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SUMMARY TECHNICAL REPORT FOR THE PERIOD APRIL 1, 1959 TO JUNE 30, 1959 - (USED AS A REFERENCE IN OU 1 RI)

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TECHNOLOGY - FEED MATERIALS 6307

ROUGH DRAFT

SUMMARY TECHNICAL REPORT

For the Period

April 1, 1959 to June 30, 1959

AEC RESEARCH AND DEVELOPMENT REPORT

DECLASSIFIED - PER AUTHORITY OF
W. J. NEYER, C.O. 8-14-92
(DATE)
BY:
(SIGNATURE)
(DATE)
8-14-92

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FEED MATERIALS PRODUCTION CENTER
NATIONAL LEAD COMPANY OF OHIO

ROUGH DRAFT

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6307

NLCO-790
Technology-Feed Materials
(M-3679, 22nd Ed.)

SUMMARY TECHNICAL REPORT FOR THE PERIOD APRIL 1, 1959 TO JUNE 30, 1959

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

EDITED BY
JOHN W. SIMMONS

Date of Issuance: July 20, 1959

NATIONAL LEAD COMPANY OF OHIO
Box 158, Cincinnati 39, Ohio
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Metallurgical Projects Relating to Fabrication, Foundry Technology and Physical Metallurgy.	C. E. Polson, Head, Metallurgical Department.
Pilot Plant Metals Development, Pilot Production, Process Engineering and Refinery Operations.	J. O. Davis, Head, Pilot Plant.
Analytical Chemistry Investigations in Wet Chemical and Instrumental Analysis.	J. W. Robinson, Head, Analytical Department.
Statistical Studies and Technical Illustration Services.	P. N. McCreery, Head, Accountability-Quality Control Department.

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SUMMARY

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Anaconda Acid, Kermac, Moab, Rifle, and Texas Zinc uranium concentrates were evaluated (the laboratory portion of feed material evaluation). 11

Laboratory equilibrium tests and Pilot Plant 2-inch-column extraction tests have demonstrated effective distribution of uranium into a TBP-kerosene solvent from aqueous phases containing as little as 0.5N HNO_3 and varying amounts of added metal nitrates ($NaNO_3$). . 17

The concentration of associated nitric acid in dilute aqueous nitric acid solutions was determined after values were obtained for the equilibrium constant for the reaction of tri-n-butyl phosphate with associated nitric acid and for the equilibrium distribution constant for the partition of associated nitric acid into tri-n-butyl phosphate.

Optimum partition of uranium into tri-n-butyl phosphate was realized in the laboratory by using an aqueous uranyl nitrate solution containing sufficient hydrogen ions to promote extraction and a low concentration of associated nitric acid. 27

An Ohmart system for controlling the uranium profile in the "A" extraction column was installed on Refinery pulse columns. Use of this system improved control but did not stop all column upsets. 37

The effect of 13 to 189 ppm sodium contamination upon hydrofluorination conversion of UO_2 to UF_4 can be decreased or eliminated by reducing the temperature at the site of the reaction.

Uranyl sulfate was shown to undergo an enantiotropic transition at 755°C and to decompose to U_3O_8 in an atmosphere of oxygen and sulfur dioxide, which gases are evolved during decomposition. 41

Decontamination of sodium, calcium, nickel, magnesium, gadolinium, and dysprosium was achieved in a laboratory investigation of the ADU process.

UO_2 produced by reductions programmed from 700° to 1100°F was hydrofluorinated at programmed temperatures of 550° to 1100°F and isothermally at 1100°F. Good conversion was obtained for material whose source was ADU calcined at 1200°F. 49

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A hydraulic separator for separating uranium from magnesium and magnesium fluoride has been fabricated. Excellent separation was obtained for +16 mesh material. 61

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A hydrochloric acid dissolution - UF_4 precipitation process for routing scrap materials to the reduction-to-metal step was examined. The purification obtained was noted, and process conditions were varied to determine their effect upon UF_4 density, UF_4 purity and precipitation time in this laboratory study.

Three types of uranium scrap were subjected to the HCl dissolution-aqueous precipitation Winlo process to determine the purification achieved. Green salt made from dolomitic bomb liner residues was found to be grossly contaminated. Acceptable green salt was made from pickle liquor treated with formaldehyde and from pickle liquor plus black oxide. . . . 67

Nominal 80 per cent yields were obtained (1) in the recovery of magnesium metal by reaction of calcium carbide with magnesium fluoride slag and (2) in the recovery of HF by the reaction of sulfuric acid with magnesium fluoride slag. 77

A sample holder for use in quantitative preferred orientation studies was fabricated. The holder, designed to fit a North American Philips Goniometer, will accommodate specimens up to 1 $^{13}/_{16}$ inches in diameter and incorporates a precision ball bearing. 81

A satisfactory technique has been developed for the analysis of uranium metal for traces of fluoride. 83

A direct flame photometric method is given for the determination of magnesium in uranium ore concentrates. No chemical separation step is required, except for high-iron-content ores. . 89

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1. FEED MATERIALS EVALUATION

C. T. Hicks J. R. Nelli

Abstract

Laboratory digestion and extraction evaluations and complete chemical analyses of five feed materials (Anaconda Acid, Kermac, Moab, Rifle, and Texas Zinc) are reported.

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 FMPC impurity tolerance limits for feed materials, as blending may be necessary to obtain acceptable processing operations with respect to column scale, corrosion, etc.

Test lots of five Colorado feed materials became available this quarter for evaluation and official assayer's samples of each lot were made available for laboratory studies.

Prior Work on Project

The feed materials evaluation program has been in existence since January, 1957. It was previously reported[1-7] that feed material evaluations of 21 feed materials had been completed.

Objective for This Quarter

To initiate and complete the laboratory part of the feed material evaluations for Anaconda Acid, Kermac, Moab, Rifle, and Texas Zinc uranium concentrates.

Summary of Results

Chemical analyses, laboratory digestion tests, and laboratory extraction tests have been completed for the five uranium concentrates. Texas Zinc has been found to exceed the FMPC impurity tolerance limit for total organic material, and Moab to contain excessive amounts of insoluble uranium.

Chemical Analyses of the Concentrates

An official assayer's sample of each concentrate investigated is submitted to the Analytical Department at this site for (1) complete spectrochemical analysis and (2) chemical analyses of constituents for which feed materials impurity tolerance limits[7] exist. Wet chemical and complete spectrochemical analyses of the five new feed materials are presented in Tables 1.1 and 1.2, respectively.

The analyses of the feed materials show that: (1) Anaconda Acid, Kermac, Moab, and Rifle concentrates meet all tolerance limits, and (2) Texas Zinc concentrate meets all tolerance limits except the limit for total organic material (0.12 per cent, uranium basis). The Texas Zinc concentrate will have to be either blended or processed further to meet this tolerance limit.

Laboratory Digestion Tests

Standard digestion tests[6] consist of (1) laboratory digestion of the concentrates in dilute nitric acid, and (2) determination of the following data from a feed slurry containing 250 ± 10 g/l uranium and having a nitric acid concentration of 3.0 ± 0.1N:

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

Digestion data are tabulated in Table 1.3. The results indicate that:

1. Anaconda Acid, Kermac, and Rifle concentrates have good digestion characteristics and

[redacted]

TABLE 1.1 Wet Chemical Analyses of Concentrates
(Results are given in per cent on a sample basis.)

Constituent	Anaconda Acid Lot AD-1604	Kermac Lot KM-13	Moab Lot M-580	Rifle Lot Ri-68	Texas Zinc Lot TZ-104
Uranium (U)	65.96	69.66	69.37	71.24	66.04
Calcium (Ca)	0.62	<0.10	<0.10	<0.10	0.11
Carbonate (CO_3^{-2})	0.74	0.13	<0.10	<0.10	0.50
Chloride (Cl^-)	0.041	0.065	<0.010	<0.010	<0.010
Fluoride (F^-)	<0.010	<0.010	<0.100	<0.010	<0.010
Iron (Fe)	0.14	0.34	1.02	0.19	1.21
Magnesium (Mg)	3.24	1.78	1.86	2.59	2.99
Sodium (Na)	2.38	1.40	0.04	2.55	0.05
Phosphate (PO_4^{-3})	0.03	0.06	0.93	0.12	0.14
Silicon Dioxide (SiO_2)	1.38	0.51	5.91	0.074	0.24
Sulfate (SO_4^{-2})	0.25	6.87	7.83	8.69	4.56
Thorium (Th)	<0.10	<0.10	<0.10	<0.10	<0.10
Total Organic Material	0.08	0.08	0.07	0.08	0.19

TABLE 1.2 Complete Spectrochemical Analyses of Concentrates
(Results are given in parts per million on a uranium basis.)

Constituent		Anaconda Acid Lot AD-1604	Kermac Lot KM-13	Moab Lot M-580	Rifle Lot Ri-68	Texas Zinc Lot TZ-104
Antimony	(Sb)	<10	<10	<10	<10	<10
Arsenic	(As)	<100	100	100	1100	400
Aluminum	(Al)	<400	450	1250	<400	<400
Boron	(B)	25	3	4	8	50
Bismuth	(Bi)	<20	<20	<20	<20	<20
Cadmium	(Cd)	<200	<200	<200	<200	<200
Chromium	(Cr)	<100	<100	650	<100	<100
Copper	(Cu)	<100	<100	<100	<100	<100
Dysprosium	(Dy)	9.6	<4	<4	<4	<4
Erbium	(Er)	5.6	<4	<4	<4	<4
Europium	(Eu)	<4	<4	<4	<4	<4
Gadolinium	(Gd)	9.6	<4	<4	<4	<4
Holmium	(Ho)	<4	<4	<4	<4	<4
Lead	(Pb)	20	80	30	<20	20
Lutetium	(Lu)	<4	<4	<4	<4	<4
Manganese	(Mn)	750	150	50	40	250
Molybdenum	(Mo)	20	30	40	750	50
Nickel	(Ni)	<20	20	30	<20	20
Samarium	(Sm)	6	<4	<4	<4	<4
Terbium	(Tb)	<4	<4	<4	<4	<4
Thulium	(Tm)	<4	<4	<4	<4	<4
Tin	(Sn)	<10	<10	<10	<10	<10
Vanadium	(V)	450	700	500	1800	<100
Yttrium	(Y)	60	16	11	48	<4
Ytterbium	(Yb)	6.4	<4	<4	27	<4
Zinc	(Zn)	<200	<200	<200	<200	<200

[redacted]

TABLE 1.3 Digestion of Concentrates

Concentrate	Acid Consumption*	Volume Change Factor**	Digestion Efficiency*** (%)	Digestion Insolubles† (%)	Digestion Reaction
Anaconda Acid	0.0071	0.946	>99.99	0.55	mild
Kermac	0.0059	0.965	>99.99	0.50	mild
Moab	0.0045	0.992	99.36	5.54	mild
Rifle	0.0049	0.984	>99.99	0.22	mild
Texas Zinc	0.0065	0.958	>99.99	<0.10	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 = Soluble U/Total U

† Per cent by weight of insolubles in the concentrate

TABLE 1.4 Uranium Distribution

The solvent used was 32.8 per cent TBP in kerosene (volume basis).
Results are in grams of uranium per liter.

UNH		Anaconda Acid Concentrate		Kermac Concentrate		Moab Concentrate		Rifle Concentrate		Texas Zinc Concentrate	
Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic
200	129	200	126.9	171	126	162	125	199	128.0	166	127
129.6	127.8	154	125.7	120	121	108	121	167	125.2	111	124
79.4	123.5	100	122.0	73.8	117	69.6	116	110	122.3	65.3	118
39.0	113.7	62.1	117.8	46.1	109	42.3	110	76.5	119.1	39.6	112
16.6	96.5	27.3	109.2	18.7	91.5	15.9	85.5	36.1	110.6	15.6	91.0
5.9	71.5	5.9	74.3	5.0	63.9	4.9	60.0	8.2	80.5	4.4	60.7
—	—	2.5	50.6	2.5	42.6	2.6	41.6	3.0	55.9	2.2	41.8

Note: The nitric acid concentration of the aqueous phase after each equilibration was 3.0N ± 0.2N.

should present no processing problems,

2. Texas Zinc contains an organic substance that floats to the top of the aqueous slurry and is soluble in 33% TBP in kerosene, and

3. Moab concentrate contains considerable insoluble uranium.

Uranium Distribution Curves

Uranium distribution curves[4] for Anaconda Acid, Kermac, Moab, Rifle, and Texas Zinc uranium concentrates were made from data collected from laboratory extraction tests, (i.e. equilibrate equal volumes of aqueous feed slurries of varying uranium concentrations with 33.5% TBP in kerosene). These curves are compared with the distribution curve for pure uranyl nitrate hexahydrate (UNH) solution in Figure 1.1. The distribution data are listed in Table 1.4. The uranium distribution curves for all five concentrates compare favorably with the uranium distribution curve for the UNH solutions. Severe emulsions were encountered when aqueous solutions of Moab were equilibrated with 33% TBP in kerosene. No serious emulsification tendencies were noted with the other four concentrates.

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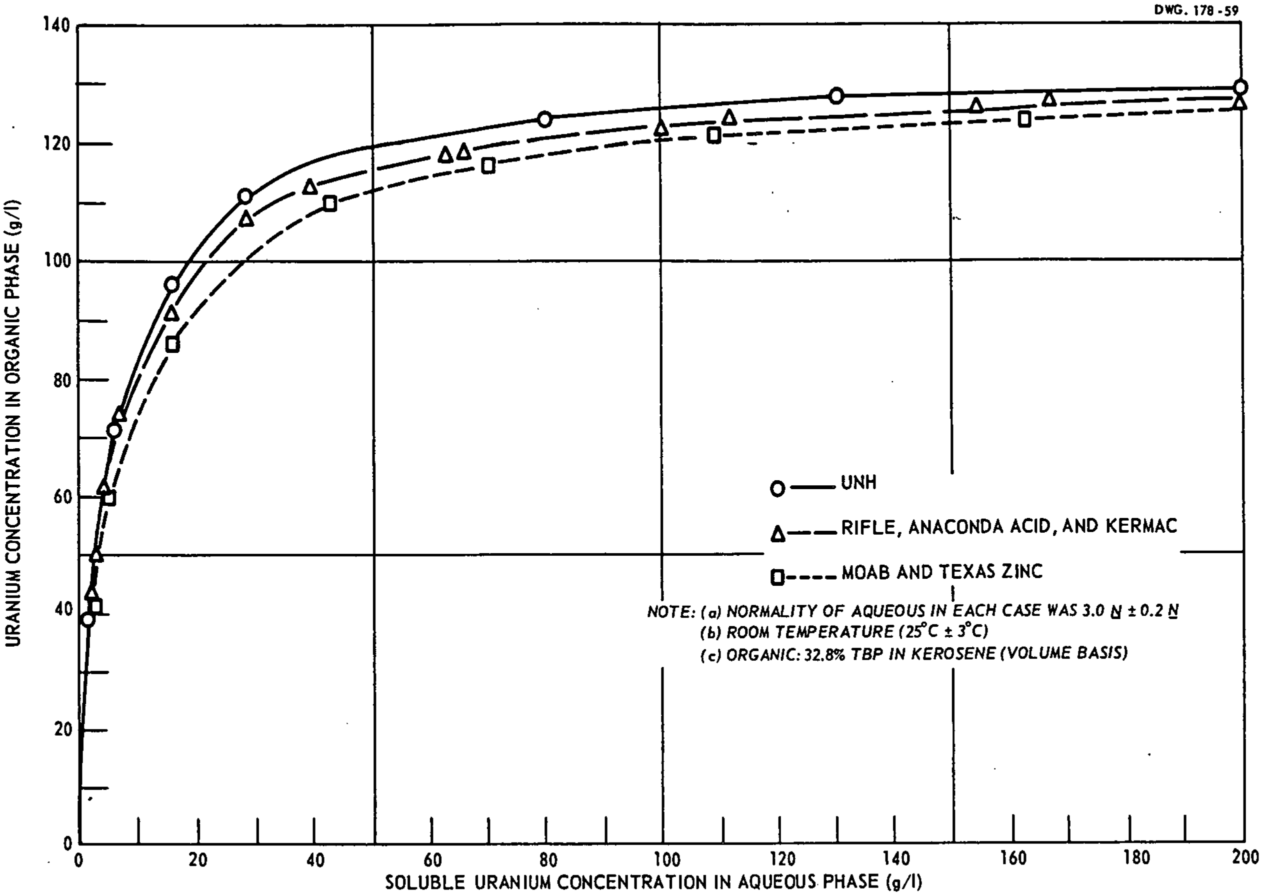

FIGURE 1.1 Laboratory Uranium Distribution Curves.

Future Work

Pilot Plant two-inch pulse column extraction tests will be made for Anaconda Acid, Kermac, Moab, Rifle, and Texas Zinc uranium concentrates. These tests will complete the feed material evaluations of these concentrates. All new concentrates which become available at this site will be evaluated.

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[1] Krekeler, J. H., Hicks, C. T., and Nelli, J. R., *Summary Tech. Rpt., pp. 13-21, NLCO-690, October 21, 1957.*

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[3] Hicks, C. T., Krekeler, J. H., Leist, N. R., and Nelli, J. R., *Summary Tech. Rpt., pp. 13-18, NLCO-725, April 18, 1958.*

[4] Hicks, C. T., Leist, N. R., and Nelli, J. R., *Summary Tech. Rpt., pp. 13-16, NLCO-750, July 18, 1958.*

[5] Leist, N. R., Hicks, C. T., and Nelli, J. R., *Summary Tech. Rpt., pp. 13-21, NLCO-760, October 24, 1958.*

[6] Hicks, C. T., Leist, N. R., and Nelli, J. R., *Summary Tech. Rpt., pp. 11-16, NLCO-775, January 22, 1959.*

[7] Hicks, C. T., Leist, N. R., and Nelli, J. R., *Summary Tech. Rpt., pp. 11-16, NLCO-785, April 15, 1959.*

[redacted]

Editor's Note – The following topical reports were issued during the report period:

NLCO-744 Laboratory and Pilot Plant Evaluation of Colorado Vitro and Canonsburg Vitro Uranium Concentrate. Nelson R. Leist, Clark T. Hicks and Joseph R. Nelli.

NLCO-776 Laboratory and Pilot Plant Evaluation of Miliken Uranium Concentrate. Nelson R. Leist, Clark T. Hicks and Joseph R. Nelli.

NLCO-777 Laboratory and Pilot Plant Evaluation of Stanleigh Uranium Concentrate. Nelson R. Leist, Clark T. Hicks and Joseph R. Nelli.

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2. SELECTIVE DIGESTION

R. K. Klopfenstein C. T. Hicks J. R. Nelli

Abstract

Laboratory tests have demonstrated more favorable uranium distribution into a TBP-kerosene solvent as a result of a reduction of the aqueous acidity from 3N excess acid to 0.5N excess acid, and addition of sodium nitrate to replace part of the removed acid.

Pilot Plant extraction column tests in which uranyl nitrate hexahydrate (UNH) feed was used have demonstrated the operability of a low acid-metal nitrate flowsheet. Similar tests, using normal uranium concentrate feed slurries, have demonstrated operability of the low acid-metal nitrate flowsheet in some cases, but in other cases have shown chemical and physical difficulties, such as emulsification, insolubility of UAP, and $CaSO_4$ scaling.

Introduction

For the past year, a laboratory investigation into the character of the bonding of the tri-n-butyl phosphate-H_2O-U-acid system has been in progress.[1] (See also Section 3 of this report.) During the course of this investigation, much work has been done on uranium partition between various aqueous systems and a tri-n-butyl phosphate (TBP) solvent. Partition has been studied in nitric, sulfuric, hydrochloric, and phosphoric acid media with nitric acid and/or nitrate ions added to either the aqueous or the organic phase. One of the significant conclusions reached during these studies was that a 3N HNO_3 excess in the aqueous phase containing uranium was not necessary to produce effective transfer of uranium into the TBP phase. Replacement of most of the nitric acid with a metal nitrate (notably $NaNO_3$, KNO_3, or NH_4NO_3) would, in fact, result in greatly enhanced distribution of the uranium toward the organic phase.[2] These conclusions, based upon equilibrium tests at only a few uranium concentrations, could not be used to predict the over-all effect of the replacement of nitric acid with metal nitrates upon dynamic pulse column uranium extraction operations throughout the normal concentration range (0 to 300 g/l uranium) encountered in the National Lead Company of Ohio Refinery.

The over-all objectives of the present studies are to thoroughly evaluate the feasibility of a low nitric acid-metal nitrate aqueous system in pulse column extraction operation, and further, to evaluate the possibility of replacing the nitric acid with the less expensive sulfuric acid in such a low acid-metal nitrate aqueous system.

A low nitric acid system or flowsheet was investigated previously in the National Lead Company of Ohio Pilot Plant.[3] At that time, results were unfavorable, but the added concept of extraction enhancement through the addition of soluble metal nitrates made a renewed investigation appear worthwhile. A low acid-metal nitrate flowsheet offered several possible advantages: reduced costs for acid, elimination of nitric acid recovery during aqueous raffinate processing, constructive use of the recycled ammonium nitrate from the recently developed ammonium diuranate (ADU) denitration process, and increased extraction capacity in the Refinery. There were, of course, a number of possible disadvantages: less efficient column operation due to emulsification and/or flooding at the lower acidity, significantly increased $CaSO_4$ scaling, borderline uranium losses in the aqueous raffinate, insolubility of the uranyl ammonium phosphate (UAP) product* from scrap recovery process, and altered decontamination during extraction of uranium values in the primary extraction columns.

---

* *The UAP is a feed to the Refinery.*

Objectives for This Quarter

Initial objectives for the investigation of a low acid-metal nitrate uranium extraction flowsheet were:

1. Laboratory determination of uranium distribution in several systems of low acid-metal nitrate vs. TBP-kerosene solvent, and
2. Pilot Plant evaluation in the 2-inch column extraction system of the several flowsheets. First uranyl nitrate hexahydrate (UNH) feed and then various uranium concentrate feeds were to be used.

Summary of Results Obtained This Quarter

Laboratory uranium distribution curves have demonstrated significant differences in uranium distribution into a TBP-kerosene solvent with varying amounts of nitric acid and/or metal nitrates in the aqueous phase. Use of an aqueous system containing $0.5\underline{N}$ HNO_3 and $2.5\underline{N}$ $NaNO_3$ results in more favorable distribution toward the solvent phase than a system containing $3\underline{N}$ HNO_3

Pilot Plant 2-inch extraction column tests have demonstrated good column operation and uranium extraction when UNH feed solutions were used with low acid and sodium nitrate. Similar tests on uranium concentrates have shown at least three problems: inability to solubilize and process UAP at the low acidity; increased $CaSO_4$ scaling due to the lower acidity, and difficulty in operating the extraction column with a 200 to 275 g/l uranium feed slurry at the low acidity. The latter problem can be alleviated by using a 400 g/l uranium feed slurry.

Laboratory Studies: Uranium Distribution Curves

Uranium distribution was determined between five different aqueous systems and a 33 volume per cent TBP-67 volume per cent kerosene solvent. The aqueous systems investigated were:

1. UNH, $3.0\underline{N}$ HNO_3 after equilibration with the solvent
2. UNH, $0.5\underline{N}$ HNO_3 after equilibration with the solvent
3. UNH, $1\underline{N}$ $NaNO_3$, $0.5\underline{N}$ HNO_3 after equilibration with the solvent
4. UNH, $2.5\underline{N}$ $NaNO_3$, $0.5\underline{N}$ HNO_3 after equilibration with the solvent
5. UNH, $1.5\underline{N}$ $NaNO_3$, $0.5\underline{N}$ H_2SO_4 after equilibration with the solvent

For each of the several systems, appropriate aqueous phases were equilibrated by shaking with equal volumes of the TBP-kerosene solvent. In all cases, the acidity of the aqueous phase was determined before separation of the equilibrated solutions. If necessary, adjustments were made, in which case the solutions were re-equilibrated. Each equilibration was sampled and analyzed for uranium in duplicate and the results were averaged. The equilibrium distribution data are presented in Tables 2.1 through 2.5, and graphical presentations of the results are given in Figures 2.1 through 2.4.

TABLE 2.1 Uranium Distribution Between $3\underline{N}$ HNO_3 and 33.5% TBP-66.5% Shell Dispersol

Aqueous Phase: UNH Solution, $3\underline{N}$ HNO_3 after Equilibration.
Organic Phase: 33.5% TBP-66.5% Shell Dispersol, Non-acidified.
Temperature: 25° ± 1°C.

Aqueous Phase		Distribution Coefficients		Organic Phase	
U (g/l)	H^+ ($\underline{N}$)	U	H^+	U (g/l)	H^+($\underline{N}$)
256.8	3.05	0.51	0.03	132.1	0.090
129.6	2.93	0.99	0.01	127.8	0.030
79.4	2.97	1.56	0.018	123.5	0.054
39.0	2.92	2.91	0.03	113.7	0.10
16.56	2.94	5.83	0.05	96.5	0.15
5.93	3.12	12.0	0.11	71.2	0.34
3.33	3.04	16.7	0.14	55.6	0.44
1.70	2.95	22.9	0.17	38.88	0.51
0.64	2.98	28.9	0.21	18.52	0.62
0.55	2.89	30.0	0.22	16.49	0.64
0.47	2.91	27.2	0.22	12.78	0.65
0.285	2.93	28.5	0.24	8.12	0.69
0.125	2.90	24.0	0.24	3.00	0.70
0.065	2.93	26.2	0.24	1.70	0.71
0.024	2.91	29.1	0.25	0.70	0.72
0.010	2.93	26.0	0.24	0.26	0.71

[redacted]

TABLE 2.2 Uranium Distribution Between $0.5\underline{N}$ HNO_3 and 32.2% TBP-67.8 Shell Dispersol

Aqueous Phase: UNH Solution, $0.5\underline{N}$ HNO_3 after Equilibration.
Organic Phase: 32.2% TBP-67.8% Shell Dispersol, Non-acidified.
Temperature: 25° ± 1°C.

Aqueous Phase		Distribution Coefficients		Organic Phase	
U (g/l)	$H^+(\underline{N})$	U	H^+	U(g/l)	$H^+(\underline{N})$
219.5	0.50	0.51	0.11	121	0.054
139	0.50	0.77	0.12	107	0.062
74.1	0.47	1.26	0.12	93.5	0.056
40.85	0.46	1.72	0.12	70.45	0.055
23.85	0.49	2.19	0.12	52.35	0.061
11.7	0.50	2.86	0.14	33.45	0.068
5.5	0.48	3.27	0.15	18.0	0.071
2.6	0.48	2.94	0.14	7.65	0.069
1.2	0.48	4.08	0.16	4.9	0.075
0.715	0.48	4.20	0.16	3.0	0.077
0.235	0.48	3.28	0.16	0.77	0.078
0.12	0.48	3.50	0.16	0.42	0.079

TABLE 2.3 Uranium Distribution Between $0.5\underline{N}$ HNO_3-$1.0\underline{N}$ HNO_3 and 32.2% TBP-67.8% Shell Dispersol

Aqueous Phase: UNH Solution, $1\underline{N}$ $NaNO_3$, $0.5\underline{N}$ HNO_3 after Equilibration
Organic Phase: 32.2% TBP-67.8% Shell Dispersol, Non-acidified.
Temperature: 25° ± 1°C.

Aqueous Phase		Distribution Coefficients		Organic Phase	
U (g/l)	$H^+(\underline{N})$	U	H^+	U (g/l)	$H^+(\underline{N})$
201.5	0.48	0.63	0.12	127.9	0.056
131.5	0.47	0.91	0.12	120	0.057
57.4	0.49	1.88	0.12	108	0.060
22.75	0.48	3.84	0.14	87.25	0.065
9.7	0.47	7.02	0.17	68.05	0.081
3.4	0.49	11.99	0.23	40.75	0.113
1.2	0.49	18.33	0.29	22.0	0.140
0.60	0.48	29.83	0.32	17.9	0.153
0.32	0.48	22.97	0.34	7.35	0.164
0.17	0.47	29.71	0.34	5.05	0.161
0.053	0.48	17.26	0.35	0.915	0.170
0.0315	0.47	17.62	0.37	0.555	0.174

TABLE 2.4 Uranium Distribution Between $0.5\underline{N}$ HNO_3-$2.5\underline{N}$ $NaNO_3$ and 32.2% TBP-67.8% Shell Dispersol

Aqueous Phase: UNH Solution, $2.5\underline{N}$ $NaNO_3$, $0.5\underline{N}$ HNO_3 after Equilibration.
Organic Phase: 32.2% TBP-67.8% Shell Dispersol, Non-acidified.
Temperature: 25° ± 1°C.

Aqueous Phase		Distribution Coefficients		Organic Phase	
U (g/l)	$H^+(\underline{N})$	U	H^+	U (g/l)	$H^+(\underline{N})$
177.5	0.52	0.74	0.11	131.5	0.057
127	0.51	1.00	0.10	126.5	0.051
45.7	0.53	2.58	0.12	118	0.066
9.15	0.49	10.51	0.19	96.15	0.094
3.1	0.50	23.11	0.28	71.65	0.142
1.1	0.51	41.14	0.40	45.25	0.202
0.365	0.48	63.42	0.52	23.15	0.249
0.155	0.52	76.81	0.55	11.75	0.284
0.074	0.49	89.46	0.59	6.62	0.857
0.040	0.49	99.75	0.61	3.99	0.297
0.013	0.49	107.69	0.61	1.40	0.300
0.0055	0.49	84.55	0.62	0.465	0.304

TABLE 2.5 Uranium Distribution Between $0.5\underline{N}$ H_2SO_4-$1.5\underline{N}$ $NaNO_3$ and 32.2% TBP-67.8% Shell Dispersol

Aqueous Phase: UNH Solution, $1.5\underline{N}$ $NaNO_3$, $0.5\underline{N}$ H_2SO_4 after Equilibration.
Organic Phase: 32.2% TBP-67.8% Shell Dispersol, Non-acidified.
Temperature: 25° ± 2°C.

Aqueous Phase		Distribution Coefficients		Organic Phase	
U (g/l)	$H^+(\underline{N})$	U	H^+	U (g/l)	$H^+(\underline{N})$
156.5	0.54	0.77	0.12	121	0.063
96.1	0.49	1.16	0.14	111.5	0.068
48.9	0.51	1.82	0.13	88.95	0.065
27.6	0.50	2.35	0.12	64.95	0.060
18.25	0.50	2.69	0.16	49.1	0.080
9.85	0.48	2.90	0.19	28.55	0.090
5.0	0.48	2.83	0.19	14.15	0.095
2.6	0.49	3.21	0.21	8.35	0.104
1.3	0.48	3.96	0.21	5.15	0.101
0.76	0.49	5.20	0.21	3.95	0.103
0.255	0.48	2.29	0.21	0.585	0.103
0.18	0.48	2.42	0.23	0.435	0.109

[redacted]

[redacted]

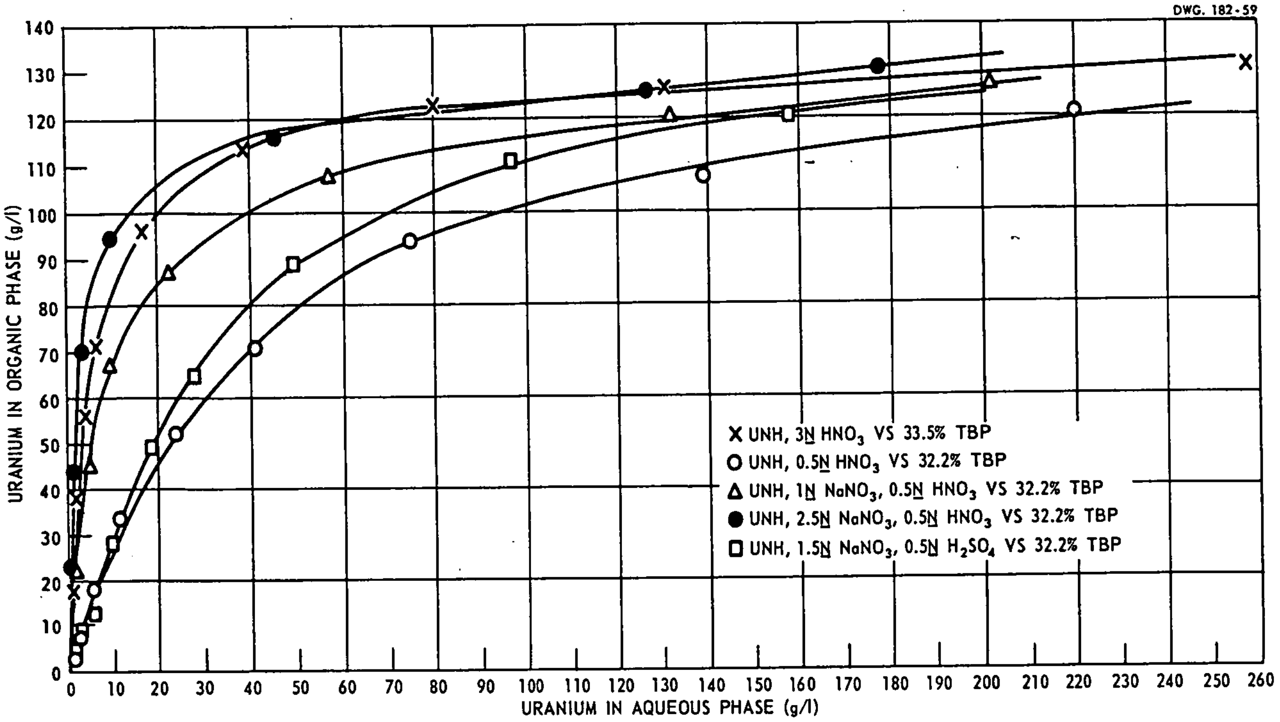

FIGURE 2.1 Uranium Distribution in Five Aqueous-Solvent Systems – 0 to 260 g/l Uranium in Aqueous Phase.

