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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

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TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	9
I. CHEMICAL-METALLURGICAL PROCESSING	20
A. Fuel-processing Facilities for EBR-II	24
B. Pyrometallurgical Development	33
C. Pyrometallurgical Research	63
II. FUEL-CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES	84
A. Direct Fluorination Volatility Process for Oxide Fuels . .	87
B. Direct Fluorination Process for Enriched Uranium- Zirconium Alloy Fuels	101
C. Metal Fluorination Studies	106
D. ADF Process Development for Enriched Uranium- Zirconium Fuel	112
E. Fused Salt Processing of Zirconium-matrix Fuels	114
F. Conversion of Uranium Hexafluoride to Uranium Dioxide	118
G. Multistage Fluidization	124
III. REACTOR SAFETY	128
A. Metal Oxidation and Ignition Studies	129
B. Metal-water Reactions	141
IV. REACTOR CHEMISTRY	154
A. Determination of Nuclear Constants - Neutron Capture Cross Sections of Uranium-236	154
B. Slurrex Chemistry Supporting Program	156
C. Reactor Decontamination	157
D. Structural Materials for Nuclear Superheaters	170
V. ANALYTICAL RESEARCH AND DEVELOPMENT	173
VI. ROUTINE OPERATIONS	176

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Comparison of Inductor Coils in Melt-refining Test Assembly	37
2.	Conditions and Results of Full-scale Skull Oxidations	46
3.	Determination of Reduction Yields by the Uranium Hydriding Method	48
4.	The Reduction of Uranium Oxide by Liquid Magnesium	49
5.	Stability of Alumina Crucibles Toward Materials Used for Reduction of Uranium Oxide	52
6.	Plutonium Material Balance in Separation of Plutonium from Magnesium Solutions by Distillation.	55
7.	Phases in Titanium-Cadmium Compacts Determined by X-ray Diffraction	65
8.	Compilation of Partition Data for the Aluminum-Cadmium System	70
9.	Compositions and Standard Free Energies of Formation of Intermetallic Compounds in the Uranium-Zinc System	75
10.	Standard Heat of Combustion of Tungsten Sulfide in Oxygen . .	78
11.	Calorimetric Combustions of Zirconium in Fluorine.	79
12.	Preliminary Data from Combustions of Boron in Fluorine . .	81
13.	Rate of Decomposition of Plutonium Hexafluoride Vapor . . .	91
14.	Reaction of Sulfur Tetrafluoride and Plutonium Hexafluoride .	95
15.	Conversion of Uranium Dioxide to Uranium Trioxide	97
16.	Results of Uranium Dioxide Fluorination Runs.	100
17.	Summary of Exploratory Runs on Direct Hydrofluorination of Zirconium Alloys in a Fluidized Bed	102
18.	Summary of Pilot-Scale Runs on Direct Hydrofluorination of Zirconium Alloys in a Fluidized Bed	104
19.	The Reaction Between Oxidized Zircaloy and Hydrogen Fluoride-Hydrogen Chloride Mixtures	107
20.	Analysis of the Residues from the Reaction of Zircaloy with a Mixture of Hydrogen Fluoride and Hydrogen Chloride. .	109
21.	Effect of Hydrogen Chloride Concentration on the Reaction $\text{Zr} + 4 \text{HF} \xrightarrow{(\text{HCl})} \text{ZrF}_4 + 2\text{H}_2$	110

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
22.	Corrosion of 304 Stainless Steel in Hydrogen Fluoride Containing Hydrogen Chloride.	111
23.	Pilot Plant Fixed-Bed Fluorination Studies	113
24.	Impurity Distribution in Fused Salt Dissolver	116
25.	Dissolution Rates of Zirconium-Uranium Alloy Fuel Plates in Sodium Fluoride-Zirconium Tetrafluoride Salt Mixtures . .	118
26.	Summary of Runs on Fluid-Bed Pyrohydrolysis of Uranium Hexafluoride to Uranyl Fluoride	119
27.	Summary of Hydrogen Reduction Runs on Uranyl Fluoride Prepared in Fluidized Beds	120
28.	Summary of Sintering Tests Performed on Uranium Dioxide Prepared by the One-step Fluid-bed Process	123
29.	Ignition Temperatures of Plutonium Alloys with Varied Aluminum Content, Thickness, and Width	135
30.	Ignition Temperatures of Preliminary 2 Atom Per Cent Plutonium Alloys	136
31.	Burning Propagations of Preliminary 2 Atom Per Cent Plutonium Alloys	139
32.	Burning Propagations of Aluminum-Plutonium Alloys with Varied Content, Thickness, and Width	139
33.	Uranium-Water Reaction Data: Condenser Discharge Method	142
34.	Summary of Results of In-pile Metal-Water Experiments with Oxide and Cermet-core Fuel Pins	147
35.	Corrosion of EBWR Turbine Metals in Alkaline Permanganate-Ammonium Citrate Solutions	158
36.	Effect of pH of Citrate Solution on Corrosion.	159
37.	Corrosion of Turbine Metals in a Modified Alkaline Permanganate Decontamination Procedure	160
38.	Corrosion of Low-chromium Steels in $2\frac{1}{2}$ Per Cent Oxalic Acid at Room Temperature	161
39.	Foam Characteristics of Surfactants	164

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
40.	Tabulated Results for Contamination Runs in Boiling Water Loop	166
41.	Amount of Uranium Corrosion Product Residues Remaining in Sampler Following Runs CL-1 and CL-2	167
42.	Summary of Irradiations Performed in Rack M-1 during April, May, June, 1960	176
43.	Per Cent of Irradiation Received in the Different Positions in Rack M-1 of Argonne's High-Level Gamma Irradiation Facility	177

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Crucible Heating Rates Used in Tests	31
2.	Long-term Sintering Test of Carbon Black Insulation (Run 27)	36
3.	Molybdenum Removal Resulting from Oxidation of Fissium . .	40
4.	Liquid Metal Process for Reclamation of Melt-refining Skulls.	41
5.	Tilt-Pour Furnace with Pressure-Siphon Attachment	42
6.	Photographs of Melt-Refining Crucibles and Uranium Skull Material Before and After Oxidation	44,45
7.	Retorting and Hydriding System for Uranium Reduction Ingots.	47
8.	Liquid Metal Process for Recovery of Plutonium from Uranium Blanket Metal	54
9.	Tantalum Baffle and Still Pot Containing Plutonium- Magnesium Distillate	56
10.	Side View of Plutonium Button After Removal from Tantalum Still Pot	57
11.	Proposed Design of Baffle and Vapor Labyrinth for Cadmium Distillation Unit.	59
12.	Solubility of Titanium in Liquid Cadmium.	64
13.	Solubility of Uranium in Lead.	66
14.	Solubility of Uranium in Liquid Cadmium	67
15.	The Solubility of Uranium in Liquid Cadmium-Magnesium Alloys at 610 C	68
16.	Solubility of Praseodymium and Neodymium in Liquid Cadmium	69
17.	Isothermal Effusion of Zinc from Uranium-Zinc Alloys.	73
18.	Vapor Pressure of Zinc Over Uranium-Zinc Alloys	74
19.	Rate of Decomposition of Plutonium Hexafluoride Vapor at 161 C for Experiments 23 through 29.	92
20.	Rate of Decomposition of Plutonium Hexafluoride Vapor at 161 C for Experiments 30 through 37.	93
21.	Rate of Decomposition of Plutonium Hexafluoride Vapor	93

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
22.	Ten-Plate Section of Uranium-Zirconium Alloy Before and After Attack by Hydrogen Chloride-Hydrogen Fluoride Gas Mixture	103
23.	Effect of Temperature on the Reaction of Oxidized Zircaloy-2 with a Mixture of Hydrogen Fluoride-Hydrogen Chloride	108
24.	Effect of Time on the Reaction Between Oxidized Zircaloy-2 and a Mixture of Hydrogen Fluoride-Hydrogen Chloride	108
25.	Effect of Hydrogen Chloride Concentration on the Reaction $\text{Zr} + 4 \text{HF} \xrightarrow{(\text{HCl})} \text{ZrF}_4 + 2\text{H}_2$	111
26.	Zirconium Dissolution in Fused Salt: Off-Gas Record in Run A-10	116
27.	Effect of Fines on Ignition Temperature of -14, +20 Mesh Spherical Uranium Powder.	131
28.	Ignition Temperatures of -200, +230 Mesh Spherical Uranium Powders as a Function of Sample Weight	133
29.	Ignition Temperatures of -200, +230 Mesh Spherical Powder as a Function of Sample Height.	133
30.	Ignition Temperatures of Spherical Uranium Powders as a Function of Specific Area.	134
31.	Ignition Temperatures of the Various Preliminary Plutonium Alloy Foils	136
32.	Interrupted Oxidation of Uranium at 200 C in 200 mm Oxygen	140
33.	Experimental Results; Uranium-Water Reaction	142
34.	Effect of Initial Temperature on the Mean Size of Uranium Particles	144
35.	Radiographs of Stainless Steel- and Aluminum-clad, Oxide-core Fuel Pins.	146
36.	Cross Section of Oxide-core Pin after Transient CEN-21 . . .	148
37.	Sector of Oxide Core from CEN-21	149
38.	Aluminum-jacketed, Oxide-core Pin after Transient CEN-22 .	150
39.	Aluminum-jacketed, Oxide-core Pin after Transient CEN-23 .	150
40.	Stainless Steel-jacketed, Oxide-core Pin after Transient CEN-24	151

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
41.	Zircaloy-2-jacketed, Cermet-core Pin after Transient CEN-25	152
42.	Zircaloy-2-jacketed, Cermet-core Pin after Transient CEN-26	152
43.	CEN-24 Oscillograph Record	153
44.	Corrosion of Low Alloy and Mild Steels in 10 Per Cent Ammonium Citrate	160
45.	Corrosion of Uranium as Monitored by Radiation Survey	167
46.	Beta Activity of Stainless Steel Type 304 Sample Strip in Runs CL-1 and CL-2	168
47.	Beta Activity of Stainless Steel Type 304 Sample Strip in Runs Cs-2 and Cs-3	169
48.	Count Rate Increase at Loop Disengaging Section as Influenced by Liquid Level	169
49.	Typical Variation of Dosimetry from Top to Bottom in Irradiation Run	178

CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

April, May, June, 1960

SUMMARY

I. Chemical-Metallurgical Processing (pages 20 to 83)

A direct-cycle fuel-reprocessing plant using pyrometallurgical procedures is being designed and constructed as part of the Experimental Breeder Reactor No. II (EBR-II) project. A Laboratory and Service Building is also included. Melt refining, liquid metal extraction, and processes involving fractional crystallization from liquid metal systems are methods being examined for the recovery and purification of EBR-II fuels. Based on these studies, process equipment is being designed and tested.

Full-scale construction of the Fuel Cycle Facility Building was resumed on March 25, 1960. The building is now about 20 per cent completed.

The Model 8 manipulators for the Junior Caves of the Laboratory and Service Building have been received at the EBR-II site and are being installed. Installation of the Junior Cave windows is completed.

The five-ton cranes for the Fuel Cycle Facility, which were unacceptable at the first inspection test, were tested again and found acceptable. The contract for the eight operating manipulators has been signed. Bids for twelve Model 8 manipulators for the Air and Argon Cells have been received.

Glass production work for the Fuel Cycle Facility windows has been completed. Porous welds in the tank units have been corrected. Design specifications for the fuel transfer coffin are essentially completed. The packet for installation of the induction heating motor generator installation was completed.

MI cable samples sealed with Temporell No. 741 have been irradiated to 3.0×10^9 rad. Insulation resistance has dropped below 150 megohms (from greater than 200 megohms). Samples of the 54-conductor manipulator power cable have been irradiated to 1.7×10^9 rad. Insulation resistance is greater than 200 megohms. The cable sheath hardened after 5.0×10^8 rad so that stress testing of the cable between gamma doses had to be terminated.

Tests of the absorber-type fume trap have been successful. Sodium trapping efficiency was greater than 95 per cent in five experiments.

Preparations have continued for high-activity-level demonstrations of the melt-refining process for EBR-II core fuel. The melt-refining furnace, designed to handle a 400-gram charge of uranium-fissium alloy irradiated to two per cent total atom burnup, has been reconditioned in preparation for the active experiments. A "dummy" experiment, closely duplicating the procedure to be followed in the active runs, has been completed. The apparatus and techniques for investigating the evolution of krypton and xenon from irradiated fuel pins on heating are being tested with unirradiated material.

Further tests were made on various insulating materials which could be employed in the melt-refining furnace. Silicon carbide powder, graphite powder and carbon black all proved to be highly effective insulating materials.

An attractive and efficient procedure for removing uranium skull material from a melt-refining crucible is to convert it to free-flowing oxide powder by oxidation with a dilute oxygen-argon mixture at 700 to 800 C. The behavior of several volatile fission product elements (ruthenium, molybdenum, and technetium) during the skull oxidation has been studied. In gram-scale experiments, fairly complete volatilization of these elements occurs or can be easily made to occur. With larger quantities of material, the rate of volatilization is reduced considerably, the difference apparently being in the ability to achieve good gas-solid contact.

Two complete runs were made for both demonstrating and pinpointing difficulties in the drag-out or skull-reclamation process. While both process conditions and equipment are in a preliminary state, all of the process steps were performed. Recovery of uranium in the skull-oxidation step exceeded 99 per cent. The introduction of zirconia from the crucibles was less than experienced in previous work, being less than 2 per cent in each case.

Investigation of the reduction of uranium oxides by liquid magnesium alloys was continued. Emphasis was placed on the use of pure liquid magnesium as the reductant. After fairly extensive calibration work, reduction yields were measured by the uptake of hydrogen to form UH_3 . Essentially quantitative (99 ± 1 per cent) reduction yields were realized with uranium dioxide. Reduction yields generally decreased with increasing particle size. Higher oxides, such as U_3O_8 , appear less susceptible to reduction than uranium dioxide, a behavior attributed to greater caking tendency.

Because of the high activity of uranium in cadmium solutions, uranium is susceptible to precipitation from such solutions by impurities. Aluminum (which was found to be introduced from alumina crucibles in the presence of a fused salt flux), graphite, and boron nitride were found to precipitate uranium from cadmium solution.

Two runs were made to demonstrate recovery of plutonium from a magnesium solution by distillation of the magnesium. This is the final step of a tentative blanket process. Essentially complete recovery of the plutonium was realized in each run. A bright, shiny plutonium ingot (about 100 grams) recovered from the second run was subsequently satisfactorily poured into a mold. The runs were made without abnormal incidents and without encountering contamination problems.

Distillation of cadmium in a fairly large experimental distillation unit has pinpointed design and operating conditions which must be met to avoid metal entrainment. This information has largely confirmed the design of the large-scale metal distillation equipment, now under construction.

Retorting studies have shown the importance of two factors for production of compact, easily removable uranium product cakes. First, uranium entrainment is reduced by having the uranium precipitated during retorting. Second, ready removal of the product is possible if the retorting is performed in ceramic or ceramic-coated crucibles. These procedures have given good quality, well-coalesced sinter cakes.

Operation of a mild steel corrosion loop for circulating a uranium-magnesium-cadmium alloy at 550 C was terminated after 4800 hours of trouble-free operation. Preliminary examination has not revealed any gross corrosion. The uranium concentration remained constant at 0.85 per cent over the last five months of operation, after an initial decrease from 0.94 per cent.

Among the fundamental physicochemical data lacking for many of the liquid metal systems of interest to pyrometallurgical processes are the solubilities of some elements in liquid metal systems. The solubility of titanium in liquid cadmium was found to vary between 0.047 atom per cent at 449 C to 0.15 atom per cent at 651 C. Two different titanium-cadmium intermetallic compounds have been found in this system. Evidence for a peritectic reaction at about 500 C was found.

The solubility of uranium in liquid lead over the temperature range from 415 to 802 C is given by the equation

$$\log (\text{atom per cent uranium}) = 3.921 - 5.121 \times 10^3 T^{-1}$$

The solubility of uranium in liquid cadmium has been redetermined below the peritectic temperature (471.5 C), using a significantly improved technique, with the result

$$\log (\text{atom per cent uranium}) = 8.115 - 7.104 \times 10^3 T^{-1} + 0.832 \times 10^6 T^{-2} .$$

Above the peritectic temperature the solubility is given by the equation

$$\log (\text{atom per cent uranium}) = 1.448 - 2.618 \times 10^3 T^{-1} + 1.189 \times 10^6 T^{-2} .$$

The solubility of uranium in cadmium-magnesium solutions containing up to 72 weight per cent magnesium at 610 C has been found to decrease smoothly from about 2 weight per cent in pure cadmium to about 0.002 per cent in 72 weight per cent magnesium. Since the solid phase in equilibrium with these solutions is α -uranium over the entire concentration range, no maximum or minimum in the solubility is expected theoretically or found experimentally.

The solubilities of praseodymium and neodymium in liquid cadmium are given by the equations

$$\log (\text{atom per cent praseodymium}) = 6.949 - 5400 T^{-1}$$

and

$$\log (\text{atom per cent neodymium}) = 6.909 - 5211 T^{-1} .$$

The partition coefficients of a number of representative fissile and fission product elements between the immiscible liquids aluminum and cadmium at 680 to 688 C have been measured. Values of the coefficient (wt per cent in aluminum phase/wt per cent in cadmium phase) are uranium: 1.45×10^5 ; palladium: 5.82×10^3 ; cerium: 1.74×10^2 ; praseodymium: 1.63×10^2 ; lanthanum: 4.61×10^1 and zirconium: 8.18×10^1 . No significant temperature dependence of the partition coefficient was found for uranium over the range from 686 to 710 C.

The activity coefficient of uranium in saturated solution in liquid lead determined by an emf method varies between 7.2 at 500 C and 5.9 at 700 C.

Effusion vapor pressure studies on the uranium-zinc system at about 440 C have shown the existence of two uranium-zinc intermetallic compounds, one at about $\text{UZn}_{11.5}$ and the other at U_2Zn_{17} .

Thermodynamic data of interest to high-temperature chemistry are being acquired by calorimetric methods.

The heat of combustion of tungsten disulfide in oxygen has been determined to be $\Delta E_C^\circ/M = -1939.29 \pm 0.55$ cal/g for the reaction

The heat of formation of zirconium tetrafluoride has been determined by combustions of zirconium in fluorine. The data lead to a preliminary value of $\Delta H_f^\circ_{298.15} = -454.5$ kcal/mole.

Two series of calorimetric combustions of boron in fluorine have been carried out. The current "best value" for the heat of formation of boron trifluoride was suspected to be in considerable error. This is not substantiated by the preliminary data which are presented in this report.

Preliminary developmental work is being carried out for combustions of cadmium and magnesium in fluorine.

II. Fuel-Cycle Applications of Volatility and Fluidization Techniques (pages 84 to 127)

Several processes have been proposed for the processing of irradiated fuels by taking advantage of the volatilities of uranium and plutonium hexafluoride and fluidization techniques. These include a Direct Fluorination Process, the Aqueous Dissolution Fluorination (ADF) Process and the Fused Fluoride Volatility Process. Current application is toward recovery of uranium from zirconium-clad or alloy-based fuels. The application of these processes to fuels containing stainless steel is also being considered. Fluidization techniques are also being used in the conversion of uranium hexafluoride to other uranium compounds of interest in the nuclear fuel cycle.

The Direct Fluorination Volatility Process is being developed to recover uranium and plutonium from spent uranium oxide, Zircaloy-clad, fuel elements of the type used in the Dresden nuclear power plant. A proposed processing procedure utilizes the reaction of zirconium with a mixture of hydrogen fluoride and hydrogen chloride for decladding. Plutonium and uranium hexafluorides, which result from the reaction of the oxide fuel with fluorine, may be separated using a combination of the variability of the rates of fluorination and chemical reactivity. Equipment has been constructed and is being tested to study the process steps using multigram amounts (10 to 100 grams) of plutonium.

A study of the kinetics and mechanism of the decomposition of plutonium hexafluoride vapor has been initiated. The reaction appears to be a heterogeneous one which is zero order with respect to plutonium hexafluoride at 160 C.

The reaction of plutonium hexafluoride with sulfur tetrafluoride was investigated. Results indicate that plutonium hexafluoride is reduced by sulfur tetrafluoride at rates suitable for process use.

The reaction of sulfur tetrafluoride with uranium trioxide to produce uranium hexafluoride may be used as a basis for a fuel-recovery process. Investigation of the stoichiometry of the reaction is in progress. Thionyl fluoride and uranium hexafluoride are the major products.

Conversion of uranium dioxide to uranium trioxide by means of air and nitric acid vapor and also by means of oxygen and nitrogen dioxide was investigated between 350 and 500 C. Excellent results were obtained with nitric acid. However, when using nitrogen dioxide and oxygen it was apparent that longer reaction times and higher gaseous pressures were needed for complete conversion of uranium dioxide.

In a continuing study of the direct fluorination of dense uranium dioxide pellets, a run in the three-inch pilot plant reactor showed (1) a lower temperature reduces the rate of fluorination of the uranyl fluoride intermediate to uranium hexafluoride and (2) a deeper inert fluidized bed retains more fines in the bed reducing the dust load on the filters.

Several aspects of the Direct Fluorination Process are being studied for the recovery of uranium from highly enriched uranium-zirconium alloy fuels. One scheme is to convert the metallic element to fluoride salts by means of mixtures of hydrogen chloride and hydrogen fluoride. A subsequent fluorination step would be expected to volatilize the uranium and permit separation. The work is being carried out with the fuel elements submerged in a fluidized bed of inert material (such as calcium fluoride) which serves as the heat transfer medium. Runs in both $1\frac{1}{2}$ -inch and 6-inch diameter columns confirmed previous results that high conversion of zirconium to the tetrafluoride may be achieved with dilute mixtures of hydrogen chloride in hydrogen fluoride (10 volume per cent or less hydrogen chloride) at temperatures of 450 to 500 C. About 95 per cent conversion was achieved on a 2-kg, 10-plate welded section of a 1.5 per cent uranium-zirconium alloy subassembly in about 12 hours. Mixtures rich in hydrogen chloride (near 40 volume per cent) were found to react less rapidly with zirconium.

Experiments incorporating a 2-zone reaction scheme for reacting zirconium with hydrogen chloride-hydrogen fluoride gas mixtures were initiated. The element is first reacted with hydrogen chloride, forming the volatile zirconium tetrachloride, which is then reacted in the upper section of the bed with hydrogen fluoride. Very little conversion was achieved in the initial trials, possibly as a result of back-mixing of the hydrogen fluoride which produced a much less reactive hydrogen chloride-rich mixture. Baffling between the two reaction zones will be required to prevent gas back-mixing.

Laboratory data have been obtained on reaction rates of Zircaloy-2 with various mixtures of hydrogen fluoride and hydrogen chloride at various temperatures. This gas mixture was found to have little effect on sintered uranium dioxide pellets contained within a short section of 30-mil thick Zircaloy tubing which completely corroded in a 6-hr period.

The ADF Process, which involves aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry powder, and fluorination of the powder to remove and recover the uranium as the hexafluoride, is directed toward recovery of uranium from enriched uranium-zirconium alloy fuels. Results of recent fluorination experiments conducted in static beds in both a 2-inch diameter by 6-foot tall reactor and a 6-inch diameter unit indicated that variations in bed heights up to $4\frac{1}{2}$ feet and gas velocities up to 0.1 ft/sec were of negligible importance with respect to uranium removal from uranium-zirconium fluoride salts prepared in the fluid-bed dryer. Residual uranium contents were about 0.03 to 0.05 per cent, representing losses of the order of 5 per cent.

A series of fused salt dissolutions of synthetic zirconium-uranium fuel assemblies has been carried out in the graphite pilot plant dissolver according to a semicontinuous flowsheet. Dissolution rates in the sodium fluoride-zirconium fluoride mixture under hydrogen fluoride sparge have been as high as 3.4 mg/(min)(sq cm), resulting in a 90 per cent dissolution of the approximately 90-mil thick plates in less than five hours. Satisfactory operation of the internal graphite heaters and other components exposed to the molten salt have continued over 1600 hours of accumulated exposure.

The conversion of uranium hexafluoride to uranium dioxide by direct reaction with steam and hydrogen is being investigated. The process involves the formation of either uranyl fluoride or uranium tetrafluoride followed by hydrogen reduction or steam pyrohydrolysis to the dioxide. In each case, the newly formed material is deposited as a dense coating on the fluidized particles in the bed. The reaction of steam with uranium hexafluoride was carried out at temperatures of 140 to 230 C using hexafluoride rates equivalent to 205 lb uranium/(hr)(sq ft reactor cross section). The temperature of the hydrogen reduction step significantly affects the rate of fluoride removal. In 4-hour batch runs 5 to 10 per cent residual fluoride remained at 550 C and only 0.024 per cent remained at 650 C. The latter value is within the fluoride specification usually set for ceramic-grade uranium dioxide powders. The reduction of uranium hexafluoride with hydrogen to a dense uranium tetrafluoride was successfully carried out in a 2.2-hour run at 600 C using a feed rate of 101 g/min and about 250 per cent excess hydrogen. The first series of pellet fabrication studies made at Mallinckrodt Nuclear Corp. on uranium dioxide prepared at ANL by direct conversion from hexafluoride resulted in sintered densities ranging from 93.5 to 97.5 per cent of theoretical for material which was ground to -325 mesh and pelleted.

The first phase of the experimental work in the 6-inch multistage fluid-bed reactor designed to achieve controlled downward transport of solids using external vibrators and without the use of internal downcomers has been completed. A correlation has been obtained for throughput rate as a function of feed particle density, shape and size, column cross-sectional area, density and superficial velocity of the fluidizing gas and the depth and size of beads used in the bed support plate.

III. Reactor Safety (pages 128 to 153)

In order to provide knowledge to minimize the hazards associated with handling the reactor metals, uranium, zirconium, plutonium, and thorium, the examination of the oxidation, ignition, and combustion processes of these metals is being continued.

The considerable inhibition of the burning propagation rates of uranium and zirconium by presence of small percentages of halogenated hydrocarbons in air has been studied further in an effort to appraise the potentiality of their use as extinguishants and to clarify the mechanism of inhibition.

The study of ignition of metal powders has continued with studies of ignition of spherical uranium powders. Ignitions of samples of varied specific area and mixtures of portions of fine and coarse particles compare favorably with ignition temperatures calculated on the basis of integrated heat generation according to isothermal oxidation kinetics. Studies of the effects of sample geometry, using various sizes of crucibles, indicate that the important parameter is the depth of the sample. Samples greater than a critical depth have constant ignition temperatures, while below this depth the ignition temperature increases with decreasing depth.

Preliminary ignition and burning propagation rate studies with plutonium binary alloy foils, containing 2 atom per cent aluminum, iron, carbon, nickel, manganese, and chromium, have been completed. Manganese appears to lower the ignition temperature and aluminum to raise it. Similar data are obtained from burning curve and shielded ignition experiments for all except the aluminum alloys. Some of the aluminum alloy samples show ignition temperatures from burning curves to be approximately 150 degrees higher than from shielded experiments. This may be due to stabilization of the delta phase, which has been reported to produce a protective oxide.

The specific area dependence, based on comparison of the iron alloy in rod form and as a foil, appears to be similar to that observed for uranium.

The development and growth of nodules observed on the surface of the oxide during isothermal oxidation of uranium on the microscope stage have been shown to cease if the oxidation is interrupted by evacuation of the cell and to resume when oxygen is readmitted. Thus, the nucleation and growth process is not independent of the formation of new oxide.

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. The principal laboratory-scale method involves the rapid melting and dispersion of metal wires in a water or steam environment by a surge current from a bank of condensers. Additional runs in the series with 30-mil uranium wires were completed. Runs have been made with initial metal temperature ranging from 662 C (solid) to 3800 C (liquid). Up to 45 per cent reaction occurred in the more energetic runs. There was no marked change in the character of the reaction at the melting point of uranium dioxide (2700 C) or any other temperature in the range studied. The uranium reaction differed in this respect from the zirconium reaction. Results of particle size measurements of the residue from the uranium runs showed that mean diameters as low as 50 μ were produced in the more energetic runs.

A second laboratory-scale method involves the rapid contact of steam with heated metal. In this method, the metal receives a "pressure pulse" of water vapor. A series of runs with aluminum gave results that were not reproducible. The difficulty was traced to interference of the aluminum mirror generated on the walls of the reaction cell during the heating process. Means to avoid this interference have been devised and the necessary modifications to the apparatus are in progress.

A series of eight experiments have been conducted in the TREAT reactor during the quarter. In these experiments, a stainless steel autoclave containing a fuel pin, gold foils, helium and water was subjected to a short burst of neutrons. Aluminum and stainless steel-clad, oxide core pins and Zircaloy-2-clad, aluminum- U_3O_8 cermet core pins were studied. The uranium was fully enriched. Only 1.4 per cent of the metal present in the fuel pin reacted in the most vigorous transient. Partial melting of both the clad and core has been obtained with the oxide pins. Penetration of the Zircaloy-2 clad and melting of the cermet core were obtained with the cermet pins. The time corresponding to a peak clad temperature lagged behind the peak flux by up to 5 sec for the oxide core pins, whereas with metal core pins less than 0.1-sec lag was noted in previous runs.

IV. Reactor Chemistry (pages 154 to 172)

Data are being obtained on the neutron-capture cross sections of uranium-236 as a function of neutron energy. Cross sections for 0.7 and 0.8-Mev neutrons have been obtained thus far.

Among the problems being examined in development of a Boiling Slurry Reactor Concept (described in ANL-6101, page 160) is preparation of spherical thoria-urania particles. Properties of the fuel particles before and after firing at high temperature have been studied.

The Reactor Decontamination Program endeavors to determine, through the operation of a loop simulating the action of a boiling water reactor, what the consequences might be if the reactor fuel cladding is ruptured. It could be expected that fission products entering the reaction water would distribute into the reactor auxiliaries, including the steam turbine. In this program, fission products are introduced into the loop, and quantities and types of these that deposit in the vapor phase are monitored. In a parallel effort, studies are being made in the laboratory to find suitable means of removing deposited activity.

Corrosion studies are being made of various turbine constructional materials in alkaline permanganate procedure solutions. The second-step reagent, ammonium citrate, was found to be the most corrosive reagent. The high chrome stainless steels (13 per cent) were quite resistant, but pH adjustments were required to reduce corrosion to reasonable levels with low alloy and mild steels. The pH adjustments had little effect on ability to decontaminate. The presence of oxygen or hydrogen in 600-psig contaminated steam was found to increase the difficulty of activity removal with the alkaline permanganate procedure. These tests are being repeated with lower oxygen contents. Foaming characteristics of seven surfactants were obtained relative to their use in a foam decontamination process.

Several loop runs were made at 200 psig with irradiated uranium. Corrosion of the uranium pellets occurred within 25 to 30 hours. Vapor phase contamination was about a factor of 10 higher when the steam velocity was increased from 0.8 to 1.2 feet per second. In a run with cesium-137 tracer, the existence of a critical liquid level was found. With a steam velocity of 0.8 feet per second at 200 psig, the rate of activity plate-out in the vapor phase was low above this liquid level and high below it.

Construction work is proceeding on apparatus to study the effects of superheated steam on materials of construction. A circulating autoclave is nearing completion, and facilities for handling a series of static autoclaves are in the design stage. Since an operating nuclear superheater is expected to contain significant quantities of radiolytic hydrogen and oxygen along with the steam, provisions will be made to include these gases in the test equipment. The exact design of the hydrogen-oxygen addition and monitoring equipment depends on the rates of reaction of these gases with each other under the test conditions. Since these rates have not been measured, additional apparatus is being assembled for this purpose.

V. Analytical Research and Development (pages 173 to 175)

A fusion technique has been developed for dissolution of plutonium oxide. It involves fusion of the plutonium oxide with ammonium bifluoride followed by dissolution of the resulting plutonium (IV) fluoride in an acid aluminum-containing solution.

Two analytical methods have been developed for determination of plutonium. One is a spectrophotometric determination of plutonium (IV) with arsenazo, the other is an amperometric titration of plutonium (VI).

VI. Routine Operations (pages 176 to 178)

The operation of the radioactive waste-processing facility and the gamma-irradiation facility continued without incident. A study has been made of dose distribution in Rack M-1 of the High-level Gamma Irradiation Facility.

I. CHEMICAL-METALLURGICAL PROCESSING

A direct-cycle fuel-reprocessing plant using pyrometallurgical procedures is being designed and constructed as part of the Experimental Breeder Reactor No. II (EBR-II) project. A Laboratory and Service Building is also included. Melt refining, liquid metal extraction, and processes involving fractional crystallization from liquid metal systems are methods being examined for the recovery and purification of EBR-II fuels. Based on these studies, process equipment is being designed and tested.

Full-scale construction of the Fuel Cycle Facility building was resumed on March 25, 1960. The building is now about 20 per cent completed.

The Model 8 manipulators for the Junior Caves of the Laboratory and Service Building have been received at the EBR-II site and are being installed. Installation of the Junior Cave windows is complete.

The five-ton cranes for the Fuel Cycle Facility, which were unacceptable at the first inspection test, were tested again and found acceptable. The contract for the eight operating manipulators has been signed. Bids for twelve Model 8 manipulators for the Air and Argon Cells have been received.

Glass production work for the Fuel Cycle Facility windows has been completed. Porous welds in the tank units have been corrected. Work continues on a number of miscellaneous equipment items for the Fuel Cycle Facility. Design specifications for the fuel transfer coffin are essentially complete. The packet for installation of the induction heating motor generator installation was completed.

MI cable samples sealed with Temporell No. 741 have been irradiated to 3.0×10^9 rad. Insulation resistance has dropped below 150 megohms (from greater than 200 megohms). Samples of the 54-conductor manipulator power cable have been irradiated to 1.7×10^9 rad. Insulation resistance is greater than 200 megohms. The cable sheath hardened after 5.0×10^8 rad so that stress testing of the cable between gamma doses had to be terminated.

Enriched fuel ingot production in Mark V mock-up furnace was suspended pending the outcome of investigations to find remedial measures to crucible cracking problems. Means of minimizing crucible cracking have now been found and fuel ingot production will be resumed next quarter.

Tests of the absorber-type fume trap have been successful. Sodium trapping efficiency was greater than 95 per cent in five experiments.

Preparations have continued for high activity-level demonstrations of the melt-refining process for EBR-II core fuel. The melt-refining furnace, designed to handle a 400-gram charge of uranium-fissium alloy irradiated to two per cent total atom burnup, has been reconditioned in preparation for the active experiments. A "dummy" experiment, closely duplicating the procedure to be followed in the active runs, has been completed. Oxidation of the "skull" remaining in the crucible provides an oxide powder which is ground in an electric mortar to provide analytical samples. The apparatus and techniques for investigating the evolution of krypton and xenon from irradiated fuel pins on heating are being tested with unirradiated material.

Work was continued on establishing optimum conditions for the melt refining of sodium-coated fuel pins.

Further tests were made on various insulating materials which could be employed in the melt-refining furnace. Silicon carbide powder, graphite powder and carbon black all proved to be highly effective insulating materials. Alternate induction coil designs of various geometries were evaluated for use in the melt-refining furnace; the present coil design, however, is considered to be satisfactory.

Rhenium-tungsten thermocouples insulated and protected by alumina appear promising for use at high temperatures.

An attractive and efficient procedure for removing uranium skull material from a melt-refining crucible is to convert it to free-flowing oxide powder by oxidation with a dilute oxygen-argon mixture at 700 to 800 C. The behavior of several volatile fission product elements (ruthenium, molybdenum, and technetium) during the skull oxidation has been studied. In gram-scale experiments, fairly complete volatilization of these elements occurs or can be easily made to occur. With larger quantities of material, the rate of volatilization is reduced considerably, the difference apparently being in the ability to achieve good gas-solid contact.

