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URANIUM DIVISION

AEC RESEARCH AND DEVELOPMENT REPORT

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Date of Issue: April 1, 1958

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PROCESS DEVELOPMENT QUARTERLY REPORT
PART I LABORATORY WORK

edited by Barbara Elliott

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GENERAL SUMMARY

Work continued during the first quarter of 1958 on nitric acid recovery, fluoride volatility, hydrogen in uranium, characteristics of raw materials, greensalt, and plant assistance projects. Analytical studies were made on the determination of non-volatile organic material and of total uranium and iron in UF_4 . In addition, leaching methods for the determination of UO_2F_2 in UF_4 and the analysis of hexane were investigated.

Specific studies are summarized as follows (Roman numeral refers to the section on which the summary is based):

- II. Twenty-one lots of Vitro concentrate were found to contain an average of 4.7% of uranium that was insoluble in nitric acid. Individual lots ranged between 0.86 - 13.4%. The amount of insoluble uranium in Vitro concentrate was found to depend on the calcination temperature at the mill site. Fixation occurred chiefly in temperature range 500 - 800°C. Use of a hydrogen atmosphere during calcination reduced the insoluble uranium content considerably.

Climax, Rifle, Uravan, and Uranium Reduction concentrates contained less insoluble uranium than the Vitro product but still averaged over 0.2% insoluble uranium.
- III. Freezing point and boiling point data on uranyl nitrate solutions in the concentration range $UO_2(NO_3)_2 \cdot 6H_2O$ to $UO_2(NO_3)_2 \cdot 1H_2O$ (32.4 - 54.9% uranium) are reported. Viscosity and surface tension measurements were made on a few solutions in this composition range.
- IV. Degradation products of the plant solvent have been found to inhibit uranium stripping. This inhibition is due to the formation of difficulty extractable complexes and also to an aggravation of solvent entrainment problems. These degradation products are probably the result of nitration reactions.
- V. The feasibility of recovering nitrate values from the Weldon Spring raffinate by additional TBP - hexane extraction stages has been demonstrated on a laboratory scale. The process utilizes sulfuric acid to displace fixed nitrate into the solvent. In contrast to distillation methods of recovering this nitrate, little chloride contamination of the recovered acid occurs.
- VI. Ammonium sulfate, when added to the plant denitration pots, was found to be as effective as H_2SO_4 in increasing the reactivity of resultant UO_3 . Uranyl sulfate seemed to be slightly less effective. A systematic study of the increase in reduction rate with the sulfate content of UO_3 is reported.

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The relatively unreactive product from the fluid-bed denitrator could be effectively activated by hydration prior to reduction.

- VII. The reaction of hydrogen fluoride with uranium metal turnings does not easily go to completion at temperatures up to 660°C . If the metal is treated first with hydrogen, then complete conversion to UF_4 can be obtained easily at $400 - 650^{\circ}\text{C}$ (98.5% yield).
- VIII. Preliminary tests of the Fluorox reaction were made with moderate success. A review of the status of research on this reaction is given.

- IX. Confirmation was obtained of the significantly faster uptake of hydrogen by liquid uranium from an H_2 atmosphere than from an H_2O atmosphere. This difference in rate was found to be greater at higher gas pressures, at least up to 590 mm Hg. The rate difference is at least eight-fold at 590 mm Hg and may be considerably greater.

- X. A mechanism is proposed that correlates the uranyl fluoride content of greensalt with (a) the dependance of the hydrogen content of uranium on the firing time of the bomb, (b) the dependance of metal yield on firing time, and (c) the dependance of firing time on greensalt composition. Experimental support for the mechanism is presented.

Hydrogen content of uranium was decreased by use of magnesium of lower surface area. This decrease was correlated with the hydrogen analysis of the magnesium. Crude bomb yields began to fall off when magnesium of surface area less than about 100 sq cm/g was used.

ZnCO_3 , UO_3 and UO_2CO_3 additives to the bomb charge all reduced the hydrogen content of resulting metal. The ZnCO_3 and UO_3 , however, reduced the metal yield.

- XI. In analytical development work, essentially quantitative recovery of TBP added to NOK and UNH solutions was achieved. Data and conditions for routine control testing of these samples are presented.
- XII. A rapid and accurate method for the infrared determination of *n*-hexane in plant hexane is presented.
- XIII. It has been demonstrated that the pyrohydrolytic method is superior to the titrimetric method for uranium assay of uranium tetrafluoride with respect to speed, accuracy, and precision. A suitable procedure for routine uranium assay of the tetrafluoride is described.
- XIV. A number of leaching procedures for the determination of uranyl fluoride in uranium tetrafluoride have been tested and found unsuitable. The use of the polarographic method following total sample dissolution is recommended.

Pilot plant work for this quarter will be reported in Part II as a separate volume.

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INSOLUBLE URANIUM IN FEED MATERIALS

by

E. N. Nelson

F. F. Harper

G. P. Lang

Summary

The survey of HNO_3 insoluble uranium in ore concentrates, a portion of which was reported previously, was continued. It was found that six of the twelve concentrates examined contain, quite consistently, greater than 0.01 percent nitric acid insoluble uranium. Of these six, four or five contain more than 0.1 percent insoluble uranium.

The effect of process variables such as calcining temperature, calcining in a reducing atmosphere, pre-drying the cake, and water washing the cake prior to calcining were investigated using Vitro concentrate. High insoluble uranium was a function of calcining temperature and was extremely high when the material was calcined in the 500 - 800°C temperature range. Calcining in a reducing atmosphere was effective in lowering the insoluble uranium content of the ore.

An unknown compound giving a well defined X-ray diffraction pattern appeared to correlate with the high nitric acid insoluble uranium content of Vitro concentrate.

Introduction

Nitric acid insoluble uranium in ore concentrates is now recognized as one of the more serious problems in the operation of the Weldon Spring refinery. It has been shown that high uranium loss to the raffinate is due chiefly to insoluble uranium.¹ Furthermore, the high insoluble uranium has generally been associated with a high concentration of iron (Fe_2O_3 , hematite produced by calcining) in the concentrate, and the appearance of an unidentified compound in the residue. This unidentified compound gives a well defined X-ray diffraction pattern with chief lines at "d" spacings of 4.05, 3.25, and 2.55 Å.²

Variations in the digestion procedure such as fine grinding, longer digestion, or the addition of hydrochloric acid were tried to aid uranium dissolution and were partially successful. Insoluble uranium was reduced about 50 percent by some of the modifications.³

¹ Lang, G. P., Varwig, J. W., and Martin, G. L. *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1399 (January 1, 1957) p 13-20

² Lang, G. P., *et. al*, MCW-1399, p 13-20

³ Lang, G. P., and Martin, G. L., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW 1401 (April 1, 1957) p 13-15

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A statistical program was started in order to obtain a history of the insoluble uranium content of ore concentrates.⁴ Data were collected to determine the variation in the insoluble uranium content of feed material from one vendor as well as the variation between vendors.⁵ A continuation of that survey is included in this report.

It has been found that the ore concentrate produced at the Vitro Mill, after the process change to dodecyl phosphoric acid (DDPA) solvent extraction, has a very high concentration of insoluble uranium. Vitro's process allows a relatively high concentration of iron to be carried through the process into the product. The ammonium diuranate product is then calcined at 500 to 600°C to remove ammonia, chloride, and water. A major portion of the iron in the final product is present as nitric acid insoluble hematite (Fe_2O_3). Samples of Vitro's HCl strip solution and precipitated wet cake were obtained and a laboratory investigation begun to find a way of processing the material without excessive uranium loss.

Experimental

Table I is a continuation from a previous report⁶ and the data was obtained by the experimental procedure described therein.

⁴ Harper, F. F., Lang, G. P., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1410 (January 2, 1958) p 13-17

⁵ Harper, F. F., Lang, G. P., MCW-1410, p 13-17

⁶ Harper, F. F., Lang, G. P., MCW-1410, p 13-17

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Table I

Insoluble Uranium in Feed Materials

Feed	Lot No.	Total U in Digest Slurry g/l	Total Dry Solids g/l	Insol. U Percent of Total Insol.	Insol. U (U Basis) %
Vitro ^a	56	245	43	0.37	0.065
	57	336	67	0.35	0.070
	58	229	111	5.4	2.6
	59	226	98	4.4	1.9 ^a
	60	209	102	11.4	5.5
	61	274	56	4.2	0.86
	62	252	42	5.8	0.96
	65	251	127	18.9	9.6
	67	282	95	18.9	6.4
	68	250	118	2.7	1.3
Uranium Reduction	283	396	25	0.18	0.011
	285	402	30	0.083	0.0064
Edgemont	60	306	0.0	- -	- -
Climax	249	286	25	25.5	2.3
	250	284	11	0.24	0.0097
	252	319	8	31.5	0.81
Western Nuclear	9	336	32	0.008	0.00078
	10	249	39	0.012	0.0019
	11	216	28	0.021	0.0027
	12	242	25	0.014	0.0015
Rifle	38	318	78	6.1	0.15
	41	265	8	4.1	0.12
	45	314	1.5	4.2	0.019
	48	305	16	10.2	0.52
	49	308	4.5	8.5	0.12

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Table I (continued)

Feed	Lot No.	Total U in Digest Slurry g/l	Total Dry Solids g/l	Insol. U Percent of Total Insol.	Insol. U (U Basis) %
Naturita	371	250	15	0.075	0.0044
	372	290	5	0.165	0.0029
	374	251	6	0.24	0.0060
Uravan	636	282	24	3.5	0.30
	637	242	22	4.7	0.44
	638	284	26	5.6	0.51
	639	300	26	4.0	0.33
	640	249	31	11	1.4
	644	284	26	1.72	0.16
Durango	518	307	8	0.108	0.0028
	519	334	12	0.136	0.0051

^aVitro process changed between Lots 58 and 59

The nitric acid insoluble and the uranium insoluble determinations reported in Table II were obtained by the following procedure which is modification of the previously mentioned procedure. The procedure was changed in order that analyses other than insoluble uranium could be carried out on the same sample.

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Table II

Insoluble Uranium in Feed Materials

Feed	Lot No.	Total Dry Solids (Percent)	Insoluble U Percent of Total U
Vitro	63	21.	4.0
	64	20.	4.9
	66	23.	5.8
	67	28.	13.4
	68	33.	1.67
	69	37.	8.0
	70	31.	5.0
	71	19.	5.4
	72	25.	7.1
	75	28.	11.8
	77	9.9	1.13
Climax	249	9.6	2.9
	250	4.2	2.79
	252	2.8	1.18
	253	2.6	1.18
	254	1.6	0.55
	256	6.2	3.1
	257	3.2	1.37
	258	1.2	0.28
	259	3.4	0.76
Uranium Reduction	319	16.	0.15
	321	12.	0.053
	322	28.	0.090
	323	26.	0.26
	324	17.	0.098
	325	11.	0.069
	326	12.	0.18
	328	11.	0.045
	329	13.	0.14
	330	14.	0.21
	331	16.	0.18
	332	11.	0.13

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Tentative Procedure

Weigh a 50.0-gram sample of ore concentrate, and transfer the sample to the 500-ml boiling flask. Connect the flask to the condenser, and add 50.0 ml of 45% (w/v) nitric acid to the flask through the condenser. Wash down the condenser with 20 ml of distilled water. Digest the sample at 91-95°C for two hours with adequate stirring. Cool the slurry.

Quantitatively transfer the slurry from the boiling flask to a 250-ml centrifuge bottle, and centrifuge at 1700 to 1800 ppm for 15 minutes. Decant the liquid. Repulp the solids with a 50-ml portion and then a 25-ml portion of distilled water, centrifuging the slurry and decanting the liquid each time. Repulp the solids with 25-ml portions of 5% (w/v) nitric acid until the centrifugate gives a negative uranium test with sodium hydroxide and hydrogen peroxide. (About five washings with 5 percent nitric acid is sufficient.) Dry the solids at 110°C overnight. Weigh the dried solids. Calculate the percent total nitric acid insoluble, dried at 110°C, in the sample.

Determine the uranium content of these insoluble solids by an X-ray spectrographic analysis. Calculate the percent nitric acid insoluble uranium in the dried solids. Calculate the percent nitric acid insoluble uranium on a uranium basis by the following equation:

$$\% \text{HNO}_3 \text{ Insoluble (U Basis)} = \frac{\% \text{HNO}_3 \text{ Insol. U in Dry Solids} \times \text{Total Insol. Solids}}{\text{Total U Content of Concentrate}}$$

Samples of the Vitro material were calcined under various conditions and the results are shown in Table III. The calcining experiments, with the exception of those carried out in a reducing atmosphere, were done in a normal laboratory muffle or oven where the samples were exposed to atmospheric oxygen during calcining. The "reducing atmospheric" ignitions were accomplished by passing hydrogen (2 liters/min) over the sample in a closed system during the calcining. The chamber was flushed with argon and the hydrogen flow started before the muffle was brought to temperature. The calcining time was two hours for the normal runs and about one hour for the hydrogen runs. The predried sample was dried in a normal oven for 16 hours at 170°C prior to calcining at 600°C. The water leached samples were repulped with an equivalent weight of water and filtered before calcining. The chloride contents of the samples were measured after calcining.

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Table III

The Effect of Calcining Conditions on Insoluble Uranium

Feed	Calcining Temperature °C	Total Dry Solids, percent	Insoluble U Percent of Total Insoluble	Insoluble U Percent of Total U	Chloride After Calcining percent
Vitro Wet Cake	No Calcining	0.5	9.0	0.05	2.05
Vitro Wet Cake (water leached)	160	2.3	1.75	0.05	0.72
Vitro Wet Cake (water leached)	215	2.9	1.83	0.06	0.90
Vitro Wet Cake	300	11.1	2.04	0.25	2.0
	400	9.7	3.24	0.32	1.1
	500	16.4	13.8	2.24	0.14
	600	20.0	15.3	3.05	0.14
Vitro Wet Cake (Predried 16 hrs at 110°C)	600	21.8	15.3	3.30	
Vitro Wet Cake (Hydrogen atmosphere)	600	2.4	0.81	0.02	0.60 ^a
Vitro Wet Cake	700	22.4	11.2	2.48	0.06
	800	27.0	19.6	5.12	
	900	21.6	0.79	0.16	
	1000	20.6	0.61	0.12	
Vitro Lot 60 (Hydrogen atmosphere)	600	8.4	0.72	0.11	
Vitro Lot 65 (Hydrogen atmosphere)	600	7.5	0.26	0.03	

^aHigh chloride probably due to the small exit tube in the closed system and the shorter ignition time

Results and Discussion

Six of the twelve concentrates quite consistently contained more than 0.01 percent insoluble uranium. The precision of the modified nitric acid insoluble uranium test as determined by twenty duplicate runs was ± 58 percent relative when insoluble uranium was < 1 percent and ± 18 percent relative in the 1 to 8 percent range. These precisions are given at the 95 percent confidence level.

The Vitro wet cake used in obtaining much of the data given in Table III is from one sample of Vitro Mill precipitated wet cake which assayed 65 percent U_3O_8 and about 12 percent iron. A qualitative spectrographic analysis showed uranium, iron, molybdenum, and vanadium to be the major metal constituents of the cake.

The insoluble uranium content of the ore concentrates depends chiefly on the calcining temperature. For the case of Vitro material the insoluble uranium content rises sharply when calcined between 400 and 500°C and drops rapidly when calcined between 800 and 900°C. Lindstrom⁷ at the Winchester Laboratory has investigated the effect of calcining temperature on insoluble uranium in concentrates from Climax, Shiprock, Moab, Tuba City, Rifle, Anaconda A and C, and Monticello A and C. With the exception of the two carbonate leach concentrates, the same characteristic correlation between calcining temperature and insoluble uranium was observed as was found in this laboratory with Vitro concentrate. The acid insoluble residues were examined by X-ray diffraction and hematite was found in all samples calcined from 160 to 1000°C. An unknown X-ray diffraction pattern, having peaks at "d" spacings of 5.10, 4.08, 3.27, 2.60, 2.03, 1.89, and 1.72 Å, was observed in the samples calcined at 500, 600, 700, and 800°C. The unknown exists in the same temperature region as the insoluble uranium and for this reason has been correlated with the insoluble uranium even though no further proof that the two are the same exists. The same compound was observed in the acid insoluble fraction of Uravan concentrate in an earlier report.⁸

If the calcining is done in the reducing atmosphere of hydrogen the insoluble uranium is considerably lower and the X-ray diffraction pattern on the residues quite different. The residue from a Vitro wet cake sample calcined in the hydrogen atmosphere contained 0.02 percent of the original uranium and no hematite or unknown X-ray diffraction pattern but did show the presence of Fe_3O_4 (magnetic iron oxide). The residue from a normal Vitro concentrate (previously calcined at 500 to 600°C at the mill) recalcined in the hydrogen atmosphere still contained

⁷ Lindstrom, R. W., Private Communication from Richard L. Philippone.

⁸ Lang, G. P., *et. al.*, MCW-1399, p 13-20

hematite but none of the unknown and very little insoluble uranium. Fe_3O_4 was not detected in this sample. The effect of calcining normal Vitro material in a reducing atmosphere can be seen by comparing the values obtained on Lots 60 and 65 given in Table III with those given in Table I.

A qualitative spectrographic analysis of the acid insoluble residues from Vitro concentrates (Lots 60 and 65, Table I) shows uranium, iron, molybdenum, and silica to be major constituents of the residue with vanadium, titanium, and aluminum present in lesser concentrations.

It should be noted that the examination of the acid insoluble residues by X-ray diffraction failed to show the presence of U_3O_8 in these residues even though the concentration of uranium was as high as 19 percent in one sample.

It is believed that uranium is a component of the compound giving the unknown diffraction pattern and the compound may or may not include iron. The iron phase of the insoluble residue does not appear to change between 800 and 900°C, the region in which much of the uranium is solubilized and the unknown disappears.

Neither water leaching nor predrying the wet cake prior to calcining appeared to have a significant effect on the insoluble uranium content of the cake; however, the effect of water leaching on samples calcined in the region of high insoluble uranium has not been investigated as yet.

Further work will be directed toward the identification of the compound or compounds present in the concentrates that are responsible for high uranium insolubility and toward a more applicable means of recovering this uranium during refining.

Acknowledgement

We wish to thank Mr. J. Starbuck for the analysis and interpretation of the X-Ray diffraction work presented in this paper and Mr. H. W. Thieman for supplying the tentative procedure for the determination of nitric acid insoluble uranium in ore concentrates.

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PHYSICAL PROPERTIES OF URANYL NITRATE SOLUTIONS

by

M. O. Nethaway

G. P. Lang

Summary

Some physical properties of uranyl nitrate solutions are presented. Boiling points and freezing points, particularly in the concentration range between uranyl nitrate hexahydrate and uranyl nitrate dihydrate, have been investigated and are compared with boiling point and freezing point curves for the entire system $\text{UO}_2(\text{NO}_3)_2 - \text{H}_2\text{O}$ as found in the literature. The temperature range over which particular compositions exist as solutions is presented graphically.

Introduction

After extraction and purification, UNH solutions in the Weldon Spring refinery are boiled to reduce volume by water removal before transfer to denitration pots for subsequent conversion to orange oxide, UO_3 . Previously the liquor has been reduced only to a concentration of about 11 pounds of uranium per gallon, which is equivalent to a solution of about fifty percent uranium by weight. Transfer of a more concentrated solution to the denitration pots would yield larger batches of UO_3 and increase production capacity.

It is known that beyond this concentration of uranium, both the boiling points and freezing points increase very rapidly, and in fact tend to converge at approximately the composition corresponding to $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}^{1,2,3}$ where decomposition occurs.⁴ In order to determine engineering requirements for the handling of these highly concentrated solutions, a determination of their physical properties is needed. It is especially important to know the magnitude of the temperature range between the freezing and boiling points in order that solutions may be maintained, with some degree of assurance, in the liquid state during transfer.

A generally accepted^{5,6} curve of freezing and boiling point temperatures for varying compositions is shown in Figure 1. Additional data^{7,8} are indicated.

¹ Marshall, W. L., Jr., Gill, J. S., and Secoy, C. H., *The Uranyl Nitrate-Water-System Above 60°C*, Oak Ridge National Laboratory, ORNL-797 (August 15, 1950) and *J. Am. Chem. Soc.*, 73, 1867 (1951)

² Lacher, J. R., *Fundamental Studies on Uranium Nitrate System*, Letter to A. E. Ruehle (May 6, 1957)

³ Bridge, J. R., Melton, C. W., Schwartz, C. M., and Vaughan, D. A., *Thermal Decomposition of Uranyl Nitrate Hexahydrate*, Battelle Memorial Institute, BMI-1110 (July, 1956)

⁴ Wendolkowski, W. S., and Kirslis, S. S., *Thermal Decomposition of Uranyl Nitrate Hexahydrate*, Union Carbide Nuclear Company, K-1086 (Feb. 22, 1954)

⁵ Hanford Atomic Products Operations, *Redox Technical Data Handbook*, HDC-826, Section C-2

⁶ Frey, F. W., *Process Data for TBP-Kerosene System*, Communication to E. K. Teter (November 11, 1954)

⁷ Dodge, E. and Ruehle, A. E., $\text{XO}_2(\text{NO}_3)_2 - \text{HNO}_3 - \text{H}_2\text{O}$ Boiling Point Diagram, Mallinckrodt Chemical Works (January, 1946)

⁸ Marshall, W. L., et al, ORNL-797

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Figure 1
FREEZING AND BOILING POINTS OF URANYL NITRATE SOLUTIONS

The variation of solution density with composition^{9,10,11} is plotted in Figure 2 and extrapolated to the uranyl nitrate dihydrate composition (55.36 percent U by weight).

Experimental and Results

The material used for investigation was Mallinckrodt plant purified uranyl nitrate hexahydrate. Uranyl nitrate dihydrate was prepared by drying the hexahydrate^{12,13} and storing under vacuum. Analysis of starting materials showed a stoichiometric ratio corresponding to uranyl nitrate hexahydrate and uranyl nitrate dihydrate to within 0.5 to 1.0 percent. Uranium determinations were made gravimetrically by ignition to the oxide, U_3O_8 .

Densities were measured at a series of different temperatures for the lower uranium concentrations (essentially all solutions at room temperature) by weighing the contents of a calibrated pipet. They are judged to be accurate within ± 0.003 g/cc.

