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ARGONNE NATIONAL LABORATORY
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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

April, May, and June, 1955

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CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

for April, May, and June, 1955

SUMMARY

I. Direct Cycle Boiling Reactor Entrainment Studies (pages 7 to 10)

The study of entrainment of dissolved radioactivity from a boiling water surface has covered the reproducibility of the data and the rate of approach to steady state. Solids have been added to the boiler water and confirmation of previous data showing an increase in decontamination factors with increased solids concentration has been obtained.

II. Solvent Extraction — Study of Dispersion and Coalescence

(page 11)

Correlations relating interfacial area to light transmission have been developed for dispersions consisting of 0.50, 0.25 and 0.10 volume fractions of the dispersed phase.

III. Fluoride Volatilization Separations Process (pages 12 to 31)

The development of flowsheets for the recovery of decontaminated uranium from enriched reactor fuels has required the main effort of the laboratory group. The current flowsheet is directed toward the hydro-fluorination of zirconium matrix fuels in a fused salt mixture of sodium fluoride-zirconium fluoride. The melt is then fluorinated with bromine pentafluoride, converting the uranium to the volatile hexafluoride which can be separated and purified by distillation. The work of the present quarter has concentrated on uranium recovery and corrosion studies.

A fused salt dissolver to be used in conjunction with the existing fluoride volatility pilot plant has been designed.

Apparatus for the preparation and handling of plutonium hexafluoride is nearly complete. This study is oriented toward rates of formation and other factors which may make feasible the processing of plutonium-uranium alloy systems by an all-volatility scheme.

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IV. Chemical Metallurgical Separations Processes (pages 32 to 67)

Laboratory efforts this quarter were devoted to construction of a versatile vacuum casting furnace for investigation of slagging on a kilogram scale, methods for drying and deoxygenating inert gas streams, determination of the reactivity of liquid oxide slags toward uranium, analytical dissolution of fissium alloys, investigation of borided tantalum as a container material for molten uranium and extraction of plutonium from uranium by molten magnesium.

In the semi-works the oxidative slagging process has been scaled up to a 2-kilogram scale. Work continued on the development of various top and bottom pouring techniques. Various techniques and materials of construction necessary in the successful extraction of plutonium by magnesium from molten uranium were studied.

V. Fluidization Studies (pages 68 to 85)

Additional studies on the continuous denitration of uranyl nitrate in a fluidized bed were devoted to the effect of sulfate in the feed. Runs were also made to determine the effect of variations in reduction step conditions on the rate of hydrofluorination.

The development of the waste calcination process was continued in the pilot scale reactor. No operating difficulties were encountered but particle size growth occurred.

Work has continued on (a) the development of a multistage reactor for countercurrent gas-solid contacting and (b) fundamental studies of particle behavior in a fluidized bed.

VI. Reactor Chemistry - Breeding Gain Determination (pages 86 to 87)

The use of proportional counters for determination of cesium-137 in burn-up determinations has been investigated.

VII. Analytical Research and Service Work (page 88)

An unsuccessful attempt was made to develop a colorimetric thiocyanate analysis for plutonium.

VIII. Waste Processing And Miscellany (pages 89 to 90)

The gamma irradiation facility has been completed and the pool filled with water. Tests are being carried out on various phases of its operation.

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I. DIRECT CYCLE BOILING REACTOR ENTRAINMENT STUDIES

(W. A. Rodger, A. J. Shor, H. T. Ward*)

The study of entrainment of dissolved radioactivity from a boiling water surface continued. The results of 21 additional runs are summarized.

Eight of these runs were of 12 to 15-hour duration to study reproducibility and the attainment of steady state conditions. Other features studied were the effect of the nature of the water used, the effect of cleanup procedures and the apparent change in activity concentration in the boiler water during operation. In four runs in which solids were injected, confirmation was made of previous evidence concerning the observed increase in decontamination factors. The effect of submergence was investigated in one run.

A. Experimental Procedure

The equipment and method of procedure used in these studies has been described previously in ANL-5333, pages 7 to 9, ANL-5388, pages 7 to 9 and in ANL-5422, pages 8 to 16. Provision has been made for sampling the boiler contents during operation. The water used in all previous runs came from the building distilled water supply which was redistilled and generally had a specific resistance of ~300,000 ohm-centimeters. Some runs were made using water from a small Barnstead still. The specific resistance of this water was ~500,000 ohm-centimeters.

B. Discussion of Results

The data obtained are summarized in Table 1. The behavior of the system during the first few hours after start-up is somewhat difficult to explain. Decontamination factors may increase, decrease, or remain constant. The following qualitative generalizations seem permissible.

- (1) As reported previously the injection of solids in solution into the boiler during operation results in finite increases in decontamination factors. In two runs, L-1 and L-2, several successive amounts of NaNO_3 solution were injected and the change in decontamination factors noted. In each injection the solids in solution in the boiler were increased approximately 300 ppm. The decontamination factor increased from 0.6×10^5 to 1.15×10^5 in one run and from 0.42×10^5 to 1.09×10^5 in the other. In

*On loan from Kansas State College, Department of Chemical Engineering under the Participating Institution Program.

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Table 1

SUMMARY OF RUNS

<u>Run</u>	<u>Feed Activity $\times 10^{-6}$, cpm/ml</u>	<u>DF (avg) Activity $\times 10^{-5}$, cpm/ml</u>	<u>Length of Run, Hours</u>	<u>Remarks</u>
L-1	4.0	0.6 to 1.15	15+	Five NaNO_3 injections; each raised solids content 300 ppm
L-2	4.0	0.42 to 1.09	14+	Six NaNO_3 injections as in L-1 above
L-2.1	4.0	1.10	5	L-2 continued after 1 week
M-1	4.0	0.23	7	Barnstead still water used. Water injection to check possible contamination from salt solutions.
M-1.1	4.0	0.26 0.36	4+	M-1 continued after 2 days. At 150 min NaNO_3 injection to give 60 ppm solids
M-2	4.0	0.22 0.27	12	Similar to M-1; NaNO_3 injection to give 15 ppm solids
M-3	4.0	0.30 0.26	8	Similar to M-1 and M-2; Barnstead still water used; at 340 min, submergence level raised to 2 inches
M-4	4.0	0.40	7+	New glass tube used; redistilled water used
M-5	4.4	0.32 to 0.50 (slow rise)	14	Old tube replaced; redistilled water used
M-5.1	4.4	0.61	6	M-5 continued after 3 days
M-5.2	4.4	0.80	5-1/2	Apparatus cleaned and feed from M-5.1, returned for use in this run
M-5.3	4.4	0.81	4-1/2	M-5.2 continued after 15 hours

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Table 1 (cont'd)

Run	Feed Activity $\times 10^{-6}$, cpm/ml	DF (avg) Activity $\times 10^{-5}$, cpm/ml	Length of Run, Hours	Remarks
M-6	4.4	0.23 to 0.29 (slow rise)	13	Barnstead still water used; apparatus cleaned but no water redistilled in it; see M-9
M-6.1	4.4	0.40	6	M-6 continued after 4 days
M-7	3.6 (avg)	0.25 to 0.40 (slow rise)	12	Redistilled water used; similar to M-5; boiler samples taken hourly in all runs hereafter
M-7.1	3.3 (avg)	0.40	5	M-7 continued after shut down and cleanup of apparatus
M-8	3.7 (avg)	0.35 to 0.40 (slow rise)	14	Apparatus not cleaned after Run M-7.1; new feed solution used however
M-9	3.5 (avg)	0.15 to 0.24	13+	Barnstead still water used after apparatus was cleaned and used to boil (or prepare) redistilled water for approximately 6 hours as in M-7; new feed used
M-9.1	2.6 (avg)	0.24	5+	M-9 continued after 2 days
M-9.2	2.55 (avg)	0.34	7	M-9.1 continued after 5 days
M-9.3	2.5 (avg)	0.37	4	M-9.2 continued after 15 hours

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Runs M-1.1 and M-2 smaller amounts of NaNO_3 were injected. Increases of the decontamination factors in these runs were less than those just mentioned.

- (2) The use of the somewhat purer distilled water resulted in lower decontamination factors in agreement with the observed effect of solids (M-6 and M-9 compared with M-5 and M-7).
- (3) Variations in cleanup procedures between runs did not seem to have an particular effect.
- (4) The increase of submergence by one inch during Run M-3 resulted in no significant change in the decontamination factor.

Effort during the coming quarter will be directed toward obtaining reproducible conditions so that a study of de-entrainment may begin.

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II. SOLVENT EXTRACTION -- STUDY OF DISPERSION AND COALESCENCE

(W. A. Rodger, V. G. Trice, Jr., L. F. Dorsey)

The effort directed toward a fundamental understanding of the processes of dispersion and coalescence in immiscible liquid systems continues. An interim topical report covering the correlation of light scattering with interfacial area for a number of pure liquid pairs is nearly complete. This work is being extended to include other classes of liquids, commercial grade compounds and also systems in which mass transfer is occurring.

Correlations relating interfacial area to light transmission similar to that presented in Figure 3, ANL-5422 have been developed for dispersions consisting of 0.50, 0.25, 0.10 volume fraction dispersed phase. These correlations have average deviations in the range of 6 to 10 per cent which compares favorably with the accuracy of the basic photographic measurement of the interfacial area.

Due to the press of other work no further studies of gross dispersions in the cylindrical mixing tanks have been made. During the coming quarter, however, these studies will be continued in the 12 and 18-inch tanks.

A program for the study of mass transfer using the light scattering measurement as a tool for determination of interfacial area is being set up.

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III. FLUORIDE VOLATILIZATION SEPARATIONS PROCESS

The development of a flowsheet for the recovery of decontaminated uranium from enriched reactor fuels has continued to represent the main effort of the laboratory group. Although this type of processing may be applicable to a variety of reactor fuel alloys, the current flowsheet development program is focused specifically on the hydrofluorination of zirconium matrix fuels in a fused mixture of sodium fluoride and zirconium fluoride. The melt is then sparged with bromine pentafluoride, converting the uranium to the volatile hexafluoride which can be separated and purified by distillation. The dissolution of zirconium and Zircaloy II by hydrogen fluoride has been demonstrated. Studies of the uranium recovery step are in progress; these will soon be extended to irradiated specimens for decontamination determinations. The corrosion testing program has been continued.

A fused salt dissolver to be used in conjunction with the existing fluoride volatility pilot plant has been designed.

The apparatus and facilities for the preparation and handling of plutonium hexafluoride are nearly completed and are being tested. This study is oriented toward rates of formation and other factors which may clarify the role of plutonium in fluoride volatilization processing schemes.

Further data have been obtained on the rates of dissolution of uranium metal in bromine trifluoride solutions. Uranium hexafluoride added to the bromine trifluoride solution increases the dissolution rate markedly; bromine gives a much smaller effect. Bromine pentafluoride also appears to increase the rate slightly over that in pure bromine trifluoride.

The investigation of the effect of potassium fluoride on the volatilization of uranium hexafluoride from bromine trifluoride solutions has been terminated. This work gives an indication of the relative stabilities of the complex compounds formed by potassium fluoride with bromine trifluoride, uranium hexafluoride, and hydrogen fluoride.

A study of the vapor phase reaction of bromine with bromine trifluoride has been initiated. Both spectrophotometric and manometric methods are used to follow the reaction.

Certain members of the engineering group have continued to work with the laboratory group on the fused salt flowsheet development program.

Consultations were held in St. Louis with W. Leaders and A. Ruehle of the Mallinckrodt Chemical Works on the possibility of recovering the uranium from magnesium fluoride slags.

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A. Laboratory Investigations

1. Enriched Reactor Fuel Process Studies
(R. K. Steunenberg)

The stepwise development of a specific flowsheet which can be tested in the semi-works facilities is the primary objective of the laboratory group. The dissolution of zirconium matrix fuel alloys by hydrofluorination in sodium fluoride-zirconium fluoride melts at 600 to 700 C appears practical on a laboratory scale. The rate at which a subassembly can be dissolved under the different conditions of scale-up and geometry in a semi-works, however, may be quite different.

The uranium recovery determinations have not been entirely satisfactory. Although the uranium remaining in the melt after sparging with bromine pentafluoride (or fluorine) represents generally less than 0.5 per cent of that charged, the amount actually recovered overhead usually has not exceeded 90 per cent of the initial charge. When it becomes possible to demonstrate adequate uranium recovery consistently, the next step will be to determine decontamination data with irradiated material.

The results of the corrosion testing program suggest that nickel apparatus is usable on a semi-expendable basis. These components in the immediate vicinity of the bromine pentafluoride sparge outlet will probably require frequent replacement.

In addition to the flowsheet development work, consideration is being given to the possible processing of other fuel alloys, ore concentrates, slags, and residues from aqueous steps from which uranium might be recovered by fluorination procedures.

a. Dissolution Studies
(S. Vogler, K. H. Schoenemann)

The equipment used in the hydrofluorination studies described in ANL-5422, page 24, was modified so that the melt could be sparged with bromine pentafluoride, hydrogen fluoride or fluorine. The technique of measuring the flow rate by weighing a nickel vessel continuously was replaced by a thermal flowmeter. This flowmeter can either be calibrated directly or used to indicate a constant flow, the total amount of material used for an experiment being determined from initial and final weights of a nickel container.

Since the hydrofluorination did not rapidly dissolve some materials, such as stainless steel (ANL-5422, page 27), bromine pentafluoride was substituted because of its stronger fluorinating potential. It was preferred over fluorine since it can be totally condensed in a cold trap along with the volatilized uranium hexafluoride. The results of these experiments on various alloys are indicated in Table 2. Essentially the same dissolution rates were found for stainless steel and aluminum as with hydrogen fluoride.

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Table 2

DISSOLUTION OF METALS BY TREATMENT WITH BROMINE PENTAFLUORIDE
IN FUSED SODIUM FLUORIDE-ZIRCONIUM FLUORIDE

Melt Volume: 50 ml

Initial Melt Composition: 1 mole NaF
1 mole ZrF₄

Coupon: Various metals 1 inch x 2 inches x 0.1 inch

Pressure: 1 atmosphere

Run No.	Material	Coupon Wt, g	Run Time, Hr	Temp, C	Amt Dissolved, Per Cent	Penetration Rate, mm/hr	BrF ₅ Add. Rate, g/m	HF Efficiency, Per Cent
48	Zirconium	20.162	3	700	26	0.11	0.48	23
50	347 SS	15.807	3	700	14	0.04	0.45	13
51	2 S Aluminum	5.602	3	600	49	0.13	1.3	11

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b. Uranium Recovery Studies

(W. J. Mecham, R. C. Liimatainen, A. L. Freeman)

A series of uranium recovery determinations are described in Table 3. Analyses of the melt indicate that uranium can be removed effectively from a fused fluoride system by sparging with fluorine or bromine pentafluoride. The uranium balances, however, have not been satisfactory.

In Table 3, Runs 25, 26, 29, 31 and 33 (see Tables 3 and 4) were conducted in the small 3/4-inch reactor described in ANL-5338, page 19, which has a melt capacity of about 50 g; all the others employed the larger 2-inch dissolver which holds a melt charge of 300 g. (ANL-5422, page 24).

