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for Plutonium and Uranium
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CHEMICAL ENGINEERING DIVISION
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April, May, June, 1956

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TABLE OF CONTENTS

	Page
SUMMARY	5
I. SOLVENT EXTRACTION - STUDY OF DISPERSION AND COALESCENCE	8
A. Light Transmittance - Interfacial Area Investigation . . .	8
B. Mass Transfer in a Continuous-Flow Mixing Chamber	8
II. FLUORIDE VOLATILIZATION SEPARATIONS PROCESS.	15
A. Laboratory Investigations	16
B. Semi-Works Operations	46
C. Fused Fluoride Process Studies	51
III. FLUIDIZATION	52
A. Green Salt Process	52
B. Direct Fluorination of Uranium Ore Concentrates	56
C. Calcination of Reactor Fuel Processing Wastes	63
D. Fundamental Studies	63
IV. REACTOR CHEMISTRY.	65
A. Metal Oxidation and Ignition	65
B. Uranium Isotope Build-Up on Recycling of Enriched Uranium through a Reactor	87
C. Dissolution of Thorium Oxide - Uranium Oxide Fuel Elements	87
D. Determination of Total Atom Burn-Up	88
V. CHEMICAL - METALLURGICAL SEPARATION PROCESSES.	91
A. Laboratory Studies	91
B. Semi-Works Studies of High Temperature Processes	112
VI. ANALYTICAL RESEARCH AND SERVICES	128
A. X-Ray Spectrophotometric Determination of Uranium in Solution.	128
B. Gamma-Ray Analyzer Facility	128
VII. ROUTINE OPERATIONS	130
A. Waste Processing Operations	130
B. Gamma-Irradiation Facility	130

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CHEMICAL ENGINEERING DIVISION

SUMMARY REPORT

for April, May, and June, 1956

SUMMARY

I. Solvent Extraction - Study of Dispersion and Coalescence
(pages 8 to 14).

Light scattering correlations have been developed for 25 per cent dispersions. Results were similar to previous results reported for 50 per cent dispersions.

Several runs have been made to investigate mass transfer in a continuous flow mixing chamber using the system isobutanol-water. The data obtained agree with literature values obtained in other types of equipment.

II. Fluoride Volatilization Separations Processes (pages 15 to 51).

Development work has continued on a fused salt process for the recovery of decontaminated uranium from enriched reactor fuels. The principal objective was to find suitable materials of construction for process equipment.

Investigations have continued on a process involving the volatilization of both uranium and plutonium fluorides. Further information was obtained on the rate of fluorination of plutonium tetrafluoride by fluorine.

The production of uranium tetrafluoride from ore concentrates by hydrogenation and hydrofluorination by fluidized-bed techniques has been demonstrated. Laboratory studies have been started to determine the feasibility of conversion of the tetrafluoride to the hexafluoride through fluorination in a fluidized bed.

Further investigations were made on the behavior of fission products in fluoride volatilization schemes.

Analysis of the data obtained in the first five pilot plant runs shows net beta and gamma decontamination factors of $>2 \times 10^5$ and $>2 \times 10^6$, respectively.

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III. Fluidization (pages 52 to 64)

The work on fluidization process development was concentrated along two lines. (1) further study of the process for the production of refined green salt from uranyl nitrate solution from the solvent extraction refineries; and (2) development of a process for the production of refined uranium hexafluoride by direct fluorination of uranium ore concentrates followed by fractional distillation.

In the refined green salt process attempts to replace the high cost porous filters in the denitration reactor with a cyclone separator were not successful in adequately removing the uranium trioxide dust from the off-gases. Alterations to improve the cyclone efficiency were started. Operation of the multistage reactor for hydrofluorination of the oxide produced some additional data on the effect of the temperature variable. The installation of pilot scale equipment for green salt production was continued.

The process for direct fluorination of ore concentrates was investigated as far as the crude green salt stage in a series of continuous single-stage runs. The reduction step was carried out at rates up to 20 lb of uranium per hour per cubic foot of bed volume in a 6-in. diameter reactor, and the hydrofluorination step at rates up to 30 lb of uranium per hour per cubic foot of bed volume.

Work continued on the fundamental study of the fluidization of mixtures of solid particles of two widely separated sizes. Considerable data were collected, but the results could not be correlated systematically. Some evidence was found that electrostatic effects may be obscuring the results.

IV. Reactor Chemistry (pages 65 to 90)

The increased use of nuclear reactors with concomitant handling of reactive metals such as uranium, thorium, zirconium and plutonium makes imperative an understanding of the factors which influence their pyrophoric nature. To elucidate these factors a study has been started on the oxidation characteristics of uranium and zirconium.

A calculation program has been carried out to determine the quantity of U^{237} produced in several cycles in a thermal reactor for various times, fluxes, initial fuel compositions (different enrichments), and modes of operation (continuous and intermittent). Most of the calculations are complete and the data are being evaluated.

A promising new fuel element consists of urania in a thoria matrix. Fuel elements of this type have shown good radiation stability but have been difficult to dissolve. Methods of dissolution are being investigated.

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A calibration experiment has been performed in order to determine the amount of Cs^{137} activity produced by a given number of fission events. This calibration factor has been determined for fast fission of U^{235} and Pu^{239} .

V. Chemical Metallurgical Separation Processes (pages 91 to 127)

The kinetics and mechanisms of ceramic oxide crucible corrosion by molten uranium and uranium alloys are being thoroughly examined. With alumina, reaction proceeds at a constant rate after a rapid initial attack by the melt. The activation energy for the linear attack is about 48 kcal/mole. Corrosion is accelerated by alloying uranium with molybdenum and ruthenium, is unaffected by aluminum, and is slowed down by carbon. Mechanisms are offered which accord with the experimental observations for thorium, zirconia, urania, and magnesia.

A study of the phase diagram of the lime-beryllia system indicates the formation of an intermediate compound, $2\text{CaO} \cdot 3\text{BeO}$. In the lime-beryllia-lanthana system a ternary eutectic melting at about 1282°C is present.

The extraction of tracer plutonium from uranium powder produced by hydriding-dehydriding cycles has been shown to be rapid and efficient. Grain boundary migration resulting from the hydriding-dehydriding cycle is postulated.

Various pilot plant components have been constructed and tested. Little effect of inductive mixing on crucible erosion has been noted. Two-inch beds of several surface active materials have been found to be effective in trapping sodium vapor used to simulate volatile fission products.

Nine magnesium distillation runs have been completed. Very little plutonium carryover has been noted. Fabrication of magnesium extraction equipment is complete.

VI. Analytic Research and Service (pages 128 to 129)

An X-ray spectrophotometric method has been devised and put into service for the rapid determination of uranium in the concentration range of 1 to 5×10^{-3} M (0.001 - 0.005).

A gamma-ray analyzer facility has been built and is being tested.

VII. Routine Operations (page 130)

Operation of the gamma irradiation facility and the radioactive waste processing building is described.

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I. SOLVENT EXTRACTION - STUDY OF DISPERSION AND COALESCENCE

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

Light scattering correlations have been developed for 25 per cent dispersions. The results are similar to those presented in ANL-5512 for 50 per cent dispersions.

Several runs have been made to investigate mass transfer in a continuous-flow mixing chamber. The initial series of runs was made using the partially miscible system isobutanol-water. The data obtained show that the mass transfer coefficients for the system tested are in agreement with literature values obtained in other types of contacting equipment.

A. Light Transmittance - Interfacial Area Investigation

The light transmittance data for 25 per cent dispersions are summarized in Tables 1 and 2. General correlations of light transmittance as a function of interfacial area, optical path length and a refractive index parameter are shown in Figures 1 and 3. Separate correlations are presented for light spectrums in the yellow and near infrared regions, using yellow sensitive (1P42) and red sensitive (1P41) phototubes, respectively. The refractive index parameter is shown as a function of the relative specific refraction or Lorentz coefficient in Figures 2 and 4. These correlations were developed by means of the procedures described in ANL-5512.

B. Mass Transfer in a Continuous-Flow Mixing Chamber

The purpose of this phase of the dispersion program is to study the film theory of mass transfer in a continuous-flow mixing chamber in which interfacial area can be measured.

A partially miscible, two-phase system consisting of isobutanol transferring from water-saturated isobutanol to pure water was selected for the first series of runs. This system was particularly attractive because of the wealth of information in the literature which may be used for comparison purposes. Other advantages included: simple, rapid analysis by refractive index, and a minimum effect from internal circulation in the drops since the composition of the dispersed phase does not change during the period of contact in the chamber.

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Table 1

SUMMARY OF EXPERIMENTAL DATA FOR 25 PER CENT DISPERSIONS

(Yellow Light Spectrum)^a

System	Symbol	Lorentz Coefficient (M)	Scattering Factor (α)	Interfacial Area sq cm/cu cm	ln (I ₀ /I) at Specified Optical Path Length		
					1.0 cm	1.5 cm	2.0 cm
Methyl Isobutyl Ketone in Glycerin - Water		0.00491	0.0167	25.4	0.500	0.620	0.746
				27.9	0.547	0.703	0.830
Isobutyl Alcohol in Water		0.0236	0.0559	46.7	2.24	2.75	3.28
				58.5	2.66	3.11	3.72
				69.3	3.22	3.78	4.38
Methyl Isobutyl Ketone in Water		0.0294	0.0660	28.4	1.69	2.15	2.58
				32.9	1.90	2.38	2.83
				37.5	2.20	2.70	3.18
Methyl Isobutyl Carbinol in Water		0.0358	0.0811	42.2	2.82	3.25	3.59
				44.0	3.02	3.52	3.81
Cyclohexane in Water		0.0421	0.0906	41.7	3.05	3.65	4.13
				47.8	3.38	3.84	4.33
Xylene in Water		0.0757	0.164	19.7	2.46	3.29	4.01
				23.4	2.85	3.51	4.26
				27.6	3.36	4.03	4.56
Chlorobenzene in Water		0.0920	0.268	13.5	3.18	3.58	4.11
				15.6	3.43	3.83	4.31
				20.9	4.10	4.43	4.90
				17.6	3.80	4.24	5.00
				19.9	3.83	4.36	4.90

^aSee ANL-5512, pages 15 through 20, for light spectrum details.

Table 2
SUMMARY OF EXPERIMENTAL DATA FOR 25 PER CENT DISPERSIONS

(Near Infrared Light Spectrum)^a

System	Symbol	Lorentz Coefficient (M)	Scattering Factor (α)	Interfacial Area, sq cm/cu cm	ln (I ₀ /I) at Specified Optical Path Length		
					1.0 cm	1.5 cm	2.0 cm
Methyl Isobutyl Ketone in Glycerin - Water		0.00491	0.0156	25.4	0.359	0.479	0.594
				27.9	0.414	0.545	0.680
Isobutanol in Water		0.0236	0.0446	46.6	2.00	2.46	2.74
				49.3	2.22	2.68	2.98
				46.7	2.18	2.60	3.13
				58.5	2.49	2.99	3.51
Methyl Isobutyl Ketone in Water		0.0294	0.0503	69.3	3.14	3.63	4.26
				28.4	-	1.87	2.25
				32.9	-	2.14	2.48
				37.5	-	2.47	2.93
Methyl Isobutyl Carbinol in Water		0.0358	0.0579	42.2	2.47	2.93	3.25
				44.0	2.69	3.13	3.47
Cyclohexane in Water		0.0421	0.0676	41.7	2.80	3.54	3.76
				47.8	3.01	3.72	4.06
Kerosene in Water		0.0497	0.0780	27.2	2.15	2.68	3.15
				31.5	2.39	2.89	3.30
				35.0	2.77	3.31	3.79
Xylene in Water		0.0756	0.123	19.7	2.38	3.11	3.62
				23.4	2.68	3.42	3.89
				27.6	3.09	3.75	4.27
Benzene in Water		0.0802	0.134	18.3	2.28	3.00	3.55
				21.3	2.65	3.41	3.94
Chlorobenzene in Water		0.0920	0.188	17.6	3.47	3.95	4.51
				19.9	3.50	4.09	4.60

^aSee ANL-5512, pages 15 through 20, for light spectrum details.

FIGURE 1
GENERAL CORRELATION OF INTERFACIAL AREA WITH
LIGHT TRANSMITTANCE FOR 25 PER CENT DISPERSIONS
(YELLOW LIGHT SPECTRUM)

FIGURE 2
SCATTERING FACTOR α AS A FUNCTION OF LORENTZ
COEFFICIENT M FOR 25 PER CENT DISPERSIONS

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FIGURE 3
GENERAL CORRELATION OF INTERFACIAL AREA WITH
LIGHT TRANSMITTANCE FOR 25 PER CENT DISPERSIONS
(NEAR INFRARED LIGHT SPECTRUM)

FIGURE 4
SCATTERING FACTOR α AS A FUNCTION OF THE
LORENTZ COEFFICIENT M FOR 25 PER CENT DISPERSIONS

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For the special case of a mixing chamber in which partially miscible phases are contacted and the organic phase is introduced at saturation:

$$k = \frac{N}{VA (x^* - x)}$$

where

N = moles isobutanol transferred per minute

k = mass transfer coefficient, moles/(min)(sq cm)(mole fraction gradient)

V = volume of the mixing chamber, cm^3

A = interfacial area per unit volume available for mass transfer

x = mole fraction of isobutanol in the aqueous phase

x^* = mole fraction of isobutanol in the aqueous phase at saturation.

A strict treatment of the data would require that activities be used. For these preliminary experiments, however, the use of concentrations is adequate. For this case, the resistance to mass transfer is in the water film and k is an individual film coefficient. Assuming that the thoroughly mixed emulsion was homogeneous, the potential for mass transfer was determined from direct sampling of the contents of the single-stage chamber and was taken as the mole fraction gradient.

About a dozen runs have been made in the mixing vessel described in ANL-5560, pages 17 to 19. Most of these were shakedown runs used to refine equipment and operating techniques. Interfacial area was determined from light transmittance. The aqueous phase was selectively sampled by the use of the fritted tip filter technique described in ANL-5560. All runs were made at organic to aqueous flow ratios of unity; flow rates of from 1 to 3.4 gpm for each phase were used.

Influents consisting of water-saturated isobutanol and pure water were introduced into the chamber at the selected flow rates. The isobutanol phase was reused without a cleanup cycle between runs. Samples of the aqueous phase in the chamber and light transmission measurements were obtained at two-minute intervals. At the end of each run a sample was withdrawn from the chamber by syringe. Comparison of these samples obtained immediately after shutdown with those obtained from the fritted tip filter usually showed identical results, indicating that the fitted tip was producing satisfactory samples.

Sufficient turbulence was supplied by the kinetic energy of the influents to provide thorough mixing without the use of the chamber impeller except at low flow rates. At flow rates above 2.4 gpm, the interfacial

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area was found to be constant within the precision of the light transmission technique over the 10- to 15-minute duration of the run. In most cases mass transfer coefficients for those runs were indeterminate because the refractive index of the aqueous effluent indicated nearly complete saturation.

In only two runs, at flow rates of 2.8 and 3.0 gpm, was the aqueous effluent not completely saturated. Values of the mass transfer coefficient k (in cgm units) were calculated for these runs in terms of mole fraction gradients. Coefficients determined for the run at 2.8 gpm, as based on five samples, showed values of k from 0.01 to 0.012 as based on mole fractions. Increasing the influent flow rate from 2.8 to 3.0 gpm resulted in an increase in the interfacial area from about 138 to 145 sq cm/cu cm. Mass transfer coefficients calculated for this run, however, ranged from 0.013 to 0.029. Surprisingly, these values of k are in fair agreement with those observed by Heertjes et al.¹ who obtained values of about 0.008 in their work with much larger drops in spray towers.

The poor results of the latter run and the inability to reproduce these results in subsequent runs led to a complete review of the experimental conditions and techniques. The sampling technique was shown not to be at fault. An increase in interfacial area was observed in duplicate runs, however, which may be attributed to an accumulation of surface active contamination in the organic phase. This indicated the undesirability of the practice of reusing the organic phase without an intermediate cleanup step.

During the next quarter the series of isobutanol-water runs will be repeated. Between runs, the organic phase will be pretreated by distillation to prevent the accumulation of contamination. The necessary accessory equipment will be installed and a few runs will be made to study mass transfer in the system methyl isobutyl ketone-acetic acid-water. In addition, light scattering data will be obtained and a correlation prepared for 10 per cent dispersions.

¹Heertjes, P. M., Holve, W. A., and Talsma, H., Chem. Engr. Sci 3, 122-124 (1954).

II. FLUORIDE VOLATILIZATION SEPARATIONS PROCESS

The development of a fused salt process for the recovery of uranium from enriched reactor fuels has been continued. The specific flow-sheet under study includes dissolution of zirconium-matrix fuels by hydrofluorination in a sodium fluoride-zirconium fluoride melt at 600° C. The dissolved uranium is volatilized as the hexafluoride, by sparging the melt with bromine pentafluoride or fluorine, and purified by fractional distillation. Since most of the basic laboratory work had been completed, the principal objective was to find suitable materials of construction for the process equipment. Materials of construction which may show better corrosion resistance than nickel, such as graphite, have been under study to determine whether they are more resistant. Both graphite and low carbon nickel appear to be superior to the commercial nickel.

Investigations have continued on a possible process involving the volatilization of both uranium and plutonium fluorides. Information obtained on the rate of fluorination of plutonium tetrafluoride by fluorine was in general agreement with previous data from other sites. Further studies have been made on the thermal stability of plutonium hexafluoride, with particular emphasis on quantitative handling of the compound in nickel equipment.

The production of uranium tetrafluoride from ore concentrates by hydrogenation and hydrofluorination by fluidized-bed techniques had been demonstrated in another group of this Division. Laboratory studies have been started to determine whether conversion of the tetrafluoride to the hexafluoride through fluorination in a fluidized bed is feasible. The addition of an easily fluidized inert diluent appears to be beneficial to the operation.

Further investigations were made on the behavior of fission products in fluoride volatilization schemes. A uranium alloy containing inactive fission product elements in concentrations corresponding to highly irradiated fuel was activated by a mild irradiation in CP-5. The active alloy was dissolved in bromine trifluoride, the volatile fractions then being examined by gamma-ray spectrometry.

Analysis of the data obtained in the first five pilot plant runs has been completed, and the net beta and gamma decontamination factors for uranium hexafluoride which has been distilled through two columns have been shown to be $>2 \times 10^5$ and $>2 \times 10^6$, respectively.

Meetings were held with personnel at Oak Ridge National Laboratory and with representatives of several industrial concerns.

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A. Laboratory Investigations
(R. K. Steunenber)

1. Corrosion Studies

a. Fused Salt Processing of Enriched Reactor Fuels
(W. Seefeldt, S. Vogler, G. Redding, R. Breyn, L. Hays)

Emphasis in the past period has been placed on finding a suitable substitute for nickel as a material of construction for fused fluoride melts through which anhydrous hydrogen fluoride is passed. In the preceding quarter a commercial nickel liner and sparge tube had failed under test conditions (ANL-5560, pages 24 to 31); failure occurred by intergranular weakening of the nickel. Graphite appears promising as a replacement; low carbon nickel also shows some promise. All tests were conducted at 600° C in equimolar sodium fluoride-zirconium fluoride. The word "attack" in this section is used in conjunction with intergranular weakening; "penetration" is used when referring to dimensional changes.

(1) Graphite as a Container Material for the Dissolution Step

Because of the poor corrosion resistance indicated for "A" nickel in fused fluoride melts with hydrogen fluoride passing through the melt, it was decided to examine other container materials. One such material is graphite which is commonly used with fused salts.

To start the testing, preliminary experiments were carried out on several types of graphite:

1. ATZ - National Carbon Company - a high density (1.70 g/cc), small particle size (max 0.006 in.) graphite with very small voids and extremely few fissures.
2. 85 - Speer Carbon Company - much larger particle size with large uneven voids and fissures.
3. Graphitite - Falls Industries - an impregnated graphite to minimize porosity; a fine-grained graphite with many voids.

Crucibles were fabricated from solid bar stock (1-1/8 in. ID, 7-1/2 in. tall, with a 3/32-in. wall thickness) such that they could be supported in the nickel liners used in previous fused salt experiments. Approximately 150 g of zirconium fluoride-sodium fluoride (1:1) were used for each test. Prior to use the melt was fluorinated in a separate nickel vessel at 600° C by passing bromine pentafluoride through the

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melt for approximately one hour and then sweeping out the excess bromine pentafluoride with helium. Then, for the test period of 4 to 7 days, hydrogen fluoride gas was passed through the melt at 600° C. At the completion of the test, the melt was poured out of the crucible. After cooling, the crucible was placed in hot water to remove the excess salt which had frozen to the wall. The crucible was sectioned about one and one-half inches from the bottom, but below the melt line. The wall thickness of the crucible was measured at various points by means of a microscope. These results were compared with measurements made before exposure to fused melt and hydrogen fluoride. The results are given in Table 3.

Table 3

GRAPHITE CORROSION IN EQUIMOLAR ZIRCONIUM
FLUORIDE-SODIUM FLUORIDE MELTS

Melt at 600° C with hydrogen fluoride sparge.

Melt prefluorinated at 600° C with BrF₅ for
1 hour in a nickel container.

Graphite	Particle Size (in.)	App Dens (g/cc)	Time (hr)	Gas Flow (g/hr)	Remarks
ATZ	0.006	1.70	78	22	No measureable corrosion. Slight amount of graphite in melt.
85	-	-	177	15	No change in wall thickness. Some of the voids were filled with salt.
Graphitite	-	-	137	23	

The ATZ graphite appeared to show the smallest penetration by the melt. Many of the voids present in the other graphites were filled with salt. Also in pouring melt from the crucibles it was apparent that the melt did not wet the graphite.

Continuing the examination of graphite, additional crucibles of regularly available graphite were fabricated. In addition, impingement plate units (Figure 5) were also fabricated, so that in a given test both the crucible and gas entry line were made of the same type graphite. As in the other tests, the melt was fluorinated in a separate nickel vessel prior to use. The graphite impingement plates were measured by micrometer and microscope before and after exposure. Initial results are given in Table 4.

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Table 4

GRAPHITE CORROSION IN EQUIMOLAR ZIRCONIUM
FLUORIDE-SODIUM FLUORIDE MELTS

Melt at 600° C with hydrogen fluoride sparge.

Graphite - Type CS (National Carbon Company)

	<u>A</u>		<u>B</u>	
Max Grain Size (in.)	0.016		0.031	
App Dens (g/cc)	1.68		1.67	

	<u>A</u>		<u>B</u>	
Run No.	65	66	63	67
HF Gas Flow Rate (g/hr)	21.7	38.9	9.1	19
Time (hr)	165	146	168	165

	<u>Dimensional Change, mil/day</u>			
ID Gas Entry Tube ^a	0.1	0.1	-	0.1
OD Gas Entry Tube ^b	0.1	<0.1	<0.1	<0.1
ID Holes Impingement Plate ^a	<0.1	<0.1	<0.1	<0.1
Thickness of Plate ^b	0.1	<0.1	<0.1	<0.1
Diameter of Plate ^b	<0.1	<0.1	<0.1	<0.1
Crucible Wall ^a	0.3	0.14		0.28

^aMicroscope Measurement

^bMicrometer Measurement

The results indicate a very low corrosion rate for graphite under the test conditions, with little variation from run to run. Examination of the impingement plates reveals that machine markings originally present are still noticeable, an indication of limited corrosion. Figure 6 shows a graphite and a commercial nickel gas entry line whose exposures have been comparable. Negligible erosive and corrosive effects are noted in the graphite, whereas attack on the nickel has been severe. In the nickel system, the gas entry line undergoes the greatest dimensional change of any of the system components.

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Figure 6

GRAPHITE AND NICKEL GAS ENTRY TUBES EXPOSED TO COMPARABLE
CONDITIONS OF HYDROFLUORINATION IN FUSED FLUORIDE MELTS

1/4-inch OD Nickel: Run 56, 115 hr,
19 grams/hr

1/4-inch OD Graphite: Run 63, 168 hr,
9.1 grams/hr

The nickel tube has undergone substantial penetration,
while very little erosion has occurred on the graphite.