Freezing points were defined as the temperature at which a solution first produced crystals while cooling. Boiling points were defined as the temperature at which either the first bubbles were evidenced during heating or the last bubbles were evidenced during cooling. The boiling point curve, shown in Figure 3, for the composition range $UO_2(NO_3)_2 \cdot 6H_2O$ to $UO_2(NO_3)_2 \cdot 2H_2O$, was obtained by sampling a melt at its boiling point during decomposition of UNH. Samples were simultaneously removed for measurement of freezing points. These data represent five different batch decompositions. The boiling point temperatures are judged to be accurate to at least $\pm 2^\circ C$. Viscosities in the range, hexahydrate - dihydrate, were determined with a Brookfield Synchro-lectric viscometer which was standardized against distilled water. The values found are in the lowest available range of the instrument where it is the least sensitive and, hence are subject to inaccuracy. The values are probably only accurate to about one-half of one scale division, or two to three centipoises.

In addition, the surface tension of uranyl nitrate hexahydrate was measured. Using a Du Nuy Tensiometer, a value of approximately 45 dynes per square centimeter was found for the molten hexahydrate at 90-100°C. The instrument was standardized against acetone and water.

Experimental data are listed in Tables I and II.

⁹ Lane, J. A., CL-697

¹⁰ Frey, F. W., Communication to E. K. Teter

¹¹ Kapustynsky, A. F., and Lipilena, E. E., "Densities of Aqueous Solutions and Apparent Molal Volumes of Uranyl Nitrate," *Yzvestia Akad. Nauk. USSR* (1956)

¹² Marshall, W. L., *et al*, ORNL-797

¹³ Katzin, L. I., Simon, D. M., and Ferrarao, J. R., *Heats of Solution of Uranyl Nitrate Hydrates in Water and Organic Solvents*, Argonne National Laboratory, Presentation at Chicago Meeting of American Chemical Society (September, 1950)

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Figure 2
DENSITY OF AQUEOUS URANYL NITRATE SOLUTIONS

Figure 3
EXPANDED BOILING POINT CURVE,
 $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

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Table I
Physical Properties of Uranyl Nitrate Solutions

U wt percent	Density g/cc	Temperature of Measurement °C	U Concentration (calculated) lbs/gal	Freezing Point		Boiling Point	
				°C	°F	°C	°F
32.4	1.753	25	4.74	14	57	106.5	224
	1.746	40					
	1.714	81					
	1.702	98					
33.1	1.786	23	4.93	20.2-20.6	69	107.8	226
	1.768	46					
	1.751	80					
	1.729	108					
34.2	1.828	23.3	5.22	23.2	75	110.	230
	1.827	28					
	1.815	42					
	1.791	76					
	1.778	96					
	1.762	110					
35.94	1.885	35.7	5.65	31.9	90	---	---
45.72	2.36	57	9.01	57	135	117	243
46.5	2.40	60	9.31	59	138	119	246
46.7	2.68	25	10.44	61	142	121	250

Table I (continued)

U wt percent	Density g/cc	Temperature of Measurement °C	U Concentration (calculated) lbs/gal	Freezing Point		Boiling Point	
				°C	°F	°C	°F
47.4	2.465 ^a	60	9.75	60	140	120	248
49.1	2.59 ^a	FP	10.5	73	163	122	252
53.1	2.86 ^a	FP	12.6	-	-	145-150	293-302
55.1	3.03 ^a	FP	13.95	175-180	347-356	180-4	356-363
55.3	3.16	25	14.5	181-184	358-363	184-6	363-7
	3.04 ^a	FP ^b	14.05				
Data from UNH Decomposition							
48.0	2.50 ^a	FP	10.0			121	250
49.6	2.60 ^a	FP	10.8			123	253
49.7	2.60 ^a	FP	10.8	85	185	125	257
50.2	2.64 ^a	FP	11.1	100	212	129	264
50.8	2.68 ^a	FP	11.4			130	266
51.4	2.71 ^a	FP	11.6			136-7	277-9
51.7	2.74 ^a	FP	11.8	108	226	139	282
52.4	2.79 ^a	FP	12.2	111	232	143	289
52.5	2.80 ^a	FP	12.3			147	297
52.6	2.81 ^a	FP	12.3			146	295
53.0	2.85 ^a	FP	12.6			152	305

Table I (continued)

U wt percent	Density g/cc	Temperature of Measurement °C	U Concentration (calculated) lbs/gal	Freezing Point		Boiling Point	
				°C	°F	°C	°F
53.3	2.88 ^a	FP	12.8	112	234	152	306
53.5	2.89 ^a	FP	12.9			154	309
53.7	2.90 ^a	FP	13.0			156	313
54.1	2.93 ^a	FP	13.2	130	266	166	331
54.2	2.94 ^a	FP	13.3			162	324
54.2	2.94 ^a	FP	13.3	132	270	164	327
54.3	2.96 ^a	FP	13.4			169	336
54.6	2.97 ^a	FP	13.5			171	340
54.7	2.98 ^a	FP	13.6	160	320	172	342
54.9	2.99 ^a	FP	13.7			173	343

^aIndicates densities assumed^bExtrapolated

Table II

Change in Viscosity During Decomposition of Molten UNH

Boiling Point of Solution °C	U wt percent	Approximate U Content lbs/gal	Viscometer Reading ^a	Viscosity Centipoises
118	45.9	8.9	3.4	17
120	47.4	9.7	3.75	19
152	53.4	12.8	5.5	28
159	53.9	13.1	6.3	32
184	55.4	14.1	8.5	43

^aNo. 1 Spindle used at 20 rpm; readings taken on 100 scale

Discussion

Uranyl nitrate solutions exhibit a very marked ability to superheat and to supercool. For this reason it is somewhat difficult to accurately determine a precise temperature of physical change. The concentration region between the hexahydrate and dihydrate is especially difficult to examine experimentally. The molten salts exhibit no sharp freezing point breaks, as would be seen in normal cooling curves. (One may observe a difference of fifteen degrees or more in successive measurements of the temperature of first crystallization of the same solution.) Solid and solution appear capable of co-existence over a wide temperature range. The best freezing point values were obtained by repeated determinations at close to equilibrium conditions. An oil bath was used as a heat transfer medium to provide slow and uniform temperature change.

Another difficulty is involved in maintaining equilibrium conditions with respect to hydrate water during melting point determinations. During heating the crystals effloresce and lose water before a definite phase change takes place. The water vapor pressure becomes appreciable,¹⁴ as is evidenced by vapor formation over the solid and condensation on the walls of the container. Thus, even keeping the system under reflux does not always insure maintenance of the same composition throughout a measurement. (All measurements were made at atmospheric pressure.)

¹⁴ Wendolkowski, W. S., K-1086

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Examination of the boiling point curve above the inflection corresponding to the trihydrate (53.1 U weight percent) will indicate another difficulty. During the decomposition of UNH by boiling, when a boiling point of 155-160°C is reached (corresponding to a composition of approximately 13 pounds of U per gallon), the dehydration becomes more rapid due to the very fast rise of the boiling point and change in composition with temperature. In this region the solution changes in color from yellow to deep orange. The temperature range between the melting and boiling point narrows, and the material becomes difficult to handle or sample. Recrystallization is sometimes observed,¹⁵ and homogeneity is probably not maintained. This region between the melting and boiling points is termed the "solution range." The magnitude of the range (defined as $\Delta T = T_B - T_F$) as it varies with composition has been plotted separately in Figure 4, since it is of special practical significance. It is seen to decrease rapidly and fall to zero below the trihydrate composition.

No NO₂ fumes were observed below the dihydrate composition. Upon heating the dihydrate to $\sim 180^\circ\text{C}$, evolution of H₂O (g) and NO₂ (g) is seen during boiling and immediately after the first sign of melting. At this composition there is no longer a difference between the boiling and melting temperatures, leaving no temperature range for the existence of solution. Three phases, solid, liquid, and gas, co-exist and rapidly decompose.¹⁶

For plant use, all data have been converted to units commonly used by plant engineers, and a curve, shown in Figure 5, has been drawn to best fit the freezing point and boiling point data. Literature values for densities have been assumed and extrapolated in order to convert weight percent uranium to pounds of uranium per gallon.

One conclusion that may be drawn is that the plant boildown liquor could be dehydrated to a more concentrated solution than is now done; however, the flexibility of handling would be decreased and temperature control would no doubt become exceedingly difficult beyond a concentration of about 13 pounds of U per gallon, where the freezing point and boiling point are only in the order of forty or less Fahrenheit degrees apart. This concentration is only one pound per gallon less than the limit of 14 pounds per gallon (the uranyl nitrate dihydrate concentration) which is unstable with respect to decomposition.¹⁷

¹⁵ Lister, B. A. J., and Richardson, R. J., *The Preparation of UO₃ by Thermal Decomposition of Uranyl Nitrate*, Atomic Energy Research Establishment, AERE-C/R-1874, (1956)

¹⁶ Wendolkowski, W. S., K-1086

¹⁷ Wendolkowski, W. S., K-1086

Figure 4
THE TOTAL RANGE IN DEGREES OVER WHICH A SOLUTION
EXISTS, *i.e.*, TBP-TFP *vs* CONCENTRATION

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Figure 5

BOILING AND FREEZING POINTS OF URANYL NITRATE SOLUTIONS

SOLVENT TREATMENT

by

E. N. Nelson
S. W. Weidman
G. P. Lang

Summary

A literature search of TBP-diluent degradation and decontamination in uranyl nitrate-TBP systems was made.

The sodium carbonate solvent treatment procedure as used in the Weldon Spring refinery was examined to determine the effects of such variables as contact time, uranium saturation of the sodium carbonate, and temperature. Equilibrium in the solvent-sodium carbonate system was attained in less than 5 minutes. Uranium saturation had little effect on sodium carbonate scrub efficiency up to 80% saturation and slightly better scrubbing was accomplished at higher temperatures. Sodium carbonate was more efficient in removing uranium from synthetic solvent containing DBP than it was in removing uranium from plant solvent. Aqueous entrainment in TBP-hexane increased with contact time and temperature and was much higher in plant solvent than in synthetic solvent containing DBP. This would seem to indicate the presence of some complexing agent and/or emulsifying agent other than DBP in the solvent.

Uranium distribution coefficients for sulfuric acid solutions and TBP-hexane were determined and it was found that 2 - 4 molar sulfuric acid is as efficient as sodium carbonate in removing uranium from TBP-hexane.

A preliminary investigation of commercial hexane degradation by nitric acid seemed to show that some product is formed which inhibits the removal of uranium from TBP-hexane by sodium carbonate.

Introduction

The refining of uranium at the St. Louis Production Center has been recently changed from a process in which the primary purification is accomplished by an extraction of uranyl nitrate with diethyl ether to a process in which the extraction is performed with tri-n-butyl phosphate (TBP) dissolved in commercial hexane. The re-purification of recycle ether was readily accomplished by a simple distillation, but this can not be done with the newer solvent, TBP-hexane, since TBP and its first hydrolysis product, di-butyl phosphate (DBP), are high boiling liquids.

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Degradation products of commercial hexane are also difficult to separate by distillation.

The only purification now being used is one in which the TBP-hexane is treated with a solution of sodium carbonate. After the uranium has been re-extracted from the solvent, the solvent is allowed to flow upward through an open column which is charged with about 300 gallons of approximately six per cent sodium carbonate. When the carbonate is spent, the column is recharged with fresh sodium carbonate, and the uranium in the spent carbonate is precipitated with sodium hydroxide and recovered by filtration.

The operation of the carbonate scrub system has been erratic due in large measure to startup difficulties. This has resulted at times in both uranium and DBP concentrations as high as 1 - 1.5 g/l in the treated solvent. With greater operating experience and with the use of higher carbonate concentrations (9%) these concentrations have leveled off to about 0.2 - 0.5 g/l.

More efficient removal of uranium from solvent feed is required in order to insure complete uranium removal in the primary extraction. This has led to a laboratory search for a more efficient treatment system as well as a better understanding of the chemistry involved in the sodium carbonate treatment.

Literature Survey

A number of investigations^{1,2,3,4,5,6,7,8} on the degradation of TBP-diluent in acidic systems have been made. The rate of formation as well as the characterization of the TBP hydrolysis products and the removal of these products by alkaline scrubs have been thoroughly studied. It is known that, if the hydrolysis products of TBP were the only impurities present in TBP-diluent, they could readily be removed by treatment with sodium carbonate.

¹ Lang, G. P., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1380 (October 1, 1955) p 59-65

² Burger, L. L., *The Chemistry of Tributyl Phosphate: A Review*, Hanford Works, HW-40910 (October 27, 1955)

³ Burger, L. L., *Partition of Dibutyl Phosphate*, Hanford Works, HW-33682 (November 8, 1954)

⁴ Ewing, R. A., Kiehl, S. A., Jr., Bearse, A. E., *Degradation Products of Tributyl Phosphate*, Battelle Memorial Institute, BMI-1073 (February 17, 1956)

⁵ Wagner, R. M., *The Hydrolysis Products of Tributyl Phosphate and Their Effects on the Tributyl Phosphate Process for Uranium Recovery*, Hanford Works, HW-19959 (April 15, 1951)

⁶ Elester, W. K., *Chemistry Division Quarterly Progress Report for Period Ending May 20, 1951*, Oak Ridge National Laboratory, ORNL-1061 (September 24, 1951) p 42-44

⁷ Haas, P. A., Jealous, A. C., *Thorex Solvent Recovery: Development of Calcium Hydroxide, Slurry Process*, Oak Ridge National Laboratory, ORNL-1784 (February 16, 1955)

⁸ Wischan, R. P., Gresky, A. T., Savolainen, J. E., Private Communication to A. C. Jealous, Oak Ridge National Laboratory, CF-54-12-89 (December 9, 1954)

Diluent degradation^{9,10,11} is much more complicated and difficult to understand because of the large number of compounds that may be present in a diluent such as kerosene. Several types of compounds have been identified in recycled TBP-kerosene. They are aliphatic nitro, nitroso, and carboxylic acid compounds; in addition the solvent is strongly indicated to contain aromatic nitro and nitroso compounds and intermediate ketones and aldehydes. Alkaline treatments will partially remove some of these products but not nitro compounds or nitrite esters, both of which have a great effect on solvent quality. Reused solvents appear to contain other products that act as metal complexers or emulsifying agents and which have never been identified.

Experimental

The data contained in Table I, which shows the effect of contact time and uranium saturation on the ability of 10% Na_2CO_3 to remove uranium from plant solvent (28% TBP-hexane), was obtained as follows. Five milliliters of fresh 10% Na_2CO_3 was shaken with successive 100-ml portions of plant solvent in a separatory funnel at room temperature for a given length of time. The uranium concentration in the clear organic phase was measured before and after each contact. E^0_A is defined as the distribution coefficient, organic to aqueous.

⁹ Moore, R. H., *Investigation of Solvent Degradation Products in Recycled Uranium Recovery Plant Solvent*, Hanford Works, HW-24502 Rev. (April 28, 1955)

¹⁰ Klopenstein, R. K., Ellerhorst, R. H., Krekeler, J. H., Hispert, R. C., Nelli, J. R., *Summary Technical Report for the Period April 1, 1957, to June 30, 1957*, National Lead Company of Ohio, NLCO-685 (July 19, 1957) p 10-24

¹¹ Ewing, R. A., Kiehl, S. A., Jr. Bearse, A. E., BMI-1073

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Table I

Distribution Coefficients of Uranium between Successive Portions
of Plant Solvent and 10% Na_2CO_3

No. of Contacts	1 Minute Contact			5 Minute Contact		
	U Organic g/l	U Aqueous g/l	$E_a^o(\text{U})$	U Organic g/l	U Aqueous g/l	$E_a^o(\text{U})$
First	0.28	9.2	0.030	0.22	10.4	0.021
Second	.17	20.6	.008	.10	23.2	.004
Third	.25	30.4	.008	.10	36.0	.003
Fourth	.18	41.6	.004	.13	48.0	.003

The synthetic solvents used in obtaining the data shown in Table II were prepared using fresh commercial hexane, carbonate-washed TBP, pure uranyl nitrate, and DBP separated from a mixture of mono- and di-butyl phosphate according to the procedure of Kennedy and Grimley.¹² The extractions were performed in a closed resin kettle under a reflux condenser. The two phases were continuously mixed and samples of the homogeneous mixture were withdrawn by siphon at various time intervals. The mixture was allowed to separate and each phase analyzed for uranium and DBP. The aqueous entrainment in the organic phase was measured by centrifuging the organic after allowing five minutes for phase separation. A twenty to one organic to aqueous ratio was used in all four experiments reported in Table II.

¹² Kennedy, J., and Grimley, S. S., *Tri-n-Butyl Phosphate Studies, Parts 1, 2, 3*, Atomic Energy Research Establishment, AERE-CE/R-968. (October 6, 1952)

Table II

The Effect of Contact Time and Temperature on the Uranium and DBP Distribution Coefficients between 1.0 M Na_2CO_3 and Various Solvents; Aqueous Entrainment as a Function of Solvent Type, Contact Time, and Temperature

Contact Time min	Temp. °C	Uranium			DBP			Aqueous Entrainment %
		Organic g/l	Aqueous g/l	E _A ^o	Organic g/l	Aqueous g/l	E _A ^o	
Plant Solvent No. 1								
1	20	0.32	5.0	0.064	0.19	0.4	0.470	0.1
5	20	.31	5.2	.060	.13	1.6	.081	0.17
10	20	.31	5.2	.060	.12	1.8	.070	0.20
20	20	.30	5.4	.056	.12	1.8	.070	0.60
40	20	.32	5.0	.064	.12	1.8	.070	0.84
Plant Solvent No. 1								
1	45	.23	6.8	.034	.07	2.8	.025	0.5
5	45	.24	6.6	.036	.07	2.8	.025	~ 2.0
10	45	.26	6.2	.042	.17	0.8	.21	~ 2.0
20	45	.21	7.2	.029	.08	2.6	.031	~ 1.2
Synthetic Solvent 28% TBP-Hexane (1 g/l U)								
1	30	<.02	19.6	<.001				
10	30	<.02	19.6	<.001				< 0.01
20	30	<.02	19.6	<.001				< .01
Synthetic Solvent 28% TBP-Hexane (1 g/l U) (0.73 g/l DBP)								
1	30	.01	19.8	<.001	.02	14.2	0.001	~ 0.01
10	30	<.01	19.8	<.001	.02	14.2	.001	~ 0.02
20	30	.02	19.6	<.001	.02	14.2	.001	~ 0.03

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The data on the distribution of uranium between TBP-diluent and sulfuric acid solutions was obtained using a similar synthetic solvent and is shown in Figure 1. The solvent used was 28% TBP-hexane which contained about 0.7 g/l each of uranium and DBP. Contacts were made at room temperature in separatory funnels using a twenty to one organic to aqueous ratio. The phases were mixed for 5 minutes to insure equilibrium. One point on the curve at 10 M sulfuric acid was obtained using a similar synthetic solvent containing no DBP.

Three liters of fresh commercial hexane were treated with 110 milliliters of concentrated nitric acid under reflux for two hours. A portion of the treated hexane (400 ml) was washed with five successive 20-ml portions of distilled water. A portion of the water washed hexane was re-distilled, collecting the fraction boiling between 66 and 69°C. Four different solvents were prepared from the variously treated hexanes and carbonate-washed TBP, and one g/l uranium was added to each of the solvents as solid uranyl nitrate hexahydrate. Each solvent was then equilibrated with 1M sodium carbonate at room temperature, using a twenty to one organic to aqueous ratio. The uranium in the solvent was determined fluorimetrically and the distribution coefficients calculated. The data is given in Table III.

Table III

The Effect of Nitric Acid Treated Hexane on the Distribution Coefficient of Uranium between 1.0 M Na_2CO_3 and TBP-Hexane

Material From Which Solvent Prepared	Uranium		
	Organic g/l	Aqueous g/l	E_A^0
Fresh Hexane	1.5×10^{-4}	1.0	1.5×10^{-4}
HNO_3 Treated Hexane	6.2×10^{-4}	1.0	6.2×10^{-4}
Water Washed Hexane	2.8×10^{-4}	1.0	2.8×10^{-4}
Re-distilled Hexane	1.5×10^{-4}	1.0	1.5×10^{-4}

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Results and Discussion

Table I shows that complete equilibrium of uranium between plant solvent and 10% sodium carbonate is not attained in one minute. About 82% of the uranium was removed from the solvent in a five-minute contact, whereas about 72% was removed in a one-minute contact. Furthermore, sodium carbonate which was loaded to about 80% of saturation with uranium appears to be just as effective as fresh sodium carbonate in removing uranium from plant solvent. In fact the distribution coefficients seem to indicate that the system became more effective as the concentration of uranium in the sodium carbonate increased. However, the concentration of uranium in the organic phase was reduced to about the same level in each case after the first contact and this may indicate that the residual uranium was held in the solvent in some form which could not be extracted from the solvent by sodium carbonate (other than the DBP complex).

A comparison of the sodium carbonate treatment on various type solvents was made and the effects of contact time and temperature on treatment efficiency were investigated. The results are shown in Table II and lead to several conclusions. Sodium carbonate was not as efficient in removing uranium and DBP from plant solvent as it was in removing uranium and DBP from a synthetic solvent. A somewhat more efficient removal of uranium and DBP was accomplished at higher temperatures. Aqueous entrainment was one to two orders of magnitude higher in the plant solvent system than in the synthetic solvent systems and it also increased with increased temperature and increased contact time. These observations would seem to show that the recycle Weldon Spring refinery solvent contained some uranium complexing agent and/or an emulsifying agent that was not completely removed by the sodium carbonate treatment. Similar characteristics have been noted in TBP-kerosene solvents at other plants and have been attributed to the degradation of the diluent kerosene. The Weldon Spring refinery diluent (commercial hexane) may be subject to the same type of degradation.

The ability of various concentrations of H_2SO_4 to remove uranium from TBP-hexane containing DBP is shown in Figure 1. The data indicates that the optimum sulfuric acid concentration is between two and four molar and the uranium distribution coefficients in this range are about as low as those obtained with 1.0 M sodium carbonate. A sample of plant solvent was also contacted with 3 M sulfuric acid and a $E_A(U)$ of 0.003 was obtained. This was an order of magnitude better than the E_A obtained with 1.0 M sodium carbonate on the same plant solvent. The mechanism by which the distribution coefficient rises with increasing sulfuric acid concentration above four molar is not understood. It is known that some sulfate extracts. The organic phases of the four and ten molar systems were found to contain one and 29 g/l sulfate, respectively. It is possible that a sulfate complex of uranium extracts into TBP from higher sulfuric acid acidities.

A sulfuric acid treatment of plant solvent prior to the normal sodium carbonate treatment has been suggested.¹³ It would allow the uranium to be recovered free of DBP and in a form which could be returned directly to the digest area without the need of precipitation. It would also allow the present sodium carbonate column to remain on steam a much longer percentage of the time. As a result, both the uranium and DBP levels in recycle solvent feed to the decanters could probably be maintained a lower level than is possible with the present system. One objection to the use of sulfuric acid is the possibility of higher corrosion rates on stainless steel. Corrosion rates appear to be the highest at about the optimum concentration for uranium removal.