The overhead product containing the uranium hexafluoride was hydrolyzed with an aqueous solution of 1.6 M nitric acid, 0.5 M boric acid, and sufficient hydrazine hydrate to reduce all the bromine present to bromide ion. The melt samples were dissolved in 4 M nitric acid containing 0.4 M aluminum nitrate. Both types of samples were then analyzed for uranium by the service analytical laboratory.

In Table 3, Runs 35 through 40, the melt was sampled over time intervals to establish the rate of uranium removal from the melt while sparging with bromine pentafluoride. It is apparent from the melt analysis that about 99.5 per cent or more of the uranium was volatilized by the end of the first hour.

In Runs 25 through 37, a small amount of helium was added to the fluorinating agent; in Runs 38 through 40, undiluted bromine pentafluoride was used as the sparge gas. There are indications that the low uranium material balances may arise from losses in the cold traps when helium is used with the sparge. Also, considerable losses appear to take place by reduction of the uranium hexafluoride by the metal surfaces to a non-volatile compound. In the two-inch dissolver, severe corrosion was noted in the annulus between the vessel and its liner, and nitric acid washes of this space have shown as much as a gram of uranium to be present. In addition, an increase in temperature appears to increase the uranium losses, as shown in Runs 35, 36, and 37. This temperature dependence may arise from the same cause. In the future, a flanged liner will be used so this annulus will be sealed off from the system.

c. Studies on the Volatilization of Uranium From the Tetrafluoride With Oxygen

(R. C. Liimatainen, A. L. Freeman)

A considerable saving in chemical costs might be realized if oxygen could be substituted for a fluorinating agent in a process fluorination of uranium. The following exploratory tests were conducted to investigate this possibility.

Three experiments were performed in which oxygen was used to convert uranium tetrafluoride to the hexafluoride by the reaction

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Table 3

SUMMARY OF DATA FROM URANIUM RECOVERY RUNS

Melt Composition: Equimolar NaF-ZrF₄
Weight Present

Run No.	Charge		Sparge Gas		Temp, C	Fluorination Time, Min	U Recovered Overhead, % of Charge	U Retained in Melt, % of Charge	U Material Balance, %
	Material	Weight, gm	Material	Excess Ratio (a)					
25	U	2.514	BrF ₅	16.7	600	75	91.7	0.4	92.1
26	U	1.163	BrF ₃	33.1	700	180	85.0	1.7	86.7
27	U	8.258	BrF ₅	8.6	600	95	77.5	0.3	80.2
28	U	18.359	BrF ₅	3.7	600	80	61.9	0.4	63.9
30	U	10.444	F ₂	8.0	600	100	70.9	0.1	71.6
32	U	18.455	BrF ₅	4.0	600	60	35.6	0.6	36.2
34	UF ₄	2.315	BrF ₅	16.8	600	30	30.3	0.2	30.5
35	UF ₄	1.000	BrF ₅	35.0	600	240	118.3	0.60 (1 hr) 0.18 (2 hr) 0.10 (3 hr) 0.12 (4 hr)	118.4
36	UF ₄	1.000	BrF ₅	39.2	700	240	86.3	0.10 (1 hr) 0.05 (2 hr) 0.05 (3 hr) 0.07 (4 hr)	86.4
37	UF ₄	1.004	BrF ₅	39.1	800	240	63.6	0.32 (1 hr) 0.09 (2 hr) 0.10 (3 hr) 0.14 (4 hr)	63.8
38	UF ₄	1.017	BrF ₅	49.4	600	240	84.0	0.12 (1 hr) 0.03 (2 hr) 0.06 (3 hr) 0.11 (4 hr)	84.1
39	U	1.359	BrF ₅	43.4	600	120	99.1	0.67 (0.5 hr) 0.13 (1 hr) 0.11 (1.5 hr) 0.05 (2 hr)	104.7
40	Zircaloy	74.936	BrF ₅	19.4	600	60	107.4	20.8 (0.5 hr) 0.14 (1 hr)	107.5

(a) Based on the reactions: $U + 3BrF_5 \longrightarrow UF_6 + 3BrF_3$
 $U + 3F_2 \longrightarrow UF_6$

$2\text{UF}_4 + \text{O}_2 \longrightarrow \text{UF}_6 + \text{UO}_2\text{F}_2$ ^{1,2} These data are given in Table 4. In Runs 29 and 31, the oxygen was sparged through a sodium fluoride-zirconium fluoride melt containing uranium tetrafluoride. At 600 C little or no reaction occurred as indicated by the very small amount of volatilized uranium and the observation that the melt retained the characteristic green color of uranium tetrafluoride. At 800 C, however, the melt was a white-yellow color at the end of the run. In Run 33 uranium tetrafluoride powder was treated with oxygen in the absence of a melt, giving substantially the same amount of conversion observed in Run 31. Again the uranium hexafluoride appeared to be reduced in the lines, suggesting that perhaps a small amount of fluorinating agent should be included in the last stages of the sparging operation.

d. Corrosion Testing
(W. B. Seefeldt, L. Hays)

The possibility of using nickel as a material of construction for equipment in which enriched fuel alloys can be processed by fluorination in a fused salt medium has been investigated further. The corrosion rates were evaluated by three general methods: (1) a coupon technique, (2) an impingement plate technique, and (3) examination of the equipment in which the tests were conducted.

The goal of the coupon tests was to obtain rates of attack as a function of time on nickel coupons partially and totally immersed in a fused sodium fluoride-zirconium fluoride melt. The system was sparged with bromine pentafluoride. The degree of attack was determined from the loss in weight and by thickness contours obtained from microscopic measurements. The procedure was to expose four totally immersed (1.5 by 0.75 inch) and two partially immersed (4 by 0.75 inch) specimens in the melt. A totally immersed coupon was removed every 48 hours, and a partially immersed one every 96 hours. The total test period was 192 hours. These results are shown in Table 5. Run 2 was terminated after 48 hours when an unexpected accumulation of a solid phase appeared in the melt in the form of a relatively hard cake at the interface, and as a looser material at the bottom of the vessel. The same effect was noted in Runs 3 through 6, in which a melt from a different source was used. The solid material, which amounted to about 5 or 10 per cent of the total melt charged, has not yet been identified. Spectrochemical analysis indicated 0.5 per cent nickel to be present.

The results in Table 5 are listed in three columns. The first two are maximum and minimum rates determined by microscopic measurements of the edge thickness; the third is the average rate of attack from weight loss data. In nearly all cases the edge attack exceeds the average rate calculated from the weight loss, indicating that the edge attack is localized. One specimen in Run 3 was sectioned through the center; in

¹Mandleberg, C. J. and Davies, D., A Study of the Reaction Between UF₄ and O₂, AERE-C/R-863, February 13, 1952.

²Katz, J. J. and Rabinovitch, E., "The Chemistry of Uranium, Part I," NNEs VIII, Vol 5, McGraw-Hill, Inc, New York (1951), page 570

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Table 4

THE VOLATILIZATION OF URANIUM FROM UF_4 BY OXYGEN

Run No.	Temp, C	State of UF_4 in Reaction Vessel	Time, hr	O_2 Flow Rate, cc/min at STP	UF_4 Charged, gram	U Volatilized, Per Cent of Theoretical Yield	Material Balance, %
29	600	$NaF-ZrF_4-UF_4$ melt	2	30	5.014	0.002	127
31	800	$NaF-ZrF_4-UF_4$ melt	1	50	3.465	22.9	23 ^a
33	800	UF_4 powder	1	40	2.217	25.3	96

^aThe low material balance is believed to be due to an error in the melt analysis.

Table 5

CORROSION STUDIES IN FUSED NaF-ZrF₄ UNDER FLUORINATING CONDITIONS

Material: Nickel
 Sparge Gas: BrF₅ diluted with He
 Sparge Rate: 1-5 g/hr BrF₅
 20 cc/min He
 Temperature: 700 C
 Melt Renewed Every 48 hours

Run	Type Exposure	Time, hours	Penetration at Edges, mils ^b		Calculated Average Penetration, mils ^c	Comments
			min	max ^d		
2 ^a	Immersed	48	6	20.5	2.5	These coupons were suspended over BrF ₅ entrance tube; a corner of one sample was completely corroded away at an average rate of about 100 mils/day.
		48	10	Complete	3.4	
		48	1.5	3	slight weight gain	
	Interface	48	2	3	slight weight gain	These coupons were suspended near container well and not subjected to direct BrF ₅ impingement.
		48	3.5	7	0.9	
		48	1	5	0.5	
3	Immersed	48	2.5 1 ^e	8.5 3 ^e	2.8	New liner used for runs 3-6.
4		96	3	8	3.6	
5		144	7	10	4.5	
6		192	3	13	6.0	
4	Interface	96	1	10*	1.9	
6		192	3	13	2.9	

^aMelt in run 2 prepared from reagent NaF and General Chemical ZrF₄.
 Melts in runs 3 to 6 purchased from ORNL.

^bMicroscopic Measurement

^cWeight loss data

^dUnless indicated by (*), the maximum figure is at the interface for partially immersed coupons.

^ePenetration rates measured at the center of a sectioned coupon.

this case the thickness measurement checked the weight loss value more closely. In general, the specimens followed a pattern. At the bottom, near the bromine pentafluoride sparge entrance, the coupons were etched heavily. In the center they were pitted, and near the top they were etched lightly. The pits were broad, shallow and flat-bottomed. The corners of specimens located very near the sparge entrance were attacked at rates approaching 100 to 125 mils per day. The most severe attack appears to occur where the bromine pentafluoride impinges on the metal. It is moderate where the gas flow parallels a vertical surface.

In order to create a more consistent type of contacting, a nickel impingement plate was installed horizontally at a level about one-half inch above the sparge entrance. The rising bubbles then hit the plate at right angles. To evaluate the rate of attack, the reduction in thickness of the impingement plate was measured.

A total of four 24-hour impingement plate tests were made, one with uranium in the melt, and three without. The results are indicated in Table 6. Run 11 was made with bromine pentafluoride sparge gas diluted with helium. In Run 12, a helium sparge only was used to determine the extent of uranium metal dissolution in the unfluorinated melt. It appeared that the uranium reduced the zirconium tetrafluoride in the melt, forming a basis for Run 14 in which uranium metal was placed in the melt below the sparge entrance. This provided a source of uranium which was gradually dissolved in the melt and volatilized upon sparging with bromine pentafluoride. Although no attempt was made to establish a fixed, known concentration of uranium in the melt, the results indicated that the rate of attack was increased by the presence of uranium. In none of the runs was the attack on the impingement plate severe. The rate was not in excess of four mils for twenty-four hours in the absence of uranium, and in its presence it was twelve mils. These low rates may be caused by a protective gas cushion formed under the plate, preventing contact with the melt. In all runs the weldment between the plate and its support was severely attacked.

The nickel liners of the vessel and the sparge tubes were also examined. The liner used in Runs 3 through 6 was sectioned for thickness measurements. The wall contours are shown in Figure 1. The area of most severe attack was not at the interface, but at the bottom. The presence of the solid phase mentioned previously may be related to this effect. The interface attack of 10 mils agrees with that measured on the partially immersed coupons.

The liner used in Runs 13 and 14 failed during Run 14. About five perforations occurred, three of them along the weld zone. It is not obvious that all of the attack occurred from the inside of the liner; there is some evidence of attack in the annulus outside the liner which was exposed to bromine pentafluoride and uranium hexafluoride vapors. The attack was very localized, some adjacent areas retaining a large part of their original thickness. The sparge tube was also penetrated completely on one side for a length of one-half inch.

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Table 6

RESULTS OF IMPINGEMENT PLATE TESTS

Material: Nickel
 Fused Salt: 50-50 mol per cent
 NaF-ZrF₄
 Temperature: 700 C

Sparge Gas: Helium diluted BrF₅ only as indicated.
 Geometry: 1/4" nickel plate mounted horizontally
 about 1/2" above inverted sparge tube.
 Time: 24 hours for each test.

Run	BrF ₅ Rate, gm/hr	Helium Dilution	Impingement Plate Thickness, mils		Comments
			Initial	Final	
11a	3.8	Yes	250	249	Wall sparge tube reduced to 10 from 32 mils.
11b	12	Yes	249	247	Sparge tube failed where plate was welded to tube.
12 ^a	0	Yes	No plate present		Not a corrosion test. Purpose was to determine whether uranium would "dissolve" in helium-sparged melt. Dissolution by ZrF ₄ reduction was complete.
13	15	No	247	243	New sparge tube walls thinned to 10 mils at end.
14	14	No	243	231	64.4 gm uranium metal placed below sparge entrance; sparge tube attacked along one side near end to length of 1/2 inch. Liner eaten through in about five locations. Liner was new at beginning of run 13.

^aThis test: 66 hours.

FIGURE 1
WALL CONTOUR OF NICKEL CONTAINER TESTED
IN A FLUORINATED FUSED SALT MIXTURE AT 700 C

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In general, the corrosion rates in this system ranged from 1 mil/day to 125 mils/day. The most important single factor appears to be the angle of incidence between the fluorinating gas bubble and the metal. Welded areas appear to be susceptible to increased corrosion rates. Uranium in the melt also accelerates the attack somewhat. Further corrosion testing will be required before definite conclusions can be reached as to the feasibility of using nickel equipment in the fused fluoride process.

2. Investigation of Methods of Preparing and Handling
Plutonium Hexafluoride
(M. J. Steindler, F. R. Linzer, R. C. Vogel)

The apparatus for the preparation of plutonium hexafluoride from the lower fluorides and elemental fluorine has been designed and built. Its assembly is now completed and testing is underway. A discussion of the objectives and orientation of this program was presented in the previous quarterly report (ANL-5422, page 35).

3. Rate Studies of the Uranium-Bromine Trifluoride Reaction
(R. C. Vogel, H. D. Tyler)

Investigation of the kinetics of the uranium-bromine trifluoride reaction has been continued. This information will be necessary when uranium-plutonium alloys are dissolved in bromine trifluoride.

Data are given in ANL-5254, page 39, obtained by the whirling cylinder method of studying metal dissolution kinetics. A different presentation of these data and brief summary of recent data are presented in Table 7. These data were collected using high purity beta-quenched uranium. At 85 C, using pure bromine trifluoride and conditions similar to those indicated in Table 7, it was found that alpha-rolled commercial grade uranium dissolved about three times as rapidly as beta-quenched pure uranium.

In pure bromine trifluoride variations in stirring speed have no discernible influence on the rate and the temperature dependence corresponds to an activation energy 6 to 7 kcal/mole. As is shown in Table 7 there is a small increase in the rate as bromine is added to the system. When 5 mole per cent uranium hexafluoride is added, however, the rate is increased by about a factor of 100 over pure bromine trifluoride and by about a factor of 30 over 5 mole per cent bromine. Since the acceleration of the reaction in the presence of uranium hexafluoride, as found by the whirling cylinder method, was unexpected, it is necessary to examine the experiments critically. It can be argued that since only a small fraction of the uranium is dissolved (a necessary condition to keep the area constant), the reaction is being studied only during an induction period. In the whirling cylinder experiments it was found that the rate for a 45-minute period was the same as that observed with a reaction time of 15 minutes, the time used in the experiments of Table 7. It is therefore believed that the whirling cylinder experiments are valid. However, it is appropriate to do a few further experiments of a semi-quantitative nature in which this possible objection is further eliminated. To do these experiments it is necessary to

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Table 7

SELECTED EXPERIMENTS OF THE DISSOLUTION^a OF PURIFIED
URANIUM IN BROMINE TRIFLUORIDE SOLUTION

<u>Dissolving Medium^b</u>	<u>Temperature, C</u>	<u>Penetration Rate,^c mm/hr</u>
BrF_3	65	0.010 $\pm$.001
	85	0.015 $\pm$.001
	105	0.036 $\pm$.001
BrF_3 - Br_2 (5 mole %)	85	0.05 $\pm$.006
(10 mole %)	85	0.08 $\pm$.006
BrF_3 - UF_6 (5 mole %)	85	1.6

^aDissolution rate is measured by the weight loss of a highly purified uranium cylinder rotating at a peripheral speed of 3000 cm/min over a 15-minute interval.