In the experiments melt passed through the crucible walls to different extents. For example, in Run 63, melt came through the crucible in sufficient quantity so that melt was found in the metal vessel supporting the graphite. In Run 66, there was a fine film of melt on the outside of the graphite crucible. In Run 67 the crucible had several spots of melt, as if the melt had just seeped through. Examination of cross sections of the crucibles (Figures 7 through 10) show that the movement of salt through the crucible apparently follows the voids and faults which may be present.

Figure 7

CS GRAPHITE (0.031-IN. GRAIN SIZE)

Before exposure to $\text{ZrF}_4\text{-NaF}$ Melt (Run 63)

Wet ground with 600 grit silicon carbide,
oblique light 35X.

Black spots are voids

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Figure 8

CS GRAPHITE (0.031-IN. GRAIN SIZE)Exposed to ZrF_4 -NaF Melt at 600°C (Run 63)

Wet ground with 600 grit silicon carbide, oblique light 35X.

White spots show salt

Figure 9

CS GRAPHITE (0.031-IN. GRAIN SIZE)Exposed to ZrF_4 -NaF Melt at 600°C (Run 67)

Wet ground with 600 grit silicon carbide, oblique light 35X.

White streak shows salt filling fault

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Figure 10

CS GRAPHITE (0.016-IN. GRAIN SIZE)

Exposed to $\text{ZrF}_4\text{-NaF}$ Melt at 600°C (Run 66)

Wet ground with 600 grit silicon carbide,
oblique light 35X.

Thin white streak shows salt filling fault

The melt after solidification shows streaks of gray, which are undoubtedly graphite, through the white melt. A sample of one such melt (Run 65) contained 34 ppm carbon for a seven-day experiment. Since less than one day is required for dissolution and the volume to surface ratio will probably be more favorable, the amount of graphite suspended in the salt and subject to oxidation in the uranium volatilization step is likely to be less than this.

These first experiments are quite encouraging and indicate that graphite might be a useful material of construction for fused salt processing. Further experiments will continue to check additional variables. If graphite is to be used as the primary container for the hydrofluorination, a back-up material must be provided. Tests are being planned to determine what metals would be satisfactory for this service.

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(2) Metals as Container Materials for the Dissolution Step

Although graphite appeared to be the most promising of the new materials, metals were also considered and tested. The run conditions for all tests of metals are shown in Table 5.

Table 5

CONDITIONS FOR CORROSION TESTS (METAL) IN HYDRO-
FLUORINATED FUSED FLUORIDE MELTS

Melt: 300 to 350 grams of equimolar NaF-ZrF₄

Temp: 600° C

Liner Area: 1.62 sq in.

All melts were prefluorinated with BrF₅ in a separate container

Run	Metal Tested	Run Time (hours)	Sparge Rate (grams/hr)
52	"A" Nickel, "L" Nickel, Inconel (all coupons)	50	20.4
53	"A" Nickel, "L" Nickel, Inconel (all coupons)	49	29.2
54	"A" Nickel, "L" Nickel, Inconel (all coupons)	48	20.3
55	"A" Nickel, "L" Nickel, Inconel (all coupons)	68	8.8
56	"A" Nickel, Hastelloy B, Copper	115	19
56A	"A" Nickel, Hastelloy B, Copper	114	21.5
57	Inconel liner and sparger	264	32.5
58	Copper liner and sparger	72	29
59	Inconel liner, graphite sparger	149	41
60	Nickel (Helium sparged)	168	750 cc/min (STP)
61	Nickel (Hydrogen sparged)	114	750 cc/min (STP)
62	Copper liner and sparger	18	19.9
64	Low carbon nickel liner ^a	381	35.9

^aStill in test

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- (a) Coupons - Coupon tests are not considered to be very reliable in two-phase systems. Uneven gas distribution and channelling can easily give distorted results. For lack of sufficient material of certain metal types for liner and sparge tube fabrication, however, coupon tests were made. In each test, two pairs of untested material were inserted with a pair of "A" nickel controls (commercial grade nickel; carbon specification: 0.05 per cent max). These were arranged to minimize uneven gas distribution effects. The test was concluded when one or both of the controls exhibited intergranular weakening. The remaining coupons were then evaluated by weight loss and metallographic examinations. The data are shown in Table 6.

Of the coupons tested, Hastelloy B appeared superior. It showed low weight losses and no evidence of intergranular attack. Low carbon nickel was affected intergranularly but not nearly as severely as regular nickel. The average depth of intergranular attack was about 5 mils with a maximum about 17 mils. Weight losses of the two nickel types were comparable. Typical intergranular attack of nickel is shown in Figure 11. Two of three copper coupons appeared satisfactory, but the third (XA) suffered severe penetration along the bottom edge where HF had impinged on it. Intergranular attack was light. Inconel showed a chromium depletion effect (Figure 12) which stratified the metal and caused the layers to separate. The actual rate of chromium depletion appeared to be about 2 mils per day. This might be an acceptable rate, but the stratification of metal followed by flaking would be objectionable. All of the above, except Hastelloy B, were subsequently tested in liner and sparger assemblies. Hastelloy B will be similarly tested as soon as materials are received.

- (b) Liners and Spargers - Three new metals were tested during the quarter in liners and spargers: Inconel, copper and low carbon nickel. None of the three had failed by intergranular weakening. Low carbon nickel appears the most promising.

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Table 6

RESULTS OF COUPON TESTS IN HYDROFLUORINATED FUSED FLUORIDE MELTS

Melt: 300 to 350 grams of equimolar NaF-ZrF₄

Temp: 600°C

Liner Area: 1.62 sq in.

All melts were prefluorinated with BrF₅ in original container

Coupon Identification	Run	Sample Area (sq cm)	Time (hr)	Rate of Attack ^a (mils/day)	Wt. Loss (mg)	Metallographic Observation
Inconel (LA)	52 through 55	16.2	215	0.82	1571	{ Both coupons ballooned, LA greater than LB; cross section shows three metallic layers; the center one is sound metal, the outside layers consist of an 8 to 12-mil layer of chromium depleted metal.
Inconel (LB)	52 through 54	16.2	147	0.62	822	
"L" Nickel ^b (H1A)	52 through 55	16.2	215	0.29	934	{ Intergranular penetration through bulk of coupons is 2 to 7 mils; edge exposed to HF impingement attacked to 17 mils.
"L" Nickel (H1B)	52 through 55	16.2	215	0.17	548	
Nickel ^c (N1)	52 through 55	16.2	215	0.28	579	{ Not examined. N1 coupon broke into 3 pieces during Run 55.
Nickel (N2)	52 through 55	16.2	215	0.18	929	
Nickel (NB9)	56, 56A	16.2	229	0.42	1479	{ Intergranular penetration has been complete. Along the sides of grain boundaries, but somewhat separated from them, are gray deposits of what may be precipitated carbon. See Figure 11.
Nickel	56A	16.2	114	1.2	2173	
Copper ^d (XA)	56	8.0	115	0.96	827.8	{ Many of the surface grains have been penetrated, but in only a few places has the attack proceeded beyond the first layer of grains.
Copper (XB)	56, 56A	8.0	229	0.14	248.1	
Copper (XC)	56A	16.2	114	0.14	241.8	
Hastelloy B	56, 56A	16.2	229	0.05	178.4	{ No intergranular penetration evident.
Hastelloy B	56A	16.2	114	0.03	47.2	

^aAssumes uniform attack.^bLow carbon nickel. Specification: <0.02 per cent C.^cNickel coupons were used as controls. The runs were continued until one or both controls showed evidence of severe intergranular attack.^dElectrolytic tough pitch grade.

Figure 11

MICROGRAPH SHOWING TYPICAL INTERGRANULAR ATTACK OF
NICKEL IN HYDROFLUORINATED FUSED FLUORIDES

Run: 55

Magnification: 400X

Figure 12

MICROGRAPH OF INCONEL LINER CROSS SECTION AFTER EXPOSURE
TO HYDROFLUORINATED FUSED FLUORIDE MELT

Run: 57

Magnification: 100X

As polished

Area of liner shown has been depleted of chromium. Note the stratification occurring. Further exposure results in detachment of the layer.

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The low carbon nickel liner was tested for 381 hr by the end of the quarter (Run 64). The average hydrogen fluoride rate was 35.9 grams/hr. No obvious metal weakening had occurred. The test will be continued for 600 hours or until failure -- whichever occurs first. The carbon specification on this material is 0.02 per cent maximum as compared to 0.05 per cent maximum for regular nickel (also known as "A" nickel). The wall thickness was 50 mils as compared to 32 mils in "A" nickel liners. No spargers were tested, as tubing stock was not on hand.

Two tests with Inconel liners were made. Run 57 for 264 hr and Run 59 for 149 hr. Hydrogen fluoride sparge rates were 32.5 and 41 grams/hr, respectively. The liners, like the coupons, showed chromium depletion effects (see Figure 12) and some stratification; intergranular effects were not evident. A typical section of Run 57 showed 42 mils of undisturbed base metal (original thickness: 62 mils) with an additional 14 mils of chromium-depleted metal adjacent, followed by a stratified layer of 8 mils of chromium-depleted metal. The latter can be separated quite readily from the remaining metal. The voids in Figure 12 characterize this stratification. The rate of chromium depletion in Run 57 was 1.8 mils per day and in Run 59 was 2.9 mils per day. A series of four sparge tubes was used in Run 57. Three "A" nickel tubes failed after 72, 21, and 47 hr, while an Inconel tube was used for the last 120 hr without failure. The Inconel tube had a chromium depletion rate of 4 mils per day on the exterior surfaces.

Two tests with copper liners and sparge tubes were made. Both resulted in early failure. Though not positively identified, the copper used was probably electrolytic tough pitch. Run 58 was made for 72 hr at an average sparge rate of 29 grams/hr, while Run 62 lasted 18 hr at a 19.9-grams/hr sparge rate. Both failures occurred by rupture. It is possible that the failures occurred prematurely due to exterior oxidation. In Run 58 about twenty blisters formed in the copper, suggesting hydrogen attack on oxygen impurities. Severe mass transfer was evidenced by large masses of sparge copper in the liner interior.

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In order to have a better understanding of the mechanism by which "A" nickel was weakening, several short tests of different types were made. It was generally thought that three mechanisms were possible:

1. That sulfur-containing materials, either in the melt or the HF, were resulting in the formation of Ni-NiS eutectic along grain boundaries and hence weakening the metal.
2. That the nascent hydrogen corrosion product from the HF-nickel reaction was diffusing through the metal and reacting with precipitated carbon to form methane under high pressure, thus causing grain separations in its effort to escape. It is known that the solubility of carbon in nickel at 600° C is about 0.03 per cent.
3. That carbon precipitation along grain boundaries was sufficient to weaken the metal intergranularly.

The following tests and observations were made:

1. Helium was passed through an equimolar sodium fluoride-zirconium fluoride melt (Run 60). If sulfur were present in the melt nickel weakening should occur. The weakening did not occur nor was NiS detected in the metal metallographically.
2. Hydrogen was passed through a similar melt (Run 61). Even though the dissociation of hydrogen is small at 600° C, it was thought that there might be sufficient to cause weakening. The latter did not occur.
3. Weakened metal from Run 51 was dissolved in hydrochloric acid, and the vapors were passed over lead acetate paper (sulfur test). The result was negative.
4. Nickel coupons were exposed to vapor phase hydrogen fluoride at 600° C for a period of 120 hr. If sulfur were present in the hydrogen fluoride, the nickel should have weakened provided that the fluoride film formed on the coupon

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was not impermeable to the sulfur compound. No weakening of the coupon occurred, nor was sulfur detected metallographically.

5. Samples of the metal from Runs 51, 60 and 61 were sent to the Corrosion Research Section of the International Nickel Company for evaluation in their laboratories. Run 51 was the first showing severe nickel disintegration. Results have not been received.
6. Emptied HF cylinders (6 lb) used in corrosion experiments have often smelled of sulfur compounds. Analytical analyses for SO_2 have shown contents of 20 ppm.

Evidences suggesting a possible hydrogen mechanism are two:

1. The blister formation in the copper liner runs is characteristic of the industrial "hydrogen sickness" occurring in electrolytic tough pitch copper. This is caused by nascent hydrogen corrosion product reacting with oxygen impurities in the metal. The nascent hydrogen can diffuse; the resulting water vapor formed under pressure cannot.
2. The failure of "A" nickel in periods of less than 100 hr, and the non-failure of low carbon nickel in 381 hr, other conditions thought to be the same, is considered to be quite significant. With the solubility of carbon being 0.03 per cent at 600°C , some carbon in "A" nickel (0.05 per cent max) will precipitate, while in low carbon nickel (0.02 per cent max) it does not. Presumably, the precipitated carbon is more available for reaction with hydrogen than that which is in solution.

Of the three postulated mechanisms for the intergranular weakening of nickel, the hydrogen mechanism appears to be most nearly consistent with the experimental evidence so far obtained. It should be added that International Nickel Company experience includes no cases of weakening and failure of nickel by a hydrogen mechanism. It is their belief that a sulfur mechanism is more likely to be responsible.

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b. Investigation of Possible Material to be Used in the Preparation of Plutonium Hexafluoride
(M. J. Steindler)

In conjunction with a study of the preparation of plutonium hexafluoride, an investigation of the behavior of materials of construction in a fluorine atmosphere has been carried out. A number of materials in coupon form have been exposed to gaseous fluorine at elevated temperatures. The equipment and procedures employed are the same as those reported previously (ANL-5560, page 34). A summary of the data is shown in Table 7. Discussion of the corrosion of metals in gaseous fluorine has been presented previously. The resistance of refractory alumina to attack by fluorine in the absence of a transport medium such as a fused salt is not surprising. The successful application of alumina in laboratory equipment wherein fluorine is handled has been recorded in the literature. The weight gain of the calcium fluoride sample can only be interpreted on the basis of reaction between the small quantity of binder present in crucible grade calcium fluoride and gaseous fluorine.

Table 7

CORROSION OF MATERIALS IN GASEOUS FLUORINE
AT ELEVATED TEMPERATURES

Material	Temp. (C)	Corrosion (penetration)(mils/yr)	
		From Weight Gain	From Film Thickness
Nickel	550	4.4	-
Nickel	650	60	310
Nickel	750	350	820
Monel	650	41	-
Monel	750	2,900	3,500
Inconel	550	3,200	4,800
Inconel	650	7,100	6,000
Inconel	750	24,000	33,000
		26,000 ^a	
Copper	550	110	-
Copper	650	430	540
Copper	750	750	1,100
Alumina (Morganite)	550	nil	-
Alumina (Morganite)	750	110	-
Calcium Fluoride (crucible grade)	750	Weight gain 2.7×10^{-4} gram/(hr)(sq in.)	

^aFrom weight loss data.

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From these data, it appears that "A" nickel may be a satisfactory material of construction for equipment to be used in the preparation of plutonium hexafluoride. Corrosion tests, however, still need to be carried out on nickel exposed simultaneously to fluorine and plutonium. In addition, extension of the data of Table 7 to include aluminum and other metals of interest to this program may be useful.

2. Processing of Uranium-Plutonium Fuels (R. C. Vogel)

The processing of uranium-plutonium alloy systems by an all volatility scheme would involve the preparation and handling of plutonium hexafluoride. Studies on the thermal stability of plutonium hexafluoride are being continued with emphasis on (1) the determination of optimum pre-fluorination conditions for handling the gas in nickel equipment, (2) the rate of thermal decomposition of plutonium hexafluoride, and (3) the rate of fluorination of plutonium tetrafluoride.

a. The Thermal Decomposition of Plutonium Hexafluoride (M. Adams, D. Steidl)

In a consideration of the thermal decomposition of plutonium hexafluoride there are two reactions which are thought to be important:

If the decomposition of the plutonium hexafluoride is being studied in the presence of fluorine the reaction of the decomposition product is also important:

The problems of the thermal decomposition of plutonium hexafluoride and proper equipment prefluorination (reactions 1 and 2) are being, by necessity, considered together. In the previous quarterly report (ANL-5560, page 53) data are presented which show that prefluorination of equipment is effective in lowering the rate of decomposition of the hexafluoride and also that the residues from the decomposition may be refluorinated at temperatures as low as 250° C if the decomposition is carried out in a fluorine atmosphere.

An apparatus, schematically shown in Figure 13, has been constructed, in which plutonium hexafluoride in either a helium or fluorine atmosphere can be passed through a heated zone packed with commercial coarse grade nickel wool. The packed zone can be pretreated with fluorine at temperatures up to 450° C and the effects of various prefluorination

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conditions and varying decomposition temperatures determined. In the apparatus used in the earlier work it was not possible to study the decomposition reaction in the absence of fluorine. The decomposition zone of the previous apparatus could also not be prefluorinated at such high temperatures.

FIGURE 13
APPARATUS FOR STUDY OF DECOMPOSITION
OF PLUTONIUM HEXAFLUORIDE

The experimental steps are the following. Plutonium tetrafluoride is weighed into a nickel boat and placed in the furnace tube at the position of the first thermocouple (TC I). The first trap and the decomposition tube are then heated by the resistance wire wrapping and, when the desired prefluorination temperature is reached, fluorine is admitted for the period of time required. The furnace is not heated during this period and no plutonium hexafluoride is formed.

After prefluorination the system is flushed with helium and the furnace heated to 500° C. The heating coil is removed from Trap I and, in order to collect the plutonium hexafluoride, replaced by a Dewar flask containing liquid nitrogen. Fluorine is then passed through the apparatus for 15 min and then swept from the system with helium. While the furnace is cooling, the temperature of the decomposition tube is regulated, the helium flow rate is adjusted to 100 cc/min, and a Dewar of liquid nitrogen placed around Trap II. After the liquid nitrogen is removed from Trap I, the heating coil is replaced and warmed to about 60° C, allowing the plutonium hexafluoride to vaporize into the helium stream. After 30 min at the decomposition temperature, the apparatus is cooled. The helium flow is maintained during cooling.

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When the apparatus is cool, it is disassembled, the individual sections of packing and the contents of both traps are dissolved and analyzed for plutonium by direct plate counting. The walls of the tubes are also washed and the washings analyzed.

In Table 8 results of these analyses and the conditions of the individual experiments are presented. For comparison some previous experiments are included in which fluorine was used as a carrier gas rather than helium.

The data presented in Table 8 are more readily understood if a rate of decomposition is calculated on some common basis for all the experiments. Table 9 shows the results of such a calculation. The rate of decomposition is expressed as the per cent of plutonium hexafluoride decomposing per second. The time is taken as a residence time of the plutonium hexafluoride in the heated zone. It is obtained by dividing the volume of the packed zone by the flow rate of carrier gas, corrected to the temperature of the packed zone. This enables a comparison to be made of all the variables, prefluorination conditions, atmosphere and decomposition temperature.

Rates of decomposition are plotted as a function of temperature in Figure 14. Separate lines are drawn connecting those rates with common prefluorination temperatures and atmospheres.

It is appropriate in attempting to understand the optimum conditions of thermal stability of plutonium hexafluoride to consider the three reactions cited above. Reaction 3, the refluorination of the decomposition product plutonium tetrafluoride, can be most easily considered independently. It has been eliminated from one series of experiments (see Table 8) by changing from a fluorine to a helium atmosphere. In experiments previously reported (ANL-5560, page 53) this refluorination was reported to take place at temperatures around 250° C. In Figure 14 this effect is shown in two types of experiment. In both cases, with prefluorinated and unprefluorinated packing, the rate of decomposition is very low at 240° C.

The effects of reactions 1 and 2 are more difficult to separate. Reaction 2, the action of plutonium hexafluoride on nickel, is best illustrated in the group of experiments with unprefluorinated packing. The rate of decomposition at 120° C is high but decreases as the temperature rises. The decrease may be a function of three factors: (1) a fluorination of nickel packing by the large excess of fluorine, (2) an increased stability of plutonium hexafluoride at higher temperatures in the presence of fluorine, and (3) refluorination of the decomposition product in the higher temperature range.

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Table 8

CONDITIONS AND RESULTS OF PLUTONIUM HEXAFLUORIDE
DECOMPOSITION EXPERIMENTS

Exp. No.	Prefluorination Conditions		Decomposition		% Pu Decomposed in Packing ^(a)	% Pu in Final Trap ^(b)	Overall Material Balance ^(b) (%)
	Time (Min)	Temp. (C)	Temp. (C)	Carrier Gas			
53	30	350	110	He ^(c)	1.1	72.7	76.1
65	30	350	120	He ^(c)	16.8	17.5	78.3
73	30	350	120	He ^(c)	13.8	13.1	89.9
59	30	350	180	He ^(c)	9.6	29.8	35.3
63	30	350	180	He ^(c)	12.9	21.6	63.7
61	30	350	240	He ^(c)	65.0	10.6	46.1
67	30	350	240	He ^(c)	61.8	19.4	59.5
71	30	450	240	He ^(c)	32.1	31.4	74.0
45	75	210	120	F ₂ ^(d)	10.5	85.6	96.1
33	-	-	125	F ₂ ^(d)	43.3	42.7	86.0
37	-	-	180	F ₂ ^(d)	38.1	37.8	75.8
47	30	250	180	F ₂ ^(d)	10.7	64.4	75.1
41	-	-	240	F ₂ ^(d)	14.5	45.3	59.8
49	30	350	240	F ₂ ^(d)	1.8	81.4	83.2

^(a)Based on amount of material passing into packing. Part of that which enters the packing is decomposed and part passes through the packing. Plutonium remaining in the first trap is not considered.

^(b)Based on amount of PuF₄ originally used. This correction is necessary because in many experiments a percentage of the plutonium remains in trap I. The reason for this is not yet clear but may be due to improper heating of the trap as the plutonium hexafluoride is vaporized into the helium stream.

^(c)Experiment carried out in equipment shown in Figure 13.

^(d)Experiment carried out in equipment shown in ANL-5566, page 57.

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Table 9

RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE AS A
FUNCTION OF TEMPERATURE AND PREFLUORINATION

Exp. No.	Carrier Gas	Prefluorination Conditions		Decompo- sition Temp. (C)	Time of Residence (Sec) ^(c)	Pu Passing into Heat Zone (mg)	Pu Decomposed (mg)	Rate of Decompo- sition (%/sec)
		Time (Min)	Temp. (C)					
53	He ^(a)	30	350	110	92	13.37	0.15	0.012
65	He ^(a)	30	350	120	91	2.87	0.47	0.18
73	He ^(a)	30	350	120	91	1.75	0.21	0.13
59	He ^(a)	30	350	180	78	5.20	0.50	0.12
63	He ^(a)	30	350	180	78	3.41	0.55	0.21
61	He ^(a)	30	350	240	69	4.02	2.61	0.94
67	He ^(a)	90	350	240	69	6.57	3.73	0.82
71	He ^(a)	30	450	240	69	5.87	1.89	0.47
45	F ₂ ^(b)	75	210	120	118	10.20	1.12	0.09
33	F ₂ ^(b)	No	No	125	72	9.44	4.75	0.70
37	F ₂ ^(b)	No	No	180	114	10.52	5.27	0.44
47	F ₂ ^(b)	30	250	180	195	11.34	1.61	0.073
41	F ₂ ^(b)	No	No	240	98	8.15	0.96	0.12
49	F ₂ ^(b)	30	350	240	143	14.13	0.31	0.022

(a) Experiment carried out in equipment described in this report, Figure 13.

(b) Experiment carried out in equipment described in ANL-5560, page 57.

(c) The time of residence is calculated from the volume of the packed zone divided by the flow rate corrected for the temperature of the heated zone.

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FIGURE 14
RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE AS A
FUNCTION OF TEMPERATURE, PREFLUORINATION AND ATMOSPHERE

Reaction 1 may be expected to predominate in the group of experiments which included prefluorination at 350° C and a helium atmosphere. The rate of decomposition increases rapidly with increasing temperature, as is shown in Figure 14. If the prefluorination temperature is 450° C, the rate of decomposition is reduced by a factor of two at a decomposition temperature of 240° C. This indicates a considerable reaction of the plutonium hexafluoride is still occurring with nickel insufficiently prefluorinated at 350° C.