Two complete runs were made for both demonstrating and pinpointing difficulties in the drag-out or skull-reclamation process. While both process conditions and equipment are in a preliminary state, all of the process steps were performed. Recovery of uranium in the skull-oxidation step exceeded 99 per cent. The introduction of zirconia from the crucibles was less than experienced in previous work, being less than 2 per cent in each case.

Investigation of the reduction of uranium oxides by liquid magnesium alloys was continued. Emphasis was placed on the use of pure liquid magnesium as the reductant. After fairly extensive calibration

work, reduction yields were measured by the uptake of hydrogen to form UH_3 . Essentially quantitative (99 ± 1 per cent) reduction yields were realized with uranium dioxide. Reduction yields generally decreased with increasing particle size. Higher oxides, such as U_3O_8 , appear less susceptible to reduction than uranium dioxide, a behavior attributed to greater caking tendency. Agitation, wetting of the container, and other factors were also briefly studied. Little reduction (15 per cent) of zirconia crucible fragments to zirconium metal by magnesium at 760 C was realized in a single experiment.

Because of the high activity of uranium in cadmium solutions, uranium is susceptible to precipitation from such solutions by impurities. Aluminum (which was found to be introduced from alumina crucibles in the presence of a fused salt flux), graphite, and boron nitride were found to precipitate uranium from cadmium solution.

Two runs were made to demonstrate recovery of plutonium from a magnesium solution by distillation of the magnesium. This is the final step of a tentative blanket process. Essentially complete recovery of the plutonium was realized in each run. A bright, shiny plutonium ingot (about 100 grams) recovered from the second run was subsequently satisfactorily poured into a mold. The runs were made without abnormal incidents and without encountering contamination problems.

Distillation of cadmium in a fairly large experimental distillation unit has pinpointed design and operating conditions which must be met to avoid metal entrainment. This information has largely confirmed the design of the large-scale metal distillation equipment now under construction. Operation of this latter unit should begin this fall.

Retorting studies have shown the importance of two factors for production of compact, easily removable uranium product cakes. First, uranium entrainment is reduced by having the uranium precipitated during retorting. Second, ready removal of the product is possible if the retorting is performed in ceramic or ceramic-coated crucibles. These procedures have given good quality, well-coalesced sinter cakes.

Equipment tested during the last quarter included externally heated liquid metal transfer lines and liquid agitator designs.

Operation of a mild steel corrosion loop for circulating a uranium-magnesium-cadmium alloy at 550 C was terminated after 4800 hours of trouble-free operation. Preliminary examination has not revealed any gross corrosion. The uranium concentration remained constant at 0.85 per cent over the last five months of operation after an initial decrease from 0.94 per cent.

Among the fundamental physicochemical data lacking for many of the liquid metal systems of interest to pyrometallurgical processes are the solubilities of some elements in liquid metal systems. The solubility of titanium in liquid cadmium was found to vary between 0.047 atom per cent at 449 C to 0.15 atom per cent at 651 C. Two different titanium-cadmium intermetallic compounds have been found in this system. Evidence for a peritectic reaction at about 500 C was found.

The solubility of uranium in liquid lead over the temperature range from 415 to 802 C is given by the equation

$$\log (\text{atom per cent uranium}) = 3.921 - 5.121 \times 10^3 T^{-1} .$$

The solubility of uranium in liquid cadmium has been redetermined below the peritectic temperature (471.5 C), using a significantly improved technique, with the result

$$\begin{aligned} \log (\text{atom per cent uranium}) = & 8.115 - 7.104 \times 10^3 T^{-1} \\ & + 0.832 \times 10^6 T^{-2} . \end{aligned}$$

Above the peritectic temperature the solubility is given by the equation

$$\log (\text{atom per cent uranium}) = 1.448 - 2.618 \times 10^3 T^{-1} + 1.189 \times 10^6 T^{-2} .$$

The solubility of uranium in cadmium-magnesium solutions containing up to 72 weight per cent magnesium at 610 C has been found to decrease smoothly from about 2 weight per cent in pure cadmium to about 0.002 per cent in 72 weight per cent magnesium. Since the solid phase in equilibrium with these solutions is α -uranium over the entire concentration range, no maximum or minimum in the solubility is expected theoretically or found experimentally.

The solubilities of praseodymium and neodymium in liquid cadmium are given by the equations

$$\log (\text{atom per cent praseodymium}) = 6.949 - 5400 T^{-1}$$

and

$$\log (\text{atom per cent neodymium}) = 6.909 - 5211 T^{-1} .$$

The partition coefficients of a number of representative fissile and fission product elements between the immiscible liquids aluminum and cadmium at 680 to 688 C have been measured. Values of the coefficient (wt per cent in aluminum phase/wt per cent in cadmium phase) are

uranium: 1.45×10^5 ; palladium: 5.82×10^3 ; cerium: 1.74×10^2 ; praseodymium: 1.62×10^2 ; lanthanum: 4.61×10^1 and zirconium: 8.18×10^1 . No significant temperature dependence of the partition coefficient was found for uranium over the range from 686 to 710 C.

The activity coefficient of uranium in saturated solution in liquid lead determined by an emf method varies between 7.2 at 500 C and 5.9 at 700 C.

Effusion vapor pressure studies on the uranium-zinc system at about 440 C have shown the existence of two uranium-zinc intermetallic compounds, one at about $\text{UZn}_{11.5}$ and the other at U_2Zn_{17} .

Thermodynamic data of interest to high-temperature chemistry are being acquired by calorimetric methods.

The heat of combustion of tungsten disulfide in oxygen has been determined to be $\Delta E_c^\circ/M = -1939.29 \pm 0.55 \text{ cal/g}$ for the reaction

The heat of formation of zirconium tetrafluoride has been determined by combustions of zirconium in fluorine. The data lead to a preliminary value of $\Delta H_f^\circ_{298.15} = -454.5 \text{ kcal/mole}$.

Two series of calorimetric combustions of boron in fluorine have been carried out. The current "best value" for the heat of formation of boron trifluoride was suspected to be in considerable error. This is not substantiated by the preliminary data which are presented in this report.

Preliminary developmental work is being carried out for combustions of cadmium and magnesium in fluorine. Progress has been made in finding a suitable support for the sample and determining unburned metal.

A. Fuel-processing Facilities for EBR-II (J. H. Schraidt, M. Levenson)

1. Design, Development and Construction of Buildings and Equipment

The Fuel Cycle Facility and the Laboratory and Service Building are described in previous quarterly reports (ANL-5789 and ANL-5820). The former building will be used for the processing of EBR-II fuel and the latter will provide radiochemical analytical and related facilities for the Idaho Division of Argonne National Laboratory. The architect-engineer is the H. K. Ferguson Company, Cleveland, Ohio.

a. Status of Laboratory and Service Building Construction and Equipment

(G. J. Bernstein, A. A. Chilenskas, M. A. Slawewski, T. W. Eckels, E. J. Petkus)

The Laboratory and Service Building was complete as of June 7, 1960 except for finishing work such as installation of laboratory furniture, painting and mechanically adjusting equipment.

The Model 8 manipulators have been delivered to the EBR-II site and are being installed in the Junior Caves. Installation of the Junior Cave windows commenced May 31 and was completed during the month of June. The location of the grout areas respective to the operators and the regions of highest radioactivity made it imperative that the density of the grout equal a minimum of 220 lb per cubic foot. Grout, periodically sampled, checked out at 220 to 238 lb per cubic foot. Illumination within any Junior Cave cell was measured to be 125 ft-candles normal to the floor and about 80 ft-candles normal to the rear wall. Additional equipment installation in the Junior Caves and the installation of Solidification Cell equipment has been started by the Package 4 contractor.

The waste evaporator was operationally tested during the second week of May in the presence of a Laboratory representative. The evaporator apparently operated as desired; decontamination data are not yet available.

The installation packet for the Radiation Monitoring System has been completed and sent to the field. The acid-fuming scrubber has been tested by the Industrial Hygiene Division. Using a mild caustic scrub solution, the scrubber alone showed about 50 per cent efficiency in scrubbing various acid fumes. The overall acid removal efficiency through the spray scrubber and AEC filter ranged from 95.3 per cent to 99.9 per cent. The unit is being held for further testing with AEC filters suitable for 100 per cent humidity gas streams.

b. Status of Fuel Cycle Facility Building Design and Construction

(E. J. Petkus, H. L. Stethers)

Full-scale construction work resumed on March 25, 1960, after a winter work stoppage. The Facility was about 20 per cent complete as of June 7, 1960. During this quarter the contractor poured concrete for all of the walls below the first floor level. During the latter part of May and the first part of June the heavy aggregate concrete (220 pounds per cubic foot) was poured to form the Argon Cell floor. Concrete for part of the operating area first floor slab has also been poured. The contractor is now doing electrical, piping, and steel work in the basement slab and

the remaining portions of the first floor slab prior to pouring of concrete. The initial submittal of shop prints is essentially complete. Approximately 1100 prints have been received to date. Of these, 78 per cent required modification or correction.

c. Cranes and Manipulators
(J. Graae, G. J. Bernstein)

The five-ton cranes were re-inspected, tested and accepted in Paceco's shop on March 28. Bus bar material has been changed to steel, and alignments of brushes, slip rings and bus bars have been improved. The cranes are being stored by Paceco until requested by the field.

The trolley lifting beam has been received at Argonne. The beam will be modified to handle manipulator carriages as well as crane trolleys, thus saving storage space for tools in the Argon Cell. It will also be used for transporting crane-trolleys through the air lock and transfer cell into the Air Cell. Lifting tools for crane and manipulator bridge drives have been ordered.

A standard General Mills Model 300-E manipulator arm (articulated arm only, exclusive of carriage, bridge and controls) for testing with the prototype operating manipulator in the mockup has been ordered. Necessary additional controls and adapter for automatic plug-in on the prototype manipulator have been ordered.

The contract for the eight operating manipulators has been signed with General Mills, Inc. Bids for twelve Model 8 manipulators for use in the Air Cell are being examined. The bidders have been asked to submit information on radiation-resistant booting which could be readily replaced without the use of elaborate booting seals.

Fabrication of control cabinets and switchboard for manipulators, cranes and blister is nearing completion. Procedures and equipment for testing are being prepared. The manufacturer of the toggle-switch control boxes has not produced acceptable switches in spite of numerous extensions of delivery time. Steps are now being taken to select another supplier.

d. Process Cell Windows
(T. W. Eckels)

Casting of glass for the Fuel Cycle Facility windows has been completed. All of the steel window liners, five of the 31 tank units, and about 40 per cent of the B slabs are now in Idaho. In addition, all of the lead dust seals for the A slab frames, and the special tools and fixtures have been delivered. The problem of the porous welds in the steel tank

units has been resolved. The technique of assembly of the glass into the units has been greatly improved and production of completed units will be at the rate of three to five per week until completion.

Light transmittance of one complete window has been measured.* It was 14.9 per cent. Previous measurements of various components seem to assure that 13 to 13.5 per cent will probably be the minimum achieved. Specifications call for a minimum of 9 per cent.

e. Miscellaneous Fuel Cycle Facility Equipment
(L. F. Coleman, R. H. Jahnke, M. A. Slawecki,
C. M. Putness, J. Graae)

Design specifications for the interbuilding fuel transfer coffin have been completed and are being reviewed. The prototype small air lock for the Argon and Air Cell is being built. The carts and track for use in the lock have been ordered. The complete unit will be set up and tested in the mockup area soon. The purchase specifications for the large and small air-lock closures have been written, and the accompanying drawings are almost ready for release to the vendor.

The packet for the installation of the induction heating units is essentially complete. The revised furnace vacuum panel has been built and installed in the mockup for testing. Drawings and specifications for the furnace control panelboard are essentially complete.

f. Material Testing
(G. J. Bernstein, A. A. Chilenskas, M. A. Slawecki)

The small Howard (1/10-hp) motors used in the General Mills mechanical arm have been redesigned by the manufacturer to provide for a larger brush. Tests made on the original design led to a predicted brush life of about 250 hours (see ANL-6101, page 23). Similar tests will be made on the new motors in dry, high-purity argon.

MI cable samples sealed with Temporell No. 741 potting compound and with Sterling Varnish P-74 have been irradiated to 3.0×10^9 rad. The samples have shown very little visible change since the start of irradiation. Insulation resistance of the samples (greater than 200 megohms up to 2.2×10^9 rad) has dropped to a range varying between 25 and 150 megohms.

*Specifications require transmittance to be measured using C.I.E. Illuminant A (2848 K) as the light source. (See ANL-6159 for procedure.)

The asbestos-covered alloy wire has been irradiated to 10^{10} rad. There has been little visible change in the insulation, but the insulation resistance of the samples has become progressively poorer, the latest readings varying between 15 and 35 megohms (initial resistance greater than 200 megohms). These samples will be irradiated further.

Wire samples with types AI, AIA, and AA insulation (1960 Electrical Code) have been irradiated to 2.3×10^9 rad. The types AI and AIA insulation became very stiff and brittle, requiring only a slight bend to rupture the insulation. Final insulation resistance varied between 1 and 50 megohms (initial resistance greater than 200 megohms). The type AA (asbestos) insulation is in good shape with only slight powdering. Insulation resistance is greater than 200 megohms.

Seven types of aluminum paints have been or are being irradiated. Of these, only one has not held up well. The other aluminum paints,* including those produced by the Tropical Paint Company, have held up well. Elastikote Heat Resisting Interior Aluminum paint has been irradiated to 1×10^{10} rad. It is discolored but is still covering. The other Tropical paints have received a dose of 3×10^9 rad and are in good condition.

Samples of Amercoat No. 33 and two other Amercoat products, Dimetecote and Zincote, have been irradiated. All the samples started to darken at 10^8 rad. After a dose of 5×10^8 rad, the samples were all badly discolored and sticky. They were removed after a dose of about 2×10^9 rad, at which time the coatings had blistered and were peeling off.

Samples of the 54-conductor manipulator power cable have been irradiated to 1.7×10^9 rad. Insulation resistance of the samples is greater than 200 megohms. Testing of the cables by twisting was terminated at 5×10^8 rad, since at this time the sheaths of the samples were too hard for the twisting machine to grip. The insulation has also become hard and brittle. Further tests are being performed to determine more accurately the useful life at which the sheath gets too stiff to function properly.

g. Transfer Cell Equipment
(G. J. Bernstein, J. Graae)

All mechanical and control equipment drawings have been approved and the vendor has started fabrication. The choice of an acceptable

-
- *1. Elastikote exterior heat-resisting aluminum
 - 2. Tropelite aluminum
 - 3. Dri-spray aluminum
 - 4. Thermalite exterior aluminum
 - 5. Argonne high-temperature aluminum (James Day Company, Chicago)

method for maintenance of pressure on the ram which holds the bottom plate of the transfer lock remains to be made.

2. EBR-II Fuel-processing Mockup

a. Manipulator and Manipulator Removal Blister (D. C. Hampson, J. Graae)

Several parts, redesigned on the basis of operating experience in the mockup, have been ordered for testing with the prototype manipulator. Design of power and control cable plug-in on bridges is being completed. Remote operability of the design, which includes features for changing cable remotely, has been demonstrated with a rough, full-scale mockup.

A forearm which can be remotely separated from the manipulator has been designed, fabricated and tested in the mockup. This type of forearm would be required should the grip jam or the grip motor fail while the manipulator was lifting an object with the double hook. Feasibility of the design has been proven.

A new, noncoated Timken tapered roller bearing lubricated with radiation resistant grease NRRG235, a product of the California Research Corporation, has been running for 60 hours at 40 rpm and 800 pounds axial load without heating or other incidents. The bearing, rated at 2500 pounds, is running with the axis of rotation vertical and is open without dust or grease shields. The run will be continued.

The two hoist drums on the manipulator carriage have been remachined so that both have diameters identical to within 0.001 inch. This has greatly improved the load distribution on the hoist cables and made the operation of the hoist much smoother.

b. Melt-refining Furnaces (D. C. Hampson, W. E. Miller)

(1) Equipment Performance

As reported last quarter, crucible cracks resulted in uranium spills during enriched Runs No. 55 and 57. As a result, production of enriched ingots for manufacture of EBR-II fuel was suspended until remedial measures could be found. About thirty crucibles have been tested in experiments.

Eleven crucibles of the same wall thickness (standard $\frac{5}{8}$ -inch thick wall) and material (Norton stabilized zirconia mix Z-300), but of varying density, were tested empty by means of the same equipment and

heating rates as used in the fuel production runs. All the crucibles cracked in a very similar manner. At least two cracks, approximately 180 degrees apart, ran vertically down the side from the top of the crucible to about one inch below the level of the top of the furnace. Observation of the crucible during the heat cycle showed that these cracks developed during the "heat-up" period. An inspection of the used crucibles from the fuel alloy preparation runs revealed that nearly all were cracked in a similar manner.

One explanation for the vertical cracks in these crucibles (Z-300 mix) is that the cracks form to relieve stresses which are set up in the wall as a result of temperature gradients. This has been checked by insulating the unheated portion of the crucible which projects about $1\frac{1}{2}$ inches above the furnace top to facilitate pouring and crucible transfer into and out of the susceptor. In no case have the vertical cracks appeared when this precaution has been taken.

Two crucibles made by Norton from Mix Z-308 were tested under identical conditions as the crucibles made from Mix Z-300. Both crucibles shattered.

Four crucibles were tested to determine the wall density variation within a given crucible. The maximum variation found was 30 per cent. The Norton Company in Worcester, Mass., was consulted concerning this and other problems associated with crucible cracking. A current crucible-manufacturing procedure inadvertently produced particle size segregation in the hopper feeding zirconia powder to the crucible mold. Since the bottom of the crucible is pressed last, it is made from larger size grains, resulting in a coarse crucible bottom. When crucibles of this type were heated, a complete circumferential crack formed at the intersection of the crucible barrel and bottom. Norton felt that the manufacturing procedure could be altered successfully by using a continuous feed system rather than the batch system which had been employed. The crucibles received in the latest shipment appear to have a uniform wall and bottom structure.

In addition to the empty crucible tests, natural uranium or natural uranium plus cerium melts were made to determine if the presence of the melt contributed in any way to crucible cracking. The results of these and the empty crucible tests are summarized below:

1. Norton stabilized zirconia Mix Z-300 proved far superior to Mix Z-308.
2. No correlation was found between wall density and cracking.
3. A coarse, grainy structure of the crucible bottom and lower side wall (caused by particle size segregation during manufacture) produced a complete circumferential crack where the side joins the bottom.

4. No vertical cracks at the top rim occurred when that part of the crucible which projects above the furnace top was thermally insulated during the heat cycle.
5. Some crucibles, as received, have fine vertical cracks at the top rim. On heat-up with no thermal insulation at the top rim of the crucible, the cracks propagated extensively, producing a crucible which was more severely cracked than one which had initially a sound structure. If the heating was done with the top rim of the crucible insulated, there was little if any propagation of the initial crack.
6. Vertical cracks occurred during heat-up in crucibles heated in the standard furnace assembly used for the enriched fuel alloy preparation.
7. Heating rates, within the range tested, did not contribute to crucible failure. This result was obtained with the top rim of the crucible insulated to minimize temperature gradients. (See Figure 1 for the heating curves.)

This test work, except for a few remaining runs necessary to check the effect of wall thickness, has been terminated. The conclusions reached as a result of the work are:

1. A crucible (made from Norton Z-300 mix) which has a sound-appearing bottom (not grainy) and no initial cracks at the top rim, will crack only slightly from a heat cycle in the uninsulated

top assembly used for fuel alloy-preparation runs. Two vertical cracks of fine to medium width about 180 degrees apart will appear at the top rim, and these will extend downward about 3 inches. A few other discontinuous cracks of hairline to fine width may or may not occur in the lower part of the crucible wall. These cracks will not pass molten metal.

2. If a crucible (made from Norton Z-300 mix) with a sound-appearing bottom is heated with the top rim thermally insulated, either no cracks or a few discontinuous cracks of hairline to fine width will occur in the lower part of the crucible wall.

Insulating the top rim of the crucible was achieved by using an inverted Fiberfrax crucible, of the type being tested for sodium-absorption efficiency, to cover the top of the furnace. The Fiberfrax crucible was attached to the fume trap rack and was thus lifted up out of the way during metal pouring. The inverted crucible thus will serve two ultimate purposes: (1) it effectively traps volatile metals evolving from the melt, and (2) being a good thermal insulator, it reduces temperature gradients in the crucible wall. Since Fiberfrax is rather hygroscopic, proper degassing procedures to avoid melt contamination are being studied at the present time.

(2) Sodium Vapor Fume Trap

Tests of the absorber-type fume trap have been essentially completed. In five runs, recoveries of sodium vapor were equal to or greater than 95 per cent. There is no difference in pickup between the "hard" and "soft" varieties of molded Fiberfrax. The material works equally well if the sodium is flashed at 600 C under vacuum or is allowed to boil at one atm pressure. There seems to be a slight improvement in pickup, 100 per cent as compared to 95 per cent, by using lowered trap-degassing temperatures, 1000 C and 1400 C, respectively. However, degassing temperature may have to be a compromise, since uranium melt contamination is a problem with poorly degassed traps.

In plant operation, metallic vapors will probably be evolved from the crucible at two distinct times during the heating cycle: the sodium coating on the pins will distill at about 600 C, and the volatile fission product metals will distill when the fuel melts. Therefore, a trap that has absorbed sodium vapor must still have some reactive surface available for reaction with metallic vapors that will be present later in the heating cycle. Two runs were therefore made to test the ability of the trap to absorb additional sodium vapor after having been previously exposed to sodium vapor. Forty grams of sodium were distilled into the trap and heating was continued to 1000 C. The furnace was then cooled, opened, and another forty grams of sodium were added to the crucible. The furnace was then heated to 1400 C. The overall recovery (including

both exposures) for one run was 99.8 per cent, and 98.6 per cent for the other. The traps were intact in each case and did not appear different from those given single exposures to sodium vapors.

B. Pyrometallurgical Development

1. Melt Refining

(R. K. Steunenberg, L. Burris, Jr.)

The melt-refining process will be used to recover fuel material from the first core loading of EBR-II. The chopped fuel pins are melted and held in a zirconia crucible for a period of 3 to 4 hours at about 1400 C. This procedure results in the removal of about two-thirds of the fission products through volatilization and selective oxidation. The purified metal is poured into a mold, producing an ingot which serves as the feed material to the fuel refabrication steps. Work on the melt-refining process was continued in the following areas: (1) preparations for demonstration runs using 400-gram charges of highly irradiated fuel, (2) development of equipment and techniques to investigate the evolution of krypton and xenon during the heating of irradiated pins, (3) studies on the oxidation of sodium-coated pins, (4) the testing of various materials and designs for the melt-refining furnace, and (5) selection of thermocouples suitable for use at high temperatures.

a. High-activity-level Melt-refining Experiments (V. G. Trice, W. H. Spicer)

Preparations continue for a series of high-activity-level melt-refining experiments. In these experiments, a fissium-uranium alloy enriched to 10 per cent in uranium-235 and irradiated to between one and two per cent burn-up will be melt refined under conditions closely approximating those planned for the EBR-II plant. In the first three experiments, 400-gram batches of alloy will be melt refined at 1400 C for three hours under an argon atmosphere in pressed lime-stabilized zirconia crucibles. This work will be performed in the Chemical Engineering Division Senior Cave.

Briefly summarized, the operational program requires the melting and casting of irradiated alloy; sampling of charge, product and crucible residue; and storage of volatiles released during melting. With the exception of the storage of volatiles, satisfactory remote procedures for the required operations have been developed, refined, and demonstrated in a pilot experiment with unirradiated fissium alloy. A dummy experiment, closely duplicating with unirradiated fissium the procedures to be followed in the active experiments, has been completed. This run will be followed by an experiment with lightly irradiated fissium.

The problem of obtaining representative samples of crucible residues apparently has been solved. After purified metal has been removed from the crucible by top pouring, a residue or "skull" remains in the crucible, consisting of oxide reaction products and unpoured metal. Skull oxidation has been demonstrated as a relatively simple method for freeing the skull from the crucible. In the oxidation process the skull is converted to a powder which can be easily poured from the crucible. The sampling problem arises from the fact that the composition of the skull oxide produced varies with particle size. By grinding and blending the skull oxide in an electric mortar, a homogeneous powder was produced as indicated by the following analyses of three random samples:

Sample	Weight per cent		
	Ru	Ce	Pd
A	1.25	4.02	0.114
B	1.22	3.91	0.103
C	1.30	4.00	0.112

Two experiments have been completed in which skulls, including the massive button of unpoured metal, were completely powdered by oxidation in air. Conditions for the oxidations were 6.5 hours at 700 C in the first experiment, and 15.7 hours at 600 C in the second run. Excellent results were obtained under both conditions. The skull oxide produced was granular and free-flowing, with no evidence of sintering. Subsequent grinding in a Mixer-Mill (produced by Spex Industries of Scotch Plains, New Jersey) reduced the skull oxide to a chemically homogeneous 300-mesh powder.

Fuel Irradiations

Irradiated fissium alloy for the first high-activity experiment was removed from the CP-5 reactor on June 14, 1960. The estimated burnup of this fuel is 1.1 atom per cent.

Capsules for the irradiation of fissium alloy in the MTR reactor are on hand and the first fuel loading is being prepared.

b. Fission Gas Release Investigation (N. R. Chellew, C. C. Honesty)

Efforts have been directed toward construction of equipment to study the release of xenon and/or krypton during heating and melting of highly irradiated uranium-fissium pins. The need for this investigation has

been discussed previously (see ANL-6145, page 35). A detailed description of the equipment will be reported at the completion of a testing program which is now in progress.

Preliminary tests of the furnace with unirradiated pins machined to a diameter approximately equal to that of an EBR-II fuel pin (0.144 in.) have indicated that: (a) clean five per cent uranium-fissium alloy can be melted under an atmosphere of commercial high-purity argon without extensive reaction product formation at the metal surface; (b) photography may be employed to record accurately the physical changes of the alloy that occur during heating; and (c) average heating rates contemplated for EBR-II plant operation (roughly 10 degrees centigrade per minute to a temperature at which the alloy is fully molten) can be duplicated in the experimental furnace.

Present plans are to perform the first of a series of experiments with irradiated alloy during July, 1960. The total atom burn-up of the initial alloy charge to be employed is expected to be about one per cent.

c. Study of Alternate Materials and Designs for the EBR-II Melt-refining Furnace

(J. Wolkoff, M. R. Cusick,* R. E. Nowak)

Efficiency tests of insulating materials that can be employed in the melt-refining furnace were continued. Such materials, as well as being efficient insulators, must be compatible with graphite, the susceptor material. A desirable result of improved insulation is lower power input and therefore lower induction coil temperatures, the coil in the melt-refining furnace being cooled only by convection and radiation. A prolonged test of Norblack carbon black was made in order to examine its sintering tendency. The test was similar to that for silicon carbide reported in the previous quarterly (ANL-6145, page 40), and it indicated some improvement over silicon carbide.

The total operating time with the crucible temperature above 1300 C was 125 hours. The equivalent of some 31 melt-refining runs was spanned by this time interval, assuming four hours at operating temperature (above 1300 C) for a typical run. Cooling to room temperature occurred eight times during the run.

The insulation was functioning effectively when the run was terminated. The carbon black had become firm and had caked sufficiently to allow withdrawal of the susceptor without major collapse, but

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there was little additional evidence of sintering. Even the worst caked material crumbled readily on handling. A number of fine cracks had formed in the inner surface of the carbon black, but none was capable of significant heat loss. In contrast, silicon carbide in the previously reported run had caked to a chalk-hard mass adjacent to the susceptor.

The data in Figure 2 show a small decrease in the insulation effectiveness with time. The effect is smaller than that observed with silicon carbide. The increase in power input with time is 0.36 kw per 100 hours at operating temperature. The corresponding value with silicon carbide was 0.63 kw per 100 hours. The changes in the uncooled copper induction coil temperature and inner wall of the grain retainer were slight and illustrate the high stability of the insulation. The temperatures are low, indicating the high efficiency of the insulation. The carbon black (Norblack) at a density of 0.6 g/ml is as effective an insulation as silicon carbide grain and, in addition, shows less loss of effectiveness with time.

A second type of carbon black insulation (Stainless Thermax) was tested in Run 28 in combination with a Lava ceramic grain retainer. A slight cracking of the grain retainer occurred. The insulation was somewhat easier to handle than Norblack and was more readily compressible to a higher density. The insulation effectiveness was equal to Norblack for this duty.

Alternate Coil Designs

Another approach to decreased power requirements and resultant low copper coil temperatures is modification of the inductor coil geometry. Three such modifications were tested in the last quarter.

All of the runs previously reported were made with a standard coil based on the design now in use in the melt-refining mockup facility. This is shown in Table 1 as coil A. The characteristics of all the coils are summarized in the table. Coils B, C, and D were assembled with the vertical side of the semicircular section in firm contact with the outer wall of the grain retainer. In contrast, coil A was a loose fit. A large cross-sectional area and a smaller effective coil diameter were investigated in the modified coils. According to theory, such configurations are desirable.

Table 1

COMPARISON OF INDUCTOR COILS IN MELT-REFINING TEST ASSEMBLY

(All coils are of solid copper with 10 in I D The inner diameter of the coil is measured between sides of the semicircular sections of coils B, C, D)

Coil Designation	Copper Section	Sectional Area (sq in)	Number of Turns	Space Factor ^b	Operating Conditions at Steady State ^a		Copper Coil Temp (max) (C)	Outer Wall Grain-retainer Temp (C)
					Run Number	Power (kw)		
A		0.20	5	0.36	21C 23C1	4.5 4.4	353 384	374 414
B		0.36	5	0.66	24C	4.1	391	386
C	Same	0.36	6	0.66	25C	4.2	417	398
D		0.21	7	0.60	26C	4.1	438	436

^aSteady-state conditions: crucible wall nominally 1400 C, under argon at atmospheric pressure. For these runs insulation was standardized at 1000 mesh silicon carbide grain with a rigid Fiberfrax grain retainer.

^bRatio of the space occupied by the conductor of a coil to the volume of solid copper that would occupy the same coil space.

The steady-state power (1400 C crucible temperatures) and the temperatures of the copper and outer wall of the grain retainer are listed in the table for five standardized test runs. The effect of the coil modifications on the power requirement is small. The three coils averaged about 7 per cent less power than standard coil A. There is no observable trend in power input with the number of turns.

The temperatures of the coils, however, were unfavorably higher than the temperature of the standard coil. This probably resulted from the firm contact of these coils with the grain retainer, since the temperature of coil A was lower than the grain-retainer outer wall, while those of coils B, C, and D were higher.

One effect of increasing the number of turns in the inductor coil is to decrease the current flow through the coil. This can be utilized advantageously to decrease the losses in the power line between the capacitors and the furnace coil, a distance of about 28 feet in the existing design for installation in Idaho. Transmission line losses and line heating, however, are not excessive; and the present coil design is, therefore, considered to be reasonably satisfactory.

d. Use of High-temperature Thermocouples
(G. A. Bennett, W. A. Pehl)

As a result of the previous tests of high-temperature thermocouples (ANL-6101, page 32), a rhenium-tungsten thermocouple was installed in the melt-refining furnace. This thermocouple was encased with alumina insulation and had an alumina protection tube. It was cycled through eight heat-up and cool-down periods, and was maintained at temperatures of 1500 C or higher for a total of 25 hours. For one hour of this period it was held at 1590 C. Based on the power input required for a given temperature, there was no change in thermocouple calibration. Failure occurred due to cracking of the alumina protection tube. To prevent further failure of this type, a tantalum-sheathed thermocouple (surrounded by an alumina protection tube) has now been installed.

Experience has shown that a platinum-platinum-10 per cent rhodium thermocouple under similar conditions would survive only two or three 1400 C cycles and would fail rapidly at temperatures of around 1500 C. The experience with rhenium-tungsten thermocouples has, therefore, been encouraging.

2. Liquid Metal Solvents Process Development (L. Burris, Jr., R. K. Steunenberg)

At the completion of the melt-refining operation, approximately ten per cent of the charge remains behind in the zirconia crucible in the form of a "skull" made up of metal and oxides. An auxiliary process is required to recover partially decontaminated uranium from the skull and return it to the melt-refining process. While highly efficient fission product removal is not necessary, a substantial amount of each fission product element must be removed in order to maintain the proper fission composition in the recycled fuel.

Mechanical methods do not appear practical for removing the skull from the melt-refining crucible. Oxidation of the skull by an argon-oxygen mixture at 700 C, however, converts it to a free-flowing oxide powder which is easily poured from the crucible.

The powder resulting from the oxidation step is reduced, either by liquid magnesium or by a solution of magnesium in liquid zinc or cadmium. In pure magnesium or in high-magnesium solutions, uranium is precipitated as the metal during reduction. Subsequent steps in the process involve uranium-fission product separations based on their different solubilities in liquid metal media, followed by a retorting operation to remove residual magnesium, zinc or cadmium from the uranium product.

a. Processing of Melt-refining Skulls

(1) Preliminary Treatment of Crucible Skulls (T. R. Johnson, R. L. Christensen)

The purpose of this program is the investigation of various means of removing melt-refining skulls from zirconia crucibles. Direct oxidation produces a finely divided material that can be conveniently separated from the crucible. The behavior of volatile fission product oxides during the skull oxidation is also of interest.

During the oxidation of small fission samples (one gram or less) in porcelain combustion boats, large fractions of the molybdenum and ruthenium can be volatilized as the oxides. Temperatures above 800 C, complete oxidation of the uranium, and flowing oxygen are necessary for the removal of ruthenium. Fairly complete oxidation of the entire sample and evacuation to one mm at a temperature greater than 900 C after oxidation are required for substantial molybdenum volatilization, as shown in Figure 3. The per cent oxidized to U_3O_8 was calculated from the weight gain of the sample corrected for volatilized oxides divided by the estimated weight gain for complete oxidation of the fission alloy to U_3O_8 .

FIGURE 3
MOLYBDENUM REMOVAL RESULTING FROM OXIDATION OF FISSION

A study of the behavior of technetium during oxidation of fission alloys has begun. One hundred milligrams of technetium metal was prepared from an aqueous solution of ammonium pertechnetate. The solution was made basic with ammonium hydroxide and was carefully dried in a flowing hydrogen atmosphere at 80 C in a molybdenum boat. The salt was decomposed and reduced at 230 C to the dioxide. Reduction to the metal with hydrogen was completed at 600 C. The technetium metal, molybdenum boat, and fifty grams of a fission alloy were melted together in a beryllia crucible at 1300 C for one hour. The nominal technetium concentration was 0.2 weight per cent. Molybdenum content resulting from the boat was 3 per cent.

Preliminary results indicate that technetium is volatilized more easily than is ruthenium. Technetium is volatilized at temperatures in excess of 700 C, which is 100 C lower than that required for ruthenium volatilization. Dark red and black deposits of technetium oxides form gradually on the cold portions of the quartz furnace tube during the oxidation. The deposits are easily soluble in water and dilute acids, which distinguishes them from ruthenium and molybdenum oxides. Technetium volatilization is less, but still significant, during oxidations under static atmospheres than during oxidations with flowing atmospheres.