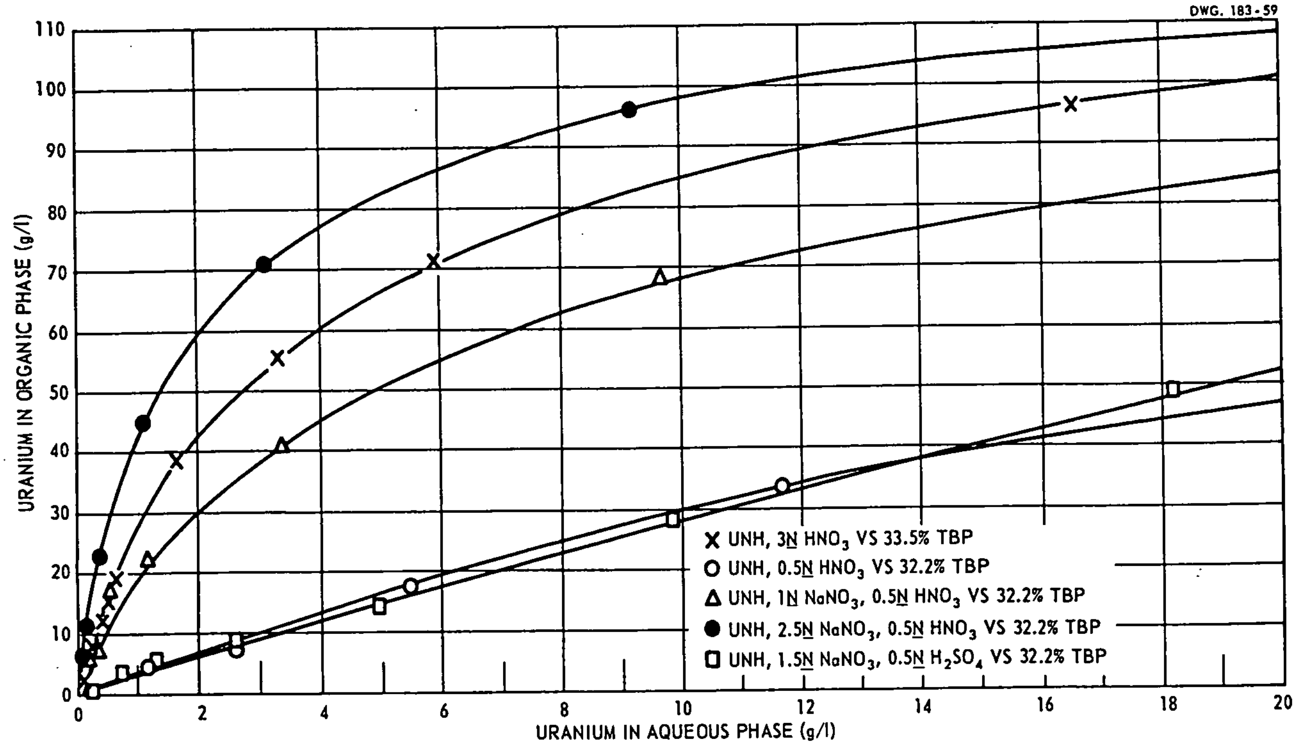

FIGURE 2.2 Uranium Distribution in Five Aqueous-Solvent Systems – 0 to 20 g/l Uranium in Aqueous Phase.

[redacted]

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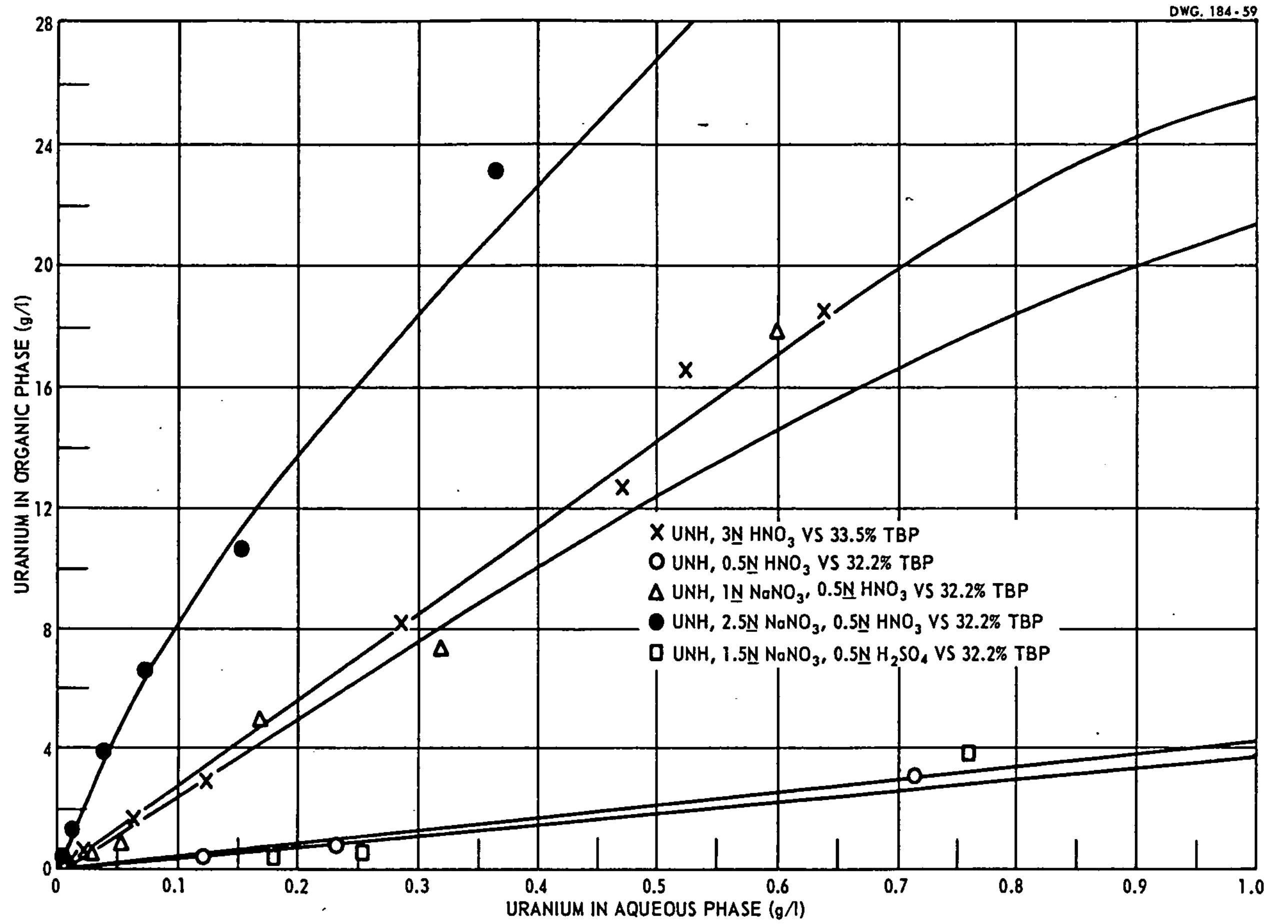

FIGURE 2.3 Uranium Distribution in Five Aqueous-Solvent Systems – 0 to 1 g/l in Aqueous Phase

The interpretation of these equilibrium distribution curves in terms of operation of a pulse column under steady-state conditions is based, at least partially, upon the presence and intensity of the "bulge" in the distribution curve at lower uranium concentrations in the aqueous phase. This means, in essence, the presence of a high distribution coefficient (D.C.) for uranium, favoring the organic phase:

$$\text{D. C.} = \left[\frac{[\text{U}]\text{org}}{[\text{U}]\text{Aq}}\right]$$

On this basis, it is readily apparent that uranium distribution into the organic phase is seriously hampered by a reduction in aqueous nitric acid concentration from 3$\underline{\text{N}}$ to 0.5$\underline{\text{N}}$. It is also apparent that addition of sodium nitrate, to replace part or all of the removed nitric acid, is very beneficial in increasing the distribution of the uranium into the organic phase. In fact, addition of 2.5$\underline{\text{N}}$ $NaNO_3$, bringing the total excess nitrate ion concentration back to 3$\underline{\text{N}}$, results in more favorable uranium distribution than that noted for 3$\underline{\text{N}}$ excess nitric acid. The 0.5$\underline{\text{N}}$ HNO_3 - 1$\underline{\text{N}}$ $NaNO_3$ system is not far removed from the 3$\underline{\text{N}}$ HNO_3 system, and it would seem that a 0.5$\underline{\text{N}}$ HNO_3 - 1.5 to 2$\underline{\text{N}}$ $NaNO_3$ system would closely approximate the 3$\underline{\text{N}}$ HNO_3 system.

Interpretation of the 0.5$\underline{\text{N}}$ H_2SO_4-1.5$\underline{\text{N}}$ $NaNO_3$ system is affected by the character of sulfuric acid as an excellent re-extraction or stripping agent for uranium. Thus, at higher uranium concentrations in the aqueous phase, this system

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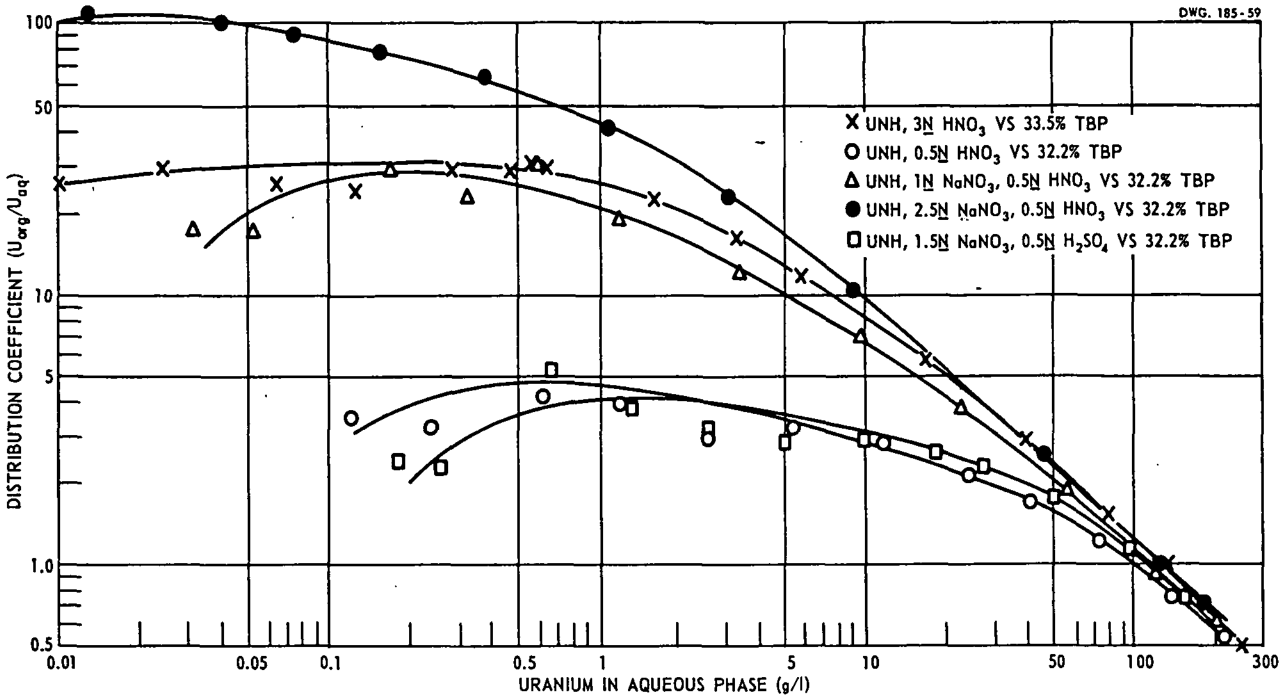

FIGURE 2.4 Uranium Distribution Coefficients for Five Aqueous Solvent Systems

closely resembles the 0.5N HNO_3 - 1N $NaNO_3$ system (the latter system has, of course, the same concentrations of hydrogen and nitrate ions). However, as the uranium concentration in the aqueous phase decreases, the distribution in the 0.5N H_2SO_4 - 1.5N $NaNO_3$ becomes less similar to the 0.5N HNO_3 - 1N $NaNO_3$, and approaches or possibly falls below the distribution in the 0.5N HNO_3 system. This behavior is interpreted in terms of the re-extracting or stripping ability of the sulfate ion at lower uranium concentrations.

Although these laboratory distribution curves revealed favorable equilibrium behavior for low acid-metal nitrate systems, predictions as to the feasibility of Refinery use of any of the systems considered could not be made until the systems had been tested in steady state pulse column use.

Pilot Plant Extraction Tests With UNH Feed Solutions

A total of six Pilot Plant 2-inch extraction column tests* were made, using standard UNH feed solutions. Each of the five aqueous systems discussed in the preceding section was tested in the primary extraction ("A") column, and the 0.5N HNO_3 system was tested using both the primary extraction column and the scrub ("B") column. The details and results of these extraction tests are presented in Table 2.6.

Extraction column behavior was good during all of these tests. In evaluating the test results, it should be noted that there were variations in the uranium content of the aqueous feed (AF), but in all but two cases (Tests No. 2 and No. 6) these were nullified or eliminated by control of the organic product (AP) density and thereby the AP uranium content. The primary point of evaluation of the remaining four tests is the variation in uranium content of the aqueous raffinate (AR) with changes in nitric acid and sodium nitrate

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* *The Pilot Plant 2-inch extraction column system has been described previously, as have the typical extraction tests using that system.*[4]

[redacted]

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TABLE 2.6 Pilot Plant 2-Inch Extraction Column Tests* Using UNH Feeds with Various Nitric Acid and Sodium Nitrate Concentrations

	Test No. 1	Test No. 2	Test No. 3	Test No. 4	Test No. 5**	Test No. 6
Aqueous Feed (AF)	205 g/l U $3.08\underline{N}$ H^+ $0\underline{N}$ $NaNO_3$	193.7 g/l U $0.64\underline{N}$ H^+ $0\underline{N}$ $NaNO_3$	207 g/l U $0.63\underline{N}$ H^+ $0.97\underline{N}$ $NaNO_3$	199.7 g/l U $0.56\underline{N}$ H^+ $2.27\underline{N}$ $NaNO_3$	188.3 g/l U $0.48\underline{N}$ H^+ $1.68\underline{N}$ $NaNO_3$	254.3 g/l U $0.61\underline{N}$ H^+ $0\underline{N}$ $NaNO_3$
Organic Extractant (AX)	0.28 g/l U 33.5% TBP	0.20 g/l U 33.3% TBP	0.16 g/l U 33.7% TBP	0.15 g/l U 33.2% TBP	0.38 g/l U 32.9% TBP	0.35 g/l U 33.9% TBP
Aqueous Raffinate (AR)	0.012 g/l U $2.98\underline{N}$ H^+	0.033 g/l U $0.56\underline{N}$ H^+	0.009 g/l U $0.46\underline{N}$ H^+	0.0055 g/l U $0.37\underline{N}$ H^+	0.053 g/l U $0.41\underline{N}$ H^+	0.082 g/l U $0.41\underline{N}$ $H^{\pm}$
Organic Product (AP)	115.7 g/l U $0.20\underline{N}$ H^+	108.3 g/l U $0.076\underline{N}$ H^+	115.3 g/l U $0.074\underline{N}$ H^+	115.9 g/l U $0.113\underline{N}$ H^+	117.3 g/l U $0.062\underline{N}$ H^+	120 g/l U $0.10\underline{N}$ H^+
Aqueous Scrub Recycle (BR)	Tests 1 through 5 did not utilize the Scrub ("B") Column					139.7 g/l U $0.533\underline{N}$ H^+
Scrubbed Organic Product (BP)						112 g/l U $0.087\underline{N}$ H^+
Flowrates						
AF	7.46 gph	7.53 gph	7.54 gph	7.87 gph	8.12 gph	6.03 gph
AX	12.74 gph	12.83 gph	12.73 gph	12.90 gph	12.45 gph	13.10 gph
AR	7.05 gph	7.06 gph	6.91 gph	7.31 gph	7.67 gph	6.36 gph
AP	13.92 gph	13.31 gph	13.63 gph	13.65 gph	13.06 gph	13.70 gph
BR	—	—	—	—	—	0.79 gph
BP***	—	—	—	—	—	13.57 gph
Column Throughput						
"A"	990 gsfh	998 gsfh	994 gsfh	1013 gsfh	1008 gsfh	976 gsfh
"B"	—	—	—	—	—	710 gsfh
Material Balance						
"A" U	+5.06%	-1.35%	+0.56%	+0.54%	-0.08%	-0.27%
H^+	+3.55%	+3.09%	-11.83%	-3.63%	+1.51%	-3.59%
"B" U	—	—	—	—	—	-0.84%
H^+	—	—	—	—	—	+16.9%
Over-all U	—	—	—	—	—	-1.18%
H^+	—	—	—	—	—	+2.31%
Raffinate U Ratio†	1.00	2.75	0.75	0.46	4.42	6.67

* Chemical analyses represent the average of three samples taken at 30 minute intervals after the column(s) reached steady-state conditions.

** For Test No. 5, the H^+ was present as H_2SO_4.

*** BP flowrate has been estimated at 99% of the AP flowrate. No measuring or metering devices are included in the system.

† Raffinate U Ratio is the ratio of the uranium in the AR for the system in question to the uranium in the AR for the $3\underline{N}$ excess HNO_3 system.

[redacted]

concentrations in the AF. Comparisons of these AR uranium losses with the distribution curves for the corresponding systems reveals essentially the variations anticipated, i.e., removal of 2.5N nitric acid is detrimental, but 1N added sodium nitrate is about as good as 3N HNO_3, and 2.5N added sodium nitrate is better than 3N nitric acid. Further, the sulfuric acid system is not as favorable as any of the others.

Pilot Plant Extraction Tests With Uranium Concentrate Feed Slurries

A total of seven Pilot Plant 2-inch extraction column tests were made or attempted, using various uranium concentrates, acidities, and sodium nitrate contents. The tests were:

Test 1. Northspan Concentrate blended with uranyl ammonium phosphate (UAP) to provide 10% $PO_4^{\equiv}$ on a uranium basis; digested to a nominal 240 g/l uranium, 0.5N H^+, with no added $NaNO_3$.

Test 2. Northspan concentrate digested to a nominal 240 g/l uranium, 0.5N H^+, with no added $NaNO_3$.

Test 3. Northspan concentrate digested to a nominal 240 g/l uranium, 3N H^+, with no added $NaNO_3$.

Test 4. South African Concentrate digested to a nominal 240 g/l uranium, 0.5N H^+, with no added $NaNO_3$.

Test 5. South African Concentrate digested to a nominal 400 g/l uranium, 0.5N H^+, with no added $NaNO_3$.

Test 6. South African Concentrate digested to a nominal 400 g/l uranium, 0.5N H^+, with 1N added $NaNO_3$.

Test 7. Dyno concentrate digested to a nominal 400 g/l uranium, 0.5N H^+, with 0.5N added $NaNO_3$.

Tests 1 through 4 were unsuccessful for the various reasons detailed below. Tests 5 through 7 were completed as planned, and the details and results are presented in Table 2.7.

Test 1. The "A" column flooded consistently, even at reduced organic extractant (AX) rates, and a persistent foam layer interfered with proper phase disengagement at the raffinate end of the column. It is quite probable that the UAP was partially insoluble at 0.5N H^+, and that this condition contributed markedly to the inoperability of the "A" column.

Test 2. The "A" column again flooded consistently, and the foam layer in the disengagement section was again harmful. The acidity of the AF was increased from 0.5N to $\sim$1.0N with no benefit to column operation.

Test 3. This test was planned to determine whether or not the Northspan concentrate lot under test would operate successfully in the "A" column at the normal 3N excess nitric acid level. The test was not successful. The column flooded badly at 1000 gsfh, and previous failures (Tests 1 and 2) were now attributed, in large part, to the uranium concentrate rather than the low acidity.

Test 4. South African concentrate was used for this test. At AF concentrations of $\sim$250 g/l uranium, 0.5N H^+, the "A" column consistently flooded at 1000 gsfh. The column was operable at 600 gsfh, but not at higher throughputs.

Test 5. South African concentrate was used for this test, but was digested to a AF of $\sim$400 g/l uranium, 0.5N H^+. This increased uranium concentration of the AF resulted in a marked decrease in "A" column volume throughput without detriment to the uranium throughput. Column operation was good, but $CaSO_4$ scaling at the raffinate end of the column was serious, and caused periodic plugging in the raffinate removal equipment.

Test 6. The details and results of this test were identical with those of Test 5 above, except that the AF contained 1N added $NaNO_3$. As in Test 5, $CaSO_4$ scaling was serious.

Test 7. In this case, Dyno concentrate was the feed material. (This concentrate has a very low Ca × SO_4 number, and should not cause $CaSO_4$ scaling). The AF contained $\sim$400 g/l uranium, 0.5N H^+, and 0.5N added $NaNO_3$. Column opera-

[redacted]

TABLE 2.7 Pilot Plant 2-Inch Extraction Column Tests, Using Uranium Concentrates with Low Nitric Acid-Sodium Nitrate

	Test No. 5	Test No. 6	Test No. 7
Aqueous Feed (AF)	416 g/l U 0.38$\underline{N}$ H^+ 0$\underline{N}$ $NaNO_3$	393 g/l U 0.4$\underline{N}$ H^+ 1$\underline{N}$ $NaNO_3$	369 g/l U 0.69$\underline{N}$ H^+ 0.5$\underline{N}$ $NaNO_3$
Organic Extractant (AX)	0.3 g/l U 33% TBP	0.15 g/l U 34% TBP	0.25 g/l U 33.7% TBP
Aqueous Raffinate (AR)	15.4 g/l U 0.27$\underline{N}$ H^+	0.36 g/l U 0.22$\underline{N}$ H^+	0.014 g/l U 0.13$\underline{N}$ H^+
Organic Product (AP)	113 g/l U 0.058$\underline{N}$ H^+	118 g/l U 0.075$\underline{N}$ H^+	104 g/l U 0.247$\underline{N}$ H^+
Aqueous Scrub Recycle (BR)	110 g/l U 0.51$\underline{N}$ H^+	85 g/l U 0.75$\underline{N}$ H^+	26 g/l U 2.56$\underline{N}$ H^+
Scrubbed Organic Product (BP)	107 g/l U 0.032$\underline{N}$ H^+	105 g/l U 0.035$\underline{N}$ H^+	100.7 g/l U 0.076$\underline{N}$ H^+
Flowrates			
AF	3.65 gph	3.91 gph	3.58 gph
AX	13.10 gph	13.10 gph	13.07 gph
AR	3.72 gph	3.51 gph	3.72 gph
AP	14.15 gph	13.62 gph	13.85 gph
BR	0.81 gph	0.81 gph	0.78 gph
BP*	14.01 gph	13.48 gph	13.71 gph
Column Throughputs "A"	860 gsfh	872 gsfh	853 gsfh
"B"	715 gsfh	690 gsfh	716 gsfh
Material Balances			
"A" U	+3.88%	-1.61%	+8.98%
"A" H^+	+2.78%	-16.4%	-12.54%
"B" U	-0.61%	-3.43%	-2.74%
"B" H^+	+6.17%	+7.84%	-11.17%
Over-all U	+3.46%	-5.20%	+5.80%
Over-all H^+	+7.19%	-17.8%	-38.2%
Scrub Ratio, AP/BR	~18/1	~18/1	~18/1

* BP flowrate has been estimated at 99% of the AP flowrate. No measuring or metering device is included in the system.

tion was good, and the test was successful.

Evaluations of these extraction tests of uranium concentrates must, of course, be based primarily on the results of the three successful tests. Suffice to say that Tests 1 through 4 indicate first, that UAP cannot be successfully processed with the tested low acid flowsheet because of its insolubility, and second, that a high uranium concentration in the AF (~400 g/l uranium) is needed to make a low acid flowsheet operable. The high uranium feed allows reduction of the "A" column volume throughput without reducing the uranium throughput.

For tests 5 and 6 (comparable except for the 1$\underline{N}$ added $NaNO_3$), the most obvious point of comparison is the very large reduction in AR uranium loss due to the 1$\underline{N}$ added $NaNO_3$ (15.4 g/l uranium for Test 5 versus 0.36 g/l uranium for Test 6). This reduction occurred despite a 5 g/l uranium increase in the AP uranium concentration. The results of Test 6, disregarding the problem of $CaSO_4$ scaling, are quite promising as regards future use of a low acid-metal nitrate flowsheet in the Refinery.

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Test 7 indicated very favorable results on a low-$CaSO_4$ concentrate. AR losses were very low (0.014 g/l uranium), while AP and BP uranium concentrations were good (104 g/l uranium and 100.7 g/l uranium).

Discussion and Conclusions

Laboratory determinations of uranium distribution between various low acid-metal nitrate aqueous systems and a TBP-kerosene solvent have demonstrated a profound effect upon uranium distribution as a result of reduction in the acid content of the aqueous phase, and as a result of subsequent addition of nitrate ions to the aqueous phase.

Pilot Plant extraction tests in which a synthetic feed was used have demonstrated successful use of a low acid-metal nitrate flowsheet. Demonstration tests in which uranium concentrates were used have been partially successful. The latter tests have pinpointed at least three major difficulties:

1. UAP cannot be solubilized and thereby processed in the Refinery in an 0.5N acid system (on the basis of present results and other unpublished data).
2. A low acid system greatly reduces the Ca × SO_4 level permissible in the feed slurry. As a result, many of the normal concentrates may be difficult to process in a low acid system due to $CaSO_4$ scaling in the "A" column.
3. Satisfactory pulse column operation is doubtful at the normal AF uranium level (200-275 g/l uranium), but this problem appears to be nullified by increasing the AF uranium concentration to ~400 g/l uranium.

Future Work

Laboratory investigations concerning (1) the processing of UAP in a low-acid system and (2) the appearance and prevention of $CaSO_4$-scaling at low acidities are anticipated.

Further Pilot Plant testing of the low acid-metal nitrate flowsheet will establish its applicability to the Refinery, and will establish the usable levels of nitric acid and metal nitrate.

References

[1] Collopy, T. J., Cavendish, J. H., Stock, D. A., and Miller, W. S., *Summary Tech. Rpt., pp 17-23, NLCO-785, April 15, 1959.*

[2] *Ibid., p. 19.*

[3] Cseplo, S. and Taylor, C. W., *Summary Tech. Rpt., p. 27, NLCO-577, October 20, 1955.*

[4] Krekeler, J. H., Hicks, C. T., and Nelli, J. R., *Summary Tech. Rpt., p. 19, NLCO-690, October 21, 1957.*

[redacted]

3. BONDING IN THE TRI-N-BUTYL PHOSPHATE-H_2O-U-ACID SYSTEM

T. J. Collopy J. H. Cavendish W. S. Miller D. A. Stock

Abstract

The equilibrium constant for the reaction of tri-n-butyl phosphate with associated nitric acid was calculated to be 20 ± 0.26. The equilibrium distribution constant for the partition of associated nitric acid into tri-n-butyl phosphate was determined as 0.19. The equilibrium constants obtained were used to calculate the concentration of associated nitric acid in dilute aqueous nitric acid solutions.

Additional data relating to uranium distribution into tri-n-butyl phosphate showed that optimum partition is realized when the aqueous uranyl nitrate solution contains (1) sufficient hydrogen ions to promote extraction and (2) a low concentration of associated nitric acid to minimize competition for the tri-n-butyl phosphate between uranium and associated nitric acid.

Introduction

The investigation of the basic chemistry of the TBP - $UO_2(NO_3)$ - HNO_3 - water - impurities system used at this site has shown that the $TBP\cdot HNO_3$ complex should be considered as a component of the extraction process. The concentration of the $TBP\cdot HNO_3$ complex in the organic phase is shown herein to limit the amount of uranium that can be extracted by TBP.

In a previous report[1], data were presented which showed that a stable, equimolar complex was formed by the reaction of associated nitric acid (HNO_3) with tri-n-butyl phosphate (TBP). It was concluded from these results that the previous postulate[2] (that this same reaction takes place between TBP and associated nitric acid in the two-phase system, TBP-H_2O-HNO_3) was valid, since associated nitric acid is present in aqueous nitric acid solutions.

This two-phase system can then be represented by (1) an equilibrium reaction in the organic phase,

$$TBP_{org} + (HNO_3)_{org} \rightleftarrows (TBP\cdot HNO_3)_{org} \qquad (1)$$

(2) an equilibrium reaction in the aqueous phase,

$$(HNO_3)_{aq} + H_2O_{aq} \rightleftarrows H_3O^+_{aq} + (NO_3^-)_{aq} \qquad (2)$$

and (3) an equilibrium distribution constant (D.C.) for associated nitric acid between phases.

$$D.C. = HNO_{3org}/(HNO_3)_{aq} \qquad (3)$$

By substituting the value for the associated nitric acid in the organic phase for Equation 3 into Equation 1 and then solving for the equilibrium constant (K_{eq}) for the equilibrium reaction shown by Equation 1, Equation 4 is obtained.

$$K_{eq} = [TBP\cdot HNO_3]_{org}/[(D.C.)(HNO_3)_{aq}].[TBP]_{org} \qquad (4)$$

The value for K_{eq} for Equation 1 can be calculated from the data[2] which were obtained in constructing the equilibrium distribution curve for nitric acid between TBP and water. For use with these experimental data, Equation 4 would take the form

$$K_{eq} = \frac{[\text{total organic acidity} - (D.C.)(HNO_3)_{aq}]}{[(D.C.)(HNO_3)_{aq}]\ [TBP]_{org}} \qquad (5)$$

Equation 5 can be applied by (1) obtaining values for the concentration of associated nitric acid in aqueous nitric acid solution from literature data, (2) assuming a value for the equilibrium distribution constant between phases, (3) calculating the concentration of uncombined nitric acid in the TBP phase, (4) calculating the concentration of $TBP\cdot HNO_3$ complex by subtracting the "uncombined nitric acid in the TBP phase" from the total titratable acid in the TBP phase, and (5) calculating the value for uncombined TBP by subtracting the value for the concentration of the $TBP\cdot HNO_3$ complex from the starting concentration of TBP and compensating for the volume change. These results, when the correct value for the

[redacted]

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distribution constant is used, would show the value of the equilibrium constant for the reaction of nitric acid and TBP in the TBP phase.

Since pure TBP was used in these studies, the theoretical molarity at which the molarity of TBP would equal the molarity of the nitric acid in the TBP phase can be calculated (i.e., 3.18M). In the two-phase TBP-H_2O - HNO_3 system, this condition in the TBP phase is reached at an aqueous nitric acid concentration of 7M (i.e., 2M associated nitric acid).[2] The equilibrium partition data and the spectral data reported previously[1,2] both showed that beyond this point, the additional nitric acid entering the TBP phase could be attributed to solvent partition rather than further complex formation. This being the case, the region above this point can be separated from the region of complex formation and examined for the value of the equilibrium distribution constant. This can be done by dividing the concentration of associated nitric acid in the TBP phase by the concentration of associated nitric acid in the aqueous phase. This latter value can be obtained from literature data. The value obtained in this way for the equilibrium distribution constant (D.C.) should be close to the assumed value used in Equation 5 for the calculation of the equilibrium constant.

Since values for associated nitric acid in aqueous nitric acid solution are unavailable for the range between 0.5 and 4M, the constants which are obtained can be used together with the data from the equilibrium curve to calculate values for the concentration of associated nitric acid in dilute aqueous nitric acid solution. These values were formerly assumed to be negligible.

Several investigators[3-8] have shown that the partition coefficient for metal nitrates-e.g., $[UO_2(NO_3)_2]$-into TBP passes though a maximum with increasing concentrations of nitric acid in the equilibrium aqueous solution. The data which have been previously reported[1,2,9-12] in this investigation of the chemistry of the TBP-uranium solvent extraction process indicate that this system can be tentatively described by the following equation:

$$(UO_2^{++})_{aq} + (2HNO_3 \cdot TBP)_{org} \rightleftarrows [UO_2(NO_3TBP)_2]_{org} + 2H^+_{aq} \qquad (6)$$

This reaction shows that a minimum amount of nitric acid is necessary to the TBP-uranium extraction process, but that excessive nitric acid in the equilibrium aqueous solution will shift the reaction to the left, thereby favoring the formation of the $HNO_3 \cdot TBP$ complex in the organic phase. In order to overcome this undesirable condition, it is believed that uranium partition into TBP can be greatly enhanced by optimizing the amounts of hydrogen and nitrate ions added to the extraction process. For example, the hydrogen ion concentration should be sufficient to furnish the amount required for extraction but low enough to prevent harmful competition for the TBP. The nitrate concentration under these conditions could be increased to give the desired uranium partition into TBP without shifting the nitric acid equilibrium in the aqueous phase to the extent that sufficient associated nitric acid for the competitive reaction with TBP would be formed.

Since the TBP-uranium extraction process used at FMPC employs nitric acid for digestion and excess nitric acid for extraction, it is possible that by optimizing the concentrations of hydrogen and nitrate ions, considerable economic benefits might be realized from a low-acid, high-nitrate flowsheet. The possibilities exist that only a small concentration of nitric acid need be added to the feed batch after digestion, assuming that sufficient salts are present in the original ore concentrate to produce the nitrate salt required for optimum extraction.