In the future more work will be done on factors influencing the decomposition rate such as higher temperature of prefluorination and the effect of surface area of the nickel packing.

b. The Rate of Fluorination of Plutonium Tetrafluoride
(M. Steindler, F. Linzer)

As indicated in previous reports (ANL-5560, pages 53 to 57) a study of the rate of fluorination of plutonium fluorides has been initiated as part of a program designed to investigate an all-volatility process for treating plutonium-uranium alloys. A simple apparatus has been devised in which the weight loss of samples of plutonium fluorides after fluorination can be measured.

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The apparatus consists of a fluorine and helium supply connected to a train consisting of a furnace tube, two U-traps, a Fluorolube bubbler, and a limestone-filled fluorine disposal section which terminates in a caustic bubbler open to the atmosphere. The fluorine supply is of the usual design, employing a 4-liter ballast tank filled with fluorine at relatively low pressures. The furnace tube is constructed of 3/4-in. nickel tubing, flared on both ends. The tube contains suitable thermocouple wells and cooling coils protecting the flare seals. The tube is heated by a standard tube furnace. The two U-traps are constructed from 3/8-in. nickel tubing. Each trap has two "Hoke No. 1103" valves and 1/4-in. flare connections on each end. They are connected in series and are cooled by boiling liquid nitrogen from the bottom of Dewars using small heaters. The temperature of the traps is maintained slightly above the boiling point of nitrogen. A fluorolube oil bubbler in a Fluorothene tube isolates the fluorine disposal system from the U-traps. Two brass cylinders filled with limestone are connected in parallel and vent to the atmosphere through a caustic scrub bottle. The whole unit serves as an efficient fluorine disposal system. The apparatus is located within a standard small hood. The front of the hood has been modified to contain two glove ports and an opening through which material is transferred by the usual bagging operation.

The thermocouples in the system are calibrated, using a boat filled with calcium fluoride. In order to determine whether plutonium tetrafluoride was being lost by dusting into the gas stream, a powdered sample of nickel fluoride was treated with fluorine at a flow rate approximately twice as high as that used in subsequent experiments employing plutonium fluoride. No loss of weight of the sample was observed.

In a typical experiment a small semi-circular boat is pre-fluorinated in the equipment and taken into the high alpha facility where a sample of plutonium tetrafluoride is weighed into the boat. The boat is introduced into the furnace tube, the sample brought to the desired temperature in a stream of helium, and fluorine is admitted. At the end of the experiment, helium is substituted for fluorine, the furnace tube cooled and the sample removed and weighed. All gases pass through the cold traps where plutonium hexafluoride is removed from the gas stream.

The data obtained in a series of experiments are presented in Tables 10 and 11 and Figure 15.

The data using Los Alamos plutonium tetrafluoride yields a straight line on the usual semi-log plot; an activation energy of approximately 11.3 kcal/mole is obtained from the graph. The activation energy for the analogous reaction with uranium is reported to be between 15.5 to 19.9 kcal/mole.² Analysis of the Los Alamos material indicates a high purity of plutonium tetrafluoride. The Rocky Flats material does not appear completely homogeneous, but a careful analysis is not available.

²RDB(CAP)/R-8120, J. Y. Labaton, A Kinetic Study of the Fluorination of Uranium Tetrafluoride (January 1955).

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Table 10

FLUORINATION OF PuF_4 USING FLUORINE GAS
AT ATMOSPHERIC PRESSURE

(Source of Plutonium Tetrafluoride - Los Alamos)

<u>Expt.</u>	<u>Temp.</u> <u>(C)</u>	<u>Time</u> <u>(min)</u>	<u>Av. Flow Rate</u> <u>(cc/min)</u>	<u>Wt. Loss</u> <u>(mg/hr)</u>	<u>Wt. Sample</u> <u>(mg)</u>
6	200	75	131	4.0	44.3
5	250	120	850	12.9	52.1
4	300	45	96	34.8	54.0
1	375	10	67	106.8	49.6
2	375	20	105	111.6	52.1
7	450	5	95	307.2	50.0
3	500	5	53	428.4	46.7
8	600	1.5	280	1060	51.8
14	375	20	210	234.9	102.5

Table 11

FLUORINATION OF PuF_4 USING FLUORINE GAS
AT ATMOSPHERIC PRESSURE

(Source of Plutonium Tetrafluoride - Rocky Flats)

<u>Expt.</u>	<u>Temp.</u> <u>(C)</u>	<u>Time</u> <u>(min)</u>	<u>Av. Flow Rate</u> <u>(cc/min)</u>	<u>Wt. Loss</u> <u>(mg/hr)</u>	<u>Wt. Sample</u> <u>(mg)</u>
11	300	45	70	20.8	52.3
10	375	20	98	96.9	57.2
13	500	5	158	369.6	57.1

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FIGURE 15
RATE OF REACTION OF PuF_4 WITH FLUORINE

Since there was some concern that plutonium tetrafluoride might sinter on excessive heating, an experiment was carried out to examine this possibility. A sample of Los Alamos plutonium tetrafluoride was heated at 750°C in a stream of helium for 3.5 hours with the result that a large proportion of the solid turned purple, presumably forming plutonium trifluoride. No evidence of sintering was obtained in this experiment. Fluorination of this 50-mg sample at 500°C gave a rate only slightly lower (409 mg/hr) than that obtained from the Los Alamos sample. It is generally assumed that plutonium trifluoride fluorinates very rapidly at 500°C to plutonium tetrafluoride, although quantitative data are lacking on this point.

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Application of these data to a volatility process requires among other things a knowledge of the type of scale-up applicable to this process. Experiment 14 (Table 10) shows the results of an experiment in which both the area and the weight of the sample were increased by approximately a factor of two. The ratio of the rates of fluorination of the large sample to those obtained on the smaller samples was 2.15. Thus far only one such experiment has been carried out.

It may be mentioned that a comparison of the data obtained by the British workers³ and those here reported shows at least two important differences. The reported threshold for the fluorination of plutonium tetrafluoride at 320° C was clearly not observed by us. In addition, the British observed a diminishing rate at temperatures above 600° C, perhaps due to sintering of their material. This, also, is not evident in our experience.

The kinetic data thus far obtained are not sufficiently complete to permit either the design of larger scale equipment or to deduce the influence of sample history on its reactivity. However, the process as envisioned will not involve carefully purified plutonium tetrafluoride such as has been used. Consequently, in the immediate future, effort is to be concentrated on samples of plutonium fluorides obtained from the dissolution of uranium-plutonium alloys in bromine trifluoride. A single dissolution has thus far been carried out on a 0.93-gm sample of 5 per cent plutonium-uranium alloy in approximately 9 ml of bromine trifluoride. The dissolution proceeded smoothly after an induction period and apparently was complete after a total of about 6 hr at room temperature. The results of this type of experiment will be reported in the subsequent summary report.

3. Feed Materials Processing - The Conversion of Uranium Tetrafluoride to the Hexafluoride. (O. Sandus, W. A. Shinn)

In the previous quarterly report (ANL-5560, page 59), experiments were described in which uranium tetrafluoride was converted to the hexafluoride by fluorine, bromine trifluoride and bromine pentafluoride. The uranium tetrafluoride had been produced directly from Rand South African ore concentrate by hydrogenation and hydrofluorination in a fluidized bed reaction (ANL-5560, page 116).

The experiments on fluorination of uranium tetrafluoride up to this point employed fixed-bed type apparatus and served to indicate the chemical feasibility of the reactions. It may be desirable to follow the fluidized-bed hydrogenation-hydrofluorination procedures with a fluidized-bed fluorination procedure. A 1-in. fluidized-bed reactor was made from

³AERE-C/R-1312, R. Hurst, et al., Plutonium Hexafluoride, Part II, (January, 1953).

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nickel and Monel and is depicted schematically in Figure 16. A sintered Monel disc at the bottom of the reactor, which served as a gas distribution plate, showed a tendency to plug when nitrogen was passed through the empty reactor at 300° C. This was remedied by drilling six 1/32-in. holes in the disc. Several other operational difficulties were encountered, consisting primarily of unexplained failures of nickel tubing used in the equipment.

FIGURE 16
SKETCH OF THE FLUIDIZED-BED APPARATUS

In early shakedown experiments with this apparatus it was believed that the uranium tetrafluoride had a tendency to cake. In order to observe the fluidization process directly, a glass column, similar to the metal one in use, was used to study the behavior of various inert fluorides which might serve as possible diluents for the uranium tetrafluoride. It was suggested that the diluent, if easily fluidized alone, might reduce the tendency toward caking shown by the uranium tetrafluoride.

Sodium fluoride ground from pellets and screened to - 40, + 100 mesh was not satisfactory because of caking, which may have resulted from the softness of the particles. Crystalline calcium fluoride,

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screened to +100 mesh and having a bulk density of 1.7 gm/cc, fluidized readily. A mixture of 50 weight per cent uranium tetrafluoride in calcium fluoride fluidized somewhat better than did the uranium tetrafluoride alone. A mixture containing 75 weight per cent calcium fluoride fluidized as easily as the calcium fluoride alone, and caking at the gas distribution disc was eliminated.

A preliminary fluorination run using 75 per cent calcium fluoride mixture was made at 450° C in the metal equipment. Twice the stoichiometric amount of fluorine was added. At the conclusion of the run, clean calcium fluoride was recovered from the reactor, indicating complete conversion of the uranium tetrafluoride. The inside surfaces of the reactor and the distribution disc were clean.

One remaining operational problem was the carryover of fine particles onto the sintered nickel filter in the off-gas line. This material does not appear to react with the fluorine perhaps due to the lower temperature (100° C) and will have to be confined to the bed.

4. Fission Product Volatilization Studies (L. E. Trevorow, G. W. Redding)

Investigations were continued on the volatility of fission product fluorides in bromine trifluoride solutions. In order to have a starting material representative of a highly irradiated fuel and still be able to work with reasonable levels of activity, a sample of Sylvania "fissium" alloy* was activated by a mild irradiation. A 0.5-gram sample of the alloy was placed in an aluminum can and subjected to a neutron flux of 10^{12} neutrons/(sq cm) (sec) in CP-5. About an hour after removal from the reactor the sample was removed from its container using manipulators in a shielded cave.

Approximately three hours after the irradiation, the alloy was dissolved in bromine trifluoride in a 3/4-in. nickel tube on a vacuum line. About 1.5 hr were required to complete the dissolution at temperatures of 50 to 70° C.

The distillation was performed in a nickel and Monel vacuum line, the volatilized fractions being collected in Fluorothene tubes. A nickel Kjeldahl trap was inserted in the system to decrease the possibility of entrainment. The entire vacuum line was maintained at a temperature of about 80° C to prevent condensation of the uranium hexafluoride. The solution was distilled slowly under vacuum at about 80° C, and the volatile materials were collected in several small fractions.

*An alloy prepared by the Sylvania Electric Products, Inc. by powder metallurgy techniques from natural uranium and inactive fission product elements.

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The volatile fractions were hydrolyzed in 100 ml of 6 M nitric acid in polyethylene bottles. The resulting solutions were then agitated overnight on a mechanical shaker. The non-volatile residue was dissolved by rinsing the still pot with several portions of 6 to 12 M nitric acid totalling 100 ml of final solution. After this treatment, no activity above background could be detected by monitoring the still pot with a hand probe. Aliquots were taken from the distillate and residue solutions and evaporated on glass fiber filter discs, which were then sealed in polyethylene films.

The gamma-ray spectra of the samples were examined by C. E. Crouthamel in the gamma-ray analyzing facility. Gamma scans of the energy spectra were made with a 256-channel pulse height analyzer used in conjunction with a sodium iodide-thallium activated crystal. Half-life characteristics were obtained by repeated scans after the elapse of various time periods. The residue activities were measured three times over a period of 184 hr. Since all the distillate fractions showed the same type of spectrum, the third fraction was chosen and scanned five times over a period of 166 hr.

The half-lives and energies of the photopeaks for the important gamma-emitters detected in the distillate are listed in Table 12. Certain of the photopeaks obtained from these samples were more suitable for quantitative decay measurements than others. For optimum counting conditions, each of the various isotopes would require a special combination of irradiation and cooling times.

Table 12

COMPARISON OF DISTILLATE ACTIVITIES
WITH LITERATURE VALUES

<u>Determined Values</u>		<u>Literature Values of Isotopes with Similar Properties</u>			
<u>Energy</u> <u>(kev)</u>	<u>Half-Life</u>	<u>Isotope</u>	<u>Energy</u> <u>(kev)</u>	<u>Half-Life</u>	<u>Reference</u>
153	65 hours	Mo ⁹⁹ -Tc ^{99m}	140-142	68 hours	4
239	70 hours	Te ¹³²	231	77 hours	5
368	6.8 days	I ¹³¹	364	8 days	5
525	22 hours	I ¹³³	530	20.5-22.4 hours	5

⁴Nuclear Science Abstracts New Nuclear Data 1954 Cumulation, 8, 46 (1954).

⁵Hollander, J. M., Perlman, I., and Seaborg, G. T., Rev. Mod. Phys. 25, 469-651 (1953).

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Volatile molybdenum in the distillate was indicated by a peak at 153 kev, which corresponded to the half-life of molybdenum-99 and the energy of its daughter, technetium-99m. Since the respective half-lives are 6 and 68 hours, the technetium energy would appear with the half-life of the molybdenum in secular equilibrium.

A peak at 239 kev strongly implied the presence of tellurium-132 in the distillate (Table 12). The energy and decay characteristics were also similar to the 230-kev gamma emission of neptunium-239, which might be expected from neutron absorption by the uranium. Neptunium-239, however, also emits a 280-kev gamma ray of about the same importance as the 230-kev gamma, and this was missing in the distillate samples.

Volatilized iodine was indicated by peaks at 368 and 525 kev which appeared to result from iodine-131 and iodine-133, respectively. The half-life of the 368-kev peak was 6.8 days, which is low for iodine-131. This might have been caused by the low activity and short counting time. Iodine-133 is a prominent product in the fission yield curve⁶ and its presence was expected for a few days after the irradiation. A good agreement of the energy and half-life data was obtained for iodine-133. The only other possibility, niobium-96, was unlikely because this isotope has an equally important peak at 1078 kev which was missing.

Two other peaks in the spectrum of the volatilized samples were not identified: they were not suitable for quantitative measurements since they were low and rather broad.

The activities found in the residue samples are given in Table 13. Peaks at 239 and 288 kev both correspond to neptunium-239 emissions. A consideration of the concentrations and cross sections of the isotopes initially present in the "fissium" suggested that sufficient neptunium-239 should be produced that its activity could obscure the presence of the fission product activities. This possibility has been avoided in the past by using irradiated enriched uranium for gamma-ray spectral determinations.⁷

A peak at 123 kev was difficult to identify, but it was suspected that the 239 and 288-kev gamma rays were exciting the X-ray emission of some element in the mixture. These energies are sufficiently high, for instance, to excite the K X ray of plutonium.

Less prominent peaks in the residue spectrum which were not well suited for decay measurements were found at 713 to 735 kev and at 640 to 663 kev. Both were suggestive of the zirconium-97 decay chain.

⁶Friedlander, G. and Kennedy, J. W., Nuclear and Radiochemistry, page 76, John Wiley & Sons, Inc., New York (1955).

⁷Peirson, D. H., British Journal of Applied Physics, 6, 444. (1955).

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Table 13

COMPARISON OF RESIDUE ACTIVITIES
WITH LITERATURE VALUES

<u>Determined Values</u>		<u>Literature Values of Isotopes with Similar Properties</u>			
<u>Energy (kev)</u>	<u>Half-Life</u>	<u>Isotope</u>	<u>Energy (kev)</u>	<u>Half-Life</u>	<u>Reference</u>
288	2.6 day	Np ²³⁹	280	2.3 day	8
239	2.8 day	Np ²³⁹	230	2.3 day	8
123	2.6 day	Pu K X ray	121-2	-	9

⁸LeFevre, H. W., Kinderman, E. M., and Van Tuyl, H. H., Phys. Rev., 100, 1374 (1955).

⁹Fine, S., and Hendee, C. F., Nucleonics, 13, 36-7 (1955).

These measurements have indicated that iodine, molybdenum and possibly tellurium are volatilized from bromine trifluoride solutions. Neptunium appears to remain non-volatile, which might be anticipated when one considers its chemical similarity to plutonium.

B. Semi-Works Operations

(W. J. Mecham, R. C. Liimatainen, R. W. Kessie, J. I. Thigpen, * and G. E. Goring**)

Analysis of the data obtained in the first five pilot plant runs has been completed and some additional information is presented. Corrosion coupons were removed from the dissolver and evaluated. Operation of fused fluoride process equipment was deferred in favor of a more complete study of the corrosion problem.

1. Pilot Plant Process Runs

In the previous quarterly report (ANL-5560, pages 62 to 72) results were given for the initial five pilot plant runs. The flowsheet consisted of batch dissolution of irradiated uranium metal slugs (10-kg scale) and subsequent separation of decontaminated uranium hexafluoride by fractional distillation in packed columns. As reported, the activity associated with the uranium hexafluoride product was largely due to that of

*Special scientific employee on loan from Mercurus Powder Company.

**Special scientific employee on loan from Union Carbide Nuclear Corp.

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the decay products of natural uranium. To obtain net fission product activity in the process samples, the activity due to the uranium daughters was subtracted from the total activity values previously reported. These corrections were based on an activity growth curve obtained from a sample of freshly distilled, unirradiated uranium hexafluoride, using the same analytical and counting procedures. The decontamination factors so obtained are believed to be conservative estimates (to a factor of ten in accuracy) and are shown in Table 14.

The behavior of the volatile fission product TeF_6 is of interest. The only definite amount of tellurium activity found (about 12 per cent of the estimated amount charged) was in the caustic solution of the waste vapor disposal scrubber. This implies that TeF_6 behaves as would be expected from its boiling point (-38.3°C). No indication of a less volatile form of tellurium was obtained.

It is planned to make further decontamination runs with higher levels of activity and shorter cooling time.

2. Corrosion in BrF_3 Pilot Plant Dissolver

Before the present series of process runs were attempted, the volatility pilot plant equipment was charged with various solutions for cleaning and testing purposes. Also, the process flowsheet in the series of Runs D-1 through D-5 called for exposure of the dissolver to both aqueous and interhalogen solutions. An initial set of corrosion coupons was present during all these operations and was removed at the end of Run D-5. Evaluation of the coupons was done by W. B. Seefeldt.

The coupon assembly was made up of 20 coupons. These were distributed equally between liquid and vapor phases and consisted of welded and unwelded nickel, Monel, and Inconel, plus nickel welded to Monel with nickel weld rod. The coupons were removed in March. Other coupons located in the pilot plant have not been disturbed.

The exposure conditions tabulated by the pilot plant group are listed in Table 15 and the data in Table 16.

Nickel and Monel gave satisfactory performance; Inconel appears to be inferior to them. Weight losses of the former two were comparable, although the Monel appears to be preferable with respect to formation of small pits. Penetration in the vapor phase is about half that in the liquid. Additional coupons were inserted into the dissolver when it was reassembled.

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Table 14

SUMMARY OF DECONTAMINATION IN RUNS D-4 AND D-5

Run	Description of Process Fraction	Plutonium		Fission Product Beta		Fission Product Gamma	
		Total amt., ^a ppb U	df ^b	Total amt., ^c % Unirradiated	df ^b	Total Amt., ^c % Unirradiated	df ^b
D-4	Overhead During Dissolution (~5% total UF ₆)	5	3 x 10 ²	9	3 x 10 ³	~ 0	>10 ⁴
	Distillation from Dissolver (First Cut, ~5% total UF ₆)	1.8	8 x 10 ²	3	7 x 10 ³	~ 0	>10 ⁴
	(Second Cut, ~25% total UF ₆)	-	>10 ³	0.6	3 x 10 ⁴	-	>10 ⁴
D-5	Distillation from Dissolver (First Cut, ~20% total UF ₆)	12.5	1 x 10 ³	20	3 x 10 ⁴	20	4 x 10 ⁵
	(Second Cut, ~80% total UF ₆)	2.5	5 x 10 ³	16	4 x 10 ⁴	4	2 x 10 ⁶
	Distillation in Purification Column	-	>5 x 10 ³	22.5	2 x 10 ⁵	~ 0	>2 x 10 ⁶
	Total Overhead ~55% total UF ₆						

^aIn parts plutonium per billion parts uranium.

^bDecontamination Factor (cumulative) = $\frac{\text{activity per gram uranium in dissolver charge}}{\text{activity per gram uranium in process stream}}$

^cUnirradiated uranium, due to daughter activity, has about 80 ct beta/(min)(mgU) and 4.5 ct gamma/(min)(mgU).

Table 15

ESTIMATE OF TOTAL RESIDENCE TIME OF CORROSION COUPONS
IN THE VOLATILITY PILOT PLANT DISSOLVER

A. Halogen Medium

1. Components: BrF_3 , UF_6 , BrF_5 , Br_2 , F_2 , ClF_3
(in decreasing order of amount used)
2. Temperature Range: 15 to 160° C
3. Pressure Range: 0 to 56 psia
- 4 Time: 600 hr.

B. Aqueous Medium

1. Components: H_2O , 45% HF , $\text{Al}(\text{NO}_3)_3$, HNO_3 , NaOH , NaNO_3 , $\text{H}_2\text{NSO}_3\text{H}^a$
2. Temperature Range: 15 to 60° C
3. Pressure: ~ 1 atm
4. Time: 25 hr

C. Cycles

1. Aqueous HF
2. Interhalogens
3. Caustic decanning solution
4. Interhalogens
5. Aluminum nitrate wash solution

^aConcentration of solutions:

Decanning Solution: 10% NaOH
 20% NaNO_3 by weight
 70% H_2O (distilled)

Wash Solution: 0.1 M $\text{Al}(\text{NO}_3)_3$
 0.01 M $\text{H}_2\text{NSO}_3\text{H}$
 pH = 0.5

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Table 16

CORROSION OF NICKEL, MONEL, AND INCONEL IN H-126
PILOT PLANT DISSOLVER

<u>Metal</u>	<u>Penetration, mils</u>	<u>Comments</u>
<u>Liquid Submerged Coupons</u>		
Unwelded Monel	0.7 0.8	Appearance: sound, no pitting.
Unwelded Nickel	1.0 0.6	Metal appears sound, but there are some minute pits.
Welded Monel-Nickel ^a	0.7	Some small scattered pits were observed on half of the sample.
Unwelded Inconel	2.7 2.8	General attack evident; bottom badly attacked and pitted; scattered pits elsewhere; some accelerated attack around identification stampings, and under Teflon separator.
Welded Inconel	8.9	Sample faces were uniformly attacked and pitted; edges were considerably worse; weld metal is intact, but thinned.
<u>Vapor Exposed Coupons</u>		
Unwelded Monel	0.3	Good appearance.
Unwelded Nickel	0.3 0.4	Good appearance.
Welded Monel	0.4	Good appearance.
Welded Nickel	0.4	Good appearance.
Welded Monel-Nickel ^a	0.3	Good appearance.
Unwelded Inconel	7.9 6.9	Coupon badly attacked, thinned in both dimensions at bottom; edges were pitted severely.
Welded Inconel	5.8	Faces were uniformly attacked; edges pitted severely; weld thinned, but intact.

^aWelded with nickel weld rod.

All nickel and Monel coupons had thin fluoride film.

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C. Fused Fluoride Process Studies

Operation of the fused fluoride process equipment referred to in earlier quarterlies has been deferred in order to make a further study of the general corrosion problem.

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III. FLUIDIZATION

(A. A. Jonke)

The work on fluidization process development was concentrated along two lines: (1) further study of the process for the production of refined green salt using uranyl nitrate solution from the solvent extraction refineries, and (2) development of a process for the production of refined uranium hexafluoride by direct fluorination of uranium ore concentrates followed by fractional distillation.

In the refined green salt process, attempts to replace the high cost porous filters in the denitration reactor with a cyclone separator were not successful in adequately removing the uranium trioxide dust from the off-gases. Alterations to improve the cyclone efficiency were started. Operation of the multistage reactor for hydrofluorination of the oxide produced some additional data on the effect of the temperature variable. The installation of pilot-scale equipment for green salt production was continued.