An attempt was made to demonstrate molybdenum and ruthenium removals from a complete crucible and skull. A skull was prepared by holding 300 grams of 0.6 weight per cent cerium-fission alloy in a zirconia crucible (2 in. OD by $3\frac{3}{4}$ in. high) for two hours at 1350 C. The total skull weight was 22.8 grams. The skull was first oxidized at 800 C in flowing oxygen for $3\frac{1}{2}$ hours. The gas composition, initially ten volume per cent oxygen in argon, was slowly increased to 100 per cent oxygen. The gas was directed into the crucible by a tube extending within $\frac{1}{2}$ in. of the bottom. The oxide was reduced with hydrogen at 700 C for two hours, then reoxidized at 850 C in undiluted oxygen for $1\frac{1}{2}$ hours.

The temperature was raised to 930 C after oxidation and the furnace was evacuated to less than one mm. The reduction-oxidation cycle was then repeated. About 70 per cent of the ruthenium and 80 per cent of the molybdenum remained in the oxide product. From the results of the small-scale experiments, greater than 90 per cent removal of molybdenum and ruthenium from the oxide would have been predicted. It is apparent that it would be difficult to design full-scale skull oxidation equipment based on the results from small samples oxidized in combustion boats. It is felt that the difficulty lies in the gas-solid contact, which is good during oxidation of one-gram samples, but very poor during the skull oxidations. Pilot experiments will continue with complete melt-refining skulls in 2-in. OD zirconia crucibles in order to investigate possible off-gas problems that may be encountered during skull oxidations in the EBR-II Fuel Cycle Facility.

(2) Drag-out Process Demonstration Runs
(R. D. Pierce, T. R. Johnson, L. F. Dorsey)

Two process demonstration runs were made, starting with crucible skulls from melt refining (prepared by liquating uranium alloys in zirconia crucibles at 1400 C for 3 hours) and attempting all of the steps in one of the proposed drag-out processes (see Figure 4) to final recovery of a uranium ingot.

FIGURE 4

LIQUID METAL PROCESS FOR RECLAMATION OF MELT-REFINING SKULLS

These runs were undertaken to pinpoint operational difficulties which may not have been anticipated; these runs were not expected to achieve optimum recovery. The process steps studied were:

1. skull oxidation and recovery from a melt-refining crucible;
2. reduction of the oxidized skull with liquid magnesium and transfer of the magnesium phase away from a bed of settled uranium;
3. washing of the uranium with fresh magnesium and transfer of the wash solution;
4. solution of the uranium and magnesium residue in zinc, and transfer of the uranium-zinc solution from any insolubles;
5. crystallization of uranium from zinc solutions as U_2Zn_{17} and transfer of the zinc from the crystals;
6. recovery of metallic uranium by retorting off zinc and magnesium; and
7. melting of the metallic uranium to consolidate an ingot.

The first crucible skull was obtained from melt refining a uranium-cerium alloy and the second skull from refining a fissium alloy of the following approximate composition in weight per cent: cerium 0.8, molybdenum 2.5, ruthenium 2.0, rhodium 0.3, palladium 0.2, zirconium 0.1, niobium 0.01, balance uranium.

For these runs the reaction pour furnace which has been used for reduction studies was modified to allow pressure siphoning of liquid from the reaction crucible (see Figure 5).

FIGURE 5
TILT-POUR FURNACE WITH PRESSURE-SIPHON ATTACHMENT

Pressure siphoning, which will be used extensively in drag-out processing, will remove the bulk of a liquid from a vessel with a minimum disturbance of any settled phase. The employment of this transfer technique on the reaction furnace permits demonstration of successive process steps with the single unit.

Two runs have now been performed. Complete information is available only for the skull-oxidation step. Therefore, only this step will be reported in detail in this report. Results for the succeeding steps will be reported later.

Skull Oxidation

The melt-refining crucibles for both demonstration runs were in fair condition prior to the oxidation step. The first had three vertical hairline cracks at the top and a crack around the circumference at the bottom. The second had only one hairline crack, about four inches long, at the junction of the crucible bottom and wall. The crucibles were supported tightly in a stainless steel secondary during the oxidation and recovery of the product.

The oxidations were performed in a 40-liter furnace. The furnace was heated to temperature, pressurized to 600 mm Hg absolute pressure with argon, and then to 800 mm Hg total pressure with oxygen to initiate the reaction. The furnace pressure was maintained at 800 mm with oxygen throughout the reaction by a regulating valve.

The skull oxide was removed from the furnace after the runs and dumped into a tray by inverting and tapping the crucible once lightly. Essentially complete removal of the uranium was realized (99.4 and 99.6 per cent).

The conditions of the burning and some characteristics of the product are presented in Table 2. Photographs of the crucibles before and after the oxidation are presented in Figures 6A and 6B.

A sample was taken of the coarsest material (>14 mesh) from the first run. X-ray diffraction indicated that the major phases were uranium dioxide and a nonstoichiometric U_3O_8 . Upon oxidation at 750 C, a sample gained $2\frac{1}{2}$ per cent in weight, indicating an approximate composition of $UO_{2.33}$. The individual particles behaved differently - some were pulverized but others remained unaffected. This same sample lost 5 per cent in weight when reduced at 700 C. Two samples of the coarse ($+14$ mesh) fraction of oxidized skull were given additional treatment to study the particle size degradation. About 50 per cent of one passed a 20-mesh screen after an oxidation-reduction-oxidation cycle. Only 15 per cent of the second sample passed through 20 mesh after a reduction-oxidation treatment.

FIGURE 6

PHOTOGRAPHS OF MELT-REFINING CRUCIBLES
AND URANIUM SKULL MATERIAL
BEFORE AND AFTER OXIDATION

A. First Demonstration Run (Cerium-Fissium Alloy Used)

Skull Before Oxidation

Oxidized Skull

Vertical Crack
in Crucible Prior to Oxidation

Horizontal Crack in
Crucible Prior to Oxidation

Crucible After Oxidized
Skull had been Dumped

Crucible Pieces After
Steel Secondary had been
Removed

FIGURE 6 (Cont'd.)

(See conditions in Table 2)

B. Second Demonstration Run (Cerium-Uranium Alloy Used)

Skull

Crucible

BEFORE OXIDATION

Skull

Crucible

AFTER OXIDATION

Table 2

CONDITIONS AND RESULTS OF FULL-SCALE SKULL OXIDATIONS

(see page 42 for the history of the skull)

	U-Ce Skull	Fissium Skull
Nominal Burning Temperature (C)	850	775
Hot Spot Temperatures (C)	875 to 950	875
Oxidation Time		
Reaction Appeared Complete (hours)	6	6
Total Exposure (hours)	8	10
Total Product (grams)	942	716
Crucible Fragment Inclusions (per cent)	<2	~5
Uranium Recovery (per cent)	99.4	99.6
Uranium Loss (grams)	4	2.1
Screen Analysis (per cent)		
+ 14 mesh	8.3	2.0
-14 + 25	18.6	14.7
-25 + 45	16.5	22.7
-45 + 80	15.5	19.7
-80 + 170	13.4	15.3
-170 + 325	11.2	12.7
- 325	16.5	12.9

(3) Pyrometallurgical Reduction Studies(A. Schneider, J. D. Schilb, J. W. Walsh,
C. R. Williams)

The objective of this program is to develop a practical method for the extensive reduction of uranium oxide to metal in a liquid metal system.

During this report period, the reduction of uranium oxide by liquid magnesium was studied in considerable detail. In addition, the reductions of zinc oxide and zirconium oxide by magnesium were also investigated to clarify certain aspects of the uranium oxide reduction and to estimate the extent of contamination of the uranium product with zirconium resulting from fragments of the crucible used during melt refining.

The Determination of Reduction Yields

The solubility of uranium is very low in liquid magnesium. It is thus not possible to follow the progress of the oxide reduction by determining the uranium content of periodically withdrawn filtered samples of the liquid metal. Various methods were considered for the

determination of reduction yields (e.g., dissolution of the ingot in cadmium or zinc, determination of the magnesium oxide formed by scavenging with a fused salt flux, metallographic examination). A procedure was finally evolved which is based on measurement of the amount of hydrogen consumed in the formation of uranium hydride (UH_3) by direct combination of the elements at 230 to 240 C.

The equipment used for this determination is shown schematically in Figure 7.

The ingot resulting from the reduction step and consisting of magnesium, uranium, uranium dioxide and magnesium oxide is transferred to the retorting still shown in Figure 7. After complete removal of the magnesium by distillation at 685 to 715 C and a still pressure of 4 to 5.5 mm Hg, a measured amount of hydrogen is introduced into the still. It was shown that of all materials likely to be present in the retorting residue, only uranium will react with hydrogen under the given conditions, forming a compound of well-defined composition (UH_3). At higher temperatures, this compound decomposes completely and the amount of hydrogen liberated is also a measure of the quantity of uranium present.

The results of several hydriding and retorting-hydriding runs under various conditions are presented in Table 3. The average of 22 determinations was 99.14 per cent of the known amount of uranium present, with limits of ± 1.21 per cent at the 95 per cent confidence level. This method was adopted for the determination of yields in all subsequent reduction runs.

Table 3

DETERMINATION OF REDUCTION YIELDS BY THE URANIUM HYDRIDING METHOD

(See page 47 and Figure 7 for description of equipment and operation)

Exp. No.	Charge Weight (g)		Operation	Hydrogen Reacted (Per Cent of Theory)	Hydrogen Released (Per Cent of Theory)
	U	Mg			
D-3-3-0	36.95	37.60	Retorting and Hydriding	105.0	Not measured
D-3-7-0	38.34	-	Hydriding	103.1	Not measured
D-3-10-0	79.80	201.33	Hydriding in Presence of Mg	102.3	99.6
F-3-14-0	29.39	19.96	Retorting and Hydriding ^b	101.3 96.6	98.3 97.5
D-3-21-0	36.85	-	Hydriding	98.3	96.2
J-4-11-0	36.75	5.35 (MgO)	Hydriding in Presence of MgO	98.0	99.9
W-5-6-0	26.60	-	Hydriding ^b	99.5 96.8	99.2 96.8
F-6-6-0	17.50	78.00	Hydriding in Presence of Mg ^a	93.4	100.0
			Retorting and Hydriding ^{a,b}	104.4 99.1	98.7 97.1

^a Graphite crucible used in place of alumina.

^b Duplicate hydriding-dehydriding runs were made on same material.

The Reduction of Uranium Oxides

It was reported previously (ANL-6101, pages 43 to 44, and ANL-6145, pages 51 to 52) that the reduction of U_3O_8 was demonstrated in liquid magnesium at temperatures above 850 C, both in the presence and absence of magnesium chloride. In those experiments the uranium oxide was dispersed in the liquid metal by a slowly rotating, close-fitting paddle stirrer. The scale-up problem associated with this stirring method and the materials of construction problems associated with the high operating temperature prompted additional exploratory experiments at lower temperatures and with more conventional stirring arrangements consisting of a paddle stirrer and four vertical baffles. The results of these experiments as well as those performed subsequently to determine the effect of various factors are shown in Table 4.

Table 4

THE REDUCTION OF URANIUM OXIDE BY LIQUID MAGNESIUM

Tantalum baffles and stirrers used in all experiments.

Magnesium to uranium weight ratio in all experiments between 2.9 and 3.1.

Total weight of charged materials: 133 to 150 g in magnesia, 200 g in graphite,
and 70 to 84 g in molybdenum crucibles.

Stirring started immediately after melting of the magnesium.

(See page 47 for description of equipment and operation)

Exp. No.	Crucible Material	O/U	Temp (C)	Duration (hr)	Oxide Particle Size (mesh)	Stirrer Speed (rpm)	Reduction Yield (% of Theoretical)
4-14-0	MgO ^a	2.02	810	7.3	See Note b	200	98.6
4-18-0	MgO	2.02	806	7.0	See Note b	200	98.0
4-28-0	MgO	2.67	810	7.0	See Note c	200	91.3
4-25-0	MgO	2.67	794	7.0	See Note d	200	41.2
5-10-0	MgO	2.02	730	3.0	100-200	450	109.0
5-11-0	MgO	2.02	800	3.0	100-200	450	102.7
5-12-0	MgO	2.02	670	3.0	100-200	450	31.0
5-13-0	MgO	2.02	730	3.0	60-100	450	55.0
5-16-0	MgO	2.02	730	1.0	100-200	450	46.4
5-17-0	MgO	2.67	800	3.0	100-200	450	30.0
5-18-0	MgO	2.41	800	3.0	100-200	450	57.7
5-20-0	Molybdenum	2.02	800	4.0	100-200	450	98.8
6-1-0	Molybdenum	2.02	800	4.0	See Note b	400	100.7
6-8-0	Graphite	2.02	800	7.0	See Note b	250	87.6
4-22-0	MgO	2.02	Retorted only ^e		See Note b	-	19.7

^aNorton, high-purity, slip-cast magnesia, Mix No. 208

^b48 per cent - 325 mesh; 18 per cent + 325-200; 13 per cent + 200-100;
11 per cent + 100-60; 10 per cent + 60

^c49 per cent - 325 mesh; 23 per cent + 325-200; 16 per cent + 200-100;
8 per cent + 100-60; 4 per cent + 60

^d40 per cent - 325 mesh; 16 per cent + 325-200; 13 per cent + 200-100;
11 per cent + 100-60; 20 per cent + 60

^eObjective of this experiment was to determine extent of reduction which may occur during retorting step.

Metallographic examination of a reduction ingot showed that the uranium product consisted of agglomerates of very small particles (about 1 to 10 microns in diameter). These particles, separated from the surrounding magnesium and magnesium oxide by leaching with acetic acid, were shown by X-ray diffraction analysis to be pure α -uranium. The quantitative reduction under certain conditions was further confirmed by determinations of the uranium metal and magnesium oxide present in the final ingot (magnesium oxide/uranium found was 0.328, compared with a theoretical ratio of 0.339 calculated for the reaction $\text{UO}_2 + 2\text{Mg} \longrightarrow \text{U} + 2\text{MgO}$).

The results in Table 4 lead to the following conclusions: The quantitative reduction of uranium oxide can be achieved by reaction with liquid magnesium at temperatures above 730 C in periods of 3 to 7 hours, depending on the efficiency of the stirring arrangement. From the results of Experiment 5-16-0 and the absence of any sharp temperature rises in all experiments, it appears that this reaction is well-controlled and thus differs from the "bomb"-type reduction reported previously (ANL-6101, page 44). A temperature threshold appears to exist between 670 and 730 C below which the reaction does not proceed. There does not appear to be any advantage to carrying the reaction out at higher temperatures. The particle size of the uranium oxide appears to be a significant factor (Experiments 5-13-0 and 5-10-0), the reduction rate being slower with coarser material. The reduction rate appears to decrease with an increase of the O/U ratio (Experiments 5-11-0, 5-18-0, and 5-17-0). It was noted that in experiments with higher oxides, the unreacted uranium oxide powder tended to cake along the crucible wall. The considerably greater tendency of $\text{UO}_{2.41}$ and U_3O_8 to cake as compared with uranium dioxide at temperatures between 730 and 800 C was shown in a separate experiment. This would support the hypothesis that the lower reduction yields obtained with the higher uranium oxides are caused by the greater sintering tendency of these materials rather than by their higher oxygen content. Magnesia, molybdenum and graphite appear to be satisfactory container materials.

Both reaction products, uranium and magnesium oxide, separated sharply from the unreacted magnesium and were located in the lower part of the ingot. Thus, it may be difficult to separate the magnesium oxide by decanting the liquid magnesium. However, the quantitative and rapid removal of magnesium oxide from a cadmium-magnesium melt was achieved by contacting with a Dow-230 flux (34 per cent magnesium chloride, 9 per cent barium chloride, 55 per cent potassium chloride, 2 per cent calcium fluoride). In this experiment, the magnesium oxide was formed by reduction of zinc oxide. The progress of reduction was obtained from the zinc content of the metal phase, while the magnesium oxide transferred to the flux was obtained from analyses of unfiltered flux samples.

The encouraging results obtained so far make liquid magnesium reduction of uranium oxide a promising step in the EBR-II drag-out processing scheme. Furthermore, this procedure may become attractive in the decontamination of uranium oxide fuels, as a possible new feed materials process, and for the production of plutonium metal from the oxide.

Reduction of Zirconium Dioxide by Liquid Magnesium

It is likely that the oxidized skull may contain fragments of the lime-stabilized zirconia crucible. An experiment was performed to determine the extent of reduction of such crucible fragments under conditions similar to those used in the reduction of uranium oxide. The zirconia charge consisted of 38 g of a pulverized section (minus 60 mesh) of a crucible used in a previous melt-refining experiment. The section used had been in contact with the molten uranium and exhibited the usual dark color. This material was reacted with 102 g magnesium at 800 C for 7 hours, by means of an alumina crucible and tantalum accessories. The resulting ingot was dissolved in 2200 g of zinc at 760 C and filtered samples were obtained at regular intervals. From zirconium analyses of these samples it appears that about 15 per cent of the zirconium oxide charged had been reduced in the first part of the experiment and that very little, if any, further reduction occurred during the zinc-dissolution step.

(4) Container Materials for the Reduction of Uranium in Cadmium Solutions

(A. Schnieder, J. C. Hesson, K. R. Tobias,
C. R. Williams)

During the reduction of uranium oxides by magnesium in cadmium solutions and in subsequent process steps, it is necessary to use container materials which do not introduce deleterious impurities into the solution. The relatively large activity coefficient of uranium in cadmium solutions cause it to be precipitated by small amounts of a variety of impurities. Several holding runs were performed to determine the suitability of various materials for the reduction of uranium oxide.

Several runs were made with recrystallized alumina crucibles. From the results shown in Table 5 it follows that alumina is satisfactory in the absence of flux, but in the presence of Dow-230 flux aluminum is introduced into the metal phase (the flux used in these experiments was based on the composition of Dow-230, but was synthesized from

reagent-grade materials). In a separate experiment, 0.19 per cent aluminum metal was added to a 6 per cent magnesium-cadmium solution containing 0.36 per cent uranium at 700 C. Dow-230 flux was present. The uranium concentration dropped from 0.36 to 0.06 per cent. Thus it appears that uranium is precipitated as the compound UAl_2 either by the direct addition of aluminum metal or by aluminum oxide in the presence of chloride flux.

The addition of boron nitride (0.26 per cent) resulted in precipitous reduction in the uranium concentration from 0.36 to less than 0.001 per cent in a 6 per cent magnesium-cadmium solution at 700 C in the presence of Dow-230 flux. An alumina crucible was used in the experiment.

A similar experiment in which 0.3 per cent graphite (filter frit material) was added to the solution showed a reduction in uranium concentration from 0.36 per cent to 0.11 and 0.026 per cent after 1.1 and 2.5 hours, respectively. No flux was present.

In another material test, a 70 per cent magnesium-cadmium melt was stirred for 6 hours at 800 to 850 C in a nitride-bonded silicon carbide crucible. The melt was contaminated by 0.5 per cent silicon, which is considered excessive. Neither uranium nor flux was present in this case.

The most satisfactory ceramic from a chemical standpoint for this application appears to be slip-cast magnesium, although alumina may be usable in the absence of flux. However, magnesia crucibles are often wet and penetrated by the magnesium-zinc and magnesium-cadmium solutions. Zinc solutions show a greater tendency to wet magnesium than do cadmium solutions, and with both solutions, the higher the magnesium concentration, the greater the tendency to wet. Pressed magnesia crucibles, which are more porous than slip-cast crucibles, were severely penetrated in most cases.

b. Development of a Process for Recovery of Plutonium from EBR-II Blanket Material
(I. O. Winsch, T. F. Cannon)

The blanket processes currently under investigation for separation of plutonium from uranium by pyrometallurgical methods are based on the solubility of plutonium in liquid magnesium and the contrasting low solubility of uranium in magnesium. A schematic process diagram is given in Figure 8.

FIGURE 8
LIQUID METAL PROCESS FOR RECOVERY
OF PLUTONIUM FROM URANIUM
BLANKET METAL

Work during the past quarter was devoted to demonstration of the final step, the recovery of a plutonium metal product from a magnesium solution by evaporation of the magnesium. A preliminary run involving 1 gram of plutonium and 100 grams of cerium as a plutonium stand-in was reported in the previous quarterly (ANL-6145, page 57). In the run made in the past quarter, 107 grams of plutonium were employed in a magnesium solution. This quantity of plutonium, which would result from processing 10 kg of blanket material in which the plutonium had been allowed to build up to one per cent, is about full-scale for process equipment which will be built for demonstration on EBR-II blanket material.

In this distillation run an alloy composed of 502.94 g of magnesium and 107.26 g of plutonium was charged to the tantalum still pot and loaded into the distillation unit (described previously in ANL-5996, page 73). Tantalum baffles were provided in the vapor space above the still pot to reduce entrainment of the plutonium. The loading, distillation, and unloading operations were again carried out smoothly and without incident.

Results for this run and the previous run are compared in Table 6. A plutonium material balance of 100.4 per cent was obtained. Analytical results indicate a lower entrainment of plutonium in this run. The de-entrainment factor was 1570, as compared to a value of 220 in the first experiment.

Table 6

PLUTONIUM MATERIAL BALANCE IN SEPARATION OF PLUTONIUM
FROM MAGNESIUM SOLUTIONS BY DISTILLATION

Charge: 1. 500.5 g magnesium, 99.2 g cerium,
1.2346 g plutonium
2. 502.94 g magnesium, 107.26 g plutonium

Run No.	Still Pot			Magnesium Distillate			Plutonium Material Balance (%)
	Charge Plutonium (g)	Product Phase Plutonium		Plutonium			
		(g)	(% of charge)	(g)	(% of charge)	(De-entrainment Factor)	
1	1.2346	1.234	99.99+	0.0055	0.45	220	101.4
2	107.26	107.6	100.3	0.0685	0.064	1570	100.4

About 1.1 g of plutonium were present on the baffles, and 106.5 g of plutonium were present in the conical bottom of the tantalum still pot as a bright, well-consolidated button. Figure 9 is a photograph of the tantalum baffle, still pot containing the plutonium bottom, and the magnesium distillate. It was possible to remove the plutonium button from the crucible by tapping the conical bottom. The resulting button, shown in Figure 10, which was about $\frac{3}{8}$ inch thick and tapered from a diameter of about $1\frac{3}{8}$ inches to a diameter of 1 inch, weighed 89.2 g. A spectrographic analysis indicated the magnesium content was 200 ppm. A tantalum value of less than 2000 ppm was reported, which is the limit of detection by this method of analysis.

Another experiment was performed to demonstrate the feasibility of pouring the final plutonium product from the tantalum still pot into a mold. The still pot with the 106.5 g of plutonium was charged to the tilt-pour furnace and heated to a temperature of 800 C under a helium atmosphere. After one hour at this temperature, the molten metal was poured into a boron nitride-coated copper mold.

About 80 per cent of the plutonium present in the crucible poured into the mold, a good recovery for this scale of operation. The resultant plutonium button was excellent in appearance and there was no

indication of plutonium reaction with the boron nitride coating on the copper mold. The heel in the pouring crucible would not be expected to build up, so that on repeated use nearly quantitative yields should be realized.

FIGURE 9
TANTALUM BAFFLE AND STILL POT CONTAINING
PLUTONIUM-MAGNESIUM DISTILLATE

This operation has demonstrated that plutonium can be easily separated from magnesium by distillation and subsequently re-melted to give plutonium of excellent quality at a high yield.

3. Engineering Development for Liquid Metal Solvents
(L. Burris, Jr.)

Development of equipment and engineering techniques is underway for the liquid metal processes under consideration. These engineering studies include work on distillation and retorting, phase separations, materials handling, and investigation of materials.

a. Distillation

Cadmium Distillation Test Unit
(I. O. Winsch, T. F. Cannon, J. Schilb, J. Hepperly)

The distillation test unit described in ANL-6145, page 62, was constructed to test several of the design concepts and operational

FIGURE 10
SIDE VIEW OF PLUTONIUM BUTTON
AFTER REMOVAL FROM TANTALUM
STILL POT

procedures of the large-scale distillation unit. Of particular interest was the feasibility of employing a removable still pot which, during distillation, is mated by means of tapered surfaces with the shell of the distillation unit. A total of six distillation runs employing 40 to 50 kg of cadmium per run have been completed in this unit. Distillation rates were 10 to 11.5 kg/hour.

In the first two runs, the distillation was carried out at a pressure of 180 mm Hg and a temperature of 650 C. Argon was maintained on the underside of the still pot at a pressure of 250 mm Hg to prevent back-diffusion of cadmium vapors if the tapered seal was not tight. The tapered seal on the still pot was engaged at between 400 and 500 C. Very tight seals were effected.

About 4 hours were required to distill the cadmium charge at a rate of about 11.3 kg per hour. The rate is limited only by the power input available. At the maximum power input, 35.2 per cent of the power was utilized in distillation of metal.

The charges in the third to sixth runs were ingots from oxide reduction studies and were composed of cadmium, magnesium, uranium and small quantities of the oxides of these metals. The distillations were carried out at a temperature of 650 C and a pressure of 180 mm Hg. After the major portion of the cadmium was distilled, the pressure was lowered to remove the remaining magnesium.

In the third, fourth, and fifth runs, a deliberate leak was provided across the tapered seal to determine the necessity of a tight seal between the still pot and shell, the extent of diffusion of cadmium vapors against a flowing stream of argon, and the overall effect of the leak on the distillation and condensation of cadmium. An argon flow rate of one cubic foot per hour was maintained through the tapered seal in each experiment. In Run 6, the tapered seal was engaged at 600 C but a leak across the seal was observed.

An examination of the heat shields below the still pot after the third run indicated that only about 60 g of metal had passed through the tapered joint and had collected below the crucible in several large drops. In this run a slight heel of magnesium, uranium, and oxides of the metal remained in the still pot. Analytical results on samples of the distillate ingot indicated a uranium concentration ranging from 64 to 16 ppm from the top to the bottom of the ingot.

In succeeding runs the distillation was carried to completion so that only uranium, magnesium oxide and uranium oxide remained in the still pot. At the completion of Run 4 it was found that about 2.1 kg of metal and metal oxide had escaped through the tapered joint. There was evidence of violent spattering in the still pot as the magnesium and cadmium concentration became low, and molten metal had evidently been physically thrown through the opening. To reduce metal escape by this mechanism, baffles were used in the vapor space above the still pot in the fifth and sixth runs. These were successful in reducing considerably the amount of metal escaping through the open tapered joint.

It is clear that with the present design it is preferable to engage the crucible securely in the mating taper of the shell. When a slight separation of the still pot was made from the shell, some leakage of metal occurred which could be reduced by use of baffles. These also eliminated entrainment of solid material. It is believed that an alternative design could eliminate leakage of metal when tight seals are not effected. Although it is not easily possible to incorporate this design in the present unit, a sketch of a suggested baffle is shown in Figure 11.

Large-scale Distillation Equipment

(P. A. Nelson, R. Jones, J. Hepperly)

FIGURE 11
PROPOSED DESIGN OF BAFFLE AND VAPOR LABYRINTH
FOR CADMIUM DISTILLATION UNIT

The installation of equipment for large-scale distillation of cadmium is proceeding. In addition to obtaining experience on large-scale distillation and retorting, this apparatus will afford operating experience on liquid transfer, liquid level, pressure and temperature measurement and control, and other operations associated with liquid metal processing.

All of the larger equipment items have been delivered. The main items which must yet be installed are the vessels, the piping and instrumentation, and the enclosure around the furnace.

b. Retorting of Uranium Concentrates

(J. T. Lenc, P. A. Nelson, M. Bowden, J. Hepperly)

Successful recovery of uranium from the final retorting operation of the liquid metal processes under consideration requires that the uranium product be in a form suitable for remote removal and handling. The work of the past quarter has shown the importance of two factors for production of compact, easily removable uranium products. First, the uranium must be precipitated during retorting in order to reduce uranium entrainment. By so doing, good quality, well-coalesced sinter cakes have resulted. Second, ceramic or ceramic-coated crucibles must be employed to enable ready removal of these sinter cakes. The general experience to date with metal crucibles is that the sintered products have adhered to the crucible and have been difficult to remove. The two charge preparation procedures were employed to give starting material in which (1) the uranium was initially in solution and (2) was initially present as a separate precipitated phase. The second condition is believed to be most representative of flowsheet conditions.

The objective for precipitating the uranium prior to retorting was twofold: (1) to obtain a more compact uranium product and (2) to reduce the amount of uranium available for entrainment in the metal vapor.

In an effort to precipitate dissolved uranium from cadmium-7 per cent zinc-1 per cent magnesium-3 per cent uranium alloys, various amounts of magnesium were added to the crucible prior to retorting. However, because of volume limitations in the equipment employed, it was not possible to add sufficient magnesium to precipitate the uranium completely. Magnesium additions were made to generally between 5 and 10 per cent, which is sufficient to precipitate only around 60 per cent of the uranium. Therefore, while good quality sinter cakes were produced, considerable entrainment still occurred, giving product yields of 75 to 90 per cent. The entrainment which occurred was manifested in part by formation of a thin foil or plating of uranium on the upper walls of the crucibles. In one run in which no uranium was precipitated prior to retorting, the entire product was deposited as a foil along the sides and bottom of the crucible. In runs in the zinc system, where precipitation has been complete, entrainment has been negligible and yields have been over 95 per cent.

In the above runs, retorting was begun at 650 to 675 C and 75 to 100 millimeters absolute pressure. During retorting the pressure was continually lowered to maintain the still temperature at 650 to 675 C. The still temperature at the completion of retorting was 900 to 940 C at less than 1 millimeter absolute pressure.

Product Removal from Crucibles

All of the above runs were made in alumina- and zirconia-coated graphite crucibles. No difficulty was encountered in removing the uranium product sinter cakes from these crucibles. Nine runs were made in tantalum crucibles, but in only one was the product removable. The products in the other eight runs very strongly adhered to the tantalum and could not be removed. It has been concluded, therefore, that tantalum is an unsatisfactory material for a retorting crucible, at least under the retorting conditions employed to date. It is expected that this same conclusion would apply to other refractory metal crucibles.

Retorting Experiments with Zinc- U_2Zn_{17} Two-phase Systems

Two experiments were made in recrystallized alumina crucibles to gain additional experience in retorting high zinc- U_2Zn_{17} two-phase systems. In the first experiment, a 2.3-kg charge of zinc-10 per cent magnesium-8 per cent uranium was retorted at 600 C with pressures less than 1 millimeter. The final temperature reached in the still was 917 C with the pressure below 0.5 millimeter. Upon exposure to room atmosphere the product ignited in less than a minute. Visual examination of the product after cooling revealed a crystalline mass that was easily removed from the alumina crucible. The amount of material deposited on the side wall was negligible.

In the second experiment, a 2.4-kg charge having the same composition as that used in the first experiment was retorted at 650 C with pressures below 5 millimeters. The final temperature and pressure were comparable to those experienced in the first experiment. The retorting temperature was increased from 600 to 650 C for this run in an effort to obtain a more compact product and thus reduce its pyrophoric nature. The product from this second experiment was again completely consolidated in the crucible bottom. Ignition was avoided by extra care in maintaining the product under an inert atmosphere. Compared to the material recovered from the first experiment, this product was less crystalline, the residue consisting of thin, metallic, foil-like laminations compacted into a single cake. Recovery of uranium was nearly quantitative.

Equipment modifications are being made to permit scale-up to about one kilogram of uranium. Runs to date have been made without fission product alloying elements present. The effect of fission products will be explored since they may materially affect the nature of the product.

c. Development of Equipment for Molten Metal Service

Resistance Heating of Liquid Metal Transfer Lines

(I. O. Winsch, T. F. Cannon)

Ability to transfer liquid metal phases from vessel to vessel in the EBR-II dragout and blanket processes is important to the successful application of these processes. A number of investigations was carried out to determine the feasibility of the transfer operation in the equipment described on page 56 of ANL-6101. The transfer line in these experiments was autoresistively heated. The major difficulty in using autoresistive heating was that differences in resistance along the pipe caused hot and cold spots to develop. Because of this difficulty, it was decided to heat the line with an external resistance heater.

A swaged, magnesia-insulated resistance heating element supplied by Continental Sensing, Incorporated was wound around the length of the transfer line. This heating element was 0.062 inch in diameter and 32 feet long. At an input of 220 volts, the heater was rated at 1325 watts. Thermon, a heat transfer medium, was spread over the transfer line and heater. Fiberfrax was used as insulation over the entire length of the heated transfer line.

For testing the transfer line, about 2.5 kg of magnesium was charged to the crucible in the transfer equipment and heated to 750 C. The transfer line was heated to 700 C and the still pot was pressurized to 15 psig with helium to effect transfer. The magnesium transferred to the receiver in a matter of seconds, after which the transfer line was blown back several times. After dismantling the equipment, an inspection of the transfer line showed it to be open and very clean in appearance.

This method of heating transfer lines appears very reliable and will be used in future runs to demonstrate phase separations of liquid metals.

Contacting of Uranium Oxide-Metal Systems for Reduction
(J. C. Hesson, K. Tobias)

Reduction of uranium oxides in liquid magnesium systems is effected by mixing the two-phase system with flat-blade paddle stirrers which have had various paddle-to-vessel diameter ratios. In full-scale equipment small stirrer diameters are desirable in order to facilitate removal and replacement of stirrers through nozzles of reasonable diameter.

The effectiveness of flat-blade and propeller stirrers having one-half and one-third the crucible diameter was investigated. With a flat-blade stirrer having a diameter one-half that of the crucible, less than 10 per cent reduction was achieved, as contrasted with nearly 100 per cent reduction realized with a paddle nearly equal to the vessel diameter. In the former case, oxide collected along the bottom and in the corners was not suspended by the agitator. This condition was alleviated to some extent by employing crucibles which were wet by the metal (stainless steel). Wetting of the crucible aided suspension of the oxide. Under these conditions apparently high reduction of skull oxide (U_3O_8) was realized with propeller stirrers having diameters of one-half and one-third the crucible diameter.

d. Liquid Metal Corrosion Studies
(J. C. Hesson, J. Pavlik)

Dynamic Tests

The second liquid metal corrosion loop fabricated of mild steel and operated at 550 C was shut down by an electric power interruption after 200 days (4800 hours) of continuous trouble-free operation. An alloy of cadmium having nominal uranium concentration of one per cent, magnesium concentration of two per cent, and fission product elements in expected concentrations (given in ANL-6101, page 62) was electromagnetically pumped at a rate of 1 gpm.

Preliminary examination of the loop did not show any evidence of internal corrosion. However, considerable external air oxidation of the loop had occurred, so that further operation would not have been possible. In the inert gas cell of the plant, such external oxidation would not occur.

Periodic samples of the circulating alloy indicated that the uranium concentration in solution had remained essentially constant for the last five months at about 0.85 per cent, after a rapid initial decrease from 0.94 per cent.

Static Tests: Corrosion of Steels by Zinc Vapor

Processes employing zinc will require the use of tantalum, tungsten, graphite, or ceramic-containing equipment. However, it is hoped that this equipment can be housed in steel or stainless steel equipment. While the steels would not come in contact with liquid zinc, there would be exposure to zinc vapor. Experience in experimental equipment has shown zinc vapor attack of steels to be slight. Some preliminary tests have confirmed this, but indicate severe attack at points of condensation.

C. Pyrometallurgical Research

(H. M. Feder)

1. Chemistry of Liquid Metal Solvents

(I. Johnson)

The chemistry of liquid metal systems is being investigated to provide basic concepts and data for the logical design of pyrometallurgical separations processes. The separation process under consideration consists of the dissolution of the spent reactor fuel in an appropriate volatile liquid metal, separation of the fission products and other extraneous elements by recrystallizations and/or extractions into immiscible liquids (either fused salts or other liquid metals), and finally recovery of the fissionable metal(s) by evaporation of the solvent.

a. Solubilities in Liquid Metals

The solubilities of the elements whose separations are being attempted are of prime importance in the design of fuel-reprocessing schemes. The dependence of solubilities on temperature and solvent composition needs to be known. When the solubilities are determined for a new system, it is useful to characterize the solid phase in equilibrium with the saturated solutions.

