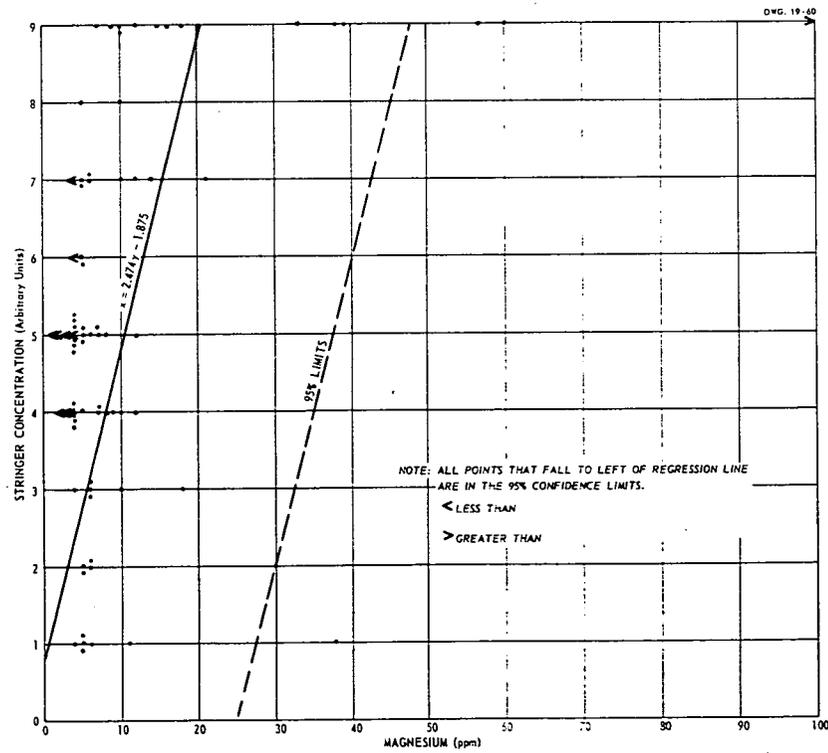


FIGURE 14.12 Stringer Concentration vs Magnesium

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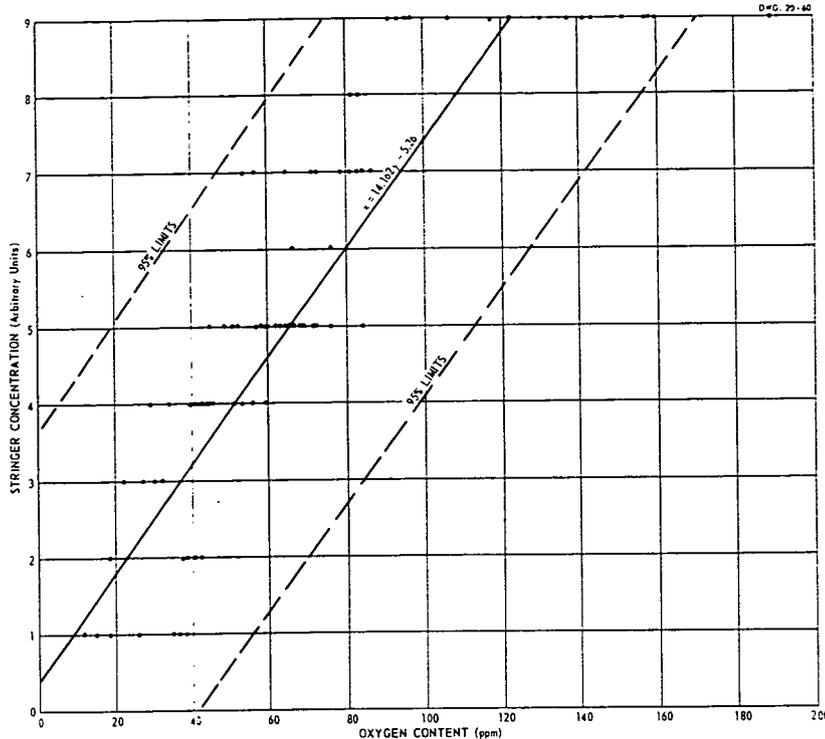


FIGURE 14.13 Stringer Concentration vs Oxygen

concentration attributed to the associated oxygen. The uranium silicon compound has been identified (on a longitudinal slug section)<sup>5</sup> as segregated stringers. The relationship derived from this study between silicon and stringer concentration gave an  $r$  of 0.545, or 27.7 per cent of the variation in stringer concentration being explainable by the associated silicon. Magnesium concentration and nitrogen concentration seem to have only a slight relation to stringer concentration.

Work to date indicates that magnesium may be associated with fluorine in the stringers, which would indicate that a slag ( $MgF_2$ ) type of stringer exists.

#### Acknowledgments

The author acknowledges the assistance and suggestions of A. Klee, W. N. Wise, and M. H.

Cornett. He also thanks M. H. Cornett, C. Carpenter, and R. J. Bieker for sample preparation and F. Hoffman, R. Verkamp, and C. Papet for photographic prints.

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<sup>1</sup>E. I. duPont de Nemours and Company. Report of the Working Committee of the Fuel Element Development Committee, USAEC Report DPST-59-142, Appendix A. January, 1959 (Classified).

<sup>2</sup>C. V. Lovoy. "The Correlation of Macro Stringers with Slug-to-Good-Slug Yield", Summary Tech. Rpt., USAEC Report NLCO-795, pp. 75-89. October 20, 1959 (Classified).

<sup>3</sup>P. G. Hoel. Introduction to Mathematical Statistics, 2nd ed., pp. 117-129, 229-233. New York: Wiley, 1954.

<sup>4</sup>E. I. duPont, op. cit.

<sup>5</sup>M. R. Tupper and J. W. Riches. Irradiation of Extruded Uranium-1.5 Atomic Per Cent Silicon Alloy, Final Report, PT-105-586-A, USAEC Report HW-43599, p. 7. June 12, 1956 (Classified).

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## 15. DESIGN, INSTALLATION, AND USE OF A HOT STAGE METALLOGRAPHIC UNIT

W. N. Wise

**Abstract**

A hot stage metallographic unit has been installed, and tests have been run to determine the best heating cycle. Samples of production uranium metal were photographed in the alpha, beta, and gamma phase ranges of temperature.

**Introduction**

Since the beta phase of uranium metal cannot be retained at room temperature, a program was initiated to design and install a hot stage metallographic unit for the observation of uranium at elevated temperatures. A series of samples could then be examined in this unit at temperatures in both the beta and gamma regions to observe any changes in the grain structure of the material.

**Objectives**

Work was initiated to design and install a hot stage metallographic unit and to study the effects of elevated temperatures on grain structure of uranium metal.

**Summary of Results**

The progress to date has been completed in two phases.

1. In the first phase, a Unitron hot stage unit, a Bausch and Lomb metallograph, and a vacuum system were assembled to constitute a hot stage metallographic unit. The system was tested and found to be satisfactory.

2. In the second phase, polished samples were photographed at 200°C, 500°C, 700°C, and 800°C. At temperatures near the alpha to beta transformation, the samples became heavily oxidized despite a vacuum of  $2 \times 10^{-4}$  mm of mercury in the hot stage.

**Design, Installation, and Testing of a Hot Stage Metallographic Unit**

It was the purpose of the first phase of the work to install a hot stage metallographic unit suitable for the study of uranium metal at temperatures above the beta to gamma transformation point. The work was completed in the following steps:

1. A commercial hot stage unit capable of providing the desired temperature range was obtained.

2. This unit was adapted for use on a Bausch and Lomb MILS metallograph.

3. A vacuum system was obtained that was capable of maintaining a vacuum ( $10^{-4}$  mm mercury) that would allow negligible oxidation of uranium at the desired temperatures.

An investigation was made of the available commercial hot stage units. The one that apparently fit our needs and was selected was the Unitron vacuum heating stage Model HHS-2 for inverted microscopes. This unit is made of stainless steel and consists of an upper portion and a lower portion, which are bolted together and sealed with a rubber gasket. Circulating water in both parts of the stage protects the gaskets and stage from overheating.

Unscrewing a pressure cap at the top of the heating stage allows the specimen to be lowered into the interior of a tungsten electric furnace. The temperature of the furnace is changed by altering the supply voltage by means of a variable transformer. The specimen is in contact with a thermocouple, and the specimen's temperature is read from a potentiometer.

The specimen is observed through a quartz window in the bottom of the stage. Between the specimen and the window is a transparent quartz shield with an aperture. The shield can be moved, by means of an external lever, to allow a clear viewing surface to be obtained if the portion of the

window being used should become clouded as a result of vaporization of the specimen.

A connection is provided that allows introduction of argon or other inert gases in order to decrease the rate of sublimation of specimens having a high vapor pressure at elevated temperatures. If sudden cooling is necessary, the argon can also serve as a quenching medium. Gases which will selectively attack the microstructure of the specimen may also be introduced, and the resulting effects may be studied at various temperatures.