The process for direct fluorination of ore concentrates was investigated as far as the crude green salt stage in a series of continuous, single-stage runs. The reduction step was carried out at rates up to 20 lb. of uranium per hour per cubic foot of bed volume in a 6-in. diameter reactor, and the hydrofluorination step at rates up to 30 lb. of uranium per hour per cubic foot of bed volume.

Work continued on the fundamental study of the fluidization of mixtures of solid particles of two widely separated sizes. Considerable data were collected but the results could not be correlated systematically. Some evidence was found that electrostatic effects may be obscuring the results.

Discussions were held with personnel from Mallinckrodt Chemical Works, Phillips Petroleum Company (ICPP), and with representatives of three industrial companies interested in feed materials production.

A. Green Salt Process (E. Petkus, N. Levitz, M. Jones, T. Cannon)

1. Uranyl Nitrate Denitration

As described in the previous quarterly report (ANL-5560, page 111), a cyclone separator was installed in the disengaging section of the fluidized-bed calciner in place of the porous filters in an attempt to find a low-cost method of dust separation. In the experimental set-up a small bank of porous filters was used for final clean-up of the gas, although it was hoped that on a production scale the use of filters might be entirely eliminated.

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In three denitration runs in which the cyclone separation was used, no difficulties due to plugging of the dip-leg were encountered and apparently the separated dust was satisfactorily returned to the fluidized bed. The amount of fine dust which passed through the separator and collected in the filter chamber, however was 11 to 13 per cent of the uranium trioxide produced. This amount is much too large to be considered satisfactory and indicates that the efficiency of the cyclone was low.

It is likely that the low separating efficiency is at least partly due to the passage of some gas up through the cyclone dip-leg rather than through the inlet tube. To provide a more dependable dip-leg seal it was decided to install a "trickle" valve (Figure 17) at the solids discharge end of the cyclone. In operation the valve remains closed until there is sufficient head of material in the dip-leg to counterbalance the pressure differential across the cyclone. The valve plate then swings open and allows discharge until the pressure differential again exceeds the material head.

A 1-in. diameter "trickle" valve has been obtained from the manufacturer (Ducon Company) and has been welded to the dip-leg of the 3-in. cyclone. Testing of the valve is planned for the next quarter.

Figure 17

TRICKLE VALVE FOR SOLIDS DISCHARGE
FROM CYCLONE SEPARATOR

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2. Reduction and Hydrofluorination

Operation of the multistage fluidized-bed reactor was continued. Originally the objective of runs made during this period was to study the effect of operating variables on the rate of conversion to green salt; however, some operating difficulties were encountered during hydrofluorination which made it necessary to alter the primary objective to an improvement of mechanical operability.

No problems were encountered in the two reduction runs made during this quarter. Smooth operation was obtained during the 13 hr of operation, representing 3.4 throughputs. The product assayed 96 to 97.5 per cent uranium dioxide under the usual operating conditions of 4-hr residence time at 575 C. The feed rate corresponded to about 60 lb/hr per cubic foot of bed volume.

On two consecutive occasions during hydrofluorination of the dioxide, the downcomer leading from the middle to the bottom stage became plugged after about one hour of operation. Investigation disclosed a loosely sintered cake in the downcomer. Since uranium tetrafluoride has a strong tendency to cake during its preparation at high temperatures unless it is well agitated, it was thought that the caking might have been caused by a somewhat erratic flow of hydrogen fluoride. A second possibility was that the high temperature on the bottom stage (600°C) might have contributed to sintering, although no trouble was encountered in the previous run at this temperature.

To smooth out the flow of hydrogen fluoride gas, the inlet line was traced with heating wire and insulated to prevent condensation, assumed to be the cause of the erratic flow. In addition, the three bed temperatures were lowered to 550, 475, and 400°C, respectively, from bottom to top. With these changes good operability was obtained and no plugging occurred.

The results of Run 25 made under the above conditions are summarized in Table 17 together with the results of two previous runs made at different temperatures. The data are too meager to draw firm conclusions, but the following tentative conclusions are indicated:

- (1) Roughly 78 percent of the conversion occurred on the top stage, 15 per cent on the second stage, and 3 per cent on third stage.
- (2) Increasing the bottom stage temperature from 450°C to 600°C definitely improved the rate of conversion of the last 10 per cent of uranium dioxide.
- (3) Increasing the second stage temperature from 450°C to 500°C appeared to increase the rate of conversion.

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Table 17

RESULTS OF MULTISTAGE HYDROFLUORINATION RUNS AT VARIOUS TEMPERATURES

Run No.	UO ₃ Source (Run No.)	Feed Rate (lb/hr)	Residence Time (hr)	Gas Composition (% HF) ^a	Gas Velocity (ft/sec)	Stage Temperatures, C			Stage Conversions (% AOI)			Product Conversion %		
						Top	Middle	Bottom	Top	Middle	Bottom	UO ₂	UO ₂ F ₂	UF ₄
20	P-75	2.1	4	66	0.57	450	450	450	21	8.9	7.0	5.2	4.0	90.0
22	P-74	1.8	4	64	0.45	400	500	600	17	1.6	0.7	0.9	0.6	98.4
25	P-81	1.8	4	44	0.50	400	475	550	28	9.4	2.5	3.1	1.8	95.2

^aGas diluted with nitrogen and hydrogen.

Further runs in the 3-in. multistage reactor are planned for the near future to investigate variables, particularly temperature and hydrogen fluoride concentration. This work was deferred for a short time in order to develop a process for crude green salt production from uranium ore concentrates.

3. Green Salt Pilot Plant

The fluidized-bed reactors have not yet been received from the fabricators. These components are nearing completion and are expected to be ready for installation early in the next quarter. The installation of the control panel is essentially completed.

B. Direct Fluorination of Uranium Ore Concentrates

Work continued on the development of a process for the production of refined uranium hexafluoride by direct fluorination of uranium ore concentrates. A block flow diagram of the proposed process is shown in Figure 18. This process appears to be economically attractive as a result of the following recent technological developments:

- (1) the development of the ion exchange process for concentrating ores has greatly increased the supply of high-grade concentrates;
- (2) knowledge gained in the development of the fluoride volatility process for spent reactor fuels indicates that a similar technique for ore purification will be feasible;
- (3) the cost of producing elemental fluorine has shown a tendency to decline.

Previous batch experiments in fluidized beds with South African Rand ore concentrate indicated that the reduction and hydrofluorination steps could be performed without apparent difficulties. It was decided to study these steps further in a series of continuous, single-stage runs using the Rand concentrate for the initial experiments--later extending this work to other types of ore concentrates.

The choice of a single-stage rather than a multistage reactor for these experiments was made for two reasons: (1) previous experiments had indicated that the Rand concentrate was very reactive (consequently the necessity for multiple stages was much reduced), and (2) the presence of a large percentage of very fine particles in the crushed concentrate would make the operation of a multistage unit somewhat more difficult.

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Figure 18

PROPOSED FLOWSHEET FOR DIRECT FLUORINATION OF URANIUM ORE CONCENTRATES

1. Reduction of Ore Concentrate

Experience had shown that when the Rand ore was reduced and hydrofluorinated in a Monel reactor an appreciable amount of scale was formed on the walls of the reactor. A spectrochemical analysis showed that the scale was composed primarily of nickel and copper, indicating corrosion. Analysis of the concentrate (Table 18) showed the presence of sulfate and nitrate in sufficient quantities to constitute a corrosion problem, and the presence of hydrogen sulfide, known to be highly corrosive to Monel, was detected in the off-gases during reduction.

Table 18

CHEMICAL ANALYSES OF RAND ORE CONCENTRATE

<u>Element</u>	<u>Analysis (%)</u>	<u>Element</u>	<u>Analysis (ppm)</u>
Uranium	69.88	As	300
Loss at 110°C	0.05	B	10
NH ₃	1.72	Ca	800
SiO ₂	2.06	Cu	50
Cl	0.018	Fe	3000
F	< 0.03	K	100
SO ₄	0.24	Mn	500
NO ₃	0.35	Mo	< 20
		Na	20
		Ni	100
		P	50
		V	< 50

To circumvent the corrosion problem it was decided to conduct the reduction step in a stainless steel reactor under the assumption that both the sulfate and nitrate would be removed in the off-gases, thus permitting the use of Monel for hydrofluorination.

The 6-in. diameter, stainless steel reactor which had been used for denitration of uranyl nitrate was modified for use in the reduction operation. This reactor was described in a previous quarterly report, ANL-5290, pages 114 to 118. The spray nozzle was removed, and the small hopper previously used for charging solids to the reactor was removed and

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replaced by a larger (5-gallon) hopper. A small screw feeder was installed to feed solids from the hopper to the reactor above the fluidized bed, and a second screw feeder was installed to remove solids from the bottom of the bed into a sealed container.

The ore concentrate was crushed in a jaw crusher and screened through a 20-mesh sieve, the oversize being returned to the crusher. The sieve analysis and bulk density of the crushed feed are given in Table 19. Three runs, ranging in duration from 7 to 14 hr, were completed and are summarized in Table 20. The first run (37) consisted of two 6-hr. periods with overnight shutdown between periods. The last run (39) was continuous for 15 hr except for a forced shutdown of about one hour due to a plug of solids in the feed line to the screw feeder. Except for this trouble the operation was smooth and without incident. The feed inlet line is being enlarged to avoid a recurrence of the plugging.

Table 19

PHYSICAL PROPERTIES OF CRUSHED RAND ORE CONCENTRATE
BEFORE AND AFTER REDUCTION AND HYDROFLUORINATION

<u>Sieve Analyses</u>			
<u>Mesh Size</u>	<u>Crushed Ore Concentrate Feed</u>	<u>After H₂ Reduction</u>	<u>After Hydrofluorination</u>
+20	0	0	0
+40	35	33	26
+60	22	24	24
+100	12	14	16
+200	16	17	21
+325	5	5	6
-325	10	7	7
<u>Bulk Densities (g/cc)</u>			
Untapped	1.16	1.44	1.48
Tapped	1.51	1.60	1.58

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Table 20

SUMMARY OF REDUCTION RUNS ON RAND ORE CONCENTRATEEquipment: 6-in diameter, stainless steel, single-stage reactorOperating Conditions:

Starting Bed: about 21 lb of reduced ore concentrate

Static Bed Depth: about 14 in

Bed Temperature: 575°C

Gas Composition: 75% H₂, 25% N₂

Gas Velocity: 0.4 ft/sec

	<u>Run 37</u>	<u>Run 38</u>	<u>Run 39</u>
Feed Rate (lb/hr)	5.2	7.8	7.1
Residence Time (hr)	5	3.5	4
Duration	12	7	14
Throughputs	2.4	2.3	3.5

Run Results:

<u>Hours After Start</u>	<u>Percentage Reduction</u>		
	<u>Run 37</u>	<u>Run 38</u>	<u>Run 39</u>
1			89.8
2	92.4	81.0 ^a	97.7
3			97.6
4	98.9	94.9	96.2
5			
6	97.0		97.0
7		88.5	95.1
8	99.4		93.2
9			94.0
10	97.0		84.6 ^a
11			96.9
12	100.0		95.1
13			93.5
14			97.7

^aSample partially oxidized due to in-leakage of air.

In Run 37 the entrained fines were allowed to pass out of the reactor with the off-gases and were collected in a separate filter chamber. The fines thus collected amounted to about 18 per cent of the total feed. For Runs 38 and 39 the porous stainless steel filters were re-installed in the disengaging section of the reactor, and the fines were returned to the bed by blowback of the filters.

It was found that the reduced ore concentrate reoxidized readily upon exposure to air at room temperature. Oxidation was detectable both by a change in color from brown to black and by the liberation of considerable heat due to the reaction. Samples for tetravalent uranium analyses were therefore taken in a nitrogen atmosphere and covered with phosphoric acid immediately after weighing. In two instances oxidation of the samples was observed despite these precautions.

The results of the runs, given in Table 20, indicate that an average of 98.5 per cent reduction was achieved with a residence time of 5 hr, and 95.8 per cent average with a residence time of 4 hr. The bed temperature for these runs was maintained at 575°C to insure that the oxide product would have a high reactivity during the subsequent hydrofluorination. However, since it is not yet known whether the reactivity of this material is sensitive to reduction temperature (as is the case for certain types of uranium oxides), additional runs are planned at higher temperatures.

2. Hydrofluorination of Ore Concentrate

For the hydrofluorination experiments the 3-in diameter Monel reactor was operated as a single-stage unit. Two runs were made using the product from reduction Run 37. Results are summarized in Table 21. In both cases the excess hydrogen fluoride was maintained at 25 to 30 per cent over the stoichiometric amount required for the uranium and impurities. The feed rate was 1.75 lb/hr in one run and 2.8 lb/hr in the other. For a linear gas velocity of 0.3 ft/sec the gas concentration required was 38 per cent hydrogen fluoride for Run 26 and 86 per cent for Run 27.

The results indicate that the uranium oxide was exceedingly reactive toward hydrofluorination, the unconverted oxide (AOI) averaging 5.0 per cent for Run 26 and 3.8 per cent for Run 27. The small excess of hydrogen fluoride required indicates that it may be feasible to neutralize and discard the off-gases rather than to attempt recovery. The use of a second stage in series with the first could reduce the excess hydrogen fluoride to even lower values.

Under the conditions of Run 27 the off-gases contained approximately 30 per cent hydrogen fluoride, 50 per cent water, and 20 per cent inerts. At the temperature used in the run (450°C) the

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Table 21

SUMMARY OF HYDROFLUORINATION RUNS
ON RAND ORE CONCENTRATE

Equipment: 3-in diameter, single-stage, Monel reactor.

Operating Conditions:

	<u>Run 26</u>	<u>Run 27</u>
Starting Bed	(7.3 lb of hydrofluorinated concentrate)	
Static Bed Depth	about 18 inches	about 18 inches
Bed Temperature	450°C	450°C
Inlet Gas Composition	$\left\{ \begin{array}{l} 38.4 \% \text{ HF,} \\ 43.5 \% \text{ N}_2, \\ 18.1 \% \text{ H}_2 \end{array} \right.$	$\left\{ \begin{array}{l} 86.3 \% \text{ HF,} \\ 9.9 \% \text{ N}_2, \\ 3.8 \% \text{ H}_2 \end{array} \right.$
Gas Velocity	0.3 ft/sec	0.25 ft/sec
HF/feed Ratio	1.25 x stoichiometric	1.3 x stoichiometric
Feed Rate	1.75 lb/hr	2.8 lb/hr
Residence Time	4.6 hr	2.2 hr
Duration	10 hr	5 hr
Throughputs	2.2	2.3

Results

<u>Hours After Start</u>	<u>AOI^a</u>	<u>UO₂F₂</u>	<u>UF₄</u>	<u>AOI^a</u>	<u>UO₂F₂</u>	<u>UF₄</u>
1	0.57	3.8	91.4	4.5	1.7	90.0
2	3.7	4.3	88.3	3.6		90.3
3	9.2	2.8	83.0	2.9		91.8
4	7.0	1.9	85.1	3.5	0.8	91.1
6	3.5	1.0	90.2	3.7	0.7	91.1
7	5.3	2.0	86.0			
9	2.8	0.7	91.5			
10	3.3	3.9	86.4			

^aAmmonium Oxalate Insoluble

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equilibrium hydrogen fluoride concentration for the reaction of uranium dioxide with hydrogen fluoride-steam mixtures is about 16 per cent.¹⁰ The latter represents the minimum concentration which could theoretically be attained in the off-gases at this temperature.

In both the reduction runs and the hydrofluorination runs the bed remained uncaked and the product was free-flowing. The sieve analyses and bulk densities of the products after reduction and hydrofluorination are compared with those of the feed in Table 19. Only a very slight reduction in particle size occurred in these operations, indicating that the amount of attrition was small. The bulk density increased about 20 per cent in the reduction step and remained constant during hydrofluorination. No scaling or other evidence of corrosion was visible in either the stainless steel (Type 304) reduction reactor or the Monel hydrofluorination reactor. In future runs it is planned to obtain additional corrosion data by inserting test specimens of several metals into the fluidized beds. Analyses for residual sulfate and other impurities in the products of the reduction and hydrofluorination steps have not yet been completed, and these will be reported next quarter.

C. Calcination of Reactor Fuel Processing Wastes (J. Loeding)

Work on this project proceeded at a reduced pace because of the press of other work. Fabrication of components and procurement of equipment was continued, but installation has not yet been started. It is hoped that installation of the calciner can begin during the following quarter.

D. Fundamental Studies (H. Katz, M. Deerwester)

Work continued on the study of particle size distribution in fluidized beds of glass beads. One further simplification in experimental procedure was made, which resulted in an appreciable shortening of the time required for a run. It was found that the two sections of the bed representing the upper, fine-particle phase and the lower, coarse-particle phase could be separated by drawing them off through a tube into a bottle by the use of suction created by an air ejector. Data obtained in this manner proved to be just as accurate as that obtained by the previous (gelatin) procedure, and a number of steps were eliminated.

In an effort to explain the unusual shape of the curve tentatively reported in ANL-5560, page 124, for the binary mixture consisting of 40-60 and 140-200 mesh particles, a considerable number of additional runs were made with this mixture and with several others. This work showed that the curves previously presented were based on insufficient data at higher gas flow rates and that the vapor-liquid analogy was an oversimplified picture of the actual situation. At the high gas velocities the data tended to scatter

¹⁰Bertram, H. W., NYO-2043 (1953) pp. 24-27

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badly. The previously reported curves appear to be valid only at the low or moderate gas velocities required for mixtures containing a small proportion of coarse particles. Additional uncontrolled experimental factors apparently remain and are being investigated.

Both visual observation and careful pressure drop measurements showed that for binary particle mixtures the following sequence of events occurs as the gas velocity is increased:

- (1) at the velocity corresponding to the onset of fluidization the bed begins to segregate into a static lower portion and a fluidized upper portion of fine particles. The amount of the upper phase increases with increasing velocity and the amount of the lower phase decreases correspondingly. The percentage of coarse particles in both phases increases with velocity.
- (2) at some intermediate velocity the lower static phase becomes fluidized, but the bed remains segregated in two distinct phases separated by a clearly visible interface. The lower phase at this point consists almost entirely of coarse particles, yet fluidization of this phase occurs at velocities considerably below the minimum velocity at which fluidization of a bed composed solely of the coarse particles normally commences. This must mean that the lower phase is not at the maximum stable fixed-bed void fraction, but is more tightly packed (lower void fraction) under the weight of the upper phase.
- (3) the relative amounts of the two fluidized phase changes with increasing gas velocity until at some higher velocity complete homogeneity is attained. Attempts to establish the velocity at which this occurs has produced somewhat scattered and non-reproducible data.

A large portion of the work during this quarter was directed toward attempting to establish the reason for the poor reproducibility of data. There is some reason to believe that the trouble may be due to variable electrostatic effects. It is also possible that the non-reproducibility is solely due to statistical variations characteristic of fluidized beds. Efforts are now being made to eliminate the electrostatic effects, and additional data will be collected.

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IV. REACTOR CHEMISTRY

A. Metal Oxidation and Ignition

(D. S. Flikkema,* H. A. Porte, G. Schnizlein, R. C. Vogel,
D. Fischer and A. Porter)

The increasing use of nuclear reactors with concomitant handling of reactive metals such as uranium, thorium, zirconium and plutonium makes imperative an understanding of the factors which influence their pyrophoric nature. To elucidate these factors a study has been started on the oxidation characteristics of uranium and zirconium. The reasoning behind the experimental approach for this program has been outlined in ANL-5494, pages 104 to 109. It is felt that conditions which accelerate the oxidation will lower the ignition temperature and increase the possibility of spontaneous ignitions. For example, it has been shown¹¹ that a direct relationship exists between oxidation rate and ignition temperature in the magnesium-aluminum system. A similar correlation may become apparent with zirconium and uranium. If such a correlation can be established it may be possible to predict the likelihood of spontaneous ignition of a metal without resorting to ignition tests of a statistical nature. By the use of such a correlation it may be possible to evaluate the variables which lead to a greater tendency toward ignition.

1 Uranium

The wide differences in the literature data on uranium oxidation have been pointed out in ANL-5494. For example, at 100° C and after 4000 minutes the extent of oxidation for various experiments under similar conditions varies by a factor of about forty. At 200° C and after 40 minutes the extent of oxidation varies by a factor of twenty. Since rather modest differences in rate could make the difference between slow corrosion and ignition (too rapid oxidation for heat loss to maintain isothermal conditions), it was considered appropriate to investigate the causes of these differences. With this background it is clear that first a base-line set of conditions for the oxidation of uranium must be established. These base-line conditions must be defined with sufficient rigidity so that oxidation data obtained on pure uranium are reproducible. After the base-line runs have established the experimental procedures, the variables of metal composition, metallurgical history and reactant gas composition must be altered individually and the effect of each variable assessed by comparison with the base line experiments on the oxidation of pure uranium

*D. S. Flikkema is a member of the analytical research group and is responsible for the X-ray diffraction studies reported here.

¹¹Fassel, W. M., et al., J. Metals 3, 522 (1951).

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a. Apparatus

The consumption of oxygen by a uranium metal sample has been followed by measuring the volume additions to the system necessary to maintain constant pressure. Figure 19 illustrates the system now in use. A furnace, 2 in. in diameter, is vertically mounted. To obtain a more uniform temperature the reactor tube is completely surrounded by a section of brass pipe. The furnace temperature is controlled by a proportional controller whose thermocouple is located outside, but near, the brass sleeve.

Figure 19

APPARATUS FOR VOLUMETRIC DETERMINATION OF METAL OXIDATION

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The reactor is constructed of 22-mm Pyrex glass tubing and has an evacuated inner envelope to minimize the volume of gas in the region of the temperature gradient at the lower end of the furnace. A semi-ball joint is provided below the furnace to facilitate introducing and removing the metal sample. The metal sample, a cube, rests on the top of a thermocouple well in the reactor.

A slant tube differential mercury manometer with electrical contacts serves as the pressure controller. The pressure in the bulb side is preset to maintain the desired pressure in the system.

A 100-ml gas buret, graduated in 0.1-ml intervals, is the oxygen reservoir during a run. A similar buret is mounted on a motorized rod runner. This buret serves as a mercury reservoir. When the regulator makes contact due to consumption of oxygen and a slight pressure lowering, the rod runner is activated, raising the leveling buret and restoring the pressure to its initial value. The ascent of the rod runner is stopped when the contact is broken in the pressure regulator. The gas buret may be refilled from the storage bulb. The rate of the oxidation is obtained by reading the gas buret at appropriate time intervals. A recording device, which plots the volume of oxygen consumed vs time, is now being tested. If successful, this device will relieve much of the tedium of buret reading.

b. Uranium Metal Samples

Fabrication - The uranium used was fabricated by the Argonne Metallurgy Division. High grade biscuit metal was melted at 1295° C and 1.2×10^{-3} mm pressure in a high purity magnesia crucible. Then it was bottom-poured into a hot graphite mold to form a hollow cylinder 2-1/2 in. OD, 1 in. ID, and 11-1/4 in. long. This casting weighed 13.5 kg. The impurities are indicated in Table 22.

A portion of the casting was quartered, rolled to flatten (coincidentally reduced somewhat from 3/4-in. thickness), and sectioned with an abrasive cutoff wheel to make 3/8-in. cubes. These cubes were presumably heated and quenched from the beta-uranium temperature region, a procedure used to randomize the crystallite orientation. However, at this point metallographic examination showed the bent twins and subgraining typical of beta-treated uranium (Figure 20). Average grain size was determined by the random line intercept method to be 0.06 to 0.08 mm. An attempt is being made to determine the nature and the degree of preferred crystallite orientation remaining.

Analysis of a typical cube is given in Table 22.

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Figure 20

MICROSTRUCTURE OF TYPICAL URANIUM CUBE

In polarized light at 100X magnification

- a - Bent twins
- b - Subgraining
- c - Inclusions (seen as white spots)

Surface treatment given photographed specimen

Mechanical polish - 80 thru 600 grit

6 micron diamond paper and cloth

3 micron diamond cloth

Electro polish

- Current - 30 milliamps /cm²

Electrolyte - 8 parts 95% ethanol

5 parts ethylene glycol

5 parts 85% ortho phosphoric acid

Cathode - Stainless steel

Anode - Uranium specimen

Touch wire - Platinum

Time - 7 minutes

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Table 22

ANALYSIS OF URANIUM USED IN METAL
OXIDATION STUDIES

Results expressed in ppm.