In order to determine the optimum concentrations of hydrogen and nitrate ions for extraction, laboratory partition data as a function of hydrogen and nitrate ions were collected. It had been shown in previously reported data[9,12] that uranium partition into TBP is a function of the amount of $TBP \cdot HNO_3$ complex present in the TBP phase and that nitrate

[redacted]

salts plus nitric acid aid uranium partition to a greater extent than does nitric acid alone. Further data at various initial uranium concentrations were collected to determine the concentrations of hydrogen and nitrate ions which should be present in aqueous uranyl nitrate solutions to provide for optimum uranium partition into TBP.

Objectives For This Quarter

1. To determine the equilibrium constants for the tri-n-butyl phosphate-water-nitric acid system.
2. To determine the effects of hydrogen and nitrate ions on uranium partition into tri-n-butyl phosphate at various initial uranyl nitrate concentrations.

Summary of Results Obtained This Quarter

Data are presented which show that the value for the equilibrium distribution constant is 0.19 and the value for the equilibrium reaction constant is 20 ± 0.26 for the partition of associated nitric acid into TBP and the reaction of this acid in TBP to form a complex. These constants were used to arrive at values for the concentration of associated nitric acid in dilute aqueous nitric acid solutions. These data are offered as indicating that only one complex forms between TBP and nitric acid in a two-phase TBP-H_2O-HNO_3 system.

Further laboratory tests of the effects of sodium nitrate and nitric acid on uranium partition into TBP showed that nitrate salts plus nitric acid aid uranium partition to a greater extent than nitric acid alone and that this effect is not dependent on the initial uranyl nitrate concentration. These results suggest that a low acid, high nitrate flowsheet be considered for the FMPC Refinery.

Equilibrium Constants for the System, TBP-HNO_3-H_2O

The procedure employed to obtain data on the nitric acid distribution into TBP was as follows: Aqueous nitric acid solutions of varying molarities were prepared by adding the required concentration of reagent grade nitric acid (70%) to distilled water. The molarities of the initial aqueous nitric acid solutions were determined by titration of samples with standard alkali to a phenolphthalein endpoint.

The nitric acid equilibrium distribution data were obtained by mixing the aqueous nitric acid solutions with tri-n-butyl phosphate (commercial grade, produced by Ohio Apex Division of the Food and Machinery Chemical Company) for a period of three minutes at constant temperature. The apparatus used was a separatory funnel equipped with an interfacial stirrer. The mixture was allowed to separate, and the phases were sampled and analyzed. The acidities of both the aqueous and organic phases were determined by titration with standard alkali to a phenolphthalein endpoint. The organic aliquot was added to an excess of distilled water and the titration was made directly on this mixture.

The equilibrium curve for the distribution of nitric acid between TBP and water at 25°C is presented in Figure 3.1 at aqueous nitric acid concentrations of 0 to 12 molar. These results show that the ratio of the total nitric acid in the TBP phase to the total nitric acid in the aqueous phase decreases with increasing aqueous nitric acid concentration until a constant value is obtained. This behavior was shown by previous reports[7,10] to be attributable to (1) the partition of associated nitric acid between TBP and water plus equimolar complex formation, and (2) partition of associated nitric acid alone between TBP and water at higher aqueous nitric acid concentrations with no additional significant complexes being formed [e.g., TBP·$(HNO_3)_2$].

By the use of Equation 5 and an assumed value for the equilibrium distribution constant, the value for K_{eq} was calculated for the region of significant complex formation (i.e., 0 to 2M associated nitric acid in the aqueous phase). This was done by first obtaining (from Fig. 3.2)[13] the values of

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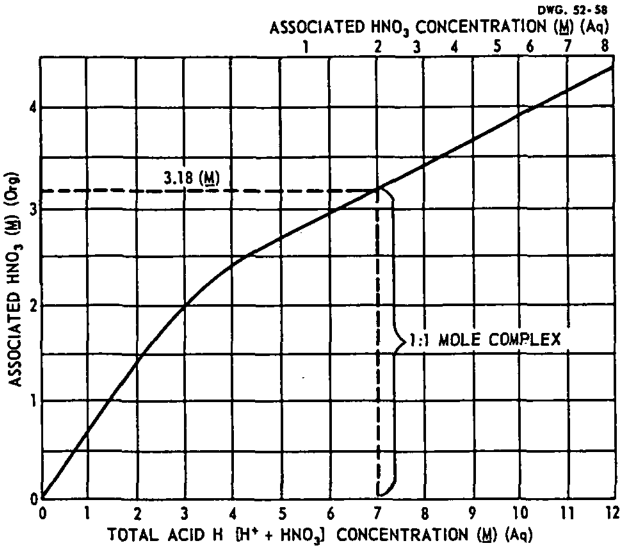

FIGURE 3.1 Equilibrium Distribution of Nitric Acid Between TBP and Water at Various Nitric Acid Concentrations (25°C).

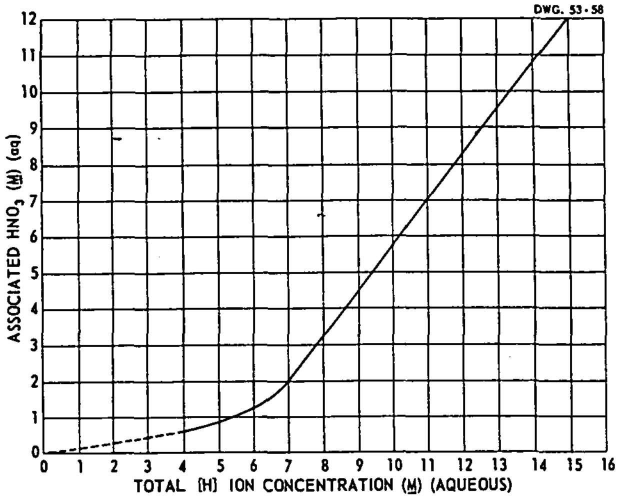

FIGURE 3.2 Concentration of Associated Nitric Acid (HNO$_3$) in Aqueous Nitric Acid Solution [Based on Redlich, O., and Bigeleisen, J., J. Am. Chem. Soc., 65, 1883 (1943)].

TABLE 3.1 Calculated Equilibrium Constant for the Reaction of Associated Nitric Acid with TBP

Assumed Value of Distribution Constant: 0.19

Total Acid Hydrogen$_{aq}$ (M)	Associated Nitric Acid$_{aq}$ (M)	Associated Nitric Acid$_{org}$ (M) [i.e.,(HNO$_3$)$_{aq}$ (D.C.)]	TBP·HNO$_3$ (M) (Total Acid in TBP) - (Free HNO$_3$ in TBP)	Free TBP (M)	K$_{eq}$ (liters/mole)
4	0.60	0.11	2.34	1.06	20
4.5	0.70	0.13	2.45	0.93	20
5	0.85	0.16	2.54	0.82	20
5.5	1.05	0.20	2.63	0.67	20
6	1.25	0.24	2.71	0.56	20
6.5	1.55	0.30	2.78	0.46	20
7	2.00	0.38	2.80	0.38	20

associated nitric acid in aqueous nitric acid solution for the various concentrations. Then the value for uncombined nitric acid in the TBP phase was obtained by multiplying the values of associated nitric acid in aqueous nitric acid solutions by the assumed value for the distribution constant. The value for the concentration of the TBP·HNO$_3$ complex was obtained by subtracting the value for the "associated nitric acid in the TBP phase" from the total titratable acid in the TBP phase. The concentration of free TBP was calculated by subtracting from the starting concentration of TBP the concentration of TBP·HNO$_3$ complex and compensating for the volume change.

Table 3.1 presents the values which were calculated for the equilibrium constant, using an assumed value for the distribution constant of 0.19. (Numerous other values ranging from 0.01 to 0.2 were evaluated as distribution constants but were not used in these calculations.) These calculations were restricted to the region above

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4$\underline{M}$ total aqueous nitric acid because below this point no data for the concentration of associated nitric acid in aqueous nitric acid solutions were available. The value of the equilibrium constant for the reaction of TBP and nitric acid to yield the equimolar complex was 20 ± 0.26.

The values for associated nitric acid in aqueous nitric acid solution (Fig. 3.2)[13] were utilized in calculating the value for associated nitric acid in the TBP phase. The equilibrium distribution constant for the partition of associated nitric acid between TBP and water (Equation 3) was then calculated. This was done by assuming that in the region above 3.18$\underline{M}$ associated nitric acid in the TBP phase and 2$\underline{M}$ associated nitric acid in the aqueous phase, nitric acid partition occurred with no further complexes being formed and with only minor shifts from the concentrations of TBP and TBP·HNO_3 which exist in the TBP phase at a concentration of 3.18$\underline{M}$.

Table 3.2 presents the calculated values for the equilibrium distribution constant at several aqueous nitric acid concentrations. These results show a value for the equilibrium distribution constant of 0.19, which corroborates the assumed value which best satisfied the calculation of the equilibrium constant by Equation 5.

By use of (1) the values obtained for K_{eq} and the distribution constant, and (2) the data obtained when constructing the equilibrium curve, the values of associated nitric acid at concentrations below the range used in the determination of K_{eq} were calculated. The equation used is shown below:

$$(HNO_3)_{aq} = \text{Total organic acidity}/[K_{eq}(D.C.)TBP_{org} + (D.C.)] \quad (7)$$

TABLE 3.2 **Equilibrium Distribution Constant for the Partition of Associated Nitric Acid Between TBP and Water**

Total Acid Hydrogen ($\underline{M}$)	Associated Nitric Acid$^*_{aq}$ ($\underline{M}$)	Associated Nitric Acid$^{**}_{org}$ ($\underline{M}$)	D.C. (O/A)
8	1.25 (3.25 - 2)	0.24 (3.42 - 3.18)	0.19
9	2.50 (4.5 - 2)	0.48 (3.66 - 3.18)	0.19
10	3.75 (5.75 - 2)	0.72 (3.90 - 3.18)	0.19
11	5 (7 - 2)	0.96 (4.14 - 3.18)	0.19
12	6.3 (8.3 - 2)	1.21 (4.39 - 3.18)	0.19

* In excess of 2$\underline{M}$

** In excess of 3.18$\underline{M}$

TABLE 3.3 **Calculated Values for Associated Nitric Acid in Dilute Aqueous Nitric Acid Solutions**

Total-Acid Hydrogen ($\underline{M}$)	Total Organic Acidity ($\underline{M}$)	Free TBP ($\underline{M}$)	Associated Nitric Acid$_{aq}$ ($\underline{M}$)
3.5	2.28	1.24	0.47
3.0	2.04	1.50	0.35
2.5	1.77	1.74	0.26
2.0	1.42	2.10	0.17
1.5	1.07	2.46	0.11
1.0	0.75	2.80	0.07
0.5	0.48	3.09	0.04

This calculation showed the amount of associated nitric acid present in aqueous nitric acid solutions below the values reported in Figure 3.2. Table 3.3 presents the data for the concentration of associated nitric acid in dilute aqueous nitric acid solution. In Figure 3.3 are presented that these data are consistent with the data previously reported.[13,14]

Determination of Uranium Distribution Coefficients into TBP

Laboratory equilibrium distribution data for uranium into TBP were determined as a function of uranyl nitrate, nitric acid, and sodium nitrate concentrations in the initial aqueous solution. The procedure used to obtain these uranium distribution coefficients was the procedure previously described[9] which was developed at these laboratories.

In Table 3.4, uranium distribution data into TBP are shown as a function of the sodium nitrate concentration in aqueous uranyl nitrate solutions at 0.1$\underline{M}$, 0.2$\underline{M}$, and 1$\underline{M}$ uranyl nitrate concentrations.

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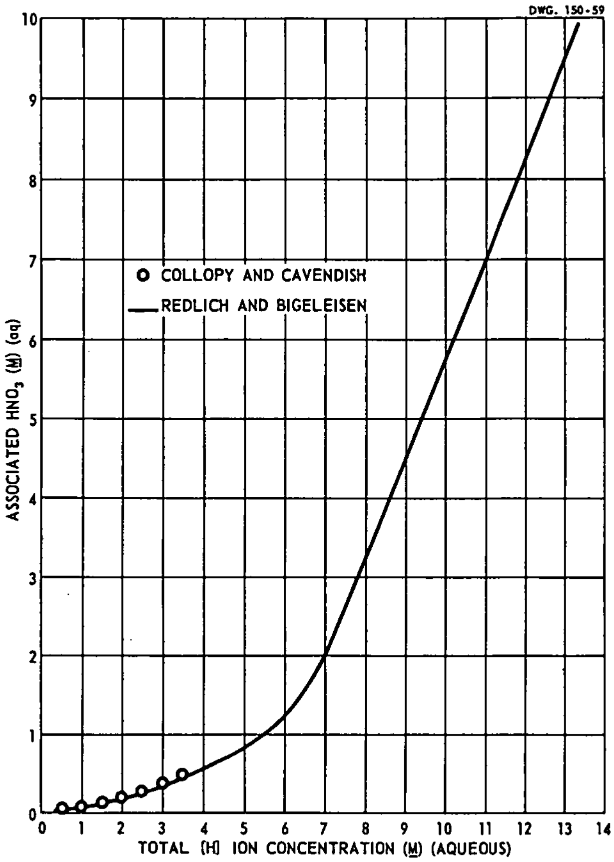

FIGURE 3.3 Concentration of Associated Nitric Acid in Aqueous Nitric Acid Solution [Based on Redlich, O. and Bigeleisen, J., J. Am. Chem. Soc., 65, 1883 (1943)]

TABLE 3.4 Uranium Distribution into TBP at Varying Concentrations of Sodium Nitrate (No Added Nitric Acid)

Aqueous			Organic		Uranium D.C. (O/A)
U Activity (cpm)	H^+ (M)	NO_3^- (M)	U Activity (cpm)	H^+ (M)	
0.1M Uranyl Nitrate					
B* 13,791	0.07	1.27	—	—	—
A* 3,840	—	—	9,881	—	2.57
B* 13,908	0.10	2.30	—	—	—
A* 1,725	—	—	11,892	—	6.89
B* 13,803	0.15	3.35	—	—	—
A* 652	—	—	12,971	—	19.91
B* 13,793	0.20	4.40	—	—	—
A* 270	—	—	13,318	—	49.25
B* 13,986	0.31	5.51	—	—	—
A* 88	—	—	13,468	—	153.04
0.2M Uranyl Nitrate					
B* 22,567	0.16	1.56	—	—	—
A* 8,540	0.15	—	15,134	—	1.77
B* 22,606	0.23	2.63	—	—	—
A* 4,353	0.18	—	18,640	—	4.28
B* 22,581	0.32	3.72	—	—	—
A* 1,842	0.22	—	20,872	—	11.33
B* 22,570	0.43	—	—	—	—
A* 773	0.27	4.83	21,839	—	28.29
B* 22,573	0.65	5.05	—	—	—
A* 277	0.32	—	22,322	—	80.64
0.1M Uranyl Nitrate					
B* 93,628	0.23	3.23	—	—	—
A* 67,562	0.36	—	38,340	—	0.567
B* 93,304	0.32	4.32	—	—	—
A* 64,646	0.33	—	40,192	—	0.619
B* 97,784	0.32	5.32	—	—	—
A* 65,630	0.35	—	40,598	—	0.622
B* 92,836	0.32	6.32	—	—	—
A* 63,530	0.33	—	40,588	—	0.639
B* 92,324	0.32	7.32	—	—	—
A* 64,000	0.33	—	41,096	—	0.642

* B-Before Equilibration with TBP; A-After Equilibration with TBP.

Data presented in Table 3.5 show the uranium distribution into TBP as a function of the sodium nitrate concentration in the aqueous uranyl nitrate solution which also contained 1M added nitric acid.

These data, when compared with the data for nitric acid alone (which are presented in Table 3.6) showed the advantage of using nitric acid plus nitrate salts for partitioning uranium from a uranyl nitrate solution into TBP. These data also indicated that

1. The effects of hydrogen plus nitrate ion was not dependent on uranium concentration
2. At very low uranium concentrations, there would be insignificant amounts of hydrolysis acid produced and some acid would have to be added for extraction. Therefore, the optimum hydrogen ion concentrations would occur between the concentration produced by the hydrolysis acid and the concentration produced by 1M acid.

Discussion

The equilibrium constant data which have been reported here are considered by the authors as an

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TABLE 3.5. Uranium Distribution into TBP at Varying Concentrations of Sodium Nitrate (1M Added Nitric Acid)

Aqueous			Organic		Uranium
U Activity (cpm)	Free H^+ (M)	NO_3^- (M)	U Activity (cpm)	H^+ (M)	D.C. (O/A)
0.1M Uranyl Nitrate					
B* 13,832	1.05	1.25	—	—	—
A* 2,063	—	—	11,707	—	5.68
B* 13,623	1.02	1.22	—	—	—
A* 1,013	—	—	12,644	—	12.48
B* 13,745	1.03	1.23	—	—	—
A* 514	—	—	13,103	—	25.49
B* 13,681	1.04	1.24	—	—	—
A* 302	—	—	13,183	—	43.65
B* 13,773	1.04	1.24	—	—	—
A* 132	—	—	13,217	—	100.13
0.2M Uranyl Nitrate					
B* 22,902	0.99	2.4	—	—	—
A* 3,757	0.80	—	19,217	0.21	5.12
B* 22,863	1.00	3.4	—	—	—
A* 2,762	0.79	—	19,961	0.23	7.23
B* 22,986	1.00	4.4	—	—	—
A* 1,510	0.74	—	21,150	0.28	14.01
B* 22,980	1.00	5.4	—	—	—
A* 828	0.68	—	21,433	0.33	25.89
B* 22,813	1.00	6.5	—	—	—
A* 494	0.64	—	21,759	0.46	44.01
1M Uranyl Nitrate					
B* 95,204	1.33	4.33	—	—	—
A* 64,150	1.29	—	41,482	—	0.647
B* 94,664	1.33	5.33	—	—	—
A* 63,420	1.29	—	42,400	—	0.669
B* 95,454	1.33	6.33	—	—	—
A* 65,014	1.33	—	42,572	—	0.676
B* 95,382	1.33	7.33	—	—	—
A* 62,278	1.28	—	42,822	—	0.697

*** B - Before Equilibration with TBP; A - After Equilibration with TBP.**

extension of the coefficient which has been calculated previously by other investigators.[15-20] These authors calculated K_{eq} for the over-all two-phase system by equations similar to that shown as Equation 8.

$$K_{over\text{-}all} = \frac{[\text{Total acid in TBP}]_{org}}{[HNO_3]_{aq}[TBP]_{org}} \qquad (8)$$

In this report, an attempt has been made to divide $K_{over\text{-}all}$ into the equilibrium reaction constant and the equilibrium distribution constant in terms of associated nitric acid.

TABLE 3.6 Uranium Distribution into TBP at Varying Concentrations of Nitric Acid

Aqueous			Organic		Uranium
U Activity (cpm)	Free H^+ (M)	NO_3^- (M)	U Activity (cpm)	H^+ (M)	D.C. (O/A)
0.2M Uranyl Nitrate					
B* 23,006	0.95	1.35	—	—	—
A* 9,839	0.85	—	13,769	0.13	1.40
B* 23,106	1.97	2.37	—	—	—
A* 6,510	1.73	—	16,668	0.28	2.56
B* 23,152	2.91	3.31	—	—	—
A* 4,874	2.57	—	17,873	0.41	3.67
B* 23,002	3.92	4.32	—	—	—
A* 4,044	3.50	—	18,578	0.53	4.59
B* 22,850	4.96	5.36	—	—	—
A* 3,562	4.48	—	18,808	0.65	5.28
B* 24,272	6.73	7.13	—	—	—
A* 3,143	6.08	—	20,334	0.72	6.47
B* 24,130	8.28	8.68	—	—	—
A* 3,439	7.65	—	19,819	0.81	5.76
B* 23,918	9.76	10.16	—	—	—
A* 3,821	9.15	—	19,430	0.90	5.09
B* 23,951	11,09	11.49	—	—	—
A* 4,414	10.70	—	19,174	0.97	4.34
1M Uranyl Nitrate					
B* 84,936	1.43	3.43	—	—	—
A* 58,425	—	—	35,400	—	0.606
B* 85,652	2.38	4.38	—	—	—
A* 57,922	—	—	35,922	—	0.620
B* 84,260	3.49	5.49	—	—	—
A* 57,408	—	—	36,106	—	0.629
B* 84,136	4.34	6.34	—	—	—
A* 57,864	—	—	35,668	—	0.616
B* 84,828	5.38	7.38	—	—	—
A* 58,332	—	—	35,950	—	0.610
B* 84,700	6.35	8.35	—	—	—
A* 59,092	—	—	34,980	—	0.592
B* 85,350	7.31	9.31	—	—	—
A* 59,272	—	—	34,648	—	0.585

*** B - Before Equilibration with TBP; A - After Equilibration with TBP.**

Nitric acid which enters the TBP phase in excess of a 1:1 ratio is considered to be dissolved acid which does not enter into a complexation reaction with the 1:1 TBP·HNO_3 complex to yield higher complexes. Supporting evidence for this is

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the fact that the partition coefficient obtained was a constant.

The data which have been reported here showed that at the equivalence point of nitric acid and TBP in the TBP phase, 90 per cent of the TBP is present as complex. In the two-phase aqueous system, it has been shown previously[16] that the TBP·H_2O complex is replaced by the TBP·HNO_3 complex as the acidity of the aqueous phase is increased. The water content of the TBP phase goes through a minimum, however, at a ratio of TBP to HNO_3 in the TBP phase of slightly greater than 1:1 rather than at 1:1. The data reported here indicate that this is due to the TBP·H_2O complex being replaced by unhydrated nitric acid to form the TBP·HNO_3 complex. The free nitric acid and the free TBP in the TBP phase are, however, hydrated, leading to the observed fact that the minimum water content is realized above the equivalence value of TBP and HNO_3 in the TBP phase.

Data on uranium distribution into TBP as a function of nitric acid in the aqueous uranyl nitrate solution has demonstrated once again that the partition coefficient passes through a maximum. It is believed that this is due to the competition for the TBP between associated nitric acid and uranium. Since in the TBP uranium extraction process employed at FMPC, ore concentrates are dissolved in nitric acid and $3\underline{M}$ excess nitric acid is employed for extraction, it is possible that the nitrate from uranyl nitrate plus the nitrate from nitrate salts shifts the nitric acid equilibrium reaction for the $3\underline{M}$ aqueous solution to the extent that sufficient associated nitric acid is formed[1,0,21] to compete with the uranium for the TBP. Because of this and the fact that $3\underline{M}$ excess nitric acid is less effective on uranium partition into TBP than a small amount of acid plus nitrate ions from a nitrate salt, the development of a low acid—high nitrate flowsheet would be advantageous from the standpoints of increased capacity, increased purity, and increased economy.

Future Work

Additional data are being assembled to show the role of the TBP·HNO_3 complex in processes in which metals are extracted by TBP from acidic solutions. Investigations being performed at this time include an infrared spectral study of the TBP·HNO_3 complex and further study of the TBP-H_2O-$UO_2(NO_3)_2$ system using isotopic exchange techniques.

Further laboratory data are being collected to determine how various ions present in uranium ore concentrates affect uranium distribution into TBP when low acid — high nitrate flowsheet conditions are employed. Pilot Plant pulse column data, which are reported in Section 2 of this report, will also be continued to determine the benefits to be gained from this flowsheet.

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

NLCO-769	Studies of the Behavior of the TBP-Kerosene Solvent in Uranium Refining: Degradation of the Kerosene Diluent. Robert K. Klopfenstein

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4. EXTRACTION COLUMN CONTROL

D. J. Stoneking F. M. Teetzel

Abstract

A gamma radiation density measurement system has been used successfully to control the extraction columns in the Refinery at this site.

Introduction

Efficient separation of uranium by the liquid-liquid extraction process [1] requires the prevention of significant losses of uranium in the raffinate waste stream. The extraction columns are designed so as to avoid these losses under normal operation conditions. However, irregularities in feed stream flow control and/or concentration occur; these upset the column equilibrium, causing increased uranium levels in the raffinate. This is especially true of the Slurrex process used here, in which the feed stream is a suspension of solids in an impure uranyl nitrate-nitric acid solution. An accurately controlled feed (in terms of flow rate and uranium concentration) is extremely difficult to maintain, and fluctuations of considerable magnitude are constantly occurring. The response of the organic product density measuring instrument presently used for column control is too slow to prevent major upsets in the column equilibrium when these fluctuations occur. An instrumental method for maintaining equilibrium operation in the extraction columns is therefore urgently needed.

Previous Work on Project

A gamma radiation density-measurement system was first tested on the FMPC Pilot Plant 6-inch extraction column, with promising results.[2] Subsequent tests performed in the Refinery were inconclusive, due to a number of variables in the system which could not be determined at that time.

Increased knowledge of the extraction process and improved instrument techniques made possible the complete evaluation of the gamma radiation density-measurement system at a later date.[3] Data taken from these tests indicated that the system was reliable for determining uranium concentrations in the extraction column. It was found from this data that the system could accurately measure the uranium concentration within ±4 grams per liter of the true value at any point in the column. This accuracy is within the limits necessary for column control. The instrument measuring the uranium profile in the column had a much faster response to impending upsets than does the organic product density instrument now used to control column operation. The profile monitoring system, having the faster response, appeared feasible for use as a controlling instrument.

Objective This Quarter

The objective this quarter was to determine if the gamma radiation profile monitoring system could be used to provide improved extraction column control.

Summary of Results

The gamma radiation density-measuring system can be used to provide improved automatic control of the extraction column. The control system tested, which does not require compensation for temperature, acid, and/or solids content changes in the column, is not capable of preventing upsets that are caused by emulsions resulting in flooding of the column. Automatic control by the gamma radiation system can improve the extraction column operation — permitting the process to be operated at a higher saturation level and thereby increasing Refinery productivity.

Equipment and Discussion

In the first control system (Fig. 4.1) tested, the density was compared at two points, 10 feet apart, in the plated section of the column. The lower measuring cell (the compensation cell) of the control system was located on the plated section of

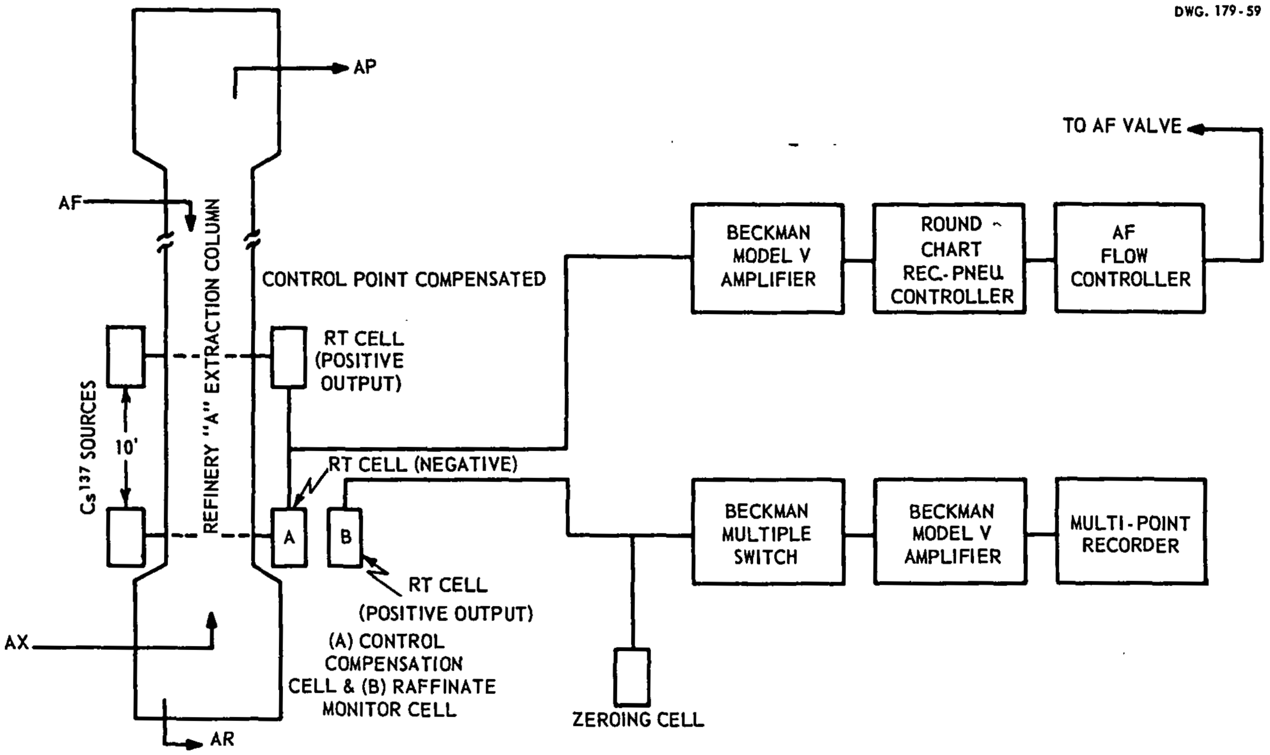

FIGURE 4.1 Ohmart Compensated Control System

the column just above the bottom disengagement section. The two cells used in this system had output currents of opposite polarity, the upper cell having a positive polarity, and the lower a negative polarity. These two cells were connected in parallel, so that the resultant output current was the difference between the two. This differential current was used as the control signal to the recorder-pneumatic controller. The recorder-pneumatic controller, (replacing the organic product density controller,) is cascaded with the aqueous feed (AF) flow controller so that the air output positions the set point of the flow controller. The flow controller operates the valve to vary the flow to the extraction column in such a way as to maintain a constant differential output from the two cells. When the differential output is controlled at a constant value, the uranium concentration profile in the column is also constant.

During normal operation, the uranium concentration at the lower cell is less than 1.0 gram per liter; therefore any changes in density at this point indicates a change in temperature, acid, and/or solids contents. Any density changes caused by changes in the value of these variables at the lower point will also be detected by the upper point; therefore, this system will compensate for these changes in density.

Also used with this system is a uranium raffinate monitor. This monitor consists of a cell mounted on the same bracket as the lower cell of the compensated control system. This cell uses the same radiation source as the other cell, but uses a zeroing cell with its own source located at the panel board. This raffinate monitor is used to indicate the amount of uranium in the raffinate; however, other density changes (due to temperature, etc.) also affect the monitor readings obtained. During several days of automatic control, the uranium raffinate monitor indicated that density changes due to temperature, etc. were negligible. Data collected during this period are shown in

Table 4.1. During this period, excellent column control was maintained.

Since the density variations at the lower cell of the profile monitoring system were insignificant, an uncompensated control system (Fig. 4.2) was installed and tested. This uncompensated control system uses the same method for controlling as the compensated system, the difference being that only one cell is located on the column. The measuring cell in this system is located in the same position as the higher cell in the other system. After the column was controlled by this uncompensated control point for a short period, it was evident the quality of control did not differ from that previously obtained.

TABLE 4.1 Readings of the Uranium Raffinate Monitor at Various Uranium Levels

Uranium in Raffinate (g/l)	Ohmart Chart Reading
0.33	5
0.72	4
0.80	3
0.75	5
0.86	5
0.69	3
0.74	4

The large uranium variations that occur throughout the column when it is manually controlled have been eliminated by the uranium profile control system. Controlling the uranium profile in the column also has maintained a more constant organic product density.

After obtaining satisfactory results for one column, it was desirable to install an Ohmart control system on another column. This was done so that the "cold side" extraction area, of which the two extraction columns are an integrated part, could be operated at a steady-state condition.

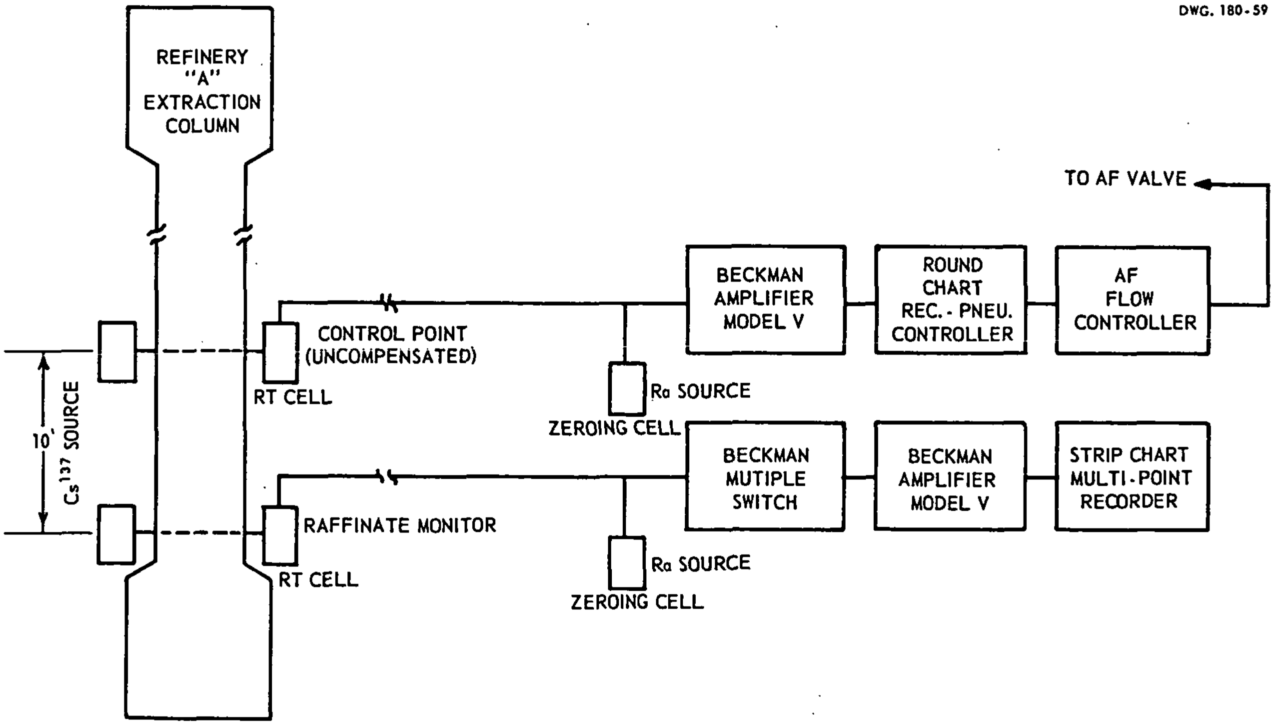

FIGURE 4.2 Uncompensated Extraction Column Ohmart Control System

[redacted]

TABLE 4.2 Organic Product Density Calibration With a Feed Containing 216 g/l Uranium

Organic Product Sp gr	Ohmart Set Point
1.009	40
1.018	60
1.022	70
1.029	86

Data

The data listed in Table 4.2 and Figure 4.3 were taken during periods in which the radiation-density instrument (the uncompensated system) was controlling the column. These data were collected by operating the extraction column at a certain organic product specific gravity for a period long enough to obtain a steady-state condition in the column (for approximately 8 hours) and then noting the set point. The uranium concentration in the aqueous feed (uranyl nitrate-nitric acid) was approximately 216 grams per liter.