Titanium-Cadmium System

(M. G. Chasanov and P. D. Hunt)

The solubility of titanium in liquid cadmium was determined by taking filtered samples of the saturated solution at various temperatures. The melt was held in an alumina crucible under an argon atmosphere and stirred with a tantalum stirrer. Samples were taken with quartz tubes coated on the inside with magnesium oxide and fitted with graphite filters. The samples were analyzed using a spectrophotometric method¹ in which the absorbance of the titanium-peroxide complex is measured. The solubility

¹Sandell, E. B., Calorimetric Determination of Traces of Metals, 3rd Ed., Interscience Publishing, Inc., New York (1959), p. 869.

data obtained in this experiment are shown in Figure 12. The results in the temperature range from 350 to 400 C appear to be high; this may be due to the passage of small solute particles through the 60 grade graphite filter. Additional solubility measurements in this lower temperature range are underway.

The ingot was sectioned and examined microscopically; small crystals of an unknown phase (or phases) were observed in the upper portion of the ingot. Spectrographic analysis of samples from the upper and lower portions of this ingot indicated no apparent contamination by materials of construction or by the sampling tubes. Chemical examination and X-ray spectroscopy of the unknown phase showed that it consisted chiefly of titanium and cadmium with minor amounts of nitride and oxides of titanium present.

X-ray diffraction studies of crystals obtained from the upper portion of the ingot by chemical leaching or by volatilization of cadmium under reduced pressure indicated the presence of two different phases:

"C" phase (cadmium rich) from leached material

"t" phase (titanium richer than "C") from the volatilized material.

To pursue this further, powder compacts of titanium and cadmium were prepared, annealed for three weeks at a temperature slightly below the melting point of cadmium, and then were examined with X-ray diffraction techniques. The results are given in Table 7.

Table 7

PHASES IN TITANIUM-CADMIUM COMPACTS DETERMINED BY
X-RAY DIFFRACTION^a

<u>Ti:Cd Atom Ratio</u>	<u>Major Components</u>	<u>Principal Minor Components</u>	<u>Minor Components</u>
1:10	Cd		phase "C"
1:7	Cd		phase "C"
1:3	Cd		phase "C"
2.3:1	phase "C"		1) β -TiH (possible) 2) Ti (possible)
5:1	phase "t"	1) phase "C" 2) β -TiH	Ti (possible)

^aX-ray diffraction studies performed by R. V. Schablaske and B. S. Tani.

Phase "C" may be the intermetallic Ti_2Cd reported by Hansen.² Additional powder compacts in the titanium-rich end of the system are planned to establish the "C" and "t" phase boundaries as well as to characterize the intermetallic compounds.

Some preliminary results of thermal analysis for two titanium-cadmium melts of 10 and 20 weight per cent titanium point to the possible existence of a peritectic transformation at about 600 C. This may be the reaction

Solubility of Uranium in Lead
(I. Johnson and R. M. Yonco)

The solubility of uranium in liquid lead was measured using both the heating and cooling method (see ANL-6068, page 66, for a discussion of the experimental method). The uranium-lead solution was prepared from high-purity lead (American Smelting and Refining Company 99.99 per cent lead) and uranium turnings. The melt was held in an alumina crucible under an argon atmosphere and stirred with a tantalum stirrer. Samples were taken with quartz tubes coated on the inside with magnesium

²Hansen, M. and Anderko, K., Constitution of Binary Alloys, 2nd Ed., McGraw-Hill Book Co., Inc., New York (1958).

FIGURE 13
SOLUBILITY OF URANIUM IN LEAD

oxide. Samples were taken from both stirred and settled melts to determine whether significant amounts of suspended particles were passing through the porous graphite filters.

The results are shown in Figure 13. These data are best represented by the equation

$$\log (\text{atom per cent uranium}) = 3.921 - 5121 T^{-1}$$

which fits the data with a standard deviation of 8.3 per cent. The solubilities found in these studies are lower than reported by Teitel³ who used a sampling method and by Frost and Maskrey⁴ who used a resistivity method.

These two previous studies are not in agreement with each other, differing by a factor of about two. The solid phase in equilibrium with these solutions is the uranium-lead intermetallic compound UPb₃ based on the data of Teitel, Frost and Maskrey.

Solubility of Uranium in Liquid Cadmium (A. E. Martin and C. Wach)

The solubility of uranium in liquid cadmium below the peritectic temperature in the cadmium-uranium system was remeasured in Morganite alumina crucibles by a technique significantly better than that which had been used in obtaining the previous data in this temperature range (ANL-5896, page 128). The longer holding times combined with vigorous agitation and longer settling periods gave more reproducible results. The new data and the previously reported (ANL-6101, page 70) data obtained above the peritectic, which together constitute the final solubility data for this system, are shown in Figure 14. The equations of the two segments of the liquidus line which were established by the least-squares method are as follows:

$$(326 \text{ to } 468 \text{ C data}); \log (\text{atom per cent uranium}) = 8.115 - 7.104 \times 10^3 T^{-1} + 0.832 \times 10^6 T^{-2}$$

³Teitel, R. J., J. Inst. Metals 85, 410 (1957).

⁴Frost, B. R. T. and Maskrey, J. T., J. Inst. Metals 82, 176 (1953).

(478 to 654 C data); $\log (\text{atom per cent uranium}) =$

$$1.448 - 2.618 \times 10^3 T^{-1} + 1.189 \times 10^6 T^{-2}$$

The per cent standard deviations of the data from these equations were 3.9 and 0.5 per cent, respectively.

The peritectic temperature in the system was determined as 471.5 C from the intersection of the two segments of the liquidus line. This may be compared with the value 473.9 C determined by thermal analysis and the value 471.8 C determined from galvanic cell studies.

The Solubility of Uranium in Cadmium-Magnesium Alloys

(A. E. Martin and C. Wach)

The solubility of uranium in cadmium-magnesium alloys containing from 10.8 to 71.8 weight per cent magnesium was measured at 610 C. Special precautions were taken to avoid the contamination of the melt with silicon. The crucible and sampling tubes were made from

Morganite alumina; the thermocouple protection tube and the stirring rod were made of tantalum. In previous experiments with Morganite alumina crucibles, the aluminum content of the melt was less than 10 ppm. In this run, analysis of the ingot showed a similarly low aluminum content.

The results from this run are shown in Figure 15. Also included to round out the data are some interpolated solubility points from previous runs made at low magnesium levels. Figure 15 shows that the solubility of uranium in the melts decreases smoothly as the magnesium content is increased. The decrease is smooth because for the entire concentration range there is no change in the identity of the solid phase, i.e., alpha uranium in equilibrium with the melt. It was previously shown, ANL-6029, page 58, that at temperatures below the peritectic in the cadmium-uranium system, i.e., below about 472 C, as the magnesium

content is increased the solubility of uranium at first increases in the range where UCd_{11} is the equilibrium solid phase and then decreases in the range where alpha uranium is the equilibrium solid phase.

Solubility of Praseodymium in Cadmium (I. Johnson and K. E. Anderson)

The solubility of praseodymium in liquid cadmium was measured by analyzing filtered samples of the saturated liquid. The saturated solution was prepared from reagent-grade cadmium (99.99 per cent cadmium) and praseodymium (99.9+ per cent) metal. The melt was held in an alumina crucible under an argon atmosphere and stirred with a tantalum stirrer. Samples were taken with quartz tubes coated on the inside with magnesium oxide. The filter was porous graphite.

The results are shown in Figure 16. These data may be represented by the equation

$$\log (\text{atom per cent praseodymium}) = 6.949 - 5400 T^{-1} ,$$

with a standard deviation of 4 per cent. The solid phase in equilibrium with these melts was not identified but is presumed to be the praseodymium-cadmium intermetallic compound PrCd_{11} .

Solubility of Neodymium in Cadmium (I. Johnson and K. E. Anderson)

The solubility of neodymium in cadmium was measured by the same method as reported above for praseodymium. The results are shown in Figure 16. These data may be represented by the equation

$$\log (\text{atom per cent neodymium}) = 6.909 - 5211 T^{-1}$$

with a standard deviation of 3 per cent. The solid phase in equilibrium with these melts was not identified but most likely is the intermetallic compound NdCd_{11} .

b. Liquid-Liquid Partition Studies (F. Cafasso and R. Uhle)

(1) Partition of Palladium, Cerium, Praseodymium, Lanthanum and Zirconium between Aluminum and Cadmium

The purpose of these studies is to investigate the utility of liquid-liquid partition for pyrometallurgical processes. Measurement

of the differential partition of a number of fissile and fission product elements between the immiscible liquids aluminum and cadmium has been completed.

The experimental procedure has been described (ANL-6068, page 75). Briefly, a charge consisting of the two immiscible metals and the solute metal was melted in an alumina crucible, was stirred for one hour and settled for one hour before the two liquid phases were sampled. Magnesium oxide-coated quartz tubes fitted with graphite filters were used for sampling. In all instances, the breakseal method (ANL-6101, page 72) was used to sample the cadmium phase.

Partition coefficients for palladium, cerium, praseodymium, lanthanum and zirconium were measured in the range from 680 to 689 C. Values of the partition coefficient, defined as the ratio of the weight per cent (average) of solute in aluminum to the weight per cent (average) of solute in cadmium, are compiled in Table 8. It is evident from this table that, without exception, the solute metals tend to concentrate in the aluminum phase. Large differences in this tendency exist between the solutes. Uranium partition into aluminum is favored by roughly a factor of 10^3 over cerium and praseodymium, and by roughly a factor of 10^2 over palladium. The small difference in values measured for cerium and praseodymium is reasonable in the light of the similarity in chemical properties usually exhibited by the rare earth series.

Table 8

COMPILATION OF PARTITION DATA FOR THE
ALUMINUM-CADMIUM SYSTEM

Solute	Average Temperature (C)	Al Phase (avg wt %)	Cd Phase (avg wt %)	$K_{avg} = \frac{w/o \text{ in Al Phase}}{w/o \text{ in Cd Phase}}$
U ^a	686	4.8 ^b	3.3×10^{-5c}	1.45×10^5
U	710	5.0 ^d	3.2×10^{-5e}	1.56×10^5
Pd	680	6.4	1.1×10^{-3}	5.82×10^3
Ce	680	4.7	2.7×10^{-2}	1.74×10^2
Pr	686	7.8	4.8×10^{-2}	1.63×10^2
La	686	8.3	0.18	4.61×10^1
Zr	688	0.09	1.1×10^{-3}	8.18×10^{-1}

^aReported in ANL-6101, page 72.

^bSolubility of cadmium in this phase was 8.0 w/o.

^cSolubility of aluminum in this phase was 1.5 w/o.

^dSolubility of cadmium in this phase was 9.6 w/o.

^eSolubility of aluminum in this phase was 1.8 w/o.

The mutual solubilities of aluminum and cadmium were only measured for the uranium systems. These values are recorded in the footnotes of Table 8.

(2) Temperature Dependence of the Uranium Partition Coefficient

In an effort to obtain an estimate of the temperature dependence of the partition of uranium between liquid aluminum and liquid cadmium, an experiment was performed at 710 C, approximately 25 C above the temperature of earlier experiments with this system (ANL-6145, page 75). Temperatures above 710 C were not attempted since cadmium boils at 765 C. The uranium charge approximated that of an earlier experiment (No. 10AC; ANL-6101, page 72). Using the average concentration values for each phase which are recorded in Table 8, the partition coefficient $\left(\frac{\text{w/o U in Al}}{\text{w/o U in Cd}}\right)$ was found to be 1.56×10^5 . The difference between these two values is within the limits of experimental error.

c. Thermodynamic Studies

Thermodynamic functions for key elements in liquid metal solvents and for the important solid intermetallic phases are being measured. Two methods are being used. Galvanic cells have proved to be especially useful for uranium-solvent systems. For those systems in which the galvanic cell method is not practical and in which only one of the components is volatile, measurement of the decomposition pressure by the effusion method is being used.

Thermodynamics of Uranium-Lead System
(I. Johnson and R. M. Yonco)

The free energy of formation of saturated solutions of uranium in liquid lead previously reported (ANL-6145, page 80) and the solubility of uranium in liquid lead reported above (page 65) may be used to compute the activity coefficient of uranium in saturated solutions. The result is found to be

$$\log \gamma_{\text{Pb}}^{\text{U}} = 2.8034 - \frac{6.7}{T} - 4.1513 \times 10^{-3} T + 2.1249 \times 10^{-6} T^2 \quad .$$

The activity coefficients were found to be 7.17 at 500 C, 6.18 at 600 C and 5.87 at 700 C, respectively. These solutions exhibit small positive deviations from Raoult's Law, in marked contrast with solutions of uranium in bismuth, where large negative deviations are found ($\gamma_{\text{Bi}}^{\text{U}} = 10^{-5}$ at 500 C).⁵

⁵Egan, J. J. and Wiswall, R. H., Nucleonics 15, 104 (July, 1957).

Thermodynamics of the Uranium-Zinc System (Effusion Studies)

(E. Veleckis and N. Goetzinger)

The low-temperature region of the phase diagram of the system uranium-zinc is being investigated by measuring the equilibrium vapor pressure of zinc over alloys of continuously varying composition. The Knudsen effusion method is being employed for these measurements. A sample of uranium-zinc alloy, initially containing approximately 17 weight per cent uranium, is placed in an effusion cell and the zinc then completely evaporated. The orifice size and the temperature range (i.e., vapor pressure of zinc) have been selected so that equilibrium conditions exist inside the cell. The progress of the evaporation process is continuously followed by observing the weight loss as a function of time.

The Knudsen effusion equation may be written in the form

$$d(r_0 - r) = \frac{KA P_{Zn} M_U}{\sqrt{2\pi} RT M_{Zn}} d\left(\frac{t}{w_U}\right) \quad (1)$$

or

$$d(r_0 - r) = 8.8996 \times 10^{-3} \frac{P_{Zn}}{\sqrt{T}} d\left(\frac{t}{w_U}\right) ,$$

where r_0 is the atomic ratio Zn/U at zero time and r the ratio at time t , $KA = 0.005182$ sq cm is the effective cell orifice area (obtained by calibration with pure zinc); M_U and M_{Zn} are the gram atomic weights of uranium and zinc, respectively, t is the effusion time in sec, w_U is the weight of uranium in the sample in g, and P_{Zn} is the pressure of zinc above the alloys in mm Hg. According to Equation (1), for a given temperature the slope of a plot of r vs t/w_U is proportional to the vapor pressure of zinc.

In Figure 17 the composition of the alloy is plotted against t/w_U for two typical runs. The curves show three distinct segments. The first segment corresponds to the evaporation of zinc from a liquid solution saturated with respect to the uranium-zinc intermetallic compound, UZn_{r_1} , according to the equation

The first break in the curve corresponds to the completion of the evaporation of the liquid phase and the beginning of the decomposition of UZn_{r_1} intermetallic according to the equation

The pressure remains constant as long as both solid phases are in equilibrium and gives rise to the first pressure plateau. At the second break in the curve, the evaporation of the intermetallic compound UZn_{r_1} has been completed and the beginning of the decomposition of the compound UZn_{r_2} occurs according to the equation

The second pressure plateau is obtained as long as the rate of evaporation of zinc from this compound is sufficient to maintain equilibrium conditions within the effusion cell.

If the standard state of zinc is chosen as pure liquid (at one atmosphere pressure), the standard free energy change, $\Delta F_{\text{tr}}^\circ$, for transformation of UZn_{r_1} into UZn_{r_2} (Equation 3) is given by

$$\Delta F_{\text{tr}}^\circ = -(r_1 - r_2) RT \ln (P'/P^\circ) \quad , \quad (5)$$

where P' is the equilibrium pressure of zinc in the effusion cell at the first pressure plateau and P° is the vapor pressure of pure zinc at the same temperature.

Similarly, for the dissociation reaction, of UZn_{r_2} (Equation 4), we have

$$\Delta F_{r_2}^0 = r_2 RT \ln (P''/P^0) \quad , \quad (6)$$

where $\Delta F_{r_2}^0$ is the standard free energy of formation of the second intermetallic phase and P'' is the pressure of zinc at the second plateau.

Upon subtraction of Equation (5) from Equation (6), one obtains the standard free energy of formation of the first intermetallic compound, $\Delta F_{r_1}^0$:

$$\Delta F_{r_1}^0 = r_2 RT \ln (P''/P^0) + (r_1 - r_2) RT \ln (P'/P^0) \quad . \quad (7)$$

The vapor pressures of the first and second plateaus as well as the vapor pressure of pure zinc⁶ are represented in Figure 18.

The results obtained from six isothermal runs using cell C (single hole area of 4.87×10^{-3} sq cm) are summarized in Table 9. In calculating $\Delta F_{r_1}^0$ and $\Delta F_{r_2}^0$, the compositions of the first and second breaks were taken to be $r_1 = 11.5$ and $r_2 = 8.5$, respectively.

As seen in Figure 17, the weight loss vs time curves exhibit extensive curvature in the vicinity of the breaks. This effect is partially due to a rapid depletion of zinc from the surface of the sample as the composition of the compounds is approached. A series of experiments are being made in which a cell with an orifice of smaller size is employed. With this cell the ratio of the mean free path to orifice radius (Knudsen number) is considerably larger; this reduces the importance of surface depletion effects and hence makes it possible to

⁶Barrow, R. F., Dodsworth, P. G., Downie, A. R., Jeffries, E. A. N. S., Pugh, A. C. P., Smith, F. I., and Swinstead, J. M., Trans. Faraday Soc. 51, 1354 (1955).

identify the breaks more accurately. The final analysis of the effusion data for the uranium-zinc system will be deferred until these additional experiments are completed.

Table 9

COMPOSITIONS AND STANDARD FREE ENERGIES OF FORMATION OF
INTERMETALLIC COMPOUNDS IN THE URANIUM-ZINC SYSTEM^a

Run No.	Temper- ature (C)	r ₁ Zn/U	r ₂ Zn/U	P' (mm Hg x 10 ²)	P'' (mm Hg x 10 ²)	P ⁰ ^b (mm Hg x 10)	$\Delta F_{r_1}^0$ (kcal/ g atom U)	$\Delta F_{r_2}^0$ (kcal/ g atom U)
50	420.8	11.67	8.47	3.82	1.44	1.61	-34.22	-28.27
49	431.6	11.64	8.57	5.68	2.14	2.22	-33.54	-27.81
48	438.8	11.65	8.49	7.86	2.72	2.73	-33.02	-27.74
51	450.5	11.54	8.64	9.53	4.06	3.79	-33.28	-27.32
52	460.8	11.38	8.73	10.71	5.61	5.02	-33.92	-27.16
53	470.6	11.37	8.69	15.22	7.52	6.50	-33.53	-27.10

^aEffusion cell orifice area: $\sim 4.87 \times 10^{-3}$ sq cm.

^bReference 5, Egan et al.

d. Magnetic Studies
(F. Cafasso and C. McMillan*)

Errata

In the previous Quarterly Report, ANL-6145, page 82,
line 5: the equation

$$M^{X_A} = (M_A) \frac{F_A}{_{295}F_S} \frac{W_S}{W_A} (_{295}X_S)$$

should read

$$M^{X_A} = (M_A) \left(\frac{F_A}{_{295}F_S} \right) \left(\frac{W_S}{W_A} \right) (_{295}X_S)$$

Page 82, line 37: the equation reading

$$X = \left(\frac{C}{T} \right) - \Delta$$

should read

$$X = \left[\frac{C}{(T - \Delta)} \right]$$

In Table 16 on page 83, table heading $[MX_{Ce}]^{-1} \times 10^2$ should read
 $[MX_{Ce}]^{-1} \times 10^{-2}$.

*Cooperating chemist, Chemistry Division

Figure 25, page 83; the abscissa scale reading

2. Calorimetry
(W. N. Hubbard)

Thermodynamic data for many compounds of interest in high-temperature chemistry are noticeably unavailable, mainly because of the experimental difficulties involved in making the necessary measurements. A program has been undertaken at Argonne to help fill the gap.

Part of the program consists of the determination of heats of formation at 25 C by oxygen bomb calorimetry. Because some of the compounds of interest are difficult to burn in oxygen and, consequently, cannot be studied by oxygen bomb calorimetry, the new technique of fluorine bomb calorimetry has been developed for their study. The accumulation of basic heat of formation data for fluorides is a necessary preliminary adjunct to fluorine bomb calorimetry and is a valuable program on its own merit.

The heats of formation at 25 C from oxygen or fluorine combustion calorimetry will be combined with the changes in enthalpy measured by a high-temperature enthalpy calorimeter to determine thermodynamic properties at high temperatures. A calorimetric system for measurements up to 1500 C has been designed and is now being fabricated in the Laboratory shops. Design concepts for an electron beam furnace to operate up to 2500 C are being tested in the Laboratory.

Some of the compounds of interest are borides, aluminides, carbides, silicides, nitrides, sulfides and selenides of metals such as uranium, zirconium, molybdenum and tungsten. Some of the compounds of uranium are being prepared for the program by Stanford Research Institute. Two compounds (the disulfides of molybdenum and tungsten) have been prepared here.

a. Combustions of Tungsten Disulfide in Oxygen
(R. L. Nuttall and D. R. Fredrickson)

The heat of combustion of tungsten disulfide in oxygen has been determined by running a series of calorimetric combustions in a platinum-lined bomb in the rotating bomb calorimeter. A value of 1939.29 ± 0.55 cal per gram was found for the heat of combustion for the reaction:

Because of uncertainties in the large corrections applied, the precision of the number given is probably fortuitous.

The combustions were carried out under the following conditions: (1) the gas phase consisted of six atmospheres of oxygen, one atmosphere of argon to lower the combustion temperature and prevent fusing, and one atmosphere of air to catalyze the conversion of sulfur to the +6 valence state; (2) the sample was a two-gram pellet of tungsten disulfide in the form of a "doughnut" suspended on the fuse wire; (3) 10 ml of sodium hydroxide (4N) was added to the bomb to dissolve the sulfur oxides formed; and (4) a 30-mg bead of sulfur on the fuse wire adjacent to the sample was used as a kindler.

Referring to Table 10, the values in columns 2 and 3, the weight of sample burned, and the percentage of sample burned were determined from original sample weights by isolating the solid residue after the combustion, dissolving the tungsten trioxide in hot sodium hydroxide, and weighing the unburned tungsten disulfide. Column 4 gives the weight of sulfur used as a kindler and Column 5 gives the heat evolved by burning this sulfur in accordance with the equation

Column 6 gives the percentages of the total sulfur which forms sulfite. These values are based on an analysis of the solution in the bomb after the combustion by titration of sulfite with standard iodine solution. The thermal effect of oxidizing this sulfite to sulfate according to the equation

is given in Column 7. Column 8 is a summation of minor corrections to the measured energy, which include dilution, vaporization and compression corrections. Column 9 gives the measured energy evolved in each combustion for the isothermal bomb process. This value contains corrections for the heat capacity of the contents of the bomb, ignition energy, and rotational

Table 10

STANDARD HEAT OF COMBUSTION OF TUNGSTEN SULFIDE IN OXYGEN

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Run	Wt WS ₂ Burned (g)	% WS ₂ Burned	Wt Sulfur Kindler (g)	Sulfur Correc- tions (cal)	Sulfur which Forms Sulfite (%)	Sulfite Correc- tions (cal)	Other Correc- tions (cal)	Total Energy (ΔE_{IBP}) ^a (cal)	n ΔE_c (cal)	$\Delta E_c/M$ (cal/g)	ΔE_c (kcal/mole)
2	1.92694	99.7	0.03354	+172.37	31.2	-350.3	-1.52	-3561.13	-3740.58	-1941.20	-481.40
3	1.94522	99.9	0.04856	+249.55	22.8	-266.0	-1.24	-3754.71	-3772.39	-1939.31	-480.93
6	1.91896	98.6	0.02923	+150.22	23.1	-256.3	-1.14	-3611.82	-3719.04	-1938.05	-480.62
7	1.88611	97.0	0.03026	+155.51	25.0	-272.0	-1.17	-3538.36	-3656.02	-1938.39	-480.71
8	1.91850	98.7	0.02982	+153.25	26.4	-292.1	-1.15	-3580.93	-3720.93	-1939.50	-480.98
Average										-1939.29	-480.71
Std Dev of Mean										0.55	0.33
or										0.03%	

^a (ΔE_{IBP}) = energy evolved in each combustion for the isothermal bomb process.

energy. A summation of Columns 5, 7, 8 and 9 gives the standard change in internal energy due to combustion of the sample alone according to equation (1). Values of this quantity, $n \Delta E_c$, for each combustion are given in Column 10. Columns 11 and 12 give the energy change for 1 gram and 1 mole of tungsten disulfide, respectively.

b. Combustion of Zirconium in Fluorine
(E. Greenberg)

A second series of calorimetric combustions of zirconium in fluorine has been completed. The data are presented in Table 11.

Table 11

CALORIMETRIC COMBUSTIONS OF
ZIRCONIUM IN FLUORINE

Run No.	Mass Zr (grams)	$\alpha \times 10^4$ (sec ⁻¹)	$-\Delta E_c^\circ/M$ (cal/gram of Zr)
8	0.99354	0.3388	4995.8
9	1.01707	0.3387	4990.7
10	1.00775	0.3372	4994.5
11	1.0370	0.3426	4998.4
12	1.03397	0.3393	4999.1
13	1.03119	0.3371	4996.6
14	1.03902	0.3355	4995.9
Average =			4995.8
Standard Deviation of Mean = 1.0 cal/gram or 0.02 per cent			
15 ^a	0.76408	0.3398	5007.1

^aZirconium sample melted.

As in the previous series (ANL-6145), the internal consistency of α (the heat transfer coefficient) and its agreement with the calibration experiments indicates that, calorimetrically, the combustions are satisfactory. With the exception of Run 15, the quantity of zirconium burned was slightly greater than in the first series and amounted to about 75 to 80 per cent of the sample introduced into the bomb. The mass of zirconium burned was determined by subtracting the mass of zirconium metal recovered after the combustion from the original mass of zirconium.

In Run 15 the zirconium sample melted and ran down onto the nickel sample holder, where it solidified. The zirconium was not bonded to the nickel and the unburned metal was recovered in the usual manner. However, there is a somewhat greater uncertainty attached to this run because the sample melted and the result was not included in computing the average.

The average value of 4995.8 ± 1.0 for $-\Delta E_c^\circ/M$, the energy change per gram of zirconium, compares with the revised value of 4987 ± 4 obtained in the first series. There does not appear to be any obvious explanation for this discrepancy except to say that the experimental techniques used were substantially better in the second series. The standard deviation of the mean for this series, 0.02 per cent, is one-fourth the value for the first series.

The values presented for $-\Delta E_c^\circ/M$ are for the reaction

with the reactants and product in standard state conditions. Corrections have been made for small amounts of hydrogen, oxygen, nitrogen, carbon, and metallic impurities in the zirconium sample. To a large extent the correction for the metallic impurities is cancelled by the correction for the nonmetallic impurities, leaving a net correction of about 0.1 calorie for this series. The data for this series lead to a value of -454.5 ± 0.1 kcal/mole for $\Delta H_{298.15}^\circ$, the standard heat of formation for zirconium tetrafluoride.

A few additional calibration experiments are now being carried out in the bomb.

c. Combustion of Boron in Fluorine
(S. Wise)

Two series of calorimetric combustions of crystalline boron in fluorine have been made. The preliminary data are presented in Table 12. Because chemical analyses of the boron sample are incomplete, corrections for impurities in the sample have not been made. The data, therefore, show only the internal precision of the calorimetry.

Several changes were made in the calorimetric technique between the first and second series. These changes probably accounted for the improved precision of the second series. In the first series of combustions (Nos. 1 through 6) the sample of crystalline (100 to 325 mesh) boron was supported by an alumina (Morganite) plate, $1\frac{1}{2}$ in. in diameter and $\frac{1}{16}$ in. thick. Although it was originally thought that the alumina would be essentially unreactive toward fluorine, it was found that the plate

changed in weight during a combustion in a manner inconsistent with the variations in the data. In the second series, fused calcium fluoride disks were used to support the boron. Thus, the possibility of supports entering into the reaction was minimized.

Table 12

PRELIMINARY DATA FROM COMBUSTIONS OF BORON
IN FLUORINE

Run No.	Boron Weight (g)	α (coding const) $\times 10^4$	$\Delta T, (C)/g \times 10^{-1}$
1	0.20955	0.3312	0.6928 ₁
2	0.22992	0.3433	0.7059 ₆
3	0.20661	0.3413	0.6982 ₄
4	0.20973	0.3403	0.6944 ₀
5	0.26531	0.3412	0.7013 ₆
6	0.25231	0.3461	0.6962 ₀
			Avg = 0.6981 ₆
			Std Dev of Mean = 0.0019 ₈
			or 0.28%
(7) ^a	(0.15403)	(0.3510)	(0.6959 ₂)
8	0.15860	0.3384	0.6926 ₇
9	0.10832	0.3175	0.6912 ₉
10	0.16489	0.3136	0.6928 ₉
11	0.16386	0.3293	0.6920 ₂
12	0.16568	0.3274	0.6910 ₅
			Avg of 8-12 = 0.6919 ₈
			Std Dev of Mean = 0.0003 ₃
			or 0.05%

^aRejected because of inconsistent stirring energy.

A second problem was that of the recovery of the unburned boron. In the first series, the unburned boron was washed from the support and weighed in a filter crucible. However, it was suspected that small amounts of the support were included in the material weighed as boron. Before the second series was started, an analytical method for recovery of the boron was developed. The calcium fluoride plate was first dissolved away from the boron in a hot aluminum chloride solution. The remaining boron was washed and then converted to boric acid by refluxing with concentrated nitric acid. The boric acid was then titrated as the mannitol

complex with standard sodium hydroxide. In the first series the amount of unburned boron ranged from 1 to 17 mg. In the second series a reduced sample size was used and the amount of unburned material was consistently less than 0.2 mg.

In both series the nickel bomb was charged with 3 atm of fluorine diluted with $2\frac{1}{2}$ atm argon. The argon was used to lower the temperature of the reaction zone. High temperatures resulting from the use of pure fluorine caused the supporting plates to crack and sometimes shatter.

X-ray analyses of the boron show that only the β -high-temperature rhombohedral crystalline form is present.

d. Combustions of Cadmium, Magnesium, Zinc and Aluminum in Fluorine
(E. Rudzitis)

Similarity of some chemical and physical properties of the group of soft metals, cadmium, magnesium, zinc, and aluminum, led to their choice for exploratory combustion experiments, since similar combustion techniques could probably be applied to them. A systematic search for optimum reaction conditions was carried out after the exploratory experiments indicated unexpectedly wide variations in reaction conditions.

By means of the wire-to-foil-to-sample ignition technique, cadmium and magnesium ignited and burned at fluorine pressures above 60 psi and 250 psi, respectively. Lower pressures resulted in melting of the ignition wire without burning of the rest of the sample. Zinc and aluminum resisted all efforts to obtain a significant amount of combustion. The use of thin foils, 500 psi fluorine pressure, and more reactive metal foils as ignitors yielded only partial melting of zinc and aluminum samples. Consequently, the experimentation with zinc and aluminum was discontinued for the time being, and efforts were concentrated on establishing conditions for calorimetric combustions of cadmium and magnesium.

The sample sizes for cadmium and magnesium, 2 g and 0.3 g, respectively, were chosen to liberate approximately 3000 cal of heat. Once the sample ignited, the burning proceeded vigorously and the intense heat melted the metal. A nonreactive and high-melting supporting material had to be found. A calcium fluoride-coated alumina support was found to be satisfactory for magnesium combustions. However, X-ray examination of the reaction products after cadmium combustion showed that calcium fluoride and cadmium fluoride had formed a solid solution, which would lead

to thermal uncertainties in calorimetric measurements. The possibility of obtaining sintered cadmium and magnesium fluoride disks for use as supports is being investigated.

Another difficulty in establishing combustion conditions was caused by incomplete combustion. During the combustion a small amount of metal was covered by the molten fluoride and remained unreacted. A method was devised to determine the amount of unburned metal by treating the melt with hydrochloric acid and separating and determining gasometrically the hydrogen evolved by dissolution of the metal. The error determining milligram amounts of cadmium and magnesium amounted to approximately one per cent.

II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES

Several processes have been proposed for the processing of irradiated fuels by taking advantage of the volatilities of uranium and plutonium hexafluoride and fluidization techniques. These include a Direct Fluorination Process, the Aqueous Dissolution Fluorination (ADF) Process and the Fused Fluoride Volatility Process. Current application is toward recovery of uranium from zirconium-clad or alloy-based fuels. The application of these processes to fuels containing stainless steel is also being considered. Fluidization techniques are also being used in the conversion of uranium hexafluoride to other uranium compounds of interest in the nuclear fuel cycle.

The Direct Fluorination Volatility Process is being developed to recover uranium and plutonium from spent uranium oxide, Zircaloy-clad, fuel elements of the type used in the Dresden nuclear power plant. A proposed processing procedure utilizes the reaction of zirconium with a mixture of hydrogen fluoride and hydrogen chloride for decladding. Plutonium and uranium hexafluorides, which result from the reaction of the oxide fuel with fluorine, may be separated using a combination of the variability of the rates of fluorination and chemical reactivity. Equipment has been constructed and is being tested to study the process steps using multigram amounts (10 to 100 grams) of plutonium.

A study of the kinetics and mechanism of the decomposition of plutonium hexafluoride vapor has been initiated. The reaction appears to be a heterogeneous one which is zero order with respect to plutonium hexafluoride at 160 C.

The reaction of plutonium hexafluoride with sulfur tetrafluoride was investigated. Results indicate that plutonium hexafluoride is reduced by sulfur tetrafluoride at rates suitable for process use.

The reaction of sulfur tetrafluoride with uranium trioxide to produce uranium hexafluoride may be used as a basis for a fuel-recovery process. Investigation of the stoichiometry of the reaction is in progress. Thionyl fluoride and uranium hexafluoride are the major products.

Conversion of uranium dioxide to uranium trioxide by means of air and nitric acid vapor and also by means of oxygen and nitrogen dioxide was investigated between 350 and 600 C. Excellent results were obtained with nitric acid. However, when using nitrogen dioxide and oxygen it was apparent that longer reaction times and higher gaseous pressures were needed for complete conversion of uranium dioxide.

In a continuing study of the direct fluorination of dense uranium dioxide pellets, a run in the three-inch pilot plant reactor showed (1) a lower temperature reduces the rate of fluorination of the uranyl fluoride intermediate to form uranium hexafluoride and (2) a deeper inert fluidized bed retains more fines in the bed reducing the dust load on the filters.

Several aspects of the Direct Fluorination Process are being studied for the recovery of uranium from highly enriched uranium-zirconium alloy fuels. One scheme is to convert the metallic element to fluoride salts by means of mixtures of hydrogen chloride and hydrogen fluoride. A subsequent fluorination step would be expected to volatilize the uranium and permit separation. The work is being carried out with the fuel elements submerged in a fluidized bed of inert material (such as calcium fluoride) which serves as the heat transfer medium. Runs in both 1½-inch and 6-inch diameter columns confirmed previous results that high conversion of zirconium to the tetrafluoride may be achieved with dilute mixtures of hydrogen chloride in hydrogen fluoride (10 volume per cent or less hydrogen chloride) at temperatures of 450 to 500 C. About 95 per cent conversion was achieved on a 2-kg, 10-plate welded section of a 1.5 per cent uranium-zirconium alloy subassembly in about 12 hours. Mixtures rich in hydrogen chloride (near 40 volume per cent) were found to react less rapidly with zirconium.