<u>Element</u>	<u>Original Casting</u>	<u>Fabricated^a Cubes</u>
O		12
C	31 (top), 44 (bottom)	21
N	43 (top), 48 (bottom)	56
H		5
Si	80	70
Fe	50	40
Ni	20	15
Al	10	10
Cr	10	5
Mn	5	2
Mg	4	3
Cu	2	3
B	<1	

^aThe analysis for those constituents not indicated were below the limits of spectrographic detection.

Surface Preparation - A series of variously finished specimens were examined for diffraction line broadening by means of an X-ray diffractometer in order to determine the surface treatment necessary to remove noticeable cold work from the surfaces of the uranium cubes. The results were obtained by point-to-point counting over the (021) alpha-uranium peak.

In this case the factors which can be involved in line broadening are crystallite size and crystallite lattice deformation. On the assumptions that the initial crystallite size in this series of specimens was similar and that the cold work caused changes in surface crystallite lattice spacings, the line broadening was taken to indicate the residuum of strain in the finished surface. The data are given in Table 23 and shown in Figure 21. Since the finest mechanical polishing left some cold work, it was decided to finish the pure metal surfaces by electropolishing technique. This consisted of a 7-minute exposure to a solution consisting of 8 parts 95 per cent ethanol,

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Figure 21

X-RAY DIFFRACTOMETER SCANS SHOWING THE (110) (021) and (002)
LINE PROFILES FROM α -URANIUM AFTER
VARIOUS SURFACE TREATMENTS

5 parts ethylene glycol, 5 parts 85 per cent ortho phosphoric acid. The current density was 30 milliamperes per sq cm; the cathode was stainless steel; the anode contact was made through a platinum touch wire.

Table 23

WIDTH AT 3/4 HEIGHT OF THE
(021) α -URANIUM LINE

<u>Final Surface Finish</u>	<u>Degrees (2θ)</u>
600 grit paper	~ 0.2
600 grit, then HNO_3 etch	0.15
1-micron diamond paste polish	0.10
Mechanical through 1-micron diamond paste and electropolish	0.052 ^a

^a Approaches the value for instrumental broadening; spectral or natural broadening is negligible in this Bragg angle region.

When the oxidation rates of alloys are compared with those for pure uranium, consideration will have to be given to the problem of preferential dissolution of one constituent, leaving the surface enriched in the other constituent. It may be necessary to use mechanical polishing through 1-micron diamond paste in these cases.

c. Results

Effect of Surface Preparation on Oxidation at 200° C -

A series of oxidations at 200° C and 200 mm oxygen pressure were made on uranium cubes surface-finished by use of either (1) 1-micron diamond paste in air, (2) 1-micron diamond paste in an inert atmosphere box or (3) electropolish.

In all cases the oxidation proceeded in two stages. The first stage appeared to have a constant rate of $0.64 \pm 0.24^* \mu\text{gm}/(\text{sq cm})(\text{min})$ for a period of 72 ± 20 minutes, or until the total oxygen consumed was $51 \pm 15 \mu\text{gm}/\text{sq cm}$. Then the reaction accelerated and another constant rate was found. This second stage rate, constant at $5.8 \pm 0.5 \mu\text{gm}/(\text{sq cm})(\text{min})$,

*In this presentation of data all the accuracies are expressed as average deviations from the mean

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was attained after 100 to 150 minutes. Most runs were carried out for approximately 300 minutes. One was followed with two interruptions for 740 minutes; each part showed the same linear rate. This indicated that the slow first stage rate was associated with the formation of the first oxide and not with the beginning manipulations in an experiment.

The only oxide detected by means of X-ray diffraction was UO_2 at all stages of the oxidation at 200 mm oxygen and 200°C . The results of examination at three points during the oxidation are tabulated in Table 24.

Table 24

PHASES DETECTED BY X-RAY DIFFRACTION

Treatment	O_2 Consumed ($\mu\text{gm}/\text{sq cm}$)	Phases Detected
In vacuo at room temp. overnight; then heated to 200°C at 10^{-5} mm	-	(a) α -U preferentially oriented. (b) UO_2 only barely detectible.
25-min oxidation at 200 mm and 200°C	20	(a) α -U preferentially oriented. (b) UO_2 preferentially oriented; crystallite size less than $100\text{ m}\mu$.
334-min at 200°C 200 mm O_2	1077	(a) α -U random, barely detectible. (b) UO_2 preferentially oriented; crystallite size less than $100\text{ m}\mu$.

Data from a typical experiment are shown in Figure 22, with an illustration of the rates in each stage. The oxidized surfaces in both stages of the oxidation at 200°C were examined by means of an X-ray diffractometer; in all cases the only oxide found was UO_2 . Extreme broadening of the diffraction peaks indicated crystallite size very much less than $100\text{ m}\mu$. As expected, crystal growth of the dioxide in these layers was oriented.

Comparison of the rates in the first and second stages and of the time and the total oxygen consumed per sq cm at the end of the first stage shows no difference due to surface preparation. These comparisons are shown in Table 25.

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Figure 22

TYPICAL RUN PLOT TO DETERMINE RATES

A number of conclusions can be drawn from the data obtained at 200° C and 200 mm. These are the following:

- (1) It has been possible to obtain reproducible data. These data are reproducible to within (a) 37 per cent for the first stage rate, (b) 27 per cent for the duration of the first stage reaction, (c) 30 per cent for the amount of oxygen consumed during the first stage, and (d) 7 per cent for the second stage rate. These accuracies are quite gratifying, considering the well-known tendency for this type of data to be irreproducible.
- (2) The method of surface treatment does not influence the rate of oxidation. The values indicated in Table 25 for various sample preparations agree, within the

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Table 25

OXIDATION OF URANIUM - EFFECTS OF SURFACE PREPARATION

Temperature: 200° C

Pressure: 200 mm

Sample: Uranium cubes, 1 cm on each edge. Analysis presented in Table 22.

Preparation	1st Stage			2nd Stage
	Rate $\mu\text{gm}/(\text{sq cm})(\text{min})$	Duration (min)	$\mu\text{gm O}_2$ Consumed	Linear Rate $\mu\text{gm}/(\text{sq cm})(\text{min})$
1- μ diamond paste in air	1.1	56	78	5.5
	0.51	85	62	6.2
	0.84	62	61	5.8
	0.35	≥ 57	≥ 54	-
Average	0.70 ± 0.26	65 ± 10	64 ± 7	5.8 ± 0.2
1- μ diamond paste in inert atm	0.66	41	42	5.7
	0.52	59	48	6.0
Average	0.59 ± 0.07	50 ± 9	45 ± 3	5.85 ± 0.15
Electropolished	1.1	38	40	6.3
				5.1
				5.0
	0.36	68	33	5.9
	0.27	86	34	-
	0.29	108	31	5.3
	1.2	35	25	6.5
	0.52	-	-	-
	0.68	92	70	6.3
	0.51	84	48	6.1
	0.62	130	82	≥ 5.1
Average	0.61 ± 0.25	80 ± 23	48 ± 16	5.7 ± 0.5
Average of all				
200° C				
200 mm O ₂	0.64 ± 0.24	72 ± 20	51 ± 15	5.8 ± 0.4

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average deviations, with those values calculated for all runs. Therefore, it can be concluded that electro-polishing is a satisfactory method of surface preparation. The data also indicate that it is feasible to use other methods of surface preparation.

Oxidation Studies at Various Temperatures - Oxidations have been conducted under 200 mm oxygen at 150, 175, 200, 225, 250, 275, 295 and 325° C. At temperatures lower than 200° C the oxidation proceeded in a manner very similar to 200° C experiments. In the first stage the rate remained constant until oxygen consumption was approximately 50 $\mu\text{gm}/\text{sq cm}$. Then the rate increased in the second stage to a higher constant value.

At temperatures above 200° C the same characteristic first stage was observed in all runs. Although the time period was very short, the rate remained constant until the same film thickness (approximately 60 $\mu\text{gm}/\text{sq cm}$) developed.

In the second stage the rate was no longer linear, but proceeded through a maximum. In runs at 295° C, a second maximum was observed.

Figure 23 illustrates typical data for each temperature. It was decided to plot rate versus total oxygen consumed to illustrate the reproducibility of the end of the first stage for all temperatures. For all runs at all temperatures this corresponds to 65 $\mu\text{gm}/\text{sq cm}$ with an average deviation of 37 per cent. It can be concluded that there is a change in mechanism of the oxidation at this point. From a more practical standpoint, if a means can be found to extend this first stage oxidation beyond this point uranium may be made more stable.

Table 26 summarizes the rates observed at each of the temperatures. Both the rate and the end of the first stage (in μgm oxygen per sq cm) are given for each temperature. In the second stage the linear rate is given for runs at temperatures up to and including 200° C. For the runs over 200° C maximum and minimum rates are given. At 295° C two maxima are shown.

X-ray diffraction study shows the product of oxidation at 295° C and 200 mm O_2 pressure is UO_2 with crystallite size very much less than 100 $\text{m}\mu$.

During higher temperature runs the temperature of the cube, as sensed by the thermocouple in the glass well, was observed to rise. Obviously this was caused by the heat of the reaction. At the higher temperatures we are therefore in the region of accelerating oxidation for our experimental conditions. An effort is being made to measure the actual temperature of the cube surface more closely during the oxidation.

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Table 26

SUMMARY RATE DATA FOR VARIOUS TEMPERATURES

Temp	Run No.	1st Stage		2nd Stage		
		Rate [$\mu\text{gm}/(\text{sq cm})(\text{min})$]	End [$\mu\text{gm}/(\text{sq cm})$]	Linear Rate [$\mu\text{gm}/(\text{sq cm})(\text{min})$]	Max Rate [$\mu\text{gm}/(\text{sq cm})(\text{min})$]	Min Rate [$\mu\text{gm}/(\text{sq cm})(\text{min})$]
150	34	0.14	45	0.54		
	36	0.18	51	0.58		
	Avg	0.16 ± 0.02	48 ± 3	0.56 ± 0.02		
175	37	0.15	41	1.3		
	39	0.28	34	1.8		
	41	0.31	51	2.3		
	Avg	0.24 ± 0.07	42 ± 6	1.8 ± 0.05		
200	15 runs avg	0.64 ± 0.24	51 ± 15	5.8 ± 0.4		
225 ^a	38	1.8	60		12.8	9.0
		0.96	60		15.5	12.1
	Avg	1.4 ± 0.4	60 ± 0		14.1 ± 1.4	10.5 ± 1.5
250 ^a	18	-	-		35	15.3
	19	-	-		45	15.3
	20	6.5	70		29	12.9
	21	2.5	55		28	13.8
	Avg	4.5 ± 2.0	67.5 ± 2.5		34 ± 6	14.3 ± 1.0
275 ^a	27	7.2	86		74.6	22.6
	28	6.4	71		49.0	20.8
	Avg	6.8 ± 0.4	78.5 ± 7.5		62 ± 13	21.7 ± 9
295 ^b	29	15.3	155		74	75
	30	8.5	98		71	64
	31	17.0	153		67	-
	Avg	14 ± 3	135 ± 25		70 ± 3	72 ± 7

Avg for all temperatures 65 ± 24

^aRuns over 225C show a decrease of rate at longer times (total O₂ consumed), as can be seen on Fig. 23. The maximum rate is obvious, but the minimum rate is chosen at the end of the run.

^bAt 295C two maxima appear (Fig. 23).

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Figure 23

OXIDATION OF URANIUM IN 200 mm O₂ AT VARIOUS TEMPERATURES

The activation energy over the entire temperature range 150 to 300° C is of the order of 16 kcal per mole.

d. Discussion

The data do not conform to any classical rate law. Experiments are still being carried out to clarify the mechanism of the reaction. Experiments are planned to study the reaction dependence on pressure, additions of certain alloying agents, gas composition and metallurgical variables.

2. Zirconium

Several recent incidents involving the "spontaneous" ignition or explosion of zirconium have re-emphasized the potential hazards which accompany the use of this metal. It is hoped that a more thorough understanding of the eccentricities of this metal could minimize many of the dangers involved in its handling and storage. With these goals in mind, a program is being initiated at this Laboratory to investigate the factors

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involved in the kinetics of the reactions of zirconium with oxygen, nitrogen and air. The results of the appropriate literature search are summarized in this section. An attempt is being made to evaluate the application of the same experimental approach to zirconium that is being used for uranium. It was found that the reaction of zirconium with oxygen has been studied rather extensively over a range of temperatures from 200 to 1100°C. These data are shown in Figures 24, 25, and 26. Some investigators have shown that the reaction follows the parabolic rate law, $w^2 = kt$, where w is the weight gain per unit area, t is the time, and k is an experimental constant which is a function of the temperature. The data for pure zirconium are compared in Table 27 through the use of the parabolic rate constant. Others¹⁵ contend that their data best fit the cubic rate law, $w^3 = kt$. Although some small pressure effects have been noted,^{12,18} most investigators agree that the effect of pressure on the reaction kinetics is negligible.

Figure 24

SELECTED LITERATURE DATA ON THE REACTION OF ZIRCONIUM
WITH OXYGEN, 300 TO 687°C

The reaction product has been identified as zirconium dioxide. At lower temperatures only the monoclinic form of the dioxide can be identified, but above 1000°C X-ray analysis has revealed the presence of a number of tetragonal lines.

¹⁵Belle, J. and Mallett, M. W., *J. Electrochem. Soc.* **101**, 339 (1954).

Figure 25

SELECTED LITERATURE DATA ON THE REACTION OF ZIRCONIUM WITH OXYGEN, 700 TO 845°C

Figure 26

SELECTED LITERATURE DATA ON THE REACTION OF ZIRCONIUM WITH OXYGEN, 900 TO 1100°C

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Some rather large differences have been found in the activation energies involved and in the ignition temperatures of the pure metal. It is believed that some of these discrepancies are due to the variations in the hafnium contents and in the metallurgical preparation of the sample. As can be seen from the data presented in Figures 24, 25 and 26, the differences between various investigators is not large. For example, if the amount of oxygen consumed by samples of various investigators at the same temperatures is compared, the data differ in extreme cases by only a factor of two. In a similar comparison for the uranium data the spread of data is a factor of twenty to forty. Using the data for the parabolic rate constant presented in Table 27, there is a similar satisfactory agreement.

Nitrogen also reacts with zirconium, but at a much slower rate than for the reaction with oxygen. There is some evidence that the presence of small traces of oxygen in the nitrogen noticeably accelerates the rate of the reaction. Most investigators, however, agree that the parabolic rate law is obeyed. The product of the reaction at all temperatures has been identified as golden-yellow zirconium nitride. Literature data are compared through the use of the parabolic rate constant and are presented in Table 28.

Some work has also been done on the reaction of zirconium and zirconium alloys with air. In general the reaction rate is higher in air than in either nitrogen or oxygen alone. Both zirconium dioxide and zirconium nitride have been identified as products of the air oxidation. The data on alloy oxidation is somewhat qualitative in nature, but it indicates that in most cases alloy addition does not markedly improve the oxidation resistance of zirconium. These data are presented in Tables 29, 30, 31, and 32.

The immediate program is, after construction of the necessary experimental apparatus, to investigate the kinetics of the reaction of pure zirconium with pure oxygen. Although the literature data for zirconium are in better agreement than for uranium, it is believed necessary to do some experiments on pure zirconium for base-line experiments. Later the effects of such variables as composition of reacting gas, purity of samples, metallurgical history of samples, alloying agents and others will be examined in detail with the hope of elucidating the fundamental processes involved in the oxidation mechanism.

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Table 27

REACTION OF OXYGEN WITH ZIRCONIUM

Results of different investigators.

Reference Temp, C	Rate Constant for Parabolic Rate Law [($\mu\text{g O}_2$ Consumed) $^2 \text{cm}^{-4} \text{min}^{-1} \times 10^{-4}$]					
	12	14	18	13	17	19a
200	0.000006					
225	0.000010					
258	0.000050					
275	0.00023					
300	0.00030					
325	0.00040					
350	0.00069					
375	0.0013					
400	0.0021					
425	0.0036					
500				0.60		
550						0.046
597		0.10				
600			0.145	0.24		0.29
650		0.48	.350			0.71
687		1.1				
700			1.17	0.94	0.50	1.5
750			2.12			3.9
757		1.6				
800			3.96	8.2	2.8	6.8
845		10.				
850			8.20			12.
900			53.0	16.	13.	31.
918		11.				
946			182.			
1000					260.	
1100					1040.	

^a2.5 wt per cent tin alloy.¹²Gulbransen, E. A. and Andrew, K. F., Trans. Am. Inst. Mining Met. Engrs. 185, 515 (1949).¹³Hayes, E. T. and Roberson, A. H., Trans. Electrochem. Soc. 96, 142 (1949).¹⁴Cubicciotti, D. J., Am. Chem. Soc. 72, 4138 (1950).¹⁷Caribotti, D. J., Green, H. M. and Baldwin, W. M., AECU-3013 (1955).¹⁸Fassell, M. W., NP-4246 (1952).¹⁹Mallett, M. W. and Albrecht, W. M., J. Electrochem. Soc. 102, 407 (1955).

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Table 28

REACTION OF NITROGEN WITH ZIRCONIUM

Results of different investigators.

Reference Temp, C	Rate Constant for Parabolic Rate Law [($\mu\text{g N}_2$ Consumed) $^2 \text{cm}^{-4} \text{min}^{-1} \times 10^{-3}$]					
	20	22	21	12	13	17
400				0.00012		
500				0.00011		
600				0.00047		
700				0.0041	0.037	
750				0.011		
800				0.031	0.086	0.034
825				0.058		
862	0.012					
890	0.031					
900			0.018		0.37	0.43
920	0.066					
928	0.066					
968	0.12					
975		1.9				
989	0.16					
998	0.22					
1000					1.2	1.9
1007	0.26					
1030		5.1				
1043	0.41					
1085		10.				
1100			1.1		7.0	9.6
1140		11.				
1195		39.				
1200			7.5		18.	34.
1300			31.			
1305		95.				
1350			100.			
1400			110.			
1420		340.				
1475		670.				
1530		1400.				
1640		1800.				

¹² Gulbransen, E. A. and Andrew, K. F., Trans. Am. Inst. Mining Met. Engrs. 185, 515 (1949).

¹³ Hayes, E. T. and Roberson, A. H., Trans. Electrochem. Soc. 96, 142 (1949).

¹⁷ Garibotti, D. J., Green, H. M. and Baldwin, W. M., AECU-3013 (1955).

²⁰ Braunieks, A., J. Am. Chem. Soc. 72, 3568 (1950).

²² Mallett, M. W., Belle, J. and Cleland, B. B., J. Electrochem. Soc. 101, 1 (1954).

²¹ Mallett, M. W., Baroody, E. M., Nelson, H. R. and Papp, C. S. BMI-707 (1951).

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Table 29

OXIDATION RESISTANCE OF ARC-MELTED ZIRCONIUM ALLOYSResults of Litton, F. B. and Ogburn, S. L.²³

In still air at 750°C for 2 hours.

Intended Composition, Balance Zr	Weight Gain (mg/dm ²)	Weight Gain Alloy	Remarks
		Weight Gain Pure Zr	
100% Zr	415	1.000	1.5% volume increase
1% Mo	368	0.987	
2.5% Mo	536	1.29	
5.0% Mo	957	2.31	
10.0% Mo	634	1.53	
1.0% Ni	219	0.527	
2.5% Ni	223	0.537	
5.0% Ni	181	0.436	
10.0% Ni	220	0.530	
1.0% W	227	0.547	
2.5% W	251	0.605	
5.0% W	209	0.504	
10.0% W	491	1.18	
1.0% Ta	433	1.04	
2.5% Ta	620	1.49	
5.0% Ta	314	0.857	
10.0% Ta	263	0.634	
17.5% Ta	-	-	Sample started to disintegrate
2.0% Al	-	-	Sample started to disintegrate
4.0% Al	550	1.32	3.5% volume increase
6.8% Al	287	0.691	
1.0% Al, 50% Ti	-	-	Disintegrated in 5 min.
4.0% Al, 50% Ti	-	-	Disintegrated in 1-1/2 hrs
6.0% Al, 50% Ti	4680	11.3	Exfoliated

²³ Litton, F. B. and Ogburn, S. L., AF-TR-5943 (1949).

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Table 30

OXIDATION RESISTANCE OF GRAPHITE-MELTED ZIRCONIUM ALLOYS

Results of Litton, F. B. and Ogburn, S. L.²³

In still air at 750°C for 6 hours.

Intended Composition, Balance Zr	Carbon %	Weight Gain (mg/dm ²)	Remarks
100% Zr	0.228	3,300	Flaky oxide.
2.25 at % Oxygen	0.226	4,200	Flaky oxide.
5% W	0.149	2,600	7.3% Expansion.
5% Mo	-	-	a
5% Cr	0.268	3,198	Flaky oxide.
5% Nb	0.265	-	a
5% V	0.351	-	a
5% Pt	0.124	-	a
5% Be	0.206	1,660	Mottled oxide.
5% Si	0.346	-	a
1% Al	0.144	-	a
3% Al	0.090	1,610	Flaky oxide.
5% Al	N. D.	413	Black adherent film.
10% Ta	0.314	5,100	
20% Ta	0.208	11,100	Striated oxide layers.
5% Tc	0.244	-	a
5% Ti, 15% W	0.378	-	a
5% Ti, 15% Cr	0.146	-	a
5% Ti, 15% Ta	0.325	-	a
5% Ti, 15% Mo	0.151	-	a
1% Ni	0.228	1,844	3.7% Expansion.
2.5% Ni	0.148	575	2.8% Expansion.
5.0% Ni	0.223	1,690	6.7% Expansion.
7.5% Ni	0.211	3,120	5.5% Expansion.
10% Ni	0.193	1,109	5.2% Expansion.
50% Ti ^b	-	-	a
1% Al, 5% Ti ^b	-	-	a
3% Al, 5% Ti ^b	-	-	a

^aAlloy disintegrated.^bIn still air at 750°C for 2 hours.²³Litton, F. B. and Ogburn, S. L., AF-TR-5943 (1949).

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Table 31

OXIDATION RESISTANCE OF GRAPHITE-MELTED
ZIRCONIUM ALLOYS

Results of Anderson, C. L., Hayes, E. L.,
Roberson, A. H. and Kroll, W. J.²⁴

Alloy	Limit of Addition, %	Weight Gain, mg/(sq dm)(day) at 649 C
Pure Zr	-	600 - 1500
Al	10	a
Be	5	a
B	5	a
Ce	5	a
Cr	10	600 - 1500
Co	46	600 - 1500
Co-Cr		
Co Content	4	
Cr Content	5	a
Nb	12	a
Cu	15	600 - 1500
Cu Ternary	5	<600
Fe, Co or Ni		
Fe	60	<600
Mn	25	a
Mo	10	a
Ni	10	<600
Si	5	a
Ag	10	<600
Ta	30	a
Th	5	a
Sn	10	a
Ti	90	a
W	10	a
V	10	a

^aAlloy disintegrates.

²⁴Anderson, C.L., et al., BM-RI-4685 (1950).

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Table 32

REACTION OF OXYGEN WITH ZIRCONIUM
AND WITH A ZIRCONIUM-TIN ALLOY

Temp C	Rate Constant for Cubic Rate Law [$(\mu\text{g O}_2 \text{ Consumed})^3$ $\text{cm}^{-6} \text{ min}^{-1} \times 10^{-7}$]	
	15 ^a	19 ^b
575	0.037	
600	0.12	0.26
625	0.24	
650	0.31	0.73
675	1.0	
700	1.7	2.3
725	3.3	
750	7.7	5.8
775	9.6	
800	28.	15.
825	14.	
850	28.	58.
875	52.	
900	134.	95.
920	133.	
950	367.	

^aPure zirconium.

^b1.5 wt % tin alloy.

¹⁵Belle, J. and Mallett, M. W., J. Electrochem. Soc. 101, 339 (1954).

¹⁹Mallett, M. W. and Albrecht, W. M., J. Electrochem. Soc. 102, 407 (1955).