The specifications of the unit are:

- Maximum Temperature 1100°C
- Maximum Electric Power 400 w (80 v, 5 amp)
- Vacuum Required 10<sup>-4</sup> to 10<sup>-5</sup> mm mercury

A Bausch and Lomb metallograph, Model MILS, was adapted for use with this heating stage. Illumination was supplied by a Bausch and Lomb ribbon filament.

The furnace is connected to the power source by a Powerstat (0 to 120 v), a voltmeter (0 to 100 v), and an ammeter (0 to 10 amp). This allows the power input to be controlled; thus, the temperature of the furnace can be raised at any desired rate. The maximum permissible rate of heating at any given temperature is determined by:

1. The need to protect the tungsten furnace coil from burning out.
2. The need to obtain sufficiently complete outgassing of the specimen and furnace parts.

The final step was the installation of a vacuum system consisting of an NRC mechanical pump and an Eimac glass oil diffusion pump. The vacuum is measured by using a thermocouple gauge in the high side of the diffusion pump to indicate roughing pressure and a hot filament ionization gauge in the high vacuum side to indicate the operating pressure. The vacuum is read from an NRC thermocouple and emission regulated ion gauge control. Results of a test of the completed vacuum unit showed that a vacuum of 10<sup>-5</sup> mm of mercury could be maintained.

The water supply for cooling the furnace was connected and adjusted to maintain the required water flow of 0.5 liter per minute.

The system was tested during outgassing. This was done by operating the stage with no specimen in it until a temperature of 900°C was attained. The procedure started with pumping down to at least 10<sup>-4</sup> mm of mercury and heating at a slow rate, gradually increasing the current input to 5 amperes. This required approximately 60 to 80 minutes. After the end of the test, the furnace was cooled to room temperature, with the vacuum pump and cooling water running.

#### Study of Grain Structures of Uranium Metal at Elevated Temperatures

The samples used in the heating stage are machined to a diameter of 8.5 millimeters and a total length of 25 millimeters. The thermocouple junction rests in a slot 1 millimeter wide and 0.5 millimeter deep, cut 2 millimeters off center in the specimen surface to be observed.

A series of samples from an alpha-rolled rod were examined, using various heating rates to determine the maximum heating rate at which a suitable vacuum could be maintained. A rise in temperature of 4°C per minute gave the most satisfactory results. A vacuum of 10<sup>-4</sup> mm mercury was maintained. The most critical range seems to be that between 100°C and 250°C. It was in this range that the most severe outgassing occurred.

The samples were ground on 60 and 400 grit grinding paper and then electropolished in a standard chromic-acetic solution. The polishing time was approximately 60 seconds. The sample was placed in the furnace chamber, and the vacuum system started. When a vacuum of 10<sup>-4</sup> mm mercury was obtained, the heating cycle was started.

At approximately 150°C, preferential oxidation occurred and the grain structure became visible under bright field illumination as shown in the sample heated to 200°C (Fig. 15.1). The heating

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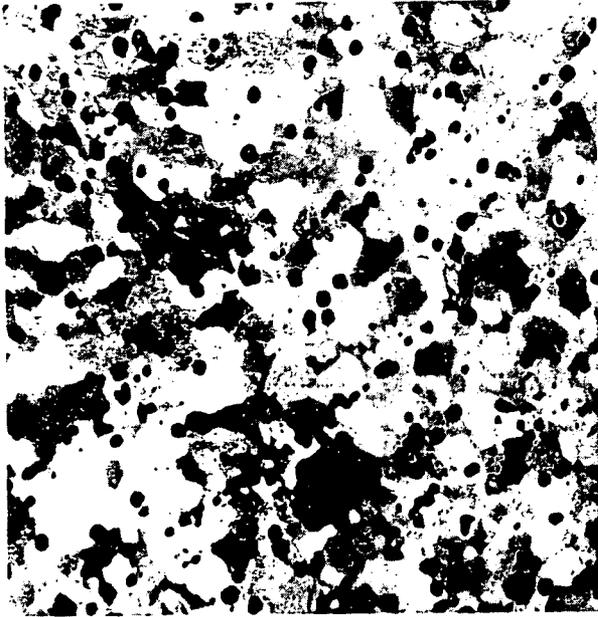


FIGURE 15.1 Alpha Extruded Uranium Heated to 200°C, 200X, Bright Field Illumination

cycle was continued at a temperature rise of 4°C per minute, and the sample was again photographed

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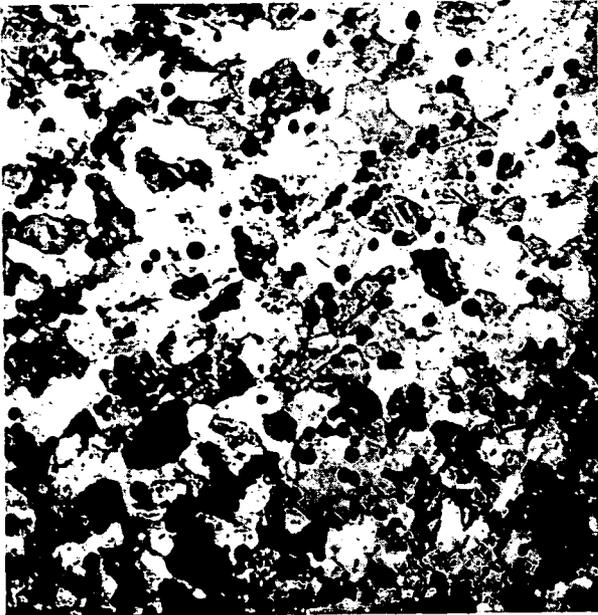


FIGURE 15.2 Alpha Extruded Uranium Heated to 500°C, 200X, Bright Field Illumination

in the high alpha range (500°C), as shown in Figure 15.2. As the temperature increased, a plateau in the heating curve was seen at the alpha to beta transformation point. The sample was photographed at 690°C in the beta range (Fig. 15.3). It is noted at this point that the sample had become heavily oxidized although the vacuum was maintained at  $2 \times 10^{-4}$  mm mercury. The temperature was steadily raised, and another plateau was seen at the beta to gamma transformation temperature. The sample was photographed in the gamma range (800°C) and is shown in Figure 15.4.

Note that there was no significant change in the grain size of the sample. The sample was cooled to room temperature, removed from the furnace, ground on 400 grit paper, and electropolished. Under polarized light, the structure appeared as seen in Figure 15.5. There were also some areas with a finer grain.

These same results were observed in every sample run to date with the exception of one: This particular sample was photographed at approxi-

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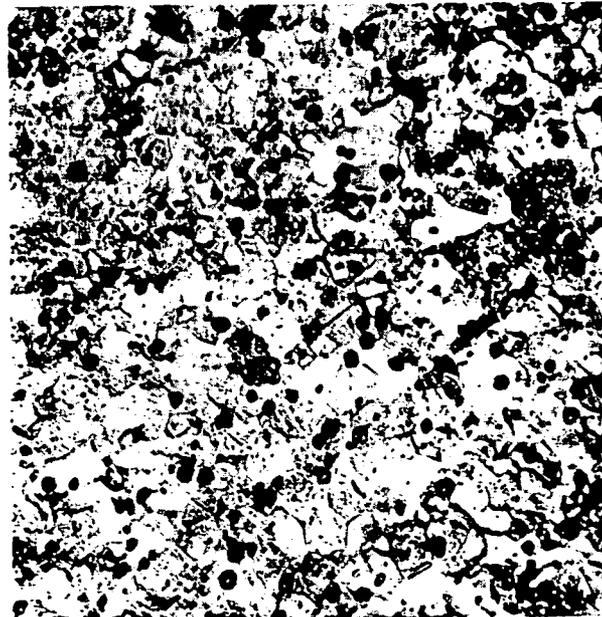


FIGURE 15.3 Uranium Shown in Figures 15.1 and 15.2, Heated to 690°C, in Beta Range, 200X, Bright Field Illumination

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mately 200°C (Fig. 15.6). Note the preferential oxidation. However, as the beta transformation was observed during further heating of this sample, the surface of the sample changed, as shown in Figure 15.7. This change took place in a matter of seconds and was uniform over the entire surface of the sample. The sample temperature was raised into the gamma range (800°C) and again photographed (Fig. 15.8). When the sample was allowed to cool to room temperature, the same structure remained, and the sample was removed from the furnace chamber. A heavy grinding was needed to remove the structure observed during the heating cycle. After grinding, the structure was similar to that shown in Figure 15.5.

This same sample was immediately placed in the furnace chamber and the heating cycle was repeated (Fig. 15.9 shows the structure at 200°C). At the alpha to beta transformation point, a change was again observed on the sample (Fig. 15.10). As noted in the photomicrograph, the surface change seems to be confined to individual grains and to changes at each grain boundary. The heating cycle

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FIGURE 15.4 Uranium Shown in Figures 15.1 to 15.3, Heated to 800°C, in the Gamma Range, 200X, Bright Field Illumination

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FIGURE 15.5 Structure of Extruded Uranium, Heated at Rate of 4°C Per Minute in Vacuum to the Gamma Range, and Air Cooled. Polarized Light, 250X.