^bNo appreciable change in concentration took place during the experiment.

^cEach value except the last is the average of several runs.

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sacrifice area control. These experiments, however, can be done at constant temperature and in such a way that the solution composition remains essentially constant. It was also of interest to determine qualitatively the effect of bromine pentafluoride on the rate of reaction.

The experimental procedure used in the dissolution experiments without area control is the following. Two hundred ml of bromine trifluoride solution is placed in a 250-ml nickel pot. A plug with a thermocouple well extending into the liquid is used to close the pot completely. A cylinder of alpha-rolled commercial uranium with a hole through the center is tied to the thermocouple. The stepwise procedure is as follows:

- (1) Insert the uranium and thermocouple in bromine trifluoride at room temperature.
- (2) Place the pot on a shaker and heat to 75°C (about 20 minutes).
- (3) Allow dissolution to proceed for one hour.
- (4) Cool rapidly to room temperature (about 10 minutes).

The dissolution data are corrected for a blank by an experiment omitting step 3. Each weight loss is converted to an approximate weight loss at 75°C by subtracting the blank found in the appropriate solution. The data are given in Table 8.

From these experiments it can be concluded that

- (1) uranium hexafluoride at 75°C does accelerate the reaction more than equivalent concentration of bromine (Run 4 vs Run 3);
- (2) bromine pentafluoride increases reaction rate slightly (Run 5 vs Run 2);
- (3) at 75°C the presence of a mixture of bromine pentafluoride with uranium hexafluoride increases the rate somewhat over that observed with uranium hexafluoride alone (Run 6 vs Run 4).

An attempt was made to do this type of dissolution experiment at 120°C. The blank of Run 7 is quite high indicating a rapid rate of dissolution. However, in the actual experiment an incident terminated the run after 25 minutes. In this incident the nickel thermocouple well corroded through where an "ear" had been silver soldered. This ear was used in wiring the uranium cylinder to the thermocouple in the nickel wire. The 200 ml of bromine trifluoride solution was blown out of the pot through the thermocouple well since the system was under pressure of about 100 mm. After the incident the uranium was recovered and it appears that a rather high rate of solution occurred.

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Table 8

RATE OF REACTION OF COMMERCIAL GRADE ALPHA-ROLLED URANIUM
WITH BROMINE TRIFLUORIDE SYSTEMS

Conditions: Each experiment started with new cylinder; area not controlled; one hour at 75 C unless otherwise indicated; volume BrF_3 200 ml; volume vapor space 50 ml; approximate initial sample area 5.6 cm^2 ; system shaken during dissolution; uranium sample tied to end of thermocouple well; data corrected by subtracting amount dissolved in heating and cooling cycle.

Run Number	2 ^a	1 ^{a,b}	3	4	5	6	7 ^c
Mol % BrF_3	100	~100	97.1	97.2	96.7	94.5	94.5
Mol % UF_6	-	0.04		2.8		2.9	2.9
Mol % Br_2			2.9				
Mol % BrF_5					3.3	2.7	2.7
Blank, wt loss ^d	0.1095	0.0487	0.1868	0.4493	0.0894	0.4280	2.5626
Original wt	11.0738	11.2916	9.8892	10.6130	11.1600	9.8377	11.3063
Total wt loss in run	0.1825	0.7259	0.3802	2.2383	0.2682	3.3879	~10
Net wt loss	0.0730	0.6772	0.1934	1.7910	0.1788	2.9599	~7
Wt loss, %	0.65	6	2.0	16.9	1.6	31.5	~70
Very approx. penetration rate, mm/hr	0.007	0.06	0.02	0.17	0.017	0.28	~0.74

^aPure BrF_3 attack giving small honeycomb type holes at the end, while Br_2 and UF_6 solutions give pits of greater diameter.

^bA possibility existed that this solution was contaminated with UF_6 ; it was analyzed and found to be 0.04 mol % UF_6 .

^cExperiment run at 120 C; due to an incident the run time was 25 minutes instead of 60 minutes. Results only approximate.

^dOn separate cylinder, taken through heating and cooling cycle only.

No further experiments of this type are planned although it is hoped that further data using the whirling cylinder approach will be collected.

4. The Volatilization of Uranium Hexafluoride from Potassium Fluoride-Bromine Fluoride Systems
(J. G. Schnizlein, R. K. Steunenberg)

This program, which was described in detail in the last quarterly report, (ANL-5422, page 41), is summarized in Table 9. The various phases of the work are essentially complete, with the exception of the experiment in which bromine trifluoride was to be added to the compound KUF_7 . This effort has been postponed until a satisfactory sample of KUF_7 can be prepared.

In Table 9, Runs 1 and 2 simply indicate that uranium hexafluoride can be volatilized from bromine trifluoride and quantitatively recovered in the equipment used. It was also found in Runs 3, 4, and 8 that most of the uranium hexafluoride could be volatilized from potassium fluoride-bromine trifluoride solutions. Approximately 0.2 per cent of the uranium hexafluoride charged, however, remained behind as an unidentified non-volatile compound when bromine trifluoride solutions containing 5 mole per cent potassium fluoride and 10 mole per cent uranium hexafluoride were distilled.

When uranium hexafluoride was refluxed over potassium bromotetrafluoride (Runs 7 and 9), a large non-volatile portion remained behind upon distillation. Despite the different ratios of starting materials, analyses on the residue indicated 67 and 58 mole per cent to be a uranium compound, the remainder being potassium bromotetrafluoride.

In Runs 5 and 6 uranium metal was dissolved in bromine trifluoride solutions containing about 5 mole per cent potassium fluoride. X-ray powder diffraction determinations indicated the same non-volatile uranium compound produced in Runs 7 and 9. These residues from Runs 5 and 6 were composed of the non-volatile uranium compound to the extent of 23 and about 30 mole per cent respectively. Further studies of the X-ray powder diffraction data are being undertaken in an effort to identify this material positively.

In addition to the work on uranium hexafluoride, the study was extended to an investigation of the relative stabilities of potassium hydrogen fluoride and potassium bromotetrafluoride. These results are outlined in Table 10. Runs 10, 11, and 12, in which the equilibrium was approached from both directions, show the potassium bromotetrafluoride to be the more stable under these conditions. In Run 10, in which potassium hydrogen fluoride was treated with excess bromine trifluoride, the weight of the non-volatile residue and the vapor pressure of the solution indicated substantially a total conversion to potassium bromotetrafluoride. The treatment of potassium hydrogen fluoride with an equivalent amount of bromine trifluoride resulted in less than 7 mole per cent of the potassium hydrogen fluoride remaining unconverted in the residue. This result was based on the weight of the residue and analyses of the volatile fractions. The vapor pressure could not be interpreted clearly because of the small amounts involved and a lack of information on the effect of the solid on

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Table 9

THE VOLATILIZATION OF UF_6 FROM $\text{KF}-\text{BrF}_3$ SYSTEMS

After reflux, the volatile material was distilled into sample tubes at temperatures up to 150 C.

	Run	Charge, millimoles				Reflux		UF ₆ Product		Unidentified U Compound in Residue, %	Material Balance	
		UF ₆	KF	BrF ₃	KBrF ₄	Time, hr	Temp, C	Volatile, %	Residue, %		UF ₆ , %	Total, %
$\text{UF}_6 + \text{BrF}_3$	1	10.4	--	85.0	--	0	--	98.5	--	--	98.5	99.3
	2	10.3	--	86.4	--	0	--	99.5	--	--	99.5	98.9
$\text{UF}_6 + \text{KF} + \text{BrF}_3$	3	10.01	5.02	90.5	--	1	75	99.7	0.14	0.28	99.8	98.4
	4	10.1	5.04	92.4	--	0.5	75	98.6	0.22	0.42	98.8	98.5
	8	10.08	4.89	87.8	--	49	75	95.2	0.53	1.0	95.7	99.7
$\text{KUF}_7 + \text{BrF}_3$												
$\text{UF}_6 + \text{KBrF}_4$	7	20.1	--	--	8.03	8	70	65.7	26.9	67.4	92.6	97.6
	9	9.90	--	--	12.07	23	70	25.8	70.6	57.9	96.4	99.0
$\text{U} + \text{KF} + \text{BrF}_3$		<u>metal</u>										
	5	2.41	5.35	91.6	--	6.5	90	33.9	61.4 ^a	28 ^a	95.3 ^a	99.4
	6	4.86	8.26	112.8	--	24	110	52.1	39.7	23.4	91.8	97.4

^aPrecipitate formed on hydrolysis; a portion used for spectrographic analysis.

Table 10

REACTIONS BETWEEN KHF_2 AND KBrF_4 SYSTEMS

	Run	Charge, millimoles				Composition of Residue, Mole %		Material Balance %
		KHF_2	BrF_3	KBrF_4	HF	KBrF_4	KHF_2	
$\text{KHF}_2 + \text{BrF}_3$	10	10.7	82.8	--	--	~100	~0	99.9
	11	22.0	21.4	--	--	93.4	7	99.7
$\text{KBrF}_4 + \text{HF}$	12	--	--	16.1	108	83.8	16	99.0

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the vapor pressure of hydrogen fluoride. In Run 12 a seven-fold excess of hydrogen fluoride was added to potassium bromotetrafluoride. The weight of the residue and analyses of the volatile material showed that 16 mole per cent of the residue was converted to potassium hydrogen fluoride.

This work has given a general indication of the relative stabilities of the complexes of potassium fluoride with bromine trifluoride, uranium hexafluoride and hydrogen fluoride. The principle value of these results probably lies in the fact that they define areas in which detailed studies might be made, such as complete characterization of the compounds present, the rate factors involved in these reactions, and the mechanism by which potassium fluoride inhibits the volatilization of uranium hexafluoride when uranium metal is dissolved in bromine trifluoride solutions. Further work on this problem is not contemplated, however, beyond a study of the reaction between KUF_7 and bromine trifluoride and an attempt to characterize the unidentified uranium-bearing residues.

5. Spectrophotometric Studies

(R. K. Steunenbergh, G. Redding and R. C. Vogel)

The purpose of this program is to study the vapor-phase reactions within the bromine-fluorine system by means of visible and ultraviolet absorption spectra. The initial stages of the work have been completed with measurements of the spectra of gaseous bromine, bromine trifluoride, bromine pentafluoride, fluorine, and uranium hexafluoride at room temperature (ANL-5254, pages 43 to 48; ANL-5422, page 44).

The current phase of this program consists of a study of the vapor-phase reaction between bromine and bromine trifluoride. That these two materials react to form a third species is strongly implied by P-V-T measurements, which show an increase in the total number of moles of gas present when their vapors are mixed (ANL-5333, pages 35 to 40). A simple explanation of this effect might lie in the reaction $Br_2 + BrF_3 \rightleftharpoons 3 BrF$. Manometric measurements at constant temperature and volume do not give a fixed equilibrium constant for this reaction, however, indicating either that it is incorrect or that other equilibria may be involved.

By combining the spectrophotometric method with simultaneous P-V-T measurements, it might be possible to characterize the reaction. The absorption peaks of bromine and bromine trifluoride are so located that their concentrations can be determined directly, and it is possible that other absorption due to a third species might appear in the mixture.

B. Semi-Works Operation

(W. J. Mecham, R. C. Liimatainen, R. Kessie)

A program has been started looking toward semi-works scale recovery of decontaminated uranium from STR-type fuel elements by a fluoride volatility process. A molten fluoride dissolver and sparge unit capable of handling a full-size STR fuel element has been designed. It will be integrated into the distillation columns of the existing fluoride volatility process pilot plant. Orders for materials of construction and major items of equipment have been placed. The installation is expected to be complete and operating

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this year. Laboratory work and engineering studies pertinent to design and operation will continue along with construction.

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IV. CHEMICAL METALLURGICAL SEPARATIONS PROCESS

High temperature laboratory studies were devoted this quarter to the following efforts: construction of a versatile vacuum casting furnace for investigation of slagging on a kilogram scale; methods for drying and de-oxygenating inert gas streams; determination of the reactivity of liquid oxide slags toward uranium; analytical dissolutions of "fissium" alloys; investigation of borided tantalum as a useful container material for molten uranium; extraction of plutonium from uranium by molten magnesium.

In the semi-works, the oxidative slagging process has been scaled up to a 2-kilogram scale. Fission product removals were essentially the same as those found previously in small scale (100 gram) laboratory experiments. Fission products added to give macro concentrations (of the order of 0.1 wt per cent) behaved in the same fashion as corresponding tracer fission product activity.

Work continued on the development of various top and bottom pouring techniques. Several samples of the metallic skulls (or slags) remaining behind in the crucibles after pouring were analyzed for oxygen content, and found to have an oxygen content equivalent to about 20 wt per cent uranium dioxide.

Work related to the magnesium extraction of plutonium from uranium involved study of phase separation, testing of various materials of construction, the construction of an experimental magnesium distillation unit, and partial design of a large scale extraction unit.

A. Laboratory Studies
(H. M. Feder)

1. Slagging Investigation
(N. Chellew, C. Cushing)

No active slagging experiments were performed this quarter because effort was directed toward the installation of the shielded vacuum casting furnace. Figures 2 to 7 show the installation and some of its component parts as they now exist. The F. J. Stokes Company built this equipment in accordance with designs and specifications supplied by the laboratory group and the design group under J. H. Schraidt.

Although a complete report on this furnace will be written after it has been thoroughly tested the following information may be useful. Versatility was stressed in the design. Operations may be conducted in high vacuum or in inert atmosphere, heating may be accomplished by an induction coil or by an electric resistance heater, and pouring may be done over the top or through the bottom.

The entire furnace assembly is enclosed in a large ventilated hood to confine the spread of activity. It is hoped that plutonium-enriched materials, in particular, may be processed. The furnace body itself is shielded with five-inch thick steel slabs capable of reducing

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Figure 2

VACUUM CASTING FURNACE

Pumping System and Movable Shields

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Figure 3

VACUUM CASTING FURNACE

Exterior Furnace Body

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Figure 4

VACUUM CASTING FURNACE

Induction Heater, Shields Charging Bucket and Molds

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Figure 5

VACUUM CASTING FURNACE

Susceptor, Stopper Rod and Water Cooled Shield in Place

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Figure 6

VACUUM CASTING FURNACE

Crucible and Heater in Pouring Position

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Figure 7

VACUUM CASTING FURNACE

Molybdenum Resistance Heater with Shields

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the radiation from a Hanford slug to tolerance level. The top and front slabs are mounted on rollers which permit their ready removal for furnace loading, unloading and maintenance. A small movable shield plug in one side permits the separate removal of the castings. The inside dimensions of the cave are 33 inches by 28 inches by 33 inches deep.