The commercial hexane used in the refinery is known to contain benzene, cyclohexane, and methyl cyclopentane as well as the isomers of n-hexane. The effect of nitrated hexane on the uranium distribution between TBP-hexane and sodium carbonate is shown in Table III. All of the distribution coefficients are lower (more favorable) than those obtained with solvents containing DBP, but the results show that nitrated hexane has a significant detrimental effect on the ability of sodium carbonate to remove uranium from TBP-hexane. Each of the four hexane samples was examined by IR and UV spectrophotometry and by gas chromatography. The presence of nitro compounds was detected in both the nitric-acid-treated sample and the water-washed sample. They were absent in both the fresh and the re-distilled samples. Concentration changes of the isomers or cyclic impurities were not great enough to be detected by the present means of comparison.

Further work will be directed toward diluent nitration, identification of unknown complexes and/or emulsifiers in recycled plant solvent, and other methods of solvent treatment.

We wish to thank Mr. C. H. McBride and Mr. H. Pena for the analysis and interpretation of infra red and ultra-violet spectra and gas chromatography separations referred to in this report.

¹³ Fariss, R. H., Private communication, Mallinckrodt Chemical Works

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RECOVERY OF NITRATES FROM RAFFINATE BY EXTRACTION WITH TBP-HEXANE

by

S. Weidman

G. Lang

I. Summary

1. The distribution coefficient (o/a) for nitric acid between raffinate and 28 percent TBP-hexane was found to have an average value of 0.3.
2. Excess H_2SO_4 in addition to that needed for nitric acid extraction increased markedly the distribution coefficient (o/a) for nitric acid.
3. Equilibrium curves for nitric acid extraction into 28 percent TBP-hexane in the presence of sodium nitrate and sodium nitrate plus sulfuric acid are presented.
4. Chloride and fluoride distribution between nitric acid solutions and TBP is reported.

II. Introduction

The recovery of nitric acid in the raffinate from the uranium refinery at Weldon Spring has been studied previously. Earlier work^{1,2,3,4,5} on nitric acid recovery from a raffinate containing 2.5 to 3.0 molar nitric acid resulted in development of the following method:

- (1) volatilization of about 85 percent of the nitric acid by a raffinate boildown;
- (2) addition of Al_2O_3 prior to the raffinate boildown to keep the fluoride in the raffinate from distilling with the nitric acid;
- (3) potassium permanganate treatment of the condensed acid stream to oxidize chloride to chlorine; and
- (4) concentration of the dilute acid to 60 percent nitric acid by means of a ten-tray, bubble cap reconcentrator.

¹ Bradford, W., Martin, G. L., Childs, C. R., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1397 (October 1, 1956) p 41

² Bradford, W., Martin, G. L., Weidman, S., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1399 (January 1, 1957) p 117

³ Weidman, S. W., Lang, G. P., Bradford, W. G., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1403 (July 1, 1957) p 13

⁴ Weidman, S. W., Lang, G. P., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1407 (October 1, 1957) p 13

⁵ Sollami, B. J., *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, MCW-1411 (February 1, 1958) p 21

REF ID: A66888

Figure 1

SCHEMATIC DIAGRAM OF PROPOSED NITRIC ACID RECOVERY

III. Experimental and Results

A. Plant Raffinate Studies

In order to obtain preliminary data on the extraction of nitric acid by TBP, with and without sulfuric acid, plant raffinate was sampled, various amounts of sulfuric acid were added, and the resulting solution contacted with 28 percent TBP-hexane. The results are tabulated in Table I.

Table I
Extraction of HNO_3 from Plant Raffinate

Date Sampled	Initial Raffinate Composition			Total Extractable ^b NO_3^- mole/l	Equilibrium Data	
	HNO_3^a mole/l	Salt ^a NO_3^- mole/l	H_2SO_4 Added mole/l		Equil. HNO_3 Organic mole/l	E_o^c
10/16/57	1.1	1.4	0.0	1.1	0.33	0.37
	1.1	1.4	0.48	1.6	.39	.32
	1.0	1.3	1.0	2.0	.49	.33
	1.0	1.2	2.0	3.0	.64	.40
10/18/57	1.7	0.31	0.0	1.7	.40	.29
	1.7	0.31	0.52	2.0	.50	.33
	1.6	0.29	1.0	1.9	.52	.37
	1.5	0.28	2.0	1.8	.76	.76
10/28/57	0.60	1.0	0.0	0.60	.16	.36
	0.60	1.0	0.52	1.1	.27	.32
	0.56	0.94	0.98	1.5	.36	.33
	0.53	0.89	2.0	1.4	.51	.56
10/31/57	1.0	0.69	0.0	1.0	.27	.37
	1.0	0.69	0.49	1.5	.42	.38
	0.94	0.65	0.99	1.6	.52	.47
	0.89	0.61	2.1	1.5	.74	.97

^a The numbers decrease because the solutions containing H_2SO_4 were made up by adding the correct amount of H_2SO_4 and diluting up to volume with raffinate. No correction was made for the amount of salt nitrate converted to nitric acid by sulfuric acid.

^b The total extractable nitrate is equal to the sum of the initial nitric acid plus the amount of salt nitrate made extractable by the addition of sulfuric acid. In calculating this number, the assumption is made that essentially none of the sulfuric acid dissociates past the bisulfate state.

^c The distribution coefficient is the organic nitric acid concentration divided by the equilibrium extractable nitrate concentration.

B. Effect of Excess Sulfuric Acid on Nitric Acid Extraction

The extraction of nitric acid by TBP may be represented as follows:

The TBP (HNO_3) complex is formed in nitric acid concentrations below about 8 molar; above 8 molar HNO_3 , TBP (2HNO_3) and other complexes are formed. From the extraction equation it is seen that excess hydrogen ion and excess nitrate ion tend to shift the equilibrium toward the organic phase. In order to measure quantitatively the excess acid effect, a series of constant temperature shakeouts were made on solutions containing various amounts of nitric and sulfuric acids. The results are plotted in Figure 2.

C. Equilibrium Curves for Synthetic Raffinate

Synthetic raffinates were prepared which contained 1 M NaNO_3 , 1 M H_2SO_4 , and various amounts of nitric acid. These were contacted with 28 percent TBP-hexane and each phase was analyzed for nitric acid; the equilibrium curves obtained from this data are shown in Figure 3.

D. Determination of the Chloride Distribution Coefficient

The distribution coefficient for chloride ion was determined in nitric acid solutions containing large amounts of sodium chloride and ferric nitrate. Two sets of determinations were carried out: one measuring the distribution coefficient of chloride in nitric acid solutions, and the other measuring the same quantity in nitric acid solutions containing ferric nitrate. The data appears in Table II. The chloride determinations were made by Volhard's method.

Table II

Determination of Chloride Distribution Coefficients in Nitric Acid Solutions

HNO_3 M	Initial Cl^- M	Initial Fe^{+3} M	Equilibrium Organic Cl^- g/l	Equilibrium Aqueous Cl^- g/l	E_A^o
0.5	2.0	0.0	9.6×10^{-3}	71.0	140×10^{-2}
1	2.0	0.0	12×10^{-3}	71.4	170×10^{-2}
3	2.0	0.0	12×10^{-3}	72.7	160×10^{-2}
0.5	2.0	0.5	1.46	68.5	2.14×10^{-2}
1	2.0	0.5	1.60	68.5	2.34×10^{-2}
3	2.0	0.5	1.53	59.5	2.20×10^{-2}
5	2.0	0.5	1.42	70.3	2.20×10^{-2}

Figure 2
EXTRACTION OF HNO_3 BY TBP FROM HNO_3 - H_2SO_4 SOLUTION

Figure 3
EXTRACTION OF HNO_3 FROM SYNTHETIC RAFFINATES

E. Determination of the Fluoride Distribution Coefficient

The distribution coefficient for fluoride ion was determined in nitric acid solutions. A high initial fluoride concentration was used in order to obtain more readily measurable amounts in the organic phase. The distribution coefficient was determined as a function of the acid concentration. In one set of determinations, Al^{+3} ion was also added. The results are shown in Table III.

Table III

Determination of Fluoride Distribution Coefficients in Nitric Acid Solution
(2 M NaF Solutions Extracted with 28% TBP-Hexane)

Initial HNO_3 M	Initial Al^{+3} M	Equilibrium Organic F^- mg/l	Equilibrium Aqueous F^- g/l	E°_A
0.5	0.0	sample lost	33.5	-
1	0.0	266	34.5	7.7×10^{-3}
3	0.0	174	35.0	5.0×10^{-3}
5	0.0	145	36.0	4.0×10^{-3}
0.5	0.5	56	36.0	1.6×10^{-3}
1	0.5	37	36.5	1.0×10^{-3}
3	0.5	33	35.5	93×10^{-3}
5	0.5	22	35.5	62×10^{-3}

IV. Discussion of Results

A. Plant Raffinate Studies

The data for the extraction of nitric acid from actual plant raffinates is presented in Table I. The table shows that the average distribution coefficient for nitric acid is approximately 0.3 up to the point where there is an excess concentration of hydrogen ion over that of the nitrate ion. At that point the distribution coefficient rises due to the salting effect of the hydrogen ion. The important thing to remember in reviewing this data is that, although the distribution coefficient does not rise significantly while adding sulfuric acid, the concentration of nitric acid in the organic phase does rise because more nitric acid becomes available for extraction.

B. Effect of Excess Sulfuric Acid on Nitric Acid Extraction

Data for the extraction of nitric acid from solutions containing nitric and sulfuric acids is shown in Figure 2. This data shows the salting effect of excess hydrogen ion on the

extraction. It is also worthwhile to report that analysis of the organic extracts did not show significant amounts of sulfate to be present; therefore, contamination of the extracted nitric acid by sulfate is not a problem.

C. Equilibrium Curves for Synthetic Raffinates

The equilibrium curves shown in Figure 3 corresponds to the curves for the two proposed methods of nitric acid recovery. The curve of 1 M NaNO_3 and HNO_3 is almost equal to the curve for 1 M NaNO_3 , 1 M H_2SO_4 , and HNO_3 , showing that the extraction will go about the same with or without H_2SO_4 present. These two curves are almost equal to the equilibrium curve used to calculate the number of stages necessary for extraction by the pilot plant.^{10,11} The equilibrium curve for pure nitric acid is added for comparison.

D. Chloride Distribution in Nitric Acid Solutions

The determinations of the chloride distribution coefficient (results shown in Table II) were done with large concentrations of chloride and ferric ions in order to obtain more readily measurable amounts of chloride in the organic phase; even then, the organic chloride analysis of the set of samples containing no ferric ion yielded very low numbers of doubtful accuracy.

The chloride in the raffinate might run as high as 0.4 g/l and the iron, 10 g/l. These conditions would yield a distribution coefficient somewhere around 10^{-3} , making the organic chloride concentration about 0.4 ppm. If a three to one organic to aqueous ratio in the aqueous stripper were used and all the chloride stripped out, the weak acid would contain about 1.2 ppm chloride. This small amount of chloride would certainly not cause corrosion in a reconcentrator operating so as to produce 35 percent nitric acid,¹² but could cause corrosion, depending on fluoride concentration, if the reconcentrator was operated to produce 60 percent acid.

E. Fluoride Distribution in Nitric Acid Solutions

The distribution coefficients for fluoride listed in Table III decrease with increasing nitric acid concentration. Aluminum addition also lowers the coefficient appreciably.

¹⁰ Farris, R. H., Letter to C. D. Harrington

¹¹ Krieg, J. T., Project Analysis 1046P

¹² Letter from R. H. Farris to Mr. E. K. Teter (June 10, 1957)

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The main purpose of these determinations was to obtain a value for the distribution coefficient in order to calculate expected fluoride contamination of the weak acid from the acid stripper. The distribution coefficient appears to be about 5×10^{-3} . Thus, the organic extract, after contacting a raffinate containing 0.1 g/l fluoride, would be expected to contain about 0.5 ppm fluoride. This would result in a weak acid fluoride concentration of about 1.5 ppm.

V. Conclusions

The data used by the pilot plant in the calculations of the feasibility of the extraction of nitric acid by TBP has been checked and verified by the equilibrium studies reported here. The process does not seem to have any serious drawbacks such as the extraction of substances other than nitric acid. The extraction of sulfate, chloride, and fluoride is very low and should not cause any corrosion problems.

VI. Future Work

The complete extraction of thorium by TBP is expected from nitric acid solutions containing nitrate salts. Sulfate and phosphate greatly lower the distribution coefficient of thorium. There is some question as to whether a one molar sulfate solution would lower the distribution coefficient enough to prohibit all of the thorium from extracting. If large amounts of thorium were extracted along with the nitric acid in either or both of the proposed methods of recovery, the entire thorium concentration in the uranium extraction system would be greatly increased due to reflux and the purity of the uranium extract would be affected.

Work on thorium distribution in nitric acid solutions containing various amounts of sulfate and phosphate is now in progress. At present, no other work is planned on this project.

VII. Acknowledgements

The help of Dr. Farris and Mr. J. T. Krieg in furnishing profile data is greatly appreciated by the author.

HYDROFLUORINATION OF UO_2 : PART VI

by

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J. A. Kennelley

I. Summary

1. Both the hydrogen reduction rate of MCW plant UO_3 at 475°C and the hydrofluorination rate of the product UO_2 at 550°C increased with increasing sulfate content over the range 220 to 700 ppm sulfate added as sulfuric acid.
2. The rate of reduction at 475°C of MCW UO_3 which contained 510 or 980 ppm sulfate added as ammonium sulfate was greater than that of non-sulfated UO_3 or UO_3 containing 190 or 380 ppm sulfate. The UO_2 samples, which were produced by reduction at 475°C of UO_3 containing 380, 510, or 980 ppm sulfate from $(\text{NH}_4)_2\text{SO}_4$ additions, hydrofluorinated at 550°C much more rapidly than UO_2 prepared by reduction of non-sulfated UO_3 .
3. The reduction-hydrofluorination reactivity of samples of UO_3 from a given pot or a production lot was enhanced to about the same extent by addition of 500 ppm sulfate either as sulfuric acid or as ammonium sulfate. Uranyl sulfate appeared to be somewhat less effective than H_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ in increasing reactivity.
4. The rates of hydrofluorination of UO_2 prepared by a 475°C -reduction of MCW sulfated UO_3 were equal at 400°C and at 550°C up to 80 percent of completion of the reaction; however, by increasing the HF temperature from 400 to 536°C after 90 percent of completion, the overall hydrofluorination rate was faster than the isothermal reaction rate at 550°C . The product from the programmed temperature hydrofluorination was purer and had not caked or sintered into aggregates.
5. As-produced, fluid-bed denitrated UO_3 was found to be very unreactive. A marked increase in reactivity was achieved by grinding to minus-100 mesh. This UO_3 , however, was still much less reactive than MCW sulfated plant UO_3 . A product which was comparable in reactivity to sulfated UO_3 was obtained by hydration of the minus-100 mesh fraction.

II. Introduction

The uranium trioxide which is produced at the MCW Weldon Spring Refinery contains approximately 500 ppm sulfate added as sulfuric acid. Certain operational difficulties in the

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pot room were encountered using this quantity of sulfuric acid. Therefore, plant experiments were carried out to determine the effects of the amount of sulfate and of the type of sulfating agent upon, (1) the reactivity of the product UO_3 , and (2) the operation of the pots.

The first part of this report deals with the thermobalance evaluation of these plant sulfated samples. Surface area measurements and X-ray analyses were made to determine if the increase in rate of both reduction and subsequent hydrofluorination with an increase in sulfate content might result from a decrease in particle and/or crystallite size of the UO_3 .

Thermobalance studies of the reactivity of UO_3 produced by fluid-bed denitration in the MCW pilot plant are presented in the second section of this report. To be specific, methods of improving the reactivity either by grinding or by hydration are discussed.

III. Experimental

The manually operated thermobalance, experimental procedure, and treatment of data are described in a previous report.¹ Bed depths of about 3 mm were maintained in all the runs described in this report. Unless otherwise specified, the UO_3 samples were studied as received from the plant. The thermobalance tube was always heated in hydrogen to 650°C before a reduction reaction was carried out.

IV. Results and Discussion

The results of the reduction and subsequent hydrofluorination of (1) MCW sulfated plant UO_3 , and (2) fluid-bed denitrated UO_3 , will be presented in two separate sections. First, the effects of the amount of sulfate and of the sulfating agent upon reactivity will be considered. Second, the enhancement of the reactivity of fluid-bed denitrated UO_3 , either by grinding or by hydration will be discussed.

A. MCW Sulfated UO_3

Plant experiments were made in which different amounts of sulfuric acid, ammonium sulfate, and uranyl sulfate were added to a given denitration pot, and the decomposition was carried out under the standard operating conditions. These samples, which contained amounts of sulfate ranging from 100 to 1000 ppm (sample basis), were reduced at 475°C in the thermobalance, and the product UO_2 was immediately hydrofluorinated at 550°C.

¹ Ludwig, F. J., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1392, (July 1, 1956) p. 37-40

1. Sulfuric Acid as the Sulfating Agent

The rates of the hydrogen reduction at 475°C of UO_3 containing sulfate added as sulfuric acid are shown in Figure 1. The presence of 220 or 490 ppm sulfate increased the reduction rate by about 20 percent, compared to that of non-sulfated UO_3 . Moreover, the UO_3 containing 700 ppm sulfate reduced approximately twice as rapidly as non-sulfated UO_3 .

The results of measurements of the chemical composition and of solid state properties of these samples are given in Table I. The UO_3 surface areas which were measured after a 16-hour outgassing at 135°C in vacuum did not correlate with the rates of reduction. The surface areas were also measured after the UO_3 samples had been heated to 475°C in argon. It is thought that these values are more significant since the sample in the thermobalance is heated to 475°C in argon before reduction is started. The surface areas of these pre-heated samples were much greater than those of the starting materials, indicating the loss of volatile components on heating. In fact, the change in surface area was linearly related to the nitrate content of the sample. The 700-ppm sulfated sample, which had a surface area after heating to 475°C of 5.4 sq m/g, reduced about twice as rapidly as the non-sulfated UO_3 of surface area 2.4 sq m/g.

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Table I

Chemical Composition and Physical Properties of Plant Sulfated UO_3 ,
Sulfating Agent: Sulfuric Acid

Property Measured	Sulfate Content of UO_3					
	Non-Sulfated	130 ppm	220 ppm	340 ppm	490 ppm	700 ppm
Surface Area UO_3 outgassed 135°C in vacuum 16 hours, sq m/g	0.99	2.36	0.85	1.70	2.0	1.83
Surface Area, UO_3 preheated to 475°C in argon, sq m/g	2.42	3.3	2.8	2.38	- -	5.4
X-ray diffraction $\frac{1}{2}$ peak breadth, at $d = 3.45 \text{ \AA}$, deg 2θ	0.19	0.20	0.24	0.20	0.23	0.27
X-ray diffraction $\frac{1}{2}$ peak breadth, at $d = 4.38 \text{ \AA}$, deg 2θ	0.19	0.22	0.20	0.21	0.22	0.27
X-ray diffraction peak height compound Y ^a at $d = 4.20 \text{ \AA}$, cps	32	4	32	12	24	38
Total U, %	82.42	83.00	82.01	82.82	82.63	80.88
Free UO_3 , %	99.00	99.69	98.54	99.52	99.26	97.18
HCl Insoluble (U basis), %	0.03	0.01	0.02	< 0.01	0.03	0.02
Iron (U basis), ppm	33	32	34	30	48	42
Nitrate (sample basis), %	- -	- -	0.70	0.31	0.37	2.0
Sulfate (sample basis), %	0.004	0.013	0.022	0.034	0.049	0.070
On 20 mesh sieve, %	15.5	22.8	21.6	17.2	28.0	9.5

^aCompound Y is an unidentified substance believed to be $\text{UO}_3 \cdot x\text{H}_2\text{O}$

X-ray diffraction analysis indicated a general decrease in crystallite size with an increase in sulfate content. For example, the UO_3 containing 700 ppm sulfate had a one-half peak breadth of 0.27 deg compared to 0.19 deg for non-sulfated UO_3 . Thus, the 700 ppm sulfated UO_3 , which was the most reactive upon reduction at 475°C, had the largest surface area and the smallest crystallite size of the series of sulfated UO_3 samples.

With some exceptions, the same trend of an increasing rate with decreasing particle and crystallite size was observed for the other members of the series. The rates of reduction did not correlate with the percent free UO_3 , the percent HCl insoluble, the ppm Fe, or the percent of plus-20 mesh fraction.

Figure 1
HYDROGEN REDUCTION AT 475°C OF MCW SULFATED PLANT UO_2
SULFATING AGENT : SULFURIC ACID

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The rates of the hydrofluorination at 550°C of the product UO_2 samples of this group are presented in Figure 2 and Table II. The reaction velocity increased with increasing sulfate content over the range 220 to 700 ppm. The UO_2 samples which were prepared from UO_3 of smallest crystallite size and largest surface area hydrofluorinated the fastest. It was found that the surface area of sulfated UO_3 increased during reduction, e.g., from 4.04 sq m/g for UO_3 heated to 475°C in argon to 5.95 sq m/g after 115 minutes reduction at 475°C. Caking of the UF_4 products was slight for all runs, indicating that the results were not invalidated by sintering.

Table II

Hydrofluorination of UO_2 Prepared from Sulfated UO_3 ; Sulfating Agent: H_2SO_4

Sulfate Content ppm SO_4	Time 100% Reduction at 475°C min	Weight UO_2 Produced g	Temp. Range HF °C	Total Time in HF min	AOI %	U(IV) %	Caking of Bed
Non-Sulfated	150	3.865	550-552	120	4.06	76.2	Slight; some hard aggregates.
130	130-140	3.915	551-553	120	1.70 ^a	75.3	Slight; some hard aggregates.
220	120	2.938	548-550	90	0.31	75.0	Slight; several hard aggregates.
340	155 ^b	3.104	549-551	90	0.98	75.2	Slight; some hard aggregates.
490	110	3.085	551-553	50	0.26	75.5	Slight to moderate; large aggregates; hard.
700	80	2.950	552-555	70	0.17	75.5	Slight; larger aggregates; hard.

^aSurface area of UF_4 = 0.22 sq m/g.

^b"HF poisoning" of the UO_3 prior to reduction is suspected.