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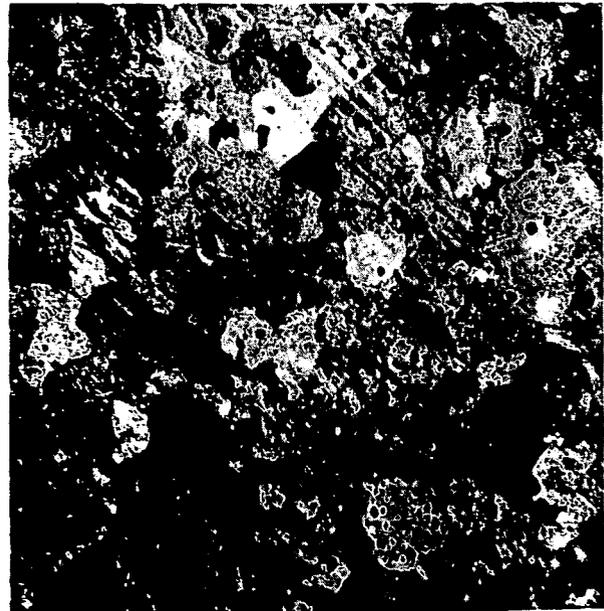


FIGURE 15.6 Alpha-Rolled Uranium, Heated to 200°C, 200X, Bright Field Illumination

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FIGURE 15.7 Uranium From Fig. 15.6, Showing Surface Oxide Lines When Heated to 700°C, in Beta Range, 200X, Bright Field Illumination

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FIGURE 15.8 Uranium From Figures 15.6 and 15.7, Showing Surface Oxide Lines When Heated to 800°C, in Gamma Range, 200X, Bright Field Illumination

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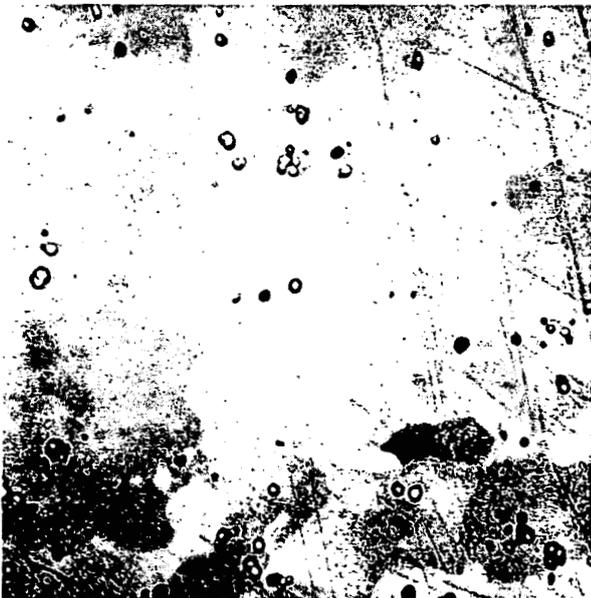


FIGURE 15.9 Uranium From Figures 15.6 to 15.8 After Surface Grinding and Reheating to a Temperature of 200°C, 200X, Bright Field Illumination

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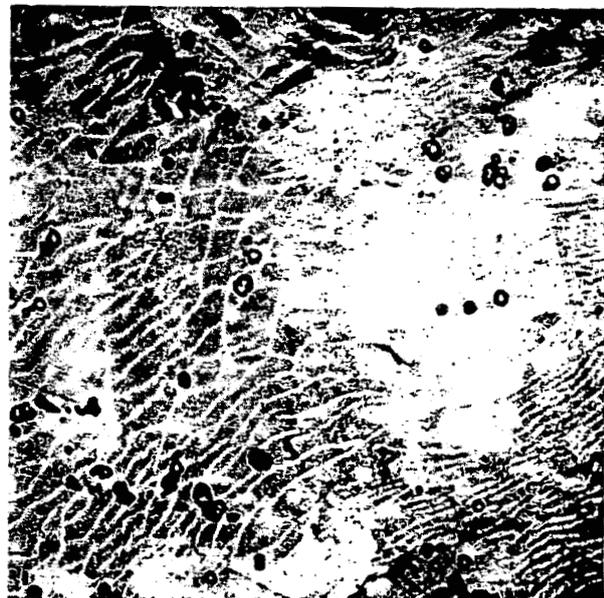


FIGURE 15.10 Uranium From Fig. 15.9 Heated to 700°C, Showing Oxide Network, 200X, Bright Field Illumination

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FIGURE 15.11 Uranium From Figures 15.9 and 15.10, Heated to 800°C, Showing Surface Oxide Network, 200X, Bright Field Illumination

was continued until the beta to gamma transformation temperature was reached. The sample surface had again changed (Fig. 15.11).

The reason for this phenomenon is unknown at this time; however, it is thought that a layer of oxide was disturbed during the transformations. The sample was submitted for chemical analysis, and the impurities were found to be at a normal level.

#### Future Work

The present vacuum system is not adequate to control oxidation of the uranium samples at elevated temperatures. Work will be performed to find a method of cleaning the surface of the sample during the heating cycle, thereby making any change in the grain structure visible. A study of the design of the furnace thermocouple is also needed to permit closer control of the temperature of the sample.

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## 16. OIL QUENCHING OF HEAT TREATED SLUG BLANKS

C. F. Hall

**Abstract**

Heat treating tests were performed, using oil as a quenching medium. A number of variables (such as slug blank\* form, temperature of salt, time in salt, air delay, temperature of oil, etc.) were investigated. The information derived from this limited study indicated that oil is a promising quenching medium.

**Introduction**

The purpose of heat treating uranium slug blanks is to obtain metal that is dimensionally stable under irradiation. To accomplish this, there should be a minimum of preferred orientation in the metal and grains should be uniformly small.

In one heat treatment process presently used, solid uranium slug blanks are beta heat treated in 50 per cent NaCl-50 per cent KCl salt and are quenched in water, which has a relatively fast cooling rate. The speed of quenching (i.e., the rate at which the metal is cooled through the beta to alpha transformation) is important, since it influences the preferred orientation. The greater the thermal gradient during the beta to alpha transformation, the greater degree of preferred orientation.<sup>1</sup>

A second heat treatment process has therefore been put into use — a bronze bath heat treatment followed by a quench in molten tin (which is a slow quench). Occasionally, metal heat treated by this procedure has undesirable large grains. There are other undesirable features in the two present heat treating processes, such as warp of water-quenched blanks, nonuniform grain size, and the high cost of the bronze-tin process.

\* A slug blank is a rough-machined right cylinder that becomes a fuel core after heat treating and finish machining. The canned fuel core is a fuel element.

Oils, which are commonly used in the metals industry as quenching media, are being investigated because they have cooling rates intermediate between those of water and molten metals. The exact cooling rate that can be obtained depends upon the properties of the oil, and the quench conditions. A recent irradiation test at Savannah River indicated that oil-quenched slugs are dimensionally more stable under irradiation than are slugs which have been heat treated in a bronze bath and quenched in molten tin.<sup>2</sup>

**Objective for This Quarter**

The objective was to investigate oil as a quenching medium for the heat treatment of uranium slug blanks. The objective of the full program is to produce a fuel element that is potentially more stable under irradiation by substituting a salt heating — oil quenching process for the two processes currently in use.

**Summary of Results Obtained This Quarter**

Oil quenches and water quenches were compared in an investigation of solid and hollow slug blanks. Time in salt, air delay before quenching, and quenching medium temperature were varied, giving the results summarized below:

1. Under the conditions investigated, the grain size of the hollow heat-treated slug blanks was slightly smaller than that of the solid slug blanks.
2. Beyond a three-minute immersion time in salt, a complete beta transformation was obtained and the grain size was relatively uniform. Various times of air delay less than 50 seconds did not appreciably affect the grain size.
3. Larger grain size resulted from quenching into 80°F oil, but the grain size remained constant at oil temperatures of 160° to 220°F.

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### Preparation of Specimens

The following steps were used in preparing samples for all of the subsequent heat treating tests: Uranium rods having 1½ inch diameters were cut into slug blanks 8.35 inches long and 1.443 inches in diameter. The slug blanks were numbered consecutively. A 0.400-inch hole was drilled through the center of the even-numbered slug blanks. For test purposes, the slug blanks were grouped in pairs, each pair consisting of one solid blank and an adjacent hollow blank. After heat treatment in the Pilot Plant furnace filled with Houghton 980\* salt and quenching, the blanks were measured for warp. Transverse and longitudinal sections were then cut from the blanks for grain size determinations.

#### Oil Quench Versus Water Quench; Time in Salt Bath

Four groups of slug blanks from one rod (four adjacent slug blanks in a group) were used in this

\* 16% NaCl, 32% KCl, 52% BaCl<sub>2</sub>

test. The slug blanks were all heat treated vertically (using a production type fixture) in a salt bath containing Houghton 980 at 1350°F. One group of slug blanks was held in the salt for one minute, the second for two minutes, the third for four minutes, and the fourth for six minutes. They were quenched after a 43-second air delay into either water or oil. One pair in each group, a solid and a hollow blank, was quenched in Sun No. 11 quenching oil; the second pair, a solid and a hollow blank, was quenched in 125°F water.