The furnace is furnished with the following: (a) a platform which holds both crucible and heating element and which can be tilted 90 degrees from the vertical to either side; (b) movable water-cooled shields over the crucible; (c) a mechanism for positioning a stopper rod and moving it vertically; (d) a movable bucket which may be used for charging while the furnace is closed; (e) top and side windows with movable shields; (f) water-cooled molds which may be moved into various positions while the furnace is in operation; (g) thermocouple junctions at strategic points. The movable parts of the furnace are operated through O-ring sealed connections by means of lazy handles extending through the shields. The furnace body is 20 inches O.D. by 28 inches high. It is internally water cooled.

The induction coil is powered by a 15 KW, 10 KC motor-generator set with an adjustable capacitor bank placed in a recess in the hood. The resistance heater is constructed from 0.2-inch diameter molybdenum rod and is fed via water-cooled copper tubes by a 10:1 step-down transformer connected to a 208 V line.

The pumping system consists of a six-inch oil diffusion pump, a four-inch booster pump and a 60 cfm mechanical pump. The design specifications require a speed of 600 liters per second at 10⁻⁵ mm. A second mechanical pump for roughing down or for backing up is included. A stainless steel liquid nitrogen trap of the thimble type is located between the furnace and the diffusion pump. A sensing thermistor in this trap triggers an automatic refilling device which draws from a large liquid nitrogen reservoir tank in the hood.

The helium purification system has not been constructed yet because it has been found experimentally that the presently used system, designed on the basis of the best available information, did not function as intended. A General Electric portable dew point indicator has been set up on a stand (Figure 8) and modified to permit the continuous estimation of oxygen and water content of inert gases by the method of Pepkowitz.³ Results obtained to date are given in Table 11.

Several observations may be made. First, Bureau of Mines pre-purified tank helium, as received, shows a wide variability of oxygen content. Pepkowitz has also pointed out that the impurity content of a given tank varies as well with degree of mixing and exhaustion. Second, the multi-component purification system previously used and described in Table 11 was

³L. P. Pepkowitz, Anal Chem, 27, 245 (1955)

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Figure 8

07

Apparatus for Continuous Indication of Moisture and Oxygen Content of Gases

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Table 11OXYGEN AND WATER CONTENT OF PREPURIFIED BUREAU OF MINES HELIUM

Test No.	Feed Gas (280 cc/min)	Further Purification	Oxygen ppm	Water ppm ^a
1	Tank 1	None	115	1
2	Tank 2	None	90	6
3	Tank 3	None	30, 35 ^b	2
4	Tank 3	System (unheated) ^c	70	4
5	Tank 3	As in 4 with uranium turnings at 800 C	39	4
6	Tank 3	Copper tubing trap and uranium turnings (unheated)	30	5
7	Tank 3	Copper tubing trap and uranium turnings at 850 C	13	5
8	Tank 3	As in 7 with trap cooled by liquid nitrogen	13	5

^aA correction for an instrumental blank of 5 ppm was found.

^bThe higher value was found when a longer feed tubing section was employed.

^cThe system used here and in earlier experimental work consisted of the following components in sequence: Anhydrone, Ascarite, copper turnings, copper oxide, glass cold trap and uranium turnings.

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ineffective. In fact, it was observed that immersion of the glass cold trap in liquid nitrogen caused a slow leak of air into the system. The system was therefore replaced by a simpler two component set-up which gave better oxygen clean-up. The linear flow rate through the uranium furnace was 68 cm/min. The linear flow rate through the cold trap, however, was 1700 cm/min. This high rate may be the source of its inefficiency for water vapor removal.

Further experimentation will be done to find efficient methods for removing the oxygen content of helium containing initially up to 150 ppm.

2. Liquid Oxide Slags

(N. Chellev, J. Fischer, H. M. Feder, J. Bingle)

Three experiments were conducted as previously described (ANL-5422, page 66) to determine the compatibility of some molten oxide slags with uranium. In each case the slag blackened as a result of reaction. The analytical data obtained are shown in Table 12. The variation in quantity of uranium oxidized may be accounted for within the precision of the data by assuming complete reduction of the magnesia and partial reduction (about 2/3) of the alumina present. Such an assumption would accord with the currently available thermodynamic data. Apparently these reactions, which proceed slowly with sintered, solid magnesia and alumina go much more rapidly when these oxides are in solution.

Additional oxide systems are being examined for their suitability for slagging purposes. The system BaO-ZrO_2 was incompletely examined by von Wartenburg.⁴ His data indicate the possibility of a eutectic in this system at about 11 mole per cent zirconia melting near 1340 C. Three mixtures, containing 9, 11, and 13 mole per cent zirconia, were made up and heated in platinum to 1400 C for two hours. Examination of the cooled materials indicated all three mixtures had fused. A preliminary trial was made of the 11 mole per cent zirconia mixture as a slagging agent with uranium at 1400 C. Darkening of the slag due to reaction did not appear to have taken place.

To speed up evaluation of possible oxide systems for use as slags apparatus has been constructed for differential thermal analysis.

3. Dissolution Studies

(M. Beederman)

The electrolytic drilling technique has been applied to the problem of determining the distribution of residual activities within a slagged ingot. An irradiated uranium slug slice, spiked with inactive fission elements, was melted in a magnesia crucible and held for four hours at 1200 C under helium. The melt was allowed to solidify and the slag layers were removed by deep etching. The ingot (8 mm high by 28 mm dia) was then sampled by electrolytic drilling with 2N HNO_3 -0.1N HF.

⁴H. von Wartenburg and H. J. Reusch, Z anorg Chem, 207, 18 (1932)

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Table 12

DISTRIBUTION OF URANIUM AFTER CONTACT
WITH MOLTEN OXIDE SLUGS

Conditions: Recrystallized alumina crucibles.
Helium atmosphere. One-half hour
at temperature.

Exp No.	Temp, C	Weight Ratio, Oxides: Uranium	Charge, mg-atoms				Uranium Recovered, mg-atoms	
			Uranium	Oxygen, as			In Ingot ^a	In Slag ^b
				CaO	Al ₂ O ₃	MgO		
8B	1390	5:100	417	41	70	7.5	--	31
11B	1390	1:100	250	5	8.4	0.9	243	3.3
13B	1430	5:100	292	31	51	None	269	13.3

^aDetermined by dissolving metal with bromine-ethyl acetate mixture. Results later shown to be probably low by about three per cent.

^bDetermined by dissolution of slag residue in aqua regia.

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Table 13

DISTRIBUTION OF RADIOACTIVITIES IN A SLAGGED INGOT

Sampled as shown in above sketch

Element	Cpm x 10 ⁻⁸ /gm Uranium					
	No. 1	No. 2	No. 3 upper	No. 4 upper	No. 3 lower	No. 4 lower
Cesium	0.17	0.06	0.15	0.67	0.08	0.10
Strontium	0.34	0.10	0.21	1.48	0.11	0.16
Rare Earths	1.66	0.92	1.51	3.91	0.46	0.69
Zirconium	0.32	0.15	0.41	0.81	0.15	0.22
Plutonium	0.029	0.020	0.029	0.031	0.029	0.028
Ruthenium ^a	0.050	0.056	0.035	0.070	0.077	0.108
Niobium	0.32	0.29	0.32	0.35	0.30	0.25

^aThese analyses are likely to be in error because of incomplete recovery.

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The ruthenium-bearing residues were dissolved in alkaline hypochlorite, acidified, and combined with the bulk solution. The analyses for radioactivities are given in Table 13.

The first result to be noted is that electrolytic sampling of ingots may lead to erroneous conclusions because of local variations in concentrations of fission elements, unless a sufficient number of drillings is made. This appears to be more particularly true of those elements removed by slagging--cesium, strontium, rare earths and zirconium--than of elements which are not removed, such as plutonium and niobium. The second result which may be noted is the existence of concentration gradients for the former elements within the ingot. The top center sample (No. 4 upper) exhibits the largest concentrations while the sample taken near the bottom periphery (No. 3 lower) shows the smallest. A conclusion which may be drawn from this fact is that convective mixing within the molten uranium is negligible. A second conclusion is that the boundary surfaces of the molten metal probably differ widely in their ability to act as sinks for the diffusing fission elements.

Alternate electrolytes were investigated for use in electrolytic drilling. Sulfuric acid, phosphoric acid, sodium bicarbonate, ammonium bicarbonate, phosphoric-hydrochloric acid mixtures, hydrochloric acid-hydrogen peroxides mixtures, and nitric acid-hydrofluoric acid mixtures were used. With many of these good drilling of uranium could be achieved but in all cases the drilling of "fissium" alloys was accompanied by the formation of residues which would require additional dissolution steps.

An alternative approach to the rather difficult problem of providing a representative solution of "fissium" alloys for analytical purposes is being investigated. In this approach the first step is reaction of the metal with molten salts. To date, it has been shown that dropping metal pellets into fused mixtures of potassium chloride with lead chloride, zinc chloride or cadmium chloride results in rapid but simple and controllable reactions. After reaction has ceased the addition of potassium nitrate to the mixture converts ruthenium into a soluble form. The fusions may be conducted in vitreous silica or porcelain. The salt mixture is finally dissolved in warm aqua regia. Analytical recovery of the elements present in a typical "fissium" alloy remains to be demonstrated.

4. Container Material Studies (C. L. Rosen, R. Sweezer)

Further testing of borided tantalum crucibles was continued. It was found that the weight of boron deposited on the tantalum during boriding is a reproducible function of the time and temperature of the boriding operation.

At temperatures in the neighborhood of 1250 C the borided crucibles seem to hold up rather well to attack by molten uranium, as compared to untreated tantalum. At temperatures in the neighborhood of 1750 C both the tantalum and borided tantalum crucibles seem to be

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corroded rather heavily. (At 1750 C it was found that uranium has a strong tendency to creep out of its containers.)

An apparatus for differential thermal analysis has been constructed for operation up to temperatures of 1200 C. With this apparatus it is hoped to obtain approximate heats of reaction and relative stabilities of the borides of transition metals and uranium. This will supplement the results reported in ANL-5422, page 68.

5. Magnesium Extraction Studies

(M. Nathans, E. Greenberg, K. E. Anderson)

The furnace and associated apparatus for studying the distribution of plutonium between uranium and magnesium have already been described in ANL-5422, page 72. Tests of the equipment and operating procedure have revealed the following:

- a. Temperature surveys of the empty furnace tube at 933 C, 1066 C, and 1180 C indicate that isothermal conditions may be established to within ± 3 C over an 8 to 9-inch long zone.
- b. Trial upheats to 950 C and 1180 C were made with a sample capsule. The top of the capsule was provided with a hole to admit a thermocouple which was embedded in a dummy charge of aluminum contained in a recrystallized alumina crucible. For an average upheat rate of about 5 C/min the temperature of the melt lagged about 10 to 15 minutes behind the furnace temperature when the control temperature was attained. The final temperature of the melt appeared to be within 5 C of the furnace temperature. The temperature distribution in the interior of the capsule was somewhat smoother than outside the capsule; high heat capacity and thermal conductivity of the sample apparently has a beneficial effect.
- c. Several materials were tested for use as a capsule suspension. The method which proved to be satisfactory consisted of screwing a cap onto the nipple at the top of the capsule, attaching a bail of two thicknesses of 50-mil tantalum wire through a hole drilled through the cap, and using 1/8-inch tantalum rod as a connecting link between the bail and the platinum-10 per cent rhodium pulley wire. In this way the platinum suspension wire does not reach into the hot test zone of the furnace.
- d. The quenching mechanism appears to operate satisfactorily.
- e. Distillation of magnesium from melts containing this metal has been eliminated by using a snug fitting graphite cap on the recrystallized alumina crucible. The cap is held in place by screwing down the top of

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the capsule. A tantalum spacer is provided between the steel capsule and graphite cap to prevent reaction at operating temperatures.

An extraction experiment was made in an alumina crucible with 106.5 grams uranium, 40.0 grams magnesium and 16.3 mg plutonium. Plutonium analyses of both the magnesium and uranium phases were made by the TTA method. A value of 0.07 was obtained at 1161 ± 5 C for the distribution coefficient, K, as defined by the following expression

$$K = \frac{\text{Pu activity in Mg phase/moles Mg}}{\text{Pu activity in U phase/moles U}} .$$

However, the plutonium recovered in the bulk phases was only 70 per cent of the initial amount. Additional samples are being submitted for analysis and duplicate runs are in progress to check this result.

Future experiments will also involve the use of lower-melting uranium-chromium alloys. Studies are therefore being carried out on the feasibility of sampling these alloys by means of an electrolytic drilling technique. Preliminary experiments indicate that a 6 M sulfuric acid 0.1 M hydrofluoric acid mixture appears to be promising.

B. Semi-Works Studies of High Temperature Processes
(L. Burris)

1. Study of Oxidative Slagging on a Kilogram Scale
(G. A. Bennett, A. A. Chilenskas, W. H. Spicer, F. B. Gast)

Study of the oxidative slagging process for purification of discharged reactor fuel continued in the past quarter with the making of three, 2 kg-scale, active tracer runs. These runs were made under essentially the same operating conditions to establish the reproducibility of the data for fission product removals and product recoveries. Both tracer fission product activity and several synthetically added fission products were present to allow comparison of the behavior of fission products from these sources. Fission product removals were in good agreement with those found in small scale (100 gm) laboratory runs. The behavior of synthetically added fission products was essentially the same as that of fission products created in fission. Product recoveries ranged between 92 and 95 per cent. Attempts are being made to improve product yields by crucible re-use and by crucible design.

Design work is also in progress to develop a pneumatically-operated piston to replace the fusible plug method (see ANL-5422, page 78) of lowering a stopper rod away from the discharge hole of a bottom pour crucible. New slagging equipment capable of handling 5-kg batches of uranium is also being designed.

a. Active Slagging Runs

Three active slagging runs were made under essentially the

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same conditions* to establish data reproducibility and to compare the behavior of synthetically added fission products and fission products originating in fission. One of the three runs was unsuccessful because of metal leakage into the mold during the course of the run. Zirconium, niobium, molybdenum, palladium, and rhodium were added to concentrations corresponding to 1 per cent burn-up of fuel atoms, and cerium to a concentration of 0.1 per cent burn-up of fuel atoms. Table 14 summarizes the compositions of materials charged and the material balances for these runs.

The recoveries of product ingot, although indicating a possible tendency toward improvement, average 93.6 per cent. Considerable work in the future will be directed toward improving the recovery or purified material as a product ingot.

The distribution of fission products between the recovered ingot and the slag layer (which includes any uranium which adheres to the slag or which fails to pour from the crucible) is shown in Table 15 for the three runs. The results are in general agreement with those of small scale laboratory runs. The elements more active than uranium are removed in the slag (rare earths, strontium, tellurium and zirconium). Cesium and a considerable fraction of the strontium are lost by volatilization. These are deposited predominantly on the surrounding Vycor tube. The elements, ruthenium, rhodium, palladium, molybdenum, and niobium, remain largely in the metal phase.