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B. Uranium Isotope Build-Up on Recycling of Enriched Uranium Through a Reactor

(Donald C. Stupegia and R. C. Vogel)

It is of interest to know the isotopic composition of uranium as it is recycled through a reactor. A typical sequence for a U^{235} enriched fuel would be as follows:

1. Enriched fuel is loaded into the reactor. It is highly diluted with an inert metal, such as zirconium, aluminum, or stainless steel.
2. The reactor is run, either continuously or intermittently.
3. The fuel elements are removed, and the short-lived fission products allowed to decay for a while.
4. Fission products and the inert diluent are separated chemically.
5. More U^{235} is added, to replace that fissioned.
6. The uranium is refabricated into new fuel elements for further use in the reactor.

The recycling continues until the total uranium becomes too great for the particular reactor arrangement.

One especially needs to know the amount of U^{237} built up after each pass through the reactor. If U^{237} builds up to such an extent that the fuel has to cool for long periods of time, then extra fuel inventory will be needed to keep the reactor operating.

A calculation program has therefore been arranged to determine the quantity of U^{237} produced in a thermal reactor for various times, fluxes, initial fuel compositions (different enrichments), and modes of operation (continuous and intermittent). Most of the calculations are complete and the data are being evaluated.

C. Dissolution of Thorium Oxide-Uranium Oxide Fuel Elements (R. P. Larsen, R. C. Vogel, C. Seils)

A promising new fuel element consists of urania in a thoria matrix. Fuel elements of this type have shown good radiation stability. They have been difficult to dissolve, however, for analytical work; the same difficulty would, of course, arise in the chemical processing of this type of fuel. It was therefore appropriate to investigate methods of dissolution.

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It has been reported by P. Murray²⁵ that beryllia will crumble when contacted with metallic sodium at 400°C. Murray states that the reaction is not chemical in nature but is the result of penetration by sodium into the microcracks of the material.

The possibility that high density thorium-uranium ceramic fuels might also crumble in molten sodium was suggested. The fuel, 90 w/o ThO_2 - 10 w/o U_3O_8 , had been compressed at 1300 psi in the form of cylindrical rods 3/8 in. long by 1/4 in. diameter, fired at 1700°C in air. The material had a bulk density of 8.3 g/ml, 80 per cent of theoretical. Tests were carried out by exposing the material to molten sodium at 500°C for 10 and 100 minutes in a Pyrex container under an argon atmosphere. At the end of the 10-minute heating period the sodium was decanted and the container allowed to cool. The sodium clinging to the pellet was dissolved in alcohol and the pellet placed in cold water. The slow evolution of gas indicated retention of sodium in the pores, but with the exception of very minor flaking the pellet not only remained intact but had apparently retained much of its original resistance to fracture. On placing the pellet in cold 12 M nitric acid - 0.0016 M fluosilicic acid, rapid disintegration to a finely divided powder resulted. When this slurry was heated to boiling, complete solution was effected in 15 minutes. This behavior in acid is in sharp contrast to the slowness with which untreated pellets dissolved in the same acid, complete solution being effected after 5 hours at the reflux temperature.

There appeared to be only small differences between pellets heated 10 and 100 minutes in sodium. At the end of the prolonged treatment there is more flaking and less resistance to fracture but the pellet is still intact. The addition of hot sodium to the pellet (rather than heating sodium and pellet together) resulted in complete rupture of the pellet. J. H. Handwerk²⁶ of the Metallurgy Division has noted similar behavior wherein thermal cycling of the pellets in sodium resulted in fracture more quickly than prolonged heating.

Tests similar to those described above were also performed on small pieces of a thorium crucible. Pieces which had been treated with sodium disintegrated and dissolved rapidly in fluoride-catalyzed 12 M nitric acid; untreated pieces remained intact and required 2.5 hours to dissolve completely.

D. Determination of Total Atom Burn-Up

(C. E. Crouthamel, P. Kafalas, M. Laug, R. Heinrich, G. Seto)

A calibration experiment has been performed in order to determine the amount of Cs^{137} activity produced by a given number of fission events. This calibration factor has been determined for fast fission of U^{235} and Pu^{239} .

²⁵Murray, P., "Reactions Between Reactive Materials," RHM-(56)-119.

²⁶Private Communication.

The experimental details have been described in ANL-5529, pages 108 to 120. The results of this experiment are summarized in Table 33. The Cs^{137} activity was measured with an end-window proportional counter. This counter is being calibrated so that the listed counting rates can be converted to disintegration rates. The absolute fission yields of Cs^{137} will then be computed using the best available value for the half-life of Cs^{137} .

A previous calibration experiment was run on U^{235} and a description of the equipment and experimental techniques used was given in ANL-4720, page 21. The determination of the cesium activity in these samples was summarized in Table 16, page 47 of ANL-4922. These data cannot be compared directly with those of Table 33 of this report. Factors for different counters, different backscattering of glass fiber versus paper filter backing, and half life corrections must be applied to make a comparison. No previous calibration was obtained for plutonium.

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Table 33

CALIBRATION FACTORS FOR BURN-UP DETERMINATIONSFast Fission of U^{235} and Pu^{239}

Heavy Sample No.	Mass of Heavy Sample Mass of Light Sample	Shadow Correction ^a	No. Fissions in Light Sample	No. Fissions in Heavy Sample	Cs ¹³⁷ Activity in Heavy Sample (c/m)	Calib Factor (Cs ¹³⁷ c/m) per 10 ¹² Fissions
U-10M ^b	0.8396 x 10 ⁶	1.039	1.76 x 10 ⁷	15.39 x 10 ¹²	10,284	668
					10,215	664
					10,035	652
					Avg = 663 ± 4	
U-10 ^b	0.8961 x 10 ⁶	1.042	1.50 x 10 ⁷	14.03 x 10 ¹²	9,316	664
					9,270	661
					9,374	668
La-Pu-C ^c	0.4441 x 10 ⁶	1.044	2.62 x 10 ⁷	12.17 x 10 ¹²	8,420	692
					8,276	680
					8,554	703
					8,676	713
						Avg = 695 ± 10
La-Pu-E ^c	0.4261 x 10 ⁶	1.042	2.58 x 10 ⁷	11.46 x 10 ¹²	7,933	692
					7,734	675
					7,974	696
					8,124	709

^aThis corrects for the shadowing of the light sample by the heavy sample.

^bSample composition: 1.02% U^{234} , 93.24% U^{235} , 5.74% U^{238} .

^cSample composition: 0.0011% Pu^{238} , 99.38% Pu^{239} , 0.61% Pu^{240} , 0.15% Pu^{241} .

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V. CHEMICAL-METALLURGICAL SEPARATION PROCESSES

The kinetics and mechanisms of ceramic oxide-crucible corrosion by molten uranium and uranium alloys are being thoroughly examined. With alumina, reaction proceeds at a constant rate after a rapid initial attack by the melt. The activation energy for the linear attack is about 48 kcal/mole. Corrosion is accelerated by alloying with molybdenum and ruthenium, unaffected by aluminum, and slowed down by carbon. Mechanisms are offered which accord with the experimental observations for thoria, zirconia, urania, and magnesia.

A study of the phase diagram of the lime-beryllia system indicates the formation of an intermediate compound, $2\text{CaO} \cdot 3\text{BeO}$. In the lime-beryllia-lanthana system a ternary eutectic melting at about 1282°C is present.

The extraction of tracer plutonium from uranium powder produced by hydriding-dehydriding cycles has been shown to be rapid and efficient. Grain boundary migration resulting from the hydriding-dehydriding cycle is postulated.

Various pilot plant components have been constructed and tested. Little effect of inductive mixing on crucible erosion has been noted. Two-inch beds of several surface-active materials have been found to be effective in trapping sodium vapor used to simulate volatile fission products.

Nine magnesium distillation runs have been completed. Very little plutonium carryover has been noted. Fabrication of magnesium extraction equipment is complete.

A. Laboratory Studies (H. M. Feder)

1. Control of Dross in Melt Refining (N. Chellew, C. Cushing, J. Schilb, D. Finucane)

A general study of the mechanisms of dross formation in melt refining has been continued. Twenty-four melts of high purity uranium and uranium alloys have been made to study the corrosion of alumina as a function of time, temperature, and alloying additive. In addition, preliminary observations of melts in alumina, thoria, beryllia and magnesia, for which complete analytical data are not available, are discussed.

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a. Uranium in Alumina Crucibles

For alumina crucibles, analysis of the liquated ingot for aluminum was used as a precise measure of the corrosion. Previous experimental work, reported in ANL-5560, page 79, has established the fact that alumina is the sole significant source of dross-forming oxygen in this corrosion reaction and that more than 96 per cent of the aluminum is recovered in the metal ingot. Table 34 is a summary of the data from twenty high purity uranium corrosion experiments. The extent of corrosion is indicated in mg aluminum per sq cm of crucible wetted. Aluminum in the ingot was determined colorimetrically with a probable analytical accuracy of five per cent. In order to minimize stirring, molybdenum resistance heating was employed and the ingots were not poured. Ten runs, covering total melt periods from 8 to 240 minutes, were made at 1200° C, and three runs with melt periods of 35 to 180 minutes were made for each of the other temperatures. Time at which the metal was molten but not at the equilibrium temperature was held to a minimum by appropriate heating conditions. Melt temperatures were determined by an optical pyrometer sighted on clean molten uranium surfaces. These were corrected by a previously determined correlation with temperatures determined with a thermocouple immersed in the melt. Surface area of alumina wetted was measured from the ingot produced.

Results from these corrosion studies are plotted in Figure 27. In contrast to earlier results obtained by the less accurate measurement of dross weight (ANL-5560, page 81), which showed a time-independent behavior, it is now apparent that the corrosion proceeds at a constant rate after a small initial attack. Hence, it may be concluded that the uranium dioxide dross formed is not protective. The non-protective nature of the dross is also revealed by photomicrography; which shows the presence of fissures and occluded uranium.

A trend line drawn from a least squares treatment of the data indicates a reaction rate of 1.68 mg Al/(sq cm)(hr) at 1200° C. Sufficient data are not available to determine reaction rates accurately for melts at 1140-1145, 1260 and 1330° C. The probable slopes are indicated by dotted lines in Figure 27. The reaction rate at 1330° C appears to be about 3.8 times as rapid as at 1200° C, implying an activation energy for corrosion of about 48 kcal/mole.

In Run 66 uranium was heated in surface contact with a standard crucible at a temperature approximately 15 degrees below the melting point for four hours. Analysis of the charge before and after heating showed no pick up of aluminum by the metal. This indicates that the initial rapid attack is by molten uranium.

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Table 34

CORROSION OF ALUMINA BY MOLTEN URANIUM

Crucible: Morgan Triangle RR recrystallized alumina.

Charge: 0.5-kilogram high purity uranium Maximum impurity concentrations - 20 ppm carbon, 5 ppm nitrogen, 11 ppm oxygen, and 33 ppm aluminum.

Conditions. Helium atmosphere. Uranium charges liquated in crucible.

Run No.	Melt Conditions			Crucible Area Wetted, sq cm	Corrosion, Milligrams of Al per sq cm of Alumina Wetted
	Equilibrium Temp, C	Time, min			
		At Equilibrium Temp	Molten		
66	1115	240	0	14.9	0.0
54	1145	39	40	40.4	0.9
75	1140	119	120	41.8	4.1
58	1140	180	180	39.1	4.65
50	1200	5	8	36.0	1.6
49	1200	24	31	36.3	2.3
72	1200	36	40	39.4	3.8
52	1200	56	62	39.2	2.9
47	1200	114	120	36.9	4.4
48	1200	119	124	37.4	5.2
53	1200	174	180	39.3	7.5
59	1200	170	180	38.9	7.8
51	1200	224	241	38.3	8.0
74	1200	235	240	40.6	7.8
57	1260	25	35	43.9	7.7
78	1260	110	120	42.2	8.5
60	1260	175	180	39.9	12.1
76	1330	26	40	41.0	10.4
77	1330	108	120	41.8	19.2
61	1330	168	180	39.6	25.2

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Figure 27

CORROSION OF ALUMINA BY MOLTEN URANIUM

b. Uranium Alloys in Alumina Crucibles

Table 35 exhibits results obtained with alumina crucibles charged with uranium alloys containing molybdenum, carbon or aluminum. The top-poured runs (42, 44 and 46) were heated at 1200 to 1210° C for 120 or 125 minutes before the temperatures were raised to 1300° C or higher for pouring. Because of the temperature increase necessary for effective pouring, one may expect that the extent of reaction with the container will be greater than in liquation experiments.

No significant change in extent of alumina corrosion was noted when uranium-1.08 w/o aluminum alloy was melted. The small difference in aluminum concentration before and after melting could not be accurately measured. Instead, the aluminum pick-up was calculated from the measured dross weight. The calculated value, 6.1 mg aluminum per sq cm, may be compared with a value of 5.8 mg aluminum per sq cm obtained from Figure 27 for a liquation in the absence of added aluminum. Mounted dross samples under high magnification appeared to be essentially similar to dross from high purity uranium melts.

Molybdenum alloys reacted more extensively than high purity uranium. The corrosion by the liquated alloy was 9.9 mg aluminum per sq cm, which may be compared with 5.0 mg aluminum per sq cm for

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Table 35

CORROSION OF ALUMINA BY MOLTEN URANIUM ALLOYS

Crucible: Morgan Triangle RR recrystallized alumina.
 Charge: 0.5 kilogram of alloy prepared from high
 purity uranium.
 Conditions: Helium atmosphere.

Run No.	Alloy Charge	Melt Conditions			Crucible Area Wetted, sq cm	Corrosion, Milligrams of Al per sq cm of Alu- mina Wetted	Corrosion, Grams of UO ₂ per sq cm of Alumina Wetted
		Equilibrium Temp, C	Time, Min				
			At Equilibrium Temp.	Molten			
44	U - 1.08 w/o Al Pour temp., 1300°C	1200	120	145	46.20	6.1 ^a	0.046 ^b
46	U - 3.99 w/o Mo Pour temp., 1355°C	1210	125	150	47.36	12.4	0.0093 ^c
79	U - 3.63 w/o Mo Liquated charge	1200	114	120	45.70	9.9	0.074 ^c
42	U - 0.045 w/o C Pour temp., 1300°C	1200	120	143	43.20	2.3	0.017 ^c

^aCalculated from observed gross weight.

^bMeasured. A correction of 12 per cent for occluded uranium metal has been made.

^cCalculated from aluminum pick-up.

unalloyed uranium obtained from Figure 27. Corrosion under top-pouring conditions was still greater. Figure 28 shows a typical dross from a molybdenum alloy. The dross is 122 microns thick and is penetrated by metal which forms a layer adjacent to the crucible wall.

Figure 28

DROSS IN ALUMINA CRUCIBLE

Uranium - 4.2 w/o molybdenum
Magnification 250X

A significant change in corrosion was noted for the uranium-carbon alloy (Run 42, Table 35). The pick-up of aluminum by corrosion is markedly reduced to less than half that for high purity uranium. The dross adhered loosely to the crucible in patches, some of which covered metal buttons retained during the pour separation. As previously noted appreciable carbon content in uranium severely limits the amount of metal which may be recovered by pouring. Analysis of a flake of the dross gave a carbon content of 2100 ppm, roughly a five-fold increase over the charged material. It would appear that uranium carbide coats the walls and lessens the attack on the alumina, but also causes considerable retention of metal.

Additional alloys, nominally 0.36 w/o cerium and 3.6 w/o ruthenium, have been melted under standard conditions in alumina. Analytical data are not available for these runs, but general observations of

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the nature of the drosses have been made. The dross from the cerium alloy (Figure 29) appears to consist of at least two phases. Irregular, soft, white and pale yellow crystalline masses are concentrated nearest the crucible wall. Further away, but with no sharp separation between phases, appears material which is typical of uranium dioxide but with some occluded yellow crystals. Width of the urania layer was approximately one-fifth of the average total dross thickness of 63 microns. Assuming the lighter colored material is oxide of cerium, the photomicrograph shows clearly the rapid preferential oxidation of the solute cerium at the crucible wall.

Figure 29

DROSS IN ALUMINA CRUCIBLE

Uranium - 0.6 w/o cerium

Magnification 500X

The dross formed by the ruthenium alloy in alumina was also markedly different from drosses formed by unalloyed uranium. This dross (Figures 30 and 31) contained many fine, irregular, white inclusions dispersed in a urania matrix, and small amounts of metal. The white inclusions may possibly be fragments of unreacted alumina. The reaction layer was unusually thick, averaging 490 microns, and the crucible showed extreme undercutting (~250 microns) in a non-uniform pattern, indicating a possible preferential penetration and loosening of the alumina grains.

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Figure 30

DROSS IN ALUMINA CRUCIBLE

Uranium - 3.6 w/o ruthenium
Magnification 100X

Figure 31

DROSS IN ALUMINA CRUCIBLE

Uranium - 3.6 w/o ruthenium
Magnification 500X

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c. Other Crucible Materials

Studies of dross formation in thoria, thoria-coated alumina, beryllia, and magnesia crucibles have been started.

Uranium was liquated in a slip-cast thoria crucible at 1200° C for 2 hours, then heated to 1325° C for top-pouring. Total dross retained by the crucible (uncorrected for occluded metal) amounted to 4.9 mg UO_2 /sq cm of crucible area wetted. This value is less than one-tenth of the amount of dross formed in comparable melts in alumina. This dross was not detachable. Similarly, when uranium was liquated at 1200° C in a beryllia crucible, no detachable dross was formed on the ingot or the crucible. Two experimental melts were made in previously degassed magnesia crucibles in which uranium was liquated at 1200° C for 2 hours. The average weight loss of crucible and ingot together, presumed to be due to the volatilization of magnesium, was 0.41 gram. This amount of volatilization would indicate reduction of 0.68 gram of magnesia and the formation of 70 mg UO_2 /sq cm of crucible area wetted. The reaction of uranium with alumina under identical experimental conditions is about one-half as extensive. The evolution of magnesium vapor left large blow holes in the frozen uranium ingots, particularly near the bottom surface of the crucible.

2. Reactions of Uranium With Refractory Oxides (C. L. Rosen, R. U. Sweezer)

This study is intended, in part, to supplement the dressing experiments of the previous section by a qualitative study of the reactions of uranium with refractory oxide. The experimental technique consists of observation of sessile drops of molten uranium on ceramic plaques in order to measure contact angles and to obtain photomicrographs of the reaction zones. The individual observations will be given first and then some possible reaction mechanisms will be discussed.

a Thoria

The contact angle of molten uranium on polished thoria plaques is approximately 135°. A reaction layer forms above the original interface. As the reaction proceeds the thoria plaque is progressively blackened. After one hour this blackening extends radially from the sessile drop a distance of eight millimeters (Figure 32). Under ideal conditions of magnification and lighting, the blackened area can be seen to consist of two areas of different shade separated by a sharp boundary. The darker area is immediately adjacent to the uranium. There appears to be no structural differences among these areas, but under polarized light the grains in the darkened areas are much more readily distinguishable. The darkened areas of the plaque gave negative tests for uranium. The tests that were applied were: leachability by boiling nitric acid, counting, and fluorescence analysis. By simply heating the blackened plaque in air, its original whiteness was restored.

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Figure 32

CROSS SECTION OF THORIA PLAQUE SHOWING RADIAL
BLACKENING UNDER SESSILE DROP OF MOLTEN URANIUM

Magnification $\sim 10X$

b. Lime-Stabilized Zirconia

The observations with this material are similar to those for thorium with respect to contact angle and blackening with two sharply defined boundaries. In these specimens the outer boundary travelled radially 30 millimeters in one hour. In a separate experiment it was shown that the rate of travel was independent of the direction. Figure 33 shows the melting and formation of the sessile drop. It was shown that the geometry of the button before melting is without effect on the final form of the sessile drop. Figure 34 shows the reaction layer above the original interface and the darkened grains below it. Figure 35 shows the contrast between the light and darkened areas of the plaque. The only apparent difference between these two areas is the accumulation of dark material at the grain boundaries in the latter. Preliminary X-ray examination indicates an expansion of the ZrO_2 lattice in the darkened area. The tests for uranium in the darkened areas were negative and heating the plaques in air restored their original cream color. Chemical analysis showed appreciable amounts of zirconium dissolved in the uranium after the sessile drop experiments.

c. Urania

Figure 36 shows that the reaction layer formed when uranium is melted on a UO_2 plaque lies above the original interface. The contact angle of the sessile drop is approximately 135° .

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Figure 33

STAGES IN THE MELTING OF URANIUM ON A ZIRCONIA PLAQUE

Figure 34

URANIUM MELTED ON STABILIZED ZIRCONIA

Magnification 500X

Bright Field

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Figure 35

GRAIN STRUCTURE OF ZIRCONIA IN LIGHT AND DARK AREAS
AS REVEALED BY "SENSITIVE TINT" LIGHT

Magnification 100X
Sensitive Tint

a. Undarkened area

b. Darkened area

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Figure 36

URANIUM MELTED ON URANIA

Magnification 250X
Bright Field

d. Alumina

Two types of alumina specimen plaques were used. On both, the contact angle is approximately 135° . With recrystallized material (density, 95 per cent of theoretical) the reaction zone takes the form shown in Figure 37. The alumina is undercut and the mixed UO_2 -U reaction layer forms below the original interface. The blackening reaction in the body of the plaque does not occur. In vacuum the reaction is accompanied by a significant weight loss which does not occur when the reaction takes place in helium at atmospheric pressure. With pressed and fired alumina of low density (62 per cent of theoretical) the same observations may be made. Undercutting proceeds rapidly at about five mils per hour. In addition, however, the blackening of the plaque below the reaction layer also occurs. This blackening travels in the downward direction only. The addition of small amounts of molybdenum or ruthenium to the uranium decreased the wetting angle of the sessile drop and the corrosion appeared to be markedly increased.

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Figure 37

URANIUM MELTED ON ALUMINA

Magnification 250X

Bright Field

e. Magnesia

On a polished specimen of single crystal magnesia the contact angle was 135° . Undercutting proceeded in the same way as on alumina (Figure 38). As with alumina, there was no blackening of the plaque adjacent to the reaction zone. With pressed and fired magnesia plaques of lower density and higher impurity content, slight blackening adjacent to the reaction zone was observed. With magnesia severe weight losses even in helium atmosphere were observed.

f. Discussion

While it is too early to form definite conclusions as to the mechanisms of attack by molten uranium on these ceramic oxides, it is clear that they fall into two categories. The dioxides of thorium, zirconium, and uranium, all of which possess fluorite-type structures, respond

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Figure 38

URANIUM MELTED ON MAGNESIA

Magnification 250X
Bright Field

by the formation of a reaction layer above the interface. As a working hypothesis it may be assumed that these react by migration of oxide ions under the influence of a concentration gradient to the uranium-reaction layer interface. Presumably the most mobile oxide ions are those at grain boundaries, impurity sites and other dislocations. It is known that all of these materials form stable phases, MO_{2-x} , where x is limited. For thorium and zirconia these compositions are black and the excess metal ion causes lattice expansion. It may be further hypothesized that on reaching the lower limit of the solid solution, disproportionation takes place to give the metal and MO_{2-x} . This hypothesis would account for the evidence of two darkened regions. Finally, this hypothesis accounts for the fact that oxidation restores the original color of the darkened areas. This hypothesis is depicted schematically in the following illustration.

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Schematic Hypothesis of the Reaction of Molten Uranium
with Thorium, Zirconia and Urania

For alumina the mechanism has already been discussed (ANL-5560, page 81). The present observations are in accord with the mechanism advanced. Two additional points remain to be added. First, in vacuum the reaction

may also occur. Secondly, with alumina having sufficiently large pores, metal may flow into the pores by ordinary (non-capillary) means and accelerate the corrosion by exposing more than the superficial area to attack. Essentially the same mechanism applies to magnesia corrosion except that in all cases the reaction proceeds as

Finally, it is hypothesized that the acceleration of corrosion by the addition of molybdenum or ruthenium to the uranium is caused largely by the increased fluidity of these melts and greater penetration of pores. Despite the observed increase in wetting it is not believed that capillarity plays a significant role in the corrosion mechanism.