After heat treatment, the slug blanks were analyzed for hydrogen, oxygen, nitrogen, carbon, and trace elements. The slug blanks were found to contain 375 ppm carbon, 25 ppm nitrogen, 27 ppm oxygen, and trace amounts of other impurities. Uranium adsorbs hydrogen from the Houghton 980 salt, the amount depending upon the slug blank form and the time in the salt.

Oil-quenched pieces were found to have less warp than water-quenched pieces.

The grain size of transverse and longitudinal sections was measured by the Heyn Line-Intercept

TABLE 16.1 Effect of Slug Blank Form, Salt Immersion Time, and Quenching Medium on Grain Size

Slug No.	Slug Blank Form	Time in Salt (min)	Quenching Medium	Grain Size (mm)			
				Transverse		Longitudinal	
					Avg		Avg
5	Solid	1	Oil	Alpha, Alpha	Alpha	Alpha, Alpha	Alpha
6	Hollow	1	Oil	Alpha, Alpha	Alpha	Alpha, Alpha	Alpha
7	Solid	1	Water	Alpha, Alpha	Alpha	Alpha, Alpha	Alpha
8	Hollow	1	Water	Alpha, Alpha	Alpha	Alpha, Alpha	Alpha
13	Solid	2	Water	Alpha, Alpha	Alpha	0.223, 0.238	0.230
14	Hollow	2	Water	Alpha, Alpha	Alpha	0.564, 0.369	0.467
15	Solid	2	Oil	Alpha, Alpha	Alpha	0.446, 0.516	0.481
16	Hollow	2	Oil	Alpha, Alpha	Alpha	0.453, 0.476	0.465
9	Solid	4	Oil	0.322, 0.294	0.308	0.330, 0.286	0.308
10	Hollow	4	Oil	0.315, 0.286	0.300	0.268, 0.323	0.286
11	Solid	4	Water	0.331, 0.390	0.360	0.315, 0.339	0.327
12	Hollow	4	Water	0.380, 0.344	0.352	0.344, 0.308	0.326
1	Solid	6	Water	0.293, 0.280	0.287	0.306, 0.299	0.303
2	Hollow	6	Water	0.293, 0.359	0.326	0.308, 0.313	0.310
3	Solid	6	Oil	0.380, 0.313	0.346	0.263, 0.248	0.256
4	Hollow	6	Oil	0.315, 0.340	0.327	0.293, 0.339	0.291

Note: The duplicate grain size measurements were made from two 20X photographs of the sample surface.

20X Method. The results are listed in Table 16.1. There was variation in grain size between duplicate measurements, hollow and solid pieces, and oil and water-quenched pieces. The hollow blanks had a slightly smaller grain size than did the comparable solid blanks. For the material held in the salt bath for two minutes, measurement of the longitudinal sections showed a large grained beta structure, because the sample was from the ends of the blanks (which had been completely transformed); the transverse sections were from the center of the slug blank and had only a small circle of beta grains around their peripheries.

The blanks were only partially transformed after two minutes in the salt and were completely transformed after four minutes in the salt. Figure 16.1 is a photograph of a transverse section of a solid

blank which had been immersed in the salt bath for two minutes and quenched in oil. Figure 16.2 is a photograph of a transverse section of the comparable hollow blank which had been immersed in the salt bath for two minutes and quenched in oil. A considerably larger volume of the hollow blank than the solid blank had been transformed, due to the hollow blanks having a smaller amount of metal (7 per cent less) which must be raised to the transformation temperature. There was no evidence of beta grains around the ID of the hollow slug blank, which indicates that the salt freezes until the temperature throughout the piece reaches the melting point of the salt.

Air-Delay; Quench Oil Temperatures;  
Time in Salt Bath

A second group of hollow and solid blanks was fabricated from a rod containing 460 ppm carbon,

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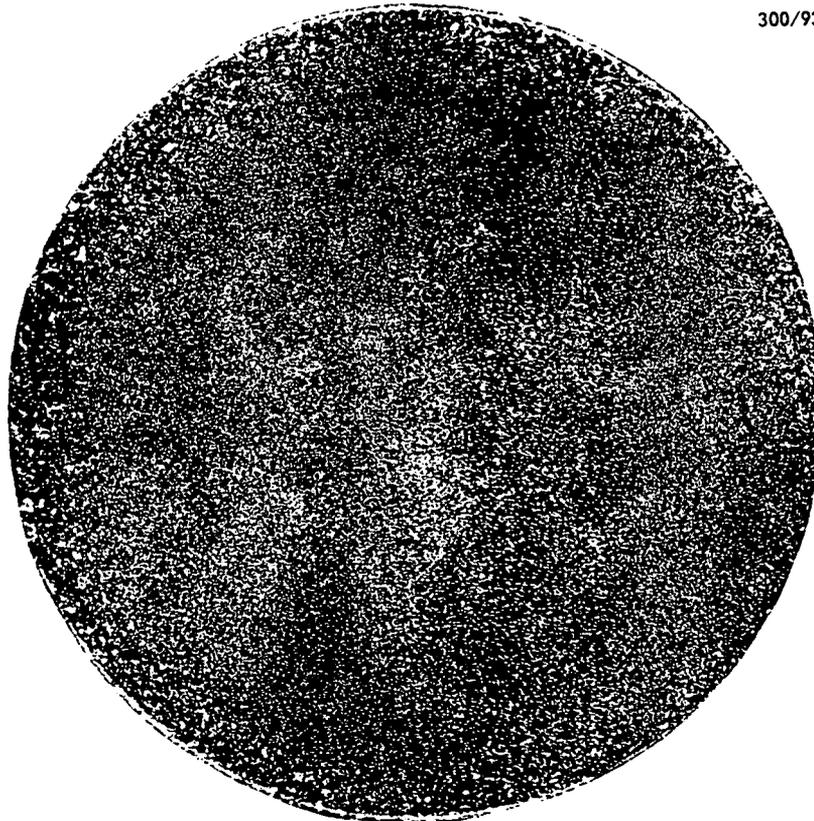


FIGURE 16.1 Transverse Section of a Solid Blank That Has Been Immersed in a Salt Bath for Two Minutes and Quenched in Oil. 3X.

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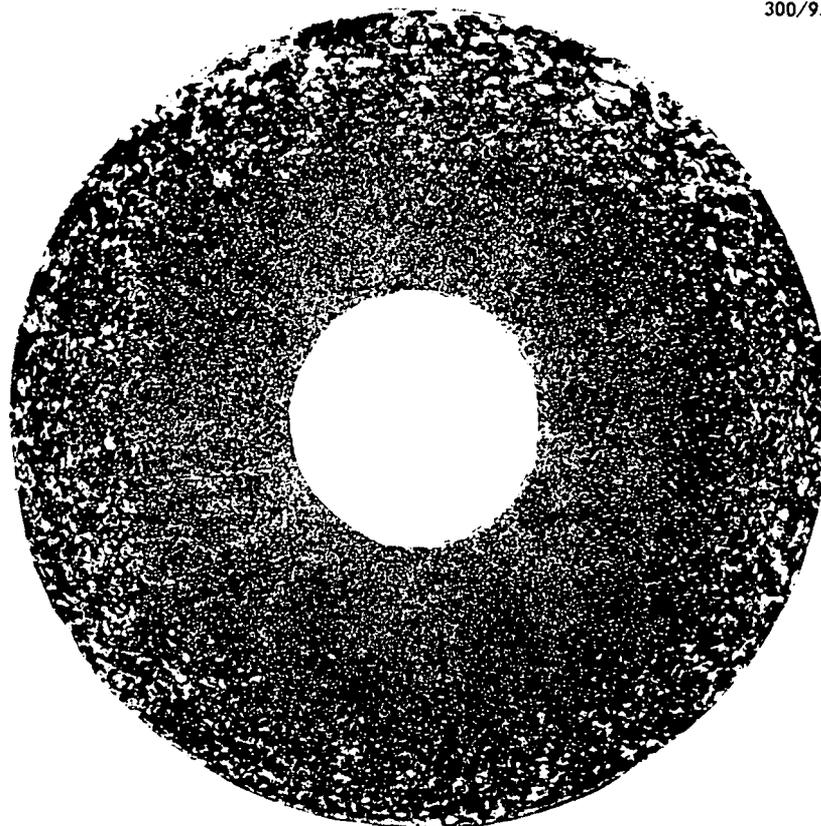


FIGURE 16.2 Transverse Section of a Hollow Blank That Has Been Immersed in a Salt Bath for Two Minutes and Quenched in Oil. 3X.

42 ppm nitrogen, 32 ppm oxygen, and trace amounts of other elements. The slug blanks from this rod were used in the following three heat treating studies.

#### A. Air Delay

Five pairs of slug blanks (one solid blank and one hollow blank in a pair) were heat treated for 12 minutes (using a production type fixture) in the Pilot Plant salt bath containing Houghton 980 salt at 1350°F. The pairs of slug blanks were quenched in Sun No. 11 quenching oil at 90°F after air delays ranging from 15 to 50 seconds.