On the basis of macro analyses of the inactive constituents, the reproducibility of the runs was very good. Reproducibility of results for the radioactive species is not as good. Some of the discrepancies may be ascribed to method of analysis rather than to any difference in the response of active and inactive species to the oxidative slagging technique. However, except for the ingot analyses for radio-zirconium, the behavior of synthetically added fission product and its radio-counterpart which originated in fission are essentially the same. This constitutes reasonably good evidence that inactive fission product stand-ins may be used to provide fission product concentrations, whose attainment would otherwise require high burn-up of reactor fuel. The confidence which can be placed on results with inactive fission products will allow the bulk of the development work to be performed at low radiation levels.

Ingot metal dissolution was relatively easily accomplished with aqua regia. Skull dissolution was considerably more difficult and involved the following sequence of steps:

- (1) Overnight cook in aqua regia.
- (2) Solution made 0.2 M in HF and 0.3 M in $\text{Al}(\text{NO}_3)_3$ at room temperature. Conditions maintained for two hours.

*These operating conditions were described in ANL-5422, pages 78 et seq. They consist of prior degassing of crucibles and other components at a temperature of 1000 C for 1/2 hour in a 6-inch diameter by 29-inch high Vycor tube. The vacuum is broken with purified helium, and after cooling the metal is charged. The contents are again degassed to a pressure of 10^{-4} mm at a temperature of 600 to 800 C. The vacuum is broken with helium and the temperature increased slowly to about 1200 C. The molten metal is held at this temperature for four hours and bottom-poured into a graphite mold.

Table 14

MATERIAL COMPOSITIONS AND BALANCES FOR
OXIDATIVE SLAGGING RUNS

Apparatus: Schematic Diagram shown in ANL-5388,
page 48, modified by bottom pour
fusible plug

Run No.	Material Charged (grams)					Charge Distribution (%)		
	Clinton ^a Slug	U-Ce ^b Alloy	Fissium ^c	Natural U	Total	Remaining in Crucible	Poured Ingot	Total
A-2	160	343	101	1249	1853	7.5	92.0	99.5
A-3	119	319	97	1453	1988	7.5	93.9	101.4
A-4	191	312	86	1765	2354	5.0	94.9	99.9

^a Clinton slug irradiated to 65 g of plutonium per ton of uranium

^b 0.35 w/o cerium

^c Contained following concentrations (w/o) of elements:
Ru = 2.48, Zr = 1.63, Mo = 1.63, Pd = 1.36, Rh = 0.05, Nb = 0.04

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Table 15

DISTRIBUTION OF ELEMENTS IN OXIDE SLAGGING RUNS

Crucible: Magnesia

Liquation Conditions: 4 hours at 1200 C

Apparatus: Schematic Diagram shown in ANL-5388, p. 48,
modified by bottom pour fusible plug

Constituent	Distribution of Constituent (%)					
	Ingot		Skull		Total Accounted For ^a	
	A-2	A-3	A-2	A-3	A-2	A-3
Uranium	92.0	93.9	7.5	7.3	99.5	101.2
Plutonium	90.0	83.5	6.9	5.6	96.9	89.1
Gross β Activity	8.1	14.5	66.7	74.2	76.4	92.8
Gross γ Activity	26.6	27.2	25.7	33.0	62.9	68.4
Total Rare Earths (FP) ^b	1.7	3.6	74.8	85.6	76.5	89.2
Cerium (Inactive)	2.9	3.4	100.0	95.2	102.9	98.6
Zirconium (FP)	11.3	25.3	77.5	82.5	88.8	107.8
Zirconium (Inactive)	35.2	34.4	70.8	67.0	106.0	101.4
Niobium (FP)	86.1	(161)	15.8	24.5	101.9	
Ruthenium (FP)	99.4	82.1	6.1	4.2	105.5	86.3
Ruthenium (Inactive)	99.2	98.9	5.6	5.0	104.8	103.9
Strontium (FP)	3.4	8.9	40.3	33.4	44.5	62.1
Cesium (FP)	3.7	9.6	23.3	46.4	54.7	78.4
Tellurium (FP)	11.7	25.3	77.5	82.5	88.8	107.8
Molybdenum (Inactive)	102.0	101.1	6.3	4.6	108.3	105.7
Palladium (Inactive)	101.8	100.1	7.1	5.1	108.9	105.2

^aIncludes additional activity found on radiation shield, Vycor tube, and crucible. Volatilized activity consisted mainly of cesium and strontium.

^bFP = fission product activity.

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- (3) Solution filtered through fine sintered glass filter and small amount black residue treated with 5 per cent NaOCl.
 - (4) Black residue boiled in aqua regia for 45 minutes.
 - (5) Solutions combined and sampled.

b. Improvement of Product Yields

Attempts are being made to increase product yields by (1) crucible design (increase pitch of surfaces over which uranium must drain and decrease surface-to-volume ratio), (2) increase in pouring temperature to increase fluidity of the molten uranium, and (3) re-use of crucible in the hope that uranium loss by adherence to the crucible walls by a melting action will occur only on the initial use of the crucible. The first and third methods have been investigated in a preliminary fashion.

By re-use of the crucible, product recovery increased in conventional runs (2 kg of metal; metal held molten for four hours at 1200 C) from 92.1 per cent in the initial use to 98.5 per cent on the second use. This indicates improvement in product recovery to have been effected by crucible re-use.

In order to ascertain the effect of crucible re-use on fission product decontamination, the uranium charges contained synthetically added cerium and zirconium in concentrations corresponding to 0.1 and 1 per cent burn-up of fuel atoms, respectively. No analytical information has been received on this last point.

A product ingot yield of 98.5 per cent of normal uranium (no added fission products) was realized on first use of crucible which had the bottom pour hole tapered and enlarged from 3/8 to 1/2 inch in diameter. This compares with a recovery of 96.2 per cent in an unaltered crucible.

Future runs for the purpose of improving product yield and simultaneously checking fission product decontamination will be made with the **fissium** supplied by Sylvania Electric Products, Inc. This is uranium in which fission products in concentrations equivalent to 2 per cent burn-up of total fuel atoms have been added by powder metallurgy techniques.

c. Ingot Quality Control in Oxide Slagging Processes

An investigation of the variables and the definition of their role in affecting the quality of the ingots produced in oxide slugging processes has been initiated. The experiments will be conducted in apparatus which has provision for sampling the inert atmosphere before entering and after leaving the slagging furnace and provision for adding known amounts of gas contaminants.

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The following areas will be investigated:

1. The effect of measured quantities of oxygen, nitrogen, and water vapor in inert atmospheres in order to define the limiting quantities of the gaseous contaminants which can be permitted under flowing and static atmospheres.
2. Degassing techniques necessary for satisfactory ingot production for both ceramic and graphite refractories.
3. Materials for mold construction.
4. Casting techniques, e.g., heated and cooled molds.

2. Oxide Composition of Pyrometallurgical Slags (D. Miller)

Metal-oxide mixtures (slags) remaining in crucibles after pouring of the metal have been analyzed for their oxide concentration. These slags are about 20 per cent uranium dioxide by weight with indications that the oxygen is taken up preferentially by elements other than uranium in systems containing cerium and zirconium.

In a pyrometallurgical process wastes occur in the form of slags and skulls. The economic recovery of fissionable material from these wastes appears to be important under the present cost structure. A factor which is important in determining the nature of such a recovery process is the oxide-to-metal ratio in the wastes.

A technique has been developed for the analysis of the oxygen in various materials.⁵ For the slag or skull, this technique involves dissolving a weighed sample in BrF_3 which reacts with the metals and oxides to yield metal fluorides, bromine and oxygen. For uranium and uranium oxide, the reactions are:

If these reactions are carried out in a system of known volume and the pressure of the oxygen evolved measured, it is possible to determine

⁵H. R. Hoekstra, and J. J. Katz, AECD-3549

the amount of uranium oxide originally present. If other elements are present as metals and oxides, similar reactions will occur. It will not be possible, however, to tell how much of each is present as metal and as oxide in such a mixture but only how much oxygen is present.

An apparatus was constructed of nickel, to resist attack by the halogens, for the purpose of carrying out the oxygen analysis and is shown in Figure 9.

Several samples from the oxidative slagging experiments have been analyzed for oxygen content. Slag from the stopper rod of a natural uranium run (U-2) gave 12.7 per cent uranium dioxide. Slag pried from the walls of the crucible used in this experiment tested 19.7 per cent oxide. A portion of the skull from the bottom of the crucible showed only 4.1 per cent oxide.

Slag from a run in which the charge was natural uranium containing 0.2 weight per cent zirconium and 0.05 weight per cent cerium (U-4) contained the equivalent of 19.4 per cent uranium dioxide.

Two measurements have been made on slag from an active Run A-2.* Powder from the crucible had a very high oxygen content, calculating as 3.20 g uranium dioxide on a 2.62 g sample. This indicates that oxygen is present as oxides of the metals other than uranium. Another possibility is that some magnesia from the crucible was included in the sample. Another sample, cut from the skull, gave 26.4 per cent uranium dioxide by weight. A third sample from lower in the skull was 22.4 per cent uranium dioxide by weight.

A sample from active Run A-3* at the top of the skull near the interface gave 65.2 per cent as uranium dioxide by weight while a sample from near the pour hole gave 98.1 per cent as uranium dioxide. A small sample from Run A-4* measured as 0.564 g uranium dioxide from a 0.485 g sample.

3. Extraction of Plutonium by Liquid Magnesium

Work is progressing in the semi-works on problems connected with isolation of plutonium from blanket or core material by magnesium extraction. In such a process, the plutonium would be recovered from the magnesium extract by distilling the magnesium away from the extracted plutonium and any uranium which may have accompanied it. Scale-up of extraction and distillation equipment is now underway. In a study which was completed, good phase separation was demonstrated by solidifying the uranium phase and pouring off the molten magnesium. The separated uranium

*Compositions of materials charged in this runs are given in Table 14, page 49.

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FIGURE 9
OXYGEN MEASUREMENT APPARATUS

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phase contained 10 to 20 ppm of magnesium. Data for the uranium content of the magnesium phase vary widely (26 to 14,700 ppm) and are inconclusive. Testing of various materials for use with the magnesium-uranium system continued.

a. Scale-up of Magnesium Extraction and Distillation Equipment
(I. O. Winsch, W. H. Spicer)

Design details are being worked out for a tantalum-lined, type 310 stainless steel batch extraction unit capable of handling together 5 kg of uranium and 5 kg of magnesium. Completion of the design and fabrication of this unit will require at least three months.

A magnesium distillation unit has been fabricated to study the feasibility of condensing magnesium as a liquid and piping the condensate to a collection vessel for recycle (Figure 10). It will be set up and tested in the next quarter.

b. Separation of Uranium and Magnesium Phases
(J. Wolkoff, W. H. Spicer, V. N. Thelen)

Further work has been done on the separation of molten magnesium from a once-molten but intentionally solidified uranium phase by pouring off the magnesium. As shown in Table 16, the average concentration of magnesium adhering to the uranium ranged from 0.35 to 1.3 g of magnesium per sq in. of total uranium surface (magnesium coated the entire uranium surface). These values are very low and indicate a negligible potential hold-up of magnesium. If other separating techniques which are now being considered (i.e., withdrawing the magnesium by vacuum or allowing it to flow by gravity through pipes) are employed, a magnesium heel of the order of 5 to 10 per cent of the magnesium charge may be deliberately left behind.

The experiments were performed in graphite and recrystallized alumina crucibles in the induction-heated, sealed steel capsules described in ANL-5422, page 82. A helium atmosphere was employed after evacuation and purging of the capsule. The magnesium and uranium charges were held for varying times at 1175 C during which periodic shaking was employed to break the continuity of any skins. After cooling to 750 C, the assembly was inverted to pour off the magnesium from the solidified uranium.

Attempts were made to determine the uranium content of the magnesium phase. However, the values scatter considerably, ranging from 26 to 14,700 ppm (Table 16). The value reported in ISC-377⁶ is 600 ppm

⁶Tracy, G. A., P. Chiotti, H. A. Wilhelm, "Magnesium-Uranium Alloy System," ISC-377.

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FIGURE 10
SCHEMATIC OF MAGNESIUM DISTILLATION UNIT

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of uranium in magnesium. As may be seen, a number of sampling methods were used, and the analyses point to lack of homogeneity throughout the magnesium ingot. Metallographic examinations did not disclose a uranium-rich phase.

The magnesium content of the uranium phase as determined by spectrographic analyses ranged between 10 and 20 ppm, except for two surface samples in which a value of >1000 ppm was reported (Table 16). Faulty sampling or the presence of magnesium or magnesium oxide inclusions may account for the high values. The concentrations of 10 to 20 ppm compare satisfactorily with a maximum concentration of 40 ppm reported in ISC-377.⁷

The likelihood of magnesium contamination of uranium particularly in those samples obtained near the surface is shown by the photomicrographs in Figure 11. (The inclusions along the top of this uranium ingot which was melted in a graphite crucible appear to be metallic magnesium.) The upper one-third of the ingot contained the "peppery" appearing black inclusions which are thought to be liquated uranium carbides. The bottom of the ingot contained the relatively sparse angular inclusions shown in Figure 12. This is also the appearance which prevailed throughout the uranium ingots from runs made in recrystallized alumina crucibles. Magnesium surface inclusions were not apparent in the ingots from the recrystallized alumina runs.

c. Materials of Construction for Molten Magnesium and Uranium
(W. Seefeldt, L. Hays, L. Marek)

Testing of possible materials of construction for magnesium and uranium at 700 C and 1150 C continued. Evaluations reported are qualitative only, and are based on visual inspection. Emphasis was placed on testing ceramic materials, and on the development of film layers that might be protective. The wetting of crucible walls by magnesium appears to be more pronounced with increasing temperature. With high density magnesia and magnesium fluoride-bonded magnesia, the wetting of the crucible wall by magnesium was sufficiently good to provide a two to four mil barrier between the uranium and the crucible wall. Improved samples of high density magnesia, and of magnesium fluoride-bonded magnesia exhibit little magnesium penetration at 700 C, and less penetration at 1150 C than earlier samples. A tabular summary of completed runs is shown in Table 17.

Three testing methods were utilized: (1) the evacuated metal capsule technique, (2) covered crucibles, and (3) elongated crucibles in which the upper section was used as a magnesium condenser. A resistance furnace was used in all runs. Temperatures at top and bottom of capsules and crucibles were monitored.

In two runs made with magnesium and uranium at 1150 C, the magnesium provided a layer that appeared to separate the uranium from the

⁷ Ibid

Table 16

SEPARATION OF MAGNESIUM AND URANIUM IN SEALED CAPSULES

(By pouring magnesium off solidified uranium at 750 C)

Charge (gm)		Materials		Time at ~1175 C (min)	Conc of Elements		Surface Density of Mg on U, (gm/sq in) ^b
Magnesium	Uranium	Crucible	Mold		U in Mg (ppm) ^a	Mg in U (ppm) ^a	
154	69.2	Graphite	Graphite	11	26	> 1000 ^a	0.9
396	118.5	Graphite	Graphite	25	26	--	1.1
393	75.4	Graphite	Graphite	31	42	> 1000-Top Half 15-Bottom Half	0.7
367	42.3	Al ₂ O ₃ ^c	Graphite	20	{ 142 3100 ^a	{ 20-Top Half 15-Bottom Half	0.35
208	35.0	Al ₂ O ₃ ^c	Mild Steel	45	{ 1,310-Outer Rad 14,700-Inner Rad 8,940-Top ^a	--	1.3
299	30.3	Al ₂ O ₃ ^c	Stainless Steel	75	{ 109-Outer Rad 80-Inner Rad	10-Bottom Half	1.2

^aOutside surface removed from every sample except those designated with superscript a.^bSurface density expressed as grams of magnesium/sq in of total uranium surface.^cMorganite Triangle RR grade of recrystallized alumina.