2. Ammonium Sulfate as Sulfating Agent

The rates of hydrogen reduction at 475°C of UO_3 samples containing from 190 to 980 ppm sulfate added as ammonium sulfate are presented in Figure 3. Reduction of non-sulfated UO_3 or UO_3 of 190 or 380 ppm sulfate content proceeded at the same rate. The UO_3 samples which contained 510 or 980 ppm sulfate were reduced in 115 - 125 minutes compared to 150 minutes for non-sulfated UO_3 . The surface areas of the

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Figure 2

HYDROFLUORINATION AT 550°C OF UO_2 PREPARED BY 475°C REDUCTION OF SULFATED UO_3 ; SULFATING AGENT SULFURIC ACID

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Figure 3
HYDROGEN REDUCTION AT 475°C OF MCW SULFATED POT UO_2
SULFATING AGENT : AMMONIUM SULFATE

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as-produced non-sulfated UO_3 and 510 ppm sulfated UO_3 were 0.99 and 2.96 sq m/g. The reduction rates did not correlate with any of the chemical or physical properties listed in Table III.

Table III

Chemical Composition and Physical Properties of Plant Sulfated UO_3
Sulfating Agent: Ammonium Sulfate

Sulfate ppm	Total U %	Free UO_3 %	HCl Insoluble (U basis) %	Fe (U basis) ppm	SO_4 (sample basis) %	NO_3 (sample basis) %	Plus-20 mesh fraction %	Other Measurements
50	81.86	98.36	0.01	33	0.005	0.53	17	--
190	82.30	98.89	.01	52	.019	.53	18	--
290	82.14	98.70	.01	23	.029	.58	23	--
380	82.32	98.90	.028	43	.038	.47	23	--
510	82.44	98.98	.09	31	.051	.44	26	Surface Area: 2.96 sq m/g; X-ray vs ^a - Type III w ^a - Type Y ^b
980	82.11	98.66	.01	74	.098	.96	12	Tap density: 3.8; X-ray: vs ^a - Type III w ^a - Type Y ^b

^aSymbols vs and w indicate very strong and weak diffraction patterns.

^bCompound Y is an unidentified substance believed to be $\text{UO}_3 \cdot X \text{H}_2\text{O}$.

The UO_2 samples, which resulted from the reduction at 475°C of UO_3 containing 380, 510, or 980 ppm sulfate hydrofluorinated at 550°C much more rapidly than non-sulfated UO_2 . (See Figure 4 and Table IV.) The UO_3 samples of 190 ppm sulfate content were appreciably more reactive than non-sulfated UO_3 .

Judging from the results for both H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ activated UO_3 , considerable increases in reactivity may be realized at sulfate contents of only 200 ppm. The maximum reactivity was obtained at 500 ppm sulfate added as H_2SO_4 and at 380 to 980 ppm sulfate added as $(\text{NH}_4)_2\text{SO}_4$. The surface area and X-ray measurements indicate that the sulfating agent may activate the UO_3 by decreasing the crystallite size and increasing the surface area.

Table IV

Hydrofluorination of UO_2 Prepared from Plant Sulfated UO_3 .
Sulfating Agent: Ammonium Sulfate

Sulfate Content ppm	Time 100% Reduction at 475°C min	Weight UO_2 Produced g	Temp. Range HF °C	Total Time in HF min	AOI %	U(IV) %	Caking of Bed
Non- sulfated	150	3.865	550-552	120	4.06	76.2	Slight; some hard aggregates
190	130	4.513	548-552	85	1.41	74.9	Very slight
380	160	2.920	547-550	80	0.05	74.3	Very slight
510	120	3.638	549-552	70	0.04	74.6	Slight; some hard aggregates
980	110-120	3.500	550-553	60	0.72	74.8	Slight; some hard aggregates

3. The Effect of the Sulfating Agent

UO_3 , which contained about 500 ppm sulfate, was prepared by the addition of sulfuric acid, ammonium sulfate, or uranyl sulfate to a given denitration pot. Samples of the resulting UO_3 were reduced at 475°C. The results are shown in Figure 5. The rate varied with the sulfating agent in the order: $\text{H}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{non-sulfated} > \text{uranyl sulfate}$. The chemical composition and physical properties of these UO_3 samples are collected in Table V. No correlation between these data and the different activating effects of the sulfating agents is apparent.

Figure 4

550°C HYDROFLUORINATION OF UO₂ PREPARED BY 475°C REDUCTION OF
SULFATED UO₂, SULFATING AGENT : AMMONIUM SULFATE

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Table V

Chemical Composition and Physical Properties of MCW Plant Sulfated UO_3 ,
 Pot 8, as a Function of Sulfating Agent

Sulfating Agent	Sulfate Content ppm	Surface Area After 475°C Heat in A sq m/g	X-ray Diffraction Analysis	Total U %	Free UO_3 %	HCl Insoluble (U Basis) %	Iron (U Basis) %	Nitrate (Sample Basis) %	Sulfate (Sample Basis) %	Plus-20 Mesh Fraction %
None	40	2.42	Type III $\frac{1}{2}$ Peak Breadth: 0.19; Height Type Y ^a Peak: 32	82.42	99.00	0.03	33	- -	0.004	15.5
UO_2SO_4	410	- -	S-Type III; w ^b - Type Y ^a ; vw ^b - U_3O_8	81.05	97.40	0.03	32	1.57	0.041	4.2
$(\text{NH}_4)_2\text{SO}_4$	510	4.04	vs ^b - Type III; w ^b - Type Y ^a	82.44	98.98	0.09	31	0.44	0.051	26.
H_2SO_4	490	- -	Type III $\frac{1}{2}$ Peak Breadth: 0.23; Height Type Y ^a Peak: 24	82.63	99.26	0.03	48	0.37	0.049	28.0

^aCompound Y is an unidentified substance believed to be $\text{UO}_3 \cdot x \text{H}_2\text{O}$

^bSymbols vw and w indicate very weak and weak diffraction patterns

Figure 5
EFFECT OF SULFATING AGENT UPON THE REDUCTION AT 475°C OF
MCW PLANT SULFATED UO_2 POR 8

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It is shown in Figure 6 and Table VI that the rate of the hydrofluorination at 550°C of UO_2 prepared from this UO_3 was influenced by the nature of the sulfating agent. The order of activation was $\text{H}_2\text{SO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{UO}_2\text{SO}_4 \gg$ non-sulfated. Since the surface area and X-ray data on these sulfated samples are incomplete, no explanation for the observed differences in rate can be offered.

Table VI

Effect of Sulfating Agent upon 550°C Hydrofluorination of UO_2
Prepared by 475°C Reduction of MCW Plant UO_3 , Pot 8

Sulfating Agent	Sulfate Content ppm	Time 100% Reduction at 475°C min	Weight UO_2 Produced g	Temp. Range HF °C	Total Time in HF min	AOI %	U(IV) %	Caking of Bed
None	40	150	3.865	550-552	120	4.06	76.2	Slight; some hard aggregates
UO_2SO_4	410	180	3.567	550-555	90	0.21	75.3	Slight to moderate; some hard aggregates
$(\text{NH}_4)_2\text{SO}_4$	510	120	3.638	549-552	70	0.04	74.8	Slight; some hard aggregates
H_2SO_4	490	110	3.085	551-553	50	0.26	75.5	Slight to moderate; some hard aggregates

Production lots were made using $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 as sulfating agents. The UO_3 samples from these lots and from a non-sulfated lot were reduced at 475°C and the product UO_2 hydrofluorinated at 550°C. It is seen from Figure 7 and Table VII that $(\text{NH}_4)_2\text{SO}_4$ is about as effective as H_2SO_4 in increasing the reactivity. In fact, up to 98 percent of completion, the rate of hydrofluorination of the $(\text{NH}_4)_2\text{SO}_4$ additive product was greater than that of UO_2 from H_2SO_4 activated UO_3 . A difference in the plus-100 mesh content of the 3-g samples would account for the lower AOI of the UO_3 activated by H_2SO_4 . The problem of securing a representative sample is more acute with UO_3 prepared in a given pot than with an entire lot. For this reason, it is believed that greater weight should be given to these results for entire lots. Therefore, it is concluded that ammonium sulfate activates UO_3 towards reduction and subsequent hydrofluorination to the same extent as sulfuric acid. The satisfactory behavior of the UO_3 lot containing 670 ppm sulfate added as $(\text{NH}_4)_2\text{SO}_4$ in the Green Salt Plant strengthens this conclusion.

Figure 6

EFFECT OF SULFATING AGENT UPON THE 550°C HYDROFLUORINATION
OF UO₂ PREPARED BY 475°C REDUCTION OF MCW PLANT SULFATED UO₂-POT 8

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Figure 7

EFFECT OF SULFATING AGENT UPON HYDROFLUORINATION AT 550°C OF
UO₂ PREPARED BY 475°C REDUCTION OF MCW PLANT UO₃ - LOT SAMPLES

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Table VII.

Effect of Sulfating Agent on Hydrofluorination of UO_2
Prepared by 475°C Reduction of Lot Samples of MCW Plant UO_3

Sulfating Agent	Sulfate Content ppm	Time 100% Reduction at 475°C min	Weight UO_2 Produced g	Temp. Range HF $^\circ\text{C}$	Total Time in HF min	AOI %	U(IV) %	Caking of Bed
None	40	165	2.600	554-557	120	1.48 ^a	75.3	Slight
H_2SO_4	500-600	120	3.687	550-553	90	0.68	74.7	Very slight; some hard aggregates
$(\text{NH}_4)_2\text{SO}_4$ ^b	670	140-150	3.363	548-550	90	1.30	74.7	Very slight

^aSurface area UF_4 = 0.31 sq m/g

^bSurface area UO_3 = 2.57 sq m/g

4. Effect of Temperature upon Hydrofluorination

The effect of temperature upon the rate of hydrofluorination of UO_2 made by reduction at 475°C of 670 ppm sulfated UO_3 (MCW Lot 054) is shown in Figure 8. The rates of hydrofluorination are equal up to 80 percent of completion at 400°C and at 550°C . Thereafter, the rate at 550°C is greater. By increasing the temperature after 90 percent of completion from 400 to 536°C , the overall hydrofluorination was faster than isothermal reaction at 550°C . The UF_4 produced in the programmed temperature run had an AOI of 0.68 percent after 65 minutes reaction whereas the UF_4 prepared at 550°C had an AOI of 1.30 percent after 90 minutes. It is probable that thermal damage, which would produce material of higher AOI, was avoided by reacting the UO_2 at 400°C for 90 percent of completion.

5. Fluid-Bed Denitrated UO_3

Fluid-bed denitration is being investigated in the MCW Pilot Plant as a method of continuous conversion of UNH to UO_3 . In the initial experiments with this reactor, the UO_3 product was composed chiefly of plus-100 mesh aggregates and was highly unreactive, e.g., see Curve 1 of Figure 9. In addition to the improved operating conditions which were realized, two well known methods of activation of UO_3 were attempted in this laboratory, namely grinding and hydration. An examination of the data given in Table VIII and Figure 9 shows that grinding to minus-100 mesh considerably improved the rate of hydrofluorination at 550°C of UO_2 prepared by 550°C

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Table VIII

Hydrofluorination at 550°C of UO_2 Prepared by Reduction of Ground Fluid-Bed Denitrated UO_3

Sieve Fraction Fluid Bed UO_3	Temp. of H_2 Red. °C	Time for 100% Reduction min	Weight UO_2 Produced g	Temp. Range HF °C	Total Time in HF min	AOI %	U(IV) %	Caking of Bed
Run 6 as-received	550-559	125	4.883	549-551	180	32.8	78.0	None
Run 6 ground to minus-100 mesh	551-555	130	3.803	546-552	180	22.0	78.6	Very slight
Run 8 ground to minus-170 plus-270 mesh	552-553	80	4.481	547-555	165	21.9	75.5	Moderate
Run 9 ground to minus-170 plus 270 mesh	554-556	43	4.275	544-550	200	13.6	76.7	Moderate
Run 8 ground to minus-100 mesh	548-645	190	3.490	558-562	120	10.9	76.0	None

Figure 8
EFFECT OF TEMPERATURE UPON THE HYDROFLUORINATION OF UO_2
PREPARED BY 475°C REDUCTION OF MCW SULFATED UO_2 (670 ppm SO_4)

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Figure 9
EFFECT OF GRINDING UPON RATE OF 550°C HYDROFLUORINATION OF UO_2 ,
PREPARED BY REDUCTION OF FLUID BED DENITRATED UO_3

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reduction of fluid-bed UO_3 . The rates of both reduction and hydrofluorination, however, were much less than those of MCW plant UO_3 .

A hydrate was prepared by heating a suspension of fluid-bed denitrated UO_3 , which was ground to minus-100 mesh, in water at 100°C for 30 minutes. The X-ray diffraction pattern of this hydrate did not match the patterns for any UO_3 hydrate which has been reported. The rate of the reduction at 475°C of this $\text{UO}_3 \cdot X\text{H}_2\text{O}$ (where probably $1 < X < 2$) was comparable to that of MCW UO_3 of 500 ppm sulfate content. The product UO_2 hydrofluorinated at 550°C as rapidly as UO_2 prepared from MCW plant sulfated UO_3 . Compare Figure 10 with Figures 2 and 4. It is shown in Figure 10 and Table IX that hydration was a much more effective method of activation than was grinding. The surface areas of the minus-100 mesh ground UO_3 and of $\text{UO}_3 \cdot X\text{H}_2\text{O}$ were 0.30 and 1.54 sq m/g, respectively. This five-fold difference in surface area is clearly reflected in the large difference in reactivity, and further supports the author's thesis that the rates of these solid-gas reactions are mainly a function of the solid state properties, particularly particle size, of the powder.

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Table IX

Hydrofluorination of UO_2 Prepared from Ground Fluid-Bed
Denitrated UO_3 and the Corresponding Hydrate

Nature of UO_3	Surface Area sq m/g	Weight Loss on Heating in A to 475°C %	Temp. Red. $^\circ\text{C}$	Time 100% Reduction min	Weight UO_2 Produced g	Temp. Range HF $^\circ\text{C}$	Total Time in HF min	AOI %	U(IV) %	Caking of Bed
Fluid-Bed Deni- trated Ground to minus-100 mesh	0.30	0.40	548-645	190	3.490	558-562	120	10.9	76.0	None
$\text{UO}_3 \cdot x \text{H}_2\text{O}^{a,b}$	1.54	6.00	475-477	90	2.511	551-554	60	0.66	75.1	Slight to moderate

^aPreparation: minus-100 mesh fluid-bed denitrated UO_3 boiled 30 min in H_2O

^bX-ray pattern did not match any published pattern for UO_3 hydrates

Figure 10
RATES OF 550°C HYDROFLUORINATION OF UO_2 PREPARED 1) FROM -100 MESH
FLUID-BED DENITRATED UO_2 , OR 2) FROM FLUID BED UO_2 HYDRATE

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V. Acknowledgement

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HYDROFLUORINATION OF URANIUM METAL: PART I

by

F. J. Ludwig

J. A. Kennelley

Summary

1. Uranium metal turnings as-received were converted to UF_4 with a 98.5 percent yield by means of the consecutive reactions with:
 - (a) commercial tank hydrogen at 400°C, and;
 - (b) anhydrous HF over the temperature range 400 to 650°C.
2. Only 30 percent of the uranium turnings were converted to UF_4 by a 130-minute reaction with anhydrous HF over the temperature range 100 to 650°C. Reaction with a 1:1 mixture of hydrogen and HF over the temperature range 180 to 660°C did not give a better yield of UF_4 than reaction with anhydrous HF alone.
3. Uranium metal cubes of different edge lengths were heated 60 minutes in purified hydrogen at 400°C and then hydrofluorinated in anhydrous HF at temperatures increasing from 400 to 660°C over a 120-minute period. During the first 5 minutes of hydrofluorination, a very rapid reaction occurred in which the percent of UF_4 formed was greater for the larger cube. For the remainder of the reaction, the rates of hydrofluorination were identical. Conversions to UF_4 of 37 and 47 percent were obtained for the 3-mm and 4-mm cubes, respectively.
4. U_3O_8 which was prepared by oxidation of uranium metal turnings was much less reactive than MCW plant UO_2 toward reduction and subsequent hydrofluorination.

Introduction

During the manufacture of acceptable slugs from dingot metal, an appreciable quantity of uranium metal scrap is accumulated. About 50 percent of this scrap metal is in the form of turnings or "sawdust." The level of the contaminants in the turnings is sufficiently low that green salt of cascade quality might be produced from them.

This conversion of uranium metal turnings into cascade-grade UF_4 is the objective of the thermobalance studies described in this report. First, it had to be demonstrated that UF_4 could be produced from uranium metal by means of relatively simple process. Then, the effect upon

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reaction rates of such variables as temperature and surface area had to be determined. Two processes were considered: (1) direct hydrofluorination of uranium metal; and (2) oxidation of uranium metal to U_3O_8 followed by reduction and subsequent hydrofluorination.

The conditions required to convert uranium turnings into UF_4 have been established in this preliminary investigation. Studies of the variation of the rate with the surface area of uranium metal cubes are in progress.

Experimental

The manually operated thermobalance is described in a previous report.¹ The following experimental procedure was used: The weighed sample of uranium metal was heated in argon up to the selected temperature at which hydrogen was introduced. The weight changes as a function of time and temperature were recorded. Anhydrous HF gas was then passed over the sample, and the gain in weight and the temperature were measured at selected times. The samples were cooled in HF to below 200°C and then in argon to about 50°C. The ammonium oxalate insoluble content, which is a measure of unreacted uranium metal and uranium oxides, was determined.

Results and Discussion

The results of the reactions of uranium metal turnings or cubes with anhydrous HF or with hydrogen followed by HF are presented in Table I. The reaction with HF alone over the temperature range 95 to 640°C was only 28 percent complete in 130 minutes. A 31 percent conversion was obtained by reaction of the turnings with a 1:1 mixture of hydrogen and HF for 190 minutes at temperatures increasing from 182 to 662°C. In each case, the metal was significantly attacked only at the edges and in grooves; certain smooth areas appeared unreacted.

¹ Ludwig, F. J., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1392 (July 1, 1956) p 37-40

Table I
Conditions of Conversion of U Metal to UF₄

Nature of Sample	Weight of Sample g	H ₂ Temp. Range °C	Total Time in H ₂ (or H ₂ + HF) min	Weight Gain in H ₂ g	Total Time in HF (or H ₂ + HF) min	HF Temp. Range °C	Conversion Calculated from Weight Gain At Given Time %	AOI of Product %	Appearance of Product
Turnings cleaned in dil HNO ₃ 10 x 10 and 5 x cm	3.480	- -	0	0.0	130	95-640	28.3 (130 min)	- -	Green around edges and in grooves; much unreacted metallic surface.
Turnings cleaned in dil HNO ₃	2.434	114-600	97	.055	300	600-606	84.8 (300 min)	16.3	Green-black popcorn-like, readily crushed lumps; X-Ray: s - UF ₄ , mw - UF ₃ ^a
Turnings as-received	3.486	98-662	147	.098	75	662-670	63.5 (11 min)	18.1	Green-black popcorn-like, readily crushed
Turnings as-received 4 pieces about 8 x 8 cm	2.512	398-408	130	.090	162	405-652	62.8 (41 min at 576°C)	1.24	Sponge-like green and dark green mass; readily powdered.
As-received turnings, One 5/8-in long piece	1.662	182-662 H ₂ + HF	190 (H ₂ + HF)	- -	190	182-662	31 (190 min)	81 (overall)	Green around edges, and in grooves; slight increase in thickness; bottom surface unreacted.
Turnings as-received 1 x 1, 0.3 x 1, 0.5 x 1, and 0.5 x 1 cm. pieces	1.757	240-422	90	.071	HF: 160 min H ₂ + HF: 26 min	399-666	82.4 (4 min 404 °c)	1.26	Voluminous sponge-like green mass; Readily powdered; UF ₄ assay 98.4%
Cube 3 mm edge	1.122	398-402	60 ^b	.017	120	396-656	36.6 (120 min)	- -	Green powder around unreacted metal cube < 3 mm on edge.

Table I (continued)

Nature of Sample	Weight of Sample g	H ₂ Temp. Range °C	Total Time in H ₂ (or H ₂ + HF) min	Weight Gain in H ₂ g	Total Time in HF (or H ₂ + HF) min	HF Temp. Range °C	Conversion Calculated from Weight Gain At Given Time %	AOI of Product %	Appearance of Product
Cube 4 mm edge	2.521	398-402	60 ^b	.030	120	396-662	47.0 (120 min)	(Powder only 7.5	Sphere of green powder surrounding smaller metal cube weighing 1.059 g

^a Symbol mw = medium weak X-ray pattern; s = strong X-ray pattern

^b H₂ was purified by passing through a deoxo purifier and over hot U and Cu turnings.

In view of the above results, it was decided to attempt to convert the surface of the metal to UH_3 prior to hydrofluorination. Two runs were carried out by heating in hydrogen from 100 to 600, and from 100 to 660°C, respectively. It was thought that the hydride would form and decompose leaving finely divided uranium metal and an "irregular" broken surface on the turning; however, the samples gained weight continuously up to 660°C. When HF was passed in at 600 or 660°C a very rapid weight gain took place, followed by a much slower reaction. Overall conversions to UF_4 , based on AOI values, of 84 and 81 percent were attained.

Two runs were made in which the hydrogen temperatures employed were 398-408°C and 240-422°C, respectively. Subsequent hydrofluorination over the temperature range 400 to 600°C gave products of 98.5 percent UF_4 assay. Thus, complete conversion of uranium metal turnings into UF_4 was realized in the laboratory by means of two simple reactions.

It is obvious that the "activation" of uranium metal by reaction in hydrogen at about 400°C is a prerequisite for the conversion of uranium to UF_4 . The nature of this reaction as it was carried out in these experiments is not yet understood. The weight changes were too great to be accounted for by the reaction

The extreme reactivity of UN_3 , or of finely divided or "clean" uranium metal towards O_2 is well known. The observed weight gains were consistent with the formation of 10 to 30 percent UO_2 . No leaks in the thermobalance tube or gas inlet system were found. The tank hydrogen was an "extra-dry" pure grade of less than 0.01 percent oxygen content. The hydrogen gas is now being passed through a "deoxo" hydrogen purifier and over hot uranium and copper turnings to remove traces of oxygen.

A uranium metal turning was heated in argon to 400°C, reacted with H_2 for 136 minutes, and then cooled in hydrogen and argon to room temperature. The 1.164-g sample gained 0.100 gram in weight whereas the theoretical weight change for $\text{U} \rightarrow \text{UH}_3$ was 0.015 gram. The X-ray diffraction pattern showed strong lines for UH_3 , UO_2 , UN , and UN_2 . In a similar experiment the sample, when removed from the reaction tube, glowed red-hot in air, probably due to reaction of UH_3 with O_2 and N_2 .