After heat treatment, the slug blanks were measured for warp. The amount of warp was small and was identical in both solid and hollow blanks.

At a 12-minute immersion time, the amount of hydrogen is nearly identical in both solid and hollow pieces. The hydrogen content of the oil-

TABLE 16.2 Effect of Air Delay on Grain Size

Slug No.	Type	Air Delay (sec)	Grain Size (mm)			
			Transverse		Longitudinal	
				Avg		Avg
5	Solid	15	0.288, 0.262	0.275	0.268, 0.243	0.255
6	Hollow	15	0.300, 0.280	0.290	0.239, 0.253	0.246
1	Solid	20	0.240, 0.267	0.254	0.276, 0.239	0.257
2	Hollow	20	0.259, 0.255	0.257	0.294, 0.321	0.307
7	Solid	30	0.282, 0.281	0.282	0.239, 0.258	0.285
8	Hollow	30	0.286, 0.248	0.267	0.277, 0.294	0.285
9	Solid	40	0.309, 0.281	0.295	0.239, 0.239	0.239
10	Hollow	40	0.275, 0.275	0.275	0.243, 0.253	0.248
3	Solid	50	0.299, 0.264	0.282	0.259, 0.253	0.256
4	Hollow	50	0.299, 0.258	0.278	0.276, 0.263	0.269

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quenched pieces was not affected by differences in air delay.

The grain size of transverse and longitudinal sections was measured by the Heyn Line-Intercept 20X Method. The results are listed in Table 16.2. There was variation between duplicate measurements and between the solid and hollow blank forms and the various air-delay intervals, but no definite correlation could be found between grain size and (a) slug blank form or (b) air delays.

### B. Quench Oil Temperature

Four pairs of slug blanks (one solid blank and one hollow blank in a pair) were vertically heat treated (using a production type fixture) in the Pilot Plant bath containing Houghton 980 salt. The pairs of slug blanks were held for 12 minutes in the 1350°F salt and were quenched after a 20-second air delay. The pairs of slug blanks were quenched in Sun No. 11 oil, which was at temperatures ranging from 80° to 220°F.

None of the slug blanks warped excessively, and there was no significant difference in warp between the solid and hollow pieces.

The temperature of the oil did not affect the hydrogen content of the metal.

The grain size of transverse and longitudinal sections was measured by the Heyn Line-Intercept

TABLE 16.3 Effect of Quench Oil Temperature on Grain Size (Sun #11)

12 Min at 1350°F, 20-Sec Air Delay

Slug No.	Type	Oil Temp (°F)	Grain Size (mm)			
			Transverse		Longitudinal	
				Avg		Avg
15	Solid	80	0.253, 0.311	0.282	0.279, 0.280	0.280
16	Hollow	80	0.248, 0.292	0.270	0.286, 0.286	0.286
11	Solid	160	0.254, 0.253	0.253	0.239, 0.269	0.254
12	Hollow	160	0.251, 0.245	0.248	0.286, 0.262	0.274
17	Solid	200	0.293, 0.264	0.278	0.286, 0.266	0.276
18	Hollow	200	0.252, 0.252	0.252	0.263, 0.244	0.254
13	Solid	220	0.247, 0.268	0.258	0.273, 0.274	0.274
14	Hollow	220	0.252, 0.258	0.255	0.237, 0.269	0.253

20X Method. The results (listed in Table 16.3) indicate that blanks quenched at 80°F had a slightly larger grain size than blanks quenched at higher oil temperatures, probably because the high oil viscosity at low temperatures resulted in a slower cooling rate.

### C. Time in Salt Bath

It was reported in a previous section that slug blanks immersed in the 1350°F salt bath for two minutes were only partially transformed and that slug blanks held for four minutes were completely transformed. This experiment was run to examine the time interval between two and four minutes.

Three pairs of slug blanks (one solid blank and one hollow blank in a pair) were beta heat treated (using a production type fixture) in the 1350°F Pilot Plant salt bath. The three pairs of slugs were held in the salt bath for 2½, 3, and 3½ minutes, respectively. The slug blanks were quenched in 100°F Sun No. 11 oil after a 43-second air delay.

The slug blanks warped slightly during heat treatment, but the amount of warp was not excessive.

The uranium adsorbed hydrogen from the salt bath; the longer the exposure to the molten salt, the greater the amount of hydrogen adsorbed. The hollow blanks adsorbed more hydrogen than did the solid blanks.

The grain size of transverse and longitudinal sections was measured by the Heyn Line-Intercept 20X Method. The results are listed in Table 16.4.

TABLE 16.4 Effect of Time of Immersion in Salt Bath on Grain Size

Slug No.	Type	Time in Salt (min)	Grain Size (mm)			
			Transverse		Longitudinal	
				Avg		Avg
23	Solid	2½	0.393, 0.402	0.387	0.383, 0.349	0.366
24	Hollow	2½	0.294, 0.304	0.299	0.360, 0.350	0.355
19	Solid	3	0.235, 0.259	0.247	0.269, 0.239	0.254
20	Hollow	3	0.249, 0.286	0.267	0.281, 0.294	0.288
21	Solid	3½	0.309, 0.276	0.292	0.252, 0.300	0.276
22	Hollow	3½	0.294, 0.263	0.278	0.307, 0.253	0.280

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FIGURE 16.3 Transverse Section of a Hollow Slug Blank That Has Been Immersed in a 1350°F Salt Bath for 2½ Minutes and Quenched in Oil After a 43-Second Air Delay. 3X.

The solid blank that had been held in the molten salt for 2½ minutes was incompletely transformed, and grain size measurements were made in the transformed region. The grains were larger in the 2½ minute blanks than in the blanks held for 3 and 3½ minutes in the salt.

Figure 16.3 shows the large grain size of a hollow slug blank which had been held in the 1350°F salt for 2½ minutes and quenched in oil after a 43-second air delay. Figure 16.4 shows the smaller grain size of a hollow slug blank which had been held in the 1350°F salt for three minutes and quenched in oil after a 43-second air delay.

**Discussion**

On the basis of available data, the amount of warp in slug blanks would be reduced if the oil-quenching process were substituted for water quenching. No significant difference in warp could be detected for the solid and hollow blank forms, whether water quenching or oil quenching was used.

Houghton 980 salt introduces hydrogen into the metal and should be replaced by 50 per cent NaCl-50 per cent KCl for heat treating. The oil quench did not affect the hydrogen content of the metal.

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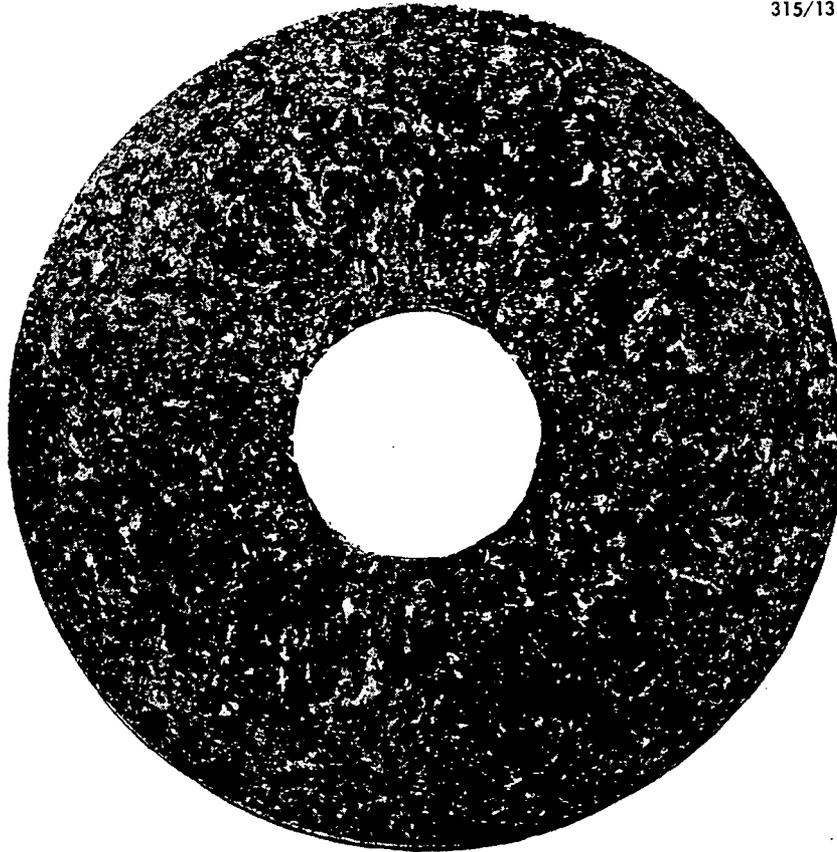


FIGURE 16.4 Transverse Section of a Hollow Slug Blank That Has Been Immersed in a 1350°F Salt Bath for 3 Minutes and Quenched in Oil After a 43 - Second Air Delay. 3X.

The range of grain size for the oil quenched metal is approximately the same as the range for production metal.