3. Search for Stable Oxidic Slags (M. Ader, J. Bingle)

Investigation of compound formation in the lime-beryllia system has continued. Experiments performed to date lead to the conclusion that the compound previously reported (see ANL-5560, page 85) is $2\text{CaO} \cdot 3\text{BeO}$. The lanthana-beryllia system, which also has a low melting

eutectic, is being studied with a view toward finding a ternary composition of lime, lanthana, and beryllia whose melting point is lower than that of either the lime-beryllia (ca 1385° C) or lanthana-beryllia (ca 1365° C) eutectics. Preliminary trials have shown that a lower melting (ca 1282° C) ternary eutectic does occur, and it is believed that these compositions will be stable toward reaction with molten uranium.

a. Lime-Beryllia Experiments

The desired compositions were prepared by premixing accurately weighed amounts of calcium carbonate and beryllia in a rolling machine, transferring the mixture to a platinum crucible, and igniting in air for from 30 minutes to several hours to a temperature between 1420 and 1570° C. The mixtures were initially held at 900 to 950° C for several hours to decompose the carbonate to oxide. During this period reaction between the oxides did not occur. After cooling, the mass was broken up and samples were taken for calcium, beryllium, X-ray powder diffraction, and microscopic analyses. Gravimetric analyses for calcium and beryllium were made on solutions prepared by dissolving samples in refluxing 10 to 12 M hydrochloric acid. Beryllium hydroxide was precipitated from solution by ammonia gas and ignited to the oxide. Calcium was determined in the filtrate by precipitation of calcium oxalate and ignition to calcium carbonate.

Table 36 lists the preparations made and the results obtained to date. Examination of the data indicates that the most probable composition of the compound is $2\text{CaO} \cdot 3\text{BeO}$. It is clear that compositions furthest away from the eutectic react very slowly. Analysis of the cooled masses has shown significantly higher BeO/CaO ratios than the nominal compositions. The reason for this is not clear at the present time, but it may be due to a systematic analytical error. The apparent discrepancies between results of X-ray and microscopic analyses (e.g., experiment MA-26) may be explained by (1) nonrepresentative sampling in the case of microscopic analyses; (2) absence of lines in powder patterns due to small scattering power of BeO ; and (3) non-attainment of equilibrium in the melt due to insufficient temperatures and/or insufficient heating time.

The pycnometrically determined density of powdered material from experiments MA-24 and MA-26 was 2.71 g/ml. Using the X-ray-determined unit cell volume of 2751 cubic angstroms (lattice constant $a = 14.012 \text{ \AA}$), the number of molecules per unit cell calculated for $2\text{CaO} \cdot 3\text{BeO}$ is 24.0. Accurate line-intensity measurements of the X-ray pattern of $2\text{CaO} \cdot 3\text{BeO}$ have been obtained from a microphotometer tracing. They are being used for a structure determination.

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Table 36

PHASE DIAGRAM STUDY: LIME-BERYLLIA SYSTEMBeO: hexagonal, refractive index $n = 1.719, 1.733$ CaO: cubic; refractive index $n = 1.837$ Compound: $2\text{CaO} \cdot 3\text{BeO}$; cubic; refractive index $n = 1.635$

Run	Max Temp, C	Nominal Composition		Mole Ratio BeO/CaO	Mole Ratio Found in Sample BeO/CaO	X-ray Pattern ^a Shows Presence of	Microscopical Analysis Indicates Presence of
		Mole Per Cent					
		BeO	CaO				
MA-27	1570	60	40	1.50	1.55	BeO + CaO ^b	BeO with some inclusions of n <1.72.
MA-28	1570	59	41	1.44	1.52	BeO + CaO ^b	BeO + CaO + small amount of isotropic crystals with n <1.70.
MA-26	1500	58	42	1.38	1.46	Compound + CaO	Compound + BeO inclusions.
MA-24	1540	57.1	42.9	1.33	1.38	Compound + CaO	Compound + in- clusions of n> 1.635; uni- axial crystals with one index >1.8.
MA-25	1500	56	44	1.27		Compound + CaO	
MA-15C	1420	50.1	49.9	1.00	1.09	Compound + CaO	Compound with isotropic in- clusions>> 1.635.
MA-17B	1420	45.8	54.2	0.845		Compound + CaO	

^aThe intensity of CaO lines relative to intensity of compound lines decreases with increasing BeO/CaO ratios.

^bX-ray powder patterns of MA-27 and MA-28 were essentially identical. A significant number of lines not belonging to either BeO or CaO were present but could not be indexed.

0371229.030

b. Lanthana-Beryllia Experiments

A eutectic between approximately 25 mole per cent lanthana (81 weight per cent) and 75 mole per cent beryllia (19 weight per cent) has been reported^{27,28} to melt at about 1410° C.

The present work has shown that compositions of 20-80 and 30-70 mole per cent lanthana-beryllia begin to melt at about 1365° C. An X-ray powder pattern taken of a melt with starting composition 25 mole per cent lanthana-75 mole per cent beryllia indicates that this system is not a simple eutectic system. However, the new phase(s) has not been identified as to composition or lattice type

Because of diminished reactivity toward molten uranium and possible use as crucible materials as temperature is lowered, effort is being given to finding ternary compositions of lime, lanthana and beryllia systems. An initial experiment with the mole per cent composition 30 2 lime - 9.2 lanthana - 60.6 beryllia showed that a substantial part of the solid material melted at 1282° C. Further experiments are planned to determine the composition of this ternary eutectic.

4. Magnesium Extraction Studies

a. Extraction From Powdered Uranium (R. Nuttall, J. Settle)

Uranium containing fission product elements was converted to a powder by two hydriding-dehydriding cycles. The powder was suspended in liquid magnesium by mechanical stirring. The liquid phase was sampled by removing portions through a filter. These samples and the unfiltered residues were analyzed. The results of these analyses are shown in Table 37. The amounts charged are based on separate analyses of pieces of untreated uranium from the same slices used in each experiment.

Run 10 was made with Sylvania "Fissium" (described in ANL-5494, page 66). Other runs were made with slices from Clinton slugs containing about 73 ppm plutonium.

It is obvious from these data that the extraction of a large fraction of the contained plutonium and rare earth activities proceeds very rapidly while the extraction of elements, such as strontium and cesium, known to be preferentially soluble in magnesium proceeds much more slowly. The most likely explanation which occurs to us is that the former elements

²⁷Dukelski, M., Z. anorg. Chem., 50, 47 (1906).

²⁸Wartenberg, H. von, Reusch, H. J. and Saran, E., Z. anorg. u. allg. chem. 230, 268 (1937).

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Table 37

EXTRACTION OF ACTIVITIES FROM POWDERED URANIUM

Run No.	10		13		14		15			16			17	
Charge	Slug 13.1 g Mg 10.14g		37.14 g 106.04 g		36.13 g 70.40 g		25.09 g 34.20 g			22.09 g 32.26 g			19.11 g 31.28 g	
Temp	800°C		800°C		800°C		800°C			800°C			800°C	
Time	6 hr		3 hr		3 hr		3 hr 5-1/2 hr			10 min 2 hr			15 min	
	% in Mg ^a	Mat. Bal. ^b	% in Mg ^a	Mat. Bal. ^b	% in Mg ^a	Mat. Bal. ^b	% in Mg ^a	% in Mg	Mat. Bal. ^b	% in Mg ^a	% in Mg ^a	Mat. Bal. ^b	% in Mg ^a	Mat. Bal. ^b
U	0.015	100.	3.9	105.9	0.02	100.	0.07	0.04	103.	0.2	0.4	97.	0.02	98.
Pu			90.		89.	90.	83.	75.	93.	72.	87.	91.	54.	89.
β			65.		71.	93.	67.	63.	97.	51.	63.	90.	27.	103.
γ			14.		16.	85.	12.	11.	98.	10.	13.	91.	0.2	89.
Ce	178.	37.	256.		78.	134.				95.	105.	88.	50.	91.
TRE ^c							85.	97.	108.					
Sr			41.		33.	88.	29.	30.	100.	9.	23.	102.	0.9	99.
Ru			6.		0.06	116.	0.4	0.3	120.	0.7	1.1	97.	1.3	81.
Cs			6.		0.2	89.	0.08	0.06	104.	0.1	0.4	92.	0.2	83.
Pd	92.	84.												
Zr	4.	100.												
Mo	0.02	56.												

^aThe filtrate samples were assumed to be representative of the composition of the liquid phase.

^bMaterial balance = $100 \frac{\text{Activity in unfiltered residue} + \text{activity in samples}}{\text{Activity in charged material}}$.

^cTotal rare earths.

have migrated to grain boundaries as a result of low temperature hydriding-dehydriding cycles and so are readily available to the solvent magnesium. This mechanism remains to be demonstrated by an independent means. Meanwhile experiments are in progress to determine whether macro-concentrations of plutonium in uranium are also rapidly extracted by this process.

b. Extraction from Molten Uranium
(E. Greenberg, M. Nathans, K. Anderson)

One additional static equilibration experiment was completed using the resistance furnace. For earlier results see ANL-5560, page 86. The data from this experiment (Run 28) follow:

	Time at Temp - 4.3 hr
Weight of Uranium - 9.82 g	Final Pu in U - 0.283 wt %
Charged Pu - 96 mg	Total Pu Recovered - 92 mg
Temp - 1186° C	K (apparent)* - 0.17

High purity sublimed magnesium was used. The plutonium was initially in the uranium phase, and the equilibration was conducted in a high purity alumina crucible with a graphite cap, inside a sealed steel capsule.

Previous Runs 26 and 27 were conducted under very similar conditions and gave values of 0.18 and 0.40, respectively, for K (apparent). The value of 0.40 is, therefore, not in line with this or earlier data and should be discarded as erroneous.

An induction furnace has been installed in the laboratory and shakedown runs have been completed. Extraction runs are currently in progress.

c. Extraction of Fission Products for Uranium Alloys

This study concerns the equilibrium distribution of individual fission products between the two immiscible liquid phases, magnesium and low-melting uranium eutectics. Efforts toward the completion and testing of equipment were continued.

*The definition of K(apparent) is mole fraction of Pu in Mg/mole fraction of Pu in U.

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5. Laboratory Equipment and Techniques (N. R. Chellew)

Copper molds have been used extensively by the laboratory group for casting uranium and uranium alloys. Previous experience has shown that a water-cooled mold with 1/4-inch walls would not alloy with metal superheated to 1300° C and poured at a slow steady rate (~10 seconds for a 1000-gram charge). In the past quarter an effort has been made to determine the temperature at which uranium would begin to alloy with a copper mold in the casting operation. For this study a 5.56-kilogram copper mold was designed to contain about 2 kilograms of uranium. Interior walls were tapered 10° and the cylindrical exterior wall was wound with a Calrod-type heating element. Two thermocouple wells were drilled to terminate 3/16 inch from the interior wall of the mold. These were located to measure temperatures at points adjacent to the top edge and center bottom surface area of the cast ingot.

Four experimental pours were carried out with the heated mold. One-kilogram uranium charges heated to 1250° C were poured at a standard rate, i. e., approximately 10 seconds for complete pouring, into the mold heated to a steady temperature of 150, 300, 450, or 555° C. Maximum mold temperature rise due to the pouring operation was found to occur in the wall of the mold adjacent to the top surface of the cast ingot and amounted to 110° C at the lowest starting mold temperature. This rise was found to decrease gradually to 70° C as the starting mold temperature was increased to 555° C. The average time necessary to attain this maximum temperature was 18 seconds. This includes the time necessary for pouring. No alloying of charge and mold occurred under the above experimental conditions. Further testing of the mold to the alloying point was limited by the capacity of the mold heater.

B. Semi-Works Studies of High Temperature Processes (L. Burris, Jr. and I. G. Dillon)

1. Design and Testing of Components for Pilot Plant (G. J. Bernstein, V. N. Thelen, L. G. Weaver*)

a Development of Top-Pour Crucible

Various top-pour crucible arrangements were tested in the past quarter. Much of this work is designed to provide experience to permit evaluation and recommendation of pouring methods to be used in a pyro-metallurgical pilot plant. Various alternate equipment designs are being considered, and some of these will be built for testing in the semi-works.

*Special scientific employee on loan from International Harvester Co.

Additional top-pour melts were made using a slip cast magnesia crucible within a graphite crucible which acted as a susceptor for induction heating. In place of the magnesia crucible used in Runs 25, 26 and 27 reported in the previous quarterly (ANL-5560, page 102), the crucible used in these runs had a skimmer tube within the crucible extending from the pouring spout to a point approximately $1/4$ inch above the bottom (see Figure 39). The purpose of this tube was to prevent contamination of the poured ingot with dross. In operation the entry to the tube passage would be sealed by metal from the previous melt and thus prevent any unliquated dross-forming metal from entering the passage.

Figure 39

SLIP CAST MAGNESIA CRUCIBLE WITH SKIMMER CHANNEL

A series of three runs (Table 38) was made in the same crucible using approximately 3-kg charges made up equally of natural uranium and fission equivalent in composition to 2 per cent burnup in a reactor. No attempt was made in the first two runs to achieve a maximum pour. On the third run the crucible was drained. In all cases very clean ingots were obtained. The overall pour for the three runs was 92.8 per cent.

Several top-pour runs were made using slip-cast magnesia crucibles with no graphite crucible susceptors. The crucible was mounted inside a stabilized zirconia pipe by wrapping the crucible in

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Fiberfrax* paper to make a snug fit. Induction heating was done by direct coupling to the uranium charge. Degassing was done by argon purging without heat. In the first pair of Runs, 31 and 32 (Table 39), the same crucible was used to melt successive charges of approximately 3 kg of natural uranium. Overall yield was 96 per cent. In the second pair of Runs, 34 and 35, the same crucible was used for successive charges of approximately 6 kg of natural uranium. Overall yield was 97.5 per cent.

Table 38

TOP-POUR CRUCIBLE RUNS USING MAGNESIA LINER
WITH SKIMMER TUBE

(Melting Time, 1-1/2 hr; Liquation time, 1 hr at 1200° C)

Run No.	Natural Uranium (gm)	Sylvania Fissium (gm)	Pour Temp (C)	Per Cent Yield
28	1460	1464	1300	63.7
29	1469	1486	1270	89.1
30	1443	1458	1300	125.8
Overall Yield				92.8

Table 39

TOP-POUR CRUCIBLE RUNS WITH DIRECT COUPLING TO CHARGE

(MgO slip-cast crucible)

Run No.	Uranium Charge (gm)	Melting Time (hr)	Holding Time (hr)	Holding Temp. (C)	Pour Temp. (C)	Per Cent Yield
31	3103	3.0	1	1200	1300	92.4
32 ^a	2860	3.5	1	1200	1280	99.5
34	5990	1.5	1	1250	1300	97.1
35 ^a	6015	1.7	1	1250	1285	97.9

^aA second run in crucible used in previous run.

*Fiberfrax is a ceramic fiber, approximately 50 per cent alumina and 50 per cent silica, made by the Carborundum Co.

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A large graphite crucible, capable of containing 10 kg of molten uranium, is being tested for possible use in the EBR-II pilot plant. The crucible has a steel support frame and tilting mechanism. It is designed to operate within the steel bell-jar furnace described in the previous report, ANL-5560, page 101. The crucible has a skimmer passage analogous to that shown in Figure 39. Two melts of approximately 10 kg each were made in this crucible after it had been sprayed with an alumina coating. The first run, No. 33, was made using the pouring passage while the second, No. 36, was made with the skimmer removed. The ingot obtained in Run 33, was made using the pouring passage while the second, No. 36, was made with the skimmer removed. The ingot obtained in Run 33 was of much cleaner appearance than that obtained in Run 36.

b. Performance of Extended Induction Coil Leads

In the proposed EBR-II pilot plant it is intended to bring the current through five-foot concrete shielding walls. In order to seal the leads properly, it may be necessary to bring them in as separate leads rather than as co-axial leads. A test series was conducted on mock-up leads to determine the restrictions which would be placed upon the allowable spacing of these leads. Bus bars were made of one-inch square copper bars, 7 feet long, with an internal water passage $5/8$ inch in diameter. These leads were tested at various spacings and with 2-, 3- and 5-turn induction coils to heat a graphite crucible. These tests indicated that effective crucible heating could be obtained even at a bar spacing of 12 inches (see Table 40). The generator power required decreased as the number of turns in the coil was increased. The data indicate that a somewhat greater number of turns would provide a more favorable heating condition. This is a consequence of lower current requirements in the coil with resultant lower power losses in the circuit.

Table 40

MAXIMUM BUS BAR SPACING FOR ACHIEVING NOMINAL
CRUCIBLE TEMPERATURE OF 1200° C

(30-kw, 10-kc, 220-volt Tocco Motor Generator Set)

Maximum Bus Bar Spacing (Inches)	No. of Turns	Power Output of Generator (kw)
4	2	11.1 ^a
8	3	8.4 ^a
12 ^b	5	6.3

^aMaximum generator output.

^bMaximum spacing tested.

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c. Performance of Air-Cooled Induction Coil

A test series was conducted to check the performance of a gas-cooled induction coil as a possible substitute for a water-cooled coil. Compressed air was used as the coolant although the principle would be applicable to an inert gas. A graphite crucible, 6-1/2 inch O.D. by 8 inches high and covered with two layers of Fiberfrax paper, was used as the susceptor. Heating was done in an argon atmosphere. Power was supplied by a 30-kw, 10-kc, 220-v Tocco motor generator set. Data are shown in Table 41. It is apparent from the low coil temperatures that gas cooling is a feasible procedure.

Table 41

PERFORMANCE OF AN AIR-COOLED INDUCTION COIL

(Nine-turn, nine-inch diameter, seven-inch high coil, 0.5-inch copper tubing, 0.032-inch wall)

Run No.	Inlet Air Pressure Psig	Exit Coil Temp. (C)	Exit Air Temp. ^a (C)	Crucible Temp. (C)	Inlet Air Velocity Scfm ^b	Total Heat Transfer to Air (Btu/hr)
3	8.8	365	291	1199	10.0	5480
4	14.7	283	223	1206	14.9	6060
5	19.0	247	193	1203	18.6	6400
6	24.7	214	159	1200	23.3	6260
7	30.0	199	144	1200	27.7	6650
2	9.7	418	310	1300	10.2	6000
8	30.4	231	167	1308	27.1	7700
9	20.8	279	211	1303	19.6	7220

^aExit air temperature measured at point after coil lead passes through bus bar connection

^bStandard cubic feet per minute at 70° F and 14.7 Psia.

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d. Performance of an Uncooled Copper Induction Coil

A test series was conducted to check the performance of an uncooled copper coil in heating the same crucible described in the previous section. The coil was made of 5/8-inch O.D. copper tubing with 0.083-inch wall. The coil had 8 turns with an inside diameter of 8-1/2 inches and a height of 8 inches. Similar uncooled coils used at Los Alamos and Rocky Flats were nickel plated before use to prevent oxidation of the copper. The coil described above was not plated to permit observation of effects of heating in an argon atmosphere. Coil temperatures in the neighborhood of 500° C (see Table 42) are not considered excessive; the results indicate that this, too, is a feasible heating method.

There was a gradual increase of oxide on the coil surface, which would indicate the desirability of plating the coil if it is to have extended use.

Tests are currently being made of a solid copper coil fabricated from 0.45-inch diameter copper wire.

Table 42

HEATING OF GRAPHITE CRUCIBLE USING
UNCOOLED COPPER INDUCTION COIL

Test No.	Crucible Temp. (C)	Time at Temp. (hr)	Coil Temp (C)			Generator Power (kw)	Coil Current (amp)
			Top Turn	4th Turn	Bottom Turn		
1	1203	1.0	522	463	467	6.2	198
2	1297	0.5	571	511	522	7.2	221
3	1205	5.0	470	451	426	4.7 ^a	170
4	1297	5.5	485	469	455	5.3 ^a	180

^aAn additional layer of Fiberfrax on the inside of the coil reduced heat loss from the crucible. In particular, the top turn of the coil was protected from radiation from the uninsulated edge of the graphite lid.

DECLASSIFIED

16

e. Fusible Metal Seal

In the previous report (ANL-5560, page 101) a steel bell-jar, in which the fuel melting crucible would be contained, was described. It is presently planned to provide a seal for this bell-jar to permit evacuation and maintenance of a high purity inert melting atmosphere. Since ordinary gaskets would be unsatisfactory under the temperature and radiation conditions anticipated, tests were conducted on a fusible seal composed of ordinary 50-50 solder. This material has a melting point of approximately 190° C. The maximum anticipated operating temperatures in the area of the seal are around 150° C. The design developed provides for a channel in the furnace base which contains the solder and a Calrod heater to provide the necessary heat for melting the solder. The edge of the bell which fits into the groove is made of copper. Once tinned, the copper will make a leak-tight seal in the solder even under adverse atmosphere conditions. With such an arrangement a leak-tight seal was made in 30 successive trials.

2. Control of Dross in Melt Refining
(G. Bennett, W. Kline)

This is a cooperative program with the laboratory group (see page 91 of this section of the report). The main efforts of the semi-works have been:

- (1) Preparation of various uranium alloys of interest;
- (2) Investigation of the effect of inductive mixing on crucible erosion by repeating in an induction furnace certain drossing runs previously performed in the laboratory resistance-heated Stokes furnace.

a. Preparation of Uranium Alloys

To date, one or more 2-kilogram batches of alloys with the following nominal compositions have been prepared:

2.4 w/o chromium
2.0 w/o zirconium
4.1 w/o zirconium
3.6 w/o ruthenium
0.5 w/o thorium
~ 0.35 w/o lanthanum
~ 0.35 w/o cerium

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b. Effect of Inductive Mixing on Crucible Erosion

Runs are underway to ascertain the effect of inductive mixing on crucible erosion. Conditions in the runs duplicate reasonably closely conditions used by the laboratory group, except for substitution of induction for resistance heating. As indicated in Table 43, little effect of inductive mixing on crucible erosion is apparent on the basis of runs made to date.

Table 43

EFFECT OF INDUCTIVE MIXING ON CRUCIBLE EROSION

(High purity Morganite alumina crucibles)

Type of Heating	Temp. (C)	Time at Temp. (hr)	F ^a	Crucible Erosion (gm Al/cm ² of wetted surface)
Resistance	1200	2	-	0.036 ^b
Induction	1200	2	0.28	0.0043
Induction	1200	2	0.53	0.0051
Resistance	1300	2	-	~0.015 ^b
Induction	1300	2	0.28	0.0125

^aF = Calculated fraction of current penetrating charge. Because of the susceptor design this fraction may be even higher than indicated.

^bFrom Figure 27 of this report.

3. Control of Volatile Fission Products
(J. Wolkoff, J. Jones)

The bell jar furnace shown in Figure 40 was built to continue study of the control of fission products volatilized when irradiated fuel material is melted. Volatilized fission products may include cesium, barium, strontium, cadmium, iodine, xenon and krypton. Control of the latter two rare gases is a separate problem and is not a part of this study.

The furnace is being used to test the efficacy of various materials for absorbing or trapping volatilized fission products. It is inductively heated with the coil outside the Vycor bell jar and is operable under vacuum or inert atmospheres. Any volatilized material not retained by the absorbing medium deposits on the relatively cool bell jar surfaces from which it may be easily washed off for analysis.

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Figure 40

PORTABLE BELL JAR FURNACE FOR VOLATILE
FISSION PRODUCT STUDIES

In the present study selected key fission elements are to be examined individually with respect to methods and conditions needed to prevent escape. Since cesium may be the most difficult fission product to control, initial work with alkali metals was undertaken. Runs to date have been made using sodium as a stand-in for cesium.

The sodium is vaporized in a nickel crucible and must pass through a 2-inch deep bed of absorbing material to escape to the bell jar atmosphere. Sodium which escapes usually forms a mirror on the bell jar. Vaporization temperature and bed temperature are varied by changing the system pressure.