Cubes of dingot uranium metal of sizes 2 to 6 mm were prepared in order to determine the effect of surface area upon the rates of the hydrogen and subsequent HF reactions. Uranium cubes of 3 and 4 mm gained 0.017 and 0.030 gram, respectively, during a 60-minute reaction in hydrogen at 400°C. The ratio of the surface areas of the two cubes was 2.37 whereas the ratio of the weight gains in hydrogen was 1.77. The total increases in weight, thus, were not directly proportional to surface area. The unknown course of the uranium metal-hydrogen reaction makes

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interpretation of the surface area effects difficult.

The hydrofluorination of these cubes proceeded very rapidly during the first five minutes of reaction. For the remainder of the hydrofluorination, the rates of hydrofluorination were approximately equal, *i.e.*, the graphs of the percent unreacted uranium *versus* time appeared to have the same slope. See Figures 1 and 2. The 3- and 4-mm cubes were 37 and 47 percent, respectively, converted to UF_4 after a 120-minute hydrofluorination. The initial rapid reactions may be attributed to hydrofluorination of UH_3 and/or UO_2 which were produced on the surfaces of the cubes. The cube of larger surface area reacted to a greater extent in both the hydrogen and HF reactions. During the second stage of both reactions it may be assumed that the overall rate of conversion was determined by diffusion of HF molecules through the UF_4 layer and by the rate of the uranium metal-HF reaction at the interface. Reactions using larger cubes are in progress to provide additional information concerning the effect of cube dimensions upon the overall process of conversion of uranium metal *via* UH_3 to UF_4 .

An alternate procedure for the conversion of scrap uranium metal to UF_4 would be oxidation to U_3O_8 prior to reduction and subsequent hydrofluorination. Therefore, a sample of U_3O_8 was prepared by air oxidation of uranium turnings over the range 25 - 600°C. Reduction of this U_3O_8 at 475°C was so slow that the temperature of the hydrogen had to be raised to 550°C to complete the reaction in 140 minutes. The product UO_2 hydrofluorinated much more slowly at 550°C than MCW plant sulfated UO_2 . The data are presented in Figure 3 and Table II. The surface area of the sulfated UO_2 was seven times greater than that of the U_3O_8 . Since it has been proved that the rate of reduction of UO_3 and the rate of hydrofluorination of UO_2 increases with increasing surface area, the very low reactivity of the U_3O_8 may be attributed chiefly to the large particle size of the powder. Unless the oxidation of uranium metal to U_3O_8 could be controlled so that material of much greater surface area were produced, this oxidation reduction-hydrofluorination process for the recovery of scrap U would be difficult on a plant scale.

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Figure 1
 RATES OF HYDROFLUORINATION AT AN INCREASING TEMPERATURE
 OF URANIUM METAL CUBES PRETREATED IN H_2 AT $400^\circ C$

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Figure 2

OVERALL RATE OF CONVERSION TO UF_4 OF U METAL CUBES
IN ANHYDROUS HF AT AN INCREASING
TEMPERATURE AFTER PREHEATING IN H_2 AT $400^\circ C$

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Figure 3
550°C HYDROFLUORINATION OF UO_2 PREPARED BY REDUCTION OF
 U_3O_8 FROM U TURNINGS

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Table II

Hydrofluorination of UO_2 Prepared by Reduction of U_3O_8

Reactant	Temp. H_2 $^{\circ}\text{C}$	Time 100% Reduction min	Weight UO_2 Produced g	Temp. Range HF $^{\circ}\text{C}$	Total Time in HF min	AOI %	U(IV) %	Caking of Product
U_3O_8^a	476-550	140	2.242	546-554	135	20.6	76.6	Slight
UO_3^b 510 ppm SO_4	474-477	130	3.638	549-552	70	0.04	74.8	Slight; some hard aggregates;

^a Surface Area: 0.41 sq m/g

^b Surface Area: 2.96 sq m/g

Acknowledgement

The author wishes to thank Mr. G. Stormont for the X-ray analyses, Mr. J. Varwig for the surface area measurements, and Mr. K. Black for technical assistance with the rate measurements.

THE REACTION OF O_2 AND UF_4 FOR UF_6 PRODUCTION

by

J. C. Coppola

J. A. Kennelley

Summary

Conversion of UF_4 to UF_6 has been effected by the use of dry O_2 at temperatures above $800^\circ C$. Complete oxidation of UF_4 , on one occasion where inefficient means of product removal was employed, yielded a small proportion of UF_6 . In a second instance where more attention was given to product removal, a significant amount of UF_6 was obtained, despite the incompleteness of UF_4 oxidation. Much systematic investigation of apparatus and experimental conditions is still required.

Introduction

The reaction of UF_4 with O_2 to form the volatile UF_6 product has been known for at least 14 years.¹ Since the use of elemental F_2 makes the conversion of UF_4 to UF_6 a fairly costly step, considerable effort has been made to control and direct the reaction which uses the much more economical O_2 reactant.

Both pilot plant and laboratory scale apparatus exist which are based on this oxidation reaction, but thus far, significant yields of UF_6 have not been successfully produced, though qualitative evidence of the desired product is quite consistently reported.

In the initial stages of investigation, suitable materials of construction posed a major problem, with apparatus capable of resisting high temperatures in the presence of oxygen and corrosive uranium fluorides being a prime requisite. Of the materials investigated for reaction chambers, Inconel and Pt-lined combustion tubes have proven satisfactory; after initial oxide scale formation the former remains quite resistant to appreciable attack while the latter is consistently satisfactory, though limited to small operations.

¹ Fried, S., and Davidson, N. R., *The Reaction of UF_4 with Dry Oxygen: a New Synthesis of UF_6* , N-1722 (November 14, 1944)

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Thermodynamically, the reaction

is favored as is shown in Table I by free energy change considerations. The reaction should, in fact, proceed spontaneously at room temperature; its failure to do so is good evidence that the mechanism of reaction is more complex than indicated by equation (1). Indication of UF_6 formation has not been obtained at temperatures below 700°C , but at $800^\circ\text{C} - 850^\circ\text{C}$ the reaction proceeds rapidly.

Table I

Free Energy Changes For the Oxidation of UF_4 at Various Temperatures²

Temperature $^\circ\text{C}$	ΔF K cal/mole UF_6
25	-9
700	-4
800	-2
830	-1
900	+1

Reaction rates were calculated³ on the following assumptions:

- (1) the reaction rate is proportional to surface area of UF_4 and oxygen partial pressure;
- (2) the catalytic effect of platinum boat containing the sample was neglected; and
- (3) the change of UF_4 surface area by sintering was neglected.

Despite these assumptions, the investigators felt that the rate constants in Table II were not in error by more than a factor of ten.

² Kirslis, S. S., McMillan, T. S., and Bernhardt, H. A., *The Reaction of UF_4 With Dry Oxygen*, Union Carbide Nuclear Company, K-567 (1950)

³ Ferris, L. M., *Laboratory Development of the Fluorox Process*, Oak Ridge National Laboratory, ORNL-2180 (1957)

Table II

Specific Reaction Rate Constants for Oxidation of UF₄ with Dry Oxygen⁴~ 10 g samples, 98% UF₄; O₂ partial pressure ~745 mm Hg

T °C	Reaction Period hrs.	UF ₄ Oxidized %	Surface Area sq m/g	Reaction Constant K moles/min-atm-sq m	UF ₄ Oxidized g/min
600	1.0	2.67	0.08	0.018×10^{-3}	0.0049
	2.0	13.4	.07	0.055×10^{-3}	0.0151
700	1.0	14.3	.07	0.12×10^{-3}	0.0329
	1.5	68.8	.07	0.59×10^{-3}	0.1617
	3.0	30.0	.07	0.09×10^{-3}	0.0247
	4.0	69.7	.07	0.23×10^{-3}	0.0630
800	0.25	68.2	.04	6.1×10^{-3}	1.67
	0.50	58.9	.04	3.1×10^{-3}	0.85
	1.0	49.7	.04	1.0×10^{-3}	0.27
	1.3	82.4	.04	1.7×10^{-3}	0.47
900	1.0	89.5	.04	3.0×10^{-3}	0.82

Discussion

The oxidation of UF₄ has been carried out on four occasions in the laboratory. The conditions employed and the results obtained are listed in Table III; the apparatus used is illustrated in Figure 1.

⁴ Ferris, L. M., ORNL-2180

Figure 1
UF₄ OXIDATION APPARATUS

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Table III

Experimental Conditions and Results of UF_4 Oxidation

Run No.	Time hrs	Temperature °C	Oxygen Flow Rate cc/min	UF_4 Sample g	Unreacted UF_4 %	UF_6 Recovered g
1	3.0	710 - 723	26	5.0	> 95	Trace
2	3.0	705 - 722	120	4.0	> 95	~ 0.1
3	1.0	800 - 810	70	10.0	< 1	~ 0.3
4	0.8	800 - 810	60	10.0	~ 80	~ 1

Although UF_6 was produced in each instance, quantitative recovery, or even approach to quantitative recovery, is a very difficult procedure which has not been effected successfully. The cold traps varied from -40°C to -190°C and at these temperatures the vapor pressure of UF_6 is extremely small (Table IV); yet the formation of UF_6 in the form of an aerosol makes it most elusive. Consequently, many of the reports dealing with completeness of reactions measure the remaining UO_2F_2 rather than UF_6 recovery. Another product yield calculation is based on the U^{+6} recovered from the off-gas stream after hydrolysis. Though each of these methods are perhaps indicative of the degree of overall reaction, they should not be used as a quantitative measure of the UF_6 produced, as usually has been done. The complex intermediates, widely differing side reactions, and as yet unsolved mechanism of UF_6 formation provide sufficient uncertainties that U^{+6} or UO_2F_2 measurement must be considered an unsatisfactory method on which to base UF_6 yields.

Table IV

Vapor Pressure of UF_6 at Various Temperatures⁵

Pressure mm	Temperature °C
760	+57
7.6	-17
0.76	-51
0.076	-60
0.008	-73
0.0008	-83

Of the four runs made, only the last two require consideration in the light of the complete oxidation of UF_4 and UF_6 production. In Run No. 3, of the 10.0 grams of starting materials, only 3.4 (~ 70%) of the theoretical 4.9 grams was left. An indeterminable amount of sublimed UF_4 , UO_2F_2 , and side reaction product deposited on the reaction tube; these, together with the 0.3 gram of UF_6 collected, left a considerable amount of unaccounted-for material. Some of this was undoubtedly UF_6 which was evidenced escaping from the last trap. Of considerable interest was a profuse bright orange powder which was deposited throughout the pyrex collection apparatus. Although no report had been previously made of such product formation during similar conditions, it was assumed that some UO_3 had been formed and swept through the system with the O_2 flow. This was not the case, however, since the material was readily soluble in H_2O . Preliminary spectrographic analysis showed chromium to be a major constituent. The sublimation of CrO_3 or CrF_4 would provide a reasonable explanation for this powder, the chromium coming from the 15% content in the Inconel combustion tube. The conditions in Run No. 4 were essentially the same as No. 3, except that the apparatus was modified slightly to contain only one dry ice (trichloroethylene) cold trap subsequent to a glass wool filter, which was used in the hope of trapping the CrO_3 and preventing its contamination of the UF_6 product. Only a small amount of chromium salt was present in the cold trap, having escaped the glass wool filter completely and, hence, formed as a vapor. The production of a relatively large amount of UF_6 with the oxidation of such a small amount of UF_4 indicates an improved efficiency which can be attributed to the

⁵ Brewer, L., Bromley, L. A., Gilles, P. W., and Lofgren, N. G., *The Thermodynamic Properties and Equilibria at High Temperatures of Uranium Halides, Oxides, Nitrides and Carbides*, MDDC-1543 (1945)

introduction of large surface area glass wool. The reason for such a large decrease in the amount of UF_4 oxidized with a decrease in reaction time of only 20% is at present inexplicable.

To avoid further chromium contamination from Inconel, a combustion tube will be fabricated of Monel, in which the chromium component is substituted by copper. A secondary approach would be to fractionally condense the two gases and, hence, isolate the UF_6 without further need for a separate sublimation step.

The multitude of side reactions and disproportionations possible with this reaction poses formidable complications. A partial list of such extraneous reactions is listed below:⁶

Further investigations will include the effects of temperature between 800 and 900°C, O_2 velocity, and reaction times on UF_6 yields. Concomitantly, the effect of various oxidizing catalysts will be explored with the hope of lowering the necessary reaction temperature to the point where the detrimental side reactions are eliminated or substantially reduced.

⁶ Ferris, L. M., ORNL-2180

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INVESTIGATION OF HYDROGEN SOLUBILITY IN MOLTEN URANIUM EXPOSED TO WATER VAPOR

by

H. W. Myers

I. Summary

Additional determinations of hydrogen solubility in molten uranium have shown that the rates of solution satisfy a simple logarithmic relationship. At a pressure of 590 mm Hg, the rate of solubility from water vapor is less than one-eighth that determined for hydrogen at the same pressure.

II. Introduction

In a continuation of the investigation¹ to determine the rate of hydrogen solubility in molten uranium exposed to water vapor as compared to that exposed to dry hydrogen, measurements have been obtained at relatively higher, controlled pressures. The purpose of this work was to aid in understanding the role of water vapor in the thermite bomb reduction process and to determine its relationship to hydrogen contamination of the uranium derby. The data reported previously on this project consisted of comparisons of initial rates for the two processes:

where $[\text{H}]_{\text{U}_{(l)}}$ denotes atomic hydrogen dissolved in liquid uranium. By employing a Sieverts' apparatus, the relative sorption rates were determined by keeping the gas volume constant and measuring the pressure drop.

Although a decreasing pressure during sorption possibly better simulates conditions within the thermite bomb, a more generally applicable rate should be realized by maintaining a constant pressure throughout the experiment. Therefore, the rate data presented in this report represent sorption under constant pressure conditions.

¹ Myers, H. W., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1410 (January 2, 1958) p 59-69

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III. Experimental

The Sieverts' apparatus utilized in this investigation was essentially the all-glass system described previously.² By using a high vacuum silicone stopcock grease (MP = 204°C), the connecting tubes as well as the stopcock bores could be regulated to 100°C-110°C by means of heating tapes. Ethylene glycol from a controlled temperature bath was circulated through the jackets of the calibrated burettes, allowing the volumes to be thermostated at 100°C ± 0.2°C.

As in the previous study, the dingot uranium samples were heated by induction and contained in quartz crucibles. The sample weights varied from 50 to 100 grams and the molten metal surface area was approximately 1.5 square centimeters.

After the desired pressure and temperature conditions were established, the gas was contacted with the molten metal and, as absorption proceeded, the pressure was maintained by forcing mercury to rise into the burettes. The volume decrease was then recorded at appropriate time intervals until there was no further change.

IV. Results and Discussion

Eight different experimental runs have been completed under a variety of pressure and temperature conditions.

The data for a typical determination can be seen in Figure 1 where s (ppm H₂ sorbed/sq cm U) is plotted with respect to t (times, minutes). The saturation solubility found for a particular pressure and temperature is represented by s_0 .

It was observed that the solution rate of hydrogen in molten uranium in each case is given by the simple relation:

$$\frac{ds}{dt} = k(s_0 - s),$$

where the gas phase is either hydrogen or water vapor. In Figures 2 and 3, the $\log(s_0 - s)$ is plotted with respect to t for two representative determinations. Since a straight line is obtained, the values for k (reaction rate constant, minutes⁻¹) in the equation $t = \frac{2.303}{k} \log \frac{s_0}{s_0 - s}$, have been calculated and appear in Table I with the corresponding experimental conditions. It can be noted that at the highest pressure and temperature conditions studied, the rate of solubility from water vapor is only one-eighth that from a hydrogen atmosphere. Over the pressure range 400-600 mm Hg, an increase in pressure at a particular temperature apparently decreases the solubility rate in water vapor and increases the rate with dry hydrogen. These relationships are plotted in Figures 4 and 5.

² Myers, H. W., MCW-1410, p 59-69

Figure 1

HYDROGEN SOLUBILITY RATE IN MOLTEN URANIUM

Figure 3
LOGARITHMIC PLOT FOR RATE OF HYDROGEN SOLUBILITY IN MOLTEN URANIUM

Figure 4
RELATIONSHIP BETWEEN HYDROGEN PRESSURE AND RATE CONSTANT

Figure 5
RELATIONSHIP BETWEEN WATER VAPOR PRESSURE AND RATE CONSTANT

Table I

Tabulation of Reaction Rate Constants

Run No.	Temp. °C	Pressure mm Hg	k' (Process 1, Hydrogen) min ⁻¹	k'' (Process 2, Water Vapor) min ⁻¹	Ratio k'/k''
11	1200	390	0.60	0.14	4.4
12	1200	439	.65	.15	4.2
13	1200	497	- - -	.10	- -
14	1200	499	.74	.09	8.7
15	1250	434	- - -	.21	- -
16	1250	483	- - -	.17	- -
17	1250	586	.94	.11	8.2
18	1300	281	- - -	.20	- -

Values for k and the interpretation of trends obviously depend on numerous experimental details which influence the measured solubility rates. Probably the two most important factors affecting this investigation are sample agitation by induction heating and the hydrogen partial pressure resulting from the reaction,

The small amount of dissolved silicon and the UO_2 produced by reaction with the crucible walls possibly have a very small effect.

In a kinetic study of the uranium-steam reaction³, Hopkinson observed that the physical nature of the UO_2 product varied greatly with the reaction temperature; between 880°C and liquid metal at 1400°C, formation of a hard compact scale with densities near the theoretical values (from UO_2 lattice parameters) offered protection against further attack. In the present study if it is assumed that the measured rate of hydrogen solubility from water vapor is inhibited by such a layer, the agitation and possible film rupture caused by induction heating would lead to erroneously high values since clean metal surfaces would occasionally be exposed to water vapor. Due to faster diffusion within the stirred melt, higher rates for dry

³ Hopkinson, B. E., *Kinetics of The Uranium-Steam Reaction*, Atomic Energy Research Establishment, Harwell, Berkshire, AERE-M/R:1281, (January, 1957)

hydrogen sorption might also be expected. Therefore, until measurements on an undisturbed sample can be determined and the effect of induction heating is established, the k values reported here can not be regarded as a property of the water vapor-hydrogen-uranium system and are of interest only in drawing comparisons.

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HYDROGEN IN URANIUM

by

R. F. Leiffield

N. F. Neumann

I. Summary

During the past quarter the investigation of methods of producing low hydrogen uranium has continued. In addition, further study has been made of the mechanism by which hydrogen contamination of bomb reduced uranium occurs. Experiments have shown that, during the bomb preheat, the UO_2F_2 content of the green salt decreases, the $\text{UO}_2(\text{AOI})$ fraction of the green salt increases, and the magnesium is filmed. In addition, the UF_4 assay generally remains constant or decreases slightly. These facts have been interpreted as indicating that a cyclic process occurs during preignition heating of the bomb according to the following scheme:

- (1) $\text{UO}_2\text{F}_2 + \text{H}_2 \longrightarrow \text{UO}_2 + 2\text{HF}$
- (2) $2\text{HF} + \text{Mg} \longrightarrow \text{MgF}_2 + \text{H}_2$
- (3) H_2 escaping to atmosphere or reacting with UO_2F_2

With this postulated mechanism the following relationships may be explained.

- (1) Hydrogen in uranium is a function of preignition time and green salt composition.
- (2) Crude yield is a function of preignition time and green salt composition.
- (3) Preignition time is a function of green salt composition.

Magnesium of decreased specific surface area (120 to 130 sq cm/g) has been used in 4-kg dingots to produce lower uranium hydrogen contents than those produced with "average" (160 to 180 sq cm/g) magnesium. Crude uranium yields averaged 94%, using magnesium with surface area averaging 130 sq cm/g (approximately minus-10 plus-20 mesh for Reade Co. magnesium). Yields were less than 90% when the magnesium surface area was decreased below approximately 100 sq cm/g. Increasing the surface area of the magnesium decreased the preignition time of 4-kg dingots. The use of magnesium with low surface area therefore offers a simple means of extending bomb preignition time and consequently lowering the hydrogen content of the uranium. Hydrogen contents of magnesium have, as reported previously, been found to increase with increasing surface area. When bombs have been fired with identical preignition times, increases of hydrogen in uranium correlate with increases in the hydrogen content of the magnesium. This effect, however, becomes less important as the bomb preheat

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is lengthened and eventually disappears.

The effect of three bomb charge additives (ZnCO_3 , UO_3 , and UO_2CO_3) on hydrogen in uranium has been studied briefly. ZnCO_3 was expected to act as an internal CO_2 purge by decomposition during the bomb preheat. UO_3 was used to convert H_2 in the atmosphere at firing to H_2O because it was found earlier that the rate of H_2 pickup by molten uranium metal is eight times slower from water vapor than from hydrogen. UO_2CO_3 , which decomposes at 515°C to UO_3 and CO_2 , was expected to combine these effects. All of the additives were of value in lowering the concentration of hydrogen in uranium; however, crude yields from charges containing ZnCO_3 and UO_3 were not favorable. Additions of UO_2CO_3 (contaminated by UO_3 and H_2O) up to approximately 1.0% of the UF_4 charge did not adversely affect yields. Carbon pickup by the uranium from UO_2CO_3 additions was found to be proportional to the bomb preheat time.

II. Introduction

Uranium produced by the dingot process, when fabricated into slugs and canned using HAPO standard procedures, has appeared to result in increased bonding interface defects. These defects have been attributed to the generally higher hydrogen content of dingot uranium (1 to 8 ppm), when compared to vacuum recast uranium (0.5 to 1.0 ppm). The approach taken in solving this problem at SLPC has been aimed at producing metal by bomb reduction with a maximum of 2 ppm hydrogen rather than treatment of fabricated forms. Previous reports ^{1,2,3,4} have shown that several different treatments of bomb components can produce low hydrogen uranium. However, the value of all treatments studied to date has been found to depend strongly on bomb preignition time with the 2-ppm target being uniformly met, on the laboratory scale, by controlling this variable alone. The general methods that have been developed to control bomb preignition heating are to use either MgF_2 -filmed magnesium or coarser mesh magnesium. A rather thorough study of filmed magnesium effects on bomb firing time was published in the last quarterly report. It was found that results obtained with filmed magnesium were very strongly dependent on the UO_2F_2 content of the UF_4 . During this quarter, major laboratory activity on the hydrogen problem centered on studies of the bomb reduction mechanism. The goal was to gain an understanding of the interrelationships of the hydrogen content of the metal, the preignition time, and the UO_2F_2 content of the green salt.