#### Future Work

Additional oil quenching studies will be made, including preferred orientation studies of the heat-treated pieces.

#### References

<sup>1</sup>J. W. Starbuck and H. C. Kloepper, Jr. "Preferred Orientation of End-Quenched Jominy Bars Sampled at Small Increments," Process Development Quarterly Report, USAEC Report MCW-1433, p. 105. November 2, 1959.

<sup>2</sup>C. E. Paetschke. Personal Communication to C. F. Hall. 1959.

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## 17. ELECTROGRAVIMETRIC ANALYSIS OF COPPER AND TIN IN TIN AND BRONZE ALLOY

E. W. Tieman

E. A. Brown

**Abstract**

Electrodeposition at a controlled cathode potential was applied to the determination of copper and tin in bronze. (Molten bronze is used for the beta treatment of uranium metal.)

Copper is deposited from a tartarate-succinate solution onto a platinum gauze electrode at a controlled cathode potential of  $-0.35$  volt (SEC) at pH 5. Hydrazine is added as an anodic depolarizer. Hydrochloric acid is then added and the tin is deposited on a clean platinum gauze electrode at a cathode potential of  $-0.60$  volt (SCE), using sulfamic acid as an anodic depolarizer.

The method may be applied without preliminary separation of the copper and tin from the sample. Macro amounts of uranium, aluminum and iron may be present in the sample without interfering. Satisfactory results were obtained upon applying this method to synthetic samples and to a NBS tin-base bearing metal.

**Introduction**

A molten bronze bath containing approximately 50 per cent copper and 50 per cent tin is used in the beta heat treatment process for uranium metal fuel elements. Molten tin is then used to slow-quench the metal to the alpha range. A small amount of aluminum is added to the tin bath to help reduce air oxidation. In order to operate the baths at the proper concentration range, analytical methods were needed for the determination of both copper and tin. A direct analytical method was needed for the determination of copper in the range of 1 to 50 per cent and tin in the range of 50 to 100 per cent. Since uranium, aluminum, and iron were known to be present in the metal baths, methods were desired which would tolerate macro amounts of these metals

Electrodeposition at a controlled cathode potential has been applied to the selective separation of metals. Metals with small differences may be conveniently separated in successive stages by this method. Electrodeposition may be made on a platinum cathode or on a mercury cathode. Many applications of the technique are given in a recent book by Lingane,<sup>1</sup> who applied the method to copper-base and tin-base alloys.<sup>2</sup> Alfonsi<sup>3,4</sup> applied the method to the determination of copper, lead, tin, and antimony in bronzes and brasses.

The basic procedure as outlined by Alfonsi was used in this work for the determination of copper and tin in the beta heat treatment metal baths. In this method, the sample is dissolved in hydrochloric acid, using peroxide as the oxidizing agent. Tartaric acid is added to complex the tin, and succinic acid is added as a buffering agent. Copper is then deposited at a controlled cathode potential. After the deposition of copper, the sample is acidified with hydrochloric acid, and tin is electrodeposited at a controlled cathode potential.

**Objective For This Quarter**

The objective of the work done during the quarter was to study and establish a satisfactory method for determining copper and tin in bronze bath materials.

**Summary of Results**

Electrodeposition at a controlled cathode potential was successfully applied to the separation and gravimetric determination of copper and tin in both tin and bronze baths. Automatic adjustments of the potential were made by means of a Potentiostat manufactured by the Analytical Instruments, Inc. Copper and tin were separated from macro amounts of uranium, aluminum, and iron with no interference from the latter. A recommended procedure is given.

### Instrumentation

A number of instruments for controlled potential electroanalysis are described by Lingane. A commercial model of a potentiostat is available from Analytical Instruments, Inc., Bristol, Connecticut. This instrument was used in this work.

The Analytical Instruments potentiostat is designed to control oxidation or reduction potentials from +3 to -3 volts across the electrode circuit. Continuous automatic adjustments of the voltage are made by means of a servo-mechanism. These adjustments maintain the potential of the working electrode at a constant value with respect to a suitable reference electrode. The servo-amplifier is designed to amplify a small d-c signal to give an a-c output sufficient to control the servo-motor. Electrolysis currents up to 12.5 amperes may be drawn at the working electrodes.

The electrolysis cell consisted of a 400-ml tall-form beaker fitted with a Plexiglass cover designed to hold the electrodes. A cylindrical platinum gauze electrode was used as the cathode, and a platinum wire spiral as the anode. A Beckman No. 29970 fiber type calomel electrode was used as the reference electrode.

### Experimental

In order to check the operation of the instrument and method, stock solutions of copper and tin were prepared from reagent chemicals. Suitable aliquots were taken, and the copper was electrodeposited on a platinum gauze cathode at a controlled cathode potential of -0.35 volt (SCE) according to the method of Alfonsi. The effect of tin on the electrodeposition of copper is shown in Table 17.1.

The results shown in Table 17.1 indicate that copper may be separated quantitatively from large amounts of tin without interference.

Satisfactory results were obtained for the electrodeposition of tin at a controlled cathode potential of -0.60 volt (SCE). The tin was deposited from a hydrochloric acid solution after the electrodepo-

TABLE 17.1 Effect of Tin on the Electroanalysis of Copper at a Controlled Potential

Tin Added (g)	Copper Added (g)	Copper Found (g)
0	0.0522	0.0524
1.00	0.0522	0.0521
1.00	0.0522	0.0518
1.00	0.0522	0.0523
1.00	0.0522	0.0518
1.00	0.0522	0.0522

sition of copper. The effect of aluminum, uranium, and iron on the determination of copper and tin was also studied. A summary of the results is shown in Table 17.2.

From the results shown in Table 17.2 it is evident that copper and tin may be determined in alloys by electrodeposition at controlled potential. The presence of aluminum, iron, and uranium does not interfere with the determination of copper and tin. After the removal of copper and tin, the electrolyte may be conveniently used for the determination of impurities in the alloy.

The results shown were the basis for a recommended procedure that was written.

TABLE 17.2 Recovery of Copper and Tin; The Effect of Foreign Ions

Ion Added	Amount (g)	Copper (g)		Tin (g)	
		Added	Found	Added	Found
None	—	0.0522	0.0522	1.0036	1.0013
None	—	0.0522	0.0522	1.0015	0.9972
None	—	0.2170	0.2161	0.2480	0.2456
None	—	0.2075	0.2076	0.2269	0.2263
Al	0.031	0.2144	0.2149	0.2643	0.2622
Al	0.062	0.2154	0.2159	0.2219	0.2220
Al	0.059	0.2289	0.2297	0.2144	0.2131
Fe	0.158				
Al	0.183	0.2063	0.2069	0.2477	0.2472
Fe	0.184				
U	0.493	0.2274	0.2278	0.2128	0.2121
U	0.474	0.0522	0.0532	1.000	*
U	0.474	0.0522	0.0518	1.000	*
U	0.502	0.2248	0.2247	0.2064	0.2069
Al	0.013				

\* Not determined

### Recommended Procedure

Weight 0.5 g of a representative sample of the bronze alloy (or a 1.0 g sample from the tin bath) into a 400-ml tall-form beaker. Dissolve the sample in 12 to 15 ml of hydrochloric acid (1-1) and 3 to 4 ml of hydrogen peroxide (30%). Warm, if necessary, to dissolve. When the sample is completely in solution, add 1 ml more peroxide and dilute to 30 to 40 ml. Boil for 15 minutes to oxidize the tin and decompose the excess peroxide. Cool the solution, and add 5 g of tartaric acid, 3 g of succinic acid, and 2 g of hydrazine dihydrochloride. Adjust the pH to 5.0 with ammonium hydroxide (1-1). Adjust the volume to 200 ml with water.

Weigh the platinum gauze cathode, insert it in the Plexiglass electrode holder, and position it in the beaker. Adjust the initial control potential across the platinum cathode - calomel electrode to give a current of 0.1 to 0.2 ampere. (If the initial current is too high, spongy copper deposits are obtained.) Finally, adjust the control potential to -0.35 volt (SCE). When the current reaches 10 milliamperes, wash the Plexiglass cover and edge of the beaker with water. After the current remains constant for 10 minutes, remove the electrode without interrupting the current, wash in acetone, dry, and weigh. The increase in weight is copper metal.

Acidify the solution with 20 ml hydrochloric acid (concentrated), and add 2 g sulfamic acid. Place the cleaned tared platinum gauze electrode in the Plexiglass holder, and adjust the potential to give a current of about 0.5 ampere. When the vigorous evolution of gas stops, adjust the control potential to -0.60 volt (SCE). When the current drops to a constant value of 0.10 to 0.15 ampere, the electrodeposition of tin is complete. Remove the electrode, rinse it in acetone, dry, and weigh. The increase in weight is tin metal.

Four samples of a National Bureau of Standards tin-base bearing metal (No. 54D) were analyzed by

TABLE 17.3 Analysis of a NBS Standard Tin-Base Bearing Metal

Sample Number	Copper Found* (%)	NBS Copper Value (%)
1	3.63	3.62
2	3.65	
3	3.54	
4	3.64	
Average	3.62	

\* The results were corrected for bismuth and silver contents of 0.02%.

the recommended procedure. The results are shown in Table 17.3.