Experiments incorporating a 2-zone reaction scheme for reacting zirconium with hydrogen chloride-hydrogen fluoride gas mixtures were initiated. The element is first reacted with hydrogen chloride, forming the volatile zirconium tetrachloride, which is then reacted with hydrogen fluoride in the upper section of the bed. Very little conversion was achieved in the initial trials, possibly as a result of back-mixing of the hydrogen fluoride, which produced a much less reactive hydrogen chloride-rich mixture. Baffling between the two reaction zones will be required to prevent gas back-mixing.

Laboratory data have been obtained on reaction rates of Zircaloy-2 with various mixtures of hydrogen fluoride and hydrogen chloride at several temperatures. This gas mixture was found to have little effect on sintered uranium dioxide pellets contained within a short section of 30-mil thick Zircaloy tubing which completely corroded in a 6-hour period.

The ADF Process, which involves aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry powder, and fluorination of the powder to remove and recover the uranium as the hexafluoride, is directed toward recovery of uranium from enriched uranium-zirconium alloy fuels. Results of recent fluorination experiments conducted in static beds in both a 2-inch diameter by 6-foot tall reactor and a 6-inch diameter unit indicated that variations in bed heights up to 4½ feet and gas velocities up to 0.1 ft/sec were of negligible importance with

respect to uranium removal from uranium-zirconium fluoride salts prepared in the fluid-bed dryer. Residual uranium contents were about 0.03 to 0.05 per cent, representing losses of the order of 5 per cent.

A series of fused salt dissolutions of synthetic zirconium-uranium fuel assemblies has been carried out in the graphite pilot plant dissolver according to a semicontinuous flowsheet. Dissolution rates in the sodium fluoride-zirconium fluoride mixture under hydrogen fluoride sparge have been as high as 3.4 mg/(min)(sq cm), resulting in a 90 per cent dissolution of the approximately 90-mil thick plates in less than five hours. Satisfactory operation of the internal graphite heaters and other components exposed to the molten salt have continued over 1600 hours of accumulated exposure.

The conversion of uranium hexafluoride to uranium dioxide by direct reaction with steam and hydrogen is being investigated. The process involves the formation of either uranyl fluoride or uranium tetrafluoride followed by hydrogen reduction or steam pyrohydrolysis to the dioxide. In each case, the newly formed material is deposited as a dense coating on the fluidized particles in the bed. The reaction of steam with uranium hexafluoride was carried out at temperatures of 140 to 230 C using hexafluoride rates equivalent to 205 lb uranium/(hr) (sq ft reactor cross section). The temperature of the hydrogen reduction step significantly affected the rate of fluoride removal. In 4-hour batch runs, 5 to 10 per cent residual fluoride remained at 550 C and only 0.024 per cent remained at 650 C. The latter value is within the fluoride specification usually set for ceramic-grade uranium dioxide powders. The reduction of uranium hexafluoride with hydrogen to a dense uranium tetrafluoride was successfully carried out in a 2.2-hour run at 600 C with a feed rate of 101 g/min and about 250 per cent excess hydrogen. The first series of pellet fabrication studies made at Mallinckrodt Nuclear Corp. on uranium dioxide prepared at ANL by direct conversion from hexafluoride resulted in sintered densities ranging from 93.5 to 97.5 per cent of theoretical for material which was ground to -325 mesh and pelleted.

The first phase of the experimental work in the 6-inch multistage fluid-bed reactor designed to achieve controlled downward transport of solids using external vibrators and without the use of internal downcomers has been completed. A correlation has been obtained for throughput rate as a function of feed particle density, shape and size, column cross-sectional area, density and superficial velocity of the fluidizing gas, and the depth and size of beads used in the bed support plate.

A. Direct Fluorination Volatility Process for Oxide Fuels

The Direct Fluorination Volatility Process is being developed to recover uranium and plutonium from spent uranium oxide, Zircaloy-clad, fuel elements of the type used in the Dresden nuclear power plant. Zircaloy cladding is removed from the fuel element by reacting the zirconium with hydrogen fluoride, containing approximately 17 weight per cent hydrogen chloride. Zirconium tetrafluoride is produced in a fluid bed of inert fluoride, such as calcium fluoride, at 500 C. In the same nickel vessel used for the decladding, uranium and plutonium oxides are subsequently converted to their respective volatile hexafluorides by reaction with fluorine at 500 C in the fluid bed remaining from the decladding operation.

During the initial reaction of the oxide fuel with fluorine (step 1), uranium is fluorinated to volatile hexafluoride faster than plutonium. Any volatile plutonium hexafluoride formed may be reduced to the nonvolatile tetrafluoride by reaction with tetra- or pentavalent uranium compounds at about 500 C in the reaction mixture, thereby enhancing the separation. The solids in this bed can be returned periodically to the fluorination vessel. The plutonium-rich fraction, remaining in the reactor toward the completion of the fluorination step, is then reacted further with fluorine to produce plutonium hexafluoride and uranium hexafluoride in step 2.

Separation of the uranium and plutonium hexafluorides from the mixture obtained in step 2, the last stage of fluorination, can be attained by reduction of the more reactive plutonium hexafluoride. Either sulfur tetrafluoride or bromine can be used as a reducing agent. The plutonium product is collected in the reducing vessel as plutonium tetrafluoride. The uranium hexafluoride is combined with that obtained in step 1 and purified by distillation, yielding highly decontaminated uranium hexafluoride.

A major portion (approximately 75 per cent) of the fission product activity should remain in the bed of calcium fluoride and zirconium fluoride, which is disposed of as solid waste. A small amount of fission products will be produced in gaseous form and the remainder of the fission products, which form volatile fluorides, will be collected in a caustic scrub solution as liquid waste.

1. Fluorine Chemistry and Fluoride Separation Studies (J. Fischer)

a. Process Development (G. J. Vogel, L. Anastasia, H. Griffin, T. Baker, G. Redding)

Equipment has been constructed and is being tested to study processing variables in the Direct Fluorination Volatility Process. This equipment, which was previously described in ANL-6145, page 100, was

designed to handle multigram quantities of plutonium and is enclosed in two glove boxes. Each box is ten feet long, 3.5 feet wide, and five feet tall. Laboratory air at fifty cubic feet per minute is passed through each box and, after being filtered, is vented to the outside of the building. The first box contains a horizontal boat reactor and the second box has a vertical fixed-bed reactor in addition to a horizontal boat reactor. Apparatus is included in the first box which will be used to transfer volatile hexafluorides from one container to another through a transfer loop containing experimental equipment. The behavior of plutonium hexafluoride during transfer operations will be studied. Apparatus in each box includes a magnetic piston pump for moving gases, gas preheaters, cold traps for trapping the volatile hexafluorides, flowmeters, and temperature and pressure indicators. A two-kilogram capacity analytical balance is included in one of the boxes.

After assembly, the Monel and nickel equipment was tested for leaks using a helium leak detector. Simulated runs were made to ensure proper operation of the controlling and recording instruments, and to study operations peculiar to glove box operations, such as changing of gloves and moving equipment in and out of the box by means of heat-sealed polyvinyl-chloride pouches. After these operations, the inside metal surfaces of the equipment were reacted with fluorine to form a protective nickel fluoride coating.

To demonstrate, before working with plutonium, that the fluorination and transfer equipment would function satisfactorily, both uranium fluoride and oxide were reacted separately with elemental fluorine at 400 C, and uranium hexafluoride was transferred through the equipment. The uranium material balances, 96.7, 99.0 and 100.8 per cent, obtained in the three fluorination runs indicated that good operational procedures were being used. Up to 104 grams were fluorinated in each experiment.

The transfer loop, consisting of 3.5 feet of $\frac{3}{8}$ -inch diameter tubing containing four Hoke 413 diaphragm valves, was also tested with uranium hexafluoride. In the three low-pressure (below 50 mm Hg) transfers, the uranium hexafluoride was moved from a warmed trap through the transfer loop to a cooled (-187 C) trap. The traps were weighed on the analytical balance before and after material was added. In four additional transfers the uranium hexafluoride was carried by a helium stream from a supply container through the loop and to the cold traps. Up to 114 grams of uranium hexafluoride were transferred in each experiment. Transfer rates ranged from 8 to 234 grams per hour, depending on the type of transfer, carrier gas flow rate, and amount of heat applied to the uranium hexafluoride supply container.

b. Rate of Decomposition of Plutonium Hexafluoride
(L. Trevorrow, W. Shinn)

Plutonium hexafluoride vapor decomposes into the less volatile plutonium tetrafluoride and fluorine when heated. The fluoride volatility process currently under development involves a transfer of plutonium hexafluoride in the vapor state, in which thermal reduction should be minimized. In another step of the process, the separation of plutonium from uranium, thermal reduction of plutonium hexafluoride might be used to advantage. Since the thermal reduction of plutonium hexafluoride occurs at an appreciable rate at a much lower temperature than the thermal reduction of uranium hexafluoride, a mixture of plutonium and uranium hexafluorides might be heated to a suitable temperature to reduce the plutonium compound preferentially.

It would be advantageous to know what factors inhibit the rate of decomposition for the purpose of plutonium transfer. It is also of interest to know under what conditions the reduction might be accelerated for a separations application. A study of the kinetics and mechanism of the decomposition of plutonium hexafluoride vapor has therefore been initiated.

Equipment has been assembled for a study of the rate of the reaction by a static method. The stoichiometry of the reaction has been established (ANL-5924, page 33). Since there is no change in the number of gas molecules in the reaction, it is not possible to follow the rate of the reaction by pressure measurement. Solid plutonium tetrafluoride is nonuniformly deposited on the inner surfaces of the reaction vessel in the course of the reaction. The deposition of solid would interfere with measurement of the partial pressure of plutonium hexafluoride by many of the common physical methods, such as spectrophotometry, thermal conductivity, sonic measurements, and density via gas balance. Thus a number of physical measurements which might be used to follow the reaction continuously are rendered inapplicable or extremely difficult due to the health hazards of handling plutonium compounds. Therefore rates have been obtained from initial and final compositions after heating a sample of plutonium hexafluoride for a given period. It is thus possible to obtain integrated rates even though the lack of a continuous measurement rules out direct determination of differential rates.

Several preliminary experiments were done in the temperature range from 140 to 200 C. These served mainly to determine the temperature range over which the magnitude of the rates permitted the use of the static method. They also served as a proving ground for the experimental technique. A set of fifteen experiments was then done at 161 C.

The preparation and purification of plutonium hexafluoride were the same as described previously (ANL-5924, page 33). Prior to each experiment, the storage vessel containing the plutonium hexafluoride was evacuated to about 2×10^{-4} mm at -196°C to remove fluorine produced by radiation decomposition. The plutonium hexafluoride was then transferred by vacuum distillation to a supply vessel where it was condensed, and fluorine was again removed by evacuation at -196°C . The 50-ml supply vessel was connected by a short length of tubing to a 50-ml decomposition vessel. The supply vessel and associated lines were heated to about 50 to 70°C to promote transfer to the decomposition vessel of adequate quantities of plutonium hexafluoride. The decomposition vessel was preheated to the experimental temperature in an aluminum block wound with Nichrome wire. An experiment was initiated by opening the valve to the evacuated decomposition vessel and allowing the warm plutonium hexafluoride to expand into it. At the end of the experiment, the furnace was lowered and the decomposition vessel was quenched in liquid nitrogen. The vessel cooled rapidly to approximately 100°C in one minute and to room temperature in two minutes. Thus the error introduced by additional decomposition during the quenching period was small, since the quenching period was short. After quenching, the decomposition vessel was warmed to room temperature, and weighed to determine the starting amount of plutonium hexafluoride (the tare weight of the vessel had been determined before the experiment). The vessel was then evacuated at 25°C to remove plutonium hexafluoride and the fluorine formed in the reaction. The vessel was weighed again to find the amount of plutonium tetrafluoride formed. From this weight, the amount of plutonium hexafluoride decomposed was calculated.

All of the experiments to date have been done in the same reaction vessel. The plutonium tetrafluoride product remained in the reaction vessel after each decomposition. Early experiments indicated that the reaction was heterogeneous in nature. The decomposition rate in the fresh vessel was quite slow compared to the rate determined in a later experiment under the same conditions but in the presence of solid plutonium tetrafluoride. This observation will be checked by further experimentation.

The results of the series of decompositions done at 161°C are given in Table 13. The weight of plutonium hexafluoride, temperature, and volume of the reaction vessel were used to calculate initial and final pressures of plutonium hexafluoride by means of the ideal gas equation. Because the partial pressure of plutonium hexafluoride is determined only for the beginning and end of each experiment, the methods available for assigning an order to the reaction are restricted. The method most commonly used in this situation is the method of integration. Various values are chosen for the order; rate constants are then calculated from the integrated rate equations for the various orders. The one which yields a rate constant that does not vary for a given temperature is accepted as the order of the reaction.

Table 13

RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE VAPOR

Reaction Temperature: 160.6 C

Reaction Vessel Volume: 51.8 cc

(See page 90 for description of
equipment and operation)

No.	Reaction time (min)	Initial Wt PuF ₆ (mg)	Wt PuF ₆ Remaining at End of Reaction Time (mg)	Initial Pressure PuF ₆ (mm)	Pressure of PuF ₆ at End of Reaction Time (mm)
23	30	171.0	162.8	253	241
24	30	142.2	134.6	210	199
25	60	138.1	126.7	204	187
26	120	137.2	110.1	203	163
27	180	124.4	62.3	184	92.1
28	45	75.4	60.7	112	89.8
29	90	76.1	39.2	113	58.0
30	60	216.4	161.9	320	239
31	60	154.0	99.1	228	147
32	90	171.9	84.3	254	125
33	90	107.0	33.5	158	49.5
34	30	134.9	101.9	200	151
35	75	132.3	60.2	196	89.0
36	15	105.5	92.3	156	136
37	45	96.3	54.8	142	81.0

There is another test of the experimental data which yields information about the order of the reaction:

The line joining the initial and the final pressures on a pressure-time graph can be referred to as a $\Delta p/\Delta t$ line. If a series of experiments are done at different initial pressures but for the same reaction time, the slope of the $\Delta p/\Delta t$ lines will decrease with initial pressure if the reaction rate is proportional to reactant pressure. If the rate is independent of reactant pressure, the slopes of the $\Delta p/\Delta t$ lines will not vary with initial pressure. Thus, the variation of the slope of the $\Delta p/\Delta t$ lines with initial pressure can be used to test whether or not the reaction rate is proportional to reactant pressure.

The results of Experiments 23 through 29 are plotted as a pressure-time graph in Figure 19. The slopes of the $\Delta p/\Delta t$ lines do not

FIGURE 19
RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE VAPOR AT 161 C
(EXPERIMENTS 23 THROUGH 29)

vary in any simple way with initial pressure. The slopes, which can be calculated from the data in Table 13, increase roughly in chronological order of the experiments. If the reaction is a heterogeneous one, it might be expected that the rate would increase in chronological order as the area of solid surface in the vessel increased with plutonium tetrafluoride accumulation.

The results of the succeeding eight experiments (30 through 37) are quite different. They are plotted as a pressure-time graph in Figure 20. The $\Delta p/\Delta t$ lines are all of comparable slope regardless of initial pressure or reaction time. The decomposition rate appears to be independent of plutonium hexafluoride pressure. For this set of experiments the rate can

be expressed by the zero-order rate equation:

$$-dp/dt = k. \quad (1)$$

The integrated rate equation is

$$p_i - p = kt, \quad (2)$$

where

p_i = initial pressure of plutonium hexafluoride,

p = partial pressure of plutonium hexafluoride at end of reaction time,

k = rate constant,

t = reaction time.

Thus a plot of $p_i - p$ versus time should be a straight line, the slope of which is k . The results of Experiments 30 through 37 are plotted in this

FIGURE 20
RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE VAPOR AT 161°C
(EXPERIMENTS 30 THROUGH 37)

FIGURE 21
RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE VAPOR
(EXPERIMENTS 30 THROUGH 37
PLOTTED IN A ZERO ORDER EQUATION^a)

way in Figure 21. The rate constant estimated from the slope of the line drawn through the points by inspection is 1.4 mm plutonium hexafluoride/min. If the reaction is heterogeneous in nature, the rate is dependent on the surface area available to the reactant. The above rate would then be a special case for the particular surface area in the reaction vessel. The area of the solid plutonium tetrafluoride has not been measured. The surface area available to the reactant might be expected to increase as the weight of residual plutonium tetrafluoride in the vessel increases. The increase of plutonium tetrafluoride in Experiments 30 through 37 was about 20 per cent of the total weight of residual plutonium tetrafluoride in the vessel, yet there was no chronological increase of reaction rate. This observation indicates either that the surface area did not increase significantly with the accumulation of plutonium tetrafluoride, or that the reaction is not very sensitive to increase in surface area.

The reason for increase in rate starting with Experiment 30 is not known. Again, the only readily available explanation is in terms of a change in surface area. The increase might have been caused by the dislodging of a large portion of the plutonium tetrafluoride from the vessel walls between Experiments 29 and 30. Such an incident would expose more solid surface area to the reactant.

c. Reaction of Plutonium Hexafluoride with Sulfur Tetrafluoride
(M. J. Steindler, D. V. Steidl)

The reaction of plutonium hexafluoride with sulfur tetrafluoride was investigated in order to determine if plutonium hexafluoride could be reduced to the nonvolatile tetrafluoride with sulfur tetrafluoride. This reaction, as shown in Equation (1),

could be utilized in the separation of uranium hexafluoride and plutonium hexafluoride after they have been produced from their oxides in the Direct Fluorination Volatility Process. It was estimated that the reaction as written has a ΔF_{298} of -46 kcal/mole and is therefore thermodynamically possible.

A small sample of plutonium hexafluoride was transferred into a weighed nickel reaction vessel for each experiment. Sulfur tetrafluoride, in excess of the stoichiometric amount, was condensed onto the plutonium hexafluoride at -196 C and the mixture was heated to the reaction temperature. The pressure in the system was observed with the aid of a Booth-Cromer pressure transmitter. At the completion of the reaction, unreacted reagents and volatile products were removed from the reaction vessel by volatilization.

The results, shown in Table 14, demonstrated that plutonium hexafluoride reacts with sulfur tetrafluoride at modest temperatures and at rates suitable for process use. The measure of the extent of reaction, as determined by pressure measurements, required that the reaction as written in Equation (1) be assumed. This assumption appears to be warranted, but additional work is in progress to determine the stoichiometry of the reaction more accurately.

d. Reaction of Uranium Oxides with Sulfur Tetrafluoride
(C. Johnson, T. Gerding)

The reaction of sulfur tetrafluoride with uranium trioxide, forming volatile uranium hexafluoride, has been suggested as a basis for a possible fuel recovery process (ANL-6145, page 93). Laboratory investigations have been concerned with the reaction of uranium trioxide and uranium oxyfluorides and the stoichiometry of these reactions, e.g.,

Table 14

REACTION OF SULFUR TETRAFLUORIDE AND
PLUTONIUM HEXAFLUORIDE

(See page 94 for description of apparatus and procedure)

Temp (C)	Time (hr)	PuF ₆ (g)	SF ₄ (g)	Extent of Reaction, %	
				Pressure Measurement	Residue
30	1	0.0753	0.0841	70	83 ^a
30	17	0.1181	0.1305	102	98 ^b
70	1.5	0.1154	0.1367	-	99 ^b
70	0.2	0.1166	0.1274	100	77 ^{b,c}

^aChemical analysis

^bWeight of PuF₄ in reaction vessel

^cReaction occurred partially outside of reaction vessel (lines and valves).

Although analytical results available at this time make it impossible to present a precise interpretation of the experimental work completed to date, the following qualitative observations have been made. In those experiments where the mole ratio of sulfur tetrafluoride to uranium trioxide was three or greater, infrared scans of the gaseous products indicated uranium hexafluoride and thionyl fluoride were the major reaction products. In one experiment where the sulfur tetrafluoride/uranium trioxide mole ratio was 1.5, the infrared scan indicated sulfur dioxide to be a product in addition to thionyl fluoride and uranium hexafluoride. Addition of sulfur tetrafluoride to uranyl fluoride showed thionyl fluoride and uranium hexafluoride to be the major species.

e. Conversion of Uranium Dioxide to Uranium Trioxide
(C. Johnson, J. Stockbar)

In a direct fluorination reprocessing scheme for spent uranium dioxide fuel elements, the separation of uranium, as the hexafluoride, from plutonium during the fluorination step is attractive. Studies (ANL-6145, page 93) have been made which indicate that sulfur tetrafluoride can be used as a specific fluorinating agent to convert uranium trioxide to uranium hexafluoride. Plutonium hexafluoride is not formed by reaction between plutonium dioxide and sulfur tetrafluoride. In attempting to utilize this unique property of sulfur tetrafluoride, avenues have been sought for the ready conversion of uranium dioxide to uranium trioxide.

A search of the literature disclosed that two different approaches to the preparation of uranium trioxide could be pursued. Sheft, Fried and Davidson⁶ prepared uranium trioxide by heating U_3O_8 with oxygen under pressure at about 500 C. Within wide limits the temperature at which the reaction is run is not critical. However, the upper limit is important. Above 750 C oxides intermediate between uranium trioxide and U_3O_8 were found. At this temperature, pressures in excess of 30 atmospheres were needed to prepare uranium trioxide.

In the procedure devised by Flook,⁷ U_3O_8 was converted to uranium trioxide by heating the uranium oxide to 400 C for a suitable period of time in the presence of vapors from a constant-boiling nitric acid solution. To prevent dissociation of the freshly formed uranium trioxide it is necessary to maintain a blanket of nitric acid vapor over the sample until the sample temperature has been cooled to 350 C or below. Below 350 C the uranium trioxide is stable toward dissociation in air.

In utilizing the procedure of Sheft *et al.*, an apparatus was constructed in which the uranium dioxide could be treated with oxygen at high pressures and high temperatures. The reactor consisted of a 2-inch, schedule 40, 347 stainless steel pipe, closed at one end and flanged at the other to allow sample boat entry. Heating was afforded by a resistance-wound furnace. A gage was fixed to the gas entrance line for pressure measurements. For each experiment some 5 to 15 g of uranium dioxide were placed in a tared 347 stainless steel boat which was placed in the center of the reactor. The front flange was then secured, and the reactor evacuated and flushed once with oxygen prior to final pressurizing. The variables of temperature, oxygen pressure and time of reaction were checked to determine the optimum conditions for conversion to uranium trioxide.

The experimental procedure used when nitric acid vapor was the oxidizing agent was as follows: A sample of uranium dioxide weighing 5 to 15 g was placed in a ceramic boat which was then positioned in the center of a Pyrex reaction tube heated by a resistance furnace. Vapors from a constant boiling solution of nitric acid were passed over the uranium dioxide for various times and at various temperatures.

It may be observed from the data of Experiments 119 to 123 in Table 15 that generally poor results were obtained when high-pressure oxygen reactions were used for the conversion of uranium dioxide to uranium trioxide. From the data it appears that the time of reaction is not as important as the oxygen pressure and that pressures in excess of 25 atmospheres will probably be needed for complete conversion. In Experiments 126 and 131, nitrogen dioxide was added in addition to oxygen. Quite

⁶Sheft, I., Fried, S., and Davidson, N., J. Am. Chem. Soc., 72, 2172 (1950).

⁷Flook, E. R., U. S. Patent 2,735,745.

Table 15

CONVERSION OF URANIUM DIOXIDE TO URANIUM TRIOXIDE

Experiment 130 was run with a flow system of equal volumes of O_2 and NO_2 . Experiments 134 to 142 inclusive were run with a flow of nitric acid vapors over the sample.

Expt No.	Initial Sample Weight (g)	Temperature (C)	Time (hr)	Initial Pressure (mm)		Fraction Converted to UO_3^a	Chemical Analysis (%)		
				O_2	NO_2		U^{+4}	U^{+6}	NO_3^-
119	5.0006	600	19.5	4000	-	0.53	-	-	-
121	5.0075	600	18.5	5000	-	0.57	-	-	-
122	5.0002	600	72	5000	-	0.58	-	-	-
123	5.0000	600	16.5	6000	-	0.59	6.2	83.0	-
126	5.0000	600	5.5	5000	800	0.57	3.0	-	0.005
131	5.0000	600	16.0	5000	1000	0.87	1.7	-	0.002
130	5.0006	450	5.0	-	-	0.26	-	-	-
134	5.0105	425	1.67	-	-	^b	0.2	79.6	1.05
140	7.3278	400	0.42	-	-	0.77	-	-	-
141	6.9235	350	0.42	-	-	0.50	-	-	-
142	5.5339	350	1	-	-	0.94	0.3	83.0	0.10
138	10.9539	290	3	-	-	0.76	-	-	-

^aFraction U_3O_8 converted to UO_3 , assuming 100 per cent conversion of UO_2 to U_3O_8 .

^bCalculated fraction converted was 1.18; excess due to nitrate in the sample.

favorable results were obtained. However, even when using nitrogen dioxide, it was apparent that much longer reaction times and higher gaseous pressures were needed for total conversion.

In Experiments 134 to 142, in which nitric acid vapors were used for the oxidation, excellent conversion to uranium trioxide was obtained. For reasonable reaction times (e.g., one hour or less), temperatures around 400 C were needed. In Experiment 134 the weight gain in excess of theoretical requirements was exactly equivalent to that amount of nitrate found in the sample. This apparently indicates that one might expect some nitrate formation in the sample if the reaction were allowed to proceed for a long period of time. As might be anticipated, lower temperatures required much longer reaction times for complete conversion.

The apparent success in using nitric acid vapors to convert the uranium dioxide to uranium trioxide suggested that an experiment be done using a pellet of arc-fused uranium dioxide as the sample. Pellets of this type are somewhat similar to the type of material that will be obtained from power reactors for reprocessing. Complete conversion was

obtained in 65 minutes at 375 C. The following data indicated that disintegration of the pellet was quite extensive, 90 per cent of the material being -325 mesh:

<u>Mesh</u>	<u>% of Material</u>
+140	4.25
+200	4.98
+325	1.17
-325	89.5

One additional experiment was done to test the action of nitric acid vapors on uranium tetrafluoride at 350 C. On termination of the experiment the deep orange color of the surface particles indicated, visually at least, that favorable conversion had taken place. Investigation of the sample disclosed that conversion to uranium trioxide was restricted solely to the surface particles. The underlying material was very dark in color, resembling somewhat the appearance of U_3O_8 . The sample had gained 7 mg in weight, whereas conversion to uranium trioxide would have resulted in a theoretical weight loss of 184 mg.

2. Engineering-scale Studies (W. J. Mecham, A. A. Jonke)

a. Direct Fluorination of Uranium Dioxide Fuels (J. D. Gabor, J. Wehrle, J. Gates, A. Rashinskas)

Uranium dioxide is a fuel in many current reactors and, therefore, a recovery process based on direct fluorination is of interest. The dense pelleted fuel material has been shown in previous reports (ANL-6101, page 118 and ANL-6145, page 103) to be capable of fluorination at practical rates. Preliminary pilot plant scale work has been directed toward the means of controlling the reaction and removing the large amount of heat evolved. Although dense pellets of the kind proposed for several nuclear reactors are too large to be fluidized directly, the use of an inert fluidizable material to cover and to fill the void spaces of a packed bed of pellets has been studied to achieve some of the advantages of fluidization for solid-gas reactions, particularly with respect to the removal of heat.

In the previous report (ANL-6145, page 103), a bed of 1-cm cylindrical dense uranium dioxide pellets was submerged in a magnesium fluoride fluid bed and fluorinated in a three-inch reactor at 500 C at concentrations of up to 30 per cent fluorine in nitrogen. Negligible fines were produced with a three-inch pellet bed under the conditions used, although substantial fines were found in deeper beds. Uranyl fluoride was identified as the major compound in the fines. The reaction rate was found to be

directly proportional to fluorine concentration. The concentration of unreacted fluorine in the off-gas decreased approximately exponentially with bed height, with corresponding increase in overall fluorine efficiency. The formation of solid intermediate uranium compounds was observed in the case of pellet beds deeper than three inches, apparently as a result of reaction between uranium hexafluoride and uranium dioxide in the upper part of the bed.

Continuing work is directed toward optimized process control for deeper pellet beds. Process variables are temperature, fluorine concentration, bed height, particle size, and gas rate. In the present period, an additional run was made at a lower temperature with a nine-inch pellet bed submerged in a much deeper inert fluid bed to retain the fines. In addition, the construction of another fluid-bed reactor system with forced air cooling to permit higher heat removal associated with deeper beds and higher fluorine concentration continued.

In this additional run (UOF-14, Table 16), a nine-inch pellet bed was submerged in a 60-inch deep bed of 60 to 100 mesh magnesium fluoride at 400 C. The general arrangement was that used previously (see Figure 31, ANL-6145, page 104). The deeper fluid bed was designed to retain the fines. The lower temperatures were expected to reduce the fluorine utilization and prevent the reaction between hexafluoride and dioxide. In a preliminary test, it was found that the ambient convective cooling of the present reactor was inadequate to maintain the desired temperature with an inlet fluorine concentration of 30 per cent. A fluorine inlet concentration of 20 per cent, however, was satisfactory at 400 ± 25 C during the run. The gas throughput of 0.5 scfm was the same as used previously. The conditions and results for Run UOF-14 are summarized in Table 16. Data for the most similar previous run, UOF-11, are also shown in the table for comparison.

The following conclusions can be drawn from the data in Table 16:

1. The uranium hexafluoride collection rate at 400 C was only about one-third that at 500 C, due to reduced reaction rate at the lower temperature.
2. The total amount of uranium fines (chiefly uranyl fluoride) was about 40 per cent higher at 400 C than at 500 C. This is attributed to the lower rate of reaction of uranyl fluoride to form uranium hexafluoride.
3. The amount of fines entrained into the filter with the deeper magnesium fluoride bed (UOF-14) was only about one-half of that for the smaller bed (UOF-11). This effect, in spite of the greater total fines in Run UOF-14, is believed to be due to the ability of the

deeper bed of magnesium fluoride to retain fines. In other respects, the two runs showed similar performances. Further studies are planned over wider ranges of conditions.

Table 16

RESULTS OF URANIUM DIOXIDE FLUORINATION RUNS

Pressure:	1 atm	
Total Gas Velocity:	0.5 scfm	
Equipment:	3-inch diameter reactor	
Inert Fluid Bed:	60 to 100 mesh (approx) MgF_2	
Inlet F_2 conc:	20 %	
UO_2 bed ht:	9 inches	
Run Time.	1.5 hr	

<u>Run Number</u>	<u>UOF-14</u>	<u>UOF-11</u>
Reaction temperature, C	400	500
MgF_2 bed ht, inches	60	18
Material charged, g		
UO_2 pellets	5244	5262
MgF_2	8541	2026
fluorine	313	377
Material at end, g		
UO_2 pellets residue ^a	3581	3696
MgF_2 phase ^b	9925	2898
UF_6 collected	207	637
filter fines	114	210
Total uranium fines ^c	1498	1082
F_2 utilization to form UO_2F_2 fines	~ 60%	~ 35%
F_2 utilization to form UF_6	21%	55%

^aBed material held on $\frac{1}{4}$ -inch screen.

^bBed material through $\frac{1}{4}$ -inch screen, includes uranium fines.

^cTotal material through $\frac{1}{4}$ -inch screen less MgF_2 charged.

B. Direct Fluorination Process for Enriched Uranium-Zirconium Alloy Fuels

(N. Levitz, A. A. Jonke)

A Direct Fluorination Process is being studied for the recovery of uranium from zirconium-based alloy fuels. The process may involve one of the following schemes, each of which may be accomplished in a single vessel: (1) reaction of the fuel with a mixture of hydrogen chloride and hydrogen fluoride followed by fluorination of the residue, (2) reaction of the fuel with hydrogen chloride to separate the bulk of the zirconium from the uranium as the volatile tetrachloride, followed by reaction with hydrogen fluoride to trap the zirconium as the solid tetrafluoride, followed by fluorination of the residue, or (3) direct fluorination using elemental fluorine. Preliminary experiments designed to permit evaluation of the best route are now in progress. The reactions are being carried out with the elements submerged in a fluidized bed of inert granular material (calcium fluoride now in use) which serves as heat transfer medium.

Preliminary work reported previously (ANL-6145, page 119) indicated rates of penetration of Zircaloy of 15 mils/hr and greater could be achieved in a 4-hour period at 540 C with 11 volume per cent hydrogen chloride in hydrogen fluoride. The test specimens were Zircaloy coupons autoclaved in steam at 350 C for 4 days to provide an oxide coating.

1. Direct Hydrofluorination of Zirconium Alloys
(J. Barghusen, N. Levitz, J. Kincinas, D. Raue)

Experimental work was continued on the direct hydrofluorination of zirconium alloys in an inert fluidized bed using anhydrous mixtures of hydrogen fluoride and hydrogen chloride gases. The hydrogen chloride functions as a catalyst, probably through the formation of zirconium tetrachloride as an intermediate. An alternate 2-reaction zone scheme is also being studied, in which the initial contact is with hydrogen chloride diluted with nitrogen. The volatile zirconium tetrachloride is then converted to the solid tetrafluoride with hydrogen fluoride which is admitted in the upper part of the fluidized bed

a. Runs with Hydrogen Chloride-Hydrogen Fluoride Gas Mixture

Several types of material were studied, including autoclaved Zircaloy coupons, uranium-zirconium alloy coupons, 30-mil thick Zircaloy tubing containing sintered uranium dioxide pellets, 10-plate welded sections of uranium-zirconium alloy (1 75 x 2.62 x 7 inches overall) and a stainless steel coupon. Experiments were conducted in both a 1½-inch diameter reactor and a 6-inch diameter unit. Calcium fluoride (-60, +325 mesh) was used as the fluid-bed heat transfer medium in all cases.

Three exploratory runs lasting 4 to 6 hours were made in the $1\frac{1}{2}$ -inch diameter column at a bed temperature of 505 C. The gas stream contained 9 volume per cent hydrogen chloride in hydrogen fluoride in two cases. In the third case, the stream contained 5 volume per cent hydrogen chloride, 51 volume per cent nitrogen diluent, and 44 per cent hydrogen fluoride. The small metal specimens were suspended in the bed in a nichrome wire basket.

Results (see Table 17) indicated the 1.5 weight per cent uranium-zirconium alloy is consumed as readily as the oxidized (steam-autoclaved) Zircaloy specimens (Runs 4 and 5, respectively). The average penetration rate was at least 11 mils per hour. The oxide layer produced by autoclaving did not appear to inhibit the reaction rate. The addition of an inert gas diluent (51 per cent nitrogen) in Run 4 did not markedly affect the reaction rate. The Zircaloy tubing was completely corroded (Run 6), while the $\frac{1}{2}$ -inch diameter sintered uranium pellets contained within the tubing were unaffected by the gases. This step thus can serve as a decladding procedure for the power reactor oxide fuels (see section C).

Table 17

SUMMARY OF EXPLORATORY RUNS ON DIRECT HYDROFLUORINATION
OF ZIRCONIUM ALLOYS IN A FLUIDIZED BED

Equipment: $1\frac{1}{2}$ -inch diameter nickel reactor
Fluid-Bed: -60, +325 mesh calcium fluoride
Bed Temperature: 505 C

Run Number	Duration of Run (hr)	Gas Velocity (ft/sec)	Nominal Inlet Gas Composition		Alloy Type	Results
			HF (v/o)	HCl (v/o)		
4	4	0.42	44 ^a	5 ^a	Autoclaved Zircaloy ($\frac{1}{16}$ -inch thick)	No metal detected in product flakes ^b
5	4	0.33	91	9	1.5 w/o U-Zr ($\frac{3}{32}$ -inch thick)	Coupon completely corroded ^b
6	6	0.34	91	9	30-mil thick Zir- caloy tubing contain- ing UO ₂ pellets	Tubing completely reacted; UO ₂ visually unaffected

^aGas stream contained 51 volume per cent nitrogen diluent.