¹ Leifield, R. F., and Neumann, N. F., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1410. (January 2, 1958) p 71

² Neumann, N. F. et al, *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1403 (July 1, 1957) p 99

³ Neumann, N. F. et al, *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1401. (April 1, 1957) p 63

⁴ Neumann N. F., et al, *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1399. (January 1, 1957) p 63

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Secondary activities were concerned with investigation of preignition time as a function of magnesium specific surface area and a brief study to evaluate addition of several different materials to the bomb charge to lower hydrogen-in-uranium values by acting as internal purges.

III. Bomb Mechanism Studies

A. Introduction

It has been shown previously⁵ that crude uranium yields, bomb firing times, and hydrogen contents of the uranium produced, are all strongly dependent on the UO_2F_2 content of the UF_4 when reduced with MgF_2 -filmed magnesium. Preignition heating times were found to be increased when the "water soluble" (UO_2F_2) content of UF_4 was increased. Yields, however, for bombs preheated the same time were found to decrease with increasing UO_2F_2 in the UF_4 . On the other hand, in any series of bombs that were fired using the same green salt, yields were found to increase, up to a point, when the preheat time was lengthened. In addition, hydrogen contents of uranium produced at identical preignition heating times were found to be lowered when the UO_2F_2 content of the UF_4 was decreased. These facts held true for UF_4 ranging from low ($\sim 1.0\%$) to high ($\sim 8.0\%$) water soluble content. In view of these results, it seemed worthwhile to investigate the changes of composition that might occur in UF_4 during the bomb preignition heating.

B. Experimental

The 4-kg dingot⁶ and the standard operating procedures were used in these experiments but were modified in the following way. After jolting-in the MgF_2 liner, alternating layers, approximately two inches thick, of green salt and magnesium were packed into the bomb. In most of the runs clean magnesium discs (1 in. diameter $\times$ $\frac{1}{8}$ in. thick) were included in the layer of granulated magnesium. After preparing the bomb in this way, a steel lid fitted with a valved exhaust pipe was bolted to the shell using a copper gasket. The bomb was then placed in a furnace at the control temperature (650°C) normally used to fire bombs. At the end of the desired heating interval the unfired bombs were removed from the furnace and cooled to 25°C under a back-fill of helium. None of the bombs treated this way fired.

⁵ Leiffield, R. F., and Neumann, N. F., *MCW-1410*, p 86 and 89

⁶ Neumann, N. F., *et al.* *MCW-1403*, p 101

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C. Results

Bomb component analyses were made before and after the heating procedure. The data available at the present time are given in Table I. In addition to the usual green salt analysis, several of the samples were analyzed for total U^{VI} and UO_2F_2 by direct polarographic techniques.⁷ Fluoride analyses were made of the minus-20 plus-30 fraction of the granulated magnesium, because the surface area of this fraction is the average of production grade material and it may be used to by-pass sampling problems.⁸ X-ray analyses for MgF_2 were made by the method previously described⁹ on the magnesium discs that were included in the granulated magnesium.

Generally the data obtained indicate that during the preignition heating of bombs:

- (1) UO_2F_2 in the UF_4 decreases
- (2) UO_2 (AOI) in the UF_4 increases
- (3) magnesium is filmed with MgF_2
- (4) UF_4 assay generally remains constant or decreases slightly, and
- (5) slight quantities of U_3O_8 are usually produced.

D. Discussion

From these results a mechanism has been formulated which can be used to explain many of the variations found to occur in bomb reductions. This mechanism is considered to be a cyclic process which is dependent upon changes in the relative rates of the following reactions:

- (1) $UO_2F_2 + H_2 \longrightarrow UO_2 + 2HF$
- (2) $Mg + 2HF \longrightarrow MgF_2 + H_2$
- (3) H_2 escaping to the atmosphere or reacting with UO_2F_2

⁷ Cf., p 155-162

⁸ Leiffield, R. F., MCW-1403, p 93

⁹ Leiffield, R. F. and Neumann, N. F., MCW-1410, p 74

Table I

Changes in Bomb Charges During Heating

Run No.	Time Heated hrs	UF ₄ Analysis								Heated Magnesium Analysis			
		Before Heating				After Heating				Location of Sample of Treated UF ₄	Percent Fluoride on -20 +30 Mesh	X-Ray ^b MgF ₂ on Mg Discs cps	Location Mg Discs
		UF ₄ %	AOI %	UO ₂ F ₂ %	U ₃ O ₈ %	UF ₄ %	AOI %	UO ₂ F ₂ %	U ₃ O ₈ %				
B148 ^a	0.75	97.0	1.18	1.77	-	96.3	2.06	1.48	-	Composites	-	-	No Sample
B130	0.75	97.2	1.22	1.78	-	97.4	0.99	1.59	-	Composites	0.30	-	-
B145 ^b	0.75	97.2	1.00	1.82	-	96.7	1.90	0.97	-	Composites	.50	-	-
B122	1.0	94.1	1.42	4.27	-	94.3	1.48	4.10	-	Composites	.34	-	-
B125	1.0	94.1	1.42	4.27	-	92.5	3.52	3.40	-	Composites	.65	-	-
B168 ^c	1.0	96.4	1.37	2.11	-	-	-	-	-	Composites	.12	24 12	Edge Center
B163	1.0	97.0	1.22	1.70	-	96.54	1.98	1.30	-	Edge	.10	23	Edge
						96.55	1.92	1.37	-	Between Edge and Center	-	-	
						96.68	1.68	1.52	-	Center	-	17	Center
						89.52	1.04	9.11	-	Edge	.30	19	Edge
B171	1.0	85.5	0.43	14.0	-	89.19	0.65	10.04	-	Between Edge and Center	-	-	
						88.78	0.66	10.43	-	Center	-	17	Center
B176 ^d	1.0	99.9	0.53	0.06 ^e	-	99.7	0.52	0.24 ^e	-	Composites	-	0.0	Edge and Center
B194 ^f	1.0	96.2	1.32	2.36	-	-	-	-	-	Composites	.00	0.0	Edge and Center
B189	1.0	96.2	1.32	2.36	-	-	-	2.84 ^e	-	Composites	No Mg Used	No Mg Used	
B128 ^f	7.5	85.5	0.43	14.0	-	79.4	14.5 ^g	0.16 ^e	0.32	Composites	-	-	
B166	16.0	87.7	0.52	11.7 12.7	0.0	82.8	13.4	3.45 0.12	1.96	-	.78	152 175	Edge Center

B167	16.0	87.7	0.52	11.7	-	80.8	13.79	4.66	-	Edge	56	360	Edge
				12.7 ^e	-	82.8	11.94	4.63	-	Between Edge			
						83.7	11.12	4.83	-	and Center		204	Center
										Center			
S89	21.1	93.8	1.32	4.72	0.26	92.9	4.50	1.97	1.96	Composite			
				4.52 ^e				0.16 ^e					

^a 0.3% ZnCO₃ added to normal bomb components

^b 0.5% ZnCO₃ added to normal bomb components

^c Bomb initially pressurized with H₂ to 800 mg Hg

^d "Wet process" UF₄ used

^e Polarographic analysis

^f He-purged throughout entire thermal cycle

^g AOI contained 2.2% U₃O₈ by direct analysis

^h The intensity in counts per second above background of the (110) MgF₂ line correlates with MgF₂ film thickness

Katz and Robinowitch¹⁰ report equation (1) as proceeding slowly at 500°C and rapidly at 600°C. Kuhlman has found the reaction to go primarily by equation (1) at 450 to 700°C with reaction (4) becoming appreciable at higher temperatures.¹¹

Ludwig has measured rates of reduction of pure UO_2F_2 with H_2 and finds reaction (1) goes to completion in 30 minutes at 593°C. In addition, a UF_4 high in UO_2F_2 (12%) was found to reduce 96% in 80 minutes at 530°C.¹² As the 4-kg bomb is heated, its atmosphere approaches 100% H_2 with time,¹³ and, this when coupled with the measured isotherms given in Figures 1 through 3, gives conditions favorable toward reduction of the UO_2F_2 within the bomb after 25 minutes in the furnace. Work reported in the last quarterly report indicated that the filming reaction (2) is rapid at 500°C but that the rate decreases with formation of MgF_2 films on the magnesium. It was also found that fluoride contents of 0.5 to 0.8% in the minus-20 plus-30 mesh fraction corresponded to a heavy film on the magnesium. It should be noted from Table I that magnesium with 0.3 to 0.8% fluoride contents was uniformly found in these heated bombs even though the magnesium was not blended with the UF_4 charge. Notice should also be taken of the UO_2F_2 and filmed magnesium gradients developed in heated bombs as shown in runs B163, B171, and B167. These gradients correspond to the temperature gradients shown above.

The mechanism postulated therefore is visualized as the result of two competing processes; one being the rate of filming of the magnesium, and the other the rate of hydrogen evolution from the bomb. When the rate of filming slows, after reaching film thicknesses of approximately 2300 Å,¹⁴ the relatively constant rate of hydrogen effusion from the bomb becomes important. The postulated cyclic movement of hydrogen is corroborated by the data of runs B128, B166, B167 and S89. If we assume that the cyclic reaction does not occur, insufficient hydrogen was present in the bomb to reduce the UO_2F_2 content to the levels found experimentally.

For example, in run B128 the UO_2F_2 content was decreased from 14.0% to 0.16% of the green salt charge. This decrease amounts to the reduction of 730 grams of UO_2F_2 which

¹⁰ Katz, J. J. and Rabinowitch, E., *Chemistry of Uranium*, McGraw Hill, New York, (1951)

¹¹ Kuhlman, C. W., *Reduction of UO_2F_2 with H_2* , Mallinckrodt Chemical Works, MCW-175, (August 2, 1949)

¹² Ludwig, F. J., Mallinckrodt Chemical Works, Private communication

¹³ Neumann, N. F., *et al.*, MCW-1401, p 65

¹⁴ Leiffield, R. F., and Neumann, N. F., MCW-1410, p 75 and 76

Figure 1
ISOTHERMS IN A 4Kg-BOMB;
BOMB CONTROL TEMPERATURE AT 650°C

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Figure 2

ISOTHERMS IN A 4Kg-BOMB;
BOMB CONTROL TEMPERATURE AT 650°C

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Figure 3

ISOTHERMS IN A 4Kg-BOMB
BOMB CONTROL TEMPERATURE AT 650°C

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would require 4.72 grams of H_2 . Assuming an average hydrogen content (in all forms) of 30 ppm in each MFL, UF_4 and magnesium¹⁵ we find a total initial H_2 content (mainly as H_2O and HF) of only 0.29 grams. The amount present, therefore is $\frac{1}{15}$ less than that needed, assuming 100% utilization of all the hydrogen available.

Auxiliary temperature cycling runs have been used to substantiate several steps in the proposed mechanism. Run B176 was made with an initially low UO_2F_2 content (0.06%) and resulted in no appreciable change of UF_4 composition and no filming of magnesium. This run demonstrates therefore that filming of the magnesium within the bomb does have its source of fluorine in the UO_2F_2 of the green salt. No increase in UO_2 was found in this run even though the initial UF_4 contained 550 ppm H_2O . This run shows that the UO_2 produced during heating comes from UO_2F_2 and not from UF_4 reversion (equation 5).

One other fact deduced from this run is that untreated MFL plays no part in magnesium filming by cyclic processes, at least when used with high purity green salt.

As this process involves oscillation of the hydrogen while acting as a fluorine carrier, between the UO_2F_2 and the magnesium, we should expect greater quantities of hydrogen to be retained in the bomb when the UO_2F_2 content of the UF_4 is increased. Bombs fired at equivalent preheat times, therefore, can be expected to show a relation between the hydrogen in uranium and the amount of UO_2F_2 in the green salt. Similarly, if the amount of UO_2F_2 in the UF_4 is decreased the production of low hydrogen content uranium should be expected even at short firing times. Bomb preignition heating times would also be a function of the UO_2F_2 content in this proposed scheme because filming of the magnesium would be proportional to the UO_2F_2 content. Again, in this mechanism crude uranium yields would be expected to decrease with increasing UO_2F_2 content because formation of the more difficultly reduced UO_2 would be proportional to the UO_2F_2 content. However, because of the increased heat input, yields using a constant quality green salt would be expected to increase with increased preignition heating. These facts have all been shown to occur¹⁶ and therefore lend further support to the postulated mechanism.

¹⁵ Gaver, R. W. and Neumann, N. F., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1407, (October 1, 1957) p 80

¹⁶ Leifield, R. F. and Neumann, N. F., MCW-1410, p 82-90

IV. Magnesium Surface Area Studies

A. Introduction

Bomb preignition heating times have been found to be a function of the particle size of the magnesium used as the reductant.¹⁷ Because the obvious relationship between particle size and surface area might be affected by geometric factors, it seemed likely that more precise measurements might lead to a correlation of preignition time with magnesium surface area.

B. Experimental

Sieved fractions of magnesium, supplied by Nelco Co., Metals Selling Corporation (MSC), and Reade Co., were measured for surface area by gas adsorption techniques.¹⁸ These fractions were nominally minus- $\frac{1}{4}$ -in. plus-10, minus-10 plus-20, minus-20 plus-30, minus-30 plus-40, minus-40 plus-50 and minus-50 A.S.T.M. mesh. Individual fractions were also analyzed for hydrogen contents and the data obtained are given in Table II. These fractions were then blended with different assay green salts and fired under normal conditions in 4-kg bombs. Preignition times as a function of magnesium surface area are shown in Figure 4 and hydrogen contents of uranium produced are shown in Figure 5 for several representative mesh fractions.

¹⁷ Neumann, N. F., *et al*, MCW-1403, p 109

¹⁸ Myers, H. W., MCW-1403, p 81

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Figure 4
THE RELATIONSHIP BETWEEN SURFACE AREA OF MAGNESIUM
AND PREIGNITION TIME OF 4 KG DINGOT BOMBS

Figure 5
THE RELATIONSHIP BETWEEN THE HYDROGEN CONTENT OF URANIUM AND THE PREIGNITION TIME

Table II

Magnesium Analyses

Sieve Fraction	Reade Magnesium		MSC Magnesium		Nelco Magnesium	
	Surface Area sq cm/g	Total Hydrogen ppm	Surface Area sq cm/g	Total Hydrogen ppm	Surface Area sq cm/g	Total Hydrogen ppm
Plus-10	130	27	87	23	-	120
Minus-10 Plus-20	130	28	120	29	770	-
Minus-20 Plus-30	160	39	160	35	-	-
Minus-30 Plus-40	380	61	230	32	-	199
Minus-40 Plus-50	390	67	360	59	-	-
Minus- $\frac{1}{4}$ -in. Plus-10 Mesh					635 ave.	

C. Results and Discussion

From the data in Figure 4 it can be seen that the length of time a bomb is heated before it ignites is a function of the specific surface area of the magnesium. In this connection it should be noted that surface area is not necessarily a direct function of the particle size. For example, in one case it was found that magnesium supplied by Nelco Co., produced by crushing magnesium "crowns" to minus- $\frac{1}{4}$ -in. plus-10 mesh, actually possessed a surface area greater than 600 sq cm/g. This surface area is greater than minus-40 plus-50 mesh magnesium supplied by either Reade or MSC and demonstrates the need to measure specific surface area rather than some parameter affecting the surface area. A comparison of the data shown in Figure 5 with average values indicates that magnesium with a surface area of 120 to 130 sq cm/g results in a decided lowering of the hydrogen in uranium. This lowering of hydrogen in uranium is probably the result of the low hydrogen content of this magnesium. However, when magnesium with high surface area is employed, the detrimental effects due to high hydrogen content of the magnesium appear to be minimized by extending the bomb preheat time. Hydrogen results were favorable when using magnesium with surface area of less than 160 sq cm/g. Crude uranium yields averaged 94% for 14 bomb runs using minus-10 plus-20 mesh (130 sq cm/g) magnesium, but dropped below 90% when plus-10 mesh (90 sq cm/g) was used.

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V. Bomb Charge Additives

A. Introduction

Measurements of hydrogen sorption by molten uranium have indicated that the rate is eight times faster from a hydrogen atmosphere than from a H_2O (gas) atmosphere.¹⁹ Therefore, it was thought that additions of UO_3 to bomb charges might decrease the hydrogen pickup of the uranium from the bomb atmosphere by converting, at least momentarily, a portion of the approximately 100% H_2 atmosphere to water vapor.

ZnCO_3 was selected for study as a charge additive primarily because of its low decomposition point.

It was thought that ZnCO_3 might result in purging and dilution of the bomb atmosphere during bomb preheating, and, hence, decrease the total H_2 concentration available to the uranium produced at firing. UO_2CO_3 was used in an attempt to combine CO_2 purging with UO_3 additions *via* equations (7) and (9).

B. Experimental

Analyses of the additives used are shown in Table III.

¹⁹ Cf., p 97-104

Table III
Chemical Composition of Additives

Additive	Assay %	H ₂ O %	UO ₃ (By Difference) %
ZnCO ₃ (as-received)	88.9	10.9	
ZnCO ₃ (dried at 125°C)	99.5	0.4	
UO ₃	98.3	1.4	
UO ₂ CO ₃	34.5	4.0	61.5
UO ₂ CO ₃	77.3	2.2	20.4
UO ₂ CO ₃	45.3	0.1	54.6
UO ₂ CO ₃	69.	0.3	~ 31.

The ZnCO₃ used was Fisher Scientific Co. Reagent Grade and was supplied as a light fluffy powder containing 11% H₂O. Additions to 4-kg bombs were made by blending both the "as-received" and dried ZnCO₃ in concentrations of 0.5 to 7.0% of the UF₄ charge. The charges were fired under normal conditions. The data obtained are given in Figures 6 and 7.

MCW production grade UO₃ was used "as-received" in concentrations ranging from 0.5 to 2.0% of the UF₄ charge. No decided difference was observed when the UO₃ was placed at the cooler charge center or when it was blended throughout the charge. The data obtained are also given in Figures 6 and 7.

The UO₂CO₃ used in these experiments was synthesized by carbonating water slurries of UO₃ at atmospheric pressures. Vigorous mechanical stirring was needed to maintain homogeneity. The method used was taken from Chernyaev, Golovnya, and Ellert, who also report 515°C as the decomposition point of UO₂CO₃.²⁰ Material synthesized this way ranged from 30 to 80% UO₂CO₃ and was generally blended with the UF₄ charge in ratios of 0.5 to 5.0%, although one bomb was fired with the additive at the charge center.

²⁰ Chernyaev, A., Golovnya, and Ellert, G.V., C.A., 54, 14458 (1957)

Figure 6

THE RELATIONSHIP BETWEEN THE HYDROGEN CONTENT OF URANIUM AND THE PREIGNITION TIME

Figure 7
RELATIONSHIP BETWEEN YIELD AND PREIGNITION TIME OF 4 KG DINGOTS USING VARIOUS CHARGE ADDITIVES

C. Results and Discussion

Consideration of the data shown in Figure 6 indicates that all of the additives studied were of value in lowering the hydrogen content when compared to uranium produced in untreated bombs. However, crude uranium yields, given in Figure 7 reveal that ZnCO_3 and UO_3 additions to the charge cause a decided drop in yield even when used with extended preignition heating. On the other hand, a comparison with the average bomb yields given in Figure 8 indicates that UO_2CO_3 additions of less than approximately 1% of the UF_4 charge do not appear to decrease yields. Yields obtained in two runs using UO_2CO_3 additions as 2.0 and 4.0% of the charge were less than 70%.

D. Conclusions

The results obtained using UO_2CO_3 appear promising and work with this additive will continue.

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Figure 8
RELATION BETWEEN PREIGNITION TIME AND CRUDE YIELD OF 4 KG DINGOT

DETERMINATION OF RELATIVELY NON-VOLATILE ORGANIC MATTER IN AQUEOUS PLANT SAMPLES, PART II

by

H. L. Christopherson

I. Summary

Although hexane may be used for extracting organic matter from aqueous samples, petroleum ether was usually preferred on account of its lower boiling point range. A steam bath was usually preferable to an infrared lamp for evaporating petroleum ether particularly if large amounts of tributyl phosphate (TBP) were present. The loss of TBP during the evaporation on a steam bath of 100 ml of petroleum ether containing 10 to 135 mg of TBP averaged a little less than 2 mg.

TBP was essentially quantitatively extracted from NOK samples by shaking with an equal volume of petroleum ether for one minute; however, the same treatment on a similar type of sample, a UNH solution, left a turbid aqueous phase that contained 20 to 30 percent of the TBP. After complete separation of this turbid aqueous phase by centrifugation, an average recovery of 97% was obtained on four samples spiked with 69 mg of TBP.

II. Introduction

This paper is a continuation of work¹ previously reported. During this investigation the routine analysis of raffinates for organic matter was discontinued, and the frequency of analysis of carbonate cakes for organic matter was changed from about three per week to not more than one per month. Accordingly, emphasis on development work was shifted to other types of samples: UNH and NOK, which are uranyl nitrate solutions, and TBP sump liquors of widely varying composition.

III. Experimental

A. Apparatus and Reagents

A Beckman Model G pH meter, equipped with the original electrodes and standardized against a 25-fold dilution of Beckman Buffer Solution pH 7 Concentrate was used for all pH measurements. A Warren Spectracord was used in all uranium determinations to measure

¹ Christopherson, H. L., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1407, (October 1, 1957) p. 97-100

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the transmittancy of uranyl tricarbonate solutions at the 436-m μ absorption maximum. An International Centrifuge Model C-50 was used, usually at its maximum speed, with 100-ml centrifuge tubes to separate emulsions or turbid solutions. A Beckman IR-4 Infrared Spectrophotometer was used to help identify some of the components in a few of the organic residues extracted from plant samples.

Mallinckrodt Chemical Works petroleum ether, AR, which contains not more than 0.0010% residue after evaporation (usually about 0.0004% non-volatile residue was found) was used for nearly all of the extractions. No correction was made for the small amount of residue from petroleum ether.

The evaporations of petroleum ether and hexane were carried out either about 3 to 6 inches beneath a 250-watt infrared lamp containing a built-in reflector, or over a Precision Scientific Company 8-hole, steam-heated water bath containing a perforated steam coil along the bottom of the bath. The flow of steam from the coil was regulated to keep the water at its boiling point and to keep a small amount of steam issuing from one uncovered small hole in the top of the bath. This bath is referred to as a steam bath throughout this report.

B. Procedure

The extent of loss of TBP during evaporation of petroleum ether or hexane was studied by evaporating the organic solvent from various amounts of TBP contained in a platinum dish placed on a steam bath or under an infrared lamp.

The recovery of TBP from various plant samples was checked by first extracting any organic matter from 100-ml samples with petroleum ether and then spiking the samples with known amounts of a solution of TBP in petroleum ether. The petroleum ether was allowed to evaporate over night. The procedure given below was followed unless otherwise noted.