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Figure 11

TOP SECTION OF URANIUM MELTED IN GRAPHITE CRUCIBLE AFTER POURING
OFF MAGNESIUM LAYER

(4 x)

Note the magnesium inclusions
along the top surface.

100x

Gray portion in upper left hand corner is a magnesium
inclusion. Fine black inclusions are thought to be
liquated carbides.

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Figure 12

BOTTOM SECTION OF URANIUM MELTED IN
GRAPHITE CRUCIBLE AFTER POURING OFF MAGNESIUM LAYER

(100 x)

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Table 17

CORROSIVE EFFECTS OF URANIUM AND MAGNESIUM IN VARIOUS CONTAINER MATERIALS

Run and Capsule Number	Liner and Capsule Material	Temperature (C)	Time (Hours)	Metals	Observations ^a
28-22	Morganite in 420 stainless	1150	5.7	Mg, U	No visible penetration ^a
33-23	Morgan battersea in 1020 steel (high purity alumina)	1150	5.5	Mg	No attack evident; Mg collected unexplained in top of capsule
34-21	430 stainless steel	1150	5.5	Mg	Capsule wall wetted; no visible penetration
35-14	Morganite in 420 stainless (high purity alumina)	1150	6.25	Mg	Capsule wall wetted; no attack
36-17	Graphite in 430 stainless	1150	6.5	Mg	Graphite not wetted; no attack
39-30	Morganite in 1020 steel	1150	24	Mg, U	No U or Mg in crucible; hole in steel wall indicates U attack; no apparent attack on crucible.
40-26	High density MgO in 1020 steel	1150	6.0	Mg, U	No attack visible; scratching sectioned crucible reveals hard, metallic like base indicating Mg penetration; crucible thoroughly wetted by Mg which completely surrounds U in layer 2-4 mils thick
41-27	Same as 39-30	700	6.0	Mg	Crucible wall not wetted; no apparent attack
42-38	Improved MgF ₂ bonded MgO	700	6.0	Mg	No attack, penetration, or wetting
43-39	Same as 42-38	1150	6.0	Mg, U	Mg wetted wall and surrounded U with one to two mil layer; little Mg in crucible; scratch test on sectioned crucible indicates Mg diffusion; no destructive attack evident
44-34	Morganite in 1020 steel	1150	72	Mg	No visible penetration, black coating on crucible wall, including that adjacent to the magnesium was 2 to 2.5 mils thick; wall wetted
45-36	Graphite in 1020 stainless	1150		Mg, U	Early capsule failure by U contact of capsule

^aAll high purity alumina crucibles acquire a black, usually thin, coating on inside and outside.

crucible wall (Runs 40-26 and 43-39). The crucibles were high density magnesia and magnesium fluoride-bonded magnesia. In the former the layer was two to four mils thick, in the latter one to two. Longer tests will be conducted to determine the effectiveness of this layer. In a single long run (72-hour; Run 44-34) with magnesium in Morganite, a black layer 2 to 2.5-mils thick isolating the magnesium from the crucible was observed.

The wetting characteristics of magnesium which probably are important in the above layer formation appear to be a function of temperature in high purity alumina, magnesia, and magnesium fluoride-bonded magnesia. With one exception (Run 35-14 with high purity alumina), the walls were wetted at 1150 C, and not wetted at 700 C. The border temperature in four-to six-hour tests appears to be about 900 C for high purity alumina.

Magnesium penetration of the magnesia crucibles was determined qualitatively by scratching the sectioned crucible. The unpenetrated crucible scratched more easily and had a dull gray appearance as compared to a bright metallic appearance in the penetrated crucible. Runs made at 700 C indicated no penetration, at 1150 C penetration that appeared less than in previous samples.

High density graphite crucibles appear to be previous to magnesium. In three runs magnesium crystals were found on the outside of the crucibles. Graphitite "A", a graphite which has been impregnated with carbon to give a thin imprevious surface layer, appeared to resist magnesium penetration.

4. Component Testing and Development

a. Development of Top Pour Uranium Melting Furnace (G. J. Bernstein, I. G. Dillon, W. H. Spicer)

This quarter was devoted principally to the development and testing of a top pour, uranium melting furnace such as would be used in the semi-works facility referred to in the preceding quarterly report, ANL-5422, page 91. The furnace tested consisted of a stainless steel tank 22 inches in diameter and 21 inches high equipped with an induction coil and tilting mechanism for top pouring the molten metal. A series of eight runs were made in which approximately 2-kg batches of copper or uranium were melted in a variety of crucible assemblies. Yields in these runs varied from 91 to 99 per cent.

The tilting mechanism consisted of a stainless steel frame supported on two bearings and capable of being tilted 100 degrees by means of a cable wound on a drum which was rotated from outside the tank. The crucible and induction coil assembly was held in the frame by means of clamps attached to the base of the frame. The maximum assembly size which would be accommodated was eight inches diameter by approximately 12 inches high. A sketch of the tilting mechanism and one of the crucible assemblies tested is shown in Figure 13.

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FIGURE 13
TILTING MECHANISM AND CRUCIBLE ASSEMBLY
FOR TOP POUR MELTING FURNACE

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In order to permit continuous application of power to the induction coil during the pouring of the melt, power leads entered the furnace through a rotating seal. Connection from these leads were made through flexible water-cooled cables to a 30-Kilowatt, 10-Kilocycle Tocco induction heater.

Temperatures of the melt were read by means of an optical pyrometer or a chromel-alumel thermocouple placed between the graphite crucible and the Alfrax container.

Two shakedown runs were made in a graphite crucible fitted into an Alfrax* crucible holder as shown in Figure 12. These runs were made using copper as the metal charge. Two uranium melting shakedown runs were then made. The first uranium shakedown run was made in a graphite crucible lined with a zirconia crucible. In this run a tough oxide skin was formed on the molten metal and the uranium did not pour. The oxide skin formation may have been due to inadequate degassing which consisted of heating the crucible for two hours at 1200 C in an argon atmosphere. There may also have been reaction between the uranium and the zirconia crucible. The second uranium shakedown run was made in a graphite crucible in which the thermal degassing time was extended to six hours at 1200 to 1300 C in an atmosphere of argon prior to charging the uranium. The uranium poured in this run giving a yield of 94.5 per cent. The ingot was covered with a thin film of oxide. This indicated that successful uranium melts could not be made without adequate degassing of the refractory and crucible holder. Therefore prior to making the subsequent melts, the Alfrax crucible holder was redesigned to permit degassing in a small vacuum induction furnace. Within this holder was a graphite crucible with a magnesium oxide crucible as a liner. This assembly was degassed under vacuum and heated at a pressure of 3×10^{-4} mm at 400 C (0.2 mm at 1150 C). It was then transferred to the melting furnace under argon atmosphere.

A series of five melting runs was then made to determine the effect of repeated use of the same crucible on ingot yield and quality. The melting technique was to heat the uranium to a temperature of 1250 to 1350 C and then pour with no appreciable liquation period. In the final run of the series a liquation period of 100 minutes was employed. The yields from these runs are given in Table 18. These data show the yields increased with re-use of the crucible in short hold runs from 95 per cent in Run 4 to 99 per cent in Run 7. The 91 per cent yield in the 100 minute hold Run 8 was probably due to excess oxide formation; this points out the need for further improvement of the atmosphere in the furnace and the need to eliminate oxygen sources.

Future work will include use of a zirconia crucible holder in place of the Alfrax one in order to improve degassing since it was

*Alfrax is a coarse crystalline alumina powder manufactured by the Carborundum Company. The cement is prepared by mixing with water to form a paste. This cement is then cast to the desired shape, dried and fired.

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Table 18

SUMMARY OF URANIUM TOP POUR CRUCIBLE RUNS

(MgO crucible used within an ATZ graphite crucible equipped with graphite pouring spout.)

Run No.	Charge (g of U)	Total Pour (g of U)	Hold Time (min)	Pouring Temp (C)	Per Cent Pour
4	1820	1729	10	1260	95.0
5	1721	1640	10	1280	95.5
6	1689	1670	10	1350	98.9
7	1880	1866	10	1360	99.2
8	2932	2662	100 ^a	1340	91.1

128 g U found in graphite crucible after Run 8

325 g U + slag in MgO crucible after Run 8

Material balance for series of runs ~100 per cent

^aPower failure interrupted intended four-hour hold.

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found that the Alfrax could not be adequately degassed. Larger crucibles will also be used to permit charges up to 5 kg of uranium. Other crucibles designs are being considered which would eliminate the need for a refractory crucible holder.

Design of Semi-Works Furnace Facility. An improved top pour furnace and auxiliary components are being designed for installation in an active semi-works area. This furnace will be capable of handling full-scale quantities of material and full-scale plutonium concentrations, but only tracer level fission product concentrations will be employed. Full fission product concentrations will be established by the use of fissium, a synthetic mixture of uranium and fission product elements.

The furnace tank is a modified design of the tank used in the runs described previously in this section. The principal changes are provisions for degassing under vacuum, for ventilation and for remote operation. The tank will contain a crucible tilting mechanism which will be removable so that it may be replaced by a bottom-pour type crucible assembly.

Preliminary design of the furnace facility to be used for melting uranium in an inert atmosphere has been made. This design includes an inert gas circulation system for use during melting and pouring operations and a vacuum system for initial degassing and subsequent removal of air prior to inert gas circulation. In addition a ventilation system of 250 cfm capacity will be provided to prevent the escape of airborne activity when the furnace tank is open.

b. Use of Fusible Metal Valve for Bottom Pouring Uranium
(D. C. Hampson, V. N. Thelen)

The use of a fusible metal valve crucible described on page 50 of ANL-5388 has been proposed as a method of bottom pouring a molten metal. In this arrangement a hollow stem or leg is attached to the bottom of the crucible. By cooling the stem, a plug of solidified metal may be maintained in the stem even through the metal in the crucible is molten. The metal plug is melted to pour the metal.

In the past quarter, tests were made of two ATZ graphite crucibles which had been coated on the inside with a 15 to 20-mil layer of alumina by the Norton Co. The inside of the stem was not coated. Four successive 2 kg-scale runs in which the metal was held molten for four hours were made in one of the crucibles. Five successive 2-hour-hold runs were made in the other. Metal failed to pour in the final run of each series. The alumina coating appeared to be unattacked after 16 hours contact with molten uranium.

The yields of product ingots in the runs in which metal pouring occurred averaged 95.3 per cent. The average ingot yield for the first runs in the crucibles was 93 per cent. This compares with values of 77 per cent for the first use and average yield values of 91.3 per cent for a series of four runs in uncoated graphite crucibles (metal held molten for four hours).

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The solidified uranium remaining in the crucible legs (from the final runs in which no pour of metal was realized) was removed and samples analyzed for carbon content. The average carbon content was 825 ppm. The carbon content of the surface layer was 2400 ppm. It is thought that the high carbon concentration of the surface layer raising the melting temperature sufficiently that melting of this material did not occur and prevented pouring. New graphite crucibles have been obtained in which both the crucible and valve sections are coated with alumina. These crucibles should eliminate the difficulty now experienced with carbon contamination.

c. Molten Metal Sampling
(D. C. Hampson, V. N. Thelen)

A "Leco Sampling Gun" was tested for sampling molten uranium. The sampler applies a vacuum on a Vycor tube which is inserted momentarily into the molten metal. Reproducible samples, 1/2 to 3/4 inch long, 1/16 inch diameter, weighing about 0.75 gram each were taken. Larger samples can be taken more easily.

d. Inert Gas Purification
(I. G. Dillon, G. J. Bernstein)

A testing apparatus is being set-up to determine the efficiency of various types of inert gas purification devices. The first type of device to be tested will be "getter" furnaces. Initially hot (600 to 800 C) uranium will be used as the getter. Later, it is planned to investigate the use of calcium and barium as "getters". The efficacy of dryers and cold traps as purifying methods will also be evaluated.

B-5. Design of Pilot Plant for Processing EBR-II Fuel by Pyrometallurgical Process
(D. C. Hampson)

Conceptual drawings and sketches have been made of both the equipment layout and of remote materials handling equipment for the EBR-II fuel processing pilot plant.

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V. Fluidization Studies

(A. A. Jonke)

Additional studies on the continuous denitration of uranyl nitrate were devoted to determining the effect on process operability of varying amounts of sulfate ion in the feed. No further work on this process is planned for the immediate future, since it is felt that sufficient data has been accumulated to permit the design of a large-scale unit.

A number of runs were made to determine the effect of variations in the conditions of the reduction step on the rate of hydrofluorination of uranium dioxide. Carbon monoxide and methanol were investigated as alternative reductants for uranium trioxide. The effect of reduction temperature on the subsequent hydrofluorination step was studied. The results indicate that the reactivity of uranium trioxide produced by fluid-bed denitration may be high under the proper operating conditions.

The development of the waste calcination process was continued in the pilot-scale reactor. No operating difficulties were encountered, but particle size growth occurred.

Work was continued on (1) the development of a multistage reactor for countercurrent gas-solid contacting, and (2) fundamental studies of particle behavior in a fluidized bed.

Consultations were held with personnel at Mallinckrodt Chemical Works.

A. Continuous Denitration of Uranyl Nitrate
(E. Petkus, M. Jones)

Much of the work on the fluid-bed denitration process has been directed toward determining the effect of operating variables on particle size growth in the fluidized bed. For continuous operation it was considered necessary that the particle size reach a steady state value, since persistent growth would eventually cause caking. For simplicity of operation it was desirable that a steady state be attained without the necessity of recycling fine particles of uranium trioxide to the bed.

Previous experiments (ANL-5422, pages 96 to 103) had shown that the correct choice of operating conditions, particularly with regard to feed concentration and denitration temperature, was necessary in order to avoid particle growth. Work during the past quarter has indicated that the amount of sulfate ion added to the uranyl nitrate feed may also have an effect on particle growth.

In the early part of this quarter several runs were made primarily to prepare uranium trioxide for subsequent process steps. It was noted that excessive particle growth had occurred in these runs, and in some cases large lumps had formed in the bed. A series of runs were then made

in an effort to determine the cause of the maloperation. Eventually the cause was determined to lie in the uranyl nitrate feed.

The feed for most of the denitration runs had been prepared by redissolution of the uranium trioxide product of previous runs in nitric acid. This recycling of the uranium had caused an increase of impurities in the feed due to corrosion and contamination. Moreover the sulfate concentration of the feed had increased to about 2000 ppm based on uranium (including the 1200 ppm which were added during each dissolution of the trioxide).