^bPenetration rate greater than 11 mils per hour.

No change in weight or dimensions of a 304 stainless steel coupon occurred in 4 hours at 510 C using a 26 volume per cent hydrogen chloride-hydrogen fluoride mixture. The use of fluorine directly on stainless steel is being considered as a decladding medium.

Ten-plate welded sections of a 1.5 weight per cent uranium-zirconium alloy were used in scale-up of the hydrogen chloride-hydrogen fluoride reaction studies. The assemblies consisted of $\frac{3}{32}$ -inch thick plates with a $\frac{5}{64}$ -inch spacing between plates. The welded side plates were $\frac{3}{16}$ -inch thick (see Figure 22). The subassembly was placed within the fluid-bed reactor on a tripod which rested on the gas distributor plate; the bottom of the fuel alloy was about 2.5 inches above the plate.

FIGURE 22

TEN-PLATE SECTION OF URANIUM-ZIRCONIUM ALLOY
BEFORE AND AFTER ATTACK BY
HYDROGEN CHLORIDE - HYDROGEN FLUORIDE
GAS MIXTURE

Run No:	ZHF-8
Temp:	500 C
Time:	3.5 hr
Gas Mixture:	15 v/o HCl - 85 v/o HF
Overall Dimensions:	$1\frac{3}{4} \times 2\frac{5}{8} \times 7$ inches
Alloy:	1.5 w/o Uranium in Zirconium

A one-inch mesh nichrome wire screen was placed just below the sub-assembly to retain large flakes of corrosion products in the reaction zone. Mixtures of hydrogen chloride and hydrogen fluoride gases containing from 9 to 41 volume per cent hydrogen chloride were tested. Neither gas was preheated except for Runs ZHF-15 and 16.

The results (see Table 18) indicate that the 10-plate, 1.5 per cent uranium-zirconium subassembly may be completely corroded under the proper conditions. Almost complete reaction was achieved in 11.8 hours using a gas mixture containing 10 volume per cent hydrogen chloride at 450 C (combination of Runs 15 and 16), while 47 per cent conversion was achieved in 7.5 hours (combination of Runs 8 and 9) with 12 to 15 volume per cent hydrogen chloride at 500 C.

Table 18

SUMMARY OF PILOT-SCALE RUNS ON DIRECT HYDROFLUORINATION
OF ZIRCONIUM ALLOYS IN A FLUIDIZED BED

Equipment:	6-inch diameter Inconel reactor
Bed:	calcium fluoride -60, +325 mesh; 15 kilograms
Fuel Specimen:	2-kg section of a welded, 10-plate, 1.5 per cent uranium-zirconium alloy subassembly, 1.75×2.625×7 inches overall
Superficial Gas Velocity:	0.45 ft sec inlet at column conditions

Run Number	Duration of Run (hr)	Temperature (C)	Nominal Inlet Gas Composition		Results
			HF (v, o)	HCl (v, o)	
ZHF-8 ^d	3.5	500	85	15	25 per cent of subassembly reacted
ZHF-9	4.0	500	88	12	47 ^a per cent of subassembly reacted
ZHF-13	5.3	405	59	41	No reaction
ZHF-14	4.6	480	63	37	No reaction
ZHF-15 ^d	5.3	450	90	10	~50 per cent of subassembly reacted
ZHF-16	6.5	450	91	9	~95 ^b per cent of subassembly reacted
ZHF-11 ^c	4.0	450	None	28 ^c	No reaction
ZHF-12	4.0	460	None	44 ^c	~12 per cent of subassembly reacted
ZHF-17 ^d	4.5	380	None	10 ^c	No reaction

^aCumulative conversion for 7.5 hours (Runs 8 and 9).

^bCumulative conversion for 11.8 hours (Runs 15 and 16).

^cTwo-zone process: hydrogen chloride diluted with nitrogen contacted subassembly. 1.5 moles hydrogen fluoride per mol hydrogen chloride introduced 4 inches above subassembly.

^dNew subassembly.

Higher hydrogen chloride concentrations in the reacting gas (~40 volume per cent used in Runs 13 and 14) produced no corrosion of the subassembly. This unexpected result was corroborated in laboratory experiments (see Figure 25), page 111 and data on page 110). The very low reaction rate with high hydrogen chloride concentrations has not yet been explained.

Chemical analyses of both the scale adhering to the residual metal and the calcium fluoride bed indicate that no chloride is retained within the zirconium tetrafluoride or the fluid bed. Evidently, the conversion of zirconium tetrachloride to zirconium tetrafluoride is rapid and complete.

The hydrofluorination of a subassembly proceeds by first producing a large quantity of scale that adheres to the metal surface and heavily plugs the interstices between the plates. Considerable swelling of the subassembly occurs perpendicular to the plates. Figure 22 shows a subassembly after 3.5 hours of attack at 500 C (Run 8), along with an unreacted section. Upon further corrosion, the plates may fall away, and various sized pieces (up to several inches in length) of scale form. In the existing equipment, the scale flakes collected on the nichrome screen supporting the assembly. This accumulation of scale restricted the turbulent mixing of the fluidized bed in this zone. This was indicated by the temperature spread which ranged from 20 to 100 degrees between the upper and lower portions of the bed. Normal differences are near 5 degrees. It may be feasible to omit the support screen to allow the reaction product to collect at the bottom of the bed.

b. Two-zone System

Since reaction of zirconium-uranium alloy with a mixture of hydrogen chloride and hydrogen fluoride gases produces a considerable quantity of scale which is not fluidized, a "two-zone" modification of the process was investigated. Hydrogen chloride concentrations of from 10 to 44 volume per cent in nitrogen were introduced at the bottom of the bed to contact the element. Approximately 50 per cent excess hydrogen fluoride was introduced 4 inches above the top of the element. Eight to ten inches of bed was provided above the hydrogen fluoride inlet to insure reasonable contact time for the tetrachloride conversion to tetrafluoride.

Essentially no reaction of the subassemblies occurred during Runs ZHF-11, 12 and 17 (see Table 18). The poor conversion of the subassembly is probably due to backmixing of the hydrogen fluoride gas and, as a consequence, the gas mixture in the vicinity of the subassembly was low in hydrogen fluoride and rich in hydrogen chloride. Although zirconium

reacts rapidly with pure hydrogen chloride gas, the presence of small amounts of hydrogen fluoride have been found to inhibit the reaction (see Figure 25, page 111). Considerable backmixing can be expected to occur in fluidized beds,⁸ and the concentration of hydrogen fluoride 4 to 8 inches below the inlet port might be as much as 20 per cent of the concentration just above the inlet port. Future studies will be directed toward preventing this backmixing, either through the use of baffles or through the use of a 2-stage reactor.

C. Metal Fluorination Studies (J. Fischer)

The conversion of zirconium to zirconium tetrafluoride has been considered for the decladding of Zircaloy-clad power reactor fuel elements and for processing of zirconium-uranium alloy fuels. The use of hydrogen fluoride gas alone for this purpose was not initially promising because of slow reactivity. It was discovered (see page 103) that a ten volume per cent (17 weight per cent) addition of hydrogen chloride to the hydrogen fluoride accelerates the reaction. The role of the hydrogen chloride in the reaction appears to be catalytic in nature. Laboratory experiments were performed to establish reaction rates under various conditions. During the course of the experimental work, it was found that the enhancing effect on the reaction was restricted to the approximate concentration range from 10 to 30 weight per cent hydrogen chloride at 400 C.

Reaction of Zircaloy-2 with Anhydrous Hydrogen Fluoride-Hydrogen Chloride Mixtures (R. L. Jarry, W. H. Gunther)

The reaction between Zircaloy-2 and hydrogen fluoride-hydrogen chloride mixtures was performed in a horizontal nickel tube reactor. The remaining system was comprised of a resistance furnace and flow metering devices. A thermal flow meter was used to measure the hydrogen fluoride flow and a rotameter was used for the hydrogen chloride. All of the lines were heated with resistance wire. The thermal flow meter base and adjacent lines were heated to approximately 60 C to prevent condensation of hydrogen fluoride. The last two-foot section of tubing located at the inlet of the reactor was heated to 125 C to serve as a preheater. The effluent was vented to the atmosphere. The hydrogen fluoride flow was calibrated by absorption of the gas in dilute sodium hydroxide solution which was then titrated with acid. In order to calibrate the hydrogen chloride flow, the rotameter was checked with nitrogen using a wet test meter, and the values obtained were corrected for hydrogen chloride flow by the relation of their

⁸Zenz, Frederick A. and Othmer, Donald F., Fluidization and Fluid-Particle Systems, Reinhold Publishing Corporation, New York (1960), pp. 300-303.

molecular weights. Subsequent checks of the flow by analyses of the gases absorbed in dilute sodium hydroxide confirmed the calibration. Both of the gases used were commercial grade.

Zircaloy-2 coupons, 1.1 x 3.8 x 0.14 cm and 1.1 x 1.4 x 0.14 cm, were oxidized in water at 350 C for a period of one week. These oxidized coupons were prepared by W. Ruther of the Metallurgy Division, who also supplied other oxidized Zircaloy-2 coupons, 1.3 x 1.9 x 0.3 cm, produced under the same conditions. The estimated oxide coating was 20 milligrams per square decimeter.

Initial runs were made with a total flow of the mixed gases of 150 ml/min with approximately 17 weight per cent hydrogen chloride. The temperature was varied over the range from 300 to 500 C. Table 19 summarizes the results of the experiments on oxidized Zircaloy-2, and Figures 23 and 24 are plots of the data. The reaction proceeded readily above 350 C. The product formed in these runs was not protective in nature, and in the experiments in which high conversion to zirconium tetrafluoride was obtained, the product was granular in appearance.

Table 19

THE REACTION BETWEEN OXIDIZED ZIRCALOY-2 AND
HYDROGEN FLUORIDE - HYDROGEN CHLORIDE MIXTURES

Flow: Combined, 150 ml min
Gas Mixture: 83 w/o HF, 17 w/o HCl

Exp. No.	Sample Weight (g)	Temp (C)	Time (hr)	Fraction Zr Converted to ZrF_4	Penetration ^a (mils/hr)
(A) Oxidized Zircaloy-2 coupons, 1.1 x 3.8 x 0.16 cm, oxidized in water 7 days at 350 C.					
Z-28	3.9161	300	3	0.019	0.2
Z-30	4.2977	350	3	0.096	1.0
Z-32	3.6599	375	3	0.97	9.7
Z-29	4.1000	400	3	0.97	9.7
(B) Oxidized Zircaloy-2 coupons, 1.3 x 1.9 x 0.3 cm, oxidized in water 7 days at 350 C.					
Zy-20	4.5542	500	0.5	0.27	32
Zy-22	4.4479	500	1.5	0.56	22
Zy-21	4.6599	500	3.0	0.85	17
Zy-23	4.4257	500	3.5	0.91 ^c	16
Zy-24	4.8491	500	4.3	0.91 ^c	12
Zy-25 ^b	3.7566	500	3.0	0.049	1.0

^aBased on half-thicknesses of 30 and 60 mils for (A) and (B), respectively, and ZrF_4 as the product.

^b100% HF.

^cIt is not believed that the reaction stops at 91 per cent converted, however, if serious practical use of this reaction is anticipated, longer experiments will be carried out.

FIGURE 23
EFFECT OF TEMPERATURE ON THE REACTION OF OXIDIZED ZIRCALLOY-2 WITH A
MIXTURE OF HYDROGEN FLUORIDE - HYDROGEN CHLORIDE

FIGURE 24
EFFECT OF TIME ON THE REACTION BETWEEN OXIDIZED ZIRCALLOY-2 AND A
MIXTURE OF HYDROGEN FLUORIDE - HYDROGEN CHLORIDE

As a check on the catalytic action of the hydrogen chloride, analyses were made for zirconium and chloride content on the products from a series of runs in the temperature range from 375 to 500 C. The results of these analyses are shown in Table 20. These analyses showed the absence of any quantity of chloride. The zirconium material balance calculated from these analytical results, corrected for the tin content in the Zircaloy-2 samples, was within the precision of the analytical method, the average material balance being 98.6 per cent. This indicated that there was no loss of metal as the tetrachloride and that the hydrogen chloride was acting as a catalyst. Considering the volatility of zirconium tetrachloride at temperatures up to 500 C, it must be immediately reacted as formed at the metal surface.

Table 20

ANALYSIS OF THE RESIDUES FROM THE REACTION OF ZIRCALOY-2 WITH
A MIXTURE OF HYDROGEN FLUORIDE AND HYDROGEN CHLORIDE

Total Flow: 150 ml/min
Gas Mixture: 83 w/o HF - 17 w/o HCl
Material: Zircaloy-2 oxidized 7 days in water at 350 C

Exp. No.	Reaction Temp (C)	Reaction Time (hr)	Fraction Converted	F/Zr Atomic Ratio ^{b,c}	Initial wt ^a Zir- conium in Sample (g)	Material Balance ^b (%)
Zy-22	500	1.5	0.56	4.61	4.381	99.8
Zy-21	500	3.0	0.85	4.55	4.5900	98.9
Zy-23	500	3.5	0.91	4.29	4.3593	98.1
Zy-24	500	4.5	0.91	4.23	4.7764	98.2
Z-32	375	3.0	0.97	4.16	3.6599	97.7
Z-26	400	3.0	0.97	4.06	4.0719	97.7
Z-29	400	3.0	0.97	4.07	4.1000	99.6

^aThe zirconium content of the samples is based on an assumed 1.5 per cent tin content.

^bAtom per cent of Cl⁻ after reaction was 0.1 or less except in Experiment No. Zy-21, for which it was 0.4 atom per cent.

^cCorrected for unreacted zirconium.

It was of interest to obtain data at hydrogen chloride concentrations higher and lower than 17 weight per cent. These results are shown in Table 21. The penetration values were based on a 30-mil half thickness and zirconium tetrafluoride as the corrosion product. Lowering the hydrogen chloride concentration to 10 weight per cent for three hours at 400 C gave the same penetration of 9.7 mils/hr as did 17 weight per cent. However, at 6 weight per cent the penetration was only 2.1 mils/hr. Increasing the temperature to 500 C with 6 weight per cent resulted in a penetration of 9.6 mils/hr. Raising the hydrogen chloride concentration above 17 weight per cent gave unexpected results. As shown in Table 21,

beyond a concentration of approximately 32 weight per cent, the reaction was inhibited. These data are shown in Figure 25, in which the penetration in mils/hr is plotted versus the weight per cent of hydrogen chloride. It is apparent that the catalytic nature of the hydrogen chloride at 400 C is effective over a limited concentration range of hydrogen chloride.

Table 21

EFFECT OF HYDROGEN CHLORIDE CONCENTRATION
ON THE REACTION

Time: 3 hours
Material: Zircaloy-2 oxidized in water
at 350 C for 7 days
Flow Combined: 150 ml/min
Area of Coupons: 2.9 to 10.5 sq cm

w/o HCl	Penetration (mils/hr) ^a at Indicated Temperature			
	300 C	375 C	400 C	500 C
0			0.6	
6			2.1	9.6
10			9.7	
17			9.7	
25			9.2	
32			9.5	
39			0.3	
56	0.1		0.2	
85			0.02	
100		~10 ^b		

^aThe penetration rate is based on a half-thickness of 30 mils and zirconium tetrafluoride as the product.

^bThe penetration rate is based on a half-thickness of 30 mils and zirconium tetrachloride as the product.

One experiment, Z-33, was performed in which a 1.2 x 1.1 x 0.14-cm oxidized Zircaloy-2 coupon was exposed at 375 C to 100 per cent hydrogen chloride at a flow of 150 ml/min for 3 hours. Almost complete conversion

to zirconium tetrachloride occurred. The product had sublimed out of the reaction zone to the cooler parts of the reactor, forming a ring which nearly plugged the reactor. A small amount of a reddish material remained in the shape of the original coupon; this turned light gray in color when exposed for a few minutes to the atmosphere.

Table 22 contains corrosion data obtained on 304 stainless steel coupons, 1 x 5 x 0.16 cm in size, which were exposed during some of the runs. The experiment numbers correspond to the matching ones in Table 19.

Table 22

CORROSION OF 304 STAINLESS STEEL IN HYDROGEN FLUORIDE CONTAINING HYDROGEN CHLORIDE

Flow: combined, 150 ml/min
Gas Mixture: 83 w/o hydrogen fluoride,
17 w/o hydrogen chloride
Reaction Time: 3 hours

Experiment No.	Temp (C)	Penetration ^a (mils/hr)
SS-28	300	0.01
SS-30	350	0.08
SS-32	375	0.07

^aBased on coupon half-thickness of 30 mils and ferrous fluoride as the corrosion product.

D. ADF Process Development for Enriched Uranium-Zirconium Fuel
(N. Levitz, A. A. Jonke)

The ADF Process, a general scheme aimed at recovery of uranium from irradiated fuels, involves the dissolution of the fuel in aqueous acids, conversion of the solution to dry granular solids, and fluorination of the solid to volatilize and separate the uranium as the hexafluoride. Initial process application was directed toward recovery of enriched uranium from zirconium-based fuels. Results of recent fluorination studies which were performed in static-bed reactors are presented below. A topical report covering the ADF Process development work is in preparation.

1. Separation of Uranium from Uranium-Zirconium Fluoride Mixtures by Fluorination
(E. Carls, L. Marek)

The planned experimental fluorination studies on the removal of uranium from mixtures of uranium-zirconium fluorides prepared in the fluid-bed dryer were concluded at the end of the last quarter and the final results are presented in Table 23. These experiments were conducted as static-bed tests at temperatures over 650 C in both the 6-inch diameter and the 2-inch diameter, deep-bed (6-foot tall) reactor, the latter designed to determine the effect of bed height on uranium removal. Previous results (ANL-6101, page 99) showed residual uranium values ranging from 0.018 down to 0.002 per cent, representing uranium removals approximating 99 per cent.

Operating conditions for both reactors were similar. Bed charges consisted of 2.5 to about 10 kg of dryer products. Run periods ranged from 5.8 to 9.9 hours, with periods at which the temperature was above 650 C ranging from 1.5 to 7.5 hours. Fluorine gas (100 per cent) was introduced at temperatures between 500 and 600 C. Gas velocities were 0.05 and 0.10 ft/sec. Since the oxygen in the dryer products was the major consumer of fluorine (>7 times that required for uranium) the fluorine requirements were based on that constituent. Fluorine excesses ranged from about 1.8 to 7.9 times the stoichiometric requirements. The dryer products were prepared at 240 and 385 C using dilute (1.2 M zirconium), low-acid feed, and intermediate (2.8 M zirconium), high-acid feed, respectively. These were hydrofluorinated at 450 C to reduce their oxygen and water contents before fluorination. Previous static-bed runs were made with product prepared at 300 C from high-acid feed containing 3.6 M zirconium.

In order to evaluate the results of a run, grab samples taken from several portions of the caked (sintered) final bed and designated as top, middle, and bottom were analyzed for uranium. Analyses of an entire bed which was crushed and blended agreed well with the grab samples (see data for Run UZr-106 given in Table 23).

Table 23

PILOT PLANT FIXED-BED FLUORINATION STUDIES

Starting Materials:^a ZCP-74 Dryer Product: 1.08 w/o uranium
1.24 w/o oxygen

ZCP-76 Dryer Product: 0.56 w/o uranium
0.63 w/o oxygen

Inlet Gas: 100 per cent F₂

Temp of F₂ Introduction: 500 to 600 C

Run No.	Starting Material ^c	Wt of Charge (kg)	Total F ₂ Used (scf)	Superficial Velocity through Reactor (ft/sec)	Mole Ratio F ₂ /O ₂	Duration of Run (hr)			Ratio of Bed Height Before and After ^d	Portion of Cake Sampled	Ratio of Residual to Initial Uranium Content
						Total	With F ₂	Above 650 C			
UZr-104	ZCP-74	10.0	10.8	0.05	1.8	5.8	2.8	2.3	-	Top	0.071
										Middle	0.012
										Bottom	0.031
UZr-106	ZCP-76	10.0	24.6	0.05	7.8	5.2	2.2	1.5	-	Middle	0.034
										Bottom	0.062
										Composite	0.059
UZr-107 ^b	ZCP-76	4.8	10.1	0.06	~6	9.9	8.1	7.5	$\frac{55}{34}$	Top $\frac{1}{3}$	0.075
										Bottom $\frac{1}{3}$	0.021
UZr-108 ^b	ZCP-76	4.8	9.8	0.10	~6	6.5	4.4	4.0	$\frac{55}{36}$	Top $\frac{1}{3}$	0.057
										Bottom $\frac{1}{3}$	0.041
UZr-109 ^b	ZCP-76	2.4	6.4	0.06	~6	6.6	4.6	4.0	$\frac{28}{18}$	Top $\frac{1}{3}$	0.093

^aIn each case, the dryer product has been hydrofluorinated for 4 hours at 450 C before fluorination.

^bThese runs were made in the 2-inch diameter 6-ft tall reactor; others were made in the 6-inch diameter unit.

^cDryer runs described in ANL-6145, page 115.

^dBed heights decreased during runs due to sintering of zirconium tetrafluoride.

Residual uranium contents were generally slightly higher than those previously reported, about 0.03 to 0.05 per cent as compared to 0.02 per cent or less. It is believed the difference may be attributable, at least in part, to the variation in characteristics of the dryer product. These residual uranium values would represent losses of about 5 per cent for a fuel alloy containing 2 per cent uranium.

The runs in the 2-inch diameter, 6-foot tall reactor indicated bed height had little effect on uranium removal. Beds of $2\frac{1}{2}$ feet and $4\frac{1}{2}$ feet (Runs 107 and 109, respectively) were used as compared to 1-foot deep beds in the 6-inch column. The gas velocity also had little effect in the range from 0.05 to 0.10 ft/sec. The pressure drop across the deep beds was less than three inches of mercury for these velocities. As the runs progressed and the cake formed, the pressure drop decreased. This may have been caused by channeling of the gas and also by the 35 per cent decrease in bed height. A gradient of uranium concentration (as noted in the tabulated values) in the final beds has been evident in most cases, with the higher concentrations being in the portion farthest from the fluorine inlet.

Contact time at the extreme temperatures (>650 C) also seemed to have no noticeable effect (compare Runs 106 and 107 in which high excesses of fluorine were used in periods of 1.5 and 7.5 hours). It was believed, on the basis of earlier small-scale work that the high temperatures were enough to insure quantitative uranium removal; however, it is now evident that on a large scale there are complicating factors involved which make it difficult to remove the last traces of uranium from the zirconium fluoride matrix.

E. Fused Salt Processing of Zirconium-matrix Fuels (W. J. Mecham, A. A. Jonke)

In the fused salt process for recovery of uranium from zirconium-matrix fuel, the alloy is dissolved in the fused salt at 600 to 700 C with a hydrogen fluoride sparge, and then the uranium in the salt is volatilized as the hexafluoride in a fluorine sparge. A pilot plant-scale graphite dissolver-hydrofluorinator has been developed for the first step to avoid corrosion incurred in metal systems. A series of dissolutions in the graphite dissolver of synthetic 10-plate zirconium-uranium fuel elements has been carried out according to a semicontinuous flowsheet. Dissolution rates in the sodium fluoride-zirconium fluoride mixture have been as high as 3.4 mg/(min)(sq cm), resulting in a 90 per cent dissolution of the ~90-mil plate assembly in less than five hours. Satisfactory operation of the internal graphite heaters and other components exposed to the molten salt has continued over an accumulated period of about 1600 hours of exposure.

Graphite Dissolver Tests

(R. W. Kessie, W. J. Mecham, J. Gates, R. Kinzler, W. Murphy, A. Rashinskas)

In the present period an additional dissolution (Run A-10) of a synthetic 10-plate zirconium-uranium fuel assembly was carried out in the pilot plant graphite dissolver according to the semicontinuous flowsheet, which calls for partial transfers of salt out of the dissolver and sodium fluoride makeup additions between dissolutions. The objective of these tests is the determination of reproducible processing rates and equipment performance.

In the previous report (ANL-6145, page 120) the procedure and results of four previous dissolutions were described. These previous dissolutions, done in fairly close succession with metal heels remaining, showed some departures from expected high-rate behavior. Elimination of various possible causes of these irregularities resulted in a smoother and more rapid dissolution, as described below.

Dissolver pressure buildup previously encountered (in Run A9) was traced to the off-gas adsorption bed. Off-gas passed through this bed directly upon leaving the dissolver; the bed was packed with $\frac{3}{16}$ -inch sodium fluoride pellets. The purpose of the bed was primarily to adsorb or desublime zirconium tetrafluoride or other volatile fluorides. (In the case of hot operation, the adsorption of fission product niobium pentafluoride would be a major function.) The 10-mesh screen used as a bed support and the bottom one-half inch of the pellet bed had plugged with powder deposit. Approximately 4000 lb of hydrogen fluoride had been passed through the fused salt to produce this plug. The adsorber was recharged with a bed support of one-half inch raschig rings in order to lengthen the period between adsorber changes. It appears that a separate, easily cleaned baffle chamber ahead of the bed would be desirable in continuous processing.

Because reduction of metal impurities during similar dissolutions was reported⁹ as possibly affecting dissolution rates and off-gas plugging, a test was made of deposits formed on a zirconium rod in the fused salt. Analysis of deposits on the zirconium rod and of off-gas deposits in the adsorber are summarized in Table 24. The results indicate no significant concentration of salt impurities, such as iron, nickel, or chromium. However, in the reported case, impurity levels in the salt were much higher, since a nickel alloy (INOR-8) dissolver was used and dissolution of Zircaloy elements rather than zirconium was carried out. A subsequent dissolution is planned with higher impurity levels corresponding to Zircaloy-2 to check this effect.

⁹ORNL Status and Progress Report for January 1960, ORNL-2906, (Unclassified AEC Report) and Chemical Technology Division Monthly Report, ORNL-CF-60-1-112 (January 1960).

Table 24

IMPURITY DISTRIBUTION IN FUSED SALT DISSOLVER
(Run A-10)

Location of Impurity	Impurity (wt per cent)		
	Fe	Ni	Cu
Molten Salt	0.03	<0.01	<0.01
Adsorber Dust	0.1	0.01	<0.01
Deposited on Zr Metal in Salt	0.02	<0.005	<0.005

Preparatory to making Run A-10, sparging of the salt with hydrogen fluoride was continued beyond the point at which any hydrogen was evolved, in order to insure starting without metal pieces in the dissolver. Sodium fluoride was also charged to the dissolver to restore salt composition to approximately forty mole per cent. A visual check of the salt sparging action eliminated the possibility of any substantial deterioration of the sparge gas distributor itself. Run A-10 was then carried out by the regular procedure. The course of dissolution is shown in detail by plots in Figure 26 of the off-gas evolution and the hydrogen content of the off-gas.

The introduction of hydrogen fluoride was taken as the start of the run; the fuel element had been charged less than an hour before. Both the total off-gas volume and the hydrogen concentration in the off-gas rose rapidly at the start. The rate of dissolution, indicated by the slope of the off-gas line, did not fall off appreciably until 90 per cent of the metal was dissolved in 4.95 hr. During this period, the hydrogen concentration in the off-gas was about 90 per cent. The approach of the off-gas line to the "100 per cent dissolution" line indicates the degree of completeness of the dissolution. The slope of this line corresponds to the 2.5 cu ft/hr of argon purge gas introduced during the dissolution.

In the period marked A, in Figure 26, the hydrogen fluoride was shut off for a hydrogen fluoride boiler change, after which the hydrogen fluoride sparge was resumed. In period B, 1.4 cu ft of argon was used to purge the volume of the off-gas scrubber. The hydrogen concentration dropped from its plateau after the 90 per cent dissolution point had been reached. The minimum in the "per cent H_2 " curve at about 8.8 hr was due to the effects of boiler change and bubbler purge. In the period from 10 to 12 hours, about 2.5 cu ft/hr of hydrogen was still leaving the dissolver system. At 13 hours, this concentration was dropping markedly, indicating that the dissolution of the last small portions of zirconium had been completed.

In Run A-10, no unusual variations of dissolution occurred during the run, and the overall rate was higher than any observed previously. The lack of variations of rate during the run is believed to be normal, and this effect in previous runs was probably due to small pieces of metal remaining from the preceding run and blocking gas and salt entry into the fuel element channels. The overall higher dissolution rate may be associated with the smooth dissolution and with the somewhat higher sodium fluoride content of the salt. A comparison of results in recent runs is shown in Table 25. During operation salt samples were taken in copper tubes through an air lock device and were analyzed volumetrically.

Results obtained in the present series of dissolutions indicate that this type of plate fuel element is dissolved rapidly up to about the 90 per cent point. This is so because the interior surfaces of the channels are effectively contacted with salt and sparge gas. Small pieces of the thicker edge sections of the plates require a longer time, and this time would be increased further if the pieces fell to a position of poorer contacting. In semi-continuous operation, while it is desired that successive fuel elements be charged quickly, sufficient time should be allowed beyond the 90 per cent point to reduce residual metal below the amount that may block gas distribution into the channels of a new fuel element. From the present data, it appears that two or three dissolutions per 24-hr day could be completed satisfactorily in semicontinuous operation.

Table 25

DISSOLUTION RATES OF ZIRCONIUM-URANIUM ALLOY
FUEL PLATES IN SODIUM FLUORIDE -
ZIRCONIUM TETRAFLUORIDE SALT MIXTURES

Temperature: 700 C
Sparge Rate: 47 to 53 lb HF/hr

Run	Dissolution Rate ^a		ZrF ₄ in Salt (mol %)	
	[mg/(min)(sq cm)]	(mils/hr)	Initial	Final
A7	2.3	8.6	46.0	48.6
A8	2.3	8.6	43.0	45.8
A9	1.6	5.8	45.8	48.5
A10	3.4	12.5	41.0	44.2

^aRate during major part of dissolution, i.e.,
to 90 per cent dissolution of metal.

The planned program on the fused salt volatility process is nearly completed. A small amount of additional work to demonstrate further the suitability of the graphite dissolver, as a means of avoiding the serious corrosion problem extant in metal systems, is expected to be completed in the next quarter.

F. Conversion of Uranium Hexafluoride to Uranium Dioxide
(I. Knudsen, N. Levitz, M. Jones)

A fluid-bed process for the preparation of uranium dioxide from uranium hexafluoride is being studied for application to the production of ceramic-grade fuel. "Simultaneous" pyrohydrolysis and reduction reactions have been carried out with uranium hexafluoride in the 3-inch diameter Monel reactor in a fluidized bed of uranium dioxide using steam and hydrogen. The newly formed material deposits as a dense coating on the particles of the bed.

The effects of temperature, reactant excess and solids residence time on conversion have been reported (ANL-6145, pages 124 to 128). Excessive amounts of fluoride remained at the higher rates of conversion of uranium hexafluoride. However, additional batch contacting with steam and hydrogen reduced the residual fluoride concentration to acceptable levels (300 ppm). The results of recent pellet fabrication tests on material so treated are included in this report.

The conversion of uranium hexafluoride to uranium dioxide may also be accomplished via two-step processes in which uranyl fluoride or uranium tetrafluoride are formed initially and subsequently converted by hydrogen reduction or steam pyrohydrolysis to the dioxide. These alternate schemes, which would permit optimization of operating conditions for each step for improved conversion and greater throughput, are now being studied. It is planned to explore these alternate methods before concentrating the development work on any specific route.

1. Pyrohydrolysis of Uranium Hexafluoride

Four runs were made in which uranium hexafluoride was reacted with steam at temperatures of 140 to 230 C. Operation was smooth at uranium hexafluoride feed rates from 66 to 118 g/min [115 to 205 lb uranium/(hr)(sq ft reactor cross section)]. These are the highest feed rates used to date. Steam excesses ranged from 400 per cent down to 175 per cent; a superficial velocity of 0.75 ft/sec was maintained with an 18-inch bed height. Individual run conditions are shown in Table 26.

Table 26

SUMMARY OF RUNS ON FLUID-BED PYROHYDROLYSIS OF URANIUM HEXAFLUORIDE TO URANYL FLUORIDE

Equipment:	3-inch diameter Monel Column
Bed Height:	18 inches
Superficial Gas Velocity:	0.75 ft/sec

Run No.	Temp (C)	Average UF ₆ Feed Rate (g/min)	Steam Excess (%)	Run Duration (hr)	Product Surface Area ^a (sq m/g)
39	230	66.5	400	2.75	0.15
40	230	118	175	2.50	0.18
43	200	91	200	1.83	-
44A	140	78	250	1.92	0.42

^a60 to 100 mesh fraction.

The uranyl fluoride deposited as a dense coating on the particles in the bed, similarly to the runs in which both pyrohydrolysis and reduction reactions were carried out simultaneously. For the run at 230 C, the reactor was maintained at temperature entirely by the heat of reaction; operation below 200 C required cooling of the reactor walls. Uranium losses to the off-gas stream amounted to less than 0.01 per cent of the material fed. Surface

area measurements on the run products (60 to 100 mesh fraction) showed increased surface area for the uranyl fluoride formed at the lower temperature, although the values were still quite low, less than 0.2 sq m/g for the material produced at 230 C and about 0.4 sq m/g for that produced at 140 C. The same ratio of surface areas existed after the materials were reduced to the dioxide although the values were about 50 per cent higher (see below).

2. Reduction of Uranyl Fluoride

Three-kilogram batches of the uranyl fluoride prepared in the above step were reduced with hydrogen to the dioxide at temperatures of 550 C and 650 C. A summary of the results is shown in Table 27.

Table 27

SUMMARY OF HYDROGEN REDUCTION RUNS ON URANYL FLUORIDE PREPARED IN FLUIDIZED BEDS

Equipment: 3-inch diameter Monel column

Run No.	UF ₆ Pyro- hydrolysis Temp (C)	UO ₂ F ₂ Reduction		Gas Composition during Reduction		Analytical Results		
		Temp (C)	Duration (hr)	(% H ₂)	(% Steam)	Residual Fluoride (%)	U ⁺⁴ (%)	U ⁺⁶ ^b (%)
41	230	550	4	100	0	7.6	-	-
			6			5.9		
42	230	650	6	100	0	0.53 ^c	-	-
45	140	550	4	100	0	11.0	-	-
		650	2 ^a	67	33	0.035	85.0	1.8
46	140	650	2	67	33	0.12	-	-
			4	67	33	0.023	85.4	2.5
			6	67	33	0.007	84.7	3.1
47	140	650	2	83	17	0.094	-	-
			4½	83	17	0.024	86.2	2.1

^aIn addition to the 4 hours at 550 C.

^bU⁺⁶ determined by difference.

^cResidual fluoride represents uranium tetrafluoride present in the starting material.

The degree of conversion was determined by chemical analysis for residual fluoride content and U^{+4} and U^{+6} content. Reduction temperature was found to have a pronounced effect. Residual fluorides of 5 to 10 per cent were obtained at 550 C (Runs 41 and 45), while an equivalent time (4 hr) at 650 C left only 0.024 per cent fluoride (Runs 46 and 47), which is within the fluoride specification usually set for ceramic-grade powders. One manufacturer gives as a typical composition 100 to 300 ppm fluoride in ADU-type oxide.¹⁰ Two additional hours at 650 C reduced the value to 0.007 per cent. The effect of and necessity for addition of steam to the hydrogen stream has not been clearly determined since similar results, 0.023 and 0.024 per cent residual fluoride after 4 hours, were achieved in Runs 46 and 47 with 17 and 33 per cent steam, respectively. In the case of Run 42 the residual fluoride represents uranium tetrafluoride present in the starting material; in this instance a trace of steam would have been desirable to convert the tetrafluoride to uranium dioxide. However, it is not likely that uranium tetrafluoride would be produced in this two-step process. Calculations based on the analyses indicate the presence of some U_3O_8 , possibly due to oxidation of the dioxide upon contact with air.