1. Thoroughly mix the sample by vigorous shaking.
2. Quickly pour 100 ml of sample into a graduated cylinder and transfer to a separatory funnel.
3. Add about 100 ml of petroleum ether to the sample.
4. Shake the mixture as vigorously as possible for 1 minute for samples which do not contain solids and for 2 minutes for samples which do contain solids.
5. Separate the two phases and discard the lower aqueous phase. Wash the inside of the separatory funnel with a small amount of water and discard the wash water. (If the separatory funnel still contains solids, it may be

desirable to transfer the organic phase to a clean separatory funnel before washing with water in order to avoid emulsion formation.)

6. Add approximately 100 ml of water to the separatory funnel and shake for 10 seconds.
7. Allow the layers to separate, then drain off and discard the lower aqueous phase. (If the water wash is yellow-colored, wash the organic phase with successive portions of water until the aqueous phase remains colorless.)
8. Pour the organic phase into a clean, dry beaker.
9. Transfer the organic phase to a clean, tared platinum dish, being careful not to carry over any water drops.
10. Place the dish on a steam bath and evaporate the petroleum ether.
11. As soon as all of the petroleum ether has evaporated, remove the dish from the steam bath, wipe off any water on the outside of the dish, cool to room temperature, and weigh on an analytical balance.

IV. Results and Discussion

A. Extractants

Both petroleum ether and hexane have been used as extractants for organic matter in this investigation and in routine analysis by the control laboratory. In many cases the two extractants evaporated about equally well (compare curves E and F in Figure 1), particularly when the aqueous sample contained only small amounts of TBP. However, when the samples contained larger amounts of organic matter, it was usually much more difficult to decide when all of the hexane had evaporated than to decide when all of the petroleum ether had evaporated. With some hexane samples (Figure 1, curve A) this difficulty was also encountered with small amounts of TBP. Petroleum ether had additional advantages in that it evaporated faster on a steam bath and was readily obtained free of significant amounts of not readily volatile material.

The only case in which hexane was found to have any advantage over petroleum ether was in the analysis of raffinates where emulsions can cause separation difficulties. However, raffinate samples are no longer tested for organic matter at the Weldon Spring Plant. Thus of the two extractants, petroleum ether is clearly preferable.

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Figure 1
EVAPORATION LOSS OF TBP FROM A PLATINUM DISH ON A STEAMBATH

B. Loss of TBP By Evaporation

Petroleum ether or hexane was added to known amounts of TBP contained in a 100-ml platinum dish which was placed on a steam bath. The time was noted at which the organic solvent first appeared to have completely evaporated. Starting from this time the platinum dish was left on the steam bath for a definite interval of time, removed, dried, cooled to room temperature, and weighed. The dish, containing the residue of TBP, was again placed on the steam bath for a definite interval of time, removed, dried, cooled to room temperature, and weighed. Sometimes this process was repeated several times. Some typical results are shown in Figure 1 where the weight of residue obtained is plotted against the total time left on the steam bath after apparent evaporation of all the organic solvent.

Some indication of the precision of the results may be obtained from an examination of curve C where data have been plotted from three identical samples. From the slope of the curves in Figure 1 it can be seen that the initial (after evaporation of the petroleum ether) rate of loss of TBP was about 3 to 5 mg per minute and was not very dependent upon the amount of TBP present. The rate usually decreased to about half of its initial value after about 5 minutes on the steam bath, which may indicate that the area of the dish covered by the TBP decreased or that TBP was not the only compound being evaporated.

The small arrows in Figure 1 intersect curves A,B,C, and D at a weight equal to the calculated amount of TBP added to the platinum dish from a measured volume of 1% (v/v) stock solution of TBP in petroleum ether. Since the intersections occurred shortly after all of the petroleum ether had apparently evaporated, it appeared at first that quantitative results would be more closely approached in future determinations by leaving the platinum dish on the steam bath for a few seconds after all of the petroleum ether had apparently evaporated. However, the actual weight of TBP added may well be greater than that calculated, because later measurements showed that the concentration of TBP in the 1% stock solution was gradually increasing, apparently due to slow evaporation of petroleum ether from the stock solution. Furthermore, later experiments (Table I) show that some TBP was always lost during the evaporation of 100 ml of petroleum ether. Therefore, quantitative recovery should be more closely approached by removing the platinum dish from the steam bath as soon as or shortly before all of the petroleum ether has apparently evaporated.

The results in Table I show that the average loss of TBP during the evaporation of 100 ml of petroleum ether was 1.5 mg for solutions (Nos. 1 - 5) removed from the steam bath as soon as the petroleum ether had evaporated, and 2.6 mg for solutions (Nos. 6 - 9) removed from the steam bath five seconds after the petroleum ether had evaporated. The difference

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is somewhat greater than the average initial rate of loss of 0.4 mg in 5 seconds obtained from the slopes of the curves in Figure 1. From a consideration of all of these results, it is estimated that the average loss of TBP during the boiling and evaporation of 100 ml of petroleum ether containing 10 to 135 mg of TBP was about 1.7 mg, and that the loss increased about 0.1 mg for each second the platinum dish was left on the steam bath after evaporation of all of the petroleum ether. The losses seem somewhat more variable and larger than might be expected if TBP were lost only by evaporation.

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Table I

Loss of TBP During Evaporation of Petroleum Ether from Platinum Dishes

Experiment No.	Method Of Evaporation	Solvent	TBP Taken mg	TBP Lost mg
1	on steam bath	100 ml Pet. Et.	131.7	1.2
2	on steam bath	100 ml Pet. Et.	134.5	2.0
3	on steam bath	100 ml Pet. Et.	68.9	1.4
4	on steam bath	100 ml Pet. Et.	69.2	1.3
5	on steam bath	100 ml Pet. Et.	64.5	1.6
6	on steam bath+5 sec	100 ml Pet. Et.	86.5	2.4
7	on steam bath+5 sec	100 ml Pet. Et.	67.5	3.0
8	on steam bath+5 sec	100 ml Pet. Et.	67.9	1.9
9	on steam bath+5 sec	100 ml Pet. Et.	13.0	3.0
10	slowly on a warm plate	50 ml Pet. Et.	13.2	0.2
11	slowly on a warm plate	50 ml Hexane	13.2	0.2
12	infrared lamp	100 ml Pet. Et.	130.1	8.3
13	infrared lamp	100 ml Pet. Et.	132.1	6.6
14	infrared lamp	100 ml Pet. Et.	12.7	1.6
15	infrared lamp	100 ml Pet. Et.	12.7	1.7
16	infrared lamp	100 ml Pet. Et.	11.1	1.9
17	infrared lamp	100 ml Pet. Et.	11.0	1.5
18	infrared lamp ^a	100 ml Pet. Et.	9.2	1.4
19	infrared lamp ^a	100 ml Pet. Et.	9.5	1.1
20	infrared lamp ^a	100 ml Pet. Et.	121.8	2.2
21	infrared lamp ^a	100 ml Pet. Et.	125.5	2.7
22	overnight at room temperature	100 ml Pet. Et.	119.6	3.7
23	overnight at room temperature	100 ml Pet. Et.	122.8	4.3
24	1 hr at room temp.	None	130.5	0.4
25	1 hr at room temp.	None	132.5	0.4
26	overnight at room temperature	None	13.2	0.5
27	overnight at room temperature	None	13.2	0.5

^aThe infrared lamp was turned off while there was still about 1 ml of petroleum ether left.

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Frequently many small droplets of liquid could be seen rising from a boiling petroleum ether solution. Most of the drops that did not completely evaporate fell back into the platinum dish, but some of them fell outside of the dish. If this were the cause of the variable and somewhat larger-than-expected losses, then one might expect the absolute loss to increase with increasing amounts of TBP taken. The results do not show any such increase; nevertheless, much of the variable loss is believed due to spray formation during boiling of the petroleum ether. The presence of larger amounts of TBP visually appears to suppress spray formation during the late stages of the boiling where any mechanical loss of liquid would be more critical due to concentration of the TBP.

The loss by spray formation can be avoided as shown in experiments 10 and 11 of Table I by a slow (20 to 30 min) evaporation that avoids boiling. Spray formation may also be avoided by the use of infrared lamps; however, with larger amounts of TBP it was difficult to decide when all of the petroleum ether had evaporated. A late decision was probably responsible for most of the 6 to 8 mg of TBP lost by this method in Experiments 12 and 13 in Table I. With small amounts (Nos. 14 - 17) of TBP the loss during an evaporation under an infrared lamp was about the same as the average loss obtained by boiling off the petroleum ether on a steam bath. Turning the infrared lamps off while there was still about a milliliter of petroleum ether left and completing the evaporation of petroleum ether by drawing air over the warm platinum dish gave slightly lower losses for small amounts (Nos. 18 and 19) of TBP, and, for large amounts (Nos. 20 and 21) of TBP, gave a loss only slightly greater than that obtained by boiling off the petroleum ether on a steam bath. Although the results of the two methods are approximately the same, the use of a steam bath is definitely preferred for routine analysis for two reasons: (1) About 15 minutes is required to evaporate 100 ml of petroleum ether under an infrared lamp, whereas only about 2 to 3 minutes is needed on a steam bath. (2) For safety reasons, electrical outlets are not available in our solvent laboratory where ether evaporations are carried out.

C. Recovery Studies

Four different kinds of samples were extracted two or three times to remove practically all of the petroleum ether-extractable organic material. Each sample was spiked with 13.2 mg of TBP, and run by the procedure described in the Experimental Section, except that the shaking time and method of evaporation were varied as shown in Table II.

Table II

Recovery Study on Samples Spiked With 13.2 mg of TBP

Sample	First Spike ^a				Second Spike ^b		
	Time Shaken With Petro- leum Ether sec	Residue Found On Extraction No. 1 mg	Residue Found After A 15-Min. Re-Extn. mg	Total Residue Found mg	Residue Found On Extraction No. 2 mg	Residue Found After A 20-Min. Re-Extraction mg	Total Residue Found mg
Carbonate Cake No. 1	60	10.7	1.5	12.2	8.6	3.5	12.1
Sump Liquor No. 26	60	12.2 ^c	1.3	13.5	10.5	1.6	12.1
NOK No. 249	30	12.2 ^c	0.4 ^c	12.9	11.6	0.3	11.9
UNH No. 81	30	7.4	3.9	11.3	9.3	2.7	12.0

^aThe petroleum ether extracts from the samples were left on the steam bath for five seconds after all of the petroleum ether had apparently evaporated.

^bEach sample was again spiked with 13.2 mg of TBP. The shaking time for the initial extraction was increased to 2 minutes for each sample, and the evaporation was carried out under infrared lamps instead of on the steam bath.

^cThe organic material recovered had a faint yellow color.

The high total recovery for extraction No. 1 on Sump Liquor No. 26 and the higher-than-normal recovery for extraction No. 1 on NOK No. 249 were probably due to the extraction of some yellow organic material that had not been completely removed in the pre-extractions.

The time of shaking on the re-extractions was increased to 15 or 20 minutes in order to be reasonably sure of extracting practically all of the remaining TBP.

Although the individual recoveries varied somewhat erratically, the total recovery for extraction No. 2 was quite uniform and averaged about 90%. The greater uniformity on extraction No. 2 may be due to the use of infrared lamps in place of evaporating on the steam bath and quantitative pre-extraction of organic matter originally present in the sample.

In both sets of data the amount of organic material recovered on the re-extraction was small for the NOK sample and surprisingly larger for the UNH sample, especially in view of the similar compositions of the two samples as shown in Table III.

Table III
Composition and Recovery Study on Altered Samples

Sample	Conc. of Uranium M	pH	pH After 1:9 Diln.	Added	pH After Addition and 1:9 diln. of a 1-ml Aliq.	TBP Added mg	Residue Found mg	Residue Found After Standing 20 Hours mg
NOK No. 249	2.3	-0.1	2.00	15 ml 1 M NaOH	2.67	13.2	11.8	
UNH No. 81	2.2	+0.7	2.41	2 ml Conc. HNO ₃	1.46	13.2	9.7	2.7

The relative concentrations of uranium and the pH of the two samples were reversed as shown in Table III. The altered samples were spiked with 13.2 mg of TBP. The initial extraction still gave a low recovery for the UNH sample and a normal recovery for the NOK sample. Apparently neither a particular pH range nor a particular concentration of uranium is the primary cause of the low recoveries obtained with one extraction on the UNH samples.

It has been noticed that all of the UNH samples used in recovery studies have been quite turbid after addition of TBP and shaking, and also after extraction with petroleum ether; whereas the aqueous phase of the NOK samples became fairly clear shortly after the same treatments. This difference in behavior was considerably less, but still noticeable for the

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sample pair in Table III after their relative acidities and uranium concentrations had been reversed. The TBP which was not removed from a UNH sample by one extraction with petroleum ether has been separated not only by an immediate re-extraction (as in Table II), but also by allowing the once-extracted, turbid sample to stand (overnight) until the TBP-uranium complex rose to the top of the solution (as in Table III) or by centrifuging. After the TBP had risen to the top, it was recovered by adding petroleum ether (without shaking), separating the two phases, and evaporating the petroleum ether layer from a platinum dish. Both centrifuging and standing overnight appeared to quantitatively remove the remaining TBP. However, a re-extraction involving only one minute of shaking did not quantitatively remove the remaining TBP from a UNH sample spiked with either a small amount (13 mg) or a large amount (134 mg, see Table IV) of TBP. Centrifugation is recommended on UNH samples when quantitative recovery is desired.

Table IV

Recovery Study on Samples Spiked with 134 mg of TBP

	<u>NOK No. 316</u>	<u>UNH No. 10</u>
Seconds shaken with 100 ml of petroleum ether	60	60
Mg of residue found on initial extraction	128.7	101.4
Mg of residue found after a 60 sec re-extn.	4.5	20.6
Mg of residue found after centrifuging		5.7
Total mg of residue found	133.2	127.7

Table IV shows that the large initial recovery difference between UNH and NOK solutions also existed at high levels of TBP.

The effect of time of shaking 100 ml of petroleum ether with UNH samples spiked with 13.2 mg of TBP is shown in Table V.

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Table V

Effect of Shaking Time on Recovery of 13.2 mg of TBP

Sample	Shaking Time min	Residue Found On Initial Extraction mg	Residue Found On Re-extraction mg
UNH No. 81	0.5	7.4	3.9
UNH No. 10	1.0	...	2.1
UNH No. 10	1.0	15.3 ^a	~2.9
UNH No. 81	1.0	11.8 ^b	0.5
UNH No. 81	2	9.5	2.1
UNH No. 81 after acidification	2	9.7	2.7
UNH No. 10	120	12.0	0.4

^aThe petroleum ether extract was not washed with water.

^bThe sample stood overnight before separation, and thus gave a higher than usual recovery on the initial extraction.

The high recovery of 15.3 mg on the initial extraction of a UNH sample shows that a water wash is necessary to remove uranium.

Increasing the time of hand shaking from 30 seconds to 60 seconds increased the amount of TBP recovered. There was no significant difference between 1 and 2 minutes of hand shaking. Shaking a spiked UNH sample for 2 hours with a Burrel wrist-action shaker left no visible amount of TBP in the sample. The 0.4 mg of residue shown in Table V for the re-extraction is equal to the blank normally obtained from 100 ml of petroleum ether. This last experiment shows that the incomplete extraction of TBP from UNH samples with petroleum ether is not due to an unfavorable distribution ratio of the TBP between petroleum ether and the sample. The low recovery with a single extraction on UNH samples appears to be due to an incomplete separation of the organic phase from the turbid aqueous phase and a far-from-equilibrium distribution of the TBP (*i.e.*, the ratio of the TBP left in the turbid aqueous phase to the TBP recovered in the petroleum ether phase has always been very much greater than the ratio of the estimated volume of organic matter in the turbid aqueous phase to the volume of the upper petroleum ether layer). The reason for this difference in behavior between UNH and NOK samples is not known.

D. Precision Study on UNH Samples

Four samples of UNH were stripped of organic matter by a preliminary extraction and then spiked with 69 mg of TBP. They were run by the procedure described in the experimental section except that the residues, which were contained in platinum dishes with a rounded bottom, were left on the steam bath for 5 seconds after all of the petroleum ether had apparently evaporated. With flat-bottom platinum dishes 5 seconds is approximately the length of time from evaporation of the last of the petroleum ether from the center of the dish to evaporation of the last of the petroleum ether from the edge of the dish bottom. Thus, the recoveries shown in Table VI are expected to be similar to the recoveries that would be obtained, with flat-bottom platinum dishes. After the initial extraction, the TBP remaining in the turbid aqueous phase was separated by centrifugation.

Table VI

Precision Study on Recovery of 69 mg of TBP from UNH Samples

Sample	Conc. of Uranium M	pH After a 10-Fold Diln.	Organic Found In 100 ml of Sample mg	TBP Recovered On Initial Extraction		TBP Recovered By Centrifuging		Total TBP Recovery percent
				mg	percent	mg	percent	
UNH No. 109	1.92	2.30	0.4	55.0	80	12.3	18	97.6
UNH No. 110	1.76	2.25	0.4	58.5	85	8.2	12	96.7
UNH No. 111	1.57	2.12	0.3	55.3	80	11.5	17	96.9
UNH No. 116	1.82	2.27	0.4	53.4	77	13.4	19	96.8

On the initial extraction of four samples of UNH spiked with 69 mg of TBP, the recovery averaged 80% with a standard deviation of $\pm 3\%$ or ± 2 mg for an individual determination. The total recovery averaged 97.0% (2-mg loss) with a standard deviation of ± 0.4 or ± 0.30 mg for an individual determination.

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DETERMINATION OF NORMAL HEXANE PRODUCT PURITY BY INFRARED ABSORPTION

by

H. E. Pena

I. Summary

A. Quantitative Determination of Normal Hexane in Commercial Hexane

A comparison-standard technique is used whereby absorption measurements are obtained at a wavelength of 13.78 microns on a sample of normal hexane of known composition prior to taking the same reading on a sample of unknown composition. The ratio of the readings is a direct measure of the amount of normal hexane present in admixture with other hydrocarbons. The maximum time for analysis is twenty minutes. No bias from the known values could be detected on statistical evaluation of the results.

B. An Iterative Procedure for the Direct Determination of Hydrocarbon Constituents Present in Commercial Grade Hexane

The low accuracy of the results from the analysis of synthetic samples of normal hexane in admixture with hydrocarbons known to be present in commercial hexane indicates that this procedure is not applicable. The use of a variable thickness absorption cell to modify this procedure is now under investigation.

II. Introduction

It is desirable to have available a rapid and accurate infrared analysis of the constituents of commercial grade hexane for specification testing and for the analysis of solvent samples from experimental investigations.

In the comparison-standard method,¹ spectra were obtained on all hydrocarbons known to be present in specification grade hexane. From these spectra, the compounds which showed interference in the wavelength region of 13.78 microns were: 3-methylpentane, 2,3-dimethylbutane, 2-methylpentane, and benzene. At this wavelength, all four of these compounds have essentially the same absorption coefficient. By using this wavelength for the analysis of normal hexane, errors caused by possible changes in the ratio of the concentrations of these interfering compounds are eliminated. The comparison standard procedure consists of determining the absorption of a sample of normal hexane of known purity at a wavelength of

¹ Hiskey, C. F., *Anal. Chem.*, 21, 1440-45 (1949)

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13.78 microns immediately prior to running the unknown sample. The ratio in absorption obtained by using the "base-line" principle,² can then be applied to a curve of absorbance ratio *versus* mole percent normal hexane. The mole percent normal hexane is then read from this chart. (Figure 1)

The investigation of an iterative procedure³ in the analysis of hydrocarbon mixtures has resulted in a technique with precision, but with an accuracy which is below the accuracy desired. This method is based on the proportionality between concentration and absorption peak height above a spectrum reference line. The steps employed in developing an iterative procedure include the determination of the spectra for all compounds present in the mixture to be analyzed, selection of the absorption peaks characteristic of the individual compounds, measurement of peaks selected, and the derivation of the equations to be used in the analyses. The time required for an individual infrared determination is one hour, which includes scanning of the spectrum and calculating the results.

III. Experimental

A. Apparatus and Reagents

The IR-4 infrared spectrophotometer was manufactured by Beckman Instruments, Inc. The IR-4 is built with a double-beam and double-monochromator optical system. Operation and specifications for the instrument have been described elsewhere.⁴

The absorption cell used had a fixed path length of 0.0570 mm.

The cell windows were made of sodium chloride.

Samples of normal hexane, the isomers of hexane, and methylcyclopentane were obtained in "Pure Grade" and "Research Grade" purity from the Phillips Petroleum Company. Cyclohexane was obtained in "Spectro Grade" purity from the Distillation Products Industries.

B. Procedure

1. Quantitative Determination of Normal Hexane

The procedure employed consists of recording the absorption of a sample of normal

² Wright, N., *Trans. Faraday Soc.*, 41, 171 (1945)

³ Heigh, J. J., Bell, M. F., and White, J. U., *Anal. Chem.*, 19, 293-97 (1947)

⁴ Beckman IR-4 Instruction Manual

Figure 1

CALIBRATION CURVE FOR NORMAL HEXANE IN
COMPARISON-STANDARD TECHNIQUE

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hexane of known purity over the range from 13.50 microns to 14.50 microns at 0.2 microns per minute. (Figure 2)

The spectrum of an unknown sample of commercial grade hexane was obtained in the same manner and in the same cell.

The IR-4 was used on double-beam operation, and the usual false energy corrections have been dispensed with because the instrument is equipped with a double-monochromator optical system.

The intensity of the absorption of each individual peak recorded is expressed as a "base-line" absorbance. This is calculated from the equation:

$$D_B = \log_{10} \frac{I_B}{I}$$

where D_B = base-line absorbance

I = transmittance of the recorded spectrum from the zero line to the selected absorption peak.

I_B = transmittance from zero to the straight line, the base-line, joining the two spectral points located on either side of the absorption peak. I_B is measured at the same wavelength as I .

The absorbances of normal hexane of known concentration and of the unknown sample are expressed in terms of the absorbance ratio a .

The following expression applies:

$$a = \frac{D_{B_X}}{D_{B_I}}$$

where a = the absorbance ratio

D_{B_I} = the absorbance of normal hexane of known concentration

D_{B_X} = the absorbance of the unknown sample

2. Iterative Procedure for the Analysis of Components in Commercial Grade Hexane

From the recorded spectra of all the hydrocarbons which are present in commercial

Figure 2

ABSORPTION PEAK OF NORMAL HEXANE AT 13.78μ

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grade hexane, it is possible to select a wavelength which is characteristic of each compound and at which all other compounds of the mixture are considerably weaker absorbers. In choosing the characteristic wavelengths, the position of the most intense absorptions are not always the best. Often other wavelengths give a more nearly linear function of the concentration.