For comparative purposes several runs were made using a new feed (MCW uranyl nitrate solution) to which only 800 ppm of sulfate was added. The results of this series of denitration runs showed that good operability was obtained whenever the new feed was used, but poor operability was obtained whenever the recycled feed solution was used. These results are summarized in Table 19. The data also show that the recycled feed (2000 ppm sulfate) yields a product containing between 1080 and 1840 ppm sulfate and having a bulk density between 3.4 and 3.8 g/cc. The new feed (800 ppm sulfate) yields a product containing between 5 and 45 ppm sulfate and having a bulk density of 4.0 to 4.1 g/cc.

Spectrographic analyses were performed on the uranium trioxide product from Runs 69 and 75, which were made with the two types of feed. The results (Table 20) reflect the appreciably higher product impurity level when recycled feed is used as compared to new feed. For those elements listed in Table 20, the product from Run 69 contained a total of 200 ppm as compared to 36 ppm for Run 75.

It is believed that the differing results obtained with the two types of feed is primarily due to the difference in sulfate content. The presence of other impurities is less likely to have an effect, since the total concentration of these elements is an order of magnitude lower than the sulfate content. The results of work at Hanford⁸ have indicated that sulfate ion increases the rate of denitration of uranyl nitrate. Thus it is possible that sulfate concentration affects particle growth in a manner similar to feed concentration and bed temperature. In other words those factors which increase the rate of denitration also increase the rate of particle growth in the fluidized bed process.

No further work on the denitration process is planned for the immediate future. The equipment is now being used for the development of a process for calcination of reactor fuel processing waste. It is felt that the fluidized-bed process for denitration of uranyl nitrate is now on a sound basis, and that only a minimum of additional work is required in order to design a full-scale unit.

⁸Moore, R. H., Factors Affecting the Reactivity of Uranium Trioxide, Hanford (HW-31670)

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EFFECT OF SULFATE CONTENT OF FEED ON PROCESS OPERABILITY

Feed Concentration: 70% UNH

Bed Temperature: 310 C

Run No.	Type of Feed	Sulfate in Feed ^a (ppm)	Sulfate in Product ^a (ppm)	Bulk Density of Product (g/cc)	Process Operability
68	recycled ^b	d	830	3.4	Excessive particle growth; lumps
69	recycled	2000	1840	3.5	Excessive particle growth
70	new ^c	800	45	4.0	No growth
71	recycled	2000	1200	3.8	Excessive growth; lumps
72	recycled	2000	1080	3.6	Excessive growth
73	new	800	8	4.0	No growth
74	new	800	5	4.0	No growth
75	new	800	10	4.1	No growth

^aSulfate content given as parts per million based on uranium.^bRecycled feed is prepared by re-dissolution of product UO_3 ^cNew feed is MCW uranyl nitrate solution^dThis feed was not analyzed for sulfate; 1200 ppm were added

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Table 20

IMPURITIES IN URANIUM TRIOXIDE PRODUCT

Element	Concentration in UO_3 (ppm)	
	Run 69 ^a	Run 75 ^b
Al	10	5
Cr	15	2
Cu	10	3
Fe	60	3
Mg	30	2
Ni	30	5
Pb	30	1
Si	<u>15</u>	<u>15</u>
Total	200	36

^aMade with recycled feed^bMade with new feed

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B. Reduction and Hydrofluorination
(N. Levitz, H. Katz, K. Olsen)

Previous experiments (ANL-5422, page 103) had shown that uranium trioxide produced by fluid-bed denitration had a low reactivity. The addition of sulfate ion to the uranyl nitrate solution before denitration increased the reactivity appreciably, but the rate of the subsequent hydrofluorination reaction, especially in the later stages of conversion, was much slower than desired.

During this quarter, work was directed toward determining the effect on reactivity of variations in the conditions of the reduction step. In previous runs the uranium trioxide had been reduced with hydrogen at 700 C prior to hydrofluorination. It was thought that a substantial decrease in the reduction temperature might have a favorable effect on reactivity. Since hydrogen reacts but slowly with uranium trioxide at temperatures below 500 C, the use of other reductants was considered. Carbon monoxide and methanol are economical reducing agents, and these were chosen for testing. Natural gas and coke-oven gas were tested by early workers, but were discarded because they produced carbon deposits in the reactor.

1. Laboratory-Scale Experiments

Preliminary experiments with carbon monoxide reductant were made in the 1-inch diameter nickel tube reactor used for the standard reactivity tests. An attempt was made to determine the temperature necessary for complete reduction of uranium trioxide using carbon monoxide. The results obtained ranged from 33.6 per cent conversion at 350 C to 94.7 per cent at 600 C. It was later found (see next section) that the uranium dioxide produced by low temperature reduction reacts considerably with air at room temperature. Since the above samples were exposed to air before analysis, it is likely that the percentage reduction was substantially greater than that indicated by the analyses.

In the course of this work it was noted that appreciable deposition of carbon on the nickel tube had occurred, due to decomposition of the carbon monoxide. Since nickel is a catalyst for this reaction,⁹ it was decided to perform further experiments in a Vycor tube using an alundum boat. This apparatus greatly reduced the amount of carbon deposited. In the absence of a catalyst the decomposition of carbon monoxide appears to be slight, since only very small amounts of carbon were noticeable in spite of the large excess of carbon monoxide used.

A few hydrofluorination experiments were performed in the nickel tube using uranium dioxide prepared by carbon monoxide reduction. The results obtained, though not highly reproducible, were sufficiently encouraging to warrant further work on a larger scale. Additional runs were

⁹Ephraim, F., "Inorganic Chemistry," 4th Ed., page 783, Edinburgh, Scotland (1943)

therefore made in bench-scale equipment as outlined in the following section.

2. Bench-Scale Experiments

a. Procedure

For the runs reported in this section the following procedure was used except where otherwise noted. The reduction step was carried out for four hours at the specified temperature using a large excess of reducing gas (five to ten times the stoichiometric amount). The hydrofluorination step was carried out at 450 C using a flow rate of hydrogen fluoride equivalent to one stoichiometric amount in two hours. The duration of hydrofluorination varied from four to twelve hours as noted. All of the runs were made batchwise using a fluidized bed. The flowrate of the fluidizing gas, including reactant and nitrogen diluent, was 0.4 to 0.5 ft/sec at the bed temperature and pressure.

b. Carbon Monoxide Reductant

Since the laboratory-scale experiments indicated that the reduction step might be carried out at moderately low temperatures using carbon monoxide, a 2-inch diameter, fluidized-bed reactor was built from brass pipe to study the reaction on a somewhat larger scale. (The Monel reactor was not used because nickel is a catalyst for carbon monoxide decomposition.)

Two exploratory batch runs were made using about one-kilogram amounts of uranium trioxide. The first run at 350 C gave essentially no reduction, the uranium trioxide being almost unchanged in color. The second run was made at 550 C. The product from this run, after cooling overnight in a nitrogen atmosphere, was poured into a tray for sampling. Within a few minutes after exposure to air the brown oxide began oxidizing to black U_3O_8 . Considerable heat was evolved, and a thermocouple placed in the batch registered a maximum temperature of 270 C. A sample taken at the start of the oxidation reaction analyzed 85.4 per cent dioxide, and a sample of the black oxidized material analyzed 66.9 per cent dioxide. Thus it was evident that dioxide produced by this method was considerably more reactive, at least toward oxygen, than that produced by hydrogen reduction at 700 C.

Because it was apparent that exposure of the reduced oxide to air must be avoided, it was decided to conduct consecutive reduction and hydrofluorination runs without intermediate cooling and sampling. For this purpose it was necessary to use the 3-inch diameter Monel reactor even though some decomposition of the carbon monoxide reductant would occur due to the presence of nickel. Two runs were made using about four-kilogram amounts of uranium trioxide. In Run RF-8 a reduction temperature of 580 C was used followed by a 4-hour hydrofluorination period. Run RF-10 was similar except that the reduction temperature was 500 C and the hydrofluorination period was twelve hours. The results of the two runs are shown in Table 21, together with data from an earlier run in which the reduction step was carried out with hydrogen at 700 C. It is apparent that

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Table 21

EFFECT OF REDUCTION CONDITIONS ON RESULTS OF HYDROFLUORINATION RUNS

Reduction: 4-hours at indicated temperature; large excess of reductant.
Hydrofluorination: 450 C, HF flow rate = one stoichiometric amount per 2 hours.
Equipment: 3-inch diameter fluid-bed reactor.

Run No.	Reducing Agent	Reduction Temp (C)	Hydrofluorination			
			4-Hours		8-Hours	
			UF ₄ (%)	AOI (%)	UF ₄ (%)	AOI (%)
RF-5	H ₂	700	73.5	25	88.2	11.7
RF-8	CO	580	84.3	12.9	-	-
RF-9	CH ₃ OH	480	98.5	1.8	-	-
RF-10	CO	500	83.5	14.5	85.7	10.5 ^a

^aAOI (ammonium oxalate insoluble) reduced to 8.4 after 12 hours.

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the carbon monoxide-reduced material was moderately reactive during the initial 4-hour hydrofluorination period. Approximately 85 per cent conversion to uranium tetrafluoride was achieved in this period for Runs RF-8 and RF-10. However, additional hydrofluorination of the material from RF-10 resulted in only a slight additional conversion. After a total of 12 hours of hydrofluorination, 8.0 per cent of unconverted uranium dioxide was present. The change in reaction rate which occurred after about 85 per cent conversion of the oxide may be due to one of the following causes: (1) the uranium dioxide consisted of a mixture of reactive and unreactive material, or (2) partial sintering of the individual particles occurred during the rapid initial hydrofluorination reaction. To resolve this point additional runs are necessary.

To determine the amount of carbon which might be present in the product as a result of carbon monoxide decomposition, an analysis was made on the uranium dioxide produced in the 2-inch diameter brass unit. The result showed 80 ppm carbon. Though carbon is an undesirable impurity, this amount may be tolerable.

c. Methanol Reductant

An exploratory run using methanol vapor for reduction was made in the 2-inch reactor. The liquid methanol was fed by a small metering pump into the gas pre-heat furnace, where it was vaporized and mixed with an equal volume of nitrogen and used to fluidize the bed of uranium trioxide. After reduction, samples of the oxide were removed and analyzed without exposure to air to avoid oxidation. After 3.5 hours at 380 C the bed contained 43.5 per cent dioxide; after an additional 2 hours at 415 C the bed contained 83.6 per cent dioxide. The relatively high conversion obtained at these low temperatures indicated that methanol was a strong reducing agent for uranium trioxide. However, an analysis of the product showed an excessive amount of carbon (700 ppm).

For comparative purposes one hydrofluorination run (RF-9) was made with methanol-reduced oxide. The reduction was carried out at 480 C, and followed by a 4-hour hydrofluorination. The product from this run was found to be caked into a solid mass and was black in color, the latter indicating the presence of considerable carbon. Analysis of this material gave 74.6 per cent U^{+4} , 21.5 per cent F, and 1.84 per cent AOI (ammonium oxalate insoluble). An X-ray diffraction analysis showed no indication of a crystalline component other than uranium tetrafluoride. The low AOI indicates that the oxide was highly reactive, which may account for the caking. It is very likely that caking could have been avoided by the use of a higher fluidizing gas flow rate to increase agitation and dissipate the heat of reaction more rapidly.

d. Hydrogen Reductant

Since the runs made with carbon monoxide and methanol as reductants indicated that an improvement in reactivity toward hydrofluorination was obtained by low temperature reduction, several runs were made to compare the efficacy of hydrogen at various reduction temperatures. In the four

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runs completed, the reduction temperature was varied from 525 C to 700 C. The reduction was complete in all cases, since analyses of the product after hydrofluorination showed less than 0.1 per cent water soluble content (uranyl fluoride). Hydrofluorination was carried out for periods ranging from four to ten hours. The results are listed in Table 22 and plotted in Figure 14.

The rate of hydrofluorination was not noticeably affected by variations in reduction temperature between 525 C and 575 C. At these temperatures the product contained about 5 per cent AOI after four hours of hydrofluorination. A reduction temperature of 700 C had a pronounced effect on the hydrofluorination reaction. At this temperature the AOI ranged from 21 to 33 per cent after four hours of hydrofluorination.

Specification grade uranium tetrafluoride (maximum 1.5 per cent AOI) was produced after 10 hours of hydrofluorination in Run RF-11, and in 8 hours in Run RF-12.

e. Discussion

It is now apparent that the rate of hydrofluorination of the uranium dioxide used in this work is strongly influenced by the temperature at which the reduction step is carried out. The reasons for this can only be surmised at the present time. British workers¹⁰ have found a correlation between the reduction temperature and the surface area of the uranium dioxide. Their findings show that high reduction temperatures cause the primary particles composing the oxide agglomerates to sinter together forming larger particles. A second possibility is that high reduction temperatures might have a tendency to remove partially the beneficial effect of sulfate treatment by annealing out strains which may have induced in the crystal lattice by the sulfate ion.

Previous work had indicated that the uranium trioxide produced by fluid-bed denitration had a low reactivity toward hydrofluorination. The results obtained during this quarter indicate that the reactivity of this material may be considerably higher than was formerly thought. It is becoming apparent that any measure of reactivity by a standard reactivity test which determines the extent of hydrofluorination under a single set of conditions, may give a completely false result.

The use of reductants other than hydrogen for production of uranium dioxide does not appear highly attractive. Though carbon monoxide and methanol will reduce uranium trioxide at somewhat lower temperatures than will hydrogen, the formation of a slight amount of carbon through decomposition would be difficult to avoid. Since encouraging results were obtained by hydrogen reduction at 575 C, further work on alternative reductants does not seem warranted.

In future runs it is planned to investigate the effect of hydrofluorination temperature on the rate of reaction. Following this work a series of continuous runs is planned to demonstrate the process more completely.

¹⁰ Anderson, J. S. et. al., The Properties and Microstructure of Uranium Dioxide, Harwell (AERE-C/R-866)

Table 22

EFFECT OF REDUCTION TEMPERATURE ON RESULTS OF HYDROFLUORINATION RUNS

Reduction: 4-hours with hydrogen gas at indicated temperature.
 Hydrofluorination: 450 C, HF flow rate = one stoichiometric amount per 2 hours.

Run No.	Reduction Temp (C)	Hydrofluorination			
		4-Hours		8-Hours	
		UF ₄ (%)	AOI (%)	UF ₄ (%)	AOI (%)
RF-3	700	75.0 ^a	21 ^a	89.0 ^a	9.8 ^a
RF-5	700	73.5 ^a	25 ^a	88.2 ^a	11.7 ^a
RF-11	575	93.2	5.0	97.2	2.2 ^b
RF-12	575	98.5	2.5	99.8	0.26
RF-13	525	94.2	5.1	-	-
RF-14	700	64.2	33	-	-

^aThese values obtained by interpolation from Figure 14

^bAOI reduced to 1.4 per cent after 10 hours.

FIGURE 14

EFFECT OF REDUCTION TEMPERATURE
ON RATE OF HYDROFLUORINATION.

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C. Multistage Fluidized-Bed Reactor
(J. Graae*)

Efforts to develop a multiple-stage fluid bed reactor have been continued. The desirability of such a unit for countercurrent contact between gas and solid is readily apparent, since it would permit smaller excesses of reactant gases without the necessity of using several reactors in series.