It has been found that feed concentrations other than 216 grams per liter will alter the profile, which means that a different set point reading on the controller will be needed to obtain the same organic product density. It was thought that perhaps a family of lines could be drawn on the graph for different feed concentrations. In the graph (Fig 4.3) a line is drawn normal to the 216 grams per liter line. On the basis of experience at this site, this normal intersects and is a common normal to every line of the family of lines. The adjusted set point for a given organic product specific gravity may be found by reading the abscissa of the intersection of the common normal with the appropriate concentration line.

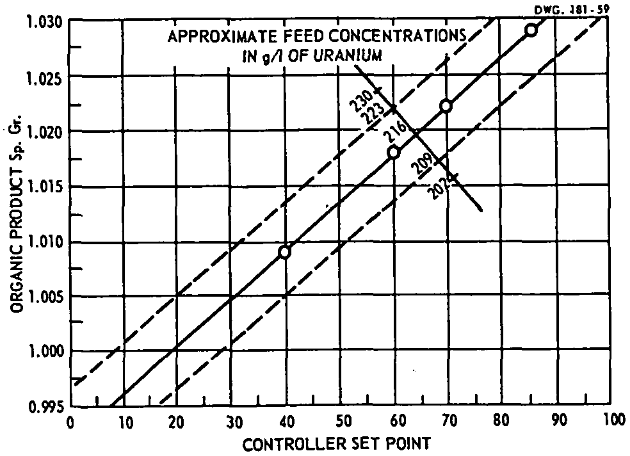

FIGURE 4.3 Determination of Ohmart Setting From Specific Gravity and Concentration of Uranium in the Feed

Example:

U Conc. in Feed (g/l)	Ohmart Set Point	Organic Product Specific Gravity
209	49	1.009
216	40	1.009
223	30	1.009

Future Work

A control system will be designed that will detect and correct for column flooding.

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5. ACTIVATION OF POT-PRODUCED ORANGE OXIDE

C. W. Huntington

Abstract

As demonstrated by uranium oxides containing up to approximately 200 ppm sodium (uranium basis), sodium contamination may increasingly retard hydrofluorination conversion; the deleterious effects can be reduced or eliminated by reducing the temperature of reaction.

Uranyl sulfate exhibits an enantiotropic transition at 755°C, and undergoes decomposition to U_3O_8 at various temperatures in the range, 690° to 825°C, depending upon the nature of the atmosphere in which the decomposition occurs. The interpretation of DTA data for decomposition reactions must involve consideration of the effective atmosphere at the site of the decomposition.

Introduction

The chemical systems involved in the production of green salt (UF_4) by reduction of orange oxide (UO_3) and hydrofluorination of the resulting brown oxide (UO_2) are very complex and are often markedly affected by seemingly minor factors. Production activities throughout the uranium industry during the last few years have repeatedly demonstrated that the achievement of optimum production potentials is dependent upon a more complete understanding of the basic aspects of the conversion processes. Thus, an integral part of the green salt development program at this site has been a series of studies encompassing such factors as reaction kinetics and mechanism, effects of activating additives, and the influence of impurities. Many of these studies have been reported in recent quarterly reports under this project category.

Work reported here involves a more definitive study of the effects of sodium on the hydrofluorination process and an investigation of the thermal decomposition of uranyl sulfate, a possible component of sulfated orange oxide systems.

Objectives for This Quarter

1. To study the hydrofluorination characteristics of uranium oxides containing up to ~200 ppm sodium.
2. To study the thermal decomposition of uranyl sulfate.

HYDROFLUORINATION OF SODIUM-CONTAMINATED URANIUM OXIDES

C. W. Huntington M. G. Mendel
D. C. Bonfer N. L. Gullion

Introduction

The relationship between hydrofluorination reactor plugging and sodium content of the Green Salt Plant feed has been well established by production experience during recent years. It is considered that reactor plugging is the result of eutectic formation in the NaF-UF_4 system, with subsequent particle aggregation[1] and increased sintering tendency.

Sintering of green salt, resulting in growth of the particles and closure of internal pores, has an adverse effect upon the hydrofluorination conversion itself, in addition to creating a physical handling problem. Thus, at certain temperatures, increasing amounts of sodium contamination will result in lower conversions. This has been demonstrated by thermobalance hydrofluorination tests performed at 1100°F.[2]

Because of the importance of the sodium contamination problem, it was desired to obtain information concerning the effects of sodium on the hydrofluorination reaction which was more definitive than that obtained to date. Previous work[2] utilized orange oxide samples produced by beaker denitration; development of the laboratory denitration pot system[3,4] has provided a more reliable means of sample generation. In addition, variation

[redacted]

in hydrofluorination technique was expected to provide more characteristic data. The previous investigation[2] involved isothermal (1100°F) hydrofluorination; it is often best to use this technique to determine whether certain factors have an effect upon the hydrofluorination reaction. Programmed-temperature conditions, however, more nearly represent the plant-scale situation. A more complete evaluation can probably be made by comparing results from both isothermal and programmed temperature tests. Such an evaluation with sodium-contaminated uranium oxides produced in the laboratory denitration pot is reported here.

Objectives of Work Completed This Quarter

To determine the hydrofluorination characteristics of sodium-contaminated uranium oxides under both isothermal and programmed thermobalance temperature control.

Summary of Results Obtained This Quarter

1. Isothermal (1100°F) hydrofluorination tests with anhydrous HF show that hydrofluorination conversion is adversely affected by sodium contamination in the 13 to 189 ppm range considered.
2. Performing hydrofluorination under programmed temperature control (500° to 1000°F) practically eliminated the effects of sodium.
3. The laboratory hydrofluorination tests demonstrate that sodium may adversely affect hydrofluorination conversion, but that this effect can be eliminated or reduced by decreasing the temperature at the site of a reaction.
4. In the range, 13 to 189 ppm sodium, with 750 ppm SO_4, sodium has no effect upon the reduction activity of orange oxide.

Methods and Data

Four orange oxide samples were prepared in the laboratory denitration pot from samples of plant boildown product containing an initial concentration of 14 ppm sodium (uranium basis). In order that the oxides would correspond to normal plant product, 750 ppm SO_4 (uranium basis), as H_2SO_4, was added to each pot charge prior to denitration. Sodium nitrate was added to three of the pot charges to give approximately 50, 100, and 200 ppm (uranium basis) sodium concentrations. The standard denitration conditions normally used for laboratory studies of this type were employed:

Vacuum	2 inches H_2O
Air Sweep	30 cfh
Agitator Speed	10 rpm
Charge	2 liters UNH
Time after Dough Stage	2 hours

Analysis of the four oxides produced is given in Table 5.1. The actual sodium series used here was found to be 13-55-89-185 ppm. As is desired in experiments of this kind, the basic composition of the oxides was essentially identical, thus eliminating variable responses due to varying volatiles content.

Reduction tests (932°F) were performed in a quartz-chamber thermobalance[5] on each orange oxide sample. The results (Table 5.2) showed no real difference among samples. The reduction number for the control sample (14 ppm Na) was ~50 seconds higher than those for the other three, but this difference is not considered significant.

TABLE 5.1 Analysis of Orange Oxide Samples

Sample No.	Na (ppm, U basis)	U (%)	NO_3 (%)	H_2O (%)	HCl-insol. (%)
1	13	83.04	0.13	0.09	0.04
2	55	83.03	0.13	0.10	0.01
3	89	83.03	0.14	0.09	0.01
4	185	83.06	0.10	0.10	0.02

TABLE 5.2 Reduction of Sodium-Contaminated Orange Oxides

Sample No.	Na (ppm, U basis)	Reduction No.* (sec)
1	13	650
2	55	595
3	89	610
4	185	600

- Time required for 97% conversion to UO_2 at 500°C (932°F).

[redacted]

Each sample was then subjected to two types of hydrofluorination tests in a Monel-chamber thermobalance:[6]

1. Isothermal reduction at 1065°F, followed by isothermal hydrofluorination at 1100°F, and
2. Isothermal reduction at 1065°F, followed by programmed temperature hydrofluorination at 500°-1000°F.

To allow for temperature correction factors, nominal (indicated) temperatures were somewhat higher than the desired temperatures; the reductions were performed at an indicated temperature of 1100°F, with hydrofluorination performed at indicated temperatures of 1150°F or 550°-1050°F. A hydrogen-nitrogen mixture (~½ volume ratio) was used for reduction; anhydrous HF was used for hydrofluorination. A reduction temperature of 1065°F was used in order to safequard against thermal damage to the U_3O_8 phase, which becomes serious above 600°C (1112°F), and thereby to insure that the hydrofluorination results were not confounded by variables originating in the reduction reaction.

Results of the hydrofluorination tests are given in Table 5.3 and are shown graphically in Figures 5.1 and 5.2.

As has been demonstrated before,[2] under isothermal hydrofluorination conditions, increasing amounts of sodium increasingly retarded hydrofluorination over the major portion of the reaction. This is especially evident for the 185 ppm sodium sample. Although the differences among the first three samples are probably not significant, the

TABLE 5.3 Hydrofluorination of Sodium-Contaminated Uranium Oxides

Time (min)	% Conversion To UF_4							
	Hydrofluorinated at 1100°F				Hydrofluorinated at 500°-1000°F			
	13 ppm Na	55 ppm Na	89 ppm Na	185 ppm Na	13 ppm Na	55 ppm Na	89 ppm Na	185 ppm Na
1	38.6	32.9	27.0	40.2	46.6	45.3	45.8	47.7
2	63.1	58.7	53.3	55.4	60.9	58.8	59.3	56.9
3	70.1	67.6	63.1	60.7	66.9	65.1	65.5	61.9
4	75.2	72.7	68.7	65.5	71.5	69.9	70.4	66.5
5	78.8	76.1	72.8	69.2	75.8	74.7	74.9	70.6
6	80.7	78.7	75.7	71.8	79.7	78.8	78.6	74.7
7	82.9	80.1	78.3	74.0	82.9	82.2	81.9	78.1
8	84.6	82.6	80.0	75.7	85.5	85.3	84.6	81.4
9	85.8	84.5	81.7	77.3	87.7	87.5	86.7	84.1
10	86.7	85.5	83.4	78.8	89.6	89.4	88.4	86.3
12	88.9	87.4	85.5	81.0	92.3	92.5	91.3	89.6
14	90.4	88.9	87.2	82.9	94.4	94.5	93.5	92.0
16	91.6	90.3	88.7	84.3	95.9	95.9	94.9	93.7
18	92.5	91.5	89.9	85.8	96.9	96.9	95.9	95.2
20	93.3	92.3	90.8	86.7	97.6	97.3	96.9	96.1
25	94.2	93.7	92.8	88.7	98.3	97.8	97.3	97.3
30	95.2	95.2	94.2	90.6	98.6	98.1	97.8	97.5
35	95.9	95.9	95.2	91.8	98.6	98.1	97.8	97.8
40	96.4	96.6	96.1	92.8				98.1
45	96.6	97.1	96.6	93.7				98.1
50	96.9	97.6	97.1	94.2				
60	97.1	97.8	97.6	95.2				
70	97.3	98.1	98.1	95.7				
80	97.6	98.3	98.1	96.1				
90	97.6	98.3	98.1	96.4				
100				96.4				

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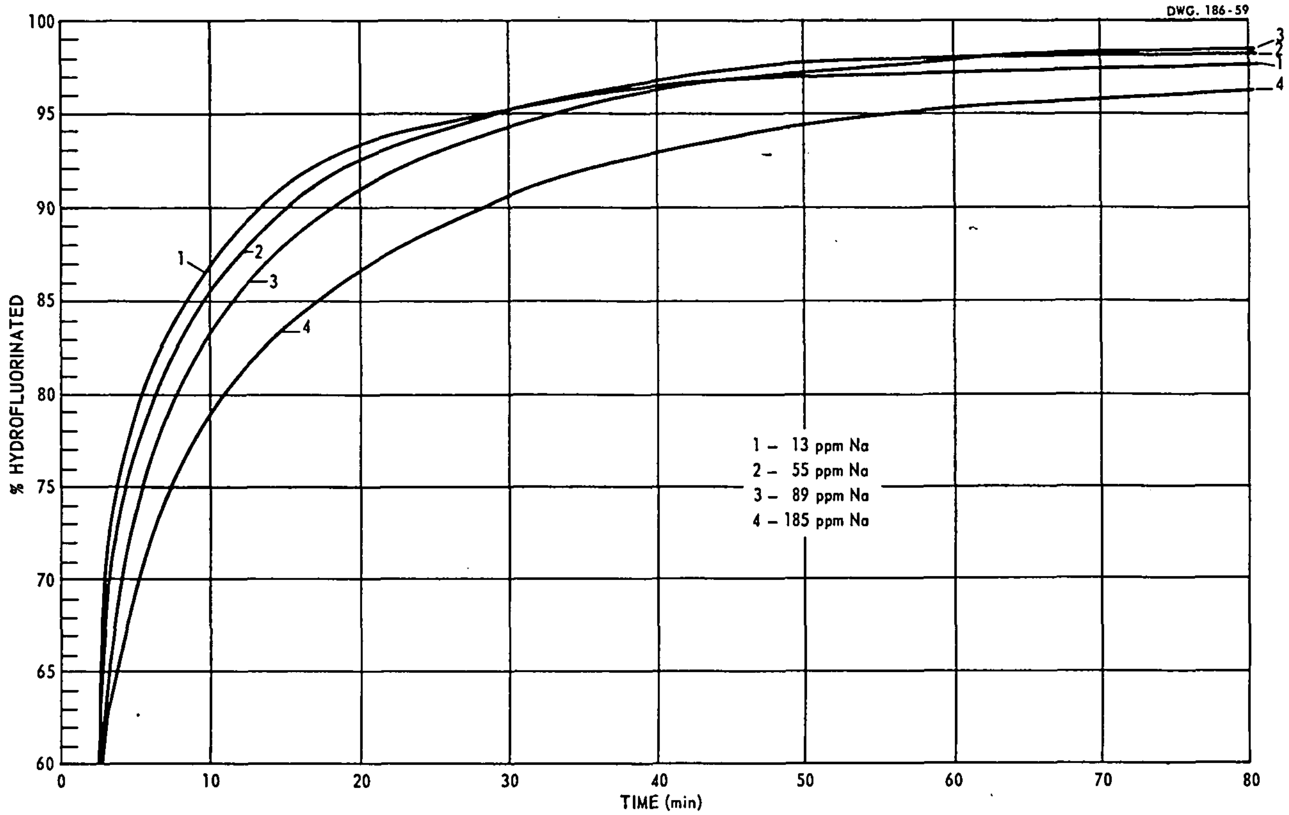

FIGURE 5.1 Isothermal (1100°F) Thermobalance Hydrofluorination. Reduction performed isothermally at 1065°F.

trend is in the predicted order up to ~95 per cent conversion (Fig. 5.1). The results of the programmed temperature hydrofluorination, on the other hand, were practically the same for all samples. In addition, the maximum conversion was achieved in a much shorter time (Cf. Fig. 5.1 and 5.2).

Discussion

It was considered that the sodium concentration range studied–up to ~200 ppm – was more than sufficient to include the probable levels of plant contamination. As shown by reduction test results, this amount of sodium has no effect upon the reduction of orange oxide containing 750 ppm SO_4.

The difference between the two hydrofluorination techniques is, of course, that conversion is effected at a much lower temperature by programmed temperature control. Together, the two sets of data obtained in these tests demonstrate that sodium may adversely affect hydrofluorination conversion, but that this effect can be eliminated or diminished by reducing the temperature at the site of the reaction.

THERMAL DECOMPOSITION OF ANHYDROUS URANYL SULFATE

K. J. Notz

In conjunction with studies of the activating effect of sulfate on orange oxide,[7] the nature of the thermal decomposition of uranyl sulfate became a matter of interest. Conflicting reports on this subject were found in the literature, Oeschner de Coninck[8] claiming UO_3 and SO_3 as the decomposition products at "dull red" heat and U_3O_8 and SO_2 as the products at "bright red" heat, while

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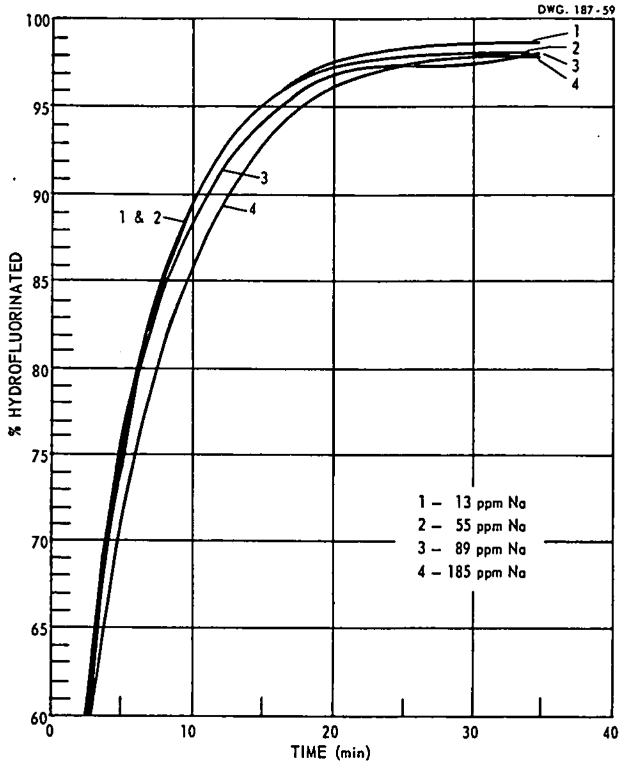

FIGURE 5.2 Programmed Temperature (500°-1000°F) Thermobalance Hydrofluorination. Reduction performed isothermally at 1065°F.

Hoekstra and Siegel[9] obtained only U_3O_8 by the thermal decomposition of uranyl sulfate. In order to resolve this uncertainty the thermal decomposition of anhydrous uranyl sulfate was studied by means of DTA (differential thermal analysis) and TGA (thermogravimetric analysis) in this laboratory. In the course of this study, some observations relevant to the correlation of DTA and TGA temperatures in decomposition reactions were also made.

Objectives of Work Completed This Quarter

To determine the temperature of decomposition and mode of decomposition of anhydrous uranyl sulfate.

Summary of Results Obtained This Quarter

Uranyl sulfate undergoes an enantiotropic transition at 755°C. At decomposition temperatures, U_3O_8, and not UO_3, is formed. The temperature at which decomposition (to U_3O_8, oxides of sulfur, and oxygen) takes place is a function of atmosphere, being 690°C in helium, 750°C in either oxygen or sulfur dioxide, and 825°C in a mixture of oxygen and sulfur dioxide (and sulfur trioxide formed by reaction between these two gases). The dependence of the decomposition temperature on atmosphere established that the DTA reaction, ostensibly carried out in an air atmosphere, actually took place in an atmosphere of the decomposition gases.

Materials and Methods

Anhydrous uranyl sulfate was prepared by drying the trihydrate (E. H. Sargent and Co., C.P. grade) for two hours at 500°C.

DTA traces were obtained with a Deltatherm unit (Technical Equipment Corporation), employing a heating rate of 10°C/min.

TGA traces were obtained by means of an automatically recording thermobalance heating at a rate of 4°C/min. Various atmospheres were maintained by flowing gases at a total rate of about 1 liter/min. The gases used were helium, oxygen, SO_2, and a 50:50 mixture of oxygen and SO_2. Each experiment was conducted at atmospheric pressure. Based on literature values of the equilibrium constant for the reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the SO_3 concentration attained while both oxygen and SO_2 were admitted was in the region of 0.15 atmosphere.

Results

Thermogravimetric decomposition of anhydrous uranyl sulfate occurred in a single step, forming U_3O_8 as the solid residue and liberating oxygen and oxides of sulfur. The reaction is very sensitive to temperature — a rough calculation using the method of Freeman and Carroll[10] gave a value of about 80 kcal/mole for the activation energy. The calculated entropy change is also large — about 70 E.U./mole. The decomposition temperature was found to depend on the atmosphere present in the

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thermobalance chamber, being 690°C in helium, 750°C in either oxygen or sulfur dioxide, and 825°C in a mixture of oxygen and sulfur dioxide.

A conventional DTA trace is shown in Figure 5.3 (Curve A), using alumina dilution of the sample. Two endotherms are displayed, at 755°C and 820°C. Since decomposition occurred in a single step, one of these endotherms must represent a phase transition. It was established by means of cooling curves that the 755° endotherm is an enantiotropic transition of uranyl sulfate. Curve B is for a sample packed in the conventional manner, with alumina dilution. The power was shut off just prior to full peak of the second endotherm. The decomposition proceeded to completion, and the cooling curve showed no thermal effects. Curve C shows results for a more heavily packed sample with no diluent, run concurrently with sample B. The larger mass of sample C delayed both endothermic reactions so that when the heat was turned off, only the first endotherm had been passed. This sample, on cooling, displayed a typical transition exotherm, thus establishing that the second endotherm is caused by decomposition.

Having demonstrated that decomposition occurs at 820°C in the DTA sample block, it is evident from the thermobalance results that the atmosphere in the DTA block is a mixture of oxygen and sulfur dioxide (and the accompanying equilibrium sulfur trioxide), these gases being formed by the decomposition reaction and not diffusing out very rapidly.

In general, it is apparent that decomposition temperatures reported on the basis of conventional DTA data do not necessarily represent the decomposition temperature in air, as is frequently reported, but rather represent the decomposition temperature in an atmosphere of the evolved gases. In particular, when correlation of DTA and TGA data is attempted, due care must be exercised to maintain an appropriate atmosphere in the thermobalance.

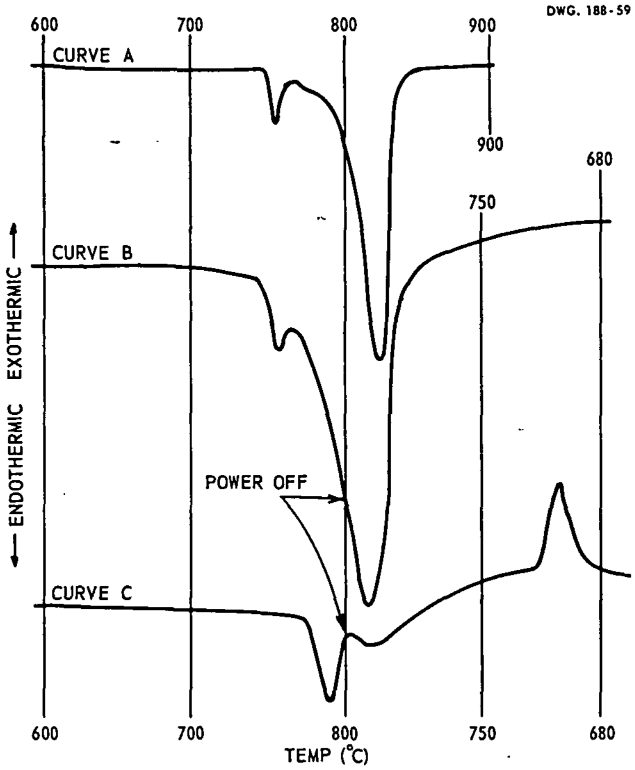

FIGURE 5.3 DTA Traces of Anhydrous Uranyl Sulfate

Curve A: Continuously increasing temperature; sample diluted with γ-alumina

Curve B: Power turned off at 800°C; sample diluted with γ-alumina

Curve C: Power turned off at 800°C; sample not diluted

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6. ADU ("AMMONIUM DIURANATE") PROCESS DEVELOPMENT

Abstract

An ADU precipitation process is being evaluated to determine its suitability as a continuous method of producing feed for the green salt plant process. A laboratory investigation of impurity decontamination by ADU precipitation indicated that decontamination of sodium, calcium, nickel, magnesium, gadolinium, and dysprosium, but not thorium, iron, or chromium, would be achieved in an ADU process.

Isothermal thermobalance hydrofluorination tests at 1050°F with ADU samples which had been calcined at 1000° to 1400°F indicated that calcination of ADU at 1200°F results in a product which is least apt to undergo thermal damage and exhibits the highest conversion. Under programmed temperature control (550°F to 1100°F), very rapid and almost complete conversions were obtained with samples calcined at 1200°F and below. It is concluded that optimum hydrofluorination reactivity would be observed with ADU which has been calcined at 1200°F.

Introduction

Because of the inherent deficiencies of the batch calcination method of producing orange oxide (UO_3), substitution of a continuous technique for producing Green Salt Plant feed would effect a major improvement in the green salt (UF_4) process. To this end, an ADU precipitation process* has been developed,[1] and ADU[2] is currently being evaluated as a Green Salt Plant feed. Work recently completed has involved further investigation of the decontamination of impurities by ADU precipitation and a study of the hydrofluorination characteristics of calcined ADU.

Objectives for This Quarter

The work reported here was performed:

1. To determine by laboratory tests the approximate degree of decontamination of commonly encountered impurities which can be expected in a plant ADU process and
2. To characterize the thermobalance hydrofluorination responses of ADU calcined at various temperatures in order to determine the product most likely to be amenable to screw reactor hydrofluorination.

LABORATORY DETERMINATION OF IMPURITY DECONTAMINATION BY AN ADU PROCESS

M. G. Mendel

Introduction

A process utilizing the chemical precipitation of a uranium compound should intrinsically offer a method of decontamination from a number of ions. One of the possible advantages of the ADU system currently being investigated would be the greater degree of decontamination which could be achieved over the present system of thermal denitration (which offers little or no decontamination). Greater flexibility of the extraction plant operation could be realized while a green salt feed within the limits of purity specifications was being produced.

Analysis of data from the ADU semi-works production operation and from preliminary laboratory studies showed that decontamination of sodium, but not thorium, could be expected in an ADU process; results for iron were inconclusive.[3] To obtain additional information on the degree of impurity decontamination which might be realized in an ADU process, a laboratory investigation was made. The distribution of certain elements when ADU is precipitated from uranyl nitrate solutions was determined.

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* *A process in which the uranium in an aqueous uranyl nitrate solution is precipitated as "ADU" by the addition of ammonium hydroxide to a pH of 5.7.*

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Objective of Work Completed This Quarter

To determine, by laboratory batch precipitation tests, the approximate degree of decontamination of commonly encountered impurities which can be expected in an ADU process.

Summary of Results Obtained This Quarter

1. No decontamination is obtained with thorium, iron, and chromium at the concentration levels investigated.
2. Decontamination is obtained with sodium, calcium, nickel, magnesium, gadolinium, and dysprosium at the concentration levels investigated.

Methods and Data

ADU samples were prepared batchwise in the laboratory under conditions corresponding, as nearly as possible, to those proposed for a plant ADU process.[4]

A pure solution of uranyl nitrate (UNH) containing 80 grams per liter of uranium was used as a feed stock. The precipitating agent was a solution of ammonium hydroxide (4% NH_3). Precipitations were carried out at room temperature in a stainless steel beaker equipped with a stirrer, pH electrodes, and a buret for adding the precipitating reagent. One liter of the uranyl nitrate was charged to the beaker and the appropriate contaminants were added. After stirring to insure complete dissolution of contaminants, a sample of the UNH was taken for analysis. The ammonium hydroxide was then added to the uranyl nitrate solution dropwise over a period of ½ hour. The precipitation agent was added until the pH of the solution increased to 5.7 and remained at that value. Retention time was 3.5 hours. The precipitate was then filtered on a Buchner funnel without washing. The filter cake obtained was dried at 110°C and blended, and one-half of the material was calcined to black oxide. The black oxide samples and the corresponding UNH samples were submitted for spectrochemical analysis.

The following impurities were added as nitrates to the UNH prior to precipitation: calcium, chromium, iron, dysprosium, gadolinium, magnesium, manganese, sodium, nickel, and thorium. Tests 1-A and 1-B were made with all of the above impurities present at a "high" level. Tests 2-A and 2-B were made with all of the above impurities present at a "low" level. The "high" and "low" levels were chosen on the basis of product specifications and operating experience. In addition, single tests were performed with only one or two impurities present.

As shown in Table 6.1, significant decontamination factors were obtained for sodium, calcium, nickel, magnesium, gadolinium, and dysprosium. The data also indicate that essentially no decontamination occurred for thorium, ferric iron, and chromium. The decontamination of manganese could not be determined, since 4 ppm is the upper detection limit by the standard spectrochemical technique.

Discussion

There appear to be two factors which determine whether decontamination does or does not occur for certain impurities in this system. The first of these is the pH at which certain ions will precipitate as hydrous oxides or hydroxides. Certainly, decontamination would not be expected for those cations which will precipitate as hydrous oxides at a pH below the pH of precipitation of the uranyl ion. (An exception to this case might be an amphoteric hydroxide.) A second factor is the very nature of the precipitate of uranium — a hydrous oxide. A precipitate of this type is very difficult to prepare pure since it tends to coprecipitate other ions in small amounts.

The pH of precipitation of a number of cations by hydroxide has been given by Moeller;[5] these data show generally the trend of decontamination which might be expected in the ADU system. However, there are other effects to be considered which also are important in a decontamination study of this system. Examples of these are readsorption

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[redacted]

TABLE 6.1 Decontamination of Various Impurities from Uranium by ADU Precipitation

	Impurity	Conc. (ppm, U Basis)		Decontamination Factor*
		UNH	U_3O_8	
Ca	Test 1-A	<6	<6	1
	Test 1-B	150	40	3.7
	Test 2-A	<6	<6	1
	Test 2-B	20	20	1
	Single Test	30	15	2
Cr	Test 1-A	18	12	1.5
	Test 1-B	30	40	1
	Test 2-A	10	<10	~1
	Test 2-B	<10	<10	1
Dy	Test 1-A	2500	230	11
	Test 1-B	2200	90	24
	Test 2-A	310	60	5.2
	Test 2-B	480	14	34
	Single Test 3 with Gd	238	14	17
	Single Test 4 with Gd	50	1.2	42
Fe	Test 1-A	100	29	3.3
	Test 1-B	78	118	1
	Test 2-A	56	62	1
	Test 2-B	47	100	1
	Single Test	250	243	1
Gd	Test 1-A	3500	340	10
	Test 1-B	2300	90	25
	Test 2-A	700	130	5.4
	Test 2-B	830	30	28
	Single Test 3 with Dy	300	17	18
	Single Test 4 with Dy	39	0.7	56
Mg	Test 1-A	24	<4	>6
	Test 1-B	50	<4	>12.5
	Test 2-A	7	<4	>1.8
	Test 2-B	55	8	7
Mn	Test 1-A	4	4	1 (?)
	Test 1-B	4	4	1 (?)
	Test 2-A	4	4	1 (?)
	Test 2-B	4	4	1 (?)
Na	Test 1-A	35	12	3
	Test 1-B	50	15	3.3
	Test 2-A	15	4	4
	Test 2-B	12	4	3
	Single Test	110	20	5.5
Ni	Test 1-A	25	<10	>2.5
	Test 1-B	66	<10	>6
	Test 2-A	26	<10	>2.6
	Test 2-B	53	<10	>5.3
Th	Test 1-A	2180	2025	1
	Test 1-B	1690	1700	1
	Test 2-A	350	352	1
	Test 2-B	388	376	1

* Decontamination Factor = Conc. in UNH/conc. in U_3O_8.

of ions, which could occur with long reaction time, and interactions with other anions, such as would occur if the ammonium hydroxide were saturated with carbon dioxide, producing insoluble carbonates (e.g., calcium carbonate). In addition, the concentration level of the impurities added would contribute to all of the considerations given above; the behavior of impurities in ppm concentrations is sometimes difficult to predict.

A comparison of the data obtained in the laboratory with that given by Moeller[5] indicates that no decontamination is achieved with those elements which form hydroxides at a pH below, or at the same pH as, the uranyl ion. Conversely, decontamination was achieved with those elements which form a precipitate at a pH higher than that governing uranium precipitation.

The results for calcium, while showing the expected decontamination, exemplify a situation in which factors other than pH considerations may influence the decontamination factor obtained. Calcium, which forms a fairly soluble hydroxide, should give a decontamination factor which is high. The fact that a relatively small decontamination factor is obtained in practice indicates that effects such as interaction with anions (e.g., carbonate) and adsorption on the hydrous oxide precipitation of uranium are operating in this system.