The surface area of the dioxide product from Run 47 was about twice that of Run 42, 0.62 and 0.30 sq m/g, respectively, the ratio being about the same as for the respective uranyl fluoride starting materials. These values are similar to those measured on the product from the single-step (simultaneous hydrolysis-reduction) process except for one batch which had a surface area of 1.94 sq m/g. The temperature of preparation may be significant in this regard, since the single-step material was not heated above 600 C.

In summary, the preparation of low-fluoride uranium dioxide is readily accomplished by pyrohydrolysis of uranium hexafluoride to uranyl fluoride followed by hydrogen reduction. The pyrohydrolysis reaction proceeded smoothly at low temperatures, 140 to 230 C; particle growth effects were similar to those noted in the simultaneous reaction tests. Significant increases in feed rates should be possible as conversion rates were at the 99.99 per cent level. The reduction of the uranyl fluoride is strongly dependent on temperature; acceptable fluoride levels were reached in four hours in batch tests at 650 C. Two-step operation has several advantages:

1. low-temperature operation of the pyrohydrolysis reactor, which minimizes equipment corrosion and product contamination;
2. high capacity - no significant losses of uranium hexafluoride in the pyrohydrolysis step have been detected yet at rates up to 205 lb uranium/(hr)(sq ft reactor cross section); and

¹⁰Chemical Engineering Progress, 54, 65-70 (March 1958).

3. simplicity of operation - separation of reactions permits optimization of reactor conditions for conversion and process control requirements, such as residual fluoride content in the reduction column or particle size in the pyrohydrolysis reactor.

3. Reduction of Uranium Hexafluoride

The reduction of uranium hexafluoride to uranium tetrafluoride with hydrogen proceeded smoothly in a 2.2-hour run at 600 C. The average hexafluoride feed rate was 101 g/min [equivalent to 176 lb uranium/(hr) (sq ft reactor cross section)]. The run was made at a fluidizing velocity of 0.75 ft/sec, using about 250 per cent excess hydrogen. As the run progressed, the product became considerably more dense than the starting material, which was green salt prepared from uranyl nitrate by denitration, reduction, and hydrofluorination. The tapped bulk density for the 60 to 100 mesh fraction increased from 3.4 to 4.2 g/cc. The tetrafluoride which formed apparently deposited as a dense coating on the fluidized particles as in previous cases. As in previous work, negligible amounts of uranium were lost in the off-gas stream, less than 0.01 per cent of the material fed. This process step may be attractive as a means of producing feed for uranium metal reduction.

4. Pellet Fabrication Tests

A series of pellet fabrication tests on a 20-lb batch of uranium dioxide prepared at ANL by the one-step fluid-bed process followed by additional treatment for 8 hours with steam and hydrogen was made by the Mallinckrodt Nuclear Corp., St. Louis, Missouri. The powder contained 130 ppm fluoride, 85.0 per cent U^{+4} and 86.7 per cent total uranium, indicating the possible presence of some U_3O_8 . The surface area was 1.94 sq m/g (60 to 100 mesh fraction). The powder was divided into 2 fractions, one ball-milled to -325 mesh and the other, covering the size range -40, +200 mesh, was used as produced. The -325 mesh fraction was divided into three portions, one to be tested as is, the second wet ball-milled for 5 hours, and the third passed through 2 oxidation-reduction cycles (1 hr oxidation and 4 hr reduction at 650 C). The coarse material was sintered both as shot and in pellet form.

A summary of the pressing and sintering conditions and results is shown in Table 28. Since each of the -325 mesh powder samples gave sintered densities near 95 per cent theoretical or better, the fluid-bed approach to preparing uranium dioxide for nuclear fuel application appears promising. In general, the powders looked good and there was little distortion in the pellets. Appreciable voids were noticed in the pellets prepared

from as-received, -325 mesh powder but these were attributed, at least in part, to an excessive use of wax. A change in binder may also reduce this problem. The voids were less obvious for material pressed at higher pressures. Few voids were noticed in the pellets from oxidized-reduced material.

Table 28

SUMMARY OF SINTERING TESTS PERFORMED ON URANIUM DIOXIDE
PREPARED BY THE ONE-STEP FLUID-BED PROCESS

(Tests made by Mallinckrodt Nuclear Corp.)

Material: UO_2 from Run 37A; Fluoride content 130 ppm

Treatment: 1. a. As produced (40 to 200 mesh)
2. a. Used as prepared.
b. Wet-ball milled for 5 hours.
c. Oxidized (1 hr) and reduced (4 hr)
at 650 C, 2 cycles.

Pelleting Pressures: 50, 70 and 90 T/sq in.

Sintering Conditions: Presinter at 900 C. Sinter 8 hours at 1650 C
plus heat-up and cool-down time.

Material	Green ^c Density (g/cc)	Sintered Density as % Theoretical	Remarks
1.a ^a	-	93	Sintered as "shot" in this test only.
1.a	-	-	Pellets found cracked.
2.a	7.4 to 7.9	~ 95	Appreciable voids present. ^b
2.b	7.34 to 7.86	93.5 to 96	Fewer voids at higher pressures.
2.c	6.87 to 7.45	96.5 to 97.5	Very few voids noticed.

^aA lower (unspecified) sintering temperature was used in this test.

^bPossibly due to excessive use of wax.

^cGreen = unsintered.

Material sintered as "shot" achieved 93 per cent theoretical density at a lower temperature (not specified), and it is believed that 95 per cent or better can be attained at higher sintering temperatures. This material might be well-suited to swaged or vibratory compacted fuel elements.

5. Discussion

The alternate fluid-bed processes investigated this quarter have shown that high capacities are attainable with the gas-gas reaction of uranium hexafluoride with steam or hydrogen only. Particle size effects in both the pyrohydrolysis and reduction reactions were consistent with the correlation of bed particle size and superficial gas velocity reported last quarter (ANL-6145, page 127). Conversion of the uranyl fluoride to the dioxide appears sufficiently rapid at high temperatures for a practicable two-step process. A sample of dioxide prepared by this two-step process is being tested for sinterability.

G. Multistage Fluidization (K. Williamson, Jr.)

The first phase of the experimental work in the 6-inch multistage fluidization column investigating the design and operational variables for controlled downward transport of solids without internal downcomers has been completed. Throughput rates as high as 15 cu ft/(hr)(sq ft reactor cross section) were obtained. The previous quarterly report (ANL-6145, pages 129 to 132) contained a description of the equipment and a discussion of the preliminary experimental results from the investigation of (1) vibrational frequency, (2) types of vibration transmitters, (3) feed particle size and particle size distribution, and (4) the percentage of vibrator on-time.

To conclude the first phase of the experimental work the variables (1) superficial gas velocity, (2) bed depth of fluidized particles, (3) plate resistance and (4) uncontrolled throughput (where no vibrator is used) were studied. A correlation of the data was obtained and is presented in summary form.

1. Experimental Results with Glass Bead-Air System

Throughput of glass beads was determined as a function of several variables as discussed below.

a. Superficial Gas Velocity

Superficial air velocities from zero to 0.4 ft/sec were used in this investigation. It was found that the maximum throughput rate occurred at an air velocity, u_m , determined by equating the velocity pressure of the

fluidizing air to the downward pressure exerted by feed particles because of gravity. This velocity, u_m , was in all cases close to the minimum fluidization gas velocity. From u_m to $4 u_m$ (~ 0.4 ft/sec) the throughput rate decreased linearly. At velocities $< u_m$ the throughput rate also decreased, but not linearly.

b. Bed Depth of Fluidized Particles

Bed depths of 3, 5, 7 and 9 inches were investigated. Above depths of 6 inches the throughput rate was found to be independent of bed depth. Below depths of 6 inches the throughput rate decreased slightly as the bed depth decreased. However, for engineering purposes the throughput rate could be considered to be independent of bed depth for beds greater than 3 inches in depth.

c. Plate Resistance

This work involved a study of the size, type of material, and depth of large nonfluidized spherical solids which serve as part of the bed supports.

(1) Size of Nonfluidized Solids

Spherical glass beads from 0.035 to 0.12 inch in diameter were used. For a given feed and vibrator on-time, the throughput rate was found to increase as the diameter of the support beads increased. For throughput to occur, the diameter of the support beads had to be at least 7 times the diameter of the average feed particle.

(2) Type of Material for Nonfluidized Solids

Throughput rates obtained with copper spheres in the bed support did not differ appreciably from those obtained with glass spheres. Runs with aluminum oxide showed a considerable decrease in throughput rate. This was caused by some degrading of the soft aluminum oxide spheres as the run progressed, causing a reduction of the diameter of the spheres. From this work it was concluded that the density of the nonfluidized solids was not a variable.

(3) Depth of Nonfluidized Solids

Throughout the range studied (0.072 to 0.436 inch), the throughput rate was found to decrease as the depth of nonfluidized solids increased. At depths < 0.109 inch, column operation was found to be unstable with large uncontrolled (vibrators not on) throughput rates occurring.

d. Uncontrolled Throughput

Uncontrolled throughput rates were found to be a function of feed particle size, nonfluidized particle size, and the depth of nonfluidized particles. The design correlation indicates that the uncontrolled throughput rates will be less than 0.27 cu ft/(hr)(sq ft reactor cross section).

2. Design Correlation

The design correlation gives the size and amount of nonfluidized beads in the bed support plate necessary to achieve a given throughput rate of feed material for the range of operating conditions tested. Two types of feed were tested, glass beads and aluminum oxide, and since these incorporate several shapes, not all spherical, and a factor of about 2 in density, the correlation may have general application.

The factor found to correlate the throughput rates is the difference between two diameters, $D_c - D_p \phi_s$. The first term, D_c , is the "critical" diameter and is defined as the largest diameter sphere that will pass between the tightly packed glass beads in the support plates. The "critical" diameter is a linear function of the diameter of the beads in the support plate. The second term, $D_p \phi_s$, is the product of a shape factor and the average feed particle diameter.

The following three equations used in the correlation account for variations in feed particle density, shape and size; column cross-sectional area; density and superficial velocity of the fluidizing gas; and the amount and size of the beads on the distributor plate.

1.
$$W_V^{u_m} = \frac{29.3 w_V^u}{A \rho P} + 127 \left(u - 1.23 \times 10^{-3} \frac{\rho_p D_p}{\rho_g \phi_s} \right)^{1/2}$$
2.
$$W_{0.218}^{u_m} = W_V^{u_m} + 100 - \exp(4.01 - 0.368 \ln V)$$
3.
$$D_s = 6.46 D_p \phi_s + 2.18 \times 10^{-4} W_{0.218}^{u_m} - 2.98 \times 10^{-3}$$

where

w_V^u = desired throughput rate of feed material, lb/hr, at gas velocity u and vibrator on-time percentage P .

$W_V^{u_m}, W_{0.218}^{u_m}$ = throughput rate, lb/hr, at u_m , based upon glass bead density and a 6-in. diameter column. Depth of support beads indicated by V ; in the second term $V = 0.218$ in.

u = operating superficial gas velocity, ft/sec.

V = depth of support beads on each plate, in.

A = cross-sectional area of column, sq ft.

P = percentage of vibrator on-time, %.

D_s = average diameter of support material, in., where
 $D_s/6.46 = D_c$.

ρ = bulk density of the feed material, g/cc.

ρ_p = absolute density of the feed material, lb/cu ft.

ρ_g = density of the fluidizing gas under column operating
conditions, lb/cu ft.

Future work will involve a mass transfer study for the absorption of water vapor by silica gel.

III. REACTOR SAFETY

In order to provide knowledge to minimize the hazards associated with handling the reactor metals, uranium, zirconium, plutonium, and thorium, the examination of the oxidation, ignition, and combustion processes of these metals is being continued.

The considerable inhibition of the burning-propagation rates of uranium and zirconium by the presence of small percentages of halogenated hydrocarbons in air has been studied further in an effort to appraise the potentiality of their use as extinguishants and to clarify the mechanism of inhibition.

The study of ignition of metal powders has continued with studies of ignition of spherical uranium powders. Ignitions of samples of varied specific area and mixtures of portions of fine and coarse particles compare favorably with ignition temperatures calculated on the basis of integrated heat generation according to isothermal oxidation kinetics. Studies of the effects of sample geometry, using various sizes of crucibles, indicate that the important parameter is the depth of the sample. Samples greater than a critical depth have constant ignition temperatures, while below this depth the ignition temperature increases with decreasing depth.

Ignition and burning-propagation rate studies with preliminary plutonium binary alloy foils, containing 2 atom per cent aluminum, iron, carbon, nickel, manganese, and chromium, have been completed. Manganese appears to lower the ignition temperature and aluminum to raise it. Similar data are obtained from burning curve and shielded ignition experiments for all except the aluminum alloys. Burning curves show some of the aluminum alloy samples to have ignition temperatures approximately 150 degrees higher than those obtained from shielded experiments. This may be due to stabilization of the delta phase, which has been reported to produce a protective oxide. The specific area dependence, based on comparison of the iron alloy in rod form and as a foil, appears to be similar to that observed for uranium.

The development and growth of nodules observed on the surface of the oxide during isothermal oxidation of uranium on the microscope stage have been shown to cease if the oxidation is interrupted by evacuation of the cell and to resume when oxygen is readmitted. Thus, the nucleation and growth process is not independent of the formation of new oxide.

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. The principal laboratory-scale method involves the rapid melting and dispersion of metal wires in a water or steam environment by a surge current from a bank of condensers. Additional runs in the series with 30-mil uranium wires were completed. Runs have been made with initial metal

temperatures ranging from 662 C (solid) to 3800 C (liquid). Up to 45 per cent reaction occurred in the more energetic runs. There was no marked change in the character of the reaction at the melting point of uranium dioxide (2700 C) or any other temperature in the range studied. The uranium reaction differed in this respect from the zirconium reaction. Results of particle size measurements of the residue from the uranium runs showed that mean diameters as low as 50μ were produced in the more energetic runs.

A second laboratory-scale method involves the rapid contact of steam with heated metal. In this method, the metal receives a "pressure pulse" of water vapor. A series of runs with aluminum gave results that were not reproducible. The difficulty was traced to interference of the aluminum mirror generated on the walls of the reaction cell during the heating process. Means to avoid this interference have been devised and the necessary modifications to the apparatus are in progress.

A series of eight experiments has been conducted in the TREAT reactor during the quarter. In these experiments, a stainless steel autoclave containing a fuel pin, gold foils, helium and water was subjected to a short burst of neutrons. Aluminum and stainless steel-clad, oxide core pins and Zircaloy-2-clad, aluminum- U_3O_8 cermet core pins were studied. The uranium was fully enriched. Only 1.4 per cent of the metal present in the fuel pin reacted in the most vigorous transient. Partial melting of both the clad and core has been obtained with the oxide pins. Penetration of the Zircaloy-2 clad and melting of the cermet core were obtained with the cermet pins. The time corresponding to a peak clad temperature lagged behind the peak flux by up to 5 sec for the oxide core pins, whereas with metal core pins less than 0.1-sec lag was noted in previous runs.

A. Metal Oxidation and Ignition Studies (J. G. Schnizlein)

1. Uranium Ignition Studies (L. Leibowitz, J. D. Bingle, L. W. Mishler)

a. The Effect of Halogenated Hydrocarbons on the Burning Properties of Uranium in Air

The burning properties of uranium have been subjected to intensive study as a result of the occurrence of a variety of fires involving the metal. Ignition temperatures and burning-propagation velocities have proven to be useful quantities for study of the effects of various factors on the pyrophoricity of this material.

It has been observed that a number of halogenated hydrocarbons, e.g., C_2H_5Br , CH_2Br_2 , CF_2Br_2 , CH_2BrCl , CHF_2Cl , and CCl_4 , markedly lower the rate of propagation of burning in air of uranium foil strips.

Concentrations of the organic compounds in air have varied from two to ten per cent by volume. These findings have been reported in ANL-6145, page 137. Some of the oxide residues were analyzed for halogen content, and small quantities of bromine or fluorine were detected in most cases. To obtain more information a sample of uranium oxide formed by burning metal foil in air containing 10 per cent CF_2Br_2 was submitted for X-ray analysis in the hope that the halide-containing phases could be identified. Chemical analysis of this oxide revealed the presence of one per cent fluoride and 0.2 per cent bromide. A microscopic examination of the oxide* revealed small thin blisters above the bulk of the oxide crust. Both the crust, free of blistered flakes, and the blistered material were examined separately by the X-ray powder diffraction technique.* Schablaske and Tani report, "A powder photogram of the blistered flake material exhibits a set of relatively sharp lines corresponding to uranium tetrafluoride and a set of fuzzy lines corresponding to uranium dioxide with the tetrafluoride as the more prominent phase. A possible minor phase is U_3O_8 . The major component of the crust material that has been freed of the blistered flakes is uranium dioxide with U_3O_{8-x} as a probable minor phase. There is no evidence of uranium tetrafluoride in this material."

It seems most reasonable to consider the uranium tetrafluoride to be formed by reaction between uranium dioxide and CF_2Br_2 . There is no information available on the rate of reaction between uranium and CF_2Br_2 although reactions of uranium dioxide with various Freons (chlorofluoro compounds) have been used to prepare uranium tetrafluoride. It seems likely that there is some interaction between uranium metal and the halogenated organic compounds in view of the observed lowering of the ignition temperature (see ANL-6145, page 137). This must occur below about 300 C, at which temperature rates of decomposition of CF_2Br_2 , CF_3Br , and other brominated hydrocarbons are quite low.¹¹ Experiments are planned in which uranium foil will be heated in the organic vapor prior to measuring burning-propagation rates and ignition temperatures in uncontaminated air.

2. Uranium Powder Ignition Studies (M. Tetenbaum, L. Mishler)

a. Effect of Fines

Previous work had shown (ANL-5974, page 29) that when a 10-mil foil of uranium (approximately 1 sq cm) was placed on top of a uranium cube, 8.5 mm on edge, ignition of the combined charge occurred at approximately the same temperature as if the foil were alone. The strong

*Microscopic examination and X-ray diffraction were conducted and interpreted by R. Schablaske and B. Tani.

¹¹Sehon, A. H., and Szwarc, M., Proc. Roy. Soc. (London), 209A 110 (1951).

dependence of ignition temperature on specific area has already been noted for foils, wires, cubes (ANL-6101, page 129), and powders (ANL-6145, page 147). As an extension of the concept that small particles initiate ignition of large particles, the effect of high specific area uranium powder on the ignition behavior of relatively coarse uranium particles was studied.

Mixtures containing various weight percentages of -230, +325 (designated as fines) and -14, +20 (designated as coarse) mesh powders were prepared. In most cases the powders were uniformly distributed throughout the mixture. However, in some cases, the fines were distributed on the bottom of the container, and the coarse uranium particles placed on top of the fines. The uranium powders, manufactured by a special process by National Lead Company, Fernald, Ohio, were smooth and spherical in shape (see ANL-6145, page 148). The container was graphite, $\frac{3}{8}$ in. ID, with a rounded bottom. The burning-curve technique was used to measure the ignition temperatures of the various mixtures. The results are shown in Figure 27.

It is apparent from the figure that small amounts of fines in coarse uranium powder lower the ignition temperature considerably, i.e., the ignition temperature of -14, +20 mesh uranium is lowered by approximately 50 degrees in the presence of 5 per cent by weight -230, +325 mesh uranium particles.

It is possible to predict the effect of fines on the ignition temperature of coarse particles by the following theoretical considerations: The heat generated by the mixture (assuming no heat losses) can be expressed as follows for oxidation obeying the parabolic rate law:

$$H = \left(\frac{M_c}{r_c} + \frac{M_f}{r_f} \right) \frac{A^{1/2} \Delta H}{21.33 \phi^{1/2} \rho} \int_0^T T^{-1/2} e^{-E/2RT} dT$$

where

E = energy of activation
 ΔH = heat of formation of oxide per mole of oxygen
 A = frequency factor in Arrhenius equation
 ρ = density of metal
 ϕ = container heating rate
 M_c = mass of coarse fraction
 M_f = mass of fine fraction
 r_c = radius of particles of coarse fraction
 r_f = radius of particles of fine fraction
 T = container temperature, and
 H = heat generated by sample.

The critical condition for ignition in this treatment requires that the temperature of the power mass due to self-heating be somewhat higher than the container temperature. Therefore, the condition for ignition of the mixture becomes

$$\left(\frac{H}{M_{c+f}} \right)_{T_i} = C_p \Delta T$$

where

C_p = specific heat of the metal
 M_{c+f} = weight of mixture
 T_i = ignition temperature of mixture
 ΔT = difference between T_i and the container temperature, T , at the time of ignition,

The specific heat of uranium in the temperature range from 200 to 400 C does not vary by more than 10 per cent from the average value. By a process of iteration, a ΔT value, approximately 25 C, was found which yielded a curve to best fit the experimental data. The calculated curve based on this value is included in Figure 27. The shape of the theoretical curve agrees reasonably well with the experimental data.

b. Effect of Sample Geometry

The effect of sample geometry on the ignition behavior of uranium powder was also investigated during this period. Stainless steel crucibles of several diameters were used in these studies to contain various charges of -200, +230 mesh spherical uranium powder. The burning-curve technique was used to measure ignition temperatures in pure oxygen. The results are summarized in Figures 28 and 29.

FIGURE 28
IGNITION TEMPERATURE OF -200,+230 MESH SPHERICAL URANIUM POWDERS
AS A FUNCTION OF SAMPLE WEIGHT

FIGURE 29
IGNITION TEMPERATURES OF -200,+230 MESH SPHERICAL URANIUM
POWDERS AS A FUNCTION OF SAMPLE HEIGHT

Figure 28 shows the measured ignition temperatures plotted against sample weights for containers of different diameters. It is apparent that for equal weights of uranium powder, the crucibles of larger diameters yield higher ignition temperature values than crucibles of smaller diameters. However, when the ignition temperatures are compared with the equivalent heights of sample charges in the crucibles of various sizes, a relatively smooth curve can be obtained from the data shown in Figure 29. From the figure, the critical depth of -200, +230 mesh uranium powder to yield constant ignition temperature values is estimated to be approximately one mm. This depth corresponds to approximately 15 particle diameters. A higher critical depth would be expected for charges of larger diameter because the effective thermal conductivity of coarse powders is greater (and therefore heat losses greater) than for fine powders. This will be investigated experimentally.

The values of ignition temperature obtained from measurements using the $\frac{1}{4}$ -in. diameter crucible are slightly higher than those obtained with larger containers. In this case, the higher ignition temperature values can be attributed to higher radial heat losses in small-diameter cylindrical vessels.

The above principles will be helpful in resolving the ignition behavior of uranium powder (as well as other materials) over a wide range of particle sizes.

c. Effect of Specific Area

A critical examination of the ignition behavior of uranium powder as a function of specific area was pursued during the last few months. Measurements, described above, on the effect of sample geometry on the ignition temperature behavior of -200, +230 mesh spherical uranium powder showed that constant ignition-temperature values are obtained if the sample height was greater than one millimeter.

On the basis of these results, duplicate ignition-temperature measurements were made for the various particle sizes studied, using generally 3- and 4-gram powder charges (in $\frac{3}{8}$ -in. stainless steel crucibles) to insure constant ignition temperatures. Larger charges of samples would be required for very low specific area powders.

The burning-curve technique was used to measure ignition temperatures in pure oxygen. The results are shown in Figure 30. Included in the figure are theoretical curves calculated on the basis of parabolic and linear oxidation rate constants (ANL-6145, page 157).

It is apparent from Figure 30 that the specific area range investigated thus far is too narrow to define the curve clearly. The measured temperature difference is only 25 C between the powders of high and low specific area. The calculated temperature difference in this specific area range on the basis of parabolic rate law behavior yields $\Delta T = 75$ C, whereas based on the theoretical

linear rate curve, $\Delta T = 36$ C. Continued study will include powders of lower and higher specific area.

3. Plutonium Ignition Studies (J. G. Schnizlein, D. F. Fischer)

Burning-propagation and burning-curve ignition experiments in air and oxygen, as well as oxygen shielded-type ignition experiments, have been completed on the preliminary two atom per cent binary alloy foils (aluminum, iron, carbon, nickel, manganese, and chromium) of plutonium which were prepared at Hanford.

a. Ignition Experiments

Summaries of the ignition temperatures obtained with the two atom per cent plutonium alloys and aluminum-plutonium alloys of varied concentrations from the air and oxygen burning-curve experiments and the oxygen shielded-type ignitions are given in Tables 29 and 30 and in Figure 31.

Table 29

IGNITION TEMPERATURES OF PLUTONIUM ALLOYS WITH VARIED ALUMINUM CONTENT, THICKNESS, AND WIDTH

Aluminum Concentration (a/o)	Foil Thickness (mm)	Foil Width (mm)	Ignition Temperatures ^a from Shielded Experi- ments in Oxygen		Ignition Temperatures from Burning Curves	
			Nonignition (C)	Ignition (C)	Air (C)	Oxygen (C)
2	0.26	3.7	350	388	-	-
2	0.26	4.4	-	-	554	-
2	0.25	3.7	-	-	-	555
10	0.24	2.8	382	455	-	-
10	0.23	3.5	-	-	620	-
10	0.24	2.9	-	-	-	590
10	0.24	4.1	-	-	-	604
10 ^b	0.12	1.9	398	402	-	-
10 ^b	0.12	6.0	-	412	-	-
10 ^b	0.14	2.3	-	-	412	-
10 ^b	0.14	1.9	-	-	-	440
10 ^b	0.82	2.1	400	432	-	-
10 ^b	0.83	2.1	-	-	425	-
10 ^b	0.82	2.0	-	-	-	390

^aIndicated is the highest temperature at which ignition did not occur and the lowest temperature at which ignition did occur upon admission of oxygen.

^bFoils received from ANL Metallurgy Division.

Table 30

IGNITION TEMPERATURES OF PRELIMINARY
TWO ATOM PER CENT PLUTONIUM ALLOYS
(approximately 0.24 mm thick and 3 mm wide)

Additive	Ignition Temperature (C)			
	from Shielded Experiments in Oxygen ^a		from Burning Curves	
	Nonignition	Ignition	in Air	in Oxygen
Mn	214	230	330	247
Ni	297	317	325	316
Cr	275	307	380	320
C	270	300	371	330
Fe	307	348	372	330
Al	350	388	554	555

^aIndicated as the highest temperature at which ignition did not occur and the lowest temperature at which ignition did occur upon admission of oxygen.

FIGURE 31
IGNITION TEMPERATURES OF THE VARIOUS
PRELIMINARY PLUTONIUM ALLOY FOILS

— SHIELDED EXPERIMENTS IN OXYGEN
○ BURNING CURVE IN OXYGEN
× BURNING CURVE IN AIR

The two atom per cent alloys were all approximately 0.24 mm thick and 3 mm wide, while the 10 atom per cent aluminum alloy samples were 0.13, 0.24, and 0.82 mm thick and of widths varying from 1.9 to 6 mm.

(1) Additive Effects

The two atom per cent manganese alloy had the lowest ignition temperatures in both the burning-curve and shielded-type ignitions of the several alloys studied. Chromium, nickel, carbon, and iron alloys had intermediate ignition temperatures. There is an indication that the two atom per cent aluminum alloy raises the ignition temperature, depending on the method of measurement (see following section).

There seems to be a slight dependence of the ignition temperature upon aluminum concentration (see Figure 31), with the 10 atom per cent, 24-mm foil indicating a somewhat higher ignition temperature than the two atom per cent foil.

(2) Comparisons of Burning-curve and Shielded Experiments

Burning-curve ignition results were similar to the shielded-type ignitions except for the aluminum alloys from Hanford. It is suspected that the latter are delta stabilized, because much higher ignition temperatures (approximately 150 degrees) were obtained from the burning-curve experiments than from shielded experiments. Since it has been reported¹² that plutonium in the delta phase oxidizes with a parabolic rate, it is suspected that a protective oxide is produced in burning curves to give the higher indicated ignition temperatures.

It should be mentioned that the minimum temperature indicated for an ignition temperature with the shielded-type experiment is the temperature of the sample at the time the oxygen is admitted. Self-heating is observed before the actual ignition takes place, and in several cases an inflection is observed in the temperature trace at or near the temperature indicated by the burning curve experiments. Therefore, the reported shielded ignition temperatures are, as expected, usually lower than values obtained from the corresponding burning-curve ignition.

(3) Considerations of Specific Area Dependence

Since no pure plutonium foil has been studied, speculations about the effects of varied size can only be made by comparing results with those obtained on plutonium alloy rod samples (see ANL-6145,

¹²Dempsey, E., and Kay, A. E., J. Institute Metals, 86, 379 (1958).

page 144). The ignition temperatures of rod and foil samples of the iron and carbon alloys of plutonium compare with uranium as follows:

	Ignition Temperature (C)	
	rod	foil
	0.6 sq cm/g	4.5 sq cm/g
2 a/o iron-plutonium alloy	520	330
2 a/o carbon-plutonium alloy	447	330
Uranium (interpolated)	570	420

The specific area dependence of the iron alloy is similar to the specific area dependence of uranium. The effect of carbon may either be interpreted in terms of absence of an additive effect in the foil region of size (~5 sq cm per g) or in terms of the fact that the specific area dependence is much smaller than for the iron alloy.

The aluminum alloys were only available as three thicknesses of foils (0.13, 0.24, and 0.82 mm). Data on these indicated essentially no change of ignition temperatures over this range of specific area.

(4) Comparison of Data of Burning-curve Experiments in Air and Oxygen

Burning-curve ignition temperatures were higher in air than in oxygen for two atom per cent alloy foils, except for the aluminum alloy, which had practically the same values in air and oxygen. This is in contrast to the data for various plutonium rod samples (6 mm diam x 6 mm high) and 10 atom per cent aluminum alloy (0.13 mm thick) which were reported as having slightly lower burning curve ignitions in air than in oxygen.

b. Burning-propagation Experiments

In Table 31 are listed the burning-propagation rates of the preliminary two atom per cent plutonium alloys. Samples were approximately 0.24 mm thick and 2 mm wide. In air, there is essentially no difference in the burning-propagation rates of the alloys. The slowest propagation rate was that of the nickel alloy, which yielded a value of 0.23 cm per sec. The fastest propagation rate was that of the chromium alloy, namely, 0.32 cm per sec. In oxygen, the propagation rates varied from 5.4 cm per sec for the aluminum alloy to 9.8 cm per sec for the chromium alloy.

Table 32 is a summary of the burning-propagation experiments of samples with varied aluminum content, thickness, and width, including those previously presented in ANL-6068, page 145. There is no effect of varied aluminum additive concentration between 2 and 10 atom per cent. It can be seen that a change in the thickness of the foil has more effect on the propagation rate than the same percentage change in the width.

Table 31

BURNING PROPAGATION RATES OF PRELIMINARY
TWO ATOM PER CENT PLUTONIUM ALLOYS
(approximately 0.24 mm thick and 2 mm wide)

Additive	Burning-propagation Rate (cm/sec)	
	In Air	In Oxygen
Mn	0.32	6.8
Ni	0.23	5.5
Cr	0.32	9.8
C	0.28	7.9
Fe	0.29	7.8
Al	0.29	5.4

Table 32

BURNING PROPAGATIONS OF ALUMINUM-PLUTONIUM ALLOYS
WITH VARIED CONTENT, THICKNESS, AND WIDTH

Aluminum Concentration (a/o)	Foil Thickness (mm)	Foil Width (mm)	Cross- sectional Area (sq mm)	Burning-propagation rate (cm/sec)	
				In Air	In Oxygen
2	0.24	2.2	0.52	-	5.4
2	0.24	2.9	0.69	-	5.1
2	0.24	1.3	0.31	0.37	-
2	0.24	2.1	0.50	0.29	-
2	0.24	3.2	0.78	0.24	-
10	0.23	2.9	0.67	-	5.5
10	0.23	3.1	0.72	0.25	-
10	0.23	3.1	0.72	0.28	-
10a	0.11	1.1	0.12	-	16
10a	0.11	1.0	0.11	0.74	-
10a	0.11	1.2	0.13	0.69	-
10a	0.11	1.2	0.13	0.68	-
10a	0.11	1.2	0.14	0.67	-
10a	0.12	2.0	0.23	0.50	-
10a	0.11	3.3	0.37	0.54	-
10a	0.82	1.2	0.99	0.20	-
10a	0.82	2.9	2.4	0.15	-

^aFoils received from ANL Metallurgy Division.

4. Isothermal Uranium Oxidation Studies (L. Leibowitz, L. W. Mishler)

The overall oxidation process found for uranium involves two stages, with a more or less abrupt rate increase occurring after roughly 50 μg per sq cm of oxygen has been consumed by the metal. The two-process mechanism outlined by Haycock¹³ seems to account for such kinetics. Briefly, in this theory it is assumed that initially the rate of oxidation depends on the thickness of the oxide layer, i.e., ordinary parabolic oxidation with $dq/dt = k_p/2q$, where q = sample weight gain, t = time, and k_p is the parabolic rate constant. When the oxide has achieved a certain thickness, a second process begins and proceeds at a constant rate. This is a transformation of the oxide from a compact to a porous form. It is the compact oxide thickness that controls the rate of the parabolic oxidation. If the rate of transformation $dq/dt = k_1$ is greater than the rate of oxidation, there will be an increase in oxidation rate until $dq/dt = k_1 = k_p/2q$. The oxidation will then continue at a constant rate. If the second process is one of recrystallization of the oxide, it would seem that, once begun, it should continue regardless of whether or not the oxidation itself continued. In order to clarify this aspect of the oxidation, two runs were carried out in the cell on the microscope stage (see ANL-6068, page 147) in which the oxidation was interrupted by removing the oxygen after the rate increase and nodule growth had begun. The temperature of the sample was not changed. After about 90 minutes, oxygen was re-introduced and the runs resumed. The results are shown in Figure 32, and it is clear that the reaction resumes at an unchanged rate.

¹³Haycock, E. W., J. Electrochem. Soc., 106, 771 (1959).

There was no change in the appearance of the surface during the interruption, and the nucleation and growth process resumed upon readmission of oxygen. Thus, the second process, whatever it may be, is not one which proceeds independently of the formation of new oxide. Indeed, because of our observation of linear initial oxidation rates and the absence of oxide higher than the dioxide on the outer oxide surface (see ANL-5974, page 71), diffusion through a compact oxide layer may not be the rate-controlling step.

B. Metal-Water Reactions
(L. Baker, M. Kilpatrick*)

1. Laboratory Studies - Condenser Discharge Method
(L. Baker, R. Warchal, T. Kato**)

The condenser discharge experiment is an attempt to obtain fundamental rate data under experimental conditions similar to those during a serious accident in a nuclear reactor. Either a nuclear runaway or a sudden loss of coolant during operation of a water-cooled reactor could result in contact between very hot fuel and cladding metals with water or steam and might involve fine particles. The condenser discharge experiment simulates the limiting case of a nuclear incident in that the heating time is very short and very fine metal particles are produced.

In the condenser discharge experiment, metal wires are rapidly melted and dispersed in a water-filled cell by a surge current from a bank of condensers. The energy input to the wire is used to calculate the initial metal temperature; the transient pressure measures reaction rate; the amount of hydrogen generated gives the extent of reaction; and the particle size of the residue indicates the surface area exposed to reaction.