The original multistage design was described in an earlier report (ANL-5333, pages 88 to 91). This reactor consisted of three stages, one above the other, the beds being supported by perforated plates and interconnected by downcomers. This unit operated successfully in several reduction runs, but there was a tendency for the perforated plates to become partially plugged with solids after long operation. Enlarging the holes in the plates eliminated the plugging but decreased the quality of fluidization seriously.

Several alternative designs have been tested using a glass column for visual observation and using air and sand as the gas and solid phases. A design which has appeared promising in preliminary tests is that shown schematically in Figure 15. A conically shaped bed is used so that the fluidizing gas enters through a single large hole at the bottom of the cone. A small baffle below the hole prevents the bed from emptying when the gas flow is turned off. The solids overflow to the bed below through a downcomer in the usual manner.

The quality of fluidization appears to be good in this unit on the basis of visual observation. Some additional work on the design of the downcomer is necessary to prevent cycling of solids up the downcomer at high gas flow rates.

D. Fundamental Fluidization Studies
(H. Katz, T. Cannon)

Studies of steady state particle distribution in beds of wide particle size range have been continued. A number of exploratory runs were made in an effort to perfect the experimental technique and check the reproducibility of the data.

The technique finally adopted was as follows. A mixture of glass beads, consisting of 66 per cent 20-40 mesh and 34 per cent 140-200 mesh, was thoroughly mixed and fluidized for two minutes at a number of different air flow rates in a two-inch lucite column after which the air flow was very rapidly shut off. Hot gelatine solution was then carefully poured into the bed so as to cause a minimum of agitation, and the bed was then frozen. After solidification, the column was sliced into one half-inch sections with a hot wire glass cutter. The beads were then removed from each section, the gelatine redissolved in hot water, and the beads filtered,

*On loan from the Lummus Company under the Industrial Participation Program.

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FIGURE 15

PROPOSED STAGE DESIGN FOR
MULTISTAGE FLUID BED REACTOR.

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washed, dried and screened on a set of standard three-inch diameter screens to determine the particle size distribution in each section.

Several runs employing this technique have been completed and preliminary results indicate a large amount of segregation of coarse particles at the bottom of the bed at low air flow rates. As the flow rate is increased the distribution becomes more nearly uniform but even at velocities in excess of the minimum fluidizing velocity of the largest particles there is still appreciable segregation. This would be quite significant in a continuous fluidized bed process where product is withdrawn from the bottom of the bed, resulting in a withdrawal of predominantly coarse particles, which may be the most difficult to convert.

Further work will be directed toward determining the velocity at which a uniform distribution is attained. This will be done for a number of particle size mixtures and a correlation will be attempted on the basis of some arbitrary type of uniformity index, as yet undefined. If this proves successful, extension to mixtures of three or more different particle sizes will be attempted.

E. Calcination of Reactor Fuel Processing Wastes
(J. Loeding, E. Petkus, M. Jones)

Previous exploratory experiments (ANL-5422, pages 105 to 108) had shown that the possibility of applying the fluidized-bed technique to the evaporation and calcination of reactor fuel processing wastes was promising. If feasible this technique would have the advantages that it is readily adapted to remote operation, that no complex, moving, mechanical parts are required, and that the calcined solid can be readily transferred to storage containers.

1. Bench Scale Experiments

Since the previous runs in the 3-inch diameter reactor had been made using 2.2 M aluminum nitrate solution at low feed flow rates (about 20 ml/min), several additional runs were made during this quarter to determine the effect of increased throughput. It was found that at feed rates above 30 ml/min the bed became caked after a few hours of operation. This caking of the bed resulted in a reduction in the rate of heat transfer through the reactor wall causing the electrical heaters to overheat and burn out.

To confirm the effect of feed flow rate, runs were repeated at both high and low throughputs. Again it was observed that at feed rates of 25 to 30 ml/min no caking occurred, whereas at 34 ml/min the bed caked seriously.

It is believed that caking occurred primarily because of the small diameter of the bench-scale reactor. When the reactor was examined at the termination of some of the runs at low feed rates, a small oxide cake was observed on the wall opposite the spray nozzle, evidently resulting from penetration of feed through the bed. At higher feed rates the amount of penetration probably increased, causing a cake to form

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across the reactor. For this reason it was decided that further waste calcination runs should be made in the 6-inch diameter reactor.

One experiment was performed in the 3-inch reactor to obtain a very approximate indication of the amount of aluminum oxide dust which might be passing through the off-gas filters. A micro cellulose filter, capable of removing sub-micron size particles of dust, was installed in the off-gas system. A representative bed of aluminum oxide was then fluidized with air at room temperature, and a portion of the exhaust air was passed through the micro cellulose filter. In a 16-hour test, 92 cu ft of exhaust air (7.1 per cent of the total off-gas) was channeled through the filter. Spectrographic analyses on this filter and a blank were identical (10 ppm) indicating little, if any, oxide dust in the off-gas. Though this experiment is not representative of actual operating conditions, it indicates that the efficiency of the off-gas filters is high.

2. Pilot-Scale Experiments

The 6-inch diameter, pilot-scale reactor was described in detail in a previous report, ANL-5290, pages 114 to 118, in connection with the denitration of uranyl nitrate. The reactor consists of a stainless steel pipe, six inches in diameter and thirty inches tall, surmounted by a twelve-inch diameter disengaging section containing porous stainless steel filters for the removal of oxide dust particles. A bed of aluminum oxide inside the reactor is fluidized by upward flowing air and is heated by electric heaters outside the reactor wall. The aluminum nitrate feed solution is introduced through a spray nozzle mounted in the reactor wall about six inches above the bottom of the bed. The calcined oxide is withdrawn through a pipe at the bottom of the bed.

Five waste calcination runs were completed using the operating conditions listed in Table 23. For the first run the starting bed consisted of commercial activated alumina, sieved between 40 and 80 mesh. Subsequent runs used oxide produced in previous runs together with activated alumina to give a mixture in the size range of 20 to 100 mesh. In the five runs completed the bed temperature was varied from 320 C to 450 C. The feed rate was varied from 103 ml/min to 210 ml/min. Other operating conditions were held constant.

No caking occurred in any of the runs, and no operating difficulties were encountered. However, it was observed that particle size growth occurred at a fairly rapid rate, as shown in Table 24. The average particle diameter was almost doubled in the 7-hour run period. For satisfactory operation of the fluid-bed calciner it is important that the particle size reach a steady state value, since continued particle growth would result in decreased agitation, eventually resulting in a caked bed. Experience on the denitration of uranyl nitrate had showed that particle growth could be eliminated by using a low denitration temperature (about 300 C). With aluminum nitrate, however, particle growth was more rapid at 320 C (Run WC-3) than at 400 C, (Run WC-2) and very slightly greater at 400 C than at 450 C (Run WC-4).

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Table 23

OPERATING CONDITIONS FOR WASTE CALCINATION RUNS

Equipment: 6-inch diameter reactor described
in ANL-5290, pages 114 to 118

	Run Number				
	WC-1	WC-2	WC-3	WC-4	WC-5 ^a
Bed Temperature, C	400	400	320	450	400
Fluidizing Air Flow Rate, cfm at STP	7.9	7.8	8.2	8.2	8.2
Nozzle Air Pressure, psig	31	31	31	31	30
Bed Level before Fluidization, inches	10	15	15	15	15
Feed (Aluminum Nitrate) Concentration, <u>M</u>	2.2	2.2	2.2	2.2	2.2
Feed Flow Rate, ml/min	103	184	210	186	200
Run Duration, hr	7	7	5	7	7

^aAluminum oxide seed particles introduced during
this run.

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Table 24

VARIATION OF ALUMINUM OXIDE PARTICLE SIZE IN WASTE CALCINATION RUNS

For run conditions see Table 23

Mesh Number	Percentage of Each Size Range									
	WC-1		WC-2		WC-3		WC-4		WC-5	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final
+20	0.1	15.9	3.1	13.0	0.8	39.1	6.4	14.3	0.6	44.0
-20, + 40	1.3	42.3	24.7	83.0	27.1	60.2	37.4	78.2	32.0	52.9
-40, + 60	14.0	40.1	35.6	3.9	29.4	0.6	28.0	5.9	22.3	2.0
-60, +100	74.3	1.3	26.8	0.1	31.4	0.0	22.0	1.1	26.3	1.0
-100	10.4	0.3	9.8	0.0	11.2	0.0	6.2	0.6	18.5	0.0

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In Run WC-5 an attempt was made to approach a steady particle size by feeding fine seed particles of aluminum oxide into the bed during the run. Oxide having a size range of 80 to 100 mesh was fed into the reactor at a rate corresponding to 15 per cent of the aluminum oxide production rate. The results of this run showed no detectable improvement over Run WC-2 which was similar except for the absence of the fine particle feed.

The nitrate content of the aluminum oxide product from these runs varied from 1.1 per cent at a calcination temperature of 450 C to 2.1 per cent at a temperature of 320 C. The untapped bulk density of the oxide was approximately 0.7 g/cc. Thus the volume concentration factor from feed to product was about six to seven.

In future runs it is planned to investigate (1) the effect of somewhat higher operating temperature, (2) the effect of increased rates of seed particle introduction, and (3) the effect of varying the particle size of both the bed and the seed. In addition it is planned to start design work on a pilot-scale unit which will be capable of processing solutions containing radioactivity.

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VI. REACTOR CHEMISTRY - BREEDING GAIN DETERMINATION

(C. E. Crouthamel, P. Kafalas, E. Rathbun*)

The Chemical Engineering Division has the responsibility for the chemical determination of the conversion ratio or breeding gain of the EBR under various circumstances. This has been done when the core was loaded with enriched uranium and the blanket was natural uranium. The reactor is soon to be loaded with plutonium and the breeding gain must again be determined.

Burn-up determination of the core material in the EBR requires a calibration experiment using plutonium to correlate the number of fission events with the formation of fission activity. The progress of the calibration experiment is described in ANL-5422, page 116. Cesium-137 has in the past been selected to monitor the number of fission events. The cesium-137 has been calibrated and counted for over four years with the halogen-filled Geiger counters. Improvements in detectors employed are discussed in the following paragraphs.

New proportional counters manufactured by Packard Instrument Company, La Grange, Illinois, have now been placed in operation and cross calibrated with cesium-137 and uranium standards. The data are given in Table 25. The samples were mounted 1.0 inch from the window of both tubes. The Geiger counters contain mica windows 1.3 mg/sq cm and the proportional counters contain aluminized nylon windows 0.8 mg/sq cm. The proportional counters were operated with a Phillips pure grade methane gas flow. The plateau with an input sensitivity of 1.0 mv extended from 2850 to 3400 volts. The slope of this plateau was 0.4 per cent per 100 volts over the 550 volt range. The tube dimensions were 1 7/8 inches by 1 1/4 inches diameter. With two inches of lead shielding a background of 12.0 counts per minute was obtained.

Absolute calibration of the proportional counters is planned in the future.

The split crystal scintillation counter is complete and has given resolutions of 10 per cent on the cesium-137 photopeak. This counter consists of two 4-inch diameter by 3 1/2-inch crystals with 1/16-inch by 1-inch diameter wells which may be opened or closed on the sample. This counter is being calibrated for barium-140 and lanthanum-140 counting. The barium-140 and lanthanum-140 will be associated with the total fissions in a sample similar to the cesium-137 in the determination of low burn-up or fission to capture ratios of critical assemblies. This work is in progress and will be reported in detail later.

*Assigned on a part-time basis by the Electronics Division.

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Table 25

CROSS CALIBRATION OF HALOGEN-FILLED GEIGER
COUNTER WITH METHANE FLOW PROPORTIONAL COUNTER

Samples placed 1.0 inch from window of each counter
 Input sensitivity of proportional counter 1.0 mv

Sample	Geiger Counter ct/min	Proportional Counter ct/min	Ratio <u>Proportional</u> Geiger
Cs ¹³⁷ -1	236 ± 2	1432 ± 8	6.068
Cs ¹³⁷ -2	253 ± 2	1532 ± 7	6.055
Cs ¹³⁷ -3	247 ± 2	1499 ± 8	6.069
Uranium-1	4637 ± 8	24690 ± 28	5.325
Uranium-2	4650 ± 8	24780 ± 31	5.329

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VII. ANALYTICAL RESEARCH AND SERVICE WORK

(C. E. Crouthamel, M. T. Laug)

Thiocyanate reactions with plutonium III, IV, V, and VI were investigated. The object was to obtain a sensitive spectrophotometric method (molar absorbance index 10^3 or greater) for plutonium analysis. Aliquots of plutonium stock solution 6.48×10^{-3} M were oxidized in 2 M hydrochloric acid with ozone for several hours. Addition of thiocyanate and acetone generated an intense brown colored complex. In strong acid the brown color rapidly disappeared. In dilute acid (~ 0.25 or less) the brown complex was relatively stable. The molar absorbance index was greater than 10^3 but erratic. It appears that thiocyanate in acid medium reduced Pu (VI) to Pu (V). The brown Pu (V) thiocyanate complex then disproportionated rapidly in high acid medium. Preparations of Pu (III) and Pu (IV) did not yield any intense colors with the thiocyanate ion. The Pu (VI) and Pu (V) complexes were judged not reproducible or stable in the presence of thiocyanate ion. Further work is not planned on this system.

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VIII. WASTE PROCESSING AND MISCELLANY

A. Processing Operations

(H. G. Swope, J. F. Harast, W. H. Kline, A. C. Rashinskas, K. Bremer, W. Palmer, M. Deerwester, J. Jones)

During this period there were a total of 35 retention tanks processed of which 13 were decontaminating solutions from the Reclamation Department. Of this total seven had to be processed because of over-tolerance strontium-90, 21 due to over-tolerance alpha activity and the 9 remaining because of high gross counts. This amounted to 4.6 per cent of the total volume of retention tank waste.

B. Gamma Facility

(H. G. Sowpe, P. Fineman, R. Juvinall)

The gamma irradiation facility has been completed and the "pool" filled with water (56,000 gallons) in order to leak test it and to allow time for the operators to become proficient in the use of the equipment. The configuration of the irradiation rack is shown in Figure 16.

The circles represent the sample ports into which the sample urns will be placed. The fuel elements are the diamond shaped openings. The sample urns were designed to hold five No. 2 cans but any material no longer than 28 in. and 4 1/8 in. in diameter will fit into them. The urns will rotate at 2 rpm during irradiations.

Four of the fuel rods are now being shipped from the MTR in Idaho and as soon as these are installed in the rack, calibration of the source will begin.

Chemical dosimetry (ferrous ion) will be used as the standard. At the same time silver activated phosphate glass dosimeters will be used in order to see if the latter will be practical in the high intensity fields.

C. Electrodeionization

(W. R. Walters)

This program (see ANL-5290, pages 138 to 156) was concluded with a 700-hour run using synthetic wastes containing added fission product activity. A final report is in preparation.

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FIGURE 16

GAMMA IRRADIATION RACK.

A-1, B-1 etc are sample ports. Sample ports are 28" high and $4\frac{1}{8}$ " in diameter.

No. 1-12 represent spaces for fuel rods.

NOTE: When there are 12 fuel elements in the rack, sample positions designated A-1, A-2, etc. will have 4 fuel elements surrounding them, whereas those designated B-1, B-2, etc. will have 2 fuel elements surrounding them.

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