The decontamination factor for sodium is relatively good, but is not as good as one would expect, considering the high solubility of sodium hydroxide. Here again, the adsorption of sodium ion on the precipitate probably limits decontamination.

Sodium, gadolinium, and dysprosium are the most important impurities among those for which decontamination was demonstrated. It should be noted that these tests indicate decontamination factors of approximately 3 for sodium and approximately 50 for the rare earths, at the concentration levels which would yield an acceptable plant product (10 ppm sodium, 1 ppm gadolinium or dysprosium).

[redacted]

This investigation has shown the approximate degree of decontamination of the commonly considered impurities which can be expected in an ADU process. Since adsorption of impurities on the precipitate is a possibility, retention time and precipitate environment may be important factors which were not fully demonstrated in the batch precipitation tests. Actual decontamination factors might be more closely estimated by a continuous precipitation arrangement which would more nearly correspond to plant conditions. Such a study is now in progress.

THERMOBALANCE HYDROFLUORINATION INVESTIGATION OF PILOT PLANT ADU

G. G. Briggs

Introduction

As reported in an earlier quarterly report,[6] a reduction and hydrofluorination test of short duration (24 hours) was made in one reactor bank of the Green Salt Plant. The 13,000 pounds of ADU used had been produced during the startup phases of the ADU semi-works facility. The results were very satisfactory, with respect to processability of the material through the fluid-bed reduction and hydrofluorination equipment, and also with respect to conversion to UO_2 and UF_4. More recently, a more extensive test was initiated with a 40-ton quantity of calcined ADU produced in the semi-works unit.[4] It soon became apparent from green salt lot analyses that the conversion to UF_4 did not meet the target specification of 97 per cent UF_4. Lot analyses ranged between 91.6 and 97.2 per cent UF_4. After about one-half of the ADU had been processed, the test was discontinued to provide an opportunity to analyze the data carefully and develop more favorable operating conditions for processing the remaining ADU.

The available data suggested that the rather poor conversion in the recent test, as compared with that achieved earlier in the brief test, resulted because HF was fed in too great an excess during much of the run. The high-surface-area ADU is known to be intrinsically much more reactive than the normally processed pot-denitrated UO_3 feed. It is thus possible that high temperatures developed during early phases of the hydrofluorination reaction caused sintering which subsequently prevented attainment of high conversion. If the HF excess is too high, the temperatures in the first hydrofluorination reactor cannot be sufficiently suppressed by taking advantage of (1) lowered HF concentrations to slow the reaction, and (2) the lowered ceiling on temperatures imposed by chemical equilibrium.

At the time of writing, the plant test has been resumed, with care being taken to hold the HF excess down so as to maintain an HF concentration in the off-gas from the hydrofluorination bank in the range of 20 to 30 per cent. Results are not yet available.

There also existed the possibility of modifying the ADU feed to improve its hydrofluorination characteristics in such a way as to permit less stringent control of reaction temperatures and HF excess in the plant. Specifically, the method involves calcination of the ADU at a temperature higher than that which is presently used for calcination in the present semi-works preparation of ADU. It is known that the specific surface area of the material can be reduced rapidly by heating at temperatures above 1000°F.[7] The decrease of surface area with increase in temperature is very great, once the material has reached a temperature sufficient to convert it to U_3O_8. Since the UO_2 which is subsequently produced from the U_3O_8 will also possess a lowered specific surface area, it should be less reactive and hence more amenable to processing in hydrofluorination equipment where adequate heat removal and temperature control are not always readily achieved.

A brief laboratory investigation was made to determine if calcination of semi-works ADU at some higher temperature would improve the hydrofluorination characteristics of the material.

[redacted]

Objective of Work Completed This Quarter

Laboratory reductions and hydrofluorinations of ADU calcined at temperatures in the range between 1000°F and 1400°F were performed in a thermobalance. It was to be determined if calcination would produce a material which could be more readily hydrofluorinated to high levels of conversion under temperature conditions which promote sintering. If successful, calcination at higher temperatures would be considered for incorporation into the semi-works flowsheet for production of ADU-type feed – particularly, if current reduction and hydrofluorination tests in the plant continue to indicate the need for such a modification.

Summary of Results

1. When ADU-source UO_2 was hydrofluorinated isothermally at the relatively high temperature of 1050°F with anhydrous HF, sintering was very evident. The best conversion under these conditions was obtained with UO_2 prepared from semi-works ADU which had been recalcined one hour at 1200°F and which possessed a specific surface area of 6.9 square meters per gram as measured by BET (nitrogen) adsorption.
2. When UO_2 produced from calcined samples of ADU was hydrofluorinated under conditions which minimize sintering (i.e., programming of the temperature from 550°F to 1100°F), very rapid and almost complete conversions were obtained with those samples which had been calcined at 1000°, 1100°, and 1200°F. The hydrofluorination rate fell off greatly for those samples calcined at 1300° and 1400°F.

Methods and Data

The semi-works ADU examined in this study was a composite sampling (designated P. O. 29100) taken from the calciner over one eight-hour shift and presumably during a period of "steady state" operation. Judging by the dark-brown color, the material appeared to have been heated to about 1000°F. Fifty-gram portions of the ADU were reheated one hour in a Lindberg furnace at temperatures of 1000°, 1100°, 1200°, 1300°, and 1400°F. The calcined samples were then subdivided for the following tests or measurements.

A. Thermobalance Reduction and Hydrofluorination

1. Hydrogen reduction of 2.700-gram samples was carried out under programmed conditions, with the temperature increasing from 700° to 1100°F. They were then hydrofluorinated under programmed conditions in anhydrous HF from 550° to 1100°F (indicated). The conversion-time curves are shown in Figure 6.1.
2. Samples (2.700-gram) were reduced as above. They were then hydrofluorinated "isothermally" at 1100°F (set-point) with anhydrous HF. Actual gas temperature near the solid sample was estimated to be 1055°F. The conversion-time curves are shown in Figure 6.2.

B. Reduction Number Determinations

The times for 97 per cent reduction of the calcined samples to UO_2 were determined at 930°F in hydrogen. The time measured in seconds is defined as the "reduction number." Results are given in Table 6.2.

C. Surface Area Measurements

The calcined samples and the uranium dioxides prepared from them were submitted for measurement of the specific surface area, using the BET nitrogen adsorption method. The results are presented in Table 6.2.

Discussion

The data of Table 6.2 illustrate the effect of calcination temperature on the specific surface area of the semi-works ADU and UO_2 derived from it. In this brief study, the effect of varying the time of calcination was not investigated; previous work by Notz[8] indicated that after a calcination time of one hour, the rate of further decrease in surface area is low. The data show that the surface area is reduced very rapidly with heating, once the samples have been fully converted to

[redacted]

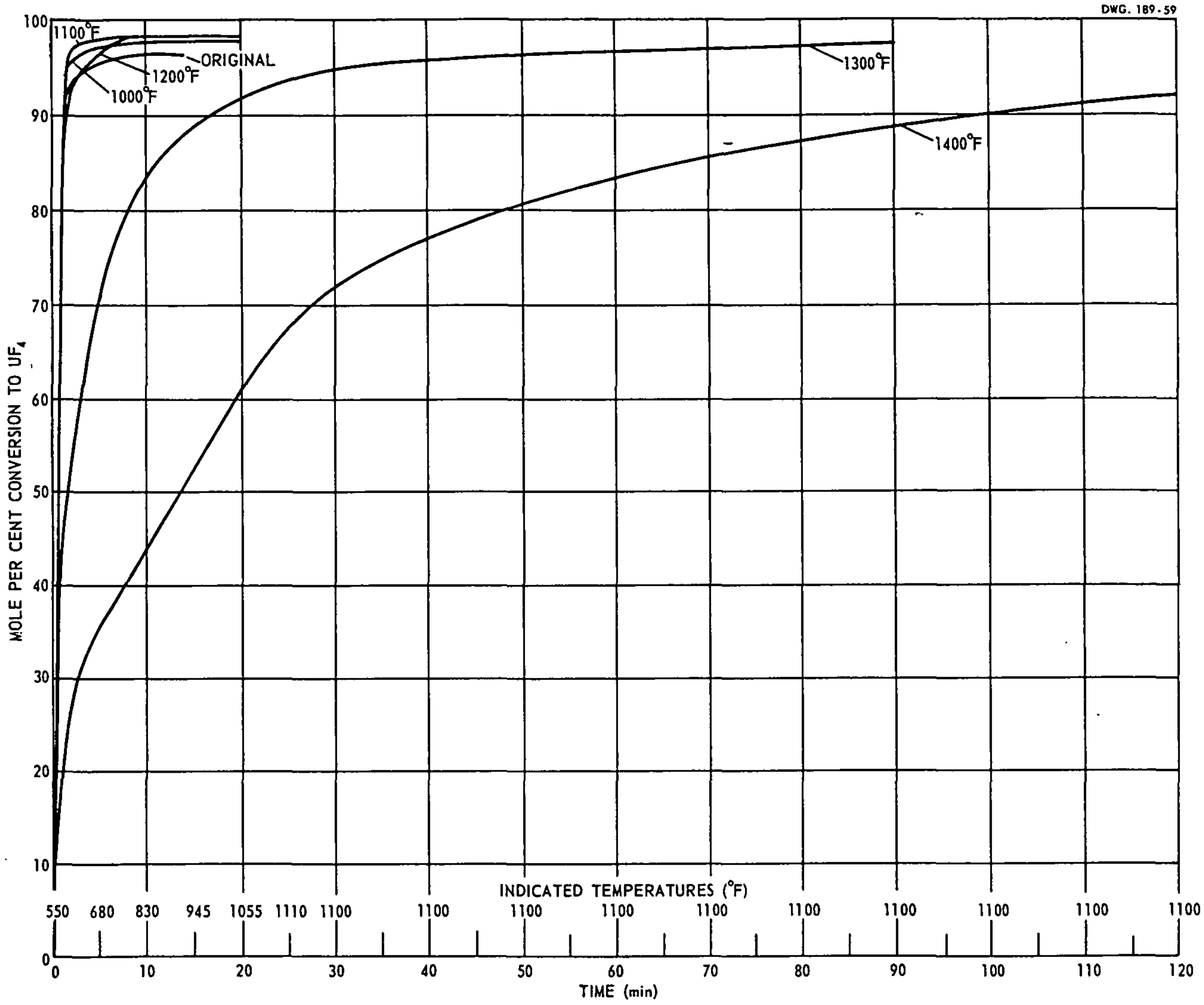

FIGURE 6.1 Thermobalance Hydrofluorination of UO_2 from Semi-Works ADU; Temperature Programmed from 550°F to 1100°F. Temperatures of Pre-Calcination Indicated on Curves.

U_3O_8 at about 1150°F. The reduction number increases rapidly as the temperature of calcination is increased above this value.

The curves of Figure 6.1 show that ADU calcined at temperatures up to 1200°F is capable of very rapid conversion to UF_4 when the temperature during the early phases of the reaction is never sufficiently great to promote sintering. For ADU calcined at 1300° and 1400°F, the hydrofluorination rate drops off rapidly, as would be expected for material having too little surface area exposed to the reactant gas.

The isothermal hydrofluorination curves of Figure 6.2 illustrate the added effect of sintering on reaction rates. For the original ADU which was not recalcined and those samples which were calcined at 1000° and 1100°F, the hydrofluorination rate fell off after initial rapid conversion to about 50 per cent UF_4. This is considered to be caused by sintering during the initial phase of the reaction, while relatively high temperatures are developed within the samples; however, precalcination of the ADU to 1200°F lessens the effect of sintering, and the maximum conversion is achieved. At the higher calcination temperatures of 1300° and

[redacted]

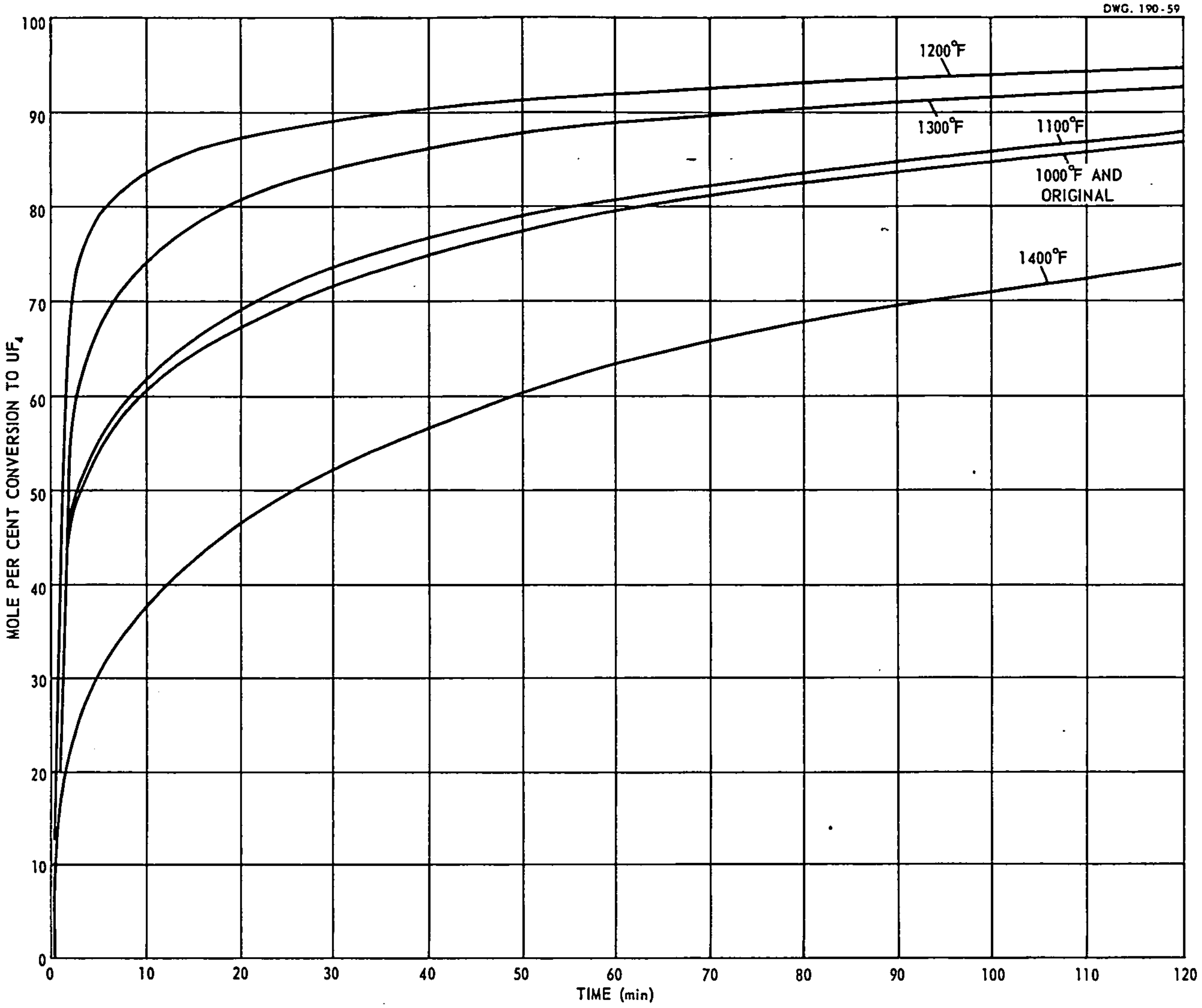

FIGURE 6.2 Thermobalance Hydrofluorination of UO_2 from Semi-Works ADU at 1055°F (Gas Temperature near Sample); Temperatures of Pre-Calcination Indicated on Curves.

1400°F, the benefit gained by diminished tendency for sintering is outweighed by the detrimental decrease in surface area to a point where diffusional resistances offered to mass transfer between gas and solid prevent rapid reaction.

Although the specific surface area of the ADU is reduced by a large percentage when calcined at 1200°F, the resulting U_3O_8 and UO_2 derived from it possess specific surface areas considerably above that normally found for a "good" UO_2 prepared from pot-denitrated UO_3 (i.e., 4 to 5 sq. m/g). Accordingly, the hydrofluorination rate obtainable with the calcined ADU is considerably greater.

In translating the laboratory results to plant-scale application, it appears desirable to have feed material possessing the hydrofluorination characteristics shown by ADU which has been calcined at 1200°F. If relatively low temperatures can be maintained in the hydrofluorination reactors during the earlier phases of the reaction by employing low HF excesses and by adequate cooling (primarily in the first hydrofluorination reactor), the ADU should hydrofluorinate as readily as mate-

[redacted]

TABLE 6.2 Surface Areas and Reduction Numbers for Calcined ADU Samples

Calcination for each sample: one hour

ADU Calcination Temp (°F)	Reduction Number (sec)	Specific Surface Area of	
		Calcined Samples (sq m/g)	UO_2 Samples* (sq m/g)
Original (1000°F, Estd.)	230	–	–
1000	230	13.3	16.0
1100	250	11.4	11.7
1200	325	7.0	6.9
1300	630	2.5	3.3
1400	1900	0.65	1.7

• ADU samples reduced at 1000°F with provision to prevent partial reoxidation of active UO_2, using procedures given in Reference 9.

rial which has not been calcined at temperatures as high as 1200°F. On the other hand, if high temperatures cannot be avoided – particularly during periods of upset – the material calcined at 1200°F should hydrofluorinate to higher levels of conversion because of its lessened tendency towards sintering.

If calcination at higher temperatures is attempted in large-scale calcining equipment, it is visualized that accurate control of temperature within a very narrow range would be essential. This is evident from the surface area determinations of Table 6.2 and the hydrofluorination results. Although uniform calcination of small samples of material is easily achieved in the laboratory, it may be difficult to accomplish when handling large volumes of material in the usual types of available calcining equipment.

Conclusions

It is concluded that a calcination temperature of 1200°F would be about optimum for the sample of semi-works ADU examined in this study. The material would be capable of very rapid hydrofluorination under conditions of increasing temperature during the course of reaction and would also be less easily damaged by sintering if relatively high temperatures could not be avoided during the initial phase of reaction.

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7. ANALYSES OF VARIATIONS IN VISUALLY DETERMINED DERBY GRADES

A. J. Klee J. E. Vath

Abstract

A number of production derbies were examined visually with respect to the surface coverage, the volume, and the weight of slag adhering to the derbies. These results were compared with the present derby grading system, and it was found that considerable overlap exists in the grades as defined presently. Quantitative data have been developed which will ultimately assist in Accountability calculations of uranium metal production.

Introduction

At the present time, Metal Production Plant derbies (produced by magnesium reduction of UF_4) are characterized by visual means into three different grades. The system is such that grade one derbies are those containing very little to no visible slag, grade two derbies are those with only a moderate amount of slag, and grade three derbies are those with a considerable amount of adhering slag. Photographs have been provided to aid the operators in the classification of these derbies. The grade of a derby is an important factor in present statistical and quality-control programs, as well as in calculations of uranium metal production for accountability purposes.

In this study, members of the Statistical Group and the Technical Measurements Group of the Accountability-Quality Control Department have examined a number of production derbies and characterized each one by:

1. Percentage of slag covering the derby
2. Amount of slag on the derby
3. Physical state of the slag on the derby
4. Geometric configuration of the derby slag

Since derby grades are presently used as a measure of derby quality, it was deemed necessary to determine whether the present system provides well-defined categories, in light of the parameters just described.

Objectives for This Quarter

This study was undertaken to improve the bases for the present method of derby grading. To this end, it was desired to determine the extent of overlap among parameters in derby grading.

Summary of Results Obtained This Quarter

1. A considerable amount of overlapping of slag parameters exists under the present system of derby grading.
2. The quantitative summaries of such overlapping, as presented in this report, can serve as a guide to a reapprasial of the present derby grading system.
3. The data obtained from this investigation can be used to estimate the amount of slag contained on production derbies and therefore assist in accountability calculations.

Data and Discussion

The derbies examined in this study, which were graded by production personnel, totalled 604. The derbies were selected by a random quota method.

Initially, frequency distributions of the data by derby grade and by group* were prepared. Several smoothing iterations by the method of moving averages were necessary, however, before the shapes of the frequency distributions could be determined. Briefly, grade one and grade two curves resembled Poisson-type distributions, while grade three curves suggested skewed normal-type distributions. Since it was difficult to determine the overlap of one grade with another from frequency distributions, a number of cumulative frequency plots were prepared.

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* *The term "group," as used in this discussion, refers to any one of the three slag parameters studied (i.e., the percentage of derby surface covered with slag, the volume of slag adhering to the derby, and the weight of the slag adhering to the derby).*

[redacted]

Figures 7.1, 7.2, and 7.3 show the over-all cumulative frequency distributions, by grade, for all three slag parameters. The lower ranges of these distributions for slag volume and slag weight are shown in Figures 7.4 and 7.5. From these plots, it was possible to obtain Table 7.1.

The slag coverage parameter is simply measured as the percentage of the top derby area covered by slag, except that these percentages are arranged into discreet classes. Thus, the 0% slag coverage parameter contains derbies with from 0 to 9% slag coverage, the 10% slag coverage parameter contains derbies with from 10% to 19% slag coverage, etc. The slag volume parameter is the cubic inches of slag adhering to the derby, arranged into discreet classes. Similarly, the slag weight parameter represents the pounds of slag adhering to the derby, grouped into discreet classes.

Table 7.1 indicates a very high degree of overlap between grades one and two and a high degree of overlap between grades two and three. The overlap between grades one and three, however, is trivial.

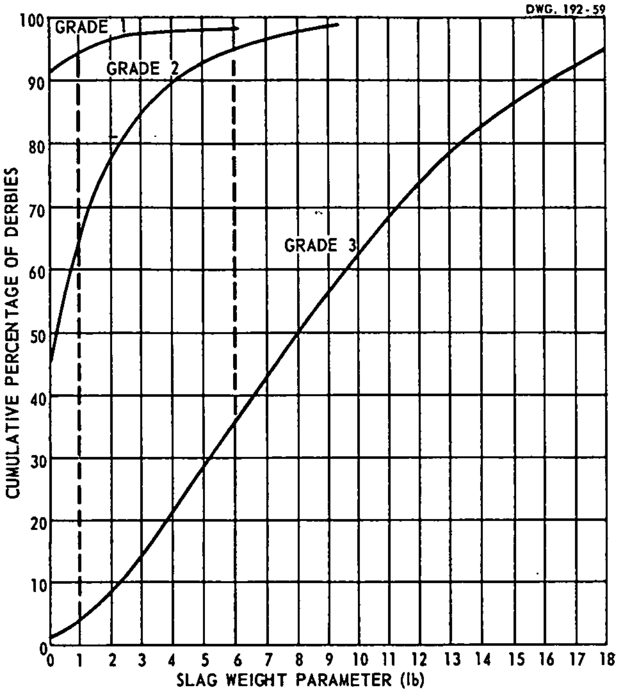

FIGURE 7.2 Slag Weight (0 to 18 lb) for the Three Grades of Derby

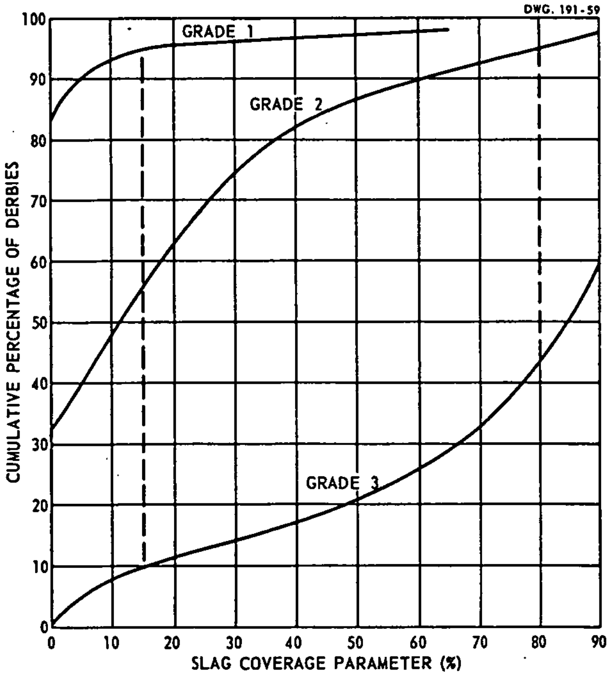

FIGURE 7.1 Slag Coverage of the Three Grades of Derby

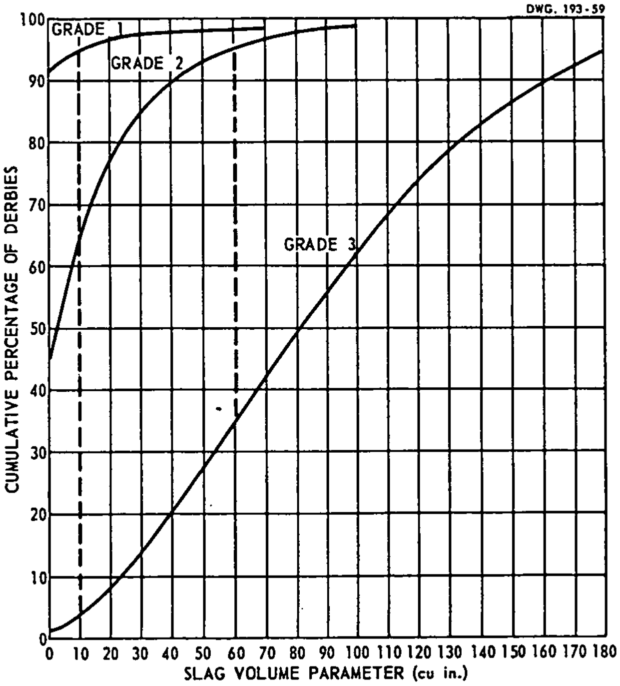

FIGURE 7.3 Slag Volume (0 to 180 cu in.) for the Three Grades of Derby

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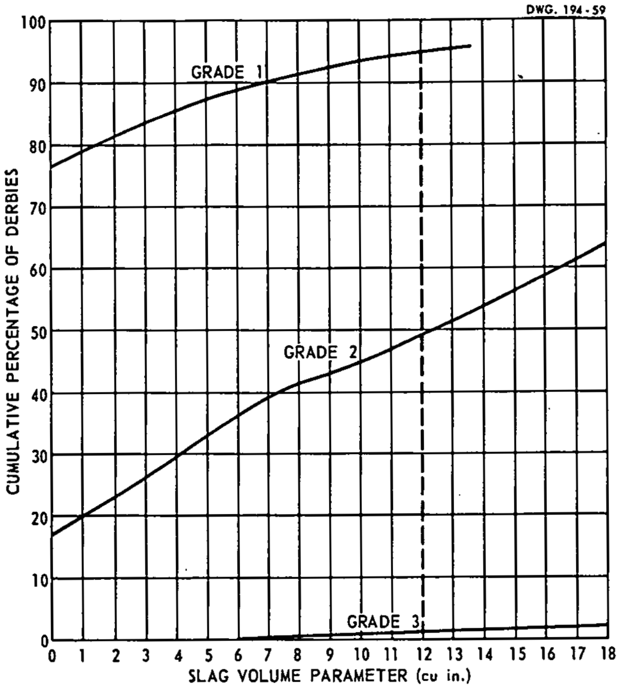

FIGURE 7.4 Slag Volume (0 to 18 cu in.) for the Three Grades of Derby

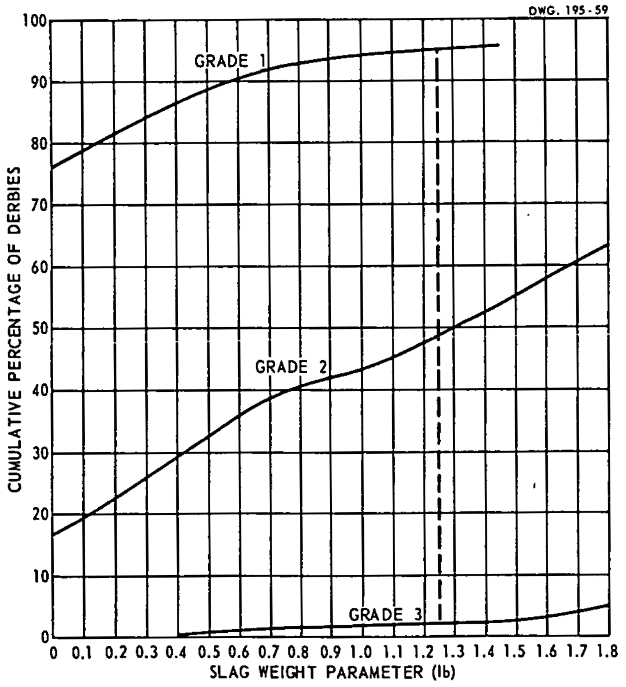

FIGURE 7.5 Slag Weight (0 to 1.8 lb) for the Three Grades of Derby

TABLE 7.1 Overlapping of Derby Grades

	% of Grade 2 Contained in 1st 95% of Grade 1	% of Grade 3 Contained in 1st 95% of Grade 2	% of Grade 3 Contained in 1st 95% of Grade 1
Slag Coverage Parameter•	56	44	10
Slag Volume Parameter*	50	35	2
Slag Weight Parameter*	51	36	2

• The parameters values were determined on the basis of the four characterizations mentioned in the Introduction.

It is also apparent that for grading purposes, slag volume and slag weight bases are comparable.

This overlap explains, to a great extent, the difficulty experienced in determining significant differences among various treatments, on a derby grade basis. Utilizing the present derby grading system, it would appear that comparisons for various factors by grade should only be made between grades one and three.

Recommendations for Future Work

Since a characterization of derby quality by the various slag parameters studied in this report appears to hold several advantages over the present grading system, especially for critical correlation purposes, it is recommended that the study be extended to include correlations of slag parameters with:

1. Green salt lot analyses
2. Reduction furnace number
3. Firing time
4. Slug reject rate
5. Crude ingot yield

In addition, it is recommended that an investigation of the effects of thermal-shocking derbies be made, utilizing these slag parameters as a measure of the slag removed by the thermal-shocking process.

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8. RECOVERY OF URANIUM FROM A MIXTURE OF URANIUM, MAGNESIUM, AND MAGNESIUM FLUORIDE

S. Cseplo H. S. Brech

Abstract

Metallic uranium in the form of prill and small pieces was recovered from the +20 mesh reject stream from the Metal Production Plant slag liner facility. Approximately 58 per cent of the total quantity of the remilled and screened reject stream was metallic uranium, of which 94 per cent was recoverable. A simple hydraulic separator was constructed to hydraulically separate the uranium from a mixture of uranium, magnesium, and magnesium fluoride.

Introduction

At this site, slag liner is used instead of the more expensive dolomite to line bomb reduction pots. This slag liner is made from reduction pot residues by ball-milling the residues, screening the overflow ball-mill stream at 20 mesh, and collecting the −20 mesh fraction for use as slag liner. The so-called "recycled Bin 3 material" which was the subject of this investigation was produced by recycling the +20 mesh fraction through the ball mill a second time, screening the ball-mill overflow at 20 mesh and collecting the +20 mesh material separately. Examination of the latter material revealed that a considerable amount of uranium was present and that it might be economical to mechanically separate the uranium from the magnesium and magnesium fluoride. The separated uranium could be consolidated by salt melting or vacuum remelt into massive metal pieces for return to the production stream as remelt stock.

Previous Work on the Project

No previous development work had been done on recovery of this material.

Objectives for This Quarter

The objectives in the Pilot Plant study were to evaluate the efficiency of (1) screening and (2) hydraulically separating the screened fractions into uranium and a mixture of magnesium and magnesium fluorides.

Summary of Results Obtained This Quarter

1. Approximately 58 per cent by weight of the "recycled Bin 3 material" is uranium; 94 per cent of the uranium content can be recovered by hydraulically separating the screened fractions.
2. The uranium prill or pieces are clean and free of magnesium or magnesium fluoride contamination. This uranium could be salt-melted or vacuum-melted into pigots for return to the production stream as remelt stock.
3. The −16 mesh fraction is too fine for remelting. Any uranium in this fraction would have to be recovered by chemical means.
4. The magnesium and magnesium fluoride from the hydraulic separator could possibly be processed for reuse in the bomb reduction step. This is yet to be evaluated.

Procedure and Discussion

A Selectro double-deck vibrating screen with a 4-mesh screen and a 16-mesh screen was used for the initial separation of the recycled Bin 3 material. Sloping of the deck 5° from the horizontal was found to be most advantageous for a rapid and effective screening rate. The feed material was dumped into a feed hopper, from which it was fed through a Syntron flow control valve directly into the top screen. A feed rate of approximately 1000 pounds per minute was used for the initial phases of the investigation. The screened fractions were collected in 30-gallon drums.

An analysis of the data obtained from the three

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fractions showed that 44 per cent of the feed was in the +4 mesh range, 45 per cent of the feed was in the −4, +16 mesh range, and 11 per cent of the feed was in the −16 mesh range (Table 8.1).

TABLE 8.1 Selectro Screen Data – Recycled Bin 3 Material

Net Weight (lb)	+4 Mesh (lb)	−4, +16 Mesh (lb)	−16 Mesh (lb)
1110	406	619	76
1408	736	596	78
1338	648	500	184
1156	366	524	250
1036	416	538	84
906	436	380	104
1032	456	492	106
1106	404	524	100
1068	604	388	84
Total	4472	4561	1142
Average (%)	44	45	11

A simple apparatus (see Fig. 8.1) was devised for gravity-separating the uranium from the magnesium and magnesium fluoride. It consisted of a 36-inch length of 1½-inch-diameter pipe with a central 1-inch-diameter pipe feed inlet, a ⅜-inch-diameter bottom discharge pipe, and a ⅜-inch-diameter bottom water inlet pipe. The entire hydraulic separator was inclined at an angle of 40° from the horizontal. Water, at an inlet pressure of 40 psig and at a rate of 11 gallons per minute, was used as the hydraulic fluid. The overflow from the 1½-inch pipe was measured at 9 gallons per minute, while the underflow was measured at 2 gallons per minute.