The results agree with the accepted NBS value.

Four samples of scrap tin metal were analyzed for copper and tin by the recommended procedure. A summary of the results obtained is shown in Table 17.4.

The results obtained were found to give a satisfactory total analysis.

TABLE 17.4 Analysis of Scrap Tin Metal

Sample Number	Sn (%)	Cu (%)	U (%)	Other* Metals (%)	Total (%)
1	97.51	1.73	0.07	1.03	100.3
2	88.38	8.08	1.45	2.20	100.1
3	96.81	2.60	0.08	0.63	100.1
4	97.46	2.06	0.11	0.76	100.4

\* Spectrographic values (total) for Al, Fe, Ni, Pb, and SiO<sub>2</sub>.

A number of samples of the bronze and tin metal used in the bath were analyzed in duplicate. Typical results for this material are shown in Table 17.5.

From the results shown, the over-all precision of the method, including the taking of duplicate samples, was calculated to be  $\pm 0.33$  per cent for copper and  $\pm 0.37$  per cent for tin at the 95 per cent confidence level.

TABLE 17.5 Analysis of Bronze Bath and Tin Metal

Sample Number	Copper (%)	Tin (%)
1a	51.09	48.30
1b	51.17	48.25
2a	49.09	48.95
2b	48.85	49.28
3a	48.67	47.54
3b	48.45	47.41
4a	1.73	97.55
4b	1.73	97.47
5a	7.96	88.26
5b	8.20	88.51

Conclusion

The direct electroanalysis of copper and tin at a controlled cathode potential is satisfactory for the

control analysis of copper and tin in bronze bath and tin bath materials. The time required for the quantitative electrodeposition of copper was found to be 20 to 30 minutes, and for tin 50 to 60 minutes.

References

- <sup>1</sup>J. J. Lingane. Electroanalytical Chemistry., 2nd ed rev. New York: Interscience, 1958.
- <sup>2</sup>J. J. Lingane. "Electrogravimetric determination of copper in copper-base and tin-base alloys by controlled potential analysis," Anal. Chem. 17: 640. 1945.
- <sup>3</sup>B. Alfonsi. "Determination of Copper, Lead, Tin and Antimony by Controlled-Potential Electrolysis. I. General Methods of Analysis," Anal. Chim. Acta 19: 276. 1958.
- <sup>4</sup>B. Alfonsi. "Determination of Copper, Lead, Tin and Antimony by Controlled-Potential Electrolysis. II. Application of the Method to the Determination of Cu, Pb, Sn, and Sb in bronzes and brasses," Anal. Chim. Acta 19: 389. 1958.

## 18. PHOTOMETRIC TITRATION OF SULFATE IN URANIUM MATERIALS

W. G. Ellis

E. A. Brown

**Abstract**

An automatic photometric titrator was successfully applied to the volumetric titration of sulfate in 80 per cent ethanol. A recommended procedure is given for the determination of sulfate in uranium materials. A preliminary separation of the sulfate from uranium and other ions is made through the use of chromatographic alumina and Dowex-50 ion exchange resin. The titration is performed with barium perchlorate, using thoron as the indicator. A photometric titrator is used for detection of the end point and has been found to overcome the limitations of the titration to a visual end point. The sensitivity of the method is thereby increased, with well defined end points given for samples containing as little as 10  $\mu\text{g/ml}$  of sulfate. The precision of the method for sulfate in the concentration range of 20 to 150  $\mu\text{g/ml}$  was found to be  $\pm 1.3$   $\mu\text{g/ml}$ .

The effect of alcohol concentration and wavelength upon the end point was studied.

**Introduction**

In the processing of uranium ore concentrates, it is necessary to monitor the sulfate content of the process streams at a number of different points. Feed materials are routinely analyzed for sulfate, since specification limits have been placed on all incoming ore concentrates. Purified uranium materials such as  $\text{UO}_3$ ,  $\text{UO}_2$ ,  $\text{UF}_4$  and  $\text{UNH}^*$  are also analyzed for sulfate. The over-all concentration range for sulfate in these materials varies widely from 20 ppm to 2 per cent.

The gravimetric method is used for the determination of sulfate in feed materials. In this method, the sulfate is precipitated, filtered, and weighed as barium sulfate. The method is accurate,

\* *UNH is uranyl nitrate hexahydrate.*

but not satisfactory for very low concentrations of sulfate.

The turbidimetric method is used at this site for the determination of small amounts of sulfate (in the concentration range of 20 to 2000 ppm). The accuracy of this method is influenced by many factors, such as the temperature, the rate of mixing the reagents, the ionic concentration of the solution, and the sulfate concentration. Rigid control of these factors is necessary in order to obtain reproducible results. Separate calibration curves are necessary for each sample type. A more precise general analytical method was needed, a method which could be applied to many different sample types over a wide concentration range.

**Objectives for the Quarter**

To develop a suitable method for the determination of small amounts of sulfate in uranium process samples.

**Summary of Results**

An automatic photometric titrator was successfully applied to the volumetric determination of sulfate in uranium process materials. The precision and accuracy of the method were found to be superior to those for turbidimetric and gravimetric methods. The photometric detection of the end point made possible the determination of sulfate in concentrations as low as 10 ppm. The optimum wavelength and alcohol concentration were established.

A recommended procedure is given for the isolation and titration of sulfate. The precision of the method was found to be  $\pm 1.3$   $\mu\text{g/ml}$  for sulfate in the concentration range of 20 to 150  $\mu\text{g/ml}$ .

**Photometric Detection of the End Point**

The most sensitive volumetric method for sulfate reported is that of Fritz and Yamamura.<sup>1</sup> In this

method, sulfate is titrated with barium perchlorate in 80 per cent ethanol. Thoron, 1-(*o*-arsonophenylazo)-2, naphthol-3, 6-disulfonic acid, is used as the indicator. With this method, it is possible to titrate 1000  $\mu\text{g}$  of sulfate in a volume of 10 ml. If a visual end point is used, an accuracy of about  $\pm 100 \mu\text{g}$  might be expected.

Titration of microgram amounts of sulfate without the aid of instruments is impractical, due to the difficulty in seeing the end point. As the amount of sulfate decreases, the end point becomes more obscure. Miller and Thomason<sup>2</sup> successfully applied the ORNL Model Q-945 Automatic Titrator to this analysis, thereby achieving a sensitivity of about 10 ppm. They determined the end point by locating the inflection point of the titration curve, which resembled a potentiometric curve. The volume of titrant was proportional to the vertical distance from the starting point to the point of inflection. When this instrument was used, the absence of a well-defined inflection point left much to be desired in selecting the end point.

The method of Fritz and Yamamura was used except that titration was performed with the automatic photometric titrator previously described.<sup>3</sup> This titrator utilizes a logarithmic attenuator circuit which monitors absorbancy changes during the titration in terms of a linear response of the chart recorder. The end point of the titration is located by a simple extrapolation of the titration curve. A typical curve for the titration of sulfate is shown in Figure 18.1. Well-defined end points are detected by projection of the two straight-line portions of the curve.

#### Effect of Wavelength

The accuracy of a volumetric method depends upon the precision with which the equivalence point can be measured. The equivalence point, in turn, depends upon the shape of the titration curve. Selection of the optimum conditions for obtaining well-defined inflection points is therefore important in improving the precision and accuracy of the method.

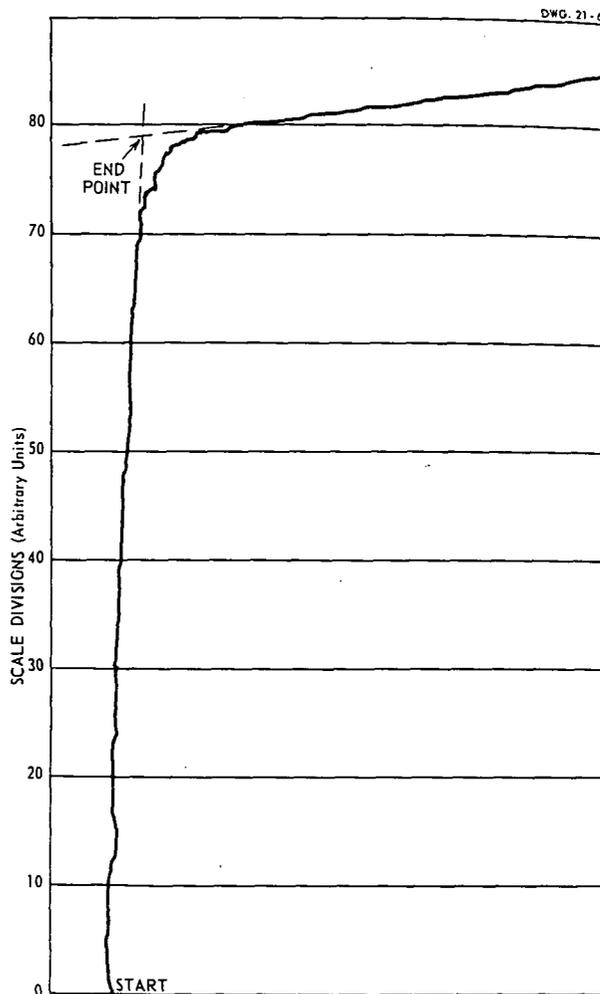


FIGURE 18.1 Typical Titration Curve (400  $\mu\text{g}$   $\text{SO}_4$ ).