In order to attempt improvement over simple condensation by virtue of the temperature gradient across the bed, materials of high surface area and porosity (surface active materials) are being tried. Comparative runs have shown that these materials completely trap sodium, whereas sodium escaped from a low surface area bed of magnesia particles or a Fiberfrax ceramic fiber (Runs 6 and 10 versus other Runs except 2 in Table 44). All of the surface active material tried to date (Molecular Sieves, activated alumina, and activated magnesia) have successfully

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Table 44

RETENTION OF VAPORIZED SODIUM ON VARIOUS ABSORBENT MATERIALS

Absorber Bed: 1-5/8 in. diameter x 2 in. deep

All runs of 30-min duration at an average pressure of 0.4 mm

Run No.	Absorbing Material	Crucible Temp. (C)	Top of Bed Temp. (C)	Degas Procedure	Results
2	none	340	-	none	39% of Na vaporized
3	Molecular sieves ^a 1/8-inch pellets	330	-	Used as received	No Na detectable in bell jar
8	Activated alumina 1/4-inch granules	400	110-140	Vacuum at 500° C	No Na detectable in bell jar
5	Activated alumina 1/4-inch granules	340	95-170	Heated 2 hr at 305° C	No Na detectable in bell jar
7	Activated alumina 1/4-inch granules	340	120-160	Vacuum at 360° C	No Na detectable in bell jar
9	"Sea Sorb 53" ^b -20 to 74 mesh	400	180-200	Vacuum at 550° C	No Na detectable in bell jar
6	High purity magnesia 1/4-inch granules	340	140-210	Vacuum at 450° C	Sodium not completely retained
10	Fiberfrax ^c Refractory wool	400	160-165	Vacuum at 600° C	Sodium not completely retained

^aA dehydrated zeolite manufactured by Linde Air Products Co.^bAn activated magnesia product manufactured by Westvaco Chemical Division.^cA ceramic fiber made by the Carborundum Co.

retained the sodium. A number of other commercially available absorbent materials will also be tested. Higher temperatures will also be employed, since it is desirable to have an absorbant which is effective at high temperatures. Cesium will be used in some of these runs.

4. Extraction of Plutonium by Liquid Magnesium
(I. O. Winsch, W. H. Spicer, L. G. Weaver*)

The design and fabrication of two units for investigation of magnesium extraction was completed during the last period. Further magnesium distillation studies were conducted in a new distillation unit.

a. Magnesium Extraction Studies

The small-scale extraction unit shown in Figure 41 has been fabricated and will be used in extraction studies planned for the next quarter. A much larger semi-works scale extraction unit, capable of handling 5 kg each of magnesium and uranium, has also been constructed and will be installed next quarter. This latter unit will provide experience in the handling of the molten magnesium and uranium phases. This will include separation of phases, transfer of molten materials from one vessel to another, mixing of phases, and observations on the suitability of various crucible and other construction materials.

Figure 41

SMALL SCALE MAGNESIUM EXTRACTION UNIT

One kilogram of a 1 per cent plutonium-uranium alloy was prepared in the Vycor tube furnace described in ANL-5529, page 89. It is reassuring that under the conditions of preparation, a temperature of about 1400° C for a period of a half hour, alpha activity was present only on the inside of the crucible.

*Special scientific employee on loan from International Harvester Co.

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b. Magnesium Distillation Studies

Nine magnesium distillation runs have been completed in the second distillation unit (see Figure 42), which was installed at the beginning of the last quarter. The results and conditions for these runs are tabulated in Table 45.

Figure 42

MARK II MAGNESIUM DISTILLATION UNIT

Table 45

SUMMARY OF MAGNESIUM DISTILLATION RUNS

See Figure 42 for description of equipment

No.	Distillation Conditions			Wt. of Charge		Wt. Distilled (gm)	Per Cent Distilled	Remarks
	Time (hr)	Temp. (C)	Pres (mm Hg)	Mg (gm)	U-Fe (gm)			
11	1.0	725	10	1930	-	1010	52	
12	1.5	730	9.5	1840	-	1450	77.3	
13	2.5	750	10	2053	1537	1950	95	Mg froze in condenser
14	1.9	740	10	1836	-	1126	61.5	
15	1.25	750	10	474	1917	472	99.9	Pu-Mg charge
16	2.75	710	10	2000	-	1930	97.0	Mg froze in condenser
17	2.9	715	10	2000	-	2000	100	
18	2.75	725	10	2018	-	2018	100	
19	3.50	730	10	2011	-	1917	95.3	

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In the initial five runs (11 through 15), induction heating was used to maintain the condenser at the proper temperature (about 670° C). Large temperature gradients existed along the condenser, and it was concluded that the heating was not uniform. Resistance heating was substituted in the last four tests (16 through 19) in an attempt to provide uniform temperature control. Uniform heating of the condenser was observed up to the time of distillation. Then, because of the insulation around the resistance heaters, it was not possible to remove this latent heat of the condensing magnesium rapidly enough. As a result, the condenser temperature would become the same as that of the still pot and all condensation of the magnesium vapor would occur in the receiver. By starting the distillation with the condenser at a relatively low temperature and by removing as much insulation as was possible, it has been possible to make successful runs (17 and 18). However, this method of condenser operation is unsatisfactory. It is now planned to use a sodium-cooled condenser, in which the condensing magnesium vapors will be allowed to vaporize sodium in a jacket. A closed sodium system will be used and the temperature of condensation will be controlled by the pressure in the sodium system.

In Runs 13 and 15, a heel of uranium-iron (melting point ~725° C) alloy was used as a material into which plutonium could transfer as distillation of the magnesium proceeded. Run 13 was made to demonstrate that the alloy melted satisfactorily. Since satisfactory melting was obtained, magnesium which initially contained 53 mg of plutonium was used in Run 15. It was reassuring to find 35 mg of plutonium in the uranium phase at the end of the distillation. However, this amount of transfer can be explained by equilibration of the phases when melting occurred, since a transfer of 35 mg corresponds to a distribution coefficient of about 0.16, the same as has been measured for extraction of plutonium from uranium by magnesium. Approximately four additional milligrams may be accounted for in an oxide film on the uranium. Probably the remainder was absorbed in the crucible walls. It is apparent that more work along this line is required.

Very little plutonium was present in the magnesium distillate (0.002 wt per cent). Entrainment of plutonium has been essentially eliminated by the use of a baffle in the still pot.

5. Inert Gas Purification (A. A. Chilenskas, K. Olson)

Work was continued on the development of procedures for removing oxygen and nitrogen contaminants from the inert argon blanketing gas for a pyrometallurgical processing facility.

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a. Removal of Oxygen from Argon

A system for the removal of oxygen by its catalytic combination with hydrogen at room temperature and subsequent removal as moisture by a drier such as "Molecular Sieves" was described in the previous quarterly, ANL-5560, page 106.

Although the catalyst efficiency was indicated as being near 100 per cent in the preliminary testing and reported²⁹ to be greater than 99 per cent at slightly elevated temperatures, the presence of even small quantities of hydrogen in the EBR-II fuel processing cell atmosphere may be undesirable. Further testing of the system for hydrogen breakthrough was undertaken in the apparatus shown in Figure 43.

Figure 43

APPARATUS FOR HYDROGEN BREAKTHROUGH DETERMINATION

Air, hydrogen, and argon are pumped together to give a composition of approximately 600 ppm oxygen and 1200 ppm hydrogen at a gas rate of 1 liter/min and fed to hydrogenation catalyst (32 ml of 0.5 per cent palladium on alumina packed in a 14-inch length of 1/2-inch copper tube). The oxygen in the presence of the palladium catalyst at room temperature combines with hydrogen to form water. The water is removed by a drier section of one-half inch copper tube, 36 inches long, packed with 1/8-inch type 4A "Molecular Sieves." The dried effluent stream is analyzed for hydrogen by converting it to moisture by the addition of oxygen to a heated section of 0.5 per cent palladium catalyst at 175° C and measuring the moisture content of the effluent gas with a continuously recording dewpoint meter.

²⁹Kuhn, D. W., et al., "The Reaction Between Hydrogen and Oxygen by Catalysis and the Thermal Reaction," ORNL-1209 (January 15, 1952)

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Tests were run in which the hydrogenation catalyst was first loaded with hydrogen using a stream of 1000 ppm hydrogen in argon and then operated for four hours with 600 ppm oxygen and 1200 ppm hydrogen while being monitored continuously for hydrogen breakthrough. The results showed that no hydrogen breakthrough occurred under conditions of catalyst space velocity* of 1875 hr^{-1} and stoichiometric proportions of hydrogen and oxygen in the argon.

The results of these tests show that for a catalytic space velocity of 1875 hr^{-1} and for a stoichiometric ratio of hydrogen and oxygen in argon, no hydrogen breakthrough occurred. The method of analysis was such that a breakthrough of 5 ppm of hydrogen would have been detected. At the same conditions, but with one-fourth of the above amount of catalyst, hydrogen breakthrough was observed.

The use of NaK at room temperatures in a bubbler system has also been studied as a possible system for the removal of oxygen. Argon contaminated with air was bubbled through 2-11/16 inches of NaK in a glass column 1-11/16 inches ID by 11-1/2 inches deep. A glass column 4-3/4 inches by 1-1/2 inches ID packed with 0.24 x 0.24 inch stainless steel Cannon protruded packing was used as a NaK de-entrainment section in series with the bubbler column. Two water-filled bubblers in series with the packed column were used to detect any NaK breakthrough in the packed column.

For a superficial gas velocity of 0.555 ft/sec, essentially complete removal of the oxygen was obtained from argon containing 3000 ppm oxygen. This removal was effected until about 16 per cent of the NaK was oxidized, whereupon the efficiency of the NaK for oxygen removal dropped sharply. Later examination suggested that the heavy crust formation permitted the argon to by-pass the remaining NaK, resulting in a rapid decrease in the oxygen removal.

Under these conditions, no NaK carryover was detected either on the column packing or in the water bubblers. At a superficial argon velocity of 0.104 ft/sec with the column operated for six hours, 9.5 mg of NaK were found on the column packing, and again none was found in the water bubblers following the packed column.

A third possibility being considered for the removal of oxygen is the use of hot copper turnings. This is attractive since regeneration can be accomplished with hydrogen. No experimental work on this procedure has been done, but a literature survey is in progress.

$$\text{*Space Velocity} = \frac{\text{Volumetric gas flow at SC}}{\text{Volume occupied by the catalyst}}$$

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b. Nitrogen Removal from Argon

An attractive possibility for nitrogen removal from the main cell atmosphere consists of purging the main cell gas with pure argon to maintain the cell atmosphere below some nitrogen tolerance concentration. This procedure is economically feasible when the cell inleakage rate is small and the nitrogen tolerance value is high, i. e., when only a small amount of argon makeup is required. Since the inleakage rate is unknown and the tolerance value of nitrogen is also unknown, additional studies of nitrogen removal by the use of metal getters has been underway to demonstrate on a small scale a purification system which will satisfactorily remove nitrogen from argon.

Preliminary investigations of the reactivity of calcium, magnesium and lithium with pre-purified grade nitrogen were conducted in a Vycor tube furnace which could be evacuated and filled with pure nitrogen. The tests indicate that calcium (electrolytic, Union Carbide and Carbon) and magnesium (Grignard reagent grade, Mallinckrodt) do not react with pure nitrogen up to temperatures of 700° C. Lithium (commercial grade) converts to nitride at a low temperature. Oxygen when introduced into the pure nitrogen at a concentration of about 500 ppm instigated the reaction between calcium and nitrogen at 575° C and between magnesium and nitrogen at 670° C.

The use of accelerators to initiate the reaction between calcium and nitrogen has been reported in the literature³⁰ and one of these, sodium, has been used repeatedly. Sodium when introduced as a lump (coated with oxide film) into a crucible containing calcium produced a vigorous reaction between calcium and pure nitrogen at 370° C. An alloy of calcium and sodium did not exhibit a noticeable reaction at any temperature up to 700° C but was found to have been smoothly converted to about 87 per cent nitride.

Apparatus has been built and will be used to estimate the gettering properties of calcium, calcium-sodium alloy, magnesium and calcium-lump sodium at the various temperatures of interest with atmospheres of 5 to 10 per cent nitrogen in pure argon and argon contaminated with about 500 ppm oxygen. The apparatus is of such design as to permit the recirculation of the test gas over the getter at a measured temperature. Measure of the decrease in system volume will show the quantity of nitrogen reacted.

³⁰Zs. Phys. Chem., 137A, 209 (1928).

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VI ANALYTICAL RESEARCH AND SERVICES

A. X-Ray Spectrophotometric Determination of Uranium in Solution

An X-ray spectrophotometric method has been devised and put in service for the rapid determination of uranium in the concentration range of 1 to 5×10^{-3} M. The details of the method are reported in ANL-5529, pages 121 to 128. As can be seen from the plot of counts per second vs uranium molarity shown in Figure 38 of ANL-5529, the counting rate deviates from linearity, the deviation being negative and greater at higher counting rates. It has been found that a coincidence-type correction of 7.2 counts per 100 counts per second to the G-M counting data gives a linear relationship. This coincidence-type correction probably includes self-absorption of the X radiation as well as the coincidence losses in the counter.

B. Gamma-Ray Analyzer Facility

(C. E. Crouthamel, Edwin R. Rathbun, Jr. and G. Seto)

The problems of building a gamma-ray analyzer facility are essentially (1) careful construction of the shielding, (2) careful packaging of the crystal and (3) determination of crystal counting efficiency for the total spectrum and the photofraction. The details of crystal packaging have been described by P. R. Bell.³¹ The standard crystal employed in this work was a 4-inch by 4-inch diameter cylindrical crystal, packaged in a partially evacuated 5-mil aluminum can and mounted on a 5-inch 6364 DuMont photomultiplier tube. The crystal was mounted inside a lead housing with inside dimensions 30 by 30 by 48 inches. A graded shield was placed on the inside surface of the lead housing and consisted of a 1/16-inch thick cadmium and 0.015-inch thick copper sheet to suppress the lead X ray by a factor of somewhat more than one hundred.

The total efficiency for the crystal was determined using the crystal geometry shown in Figure 43 and total cross section data. The total number of gamma rays striking the crystal will be $I_0 \Omega_T$ and $I_0 d\Omega$ is the total number of gamma rays striking the crystal in the solid angle $d\Omega$. The gamma rays detected in the solid angle $d\Omega$ will be $(1 - e^{-\mu_T \ell}) I_0 d\Omega$ and $\epsilon_T \Omega_T = \int_0^T (1 - e^{-\mu_T \ell}) d\Omega$. The total absorption coefficient for sodium iodide-0.1 per cent thallium-activated crystal is μ_T ; the total efficiency is represented by ϵ_T . The path length of the photon through the crystal is ℓ . The integral above cannot be evaluated directly, but values were obtained by the Argonne computer, AVIDAC. Geometries ranged from 50 to 0.5 per cent and μ_T from 0.090 to 10.0.

³¹Siegbahn, K., "Beta and Gamma-Ray Spectroscopy," Ch. 5, page 149. Interscience Publishers Inc., (New York, 1955).

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Figure 44

GEOMETRY FOR CALIBRATION OF
SODIUM IODIDE - THALLIUM ACTI-
VATED CRYSTAL

The total efficiency is relatively simple to calculate. However, the photofraction efficiency is very difficult to calculate directly because of the high probability of coincident multiple events occurring in the crystal. The photofraction efficiency is defined as the number of gamma rays of a given energy emitted by a source which strike the crystal and interact in such a manner that all of the energy of the incident gamma ray is totally absorbed by the crystal, divided by the total number of interactions of any kind due to photons possessing the energy of interest. After appropriate corrections are applied, this definition may be written as:

$$E_p = \frac{\text{Area under photopeak}}{\text{Total area under the pulse height distribution}}$$

We have measured the ratio of the area under the photopeak and the corrected area under the total spectrum for sources that emit only one gamma ray. Thus experimental values for E_p have been obtained. Separate experiments must be made at each geometry. Suitable single gamma sources range from 0.128-Mev Cs^{134m} to 1.114-Mev Zn^{65} . Our range of interest and practical application extends to 5.0 Mev. We have programmed Monte Carlo calculations on the new Argonne computer. These calculations have been set up for a divergent beam and point source geometries as shown in Figure 43 and the 4-inch by 4-inch diameter cylindrical crystals. The results of this computation and the experimental determinations of the photofraction will be reported later.

The analyzer associated with this facility is the Argonne 256-channel magnetic core memory unit. Both digital and graphical read out of the data are employed.

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VII. ROUTINE OPERATIONS

(H. G. Swope)

A. Waste Processing Operations

(J. F. Harast, K. Bremer, T. Emmering)

There were 54,000 gallons of liquid wastes processed during this quarter, as compared to 28,000 gallons in the previous quarter. The 54,000 gallons were reduced to 1,900 gallons by evaporation and concentration, 160 gallons were absorbed in vermiculite, and 120 gallons were made into concrete.

B. Gamma-Irradiation Facility

(H. G. Swope, J. Harast, A. Rashinskas, L. Marek, R. Juvinall, K. Clark)

The number of samples irradiated in the quarter ending March 31 was 740, whereas for the quarter ending June 30 it was 1427. The sample irradiations in the gamma irradiation facility during April, May and June are summarized below:

TOTAL NUMBER OF SAMPLES AND URN UNITS

	No. of Samples	No. of Urn Units ^a			No. of Re-immersions	Total Units
		Loadings	Day	Night		
April	497	212	335	313	21	881
May	338	170	230	67	5	472
June	592	208	467	249	134	1058
Totals	1427	590	1032	629	160	2411

^a1 loading = 1 unit

1 day unit = 2 million roentgens

1 night unit = 1/3 day unit

1 re-immersion = 1 unit

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LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	Summary of Experimental Data for 25 Per Cent Dispersions.	9
2	Summary of Experimental Data for 25 Per cent Dispersions.	10
3	Graphite Corrosion in Equimolar Zirconium Fluoride-Sodium Fluoride Melts	17
4	Graphite Corrosion in Equimolar Zirconium Fluoride-Sodium Fluoride Melts	19
5	Conditions for Corrosion Tests (Metal) in Hydrofluorinated Fused Fluoride Melts	24
6	Results of Coupon Tests in Hydrofluorinated Fused Fluoride Melts.	26
7	Corrosion of Materials in Gaseous Fluorine at Elevated Temperatures	31
8	Conditions and Results of Plutonium Hexafluoride Decomposition Experiments	35
9	Rate of Decomposition of Plutonium Hexafluoride as a Function of Temperature and Prefluorination	36
10	Fluorination of PuF_4 Using Fluorine Gas at Atmospheric Pressure	39
11	Fluorination of PuF_4 Using Fluorine Gas at Atmospheric Pressure	39
12	Comparison of Distillate Activities with Literature Values	44
13	Comparison of Residue Activities with Literature Values	46
14	Summary of Decontamination in Runs D-4 and D-5	48
15	Estimate of Total Residence Time of Corrosion Coupons in the Volatility Pilot Plant Dissolver	49
16	Corrosion of Nickel, Monel, and Inconel in H-126 Pilot Plant Dissolver	50
17	Results of Multistage Hydrofluorination Runs at Various Temperatures	55
18	Chemical Analyses of Rand Ore Concentrate	58
19	Physical Properties of Crushed Rand Ore Concentrate Before and After Reduction and Hydrofluorination	59
20	Summary of Reduction Runs on Rand Ore Concentrate.	60
21	Summary of Hydrofluorination Runs on Rand Ore Concentrate.	62
22	Analysis of Uranium Used in Metal Oxidation Studies	69
23	Width at $3/4$ Height of the (021) α -Uranium Line	71

DECLASSIFIED

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
24	Phases Detected by X-Ray Diffraction	72
25	Oxidation of Uranium-Effects of Surface Preparation	74
26	Summary Rate Data for Various Temperatures	76
27	Reaction of Oxygen with Zirconium	81
28	Reaction of Nitrogen with Zirconium	82
29	Oxidation Resistance of Arc-Melted Zirconium Alloys	83
30	Oxidation Resistance of Graphite-Melted Zirconium Alloys	84
31	Oxidation Resistance of Graphite-Melted Zirconium Alloys	85
32	Reaction of Oxygen with Zirconium and with a Zirconium-Tin Alloy.	86
33	Calibration Factors for Burn-Up Determinations	90
34	Corrosion of Alumina by Molten Uranium	93
35	Corrosion of Alumina by Molten Uranium Alloys	95
36	Phase Diagram Study: Lime-Beryllia System	108
37	Extraction of Activities from Powdered Uranium	110
38	Top-Pour Crucible Runs Using Magnesia Liner with Skimmer Tube	114
39	Top-Pour Crucible Runs with Direct Coupling to Charge	114
40	Maximum Bus Bar Spacing for Achieving Nominal Crucible Temperature of 1200° C.	115
41	Performance of an Air-Cooled Induction Coil	116
42	Heating of Graphite Crucible Using Uncooled Copper Induction Coil	117
43	Effect of Inductive Mixing on Crucible Erosion	119
44	Retention of Vaporized Sodium on Various Absorbent Materials	121
45	Summary of Magnesium Distillation Runs	123

037029.000

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1	General Correlation of Interfacial Area with Light Transmittance for 25 Per Cent Dispersions	11
2	Scattering Factor α as a Function of the Lorentz Coefficient M for 25 Per Cent Dispersions	11
3	General Correlation of Interfacial Area with Light Transmittance for 25 Per Cent Dispersions	12
4	Scattering Factor α as a Function of the Lorentz Coefficient M for 25 Per Cent Dispersions	12
5	Graphite Sparge Tube	18
6	Graphite and Nickel Gas Entry Tubes Exposed to Comparable Conditions of Hydrofluorination in Fused Fluoride Melts	20
7	CS Graphite (0.031-in. Grain Size)	21
8	CS Graphite (0.031-in. Grain Size)	22
9	CS Graphite (0.031-in. Grain Size)	22
10	CS Graphite (0.016-in. Grain Size)	23
11	Micrograph Showing Typical Intergranular Attack of Nickel in Hydrofluorinated Fused Fluorides	27
12	Micrograph of Inconel Liner Cross Section after Exposure to Hydrofluorinated Fused Fluoride Melt	27
13	Apparatus for Study of Decomposition of Plutonium Hexafluoride	33
14	Rate of Decomposition of Plutonium Hexafluoride as a Function of Temperature, Prefluorination and Atmosphere	37
15	Rate of Reaction of PuF_4 with Fluorine	40
16	Sketch of the Fluidized-Bed Apparatus	42
17	Trickle Valve for Solids Discharge from Cyclone Separator	53
18	Proposed Flowsheet for Direct Fluorination of Uranium Ore Concentrates	57
19	Apparatus for Volumetric Determination of Metal Oxidation	66
20	Microstructure of Typical Uranium Cube	68
21	X-Ray Diffractometer Scans Showing the (110) (021) and (002) Line Profiles from α -Uranium after Various Surface Treatments	70
22	Typical Run Plot to Determine Rates	73
23	Oxidation of Uranium in 200 mm O_2 at Various Temperatures	77
24	Selected Literature Data on the Reaction of Zirconium with Oxygen, 300 to 687°C	78

DECLASSIFIED

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
25	Selected Literature Data on the Reaction of Zirconium with Oxygen, 700 to 845°C	79
26	Selected Literature Data on the Reaction of Zirconium with Oxygen, 900 to 1100°C	79
27	Corrosion of Alumina by Molten Uranium	94
28	Dross in Alumina Crucible	96
29	Dross in Alumina Crucible	97
30	Dross in Alumina Crucible	98
31	Dross in Alumina Crucible	98
32	Cross Section of Thoria Plaque Showing Radio Blackening Under Sessile Drop of Molten Uranium	100
33	Stages in the Melting of Uranium on a Zirconia Plaque	101
34	Uranium Melted on Stabilized Zirconia	101
35	Grain Structure of Zirconia in Light and Dark Areas as Revealed by "Sensitive Tint" Light	102
36	Uranium Melted on Urania	103
37	Uranium Melted on Alumina	104
38	Uranium Melted on Magnesia	105
39	Slip Cast Magnesia Crucible with Skimmer Channel	113
40	Portable Bell Jar Furnace for Volatile Fission Product Studies	120
41	Small Scale Magnesium Extraction Unit	122
42	Mark II Magnesium Distillation Unit	123
43	Apparatus for Hydrogen Breakthrough Determination	125
44	Geometry for Calibration of Sodium Iodide-Thallium Activated Crystal	129

037029.030