A larger separator was built on the same principle, with a 36-inch length of 2-inch-diameter pipe, a 1¼-inch-diameter feed inlet, a 1-inch-diameter water inlet pipe, and a semi-circular discharge opening in the bottom of the inclined central pipe. Because of the large-diameter piping used in this adaptation, the supply water pressure was only 19 psig. The water rate through the large separator was estimated at 30 gallons per minute.

After the water is turned on, the feed (consisting of magnesium, magnesium fluoride and uranium) is slowly fed into the inlet pipe. Because of the differences in density of the three types of particles,

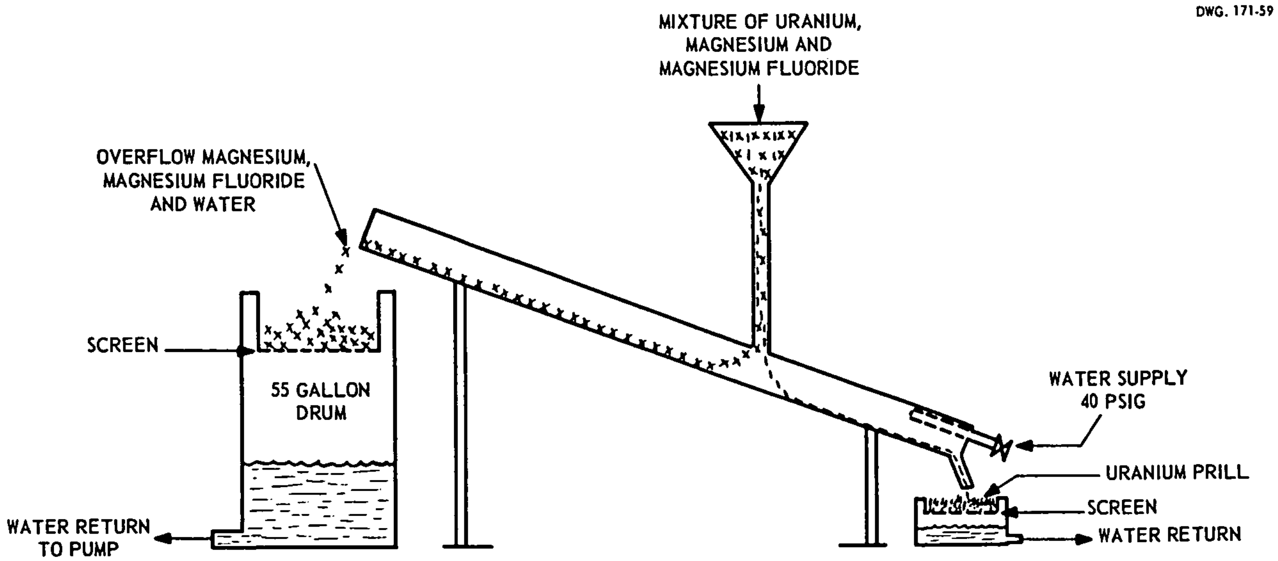

FIGURE 8.1 Hydraulic Separator

the uranium prill sinks to the bottom of the pipe, where it emerges with the underflow stream. The magnesium and magnesium fluoride are swept out with the overflow stream.

When the small hydraulic separator was used, a feed rate of 200 pounds per hour of the mixture yielded a uranium prill rate of 120 pounds per hour and a combined magnesium-magnesium fluoride rate of 80 pounds per hour. The larger hydraulic separator was able to handle a feed rate of 400 pounds per hour of feed, yielding a uranium prill rate of 252 pounds per hour and a magnesium-magnesium fluoride rate of 148 pounds per hour.

Examination of the uranium product showed that there was very little magnesium or magnesium fluoride contamination present. As can be seen from the photograph of the uranium prill (Fig. 8.2), most of the prill is uranium, but a few particles of the prill are agglomerates of magnesium and uranium (Fig. 8.3). These magnesium-uranium prill pieces (Fig. 8.3) can not be separated from the uranium mechanically, but could probably be acid-washed to dissolve the magnesium from the uranium. A typical sample of prill had a magnesium content of 0.03 per cent. The hydraulic action of the water very effectively scoured the uranium prill free of any adhering magnesium fluoride dust.

The magnesium-magnesium fluoride residue (Fig. 8.4) was essentially free of uranium contamination and could possibly be recycled for reuse in the bomb reduction step. A typical sample of this material showed a uranium content of only 0.5 per cent. This uranium content was attributed to very small pieces of uranium that were swept up with

699-3

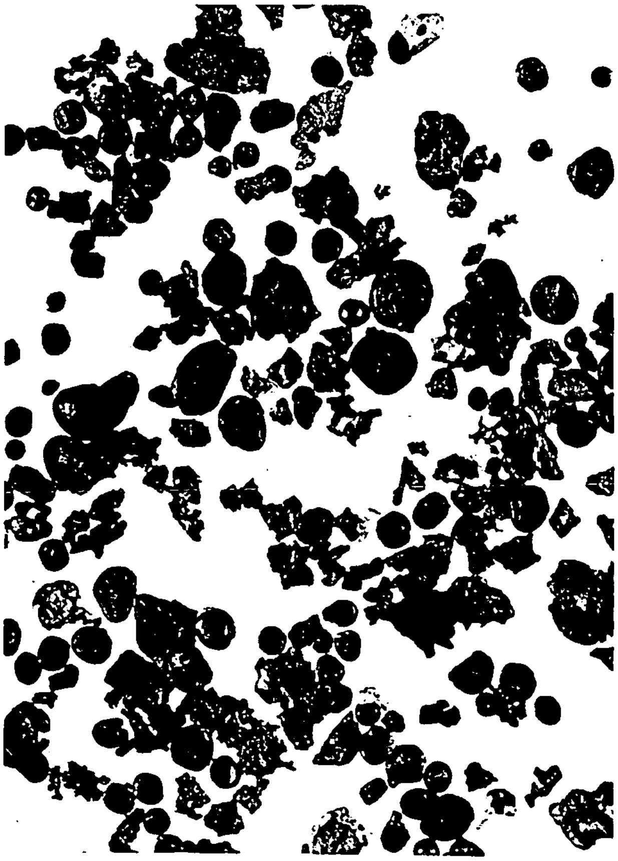

FIGURE 8.2 Uranium Prill, 3X

699-1

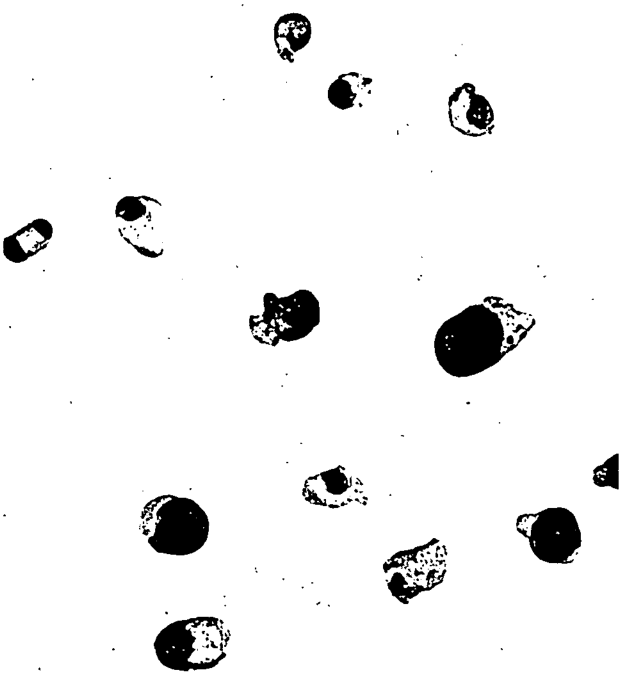

FIGURE 8.3 Magnesium-Uranium Agglomerates, 5X

[redacted]

TABLE 8.2 Hydraulic Separation

	−4, +16 Mesh Fraction			+4 Mesh Fraction		
	Net Weight of Fraction (lb)	Uranium (lb)	Yield (%)	Net Weight of Fraction (lb)	Uranium (lb)	Yield (%)
	619	410	60	1810	926	51.8
	702	531	75			
	630	400	73			
	664	418	63			
	542	316	67			
	492	286	59			
	524	251	50			
Total	4173	2672	xxx	1810	926	xxx
Avg	xxx	xxx	63.2	xxx	xxx	51.8

Over-all average Yield from the +4 and −4, +16 mesh fractions $= \frac{4561\,(0.632) + 4472\,(0.518)}{9033}$

$$= \frac{2885 + 2320}{9033}$$

$$= \frac{5205}{9033}$$

$$= 57.8\%$$

Total uranium content of recycled Bin 3 material $= \frac{4561\,(0.632) + 4472\,(0.518) + 1142\,(0.29)}{10175}$

$$= 54.5\%$$

Maximum Uranium Yield Obtainable $= \frac{4561\,(0.632) + 4472\,(0.518)}{4561\,(0.632) + 4472\,(0.518) + 1142\,(0.29)}$

$$= 93.8\%$$

the lighter magnesium and magnesium fluoride particles.

An average 58 per cent yield of cleaned uranium prill was obtained from the +4 and −4, +16 mesh fractions together (Table 8.2). This amount of uranium accounted for 93.8 per cent of all of the uranium present in the recycled Bin 3 material. The prill was judged suitable for salt-melting into "pigots" for return to the production stream. The −16 mesh fraction contained 29 per cent uranium (6.2% of the total uranium content in recycled Bin 3 material), but could not be separated because of the fineness of the material. Visual examination of this fraction did not show distinguishable particles of free metal; the uranium is evidently present largely as very fine particles or as uranium oxides.

The uranium prill as obtained from the hydraulic separator was too wet for salt-melting tests. Methods of drying it were tried. Oven-drying the prill, using hot air (180°F) blowing over the prill, proved to be effective, but was too hazardous because prill damp with water is easily ignited when heated. The prill was safely dried by placing it in a perforated-metal basket and immersing the basket in a drum of safety-solvent (methyl chloroform). The basket was raised and lowered in the safety-solvent several times, and the basket was then removed and allowed to drain freely. A stream of warm air (150°F) was blown over and through the basket with a fan to drive off the remaining safety-solvent. In this manner, 80 pounds of wet prill containing 1.5 pounds of water was dried thoroughly in 40 minutes; 1.5 pounds of safety-solvent was lost in the process.

[redacted]

[redacted]

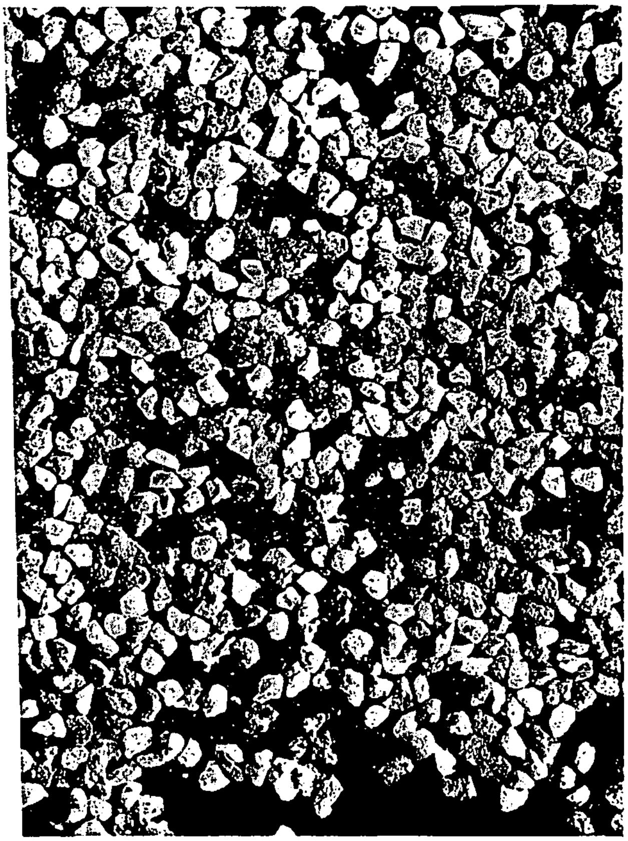

FIGURE 8.4 Magnesium-Magnesium Fluoride Residue, 3X

Future Work

Future work on this project will consist of the following:

1. Design and testing of an improved design of hydraulic separator, with greater throughput capacity.
2. Testing of magnetic separation for removal of metallic iron contamination.
3. Evaluation of a process for hydraulically separating uranium in Bin 3 material from magnesium and magnesium fluoride directly with no prior screening.

[redacted]

9. SCRAP PROCESSING BY AN AQUEOUS UF_4 PROCESS

Abstract

The product obtained by subjecting low-grade MgF_2 type scrap to the currently employed UAP Process was found to be sufficiently pure for subsequent hydrochloric acid dissolution and aqueous precipitation of metal grade UF_4.

Several of the high-grade scrap streams (black oxides resulting from the burning of chips, turnings, sludges, etc.) were found to be sufficiently pure to be amenable to a hydrochloric acid dissolution – aqueous UF_4 precipitation process.

Pilot Plant tests have shown that metal grade UF_4 can be made from impure uranium-containing pickle liquor* by the Winlo process.** High nitrate content in the starting solution acts as a retardant, and can be decreased either by adding formaldehyde and heating or by digesting high nitrate feeds with black oxide. Solutions prepared from dolomitic reduction pot residues*** were not suitable for precipitation of UF_4.

Introduction

Scrap generation at FMPC is divided between normal and enriched scraps of various types. The two classes of scrap are chemically similar, and processing techniques are interchangeable between the classes. However, separate facilities must be provided to prevent cross contamination and unacceptable variation in isotopic assay of both normal and enriched products. The general objective of scrap development work has been to provide optimum processing techniques for both classes of scrap. Laboratory work during the past quarter has been concerned with testing the feasibility of processing current normal scrap generation by the Winlo Process to produce metal grade UF_4. The Pilot Plant program has been directed toward refinement of the techniques, reported previously,[1] for processing enriched scrap by the Winlo Process.

Objectives for This Quarter

1. Determine the quality of UF_4 (from the chemical purity and physical property standpoint) which could be produced by the Winlo Process from (a) uranyl ammonium phosphate (UAP)[2] and (b) black oxide products from the normal Metals Recovery operation.
2. Determine optimum operating conditions for production of UF_4 from these normal scraps.
3. Determine the quality of UF_4 that could be produced from enriched dolomitic bomb liner, black oxide, and pickle liquor scraps without purification of the leach liquor prior to UF_4 precipitation.
4. Determine the best method for reducing the nitrate content of pickle liquor prior to UF_4 precipitation.

LABORATORY PREPARATION OF GREEN SALT FROM PLANT-PRODUCED UAP AND BLACK OXIDE

E. D. Rutenkroger J. H. Cavendish

Introduction

In the production of uranium metal at FMPC, considerable quantities of uranium-containing scrap are generated. A portion of the scrap from the metal fabrication operations is amenable to direct remelt and re-introduction into the process stream at that point. The remainder of the metallic scrap is too highly contaminated for remelt, and is oxidized in the Metals Recovery Plant and recycled through the entire purification cycle. Low

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* *Pickle liquor is a mixture of nitric acid, uranyl nitrate, and water produced when uranium chips are pickled prior to briquetting.*

** *The HCl dissolution-aqueous precipitation process developed at Winchester Laboratory and this site is hereafter referred to as the Winlo Process.*

*** *A mixture of MgF_2, dolomite, uranium, and magnesium.*

grade scraps (such as MgF_2 reduction bomb liners) are processed through the Recovery Plant uranyl ammonium phosphate (UAP) process,[2] and the resulting UAP product fed to the Refinery for recycle through the purification process. Recycle of this scrap uranium through the entire purification process is expensive; a more direct recovery is desirable. The Winlo process for direct conversion of uranium from a scrap leach liquor to metal grade UF_4 has been investigated for this purpose. Product purity and capital cost of equipment involved were the criteria used in the investigation.

Purification of MgF_2 type scrap leach solutions by amine extraction, prior to UF_4 precipitation, has been investigated and a satisfactory flowsheet has been developed.[1] Scoping tests have indicated that another process, the currently employed UAP process, may provide sufficient purification that the UAP may subsequently be dissolved in HCl and subjected to an aqueous precipitation of metal grade UF_4. This approach would require considerably less capital investment than the amine extraction purification process. Therefore, a laboratory investigation has been conducted to determine its feasibility.

The high-grade scraps (black oxide resulting from the burning of chips, turnings, sludges, etc.) are not sufficiently pure for direct conversion to UF_4 and are now processed through the Refinery concurrently with ore concentrates. However, it appears that these scraps might be sufficiently pure to be amenable to hydrochloric acid dissolution-aqueous UF_4 precipitation by the Winlo process. Therefore, a second laboratory study has been conducted. In this study, the purification which could be obtained by this method of processing was to be determined.

Objectives of Work Completed This Quarter

1. With a feed obtained by subjecting low-grade (MgF_2 type) scrap to the UAP process, it was desired to determine the purification which could be accomplished by hydrochloric acid dissolution and UF_4 production by the Winlo process.
2. It was desired to determine the effect of uranium concentration and acid concentration on the UF_4 precipitation.
3. It was desired to determine which of the high-grade scrap streams (black oxides) are of sufficient purity to be amenable to Winlo processing.

Summary of Work Completed This Quarter

1. Laboratory tests have shown that a high-grade UF_4 can be produced from plant-produced UAP. Calcination of the UAP to remove the NH_3 prior to hydrochloric acid dissolution was found to be necessary.
2. The uranium concentration and hydrochloric acid excess employed in dissolution of the UAP had little effect on the resulting UF_4; however, both had considerable effect on the SO_2 efficiency and the total time required for precipitation. The optimum conditions appear to be a uranium concentration of approximately 200 g/l and the use of a stoichiometric amount of hydrochloric acid.
3. Metal grade UF_4 was produced from all of the high-grade (black oxide) materials tested. The streams tested represented a very high percentage of the high-grade scraps currently being processed at National Lead Company of Ohio.

Aqueous UF_4 Precipitation From Solutions of UAP in Hydrochloric Acid

A series of dissolutions and aqueous UF_4 precipitations were conducted in the laboratory to study the effect of uranium concentration and acid concentration on the purity of the resulting UF_4. In initial scoping tests, uncalcined UAP and calcined UAP were used. Both samples were taken from the Metals Recovery Plant production operation. The UF_4 produced from uncalcined UAP was found to contain 1 to 2 per cent NH_3 and had a relatively low tap density (2.5 g/cc). Therefore, all subsequent tests were conducted with calcined (1200°F) UAP – presumably $(UO_2)_2P_2O_7$. Karbate beakers were used for both the digestion and pre-

[redacted]

cipitation steps involved in these tests. The Karbate was apparently unaffected by the solutions used.

A. Effect of Uranium Concentration on UF_4 Precipitation

A series of HCl dissolutions were conducted to produce solutions assaying approximately 100, 200, and 300 g/l uranium. The dissolutions were performed employing the stoichiometric amount of HCl (based on the reaction, $(UO_2)_2P_2O_7 + 4\ HCl + H_2O \rightarrow 2UO_2Cl_2 + 2H_3PO_4$) plus a $1\underline{N}$ excess. In order to obtain complete dissolution, it was necessary to use elevated temperatures (80° to 90°C) and an oxidant. Both H_2O_2 and HNO_3 were found to be satisfactory oxidants, and HNO_3 was employed for the tests reported. Following dissolution of the uranium pyrophosphate, the solutions were filtered to remove the insoluble filter aid which was present in the UAP cake. Uranium tetrafluoride was precipitated by the addition of 22 g/l $CuSO_4 \cdot 5H_2O$ and a 15 g/l excess of HF (added as a 50% solution), followed by bubbling SO_4 into the solutions. All of the precipitations were conducted at 90° to 95°C. The product UF_4 from the precipitations was oven-dried at 110°C and was analyzed "wet chemically" and spectrochemically. The results of these tests are shown in Table 9.1.

As may be seen, good purification was obtained, and the impurity levels of the product UF_4 are very low except for calcium, magnesium, sodium, and possibly phosphorus. (The wet chemical and spectrochemical analyses do not agree on phosphorus.) It is considered probable that good decontamination of these materials would be obtained during metal reduction.

The tap density of the UF_4 varied from 2.9 to 3.2 g/cc, which is slightly lower than that previously produced from purified HCl solutions. However, grinding of the sample produced in the 200 g/l test increased the tap density from 2.9 g/cc to 3.5 g/cc.

TABLE 9.1 Effect of Uranium Concentration on UF_4 Purity

	Calcined UAP Feed	Test No. 1	2	3
		HCl Leach Solution		
U (g/l)		95	176	293
PO_4 (g/l)		38	67	—
H^+ ($\underline{N}$)*		1.9	2.4	3.4
		UF_4 Product**		
Wet Chemical				
AOI (%)		0.02	0.02	0.04
UO_2F_2 (%)		0.75	0.83	1.20
U (%)	61.7	72.98	73.22	73.70
U^{+4} (%)		72.40	72.58	72.77
UF_4		96.33	95.53	95.99
H_2O (%)		2.90	3.62	2.77
F (%)		23.00	23.04	23.24
PO_4 (%)	26.5	0.13	0.09	0.08
Tap Density (g/cc)		2.91	2.91†	3.26
Spectrochemical (ppm)††				
Al	400	15	20	15
Ba	—	30	—	45
Bi	<20	<1	<1	<1
Ca	—	180	—	150
Cd	<200	<0.2	<0.2	<0.2
Cr	<100	<10	<10	<10
Cu	300	35	25	6
Fe	3000	50	80	99
Li	—	<2.5	—	<2.5
Mg	1600	>100	>100	>100
Mn	650	<4	<4	<4
Mo	<10	<6	<6	<6
Na	—	75	—	>200
Ni	<20	<10	<10	<10
P	>60,000	<20	<20	<20
Pb	80	2	2	<1
Sn	150	<1	<1	<1
Sr	<20	<10	—	<10
V	<100	<40	<40	<40
Zn	<200	<20	<20	<20

* As titrated with NaOH to pH 6.05.

** Oven-dried at 110°C.

† Grinding of sample in mortar increased the tap density to 3.51 g/cc.

†† On uranium basis.

The initial uranium concentration of the leach solution appeared to have little effect on impurity level except for iron and sodium. These two impurities seemed to increase as the uranium con-

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centration in the HCl leach solution was increased. The precipitation times for the runs at 100, 200, and 300 g/l were 1.5, 3.0, and ~7 hours, respectively. This indicates a reduction in SO_2 efficiency at the 300 g/l level (probably due to decreased solubility of SO_2 in H_3PO_4). On the basis of these tests, the optimum starting uranium concentration would be near 200 g/l.

B. Effect of Acid Concentration on UF_4 Precipitation

A series of dissolutions and aqueous UF_4 precipitations were conducted in which the HCl excess used in dissolution of the uranium pyrophosphate was 0.0N, 1.0N, and 2.0N. The dissolutions and precipitations were conducted in the same manner as those described in the previous section and at the 200 g/l uranium level. The results of these tests are shown in Table 9.2.

The results show that the HCl excess (in the range studied) has no significant effect on the resulting UF_4. However, the time required for complete precipitation increased as the HCl excess was increased. The times for the runs at 0.0N, 1.0N, and 2.0N excess were 2.4, 3.0, and ~3.5 hours. Previous work has shown this same effect to be much more pronounced in an H_2SO_4-HCl system than in a starting system of HCl alone. It appears that the H_3PO_4-HCl system is similar to the H_2SO_4-HCl system in this respect. The results of these tests indicate that the optimum HCl concentration would be as near the stoichiometric requirement as possible.

TABLE 9.2 Effect of Acid Concentration on UF_4 Precipitation

	Test No.		
	1	2	3
	Leach Solution		
HCl Excess (calculated)	0	1	2
Total Acidity N*	1.5	2.4	3.3
U (g/l)	190	176	187
PO_4 (g/l)	75	67	80
Precipitation Time (hr)	2.4	3.0	~3.5
	UF_4 Product**		
Wet Chemical			
AOI (%)	0.09	0.02	0.07
UO_2F_2 (%)	0.70	0.83	0.93
U (%)	72.90	73.22	73.34
U^{+4}	72.36	72.58	72.62
UF_4 (%)	95.37	95.53	95.42
H_2O (%)	3.84	3.62	3.58
F (%)	23.22	23.04	23.46
PO_4 (%)	0.039	0.084	0.014
Tap Density (g/cc)	3.34	2.91	3.16
Spectrochemical (ppm)†			
Al	34	20	100
Ba	25	—	30
Bi	<1	<1	<1
Ca	40	—	180
Cd	<0.2	<0.2	<0.2
Cr	<10	<10	<10
Cu	35	25	12
Fe	130	80	131
Li	<2.5	—	<2.5
Mg	>100	>100	>100
Mn	<4	<4	<4
Mo	<6	<6	<6
Na	190	—	>200
Ni	<10	<10	<10
P	>200	<20	>200
Pb	5	2	1
Sn	<1	<1	<1
Sr	<10	—	<10
V	<40	<40	<40
Zn	—	<20	<20

• As titrated with NaOH to pH 6.05.

** Oven-dried at 110°C.

† On uranium basis.

Uranium Recovery From High-Grade Black Oxide Scrap Streams By HCl Dissolution — Aqueous UF_4 Precipitation

Several of the high-grade scrap streams (black oxides resulting from the burning of chips, turnings, sludges etc.) have been investigated in the laboratory to determine their amenability to an HCl dissolution-aqueous UF_4 precipitation process. The purification which could be obtained by this technique was of primary interest. Samples used for laboratory testing were composite lot samples which were representative of the past three months' production operation. Samples of the following

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types were investigated:

Source

- Crucible Burnout Black Oxide[3]
- Oxidation Furnace Ash[3]
- Graphite Furnace Ash[4]
- Box Furnace Ash*
- Alloyed Black Oxide**

Two samples of each of the above types were tested in the laboratory.

The laboratory tests were conducted by dissolution of the black oxides in HCl (using HNO_3 as an oxidant) to produce solutions for precipitation assaying approximately 200 g/l uranium and 1N excess HCl. The insolubles were removed prior to UF_4 precipitation. Uranium tetrafluoride was precipitated from the clarified solutions by the addition of 22 g/l $CuSO_4 \cdot 5H_2O$ and a 15 g/l excess of HF after which SO_2 was bubbled into the solution. The precipitations were all conducted at 90° to 95°C, 2 to 2.5 hours being required for complete precipitation. The feed used in each test was analyzed spectrochemically and the resulting UF_4 was analyzed both "wet chemically" and spectrochemically. The results of the tests are shown in Table 9.3.

As may be seen, all of the samples tested produced high-quality UF_4 which was low in impurities. The UF_4 produced from all of the materials tested had an average assay of 0.19% AOI, 0.44% UO_2F_2, 96.03% UF_4 and 3.35% H_2O.*** It appears that dehydration to remove the water content would produce a UF_4 which would meet metal grade specifications in all respects. No laboratory work was done on dehydration, since a very promising technique has been developed and tested on a laboratory scale at the Winchester Laboratory.[5]

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* *The feed to the box furnace includes chips, turnings, sawdust, and metal spills.*

** *Alloyed black oxide is produced by passing metallic alloys through first the box furnace and then the oxidation furnace.*

*** *Confidence Limits on Analyses.*

	LE_x	Avg Level
AOI	±0.137%	1.9%
UO_2F_2	±0.241%	1.9%
UF_4	±0.320%	96.19%

Future Work

1. Cost figures will be developed for the hydrochloric acid dissolution-aqueous UF_4 precipitation process.
2. Pilot Plant testing will be carried out, with the main emphasis on metal reduction evaluation.
3. Pilot scale dehydration tests will be conducted if dehydration is found to be necessary.

GREEN SALT PREPARATION FROM PICKLE LIQUOR, BLACK OXIDE, AND REDUCTION POT RESIDUES

S. Cseplo C. C. Fogel

Introduction

The Winlo UF_4 process is a process for the preparation of metal grade UF_4 from various "scrap" materials. Scrap materials such as black oxide, UO_3, pickle liquor, and scrap UF_4 are dissolved in hydrochloric acid in the presence of an oxidizing agent. A soluble copper salt is added as a catalyst along with an excess of hydrofluoric acid. Sulfur dioxide gas is introduced which reduces the copper catalyst from the cupric to cuprous state. The cuprous copper reduces uranium from +6 to +4 and is in turn oxidized back to cupric copper; the uranium is thus precipitated as UF_4. The UF_4 produced is crystalline in nature and is accompanied by ¾ mole of water of hydration.

The process is well suited for producing metal-grade UF_4. Decontamination factors are relatively high and, as a result, many impure scrap materials can be recovered directly without a prior purification step. The Winlo process is also attractive as a means of returning many uranium scrap materials directly to the process stream as metal grade UF_4, thus bypassing the expensive solvent extraction, denitration, reduction, and hydrofluorination steps.

Previous Work Done on the Project

Earlier work on this process has been reported.[1,6,7] Previous work had been directed toward the preparation of quantities of green salt

[redacted]

[redacted]

TABLE 9.3 Purification of Black Oxide Scraps by HCl Dissolution – Aqueous UF_4 Precipitation

Precipitation Conditions: Feed Solution Assay ~200 g/l Uranium and 1N Excess HCl; Temperature 90° to 95°C; Time 2-2½ hr

	Crucible Burnout Black Oxide				Oxidation Furnace Ash				Graphite Furnace Ash				Box Furnace Ash				Alloyed U_3O_8			
	Sample 1		Sample 2		Sample 1		Sample 2		Sample 1		Sample 2		Sample 1		Sample 2		Sample 1		Sample 2	
	Feed	UF_4	Feed	UF_4	Feed	UF_4	Feed	UF_4	Feed	UF_4	Feed	UF_4	Feed	UF_4	Feed	UF_4	Feed	UF_4	Feed	UF_4
Wet Chemical																				
Tap Density (g/cc)		3.21		3.13		3.20		3.05		3.17		3.09		3.18		3.43		3.25		3.20
AOI (%)		0.00		0.06		0.13		0.13		0.14		0.14		0.13		1.14		0.02		0.01
UO_2F_2 (%)		0.38		0.41		0.32		0.25		0.12		0.10		0.14		1.75		0.19		0.69
UF_4 (%)		97.45		97.47		95.28		95.99		96.20		95.40		95.86		93.13		97.12		96.40
U (%)		73.56		73.08		72.81		73.37		73.26		72.74		73.06		73.01		72.99		73.39
U^{+4} (%)		73.27		72.76		72.56		73.18		73.17		72.66		72.95		71.66		72.84		72.86
F (%)		23.34		23.16		23.34		23.28		23.20		22.96		23.28		23.29		23.20		23.14
H_2O (%)		2.17		2.06		4.27		3.63		3.54		4.36		3.87		3.98		2.67		2.90
Spectrochemical (ppm)*																				
Al	>100	<6	>100	<6	<6	<6	>100	<6	<6	<6	<6	<6	45	<6	10	10	<6	<6	–	<6
B	<0.2	–	<0.2	–	<0.2	–	0.35	–	<0.2	–	<0.2	–	<0.2	–	<0.2	–	<0.2	–	–	–
Ba	11	10	11	12	8	10	6	10	12	5	20	12	10	6	150	70	–	80	–	150
Bi	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	–	<1
Ca	–	30	>200	30	>200	130	>200	200	–	25	–	75	>200	50	>200	>200	–	100	–	>200
Cd	<0.2	–	<0.2	–	<0.2	–	<0.2	–	<0.2	–	<0.2	–	<0.2	–	<0.2	<0.2	0.9	–	–	<0.2
Cr	20	<10	10	<10	<10	<10	33	<10	10	<10	<10	<10	100	<10	15	<10	<10	<10	–	<10
Cu	6	10	13	15	11	6	>100	6	30	6	2	8	85	5	27	25	2	15	–	40
Fe	690	<10	1270	<10	5490	26	3925	<10	641	<10	<10	<10	1532	<10	1871	26	<10	<10	–	<10
Li	–	<5	8	<5	>20	<5	>20	5	20	<5	10	<5	>20	<5	>20	<5	–	<5	–	<5
Mg	>100	6	>100	50	>100	8	>100	<4	95	<4	14	10	>100	6	>100	>100	<4	30	–	>100
Mn	>100	<4	80	<4	5	<4	>100	<4	10	<4	<4	<4	>100	<4	8	<4	<4	<4	–	<6
Mo	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	<6	–	<4
Na	30	15	50	20	>200	175	>200	185	>200	35	200	20	>200	45	>200	>200	–	105	–	75
Ni	72	<10	28	<10	<10	<10	<10	<10	26	<10	<10	<10	65	<10	36	<10	<10	<10	–	<10
P	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	–	<20
Pb	>30	<1	>30	<1	2	<1	>30	<1	2	<1	<1	<1	>30	<1	2	2	<1	1	–	<1
Si	100	<10	>100	<10	40	<10	>100	<10	48	<10	<10	<10	58	<10	32	–	<10	<10	–	–
Sn	3	<1	15	<1	11	<1	>25	<1	16	<1	<1	<1	25	<1	2	<1	<1	<1	–	<1
Sr	–	<10	<12	<10	<12	<10	<12	<10	<10	<10	<10	<10	15	<10	>200	35	–	<10	–	<12
V	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	<40	–	<40
Zn	<20	<20	25	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	–	<20

* ppm on U basis.