The values obtained from the base-line optical densities of all the absorption peaks are used to derive equations which express concentration of the individual constituents in terms of volume percent. The use of these same equations in future sample analysis will result in a considerable saving of time because derivation of the equations is required only once during calibration.

The concentration, $C_{(A)}$, for the principal absorber is expressed in the following equation:

$$C_{(A)} = \frac{D_{A(n)}}{K_{(n,A)}} - \frac{K_{(n,B)}}{K_{(n,A)}} C_{(B)} - \frac{K_{(n,C)}}{K_{(n,A)}} C_{(C)} - \dots$$

where $-\frac{K_{(n,B)}}{K_{(n,A)}} - \frac{K_{(n,C)}}{K_{(n,A)}} = \text{correction coefficients}$

$D_{A(n)}$ = the base-line absorbance of A at any wavelength η , and

$C_{(B)}, C_{(C)}$ = concentration of components B and C, respectively.

The spectra for determination of the explicit equations and the spectra of the unknown samples should be determined on cells of equal thickness or the same cell.

A synthetic blend, No. 66, has been calculated by the iterative process as shown in Table I. The blend consisted of the following components:

2,2-Dimethylbutane (2,2-DMB)	2.0 % (v/v)
2,3-Dimethylbutane (2,3-DMB)	2.0
Normal hexane	75.0
2-Methylpentane (2-MP)	6.0
3-Methylpentane (3-MP)	4.0
Methylcyclopentane (MCP)	7.0
Cyclohexane (CH)	2.0
Benzene	2.0

Table I

Calculation Sheet for Synthetic Blend 66

First Approximation

	<u>Benzene</u>	<u>n-Hexane</u>	<u>2,2-DMB</u>	<u>Cyclohexane</u>	<u>3-MP</u>	<u>2,3-DMB</u>	<u>MCP</u>	<u>2-MP</u>
Benzene	= 0.04004							
n-Hexane	.0334	= - 0.7805						
2,2-DMB	.541	- .069	= 0.04967					
Cyclohexane	.000	- .018	.000	= 0.01429				
3-MP	.000	.000	.000	.000	= 0.01843			
2,3-DMB	.000	- .167	.000	.430	.000	= 0.02062		
MCP	.000	- .138	.351	.000	.508	.136	= 0.05429	
2-MP	- .170	- .175	.000	.000	- .332	.348	- .163	= 0.0541

Second Approximation

		<u>2-MP</u>	<u>MCP</u>	<u>2,3-DMB</u>	<u>3-MP</u>	<u>Cyclohexane</u>	<u>2,2-DMB</u>	<u>n-Hexane</u>	<u>Benzene</u>
MCP	0.0543	0.067	= 0.0589						
2,3-DMB	.0206	.000	.000	= 0.0206					
3-MP	.0184	.288	.059	.000	= 0.0416				
Cyclohexane	.0143	.014	- .016	.000	.000	= 0.0145			
2,2-DMB	.0497	.040	.000	.162	- .303	- .336	= 0.0326		
n-Hexane	.7805	- .541	- .591	.266	.000	1.053	.000	= 0.7295	
Benzene	.0400	.004	.007	- .199	- .014	- .121	.024	- .021	= 0.0198

Table I (continued)

Third Approximation

		Benzene	2,2-DMB	Cyclohexane	3-MP	2,3-DMB	MCP	n-Hexane	2-MP	%(v/v) ^a
n-Hexane	0.77916	0.033	0.000	1.053	0.000	0.266	-0.591		-0.541	= 71.78
2,2-DMB	.08186	.541		-0.336	- .303	.162	.000	-0.069	- .040	= 1.97
Cyclohexane	.02834	.000	.000		.000	.000	- .016	- .018	.0143	= 2.40
3-MP	.01843	.000	.000	.000		.032	.059	.000	.288	= 4.22
2,3-DMB	.14482	.000	.000	.430	.000		.000	- .167	.000	= 3.54
MCP	.13251	.000	.351	.000	.508	.136		- .138	.067	= 7.12
2-MP	.13251	- .170	.000	.000	- .332	.348	- .163	- .175		= 7.71
Benzene										= 1.98
									Total	= 100.75

^aElements multiplied by 100 to give results as percent

IV. Discussion and Results

A. Comparison Standard Technique for the Quantitative Determination of Normal Hexane

A statistical evaluation determined that an average of eight results on each synthetic sample does not differ from the known amount. That is, there is no evidence that an inaccuracy exists, based on the assumption that the synthetic is without error. If there is an inaccuracy, it is not more than 0.5 mole percent on the average for the 73 mole percent level and 1.2 mole percent on the average for the 84 mole percent level.

The observed difference between the average of eight determinations and the known is 0.13 for the 73 mole percent level and 0.33 for the 84 mole percent level.

B. Iterative Procedure for Quantitative Determination of Components in Commercial Grade Hexane

A comparison of the results obtained by this procedure shows that the probable error in the determination of each of the individual components in a synthetic blend which simulates commercial grade hexane is greater than 50 percent relative for some of the components present in small concentrations. It is believed that the accuracy of the procedure can be improved to a very large extent if it is modified by the use of a variable cell to eliminate the absorption of hexane. The iterative procedure can then be applied to the minor components present. Comparison of the results obtained by this method on a synthetic blend is shown in Table II.

Table II

Comparison for Analytical Accuracy in Iterative Procedure

	Synthetic Blend %(v/v)	Found %(v/v)
2,2-Dimethylbutane	2.0	2.0
2,3-Dimethylbutane	2.0	3.5
Normal Hexane	75.0	71.8
2-Methylpentane	6.0	7.7
3-Methylpentane	4.0	4.2
Methylcyclopentane	7.0	7.1
Cyclohexane	2.0	2.4
Benzene	2.0	2.0

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V. Acknowledgement

The author is grateful to Mr. Samuel H. Huston for his statistical evaluation of the data, and to Mr. Clifford McBride for his critical review of the methods.

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DETERMINATION OF TOTAL URANIUM AND IRON IN URANIUM TETRAFLUORIDE

by

W. M. Wise

J. J. Scopel

I. Summary

The results of this investigation show that, with respect to precision, accuracy, and rapidity, the pyrohydrolytic method is superior to the titrimetric method for determining total uranium in uranium tetrafluoride. In addition, the former does not require the use of a hazardous chemical such as perchloric acid. The sample is pyrohydrolyzed for 20 minutes at 850°C and ignited for 10 minutes at 850°C. The residue (U_3O_8) can be used for the determination of iron. Nickel could also be determined if a nickel-free apparatus were constructed.

II. Introduction

The titrimetric method used in this laboratory for determining total uranium in uranium tetrafluoride requires constant attention and is time-consuming. In search for a more rapid method it appeared as if pyrohydrolysis of the uranium tetrafluoride to U_3O_8 at 850°C and gravimetric measurement of the residue offered the best solution to the problem.¹

III. Experimental

A. Apparatus

The pyrohydrolysis apparatus is described in a previous report²; however, several modifications were made. Air was passed through a Koby Air Purifier and then into the steam generator to allow the passage of a mixture of steam and air over the sample. The temperatures of the steam-preheater and the pyrohydrolysis furnace were maintained at 650 and 850°C, respectively. A nickel tray 18 cm long and 1.5 cm wide was employed to hold four platinum sample boats. The tray was introduced and removed from the platinum tube with the aid of a wire rod.

¹ Hibbits, J. O., *Anal. Chem.*, 29, 1760-2 (1957)

² Wise, W. M., "Titrimetric Determination of Fluoride with Aluminum (III)," *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MGW-1385 (April 1, 1956) p 87-94

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B. Procedure

The pyrohydrolysis procedure was essentially the same as the one described in the previous report.³ Air was passed into the steam generator at a rate of 3-4 bubbles per second, and steam was generated at a rate of 2.5 g per minute. Samples were ground in a mullite mortar and weighed into previously ignited platinum boats. The boats were placed on the tray and introduced into the hottest portion of the platinum tube. The tube was closed, and the pyrohydrolyses were conducted for the desired lengths of time. The samples were removed, ignited in a furnace at 850° C for 10 minutes, cooled in a desiccator for 1 hour, and weighed. It was assumed that the residue contained 84.80% uranium.

Each sample of U_3O_8 was dissolved in 8 M nitric acid, and iron was determined spectrophotometrically using hydroxylamine sulfate and 1,10-phenanthroline.⁴

IV. Results and Discussion

Hibbitts⁵ showed that pyrohydrolysis in the presence of oxygen is a satisfactory method for determining total uranium in uranium tetrafluoride. However, he worked with samples whose sizes were approximately one-tenth the amounts used in this investigation. Since it seemed desirable to employ a larger sample in order to use the residue for the determination of iron and nickel, it was necessary to establish how much time is required for complete conversion of 2 g of uranium tetrafluoride to U_3O_8 in this apparatus.

Uranium tetrafluoride, which the New Brunswick Laboratory had selected as a standard, was pyrohydrolyzed for different amounts of time. The results are given in Table I. These data show that a pyrohydrolysis time of 15 minutes is satisfactory. It was observed that at the conclusion of this period the condensate no longer gives an acidic test with "Hydrion Paper." It was also found that after pyrohydrolysis the sample should be ignited at 850°C for at least 5 minutes. On the basis of these results, it is suggested that pyrohydrolysis and ignition be conducted for 20 and 10 minutes respectively.

³ Wise, W. M., MCW-1385, p 87-94

⁴ Perkins, M. A., ed., *Sampling and Testing Procedures for Special Products*, Mallinckrodt Chemical Works, MCW-1396, (January 1, 1956) p 64-65

⁵ Hibbitts, *Anal. Chem.*, 29, 1760-2

Table I

Uranium Assays and Iron Results Using Different Pyrohydrolysis Times

Time min	Total U %	Average Total U ^a %	Fe ppm (U Basis)	Average Fe ppm (U Basis)
15	75.78, 75.78, 75.80, 75.80 75.79, 75.78, 75.80, 75.78	75.79	17, 18, 16	17
20	75.78, 75.77, 75.81, 75.80 75.79, 75.77, 75.80, 75.79	75.79	18, 18, 17, 17	18
30	75.78, 75.79, 75.81, 75.80 75.78, 75.76, 75.80, 75.80	75.79	15, 16, 18, 19	17
45	75.76, 75.78, 75.79, 75.77 75.78, 75.77, 75.79, 75.80	75.78	16, 17, 18, 16	17
60	75.78, 75.79, 75.80, 75.79 75.79, 75.79, 75.82, 75.78	75.79	20, 17, 18, 19	18

^aAccepted value for N. B. L. Standard 7656 (No. 17A) = 75.77% Total U

A statistical analysis of the assay data in Table I reveals that at the 95% confidence level a single total uranium determination has an absolute precision of $\pm 0.028\%$. In all cases excellent accuracy is evidenced by the close agreement with the accepted value.

The determination of nickel⁶ was complicated by contamination, apparently from the nickel tray used to hold the boats, and erratic results were obtained. This difficulty could be alleviated by using an apparatus devoid of any nickel-containing components.

Iron was determined by the 1,10-phenanthroline method,⁷ and the results are given in Table I. An investigation is being conducted to ascertain whether there is any bias between this procedure and the direct ammonium oxalate fusion method.

⁶ Perkins, M. A., MCW-1396, p 101-4

⁷ Perkins, M. A., MCW-1396, p 64-65

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A STUDY OF LEACHING METHODS FOR THE DETERMINATION OF URANYL FLUORIDE IN URANIUM(IV) FLUORIDE

by

T. J. Kneip

J. D. Dowdy

I. Summary

No suitable leaching procedure has been found for the determination of uranyl fluoride in uranium(IV) fluoride. The methods studied are subject to either incomplete leaching or excessive hydrolysis of the uranium(IV) fluoride.

II. Introduction

The uranyl fluoride content of uranium(IV) fluoride generally has been obtained in one of two ways.¹ The first method is a calculation based on the difference between the total uranium content and the uranium(IV) content, while the second is the measurement of the amount of uranium dissolved by a leaching solution. Both involve conversion to uranyl fluoride content by the use of a suitable molecular weight factor.

$$\frac{\text{Mol. Wt. } \text{UO}_2\text{F}_2}{\text{At. Wt. U}} = 1.294$$

Results obtained by the first method are subject to at least two sources of significant errors. Since the uranyl fluoride is a minor constituent of normal uranium(IV) fluoride, the difference between total uranium and uranium(IV) assays is small and is subject to large relative errors caused by small relative errors in the two assays. The presence of uranium(VI) in a form other than uranyl fluoride would not be corrected for and would constitute a second error in the value reported. For example, significant amounts of uranium(VI) may be present in the "ammonium oxalate insoluble" (AOI) fraction of the sample.

¹ Rodden, C. J., *Current Procedures for the Analysis of UO₃, UF₄, and UF₆*, New Brunswick Laboratory, TID-7003 (February, 1956) p 34-5

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Several leaching methods have been reported.^{2,3,4,5,6} Two methods have been reported involving dissolution of the sample without valence change of the uranium and polarographic determination of the uranium(VI).^{7,8}

A direct, accurate, and rapid determination of the uranyl fluoride is desirable. Since the leaching methods are the most rapid of those reported, the present work was done to define the effects of the many variables present in the various procedures already reported.

III. Experimental

A. Equipment

The leaching was carried out in glass containers, which were suspended in a constant temperature water bath. The solvent and sample were agitated by glass stirrers driven by variable speed electric motors.

The solvent was separated from the leached solids by either centrifugation or suction filtration. An International Clinical Centrifuge, Model CL, was used at the maximum speed with 15-ml Pyrex centrifuge tubes. The filtration was carried out through two sheets of Whatman No. 2 filter paper in a No. 2 Buchner funnel.

The uranium content of the leach solutions was determined by the alkaline-peroxide colorimetric method. A Beckman Model B spectrophotometer was used with 1-cm Corex cells to obtain the absorbances at 400 mμ.

B. Procedure

A 10 - to 15-g portion of the uranium(IV) fluoride sample was ground to a smooth, flour-like powder. A known weight of sample was taken from this ground material. The required volume of solvent was placed in the glass container, and the stirrer was started. The

² Eberle, A. R., and Rodden, C. J., Manhattan Project, A-1018, Section 2C

³ *Tentative Methods for Analyzing UF₄*, A-1008 (May 7, 1943).

⁴ Marshall, E. D., Union Carbide Nuclear Company, K-25 Plant, *Laboratory Manual File, SA-U-6*

⁵ Gilles, G. M., et al, *The Determination by Pyrohydrolysis of Uranium, Fluorine, and Oxide Impurity in Uranium Tetrafluoride*, Atomic Energy Research Establishment, AERE-C/M-225 (October 26, 1954) p 2

⁶ Kirkland, J. D., Eldorado Mining and Refining, Ltd., Research and Development Division, *Method U-6* (October, 1956)

⁷ Letner, M. W., and Jaffa, F., *The Polarographic Determination of Uranium(VI) in Uranium Tetrafluoride*, New Brunswick Laboratory, NBL-132 (October, 1956)

⁸ Kneip, T. J., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1397 (October, 1956) p 183-7

weighed sample was then added to the solvent, and the stirrer was adjusted for maximum agitation without spattering. Addition of the sample in this way prevented caking and resulted in more uniform contact with the solvent.

The stirring was stopped at a known time, the sample and solvent were brought rapidly to room temperature, and the mixture was transferred to a graduated mixing cylinder. The mixture was diluted to a known volume (usually 100 ml), while the solvent was kept at a constant composition, and the mixture of sample and solvent was mixed by inverting the cylinder ten times. The solids were allowed to settle for 5 minutes. A 10-ml aliquot was then withdrawn from the upper 20 ml of solvent.

The aliquot was transferred to the centrifuge tube and centrifuged for 5 minutes. The supernate was then transferred to a clean 100-ml mixing cylinder. The centrifuge tube was allowed to drain and the lip was rinsed. No further washing was found necessary, since only a small amount of solids was present in the aliquot taken after the settling period.

An alternate separation scheme was the suction filtration of the entire sample. The filtrate was diluted to a known volume, and the uranium was determined by the alkaline-peroxide spectrophotometric method.

IV. Results and Discussion

An MCW reference standard uranium(IV) fluoride was chosen for the sample material. The known values for this material are given in Table I.

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Table I

Standard UF₄ (SH-53)

Constituent	% (Sample Basis)
U (Total)	75.89
U(IV)	74.71
U(VI)	1.18 ^a
U(VI) found	1.22 ^b
U(VI) from UO_2F_2 found	1.00 ^b
UO_2F_2	1.29 ^c
UO_2F_2	1.54 ^d

^aDifference of total uranium and uranium(IV)^b Direct polarographic determination^cCalculated from U(VI) result for UO_2F_2 ^dCalculated from 1.18% U(VI).

The results of a sieve analysis of the sample after grinding are shown in Table II.

Table II

Sieve Analysis of 100 g of SH-53 Uranium(IV) Fluoride after Grinding

U. S. Standard Sieve No.	Material on Sieve, %
100	1.45
270	14.6
325	11.8
<325	72.0
Total	99.85

The initial experiments were designed to obtain a precision figure and, if possible, to eliminate or standardize some of the variables. The major variables to be considered were: (1) solvent composition, (2) temperature, (3) method of contact, and (4) time of contact. Power driven glass stirrers were chosen to provide the most reproducible contact between

the solid sample and the solvent.

Table III contains the results of the evaluation of various glass containers, and the effect of grinding the sample.

Table III
Evaluation of Contact Method and Sample Condition

Conditions: solvent - 60 ml of 20% v/v methanol
5 g sample
70°C
15 minutes contact time

Sample	Container	UO ₂ F ₂ Found, Average %	Precision ^a of Single Result, % Absolute
Unground SH-53	200-ml Berzelius Beaker	1.49	± 0.18
Ground SH-53	200-ml Berzelius Beaker	1.53	± 0.06
Ground SH-53	250-ml Erlenmeyer Flask	1.37	± 0.06
Ground SH-53	100-ml Centrifuge Tubes	1.39	± 0.18

^aAll precision statements will be given at the 95% confidence level unless otherwise stated.

The difference between averages of ground and unground samples contacted in 200-ml beakers was significant at the 95% level. The precisions were also significantly different at the same level. The 200-ml beakers showed a significantly higher average than either of the other containers, although the precision was significantly different from only that of the centrifuge tubes.

These data show the most reproducible and probably most efficient system to be stirring a ground sample in a 200-ml Berzelius beaker.

The solvent composition, temperature, and time of stirring were then varied with the chosen stirring conditions. The curves obtained are shown in Figure 1. Various ratios of methanol and water were used as solvent in all but one case in which the solvent was a saturated sodium fluoride solution in water.

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Figure 1
EFFECT OF VARIABLES ON
LEACHING OF UO_2F_2 FROM UF_4

As is shown, only two solvents (methanol, and water saturated by sodium fluoride) prevented the hydrolysis of the uranium(IV) fluoride. In both cases, the ultimate uranyl fluoride value fell well beneath those shown in Table I.

All of the water-methanol mixtures show the effect of hydrolysis of the uranium (IV) fluoride. The effect increases with increasing temperature and increasing concentration of water.

V. Conclusions

It is evident that the result obtained can be made to coincide with a pre-chosen answer by the proper choice of conditions. The result obtained would remain dependent on fluctuations in solvent, temperature, and time if the method of stirring were reproducible.

Since the result would be largely dependent on the physical character of the sample, it seems most unlikely that such a method would consistently produce a correct answer on a variety of samples. Therefore, the various leaching methods would not provide a reliable replacement for the calculation based on the total uranium and uranium(IV) values. Since the small value calculated from the two large numbers, may have a large error and a possible positive bias from uranium(VI) not in the form of uranyl fluoride, the polarographic methods previously mentioned remain the best for the determination of uranyl fluoride in uranium(IV) fluoride.

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Glossary of Specialized Terms

<u>AOI</u>	- ammonium oxalate insoluble
<u>billet</u>	- a bar of forged dingot uranium suitable for subsequent rolling
<u>black oxide</u>	- U_3O_8
<u>brown oxide</u>	- UO_2
<u>derby</u>	- the uranium metal product of the nominal 300, 100 and 50 lb. reduction bombs which is subsequently recast.
<u>dingot</u>	- (direct ingot) the uranium metal product of 1400 and 3300 lb. reduction bombs. This metal not recast.
<u>DMFL</u>	- dingot magnesium fluoride liner
E_o <u>A</u>	- distribution coefficient (organic to aqueous)
<u>ESU</u>	- easily soluble uranium
<u>green salt</u>	- UF_4
<u>I & E slug</u>	- (hollow) internally and externally cooled slug
<u>ingot</u>	- recast uranium metal
<u>MFL</u>	- magnesium fluoride liner
<u>NOK</u>	- an aqueous uranyl nitrate solution obtained by stripping uranyl nitrate from tributyl-phosphate-hexane solvent with water
<u>OK-liquor</u>	- the uranyl nitrate liquor of highest purity used as a feed to the denitration pots
<u>orange oxide</u>	- UO_3
<u>P = D</u>	- pumper decanter
<u>raffinate</u>	- the aqueous residue remaining after tributyl phosphate extraction of a uranium concentrate previously digested with HNO_3

(continued on next page)

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<u>RMF</u>	- reject magnesium fluoride
<u>rod</u>	- cylindrical length of uranium produced by rolling or extruding uranium billets and ingots
<u>shotgun</u>	- a percent increase of neutron absorption cross section due to impurities in the product; pure U_3O_8 has a shotgun of zero
<u>slag</u>	- magnesium fluoride, containing small quantities of uranium and magnesium formed in the thermite bomb reaction
<u>slug</u>	- rods of uranium machined to specific diameter and lengths. Slugs, when canned are used as fuel elements
<u>soda-salt</u>	- sodium diuranate; usually applied to raw materials of that composition
<u>UNH</u>	- uranyl nitrate hexahydrate
<u>U-Con</u>	- a product of the physical separations plant consisting of a mixture of fine metal particles, uranium oxides, and magnesium fluorides, screened to -10 mesh and assaying 70 - 75% uranium
<u>U-Mag</u>	- an intermediate product of the physical separations plant consisting of the +10 mesh oversize from the screening of ground RMF. It is further separated to 701-metal and C-701
<u>701-metal</u>	- the metal concentrate product of the physical separations plant consisting of uranium metal particles ranging in size from +10 mesh to $\frac{1}{2}$ inch and assaying 95% uranium
<u>C-701</u>	- the reject product of the physical separations plant consisting chiefly of finely ground magnesium fluoride

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