The instrument adjustments, such as recorder span, millivolt range, slit width of the spectrophotometer, were found to be more or less interdependent in their effects on the curve. Variations in these settings did not materially improve the inflection point-chart recording relationship. However, a change in the wavelength setting was found to materially change the shape of the titration curve.

A series of solutions, each containing 233  $\mu\text{g}$  of sulfate, were titrated, using the photometric method. The ratio of water to ethanol was 1 to 5. A total

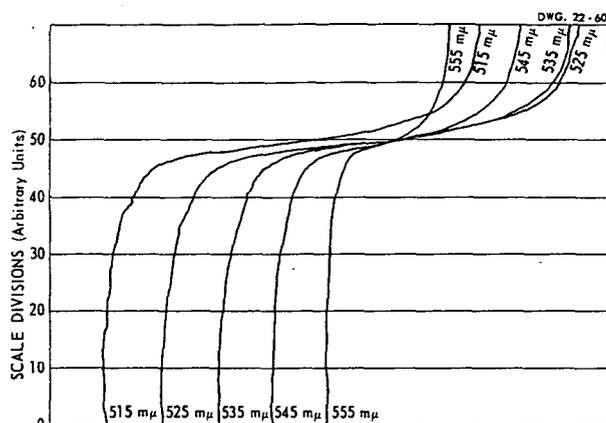


FIGURE 18.2 Effect of Wavelength on the Titration Curve (233  $\mu\text{g}$  of Sulfate Added).

volume of 60 ml was used in the titration cell in order to avoid turbulence during the stirring. The results of these tests are shown in Figure 18.2. On the basis of the results given, a wavelength setting of 525  $m\mu$  will produce the maximum change in the absorbancy at the end point. However, satisfactory titration curves may be obtained at any wavelength between 515 and 535  $m\mu$ .

#### Effect of the Water to Ethanol Ratio

The shape of the titration curve was found to depend on the water to ethanol ratio. A series of samples, each containing 233  $\mu\text{g}$  of sulfate, were analyzed to determine the effect of varying ethanol content. The effect of ethanol on the titration at 525  $m\mu$  is shown in Figure 18.3. The titration curves showed well-defined inflection points in A and B, which would indicate an optimum water to ethanol ratio between 20 to 40 and 15 to 45. Figure 18.4 illustrates more effectively the influence of the alcohol concentration on the titration at 545  $m\mu$ .

It is apparent from these experiments that the results of an analysis are not affected by small variations in alcohol content or wavelength settings. The sharpness of the break at the equivalence point may vary, but the intersection of the

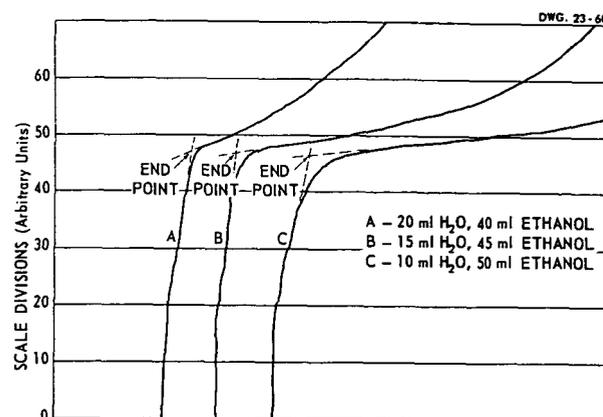


FIGURE 18.3 Effect of Water to Ethanol Ratio at 525  $m\mu$  (233  $\mu\text{g}$  of Sulfate Added).

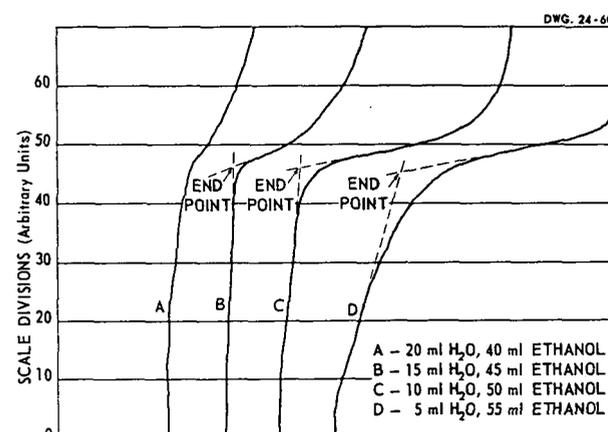


FIGURE 18.4 Effect of the Water to Ethanol Ratio at 545  $m\mu$  (233  $\mu\text{g}$  of Sulfate Added).

extrapolated lines was found to be reproducible (Fig. 18.3).

#### Recommended Procedure

Dissolve the sample containing 1 to 10 mg of sulfate in hydrochloric or perchloric acid, and adjust the excess acid between 0.1 and 2.0M. A 10 to 20 g sample of uranium oxide may be used, if necessary. Pass the sample through the activated alumina column in order to adsorb the sulfate. (Details on the preparation of the alumina and cation

exchange resin columns are given in the original paper by Fritz et al.)<sup>4</sup> Elute the sulfate from the alumina with dilute ammonium hydroxide. Then pass the solution through the prepared Dowex-50 column in order to remove cations. Dilute the solution to 50 ml, and transfer a suitable aliquot containing 0.5 mg sulfate to the titration cell. Adjust the volume to 10 to 12 ml, and add 2 drops of 0.2 per cent thoron indicator and 50 ml of ethanol. Position the cell in the automatic titrator, and titrate with 0.005M barium perchlorate, recording the absorbancy changes on an automatic photometric titrator. Details of the operation of the photometric titrator used at this laboratory are given in a previous report.<sup>3</sup>

A calibration factor (in terms of micrograms of sulfate per unit chart travel) is determined by titrating sulfate standards as in the recommended procedure.

This method may be applied to any type of uranium-bearing material. Such materials as  $UO_2$ ,  $UO_3$ ,  $UF_4$ , UNH, and uranium ore concentrates were analyzed by the method (results not shown), with satisfactory precision.

#### Precision and Accuracy of the Method

A stock uranium solution was prepared from sulfur-free uranium metal by dissolving the metal in hydrochloric acid and hydrogen peroxide. Sulfate standards were prepared by adding a standard sodium sulfate solution to the stock uranium solution. The samples were coded, submitted to the laboratory in replicate, and analyzed by the recommended procedure. A statistical evaluation was made from the analytical data. A summary is given in Table 18.1.

The results shown in Table 18.1 indicate that the photometric method for determining sulfate in uranium materials is precise and accurate. The precision compares favorably with titrations per-

TABLE 18.1 Precision and Accuracy of the Photometric Method for Sulfate

Uranium Added (g/l)	Sulfate Added ( $\mu$ g/ml)	Estimate of Bias* ( $\mu$ g/ml)	Precision** ( $\mu$ g/ml)
20	20	+0.61	$\pm 1.33$
20	87	-0.14	$\pm 1.30$
20	150	-0.84	$\pm 1.33$

\* Estimates of bias were made by fitting a regression line to differences between the amounts of sulfate added and found.

\*\* Precision at 95 per-cent confidence level.

formed with macro materials, using a visual end point.

#### Conclusions

The photometric titration method given has a number of advantages over conventional volumetric or colorimetric methods. The tedious approach to the end point used in visual titrations is eliminated by use of the chart recorder. A simple projection of the straight segments of the chart recording serves to position the end point with great precision. Furthermore, the titration is fully automatic, which makes the method rapid. The time required for performing the titration is approximately five minutes. Separation of the sulfate by passing the sample through alumina and Dowex-50 makes possible the use of a large sample, thereby extending the method to the determination of sulfate in the ppm concentration range.

The sulfate separation method described will tolerate large amounts of foreign ions. A detailed study of these interfering ions has been reported.<sup>2,4</sup> Only fluoride and phosphate are not separated in the column separation step. Fluoride may be removed by fuming with perchloric acid.

## References

<sup>1</sup>J. S. Fritz and S. S. Yamamura. Rapid Microtitration of Sulfate, USAEC Report ISC-540. November 12, 1954.

<sup>2</sup>F. J. Miller and P. F. Thomason. Automatic Photometric Titration of Sulfate, USAEC Report ORNL-2040. March 15, 1956.

<sup>3</sup>W. G. Ellis and E. A. Brown. "Automatic Photometric Titrator," Summary Tech. Rpt., USAEC Rpt., USAEC Report NLO-795, p. 113. October 20, 1959 (Classified).

<sup>4</sup>J. S. Fritz, S. S. Yamamura, and M. J. Richard. "Titration of Sulfate Following Separation with Alumina," Anal. Chem. 29: 158. 1957.