[redacted]

from various scrap streams for the purpose of evaluating its reduction-to-metal characteristics and for equipment evaluation. Both laboratory and Pilot Plant semi-works development work is reported in the references.

Objectives for This Quarter

The main objective of laboratory work done this quarter was to evaluate the conditions needed to produce an acceptable Winlo UF_4, using the principal "problem" scrap materials as sources of feed.

Summary of Results Obtained This Quarter

1. Green salt made by the Winlo process from a feed solution containing digested dolomitic-liner reduction residues (along with pickle liquor and black oxide) was grossly contaminated with impurities, because of the high soluble-magnesium and soluble-calcium content of the dolomitic liner. This indicates that reduction pot residue leach liquor will require additional treatment to reduce the soluble magnesium and calcium content before precipitation of UF_4.
2. Precipitation of an acceptable grade of UF_4 from pickle liquor alone was shown to be feasible. The use of formaldehyde to reduce the nitrate content of the pickle liquor before precipitation of UF_4 reduced the total precipitation time by 50 per cent. The green salt prepared from formaldehyde-reduced solutions is acceptable chemically and spectrochemically, but is lower in tap density than green salt prepared from non-reduced solutions.
3. Total precipitation time is dependent on the initial nitrate content of the feed solution. Apparently, the SO_2 gas preferentially reduces the nitrate ion before reducing the copper catalyst. Since the copper catalyst must be reduced before precipitation of UF_4 commences, rapid precipitation should be achieved if the nitrate concentration of feed solutions is decreased before the introduction of SO_2 gas.
4. The addition of formaldehyde to feed solutions containing high nitrate values was shown to be a rapid and efficient method for decreasing the nitrate content. Over 93 per cent of the original nitrate content in a feed solution was removed by adding formaldehyde and heating. Much of the free nitrate content of high-nitrate feeds was removed by digesting with black oxide.

Procedure and Discussion

The following experiments were conducted in the Pilot Plant laboratory and utilized two-liter Pyrex beakers for the digestions and two-liter high-temperature, high-density polyethylene beakers immersed in a water bath for the green salt precipitation. Three of the principal scrap streams are: pickle liquor from the enriched uranium briquetting line, dolomitic liner reduction pot residues containing enriched uranium, and black oxide from the crucible burnout station. The pickle liquor, as obtained from the pickling line, assayed 250 to 325 g/l uranium; the dolomitic-liner reduction residues assayed 2 per cent uranium; and the black oxide assayed 82 per cent uranium.

A digestion was made of 204 grams of black oxide, 2.57 liters of pickle liquor, 567.5 grams of reduction pot residues, and 0.76 liter of 36 per cent HCl. After the slurry was digested at 85°C for 2 hours, the slurry was filtered, yielding a solution containing 84 g/l uranium and $1.47\underline{M}\ H^+$. The residual cake assayed 0.018 per cent uranium, which indicated excellent uranium recovery. Two standard Winlo green salt precipitation* runs were made, using the filtrate from this digestion. Spectrochemical analyses were obtained on the feed solution and the green salt produced to determine if sufficient decontamination was achieved to justify further experiments. The analytical results of the above experiment are given in Table 9.4.

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* *Standard Winlo precipitation conditions are as follows: Add to the uranium solution six grams per liter of copper and 15 grams per liter in excess of the stoichiometric requirement for hydrofluoric acid (anhydrous HF basis). Bubble through the solution 80 to 100 per cent excess of SO_2 gas at 95°C, with agitation.*

TABLE 9.4 Contaminant Levels Before and After Precipitation

	Feed Solution	UF_4, Run 1	UF_4, Run 2
Al	<400	<400	15,000
B	120	–	–
Bi	<20	<20	<20
Cd	<200	<200	<200
Co	<100	<100	<100
Cr	3500	<100	200
Cu	100	<100	<100
Fe	>1000	>1000	700
Mg	>6000	>6000	>6000
Mn	>100	20	<40
Mo	30	<10	<10
Ni	1500	20	30
P	<400	<400	<400
Pb	<20	<20	<20
SiO_2	<400	–	–
Sn	100	60	20
V	<100	<100	<100
Zn	<200	<200	300

It was concluded that direct precipitation of a feed solution containing digested dolomitic-liner reduction residue would not be feasible because of the poor decontamination obtained.

Failure of the initial experiment to produce acceptable quality green salt prompted an investigation of the precipitation qualities of pickle liquor alone. A Winlo precipitation run was made, using pickle liquor assaying 95.2 g/l uranium, 2.3M H^+, and 91.8 g/l NO_3. Total precipitation or SO_2 gassing time for complete uranium depletion was six hours. Since copious amounts of NO_2 fumes were observed during the run, it was concluded that the SO_2 gas was preferentially reducing the nitrate ion rather than the copper ion and thus retarding the reduction of the hexavalent uranium ion to the quadrivalent uranium ion. As can be seen from the wet chemical and spectrochemical analyses given in Table 9.5, the green salt produced was of acceptable quality.

In order to check the postulation that high nitrate values were deleterious to the Winlo process, an experiment was conducted in which the nitrate content of the feed solution was reduced to 44 g/l. One hundred and twenty grams of black oxide was digested in 2.6 liters of pickle liquor assaying 65 g/l uranium, 51.1 g/l NO_3, 0.44N HNO_3, and 378 cc of 36% HCl in order to utilize the free HNO_3 content. After digestion for 3 hours at 95°C, the slurry was filtered and diluted to yield a feed solution assaying 89.6 g/l uranium, 1.6M H^+ and 44 g/l NO_3^-. A normal Winlo precipitation run was made in which the total SO_2 gassing time for complete UF_4 precipitation was only three hours. The filtrate obtained when the green salt was filtered contained 0.02 g/l uranium. The analytical data for this experiment are listed in Table 9.6. The results of this experiment seem to strengthen the original postulation that high free nitrate values in the feed solutions are a retardant for efficient UF_4 precipitation. This statement seems to hold true, since the previous solution containing 92 g/l NO_3^- took six hours for the total precipitation of the uranium, as opposed to three hours when a low nitrate level was used.

In order to further check the dependence of precipitation time on the original free nitrate value in the feed solution, an experiment was performed utilizing formaldehyde to remove the free nitrate content. About 0.5 mole of formaldehyde was added to a pickle liquor solution assaying

TABLE 9.5 UF_4 Made From Pickle Liquor Alone (91.8 g/l NO_3)

Chemical Analysis of UF_4

AOI*	– 0.06%	U^{+4}	– 72.86%
UO_2F_2	– 0.53%	Tap Density	– 2.55 g/cc
UF_4	– 95.97%	Moisture	– 3.44%
U	– 73.27%	F	– 23.20%

Spectrochemical Analysis (ppm, Uranium Basis)

	Feed Solution	UF_4		Feed Solution	UF_4
Al	<6	<6	Li	>20	<2.5
B	<0.2	–	Mg	<4	40
Ca	>200	>200	Mn	<4	<4
Cr	<10	<10	Na	>200	95
Cu	2	100	Ni	<10	<10
Fe	<10	12	Si	<10	–
K	35	12			

* A measure of UO_2 content.

[redacted]

TABLE 9.6 UF_4 Made From Pickle Liquor – Black Oxide Feed Solution Containing 44 g/l NO_3^-

Chemical Analysis of UF_4

AOI	– 0.00%	U^{+4}	– 73.24%
UO_2F_2	– 0.31%	Tap Density	– 3.86 g/cc
UF_4	– 96.69%	Moisture	– 3.00%
U	– 73.48%	F	– –

Spectrochemical Analysis (ppm, Uranium Basis)

	Feed Solution	UF_4		Feed Solution	UF_4
Al	<400	<6	Mo	<10	<6
Bi	<20	<1	Ni	<20	<10
Cr	<100	<10	P	<400	<20
Cu	<100	18	Pb	60	<1
Fe	700	<10	Sn	6	2
Li	–	5	V	<100	<40
Mg	300	6	Zn	<200	<20
Mn	20	<4			

116 g/l uranium, 108 g/l NO_3^-, and 1.4M HCl. The resulting solution was heated to 95°C, copious amounts of NO_2 fumes being evolved. Heating at 95°C was continued until no evolution of NO_2 fumes was noted. A sample of solution was analyzed and found to contain 116 g/l uranium, 1.4M HCl, and 5.3 g/l NO_3, which constituted a reduction of nitrate content of 94.5 per cent. A normal Winlo precipitation run was made in three hours (Table 9.7), but the UF_4 product was fluffy (tap density of 1.06 g/cc).

TABLE 9.7 UF_4 Made From Formaldehyde Reduced Pickle Liquor (5.3 g/l NO_3^-)

Chemical Analysis of UF_4

AOI^-	– 0.02%	U^{+4}	– 73.42%
UO_2F_2	– 1.90%	Tap Density	– 1.06 g/cc
UF_4	– 96.66%	Moisture	– 1.42%
U	– 74.89%	F	– 23.60%

Spectrochemical Analysis (ppm, Uranium Basis)

	Feed Solution	UF_4		Feed Solution	UF_4
Al	<6	<6	Mg	100	<4
B	0.65	–	Mn	12	<4
Cr	<10	<10	Ni	10	<10
Cu	90	100	Pb	<1	<1
Fe	15	17	Si	>3	<10
Li	>20	<5			

TABLE 9.8 UF_4 Made From Pickle Liquor – Black Oxide Feed Solution in Semi-Works Unit

Chemical

AOI – 0.05 to 0.85%
UO_2F_2 – 0.12 to 1.19%
UF_4 – 95 to 97%
H_2O – 2 to 4%
Tap Density – 2.5 to 3.0 g/cc

Spectrochemical (ppm, Uranium Basis)

Al	– <6	Ni	– <10
Bi	– <1	P	– <20
Cd	– <0.2	Pb	– <1
Cr	– 10	Sn	– <1
Cu	– 10	Vn	– <40
Fe	– 50	Zr	– <20
Mg	– 20	Na	– 30
Mn	– <4	K	– 30
Mo	– <6	Ca	– >200
		Li	– <5

200-Gallon Semi-Works Unit

Due to the success achieved in the laboratory on producing acceptable UF_4 from liquors made from a digestion of black oxide in pickle liquor, semi-production-scale runs were made in which the 200-gallon semi-works unit[3] was used. A typical semi-production run consists of digesting 113 pounds of black oxide in 98 gallons of diluted pickle liquor (11 g/l uranium, 9 g/l NO_3, 0.13N HNO_3) and 39 gallons of 36% HCl at 95°C for 2½ hours. The feed liquor, after filtration of undigested solids, assayed 90 g/l uranium 2.2N $H,^+$ and 4 g/l NO_3. Total precipitation time, after addition of the required amounts of copper and hydrofluoric acid, averaged 3 hours. The uranium content of the filtrate averaged 0.02 to 0.1 g/l uranium. The average analyses of the UF_4 produced are shown in Table 9.8.

The UF_4 produced was of acceptable quality, and will be blended with straight 6-to-4 green salt prior to use in derby production.

Two different types of rubber linings being used in the Winlo process equipment are being evaluated for service life. Rubber linings for the Winlo-

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process digestion, precipitation, and filtrate-hold tanks have given satisfactory usage in continued service up to 900 hours.

Future Work

Future work on the Winlo process will consist of the following:

1. Adapting of the process to accommodate scrap materials such as UAP (uranyl ammonium phosphate), sump cake, scrap green salt, etc. UAP is a scrap material made by ammonia addition to a hydrochloric acid leach of bomb liner residues. Sump cake is an alkaline precipitate formed when lime is added to a uranium solution. This material (essentially a calcium-uranium complex) is very high in calcium.
2. Investigation of alternative methods for reducing the moisture content of the product green salt.
3. Determination of cost factors — cycle time, labor, and chemical requirements.

References

[1] Rutenkroger, E. O. and Cavendish, J. H., *Summary Tech. Rpt., pp. 61-72, NLCO-785, April 15, 1959.*

[2] Johnson, E. R., Rutenkroger, E. O., Kreuzmann, A. B., and Doumas, B. C., *Recovery of Uranium from MgF_2 Slag by a Phosphate Precipitation Process, pp. 15-30, TID-7528 (Pt. 2), December, 1959.*

[3] Rutenkroger, E. O., *Summary Tech. Rpt., pp. 133-140, NLCO-670, April 18, 1957.*

[4] *Catalytic Construction Co., Process Engineering Staff, Integrated Process Design Report on Feed Materials Production Center, Fernald, Ohio, p. 309, NYO-1177, October 20, 1952.*

[5] Whitman, A. and Lindstrom, R. W., *The Dehydration of Green Salt, UF_4, WIN-95, May 1, 1959.*

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10. THE RECOVERY OF MAGNESIUM AND HF FROM MgF_2 SLAG

E. W. Mautz

Abstract

Study of the recovery of magnesium and HF from MgF_2 slag (obtained in the reduction of UF_4 to uranium metal by magnesium) has continued in the laboratory.

Experiments were conducted on the reduction of MgF_2 slag by calcium carbide, using 100 grams of slag in each run, to determine magnesium product purity, reaction rate, and yield data.

Additional study of the MgF_2 slag – H_2SO_4 reaction for the preparation of HF indicates that a two-step reaction best explains the results obtained.

Introduction

Anhydrous HF (used in the preparation of UF_4) and magnesium metal (employed in the reduction of UF_4 to uranium metal) contribute substantial costs to the uranium metal production operation. The recovery of magnesium and HF from MgF_2 slag represents a potential means of reducing uranium metal costs. Additional work on this subject has been published previously.[1]

Objectives for This Quarter

1. The reduction of MgF_2 slag with calcium carbide was to be investigated on a small scale, and magnesium purity, reaction rate, and yield data were to be obtained.
2. The variables influencing the HF yield in the reaction of MgF_2 slag with sulfuric acid were to be defined.

THE RECOVERY OF MAGNESIUM FROM MgF_2 SLAG

D. C. Bonfer N. L. Gullion
R. E. DeMarco

Introduction

Preliminary small-scale laboratory experiments[1] confirmed the conclusions of a literature survey which had indicated that the most feasible method of magnesium preparation from MgF_2 slag is based on the MgF_2-CaC_2 reaction.

Objective for This Quarter

Laboratory experiments (in which 100 grams MgF_2 was used in each run) were conducted to determine magnesium product purity, reaction rate, and yield data.

Summary of Results Obtained This Quarter

1. Essentially complete reduction of MgF_2 with CaC_2 to produce magnesium metal was obtained in two hours at 1000°C and 350μ absolute pressure.
2. A nominal 80 per cent yield of magnesium (based on the active CaC_2 content of commercial calcium carbide) was obtained by the MgF_2-CaC_2 reaction.
3. The raw magnesium produced by the MgF_2-CaC_2 reaction after melting and fluxing appears to be satisfactory for use in UF_4 reduction to metal.

Experimental

The stainless steel apparatus used for 100-gram scale testing of the magnesium fluoride – calcium carbide reaction is depicted in Figure 10.1. The magnesium vapors produced by this reaction were condensed on carbon steel sleeves at either end of the reaction tube.

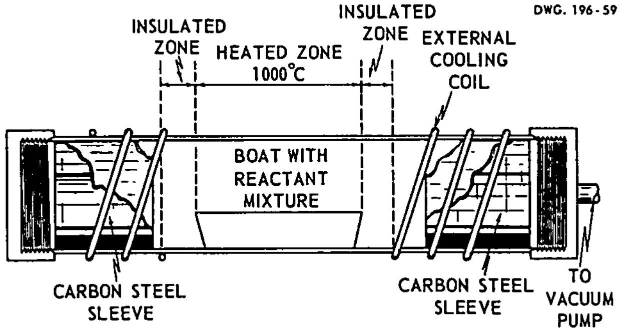

FIGURE 10.1 Magnesium Retort

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Samples of the blended reactant mixture were degassed, in situ, from room temperature to 450°C. The furnace temperature was then raised as rapidly as possible to the desired 1000°C reduction temperature. Prior to weighing, the magnesium collected on the cooled steel sleeves was washed with water. The yield data obtained are summarized in Table 10.1.

A qualitative test for the presence of unreacted calcium carbide was made on the reaction residues. No unreacted calcium carbide was noted in the residues from Runs III and IV. This information and the fact that commercial calcium carbide usually contains 80 to 85 per cent active calcium carbide was used as the basis for the recalculated reaction yields (based on 85 per cent CaC_2) of Table 10.1. It is believed that the nominal 80 per cent yield figure thus calculated better represents the practical maximum attainable for the given reaction conditions.

TABLE 10.1 Process Conditions and Yields for Reaction of MgF_2 with CaC_2

	Run I	Run II	Run III	Run IV
Reaction Time	4 hours			2 hours
Reaction Temperature	1000°C	1000°C*	1000°C	1000°C
Reaction Pressure	350μ			
Weight MgF_2 Slag (~90% MgF_2)	100 grams			
Weight Commercial Grade CaC_2 (~85% CaC_2)	120 grams	100 grams		
Reducible Mg (based on 90% MgF_2 in Slag)	38 grams			
Reducible Mg (based on 85% CaC_2)	38 grams	32 grams		
Mg Recovered	30 grams	21 grams	25 grams	26 grams
Mg Yield (based on 90% MgF_2 in Slag)	79%	55%	66%	68%
Mg Yield (based on 85% CaC_2)	79%	66%	78%	81%

* A large-scale deposit and cracked glow-bar heating element probably resulted in a reaction temperature significantly less than the measured value.

LABORATORY AUTOCLAVE STUDY OF THE MgF_2 SLAG – H_2SO_4 REACTION FOR THE PREPARATION OF HF

D. C. Bonfer N. L. Gullion
R. E. DeMarco

Introduction

The recovery of HF from MgF_2 slag (generated in the reduction of UF_4 to metal) has been proposed as a possible in-plant recycle process. Previous laboratory studies[1] have shown that the MgF_2-H_2SO_4 reaction may be a suitable means for producing HF from slag.

Objectives for This Quarter

To define the variables influencing HF yield in the reaction of MgF_2 slag with H_2SO_4.

Summary of Results This Quarter

HF may be generated, in 80 per cent yield, from magnesium fluoride slag by either of two processes:

The first process involves the reaction of MgF_2 slag with a 100 per cent stoichiometric excess of H_2SO_4. At temperatures approximating 400°F, it is estimated that 75 minutes is the minimum retention time required to produce HF in an 80 per cent yield.

A second process involves reacting the MgF_2 slag with the theoretical requirement of H_2SO_4. The reaction for 30 minutes at 400°F will produce HF in a 40 per cent yield. This reaction residue may be thermally decomposed by calcination at 700°F to yield HF and $MgSO_4$. Calcination of the residue for twenty-five minutes or less will produce sufficient HF to give an 80 per cent over-all reaction yield.

Of the two proposed processes, that involving calcination of the intermediate fluoride residue [$MgF(HSO_4)$] appears more favorable. The benefits of this method accrue from: (1) shorter residence time – 55 minutes versus 75 minutes, and (2) the use of mole-to-mole rather than mole-to-two mole MgF_2-H_2SO_4 ratios.

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Experimental

The modified autoclave previously described[7] was employed in this study of the MgF_2-H_2SO_4 reaction. The only change in the experimental procedure was the maintenance of a constant power input during the course of a run.

Table 10.2 summarizes the data obtained for reaction of 400 grams of MgF_2 slag (−100 mesh) with the stoichiometric quantity of H_2SO_4 required by the equation

$$MgF_2 + H_2SO_4 \rightarrow MgSO_4 + 2HF \qquad (1)$$

Power input to the autoclave was varied, between runs, in 10 per cent intervals from 70 per cent to 100 per cent of full power (2100 watts).

The results of a similar series of runs employing a 100 per cent stoichiometric excess of concentrated sulfuric acid are given in Table 10.3.

Isothermal runs at temperatures of 350°F, 400°F, 450°F, and 500°F were conducted to determine the effect of temperature on the yield of HF from the MgF_2-H_2SO_4 reaction. The data reported in Table 10.4 are based on the reaction of 400 grams of MgF_2 slag (−100 mesh) with a 100 per cent stoichiometric excess of H_2SO_4.

Interpretation of Results

The experimental data summarized in Tables 10.2, 10.3, and 10.4 indicate that the MgF_2 slag – H_2SO_4 reaction is not a simple, uninhibited, one-step reaction. The most probable reaction mechanism involves the reaction of one mole of MgF_2 with one mole of H_2SO_4 to form the acid fluoride, as shown by Equation 2

$$MgF_2 + H_2SO_4 \rightarrow MgF(HSO_4) + HF \qquad (2)$$

A second mole of HF can then be released by reaction of this acid fluoride with an additional

TABLE 10.2 MgF_2 Slag* – H_2SO_4 Reaction – No Excess H_2SO_4

	100%** Power Input	90%** Power Input	80%** Power Input	70%** Power Input
Heating Rate before Plateau (°F/min)	10.0	8.5	6.5	5.0
Heating Rate after Plateau (°F/min)	10.0	8.5	5.0	3.0
Start of Plateau (°F)	360	355	345	340
Midpoint of Plateau (°F)	397	394	390	385
End of Plateau (°F)	430	430	425	420
Time in Plateau (min)	30	35	50	69
HF Yield (%)	41.80	42.30	42.60	42.60
H_2SO_4 Boilover (%)	2.22	1.85	1.48	1.24
SO_3 Decomposition (%)	0.30	0.50	0.34	0.35

* 400-gram sample in each run.

** % of rated maximum.

TABLE 10.3 MgF_2 Slag – H_2SO_4 Reaction – 100% Stoichiometric Excess H_2SO_4

	100%* Power Input	90%* Power Input	80%* Power Input	70%* Power Input
Heating Rate before Plateau (°F/min)	10.0	8.0	6.5	5.0
Heating Rate after Plateau (°F/min)	8.5	7.0	5.0	1.5
Start of Plateau (°F)	370	370	355	350
Midpoint of Plateau (°F)	390	400	395	390
End of Plateau (°F)	420	430	430	425
Time in Plateau (min)	26	28	48	87
HF Yield (%)	73.03	72.9	75.1	82.6
H_2SO_4 Boilover (%)	3.21	3.03	2.52	1.66
SO_3 Decomposition (%)	5.16	0.42	0.56	0.47

* % of rated maximum.

TABLE 10.4 Isothermal Study of MgF_2 Slag – H_2SO_4 Reaction – 100% Stoichiometric Excess H_2SO_4

	500°F	450°F	400°F	350°F
Time at Temperature (min)	90	180	270	360
HF Yield (%)	79.55	78.55	79.55	26.42
H_2SO_4 Boilover (%)	1.40	1.32	1.01	0.21
SO_3 Decomposition (%)	0.77	0.53	0.83	0.02

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mole of H_2SO_4

$$MgF(HSO_4) + H_2SO_4 \rightarrow Mg(HSO_4)_2 + HF \quad (3)$$

Disproportionation and recombination of this acid sulfate to form the double salt, as shown by Equation 4, probably occurs as the final step of the cycle.

$$Mg(HSO_4)_2 \rightarrow MgSO_4 \cdot H_2SO_4 \quad (4)$$

The preceding reaction sequence (Equations 2, 3, and 4) suitably explains the following summary observations noted in the course of the MgF_2-H_2SO_4 reaction.

1. Only one-half of the available HF is released when one mole of MgF_2 is reacted with one mole of H_2SO_4.
2. In the reaction of two moles of H_2SO_4 with one mole of MgF_2, one-half of the available HF is rapidly released.
3. X-ray identification indicates that $MgSO_4$ is the primary reaction product.

The existence of an intermediate reaction compound, $MgF(HSO_4)$, prohibits the direct use of data reported in Tables 10.2 and 10.3 for establishment of minimum retention times. The time during which the reaction curves were in the plateau region probably corresponds to the reaction of Equation 2. The rate at which the acid fluoride reacts with a second mole of sulfuric acid (Equation 3) was estimated to be one-half to one-third the rate of the first reaction. The over-all minimum time for the reaction of one mole of MgF_2 with two moles of H_2SO_4 to produce HF in an 80 per cent yield is estimated as 75 minutes.

Thermal decomposition studies of the intermediate compound, $MgF(HSO_4)$, were conducted to determine the temperature and mode of decomposition.

These preliminary thermogravimetric experiments indicate that $MgF(HSO_4)$, decomposes rapidly at 700°F to HF and $MgSO_4$. Sulfuric acid contamination of the product HF was not determined.

Reference

[1]Mautz, E. W., DeMarco, R. E., Bonfer, D. C., and Gullion, N. L., *Summary Tech. Rpt., NLCO-775, pp. 139-150, January 22, 1959.*

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11. A ROTATING SAMPLE HOLDER FOR PREFERRED ORIENTATION STUDIES

F. H. Ford* R. N. Thudium

Abstract

A sample holder used in preferred orientation studies was designed and fabricated. Design considerations included the requirement that it accommodate larger diameter specimens than do commercial sample holders of this type and the requirement that it incorporate a precision ball bearing.

Introduction

Essentially monochromatic X-radiation is commonly employed in quantitative preferred orientation studies. In a polycrystalline aggregate, diffraction occurs only for those crystallites which have a set of diffraction planes properly oriented with respect to the incident X-ray beam.

In inverse pole figure studies, it is common practice to maintain the plane of the sample surface (A, Fig. 11.1) so that (1) a surface normal through the point of intersection of the center of the incident beam with the sample surface forms equal angles with lines drawn from the point of intersection to the centers of the divergence (B, Fig. 11.1) and receiving slits (C, Fig. 11.1), and (2) the surface normal lies in the plane formed by these lines.

For a given set of diffraction planes, the observed diffracted intensity is then proportional to the volume fraction of crystallites irradiated by the beam which have that set of diffraction planes parallel to the surface.

The effect of large crystallite size is to reduce the size of the statistical sample, reducing both the precision and probable accuracy of the results. This effect may be partially offset by employing mechanical "integrating" techniques to sample a larger number of crystallites. In cases where radial symmetry exists, or where results on the average orientation for a given surface are desired, the sample may be rotated about an axis normal to its surface. Commercial sample holders of this type are limited to samples less than one inch in diameter and have unsatisfactory bearings. A sample holder was desired which would permit examination of larger diameter samples and would incorporate a precision ball bearing to insure improved sample alignment and positioning.

Objective

The objective was the development of a sample-rotating device which would permit the examination of larger specimens and incorporate a precision ball bearing.

Summary of Results

The holder, shown in Figure 11.1, will accommodate specimens up to $1\frac{13}{16}$ inches in diameter and incorporates a Fafnir M9311K special-precision bearing. It is designed to fit a North American Philips Goniometer.

Equipment

The holder was constructed of stainless steel. The bearing housing (D, Fig. 11.1) and the shaft (which is inserted in the goniometer axle) were machined from a single piece of stainless steel. The shaft was drilled and tapped to accept the bolt employed with the flat sample holder supplied with the goniometer (E, Fig. 11.1).

The holder was machined so that the axis of the shaft coincided with the surface of the sample when the bearing was seated in the housing, the ring flange fitted in the bearing, the cover plate mounted on the ring flange, and the sample seated up against the cover plate. The sample is held against the cover plate by a threaded rod which engages the ring flange. The rod is locked in position by a set

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* *Presently with Radio Corporation of America, Electronic Tube Division.*

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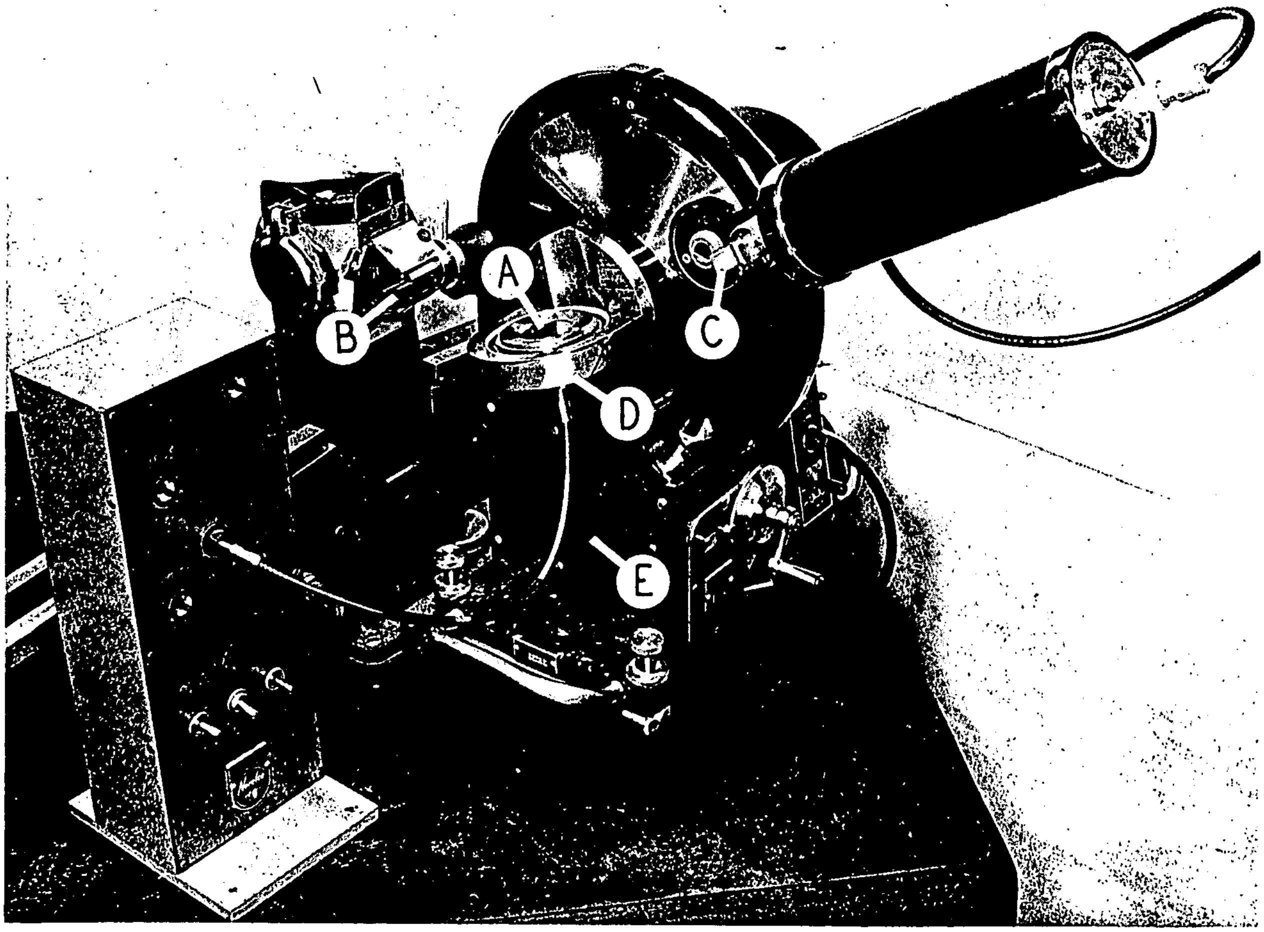

FIGURE 11.1 Rotating Sample Holder. (A. Sample Surface; B. Divergence Slit; C. Receiving Slit; D. Bearing Housing; E. Goniometer).

screw through the ring flange which contacts the rod below the threaded portion. Another set screw holds the flexible shaft drive in the rod.

The sample is loaded from the bottom by removing the flexible shaft and threaded rod. Cover plates were designed to accept commonly encountered production uranium transverse slug sections. The edges of the cover plates were beveled to permit examination near the edge of the sample without reflections from the cover plate.

Acknowledgment

The authors are indebted to J. May for machining the holder.

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12. DETERMINATION OF MICROGRAM AMOUNTS OF FLUORIDE IN URANIUM METAL

W. G. Ellis E. A. Brown

Abstract

A technique is described for the dissolution and analysis of uranium metal for traces of fluoride. The sample is dissolved anodically in a specially designed distillation flask. Sulfuric acid is used as the electrolyte, and the current is 6 amperes. The optimum conditions for the steam distillation of fluoride as fluosilicic acid are described. The effect of sulfate on the thoron spectrophotometric method for fluoride was studied, and a recommended procedure is given to minimize sulfate carry-over in the steam distillation step.

Introduction

Magnesium fluoride is used as a liner material in the reduction of uranium tetrafluoride to uranium by the thermal process. Occlusions of the liner material and other fluoride compounds are sometimes found in the metal. Evaluation studies on the effect of impurities on the physical characteristics of the metal made necessary the development of a suitable method for the determination of traces of fluoride in uranium metal.

The acid dissolution methods normally used for uranium metal, such as dissolution in nitric acid, could not be used in the determination of traces of fluoride. Many anions such as nitrate are distilled with the fluoride and tend to interfere with the spectrophotometric determination of fluoride. Therefore, a method was needed for the dissolution of the sample at a relatively low temperature without the introduction of interfering volatile anions.

Anodic dissolution of the uranium metal in sulfuric acid was selected for investigation. Safranski, Straetz, and Spence[1] dissolved uranium anodically by using a current of 1.5 amperes and a potential of 3 volts. No information could be found on the application of this method to the determination of fluoride in uranium metal.

Objectives for the Quarter

The objective of the work done during the quarter was to establish a satisfactory method for the dissolution of uranium metal and the determination of traces of fluoride.

Summary of Results

A suitable technique was developed for dissolving the uranium metal anodically in sulfuric acid. A special distillation flask was devised which made it possible to dissolve and distill the sample in a closed system, thereby minimizing the loss of fluoride. By use of a current of 6 amperes, up to 10 grams of metal could be dissolved in 1 hour.

A satisfactory modification of the thoron colorimetric procedure for fluoride was established. Sulfate was found to interfere with the method. The optimum distillation temperatures were found to be 145°-150°C for quantitative recovery of fluoride and minimum interference of sulfate.

Dissolution of the Uranium Metal

Uranium metal is readily soluble in nitric acid and in mixtures of nitric and hydrochloric acid. If these acids are used in dissolving the sample, appreciable amounts are distilled over with the fluoride in the Willard-Winter method,[2] interfering with most colorimetric procedures for determining fluoride. Therefore, it was necessary to devise a suitable method for dissolving the sample without using volatile acids. It was also necessary to dissolve the sample directly in the distillation flask in order to prevent the loss of fluoride.

The anodic dissolution of the sample in sulfuric acid (Fig. 12.1) eliminated the difficulties encoun-

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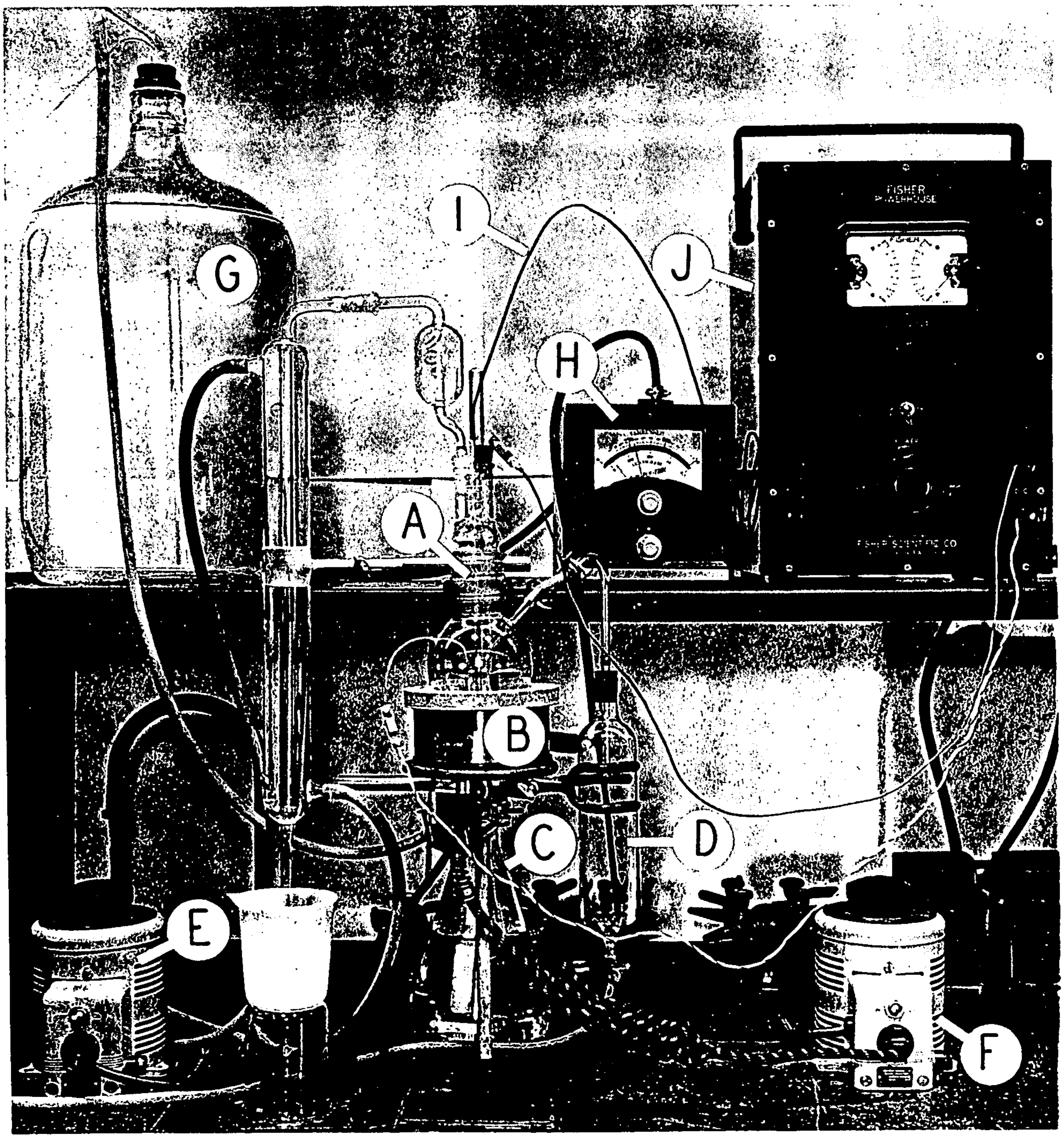

FIGURE 12.1 Fluoride Apparatus. A-Modified Willard-Winter Fluoride Still, B-Electric Heater, C-Steam Generator, Electric, D-Condensate Trap for Steam Inlet, E-Steam Control Powerstat, F-Distillation Control Powerstat, G-Distilled Water for Steam Generator, H-SIM-PLY-TROL for Controlling the Temperature of the Distillation Flask, I-Thermocouple, and J-Direct-Current Supply for the Electrolysis.

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tered in dissolving the sample. A detailed study was made of the electrolytic dissolution technique in order to establish the optimum operating conditions. Supporting the sample in a platinum wire basket proved to be too slow, since the platinum basket made it necessary to limit the potential applied to about two volts, the potential at which oxygen is discharged. Above two volts, large amounts of oxygen were released at the surface of the platinum basket, which, when mixed with the hydrogen from the anode, represented a safety hazard.

The release of oxygen was prevented by changing the form of the sample holder at the anode. A spring-type holder (L, Fig. 12.2) was constructed of 12 gauge platinum-iridium wire in such a form that the sample dipped into the acid, but not the platinum. This arrangement allowed all of the current to pass through the sample (M, Fig. 12.2) and none through immersed wire. This type of suspension eliminated the production of oxygen and made it possible to use currents as high as 8 to 10 amperes. The current finally adopted (5 to 6 amperes) prevented entrainment of sulfate by the hydrogen given off. By use of a current of 6 amperes, 10 grams of uranium could be dissolved in about 1 hour.

The preheating of the solution effected by the electrolysis served to reduce the time required to distill the sample after dissolution. Loss of fluoride during electrolysis was prevented by placing the receiver in position in such a manner that water covered the tip of the condenser. The water was made alkaline with 1 or 2 drops of ammonium hydroxide.

The one disadvantage of the electrolytic process is that essentially all of the uranium dissolved is reduced to the tetravalent form because of reduction at the cathode. The resulting uranous sulfate is only partially soluble and forms a rather thick slurry. It was found by experiment that fluoride recovery was not affected by the presence of the slurry. Therefore, no provision was made for completely dissolving the precipitate.

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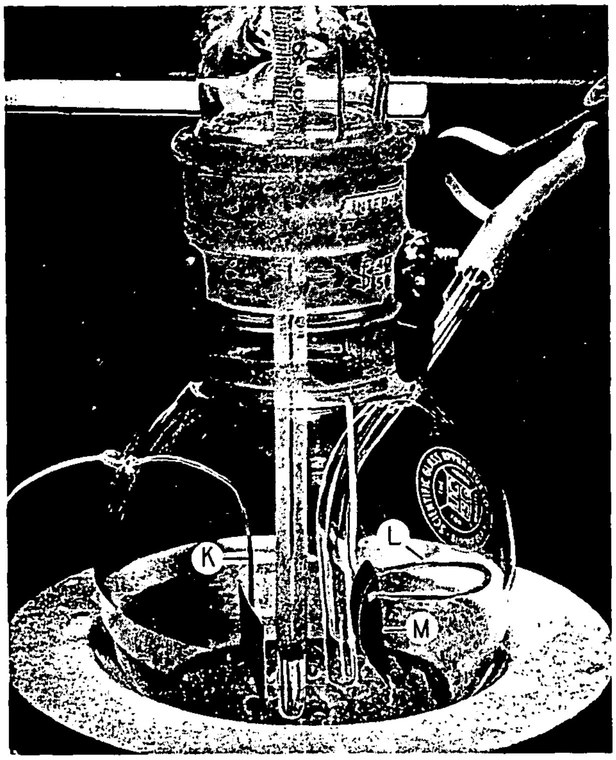

FIGURE 12.2 Details of Reaction Flask. (K) Platinum Cathode, (L) Platinum-Iridium Sample Holder, and (M) Uranium Metal Sample.

Distillation of the Fluoride

Sulfuric acid is used in this laboratory for the distillation of fluorides by the Willard-Winter method.[2] Perchloric acid is also recommended by some workers. Sulfates and perchlorates interfere in the thoron method[3] for fluoride, and care must be taken to prevent any carryover of the acids in the distillation step. The effect of sulfate on the thoron color development is shown in Figure 12.3. Sulfate forms a complex with the thorium present in the reagent, thereby bleaching the color in proportion to its concentration. The maximum sulfate concentration that can be tolerated in the final distillate is 10μg/ml.

Initial experiments were conducted, using the Willard-Winter distillation apparatus without a spray trap. Considerable amounts of sulfate were carried over into the distillate, giving a blank

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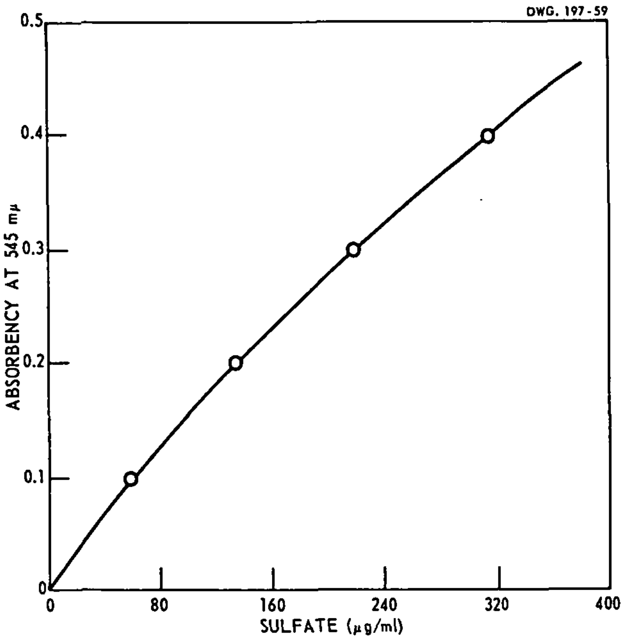

FIGURE 12.3 Effect of Sulfate on the Thoron Color Method for Fluoride

equal to several parts per million fluoride. Introduction of the spray trap into the vapor line reduced the sulfate to less than 10 μg per ml.

Control of the distillation temperature was found to be a factor in obtaining satisfactory results. Distillation temperatures below 145°C were found to result in incomplete recovery of fluoride.* Temperatures above 150°C were found to result in an increase in the sulfate carryover. Therefore, it was necessary to control the distillation temperature within narrow limits (145° and 150°C). The use of a SIM-PLY-TROL (H, Fig. 12.1) in conjunction with an electric heater was found to be satisfactory for this purpose.

Colorimetric Estimation of the Fluoride

The "Thoron" method of Horton, Thomason, and Miller[3] was modified and used in this investigation. With suitable control of the sulfate interference, the method was found to be capable of good precision and accuracy. As little as 0.05 μg of fluoride may be detected with an accuracy of ±0.02 μg. In terms of uranium metal, this amounts to about 1 ppm when analyzing a 10-gram sample.

The modification of the "Thoron" method was designed for general application to the analysis of solutions of fluorides. Reagent strengths and volumes were adjusted for the greatest handling convenience. The thorium and thoron reagents were combined into one reagent and proved to be stable for at least six months. The concentration was adjusted so that one 5-ml aliquot of mixed "color" reagent was used in place of two 1-ml aliquots of the respective components. Previous experience with the method had shown that the optimum pH was 1.5, obtained by the dropwise addition of 6N HCl to the sample aliquot.

Recommended Procedure

A. Apparatus

The apparatus used was constructed from the standard Willard-Winter fluoride still, as supplied by the Scientific Glass Apparatus Company. Figures 12.1 and 12.2 show the modified construction. The cathode was constructed from platinum wire and sheet and was fused into the side of the distillation flask. The sample holder was formed from a piece of platinum-iridium wire, as shown in Figure 12.2. A steam inlet was also provided to convert the unit to steam distillation instead of adding water through the funnel.

The power source is a standard Fisher Powerhouse, supplying d-c voltage up to 10 volts and 8 amperes.

The Beckman DU spectrophotometer was used for all optical density measurements.

Sim-Ply-Trol pyrometer control range: 0-400°C.

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* *The loss of fluoride below 145°C is believed to be due in part to the composition of the distillation mixture. With more dilute uranium solutions (1g samples), complete recovery is obtained at temperatures as low as 135°C.*

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B. Reagents

Thorium nitrate. Dissolve 0.4750 g of $Th(NO_3)_4 \cdot 4H_2O$ in distilled water, and dilute to one liter.

Thoron solution. Dissolve 1.250 g of Thoron reagent, 1-(O-arsonophenylazo)-2-naphthol-3,6-disulphonic acid, in distilled water, and dilute to one liter.

Color reagent. Transfer 100 ml each of the thorium and thoron reagents to a 500-ml volumetric flask, and dilute to volume.

Standard fluoride. Dissolve 0.2210 g of NaF (previously dried for one hour at 110°C) in distilled water, and dilute to one liter. Fifty milliliters of the above solution diluted to one liter will contain 5.00 μg of fluoride per milliliter.

C. Method

Place 80 ml of sulfuric acid (1-2) in the distillation flask (A, Fig. 12.1). Weigh the sample, clean in acetone, and attach to the platinum-iridium sample holder. Adjust the sample so that the liquid level is about ⅛ inch below the wire. Close the distillation flask, and place a 250-ml polyethylene beaker containing a few drops of NH_4OH in 25 ml of water just under the condenser tip.

Dissolve 5 to 10 grams of the metal by passing through it a current of 6 amperes (approximately 10 g will dissolve in 1 hour). Turn off the current and, without removing the undissolved portion of the sample, steam-distill the fluoride until approximately 150 ml of distillate is collected in 30 to 40 minutes. The temperature of the distillation flask should be maintained at 145°-150°C by the use of an auxiliary heating element controlled by the SIM-PLY-TROL unit.

Dilute the distillate to 250 ml. Transfer duplicate 20-ml aliquots of the sample to 50-ml beakers. Prepare duplicate blanks in similar manner, using 20 ml of water. Add 5 drops of 6N hydrochloric acid and 5 ml of the "Color Reagent" to each beaker with stirring. Program the addition of reagents so that each solution will have stood fifteen minutes at the time the optical density is to be read. Determine the cell correction by transferring the two blanks to two 5-cm matched absorption cells. Compare the cells in the Beckman DU spectrophotometer at 545 mμ and 0.100 mm slit width. Retain the blank that is in the normal sample cell. Compare the samples with the blank by placing each in turn in the reference cell. This technique is used because the sample solutions are less dense than the blank. Correct for the density of the blank, and determine the fluoride content of the samples by reference to a calibration curve prepared by the analysis of known solutions of the standard fluoride. Weigh the undissolved portion of the sample, and determine the sample weight by difference.

Experimental

By use of the recommended procedure, a series of blank determinations were made with no uranium in the still to establish the average blank correction required. Table 12.1 illustrates the amount of correction to be expected in routine work.

A series of samples of a metal known to be fluoride-free were then dissolved and spiked with known amounts of fluoride. The recoveries are shown in Table 12.2.

Samples of production material were then selected which were known to have occlusions and were believed to have fluoride as an impurity. These were analyzed according to the proposed procedure and were found to contain varying amounts of fluoride, as shown in Table 12.3.

TABLE 12.1 Determination of the Blank Correction for the Still

Determination No.	Absorbency at 545 mμ	Fluoride Found (μg)
1	0.015	0.6
2	0.019	0.7
3	0.015	0.6
4	0.021	0.8
5	0.009	0.4
Average		0.6 ± 0.2

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TABLE 12.2 Analysis of Known (Spiked) Samples

Sample No.	Fluoride Added (ppm)	Fluoride Found (ppm)
1	10.0	9.9
2	10.0	9.9
3	10.0	10.7
4	10.0	9.6
5	10.0	11.3
6	10.0	10.1
7	10.0	10.1
8	10.0	9.6

TABLE 12.3 Analysis of Unknown Metal Samples

Sample No.	Weight (g)	Fluoride Found (ppm)
11-1443	11.3	6.1
11-1444	11.1	5.0
11-1445	12.2	37
11-1446	8.6	48
11-1447	9.4	18
11-1448	9.8	4.8

Discussion

The reliability of the analytical results depends to a large extent on the technique used in sampling the metal. The dissolution technique described tends to dissolve occluded areas to a greater degree than solid areas. For this reason, it is desirable to cut the samples to a uniform size and surface area. While the uniform size may not guarantee-precise analytical results, it will give comparative data on the fluoride content. The most accurate results will be obtained by first cutting approximately 10 to 15 g samples across the grain structure of the metal and then dissolving nearly all of the sample. In this way, the original proportion of fluoride to metal content is most nearly preserved.

Conclusion

The method as outlined is capable of producing satisfactory results as a routine control procedure.

References

[1] Safranski, L. W., Straetz, R. P., and Spence, R. W., *pp. 3-11, CC-934, September 11, 1943.*

[2] Willard, H. N. and Winter, O. B., *Ind. Eng. Chem., Anal. Ed., 5, 7, (1933).*

[3] Horton, A. D., Thomason, P. F., and Miller, F. J., *Anal. Chem., 24, 548 (1952).*

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13. DIRECT FLAME PHOTOMETRIC DETERMINATION OF MAGNESIUM IN URANIUM ORE CONCENTRATES

J. A. Freitag E. A. Brown

Abstract

The Beckman DU Recording Flame Photometer was applied to the direct determination of magnesium in uranium ore concentrates. Satisfactory results were obtained, using the "standard addition" method in which a standard magnesium solution is added to the sample and the concentration is calculated from the emission-concentration relationship. A separation from other anions and cations normally found in the sample is not necessary, since the method automatically compensates for radiation effects of other ions.

A recommended procedure is given which is based upon measurements of the magnesium flame emission at 371 mμ and background at 355 mμ. Satisfactory results were obtained by this procedure, using an NBS dolomite sample and Canadian uranium ore concentrates. At the concentration level of 2 to 6 per cent, the precision of the method was found to be ±0.15 per cent (95 per cent confidence level).

Introduction

This investigation resulted from the need for a rapid analytical method for the determination of magnesium in uranium ore concentrates. Volumetric and gravimetric methods for determining magnesium are time-consuming, due to the need for multiple separations from interfering ions. The separation from phosphate (which is frequently found in uranium ore concentrates) is particularly troublesome. A direct method in which the magnesium could be determined in the presence of the sample matrix material was desirable.

The direct flame photometric determination of calcium is described in a previous report.[1]

The investigation reported herein was made in order to study the flame emission spectra of magnesium and to apply the "standard addition" technique to the determination of magnesium. The sensitivity of the magnesium flame emission is weaker than that for calcium and the alkali metals. The magnesium emission, for example, is about one-seventieth that of calcium. Due to the high concentration level of magnesium in many ore concentrate samples,* this lack of sensitivity is not objectionable.

Prior Work on Project

In a previous report,[2] a number of elements (including magnesium) normally present in uranium ore concentrates were identified in the recorded flame emission spectra. The recording technique was found to offer many advantages over conventional flame photometry.

A direct flame photometric method for calcium has been reported.[1] This method is based upon the "standard addition" principle, in which the concentration is calculated from the recorded emission-concentration relationship.

Objectives for The Quarter

The objective of the work done during the quarter was to study and establish a satisfactory method for determining magnesium in uranium ore concentrates.

Summary of Results

The Beckman DU Recording Spectrophotometer was used for the direct determination of magnesium in uranium ore concentrates. The "standard addition" method was found to give satisfactory results for magnesium, no preliminary separations being needed. Satisfactory results were obtained on

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* *Magnesite is frequently used as a precipitating agent at the mill, thereby producing uranium concentrates containing up to 8 per cent magnesium.*

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N.B.S. standard dolomite and Canadian uranium ore concentrates. The precision of the direct flame method for 2 to 6 per cent magnesium was found to be ±0.15 per cent at the 95 per cent confidence level.

Magnesium Flame Emission Spectra

The magnesium spectrum consists of two molecular bands in the vicinity of 371 and 383 mμ and an arc line at 285.2 mμ. Typical recordings of the magnesium spectra, using the Beckman DU Recording Flame Photometer, are shown in Figure 13.1, Curve A, and Figure 13.2, Curve A.

A study was made of how the magnesium flame emission is affected by anions and cations that normally are present in uranium ore concentrates. Standards were prepared by adding the anion or cation to a magnesium stock solution. The final magnesium concentration was 25 μg/ml in all cases. The flame emission was measured on the recording spectrophotometer at 285, 371, and 383 mμ. The relative emission ratio (representing flame emission of magnesium plus added ion to magnesium) is shown in Table 13.1.

From the relative flame emission measurements shown in Table 13.1, the 285.2 mμ line shows the minimum interference from other ions. However, the emission-concentration relationship at this wavelength was not found to be linear, as shown in Figure 13.3. Self absorption of the magnesium emission was evident at higher concentration levels, which prevented the application of the "standard addition" method. Attention was therefore directed to measurements in the molecular band region at 371 and 383 mμ.

Iron was found to be the most troublesome element encountered. The flame emission of the iron

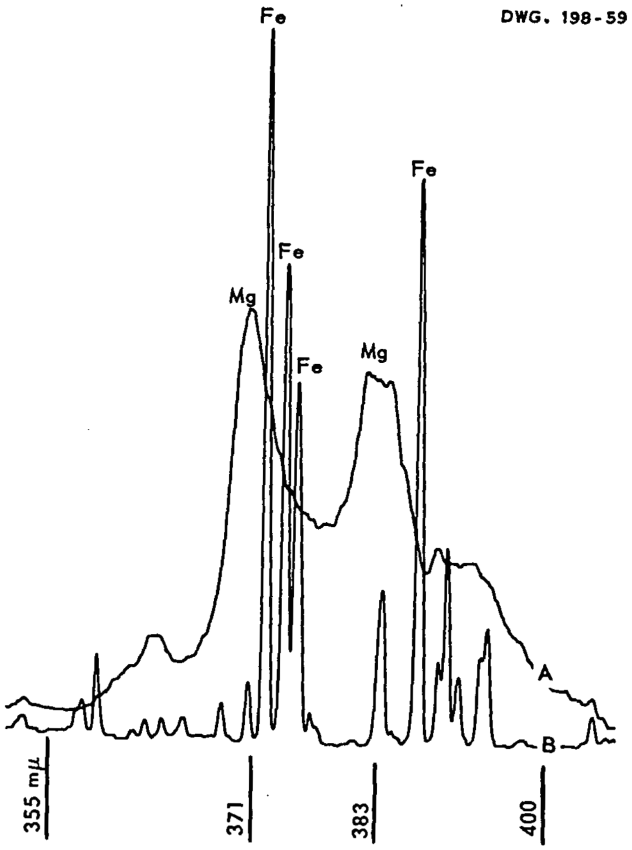

FIGURE 13.1 Recordings of Flame Emission Spectra. A - Magnesium 100μg/ml, 0.035 mm Slit; B Iron 100μg/ml, 0.035 mm Slit.

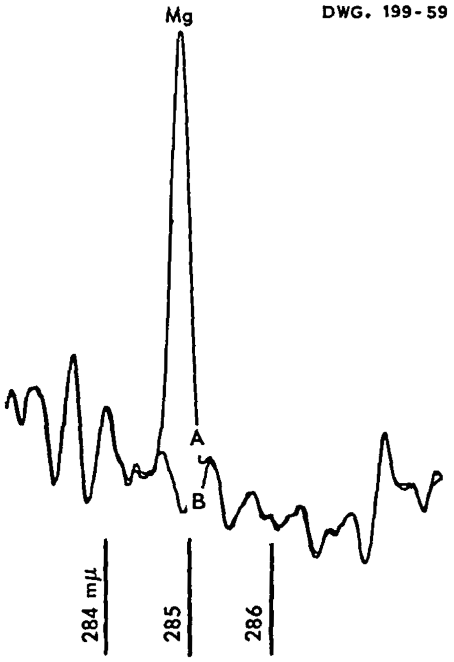

FIGURE 13.2 Recordings of Flame Emission Spectra. A - Magnesium 100μg/ml, 0.025 mm Slit; B - H_2O Background.

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TABLE 13.1 Effect of Foreign Ions on Magnesium Flame Emission

Magnesium concentration of each sample: 25 μg/ml

Ion Added	Weight Ratio, Ion: Magnesium	Magnesium Emission Ratio* at Various Wavelengths 371 mμ	383 mμ	285 mμ
None	—	1.00	1.00	1.00
Aluminum	1	0.65	0.57	0.84
	10	0.15	0.14	0.32
Iron	1	1.13	1.44	1.00
	10	1.22	5.70	0.96
Sodium	1	1.06	1.04	1.00
	10	1.05	1.11	1.01
Calcium	1	1.10	1.07	1.04
	10	0.98	0.90	1.05
Sulfate	1	0.95	0.98	0.97
	10	0.54	0.52	0.77
Phosphate	1	0.85	0.84	0.95
	10	0.41	0.41	0.65

$$*\text{Magnesium Emission Ratio} = \frac{\text{Flame emission of magnesium plus ion added}}{\text{Flame emission of magnesium}}$$

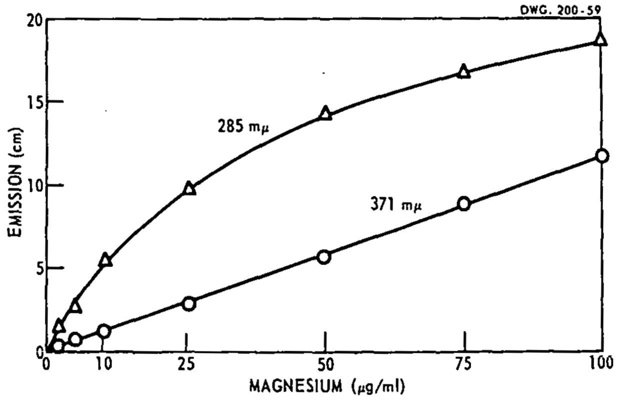

FIGURE 13.3 Magnesium Emission-Concentration Curves at 285 and 371 mμ.

spectra is shown in Figure 13.1, Curve B. It is evident that serious interference is encountered in the vicinity of 383 mμ. However, at 371 mμ, the interference due to iron is minimized. A relatively weak iron line is found at 371 mμ; however, the iron-magnesium concentration level in uranium ore concentrates was below the level required to give interference at this wavelength. Furthermore, the concentration-emission relationship at 371 mμ was found to be linear (Fig. 13.3). Background measurements at 355 mμ, which is the minimum transmission value for our instrument, were found to be relatively free from interferences. Therefore, flame photometric measurements were made for magnesium emission and background at 371 and 355 mμ, respectively.

Recommended Procedure for Magnesium in Uranium Ore Concentrates

Dissolve 1 gram of the ore concentrate in 5 ml of nitric acid and 3 ml perchloric acid, and evaporate to near-dryness. Add 5 ml of hydrochloric acid, and evaporate to near-dryness. Dissolve the residue in 10 ml of 6M hydrochloric acid, transfer to a 100-ml volumetric flask, and dilute to volume. Filter a portion of the solution through a dry No. 42 Whatman paper, discarding the first 20 ml of the filtrate. Transfer a 10-ml aliquot to each of two 100-ml volumetric flasks. Add 10 ml of magnesium standard (500 mμ/ml) to one of the flasks, and dilute both to volume.

Turn on the flame photometer, and adjust according to the manufacturers' directions. The following settings were suitable for the measurements:

Oxygen pressure	10 psi
Hydrogen pressure	4 psi
Photo tube load resistor	position 2
Slit width	0.035 mm
Photomultiplier sensitivity	Full
100% adjust	2 turns from clockwise

Set SERA control to record and wavelength drive to DECR. Place the spiked sample in the sample holder, and position it under the burner. Open the phototube shutter and set the recorder pen at 5 per cent of full scale. Set the wavelength scale at 355 mμ, and record the background for 2 to 3 cm. Manually turn the wavelength dial to 371 mμ, and adjust for greatest response. (The dial may be

[redacted]

set to 373 mμ and the peak scanned to use as a guide.) Record the emission for 2 to 3 cm. Remove the spiked sample, rinse the burner, and aspirate the unspiked sample through the burner. Record the emission of the unspiked sample for 2 to 3 cm. Turn the wavelength dial to 355 mμ, and record the background of the unspiked sample.

Measure the peak height of the individual recordings with a millimetric rule from the background in order to obtain values of T_1 and T_2. (See Figure 13.4 for a typical recording of a sample.) Substitute the values of T_1, T_2, and S in the equation in order to calculate the concentration of magnesium in the sample.

Calculations

$$\% \text{ Mg} = \frac{T_1 \times D \times S}{W (T_2 - T_1) \times 10{,}000}$$

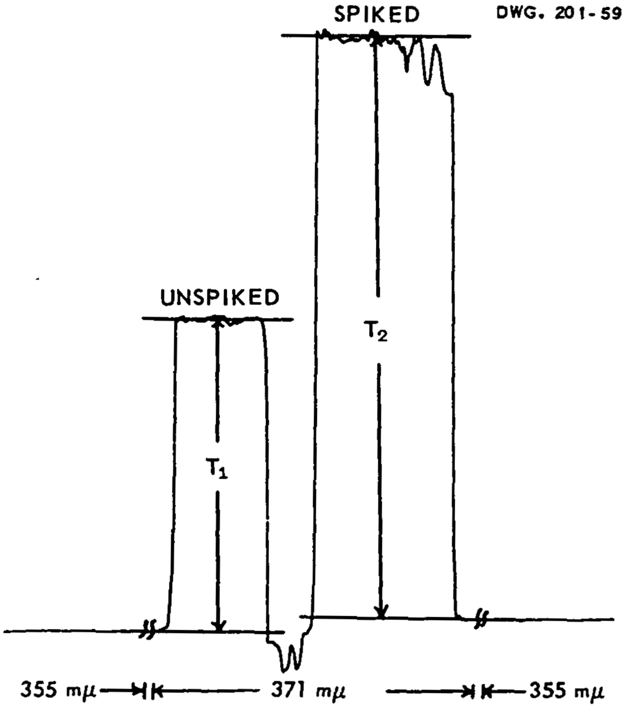

FIGURE 13.4 Recording of Flame Emission Spectrum. Magnesium in an Ore at 371 mμ.

where

T_1 = Emission of unspiked sample

T_2 = Emission of spiked sample

W = Sample weight in grams

$$S \text{ (Spike)} = \frac{\text{ml of spike} \times \mu\text{g Mg/ml spike}}{\text{final volume in ml}}$$

$$D \text{ (Dilution)} = \frac{V_1 \times V_2 \cdots V_n}{a_1 \times a_2 \cdots a_n}$$

V is the volume in milliliters

a is the aliquot in milliliters

Magnesium in N.B.S. Samples

Four samples of N.B.S. Dolomite No. 88 were analyzed for magnesium by the recommended procedure. The results are shown in Table 13.2.

The results shown in the above table agree with the accepted value for samples containing over 12 mg of magnesium in the sample taken.

Magnesium in Uranium Ore Concentrates

Seven Canadian uranium ore concentrates were selected for a comparative study of the flame photometric method. These samples were analyzed by the classical gravimetric method, as well as by the recommended flame method, In the gravimetric procedure, a double ammonium hydroxide - double oxalate separation was used to remove interfering ions, followed by the determination of the magnesium by the phosphate method.[3] A summary of the results obtained will be found in Table 13.3.

TABLE 13.2 Determination of Magnesium in N.B.S. Dolomite No. 88

No.	Sample Weight (g)	Magnesium Found (%)	Magnesium N.B.S. Value (%)
1	0.4115	12.9	12.96
2	0.3337	12.9	
3	0.1939	12.6	
4	0.0932	11.9	

[redacted]

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TABLE 13.3 Determination of Magnesium in Uranium Ore Concentrates

Sample Source	Per Cent Magnesium		
	Gravimetric*	Flame Photometric*	d**
Bicroft	5.57	5.63	0.133
Denison	4.84	4.94	0.013
Faraday	3.80	3.80	0.080
Pronto	3.82	4.25	0.153
Can Met	5.56	5.30	0.070
Lorado	5.24	5.34	0.030
Dyno	1.95	2.01	0.000

* Average of duplicate determinations.

** Difference between duplicate determinations for the flame photometric method.

From the results shown in Table 13.3, the precision of the flame photometric method in the range of 2 to 6 per cent magnesium was found to be ±0.15 per cent (95 per cent confidence level). This precision is based upon the average of duplicate determinations. The two methods gave inconsistent results for Pronto, which is believed to be due to the abnormally high iron content of the sample, 3.9 per cent. A preliminary ammonium hydroxide separation is recommended for samples containing more than 2 per cent iron.

The direct flame photometric method described is satisfactory for the routine analysis of uranium ore concentrates for magnesium. The method is rapid, since a preliminary separation from other elements present in the sample is not necessary. The method was found to be well adapted to the routine examination of a large number of samples. The time required to process ten samples was found to be 4 to 4.5 hours, which is only a fraction of the time required to analyze the samples by gravimetric methods.

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[1]Brown, E. A. and Ellis, W. G., *Summary Tech. Rpt., pp. 159-162, NLCO-775, December 31, 1958.*

[2]Brown, E. A. and Ellis, W. G., *Summary Tech. Rpt., pp. 99-106, NLCO-760, October 24, 1958.*

[3]Furman, N. H., *"Standard Methods of Chemical Analysis," Vol 1, p. 532, Van Nostrand, New York, 1939.*

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