Analysis of the results is based on one of the usual laws of metal oxidation and a simple heat transfer model. In this way, it has been possible to obtain rate constants which in turn may be applied toward a detailed analysis of particular reaction conditions.

a. Runs with Uranium

A brief series of runs with 30-mil uranium wires was reported in the previous quarterly report (ANL-6145, page 161). A more extensive series of runs has now been completed. Runs have been made with initial metal temperature ranging from 662 C (solid) to 3800 C (liquid). Results for the previously unreported runs are summarized in Table 33.

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**Summer employee.

Table 33

URANIUM-WATER REACTION DATA:
CONDENSER DISCHARGE METHOD

Run	Energy Input (cal/g)	Calc Initial Metal Temp (C) and Phys State	Per Cent Reaction	Appearance of Residue
166	40	900, solid γ	1.4	Intact
167	46	1050, solid γ	1.6	Elliptical
165	54	1133, 40% liq	2.3	Elliptical
168	56	1133, 60% liq	3.4	Coarse particles
169	61.5	1200, liq	4.4	Coarse particles
170	62	1200, liq	4.6	Coarse particles
164	64	1200, liq	5.1	Coarse particles
160	80	1650, liq	10.7	Some fines
159	88	1900, liq	16.1	Some fines
172	136	3200, liq	40.9	Powder
171	145	3450, liq	40.1	Powder
173	147	3500, liq	45.4	Powder
174	152	3650, liq	45.4	Powder
176	156	3800, liq	41.7	Powder

Results for the total extent of reaction, determined from the hydrogen analysis, are plotted as a function of initial metal temperature for all of the runs in Figure 33.

FIGURE 33
EXPERIMENTAL RESULTS URANIUM-WATER REACTION

The results of the uranium runs may be compared to results reported in previous quarterlies for the zirconium-water reaction. The total extent of reaction for 30-mil wires was roughly twice that for 60-mil wires at initial temperatures through the melting point for zirconium. There is no significant difference, however, in the data for 30- and 60-mil wires for uranium. The zirconium data were successfully correlated through the melting point by means of the parabolic law of oxidation. It can be shown that the same heat transfer model when used with a linear rate law gives a total extent of reaction that is independent of particle size. This suggests that this rate law may be the appropriate one for uranium. Small particles are consumed more rapidly; however, they also cool

more rapidly so that the reactions are quenched to roughly the same degree.

The nature of the zirconium-water reaction changed from a smooth reaction to an explosive reaction at an initial temperature of 2600 C, which corresponded approximately to the melting point of zirconia. Melting oxide apparently destroyed the protectiveness of the oxide film. A recent determination of the melting point of uranium dioxide gave a value of 2700 C.¹⁴ The oxide melting point is indicated in Figure 33. The uranium reaction shows no critical change throughout the temperature range studied. This behavior is consistent with the concept of a linear rate law in that ion diffusion through a thickening protective film is not the rate-determining step. Preparations for a detailed computer study using the linear rate law and a simple heat transfer model are under way. The possibility exists that the runs at higher temperature are controlled by the diffusion of water vapor through a hydrogen barrier. The equations governing diffusion behavior are under study.

b. Nature of the Solid Products of the Reaction

Particle size determinations for residues from runs with zirconium were reported previously (ANL-5996, page 241). The particles were approximately spherical. The same optical technique was used to determine mean particle diameters of the residues from runs with uranium. The particles did not have a characteristic spherical shape, so that the results are only qualitative. Some of the larger pieces were considered as having a cylindrical shape while most of the particles were calculated as spheres. In all cases the pertinent dimensions referred to a minimum chord of irregularly shaped particles. The spherical character of particles obtained in condenser discharge runs with zirconium, platinum, copper, and stainless steel in water environment and with uranium in inert gas suggest that uranium particles in water are formed as spheres and assume an irregular shape through subsequent processes. The effective surface area and particle diameter to be used in the data analysis are those of liquid spheres and not of the solid pieces that are eventually recovered. The method used is believed to provide an approximation to the desired sphere diameter.

The mean particle diameters [$D = 6 \text{ (total sample volume) / (total sample surface)}$] are plotted in Figure 34 as a function of initial metal temperature. The calculated particle sizes are very similar to those obtained with zirconium at corresponding temperatures.

c. High-pressure Apparatus

The design and construction of a high-pressure reaction cell is nearly complete. It will be possible to carry out the condenser

¹⁴Newkirk, H. W., and Bates, J. L., The Melting Points of Uranium Dioxide, Uranium Monocarbide and Uranium Mononitride, HW-59468 (March 4, 1959).

discharge experiments in liquid water at temperatures up to 600 F (315 C) and pressures up to 1500 psi.

2. Laboratory Studies - Pressure pulse Method (D. Mason, P. Martin)

The pressure-pulse method has been developed to study the reaction of molten metals with water vapor under conditions as nearly isothermal as possible. The molten metal, contained in a crucible, is heated in vacuum. When the desired temperature is attained, two electronically operated valves are used to produce contact of water vapor with the metal for a specific period of time. The apparatus and procedure are described in a previous report (ANL-6068, page 153).

Isothermal rate data obtained by this method should provide a check on the results of both the condenser discharge and the in-pile studies. The method should give the best determination of the form of the rate law to be used to interpret the results of the other methods.

Preliminary results on zirconium have been reported (see ANL-6145, page 166). The metal, however, was found to be contaminated with up to 7 per cent thorium from the thoria crucible used to contain the molten zirconium.

It was decided to evaluate the method of study using a metal which could be contained without crucible contamination. Aluminum was chosen because it can be readily contained in high-purity alumina crucibles and because of the intense interest in the aluminum-water reaction. A series of runs with aluminum was carried out but reproducible results could not be obtained. The poor reproducibility is now attributed to interference from the small quantity of metal that is vaporized from the melt and plated on the walls of the reaction cell as a mirror. Experiments showed that the mirror reacted with water vapor extensively even though its temperature was below 200 C.

Vaporization of the molten metal was readily suppressed in the presence of a low pressure of highly purified argon gas. It was believed, however, that even a few mm of inert gas might constitute a serious diffusion barrier between the metal surface and the water vapor when the

total water vapor pressure is only 20 mm (room temperature apparatus). It was decided, therefore, to complete construction of a heated apparatus in which the total pressure of water vapor will be approximately 1 atm. The necessary modifications to the apparatus are in progress.

3. In-pile Testing in the TREAT Reactor*

(R. C. Liimatainen R. O. Ivins, M. Deerwester, F. Testa, J. DeAcetis**)

The purpose of this program is to study metal-water reactions initiated by a nuclear transient. This is accomplished by exposing a small reactor fuel pin to conditions simulating either a power excursion or a loss of coolant incident. Another important purpose of the program is to determine how the fuel pins break up under the influence of reactor excursions of sufficient energy to cause either partial or complete melting.

Results have been reported on unclad uranium metal pins (ANL-6101, page 149), and on Zircaloy-2 clad ("pin-hole" type) metal core pins (ANL-6145, page 167). During the past three months the effort was concentrated on oxide- and cermet-core pins which were jacketed with aluminum, stainless steel and Zircaloy-2.*** Figure 35 shows the details of the oxide core pins (X-ray photographs taken before the transient experiment).

Table 34 gives a summary of the latest metal-water transients. It is interesting to note that even though the energy inputs to the pins are quite high (relative to the energy imparted to metal pins in previous transients), the extent of metal reacted is quite low. The amount of metal reacted ranges from 0.7 to 1.4 per cent.

The amount of metal reacted was obtained from the hydrogen analysis (by mass spectrometer), assuming that the reactions were

The metal in the end plugs was not included in the calculation. An average molecular weight was used for the stainless steel to take into account the presence of nickel and chromium. For the cermet pins it is possible that a thermite-type reaction contributes to the heating. However, for the oxide-core, aluminum-clad pins, this is unlikely since there is no intimate contact. This point will be checked experimentally.

*The cooperation of the TREAT operating personnel of the Idaho Division is gratefully acknowledged.

**Summer employee.

***The fuel pins were fabricated by ANL Metallurgy Division.

FIGURE 35
RADIOGRAPHS OF STAINLESS STEEL AND ALUMINUM-CLAD, OXIDE-CORE FUEL PINS

In transients where the metal clad does not melt, some interesting structural changes take place in the oxide core, as indicated in Figures 36 and 37, for Run CEN-21, a 420-megawatt-second burst. Figure 36 shows a distinct circular area which divides the relatively hot, central region of the core from the cooler region near the edge of the core. Figure 37 shows a sectional view at higher magnification; the cracks and changes in porosity caused by sintering are clearly evident.

Figures 38, 39, and 40 show the physical changes which took place in the oxide-core pins during the transient. In Experiments CEN-22 and -23, the aluminum jacket was melted in the central region near the core pellet. Also, considerable distortion took place. The relatively massive end plugs were not melted. In each case the oxide core was fragmented and partially discharged through the holes produced in the jacket. For an average energy input of 500 cal/gram, the maximum temperature of the oxide core was 2750 C (adiabatic). The oxide core was fragmented in CEN-24 and came out of the jacket; however, Figure 40 shows only the jacket.

Table 34

SUMMARY OF RESULTS OF IN-PILE METAL-WATER EXPERIMENTS
WITH OXIDE AND CERMET-CORE FUEL PINS

oxide core composition, w/o: 81.51 ZrO₂, 9.06 CaO, 8.69 U₃O₈, 0.74 Al₂O₃, 93% enriched

cermet core composition, w/o: 90 Al, 10 U₃O₈, 95% enriched

	CEN Transient Number							
	19	20	21	22	23	24	25	26
<u>Fuel Pin Material</u>								
Clad	Al	Al	SS	Al	Al	SS	Zr-2	Zr-2
Core	oxide	oxide	oxide	oxide	oxide	oxide	cermet	cermet
<u>Environment of Pin</u>								
	in	in	in	in	above	above	in	in
	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	He	H ₂ O
<u>Reactor Characteristics</u>	(final burst)						(final burst)	
Mw-sec burst	169	260	420	490	540	560	340	240
Mw peak power	594	590	765	1550	1710	1705	1670	1660
Ms period	101	105	78	65	60	65	64	63
<u>Thermal Neutron Dose,</u> nvt x 10 ⁻¹⁴ ,	3.6	4.8	6.5	8.7	8.2	10.5	4.5	4.8
by gold foil activation					9.6			
<u>Core Fission Energy Input</u> by Mo ⁹⁹ Analysis,	95	-	-	462	504	363	-	502
calories/gram								
<u>Per Cent of Metal</u> <u>Reacted with Water</u>	0	0	0	0.8	0.7	1.4	-	-
<u>Appearance of Fuel</u> <u>Pin after Transient</u>								
Clad	no change	no change	no change	melted	melted	melted	penetrated	penetrated
Core	-	-	cracked	fragmented, partially fused	fragmented, partially fused	fragmented, partially fused	melted	melted
<u>Peak Surface Temp</u> <u>of Pin, C</u>	660	>140	>140	735	>245	>640	360	-
<u>Peak Pressure Rise, psi</u>	-	42	10	250	-	12	20	186

The typical amounts of material involved in these oxide and cermet pin transients are as follows for one fuel specimen, in grams:
oxide core: 4, cermet core: 2, aluminum clad: 4, stainless steel clad: 9, Zircaloy-2 clad: 14.

FIGURE 36
CROSS SECTION OF OXIDE-CORE PIN
AFTER TRANSIENT CEN-21

10X Magnification

FIGURE 37
SECTOR OF OXIDE CORE FROM CEN-21

35X Magnification

FIGURE 38
ALUMINUM-JACKETED, OXIDE-CORE PIN
AFTER TRANSIENT CEN-22

FIGURE 39
ALUMINUM-JACKETED, OXIDE-CORE PIN
AFTER TRANSIENT CEN-23

FIGURE 40
STAINLESS STEEL JACKETED,
OXIDE-CORE PIN AFTER
TRANSIENT CEN-24

Figures 41 and 42 show how the molten aluminum- U_3O_8 cermet core penetrated through the Zircaloy jacket and dispersed with the production of particles. An interesting observation in connection with the transients on the oxide core fuel pins is the long thermal lag as shown in Figure 43. As previously noted in ANL-6101, page 149, and ANL-6145, page 172, the peak temperature of metal pins occurs within 0.1 sec of the flux peak. However, lags of 1 to 5 seconds have been observed with the oxide-core pins. In some runs, the thermocouple became dislodged from the jacket during the transient; hence, the peak temperature did not coincide with observation of melting of the metal.

The next major study in this program will be the investigation of preirradiated fuel specimens which contain entrapped fission product gases.

FIGURE 41
ZIRCALOY-2-JACKETED, CERMET-CORE PIN
AFTER TRANSIENT CEN-25

FIGURE 42
ZIRCALOY-2-JACKETED, CERMET-CORE PIN
AFTER TRANSIENT CEN-26

FIGURE 43
CEN-24 OSCILLOGRAPH RECORD

IV. REACTOR CHEMISTRY

Data are being obtained on the neutron-capture cross sections of uranium-236 as a function of neutron energy. Cross sections obtained for 0.5, 0.7 and 0.8-Mev neutrons are 0.26, 0.29, and 0.32 barn, respectively.

Among the problems being examined in development of a Boiling Slurry Reactor Concept (described in ANL-6101, page 160) is preparation of spherical thoria-urania particles. Properties of the fuel particles before and after firing at high temperatures have been studied.

In the Reactor Decontamination Program, the corrosion in decontamination reagents of various steam turbine constructional materials, typical of those used in boiling water reactor steam systems, was evaluated. The second step of the decontaminating procedure, which employs ammonium citrate, was the most corrosive. The high-chromium stainless steels (13 per cent) were more resistant than low alloy and mild steels. Adjustments of the solution pH reduced the attack on the latter without significantly reducing the ability to decontaminate. The presence of oxygen or hydrogen in 600-psi contaminated steam reduced the effectiveness of the decontamination procedure.

Several loop runs simulating boiling water reactor conditions were made at 200 psig with irradiated uranium to ascertain the amount of contamination of metal surfaces in the vapor phase. Vapor-phase contamination was about a factor of 10 greater when steam velocity was increased from 0.8 to 1.2 feet per second.

Construction work is proceeding on apparatus to study the effects of superheated steam on materials of construction. A circulating autoclave is nearing completion, and facilities for handling a series of static autoclaves are in the design stage. Since an operating nuclear superheater is expected to contain significant quantities of radiolytic hydrogen and oxygen along with the steam, provisions will be made to include these gases in the test equipment. The exact design of the hydrogen-oxygen addition and monitoring equipment depends on the rates of reaction of these gases with each other under the test conditions. Since these rates have not been measured, additional apparatus is being assembled for this purpose.

A. Determination of Nuclear Constants - Neutron-capture Cross Sections of Uranium-236

(C. E. Crouthamel, D. Stupigia and R. Heinrich)

1. Fast-neutron-capture in Uranium-236 (D. Stupigia and R. Heinrich)

The neutron-capture cross section of uranium-236 as a function of neutron energy has been determined at several energies using the

Van de Graaff accelerator of the Reactor Engineering Division. Monoenergetic neutrons are obtained from the proton beam by the reaction $\text{Li}^7(\text{p}, \text{n}) \text{Be}^7$. The data are shown below:

Neutron Energy (Mev)	Cross Section (barn)
0.5	0.26
0.7	0.29
0.8	0.32

These values are much lower than the preliminary result quoted in the last quarterly report (ANL-6145, page 177), because the neutron flux, now having been determined, was estimated only roughly at that time. It is seen that the cross section is rising with energy, although the reverse is expected in this energy region. This effect has also been observed by other workers for the species thorium-232 and uranium-238.¹⁷ The shape of the cross-section curves has been explained for the uranium-238 and thorium-232 data.¹⁸ These authors have shown that the cross sections are determined by the ratio of the energy level density in the compound nucleus to the number of levels in the target nucleus below the incident neutron energy. An attempt will be made to compare the present data with this type of calculation.

The cross-section determination is based upon an absolute calibration which relates the gamma counting rate of uranium-237 in a uranium dioxide disc to the disintegration rate. The absolute disintegration rate of the activation product, uranium-237, is determined by 4π beta counting. A known amount of this activity is then introduced into uranium discs geometrically similar to the target discs, and the counting rate is determined for a particular gamma ray of uranium-237, using the scintillation spectrometer. Although the 4π beta count seems to be valid and reproducible, further refinements in this measurement are being sought, since the preparation of the sources is generally difficult.

2. Capture-to-fission Ratios in EBR-I, Mark III (C. E. Crouthamel, D. Stupigia and R. Heinrich)

Samples of uranium-233, -235 and -238, and of plutonium-239 and -240 have been undergoing irradiation in the fast breeder reactor EBR-I since May 23, 1960. The required total exposure of about 800,000 kilowatt-hours should be reached by the end of August, 1960. Thereafter, the samples will be brought here for analysis.

¹⁷Hanna, R. C. and Rose, B., J. Nucl. Eng., 8, 197 (1959).

¹⁸Lane, A. M. and Lynn, J. E., Proc. Phys. Soc., A70, 557 (1957).

B. Slurrex Chemistry Supporting Program
(C. E. Crouthamel)

Preparation of Spherical Thoria-Urania Particles
(W. G. Knapp)

Spherical thorium-10 per cent uranium dioxide particles have been prepared and fired up to 1600 C without appreciable sintering. The method of preparation begins with the preparation of a thorium nitrate stabilized sol, 3.0 molar in thorium concentration, which is adjusted to a pH of about 3.8 with concentrated ammonium hydroxide. Acid-free uranyl nitrate crystals are dissolved in the sol and the pH will drop to approximately 3.6. No additional adjustment of the pH can be made as the uranium will precipitate and cannot be redissolved with small additions of nitric acid. The sol is then sprayed into an atmosphere of ammonia vapor which gels the liquid droplets of the thoria sol very rapidly. The material is washed with 7 molar ammonium hydroxide and finally with methanol. The material is then dried and fired.

Spherical thorium oxide particles in the 1 to 50-micron size range and with 10 per cent uranium dioxide prepared as described above have been fired at high temperatures to determine the sintering temperature of this material. The sintering point is the temperature at which bulk samples of the material tend to agglomerate into a caked mass. This represents a possible serious limit to the compacting and hardening of individual particles by firing bulk samples. Sintering of similar material prepared by other methods has previously been observed to occur above approximately 1050 C with 10 per cent uranium oxide in a thorium oxide matrix. However, the test samples made in this laboratory have not sintered at 1600 C. This unusual inert behavior is attributed to the homogeneity of the distribution of uranium oxide throughout the thorium oxide matrix, which was achieved in the method of fabrication of the individual particles. The 1600 C fired material has a high density (9.9 g/cc) and a low surface area (<0.2 sq m/g).

Spherical thoria gel material which had been dried between 110 and 650 C yielded an unstable particle. Periodic observation of the individual spheres of thorium oxide over periods of days to weeks on a glass slide with a 400 to 600-power microscope revealed a series of changes. The individual spheres, which at first appeared clear and glassy, gradually became a diffuse white, with protrusions extending out of the spherical surface. Finally, the individual spherical particles shattered into irregular crystalline fragments. Material fired up to 650 C and cooled to room temperature was observed to shatter at room temperature over a period of several days to a week until all the spherical particles were destroyed.

Material which was dried and fired in a short period (4 to 8 hours) at 950 C or higher kept its clear glassy appearance and remained stable as

a spherical particle. Apparently the growth of large crystals in the hydrated oxide is responsible for the fragmentation of the spheres. If the water is removed rapidly, large crystals are not formed. Gel stored under aqueous ammonium hydroxide for months showed no deformation of the spherical particles.

It is necessary in the fabrication of large quantities of material to remove water and methanol at low temperature, i.e., at about 110 to 230 C. However, storage of this partially dried material over extended periods of time (>10 hours) may cause a fraction or even all of the particles to deform from their original spherical shape.

C. Reactor Decontamination (W. B. Seefeldt)

1. Laboratory Program (S. Vogler, H. Tyler)

Laboratory studies are being made to evaluate decontamination methods that may be useful in boiling water reactor systems. Efforts to date have been focused on the decontamination of stainless steel type 304 with liquid reagents.

A recommended procedure for the decontamination of metallic surfaces contaminated by high-pressure steam (~600 psig) involves the use of alkaline permanganate followed by the use of ammonium citrate or citric acid. Current investigations are aimed at exploiting the use of foam with these reagents in an effort to achieve decontamination with smaller volumes of solution than are necessary with liquid-phase decontamination.

a. Corrosion Behavior

Corrosion tests were run on four metals used in EBWR, which are typical of those found in many turbine-generator systems. These metals are

1. 13 per cent chromium alloy (buckets)
2. 13 per cent chromium, nonhardening alloy (nozzle elements)
3. AISI 4140 (wheels)
4. 1 per cent chromium- $\frac{1}{2}$ per cent molybdenum (shaft).

The metals were exposed to solutions representative of the alkaline permanganate-ammonium citrate decontamination procedure. In preliminary tests, a sample of steel was immersed in a solution of 3 per cent potassium permanganate in 20 per cent sodium hydroxide at 90 C for five hours. After removal from the permanganate solution the

metal was rinsed with distilled water and placed in a solution of 10 per cent ammonium citrate or 10 per cent citric acid for two hours at 85 C. At the completion of this exposure, the metal was rinsed in distilled water and dried. Weighings before and after the exposure gave the weight loss due to reaction in the two solutions. The results are shown in Table 35. These results indicate that the higher chromium alloys are more corrosion resistant than the other steels.

Table 35

CORROSION OF EBWR TURBINE METALS IN ALKALINE
PERMANGANATE-AMMONIUM CITRATE SOLUTIONS

Step 1: 3 per cent KMnO_4 }
 20 per cent NaOH } 90 C for 5 hours

Step 2: 10 per cent ammonium citrate or citric acid, 85 C for 2 hours

Metal: 1-inch square specimen

Material	Weight Loss (mg) ^a	
	10% Ammonium Citrate (pH 4.8)	10% Citric Acid
13% Chromium steel	8.3	13.7
13% Chromium steel (nonhardening)	9.8	15.4
AISI-4140	374	1247
Chromium-molybdenum steel (1% Cr-0.5 Mo)	559	1226

^aA weight loss of one mg represents a penetration of 4×10^{-3} mil.

An effort was made to separate the corrosive effect of each of the solutions. This was done by placing a sample of 13 per cent chromium steel in a 10 per cent citric acid solution. The results for 2- and 6-hour exposure periods showed weight losses of 243 and 220 mg, respectively, compared to 15 mg when samples were first exposed to alkaline permanganate, then to citric acid. These results indicated that the exposure of the metal to the alkaline permanganate solution prior to immersion in citric acid results in an inhibition of the corrosion for citric acid alone. It was also indicated that the bulk of the corrosion with citric acid occurred during the early period of the exposure.

Additional tests were made on the 13 per cent chromium steel to determine if additional exposure to the citric acid solution after

the alkaline permanganate solution would result in a loss of the inhibiting effect produced by the permanganate. For example, the first two-hour exposure to citric acid resulted in a weight loss of 9.4 mg. Two additional four-hour exposures resulted in a weight loss of 0.3 mg in each case. Thus, for the limited test times, the corrosion inhibition produced by the alkaline permanganate was not destroyed after a ten-hour exposure to the citric acid solution. This effect was also noted with the ammonium citrate solutions.

A ten per cent solution of ammonium citrate in water has a pH of approximately 4.8. In an effort to reduce the corrosiveness of the ammonium citrate solution, several tests were made in which the pH was raised by the addition of sodium hydroxide. This resulted in the release of ammonia; the subsequent solution contained sodium citrate, and possibly some ammonium ions. In these tests, exposure to citrate solutions followed a regular alkaline permanganate exposure. The results as given in Table 36 clearly indicate the improvement of corrosion with an increase in the pH of the citrate solution.

Table 36

EFFECT OF pH OF CITRATE SOLUTION ON CORROSION

Step 1: 3 per cent KMnO_4 } 90 C for 5 hours
 20 per cent NaOH }

Step 2: 10 per cent ammonium citrate,
 pH adjusted with sodium hydroxide

Time: 4 hours

Temp: 85 C

Coupon: One inch square

Material	Weight Loss (mg) ^a		
	pH 7	pH 9	Sodium Citrate, pH 10
AISI-4140	756	13	5
Chromium-Molybdenum Steel (1% Cr-0.5% Mo)	48	13	6

^aWeight losses of 500 to 1000 mg were obtained with ammonium citrate solution which was not pH adjusted.

To summarize these results and also to confirm them, additional experiments were made. Results, given in Table 37, show that for the high-chromium steels changes in the pH of the citrate solution do not affect the corrosion of these metals. For the other steels, the corrosion rate is very much a function of the pH of the citrate solution. Several experiments were run in order to ascertain whether pH changes of the citrate solution affected the decontamination of stainless steel by the alkaline permanganate procedure. The first results indicated that the higher pH did not materially change the decontamination obtained from the standard alkaline permanganate-citrate procedure.

Table 37

CORROSION OF TURBINE METALS IN A MODIFIED ALKALINE
PERMANGANATE DECONTAMINATION PROCEDURE

Step 1: Alkaline permanganate solution,^a 90 C for 5 hr

Step 2: Citrate solution, 85 C for 2 hr

Sample: One inch square

Material	Weight Loss (mg)	
	10% Ammonium Citrate	10% Citric Acid (pH 9) ^b
13 Chromium Steel	9	14
13 Chromium Steel (nonhardening)	9	9
AISI-4140	33	7
Chromium-Molybdenum Steel (1% Cr, 0.5% Mo)	20	9

^aAlkaline permanganate solution: 3 per cent KMnO_4 and 20 per cent NaOH .

^b10 per cent citric acid solution adjusted to pH 9 with sodium hydroxide.

Contemplated procedures for decontamination of reactor systems involve the use of the reagents at room temperature. Experiments were carried out with the low-chromium steels in ten per cent ammonium citrate at room temperature. The results have been summarized in Figure 44. These results showed significant corrosion with no indication of a diminution of the corrosion rate with time.

Oxalic acid has been found to be a promising decontamination reagent for mild steel and stainless steel exposed to water at elevated temperatures. In addition, it has been used with

reasonable success for the decontamination of stainless steel exposed in the HRE (Homogeneous Reactor Experiment) and for the decontamination of separations process equipment. On the basis of its possible utility, the corrosion resistance of samples of mild steel used in the EBWR system to oxalic acid was examined. Samples of the metal were immersed in 2.5 per cent oxalic acid at room temperature. These results, given in Table 38, indicate that the corrosion rate decreases with time, in contrast with results in citric acid, which showed no decrease in corrosion rate with time.

Table 38

CORROSION OF LOW-CHROMIUM STEELS
IN $2\frac{1}{2}$ PER CENT OXALIC ACID AT
ROOM TEMPERATURE

Metal: One inch square

Time (hr)	Total Weight Loss (mg) ^a	
	Cr-Mo Steel	AISI-4140
2	26.6	33.1
9	45.4	43.3
25	71.5	62.8

^aA weight loss of 1.0 mg represents a penetration of 0.004 mil.

b. Effect of Oxygen or Hydrogen in Steam on the Decontamination of Stainless Steel by the Alkaline Permanganate-Citrate Procedure

In a boiling water reactor such as EBWR, the steam entering the turbine contains from 5 to 20 ppm of oxygen, which is produced by the radiolysis of the water in the reactor vessel. The oxygen which is formed is stripped from the water and is carried along with the steam. Hydrogen would be expected to exist in corresponding stoichiometric proportions.

The effect on decontamination of the presence of oxygen and hydrogen during contamination was studied. Three parallel experiments were performed in which contamination conditions were varied. Prefilming conditions and decontamination procedure were held constant. Prefilming consisted of exposure of the specimen liner to 600 psig steam (100 ml of deionized water present in autoclave) for $6\frac{1}{2}$ days. In each of the three contamination cycles, 2 to 3 g of irradiated uranium were charged to the specimen liners, together with 100 ml of deionized water prior to heating to 600 psig.

In the first experiment, extraneous gases were removed by first pumping out the assembled autoclave and then flashing off small amounts of steam at low pressures. In the other experiments, two autoclaves were pumped down and then 80 psig oxygen was added to one and 80 psig hydrogen was added to the other autoclave. The samples of specimen liners from each experiment were subjected to the decontamination method described below.

Using the foam decontamination technique at room temperature with a solution consisting of 0.5 per cent potassium permanganate, one per cent sodium hydroxide, and 0.2 per cent Makon 10 for four hours, followed by 10 per cent ammonium citrate, 0.2 per cent Makon 10 for one-half hour, the following results were obtained. A sample of the liner from the degassed experiment gave a decontamination factor of approximately 100, whereas a sample from the oxygen experiment gave a decontamination factor* of two. A sample from the hydrogen experiment gave a decontamination factor of six. Similar results were obtained in beaker tests under slightly different conditions.

Current experimentation is aimed at measuring the effects of more realistic concentrations of oxygen in the steam phase upon the decontamination. Decontamination experiments similar to those previously mentioned were carried out in which the steam phase during the contamination period contained approximately 200 ppm of oxygen. The results showed a decontamination factor of four as compared with a decontamination factor of 16 for metal contaminated in a steam phase in the absence of oxygen.

These results indicate that the presence of oxygen in the steam phase during the contamination period results in a decrease in the decontamination obtained by the alkaline permanganate-citrate method. Future experiments will be aimed toward measuring the effect of lower concentrations of oxygen.

c. Foam Characteristics

Boiling water reactor systems involve large volumes of piping and vessels. Decontamination of such systems by filling with liquid would result in large volumes of liquid waste. Attempts have been made to reduce the volume of liquid handled by techniques involving the wetting of the system walls. One such technique is the use of vapors. Another somewhat analogous technique is the use of foam as a vehicle for transporting

*Decontamination factor is the ratio of the counting rate before to the counting rate after the decontamination step, as measured with a single-channel scintillation spectrometer using a 4 x 4-in. sodium iodide, thallium-activated crystal and a 50-kev threshold energy.

the decontaminating reagent to the proper metallic surfaces. Preliminary decontamination experiments using the foam technique with the alkaline permanganate and ammonium citrate reagents have yielded gamma-decontamination factors of 10 to 15.

A number of surfactant materials were tested for their ability to generate and sustain foams in alkaline permanganate solutions.

The procedure consisted of preparing solutions of 0.5 per cent potassium permanganate, one per cent sodium hydroxide, and 0.2 per cent of the surfactant. These solutions were allowed to stand and a qualitative appraisal of the solution stability was made by observing the color of the permanganate solution; a change in the color was taken as a measure of chemical instability.

The ability to generate foam was measured by placing 200 ml of the permanganate solution in a 2-liter measuring cylinder. Nitrogen was bubbled through the solution at a rate of 300 cc/min through a fritted disc until the foam reached the 2000 ml mark. At this time the liquid foam interface was noted from the volume markings of the cylinder. From the observed values, the volume of foam generated was determined as well as the volume of liquid expended in this foam. From these two numbers a foam ratio was calculated for each solution. This is defined as cc of foam volume generated per cc of liquid. In addition, the foam half-life was determined for several of the surfactants by measuring the change in foam volume with time.

The surfactants tested were

1. Solvidine G	- Ciba Chemical Co.	(an alkyl aryl sulfonate)
2. Sodium lauryl sarcosine		
3. Sodium dibutyl naphthalene sulfonate		
4. FC - 95	} Minnesota Mining
and
Manufacturing Co.	an anionic surfactant
5. FC - 98		an anionic surfactant
6. FC-128		an anionic surfactant
7. FC-134		a cationic surfactant

Solvidine G, sodium lauryl sarcosine, FC-95, FC-98, and FC-128 showed a stability in alkaline permanganate solution of more than several hours. The sodium lauryl sarcosine indicated marked instability after 48 hours. The results obtained with these surfactants are summarized in Table 39.

The foam ratio is a measure of the volume of foam produced by one cc of liquid and indicates the volume of liquid which may be saved in a plant operation. On the other hand, if foam ratios are too large, then very little of the decontaminating reagents are brought to the metal surface requiring decontamination.

Table 39

FOAM CHARACTERISTICS OF SURFACTANTS

Solution Foamed: 0.5% KMnO_4
 1.0% NaOH
 0.2% Foamer

Temperature 25 C
 Gas Flow Rate: 300 cc/min

	Foaming Agent						
	Solvidine G	Sodium Lauryl Sarcosine	Sodium Dibutyl Naphthalene Sulfonate	FC-95	FC-98	FC-128	FC-134
Time to Generate Foam (sec)	46	41	36	46	-	43	44
Foam Ratio ^b	29 ^c	14	14	17	10 ^a	73 ^d	37
Foam Half-life (min)	54 ^c	15	5	15	0.5	39 ^d	23

^aWith nitrogen flow the foam did not rise above 1230 cc.

^bVolume of foam produced by one cc of liquid.

^cAverage of four determinations.

^dAverage of two determinations.

Of the foaming materials tested, the Solvidine G, FC-95, and perhaps FC-128 appear to be the most useful surfactants. For the FC-128, the foam ratio is high, indicating a rather dry foam; this may affect decontamination characteristics.

2. Loop Operations (D. Grosvenor, C. Bally)

A stainless steel loop which simulates the action of a boiling water reactor has been installed in a shielded cell for the purpose of studying the effects of fuel ruptures. A description of the equipment appeared in ANL-5858, page 66. The primary objective is the study of the deposition characteristics of various fission products in the vapor phase of the loop as a result of introducing them into the liquid phase. Single or mixed fission products are introduced into the equipment as tracers or in irradiated uranium. A metal sample strip of suitable composition (stainless steel type 304 in experiments conducted to date) is inserted into the vapor-phase disengaging section. This is removed following a run to determine the types and quantities of fission products deposited. In addition, a scintillation detector is located on the outside of the disengaging section at an elevation eight inches below the steam exit line to monitor the deposition of

gamma activities at that point. All elevations referred to in the text, figures, and tables were measured from a common reference point, namely, the liquid sampler line. A figure showing the elevations of pertinent equipment items appeared in ANL-6145, page 182.

Initial runs made in the equipment utilized yttrium-90 and cesium-137 tracer activities. Early runs were made at the design pressure level of 600 psig; because of equipment difficulties, more recent runs have been made at 200 psig.

Four runs were completed during the past report period. In three of these (CL-1, CL-2, and U-1) mixed fission products were introduced in the form of irradiated uranium. The fourth run (Cs-4) was conducted with cesium-137 tracer in order to study the effect of liquid level on activity buildup in the vapor section. Cylindrical discs of uranium weighing 20 to 25 grams were used in Runs CL-1 and CL-2. The radiation level was 390 MWD/ton and cooling time was 3 years. This corresponds to a cesium-137 content of 2.74×10^9 disintegrations per minute per gram of uranium. The uranium for Run U-1 was irradiated in the CP-5 reactor for 15 days and cooled for 37 days (10.9 MWD/ton). Operating conditions and tabulated results are shown in Table 40.

The loop instrumentation senses "liquid level" by monitoring the weight of liquid above the reference elevation. To calculate true liquid level requires knowledge of liquid density and steam void fraction. In previous reports, a void fraction of 0.10 was assumed. More recent information from the Heat Engineering Section of the Reactor Engineering Division has resulted in new assumptions that are reflected in the data for this report period. At the present operating pressure of 200 psig the following void fractions were used: 0.31 at 0.8 feet per second, and 0.36 at 1.2 feet per second.

The corrosion of the uranium inserted into the loop was monitored by placing a beta-gamma probe at the liquid crossover line. Physically this line is located about 7 feet above the point where the uranium is introduced. As corrosion proceeds and fission products pass into the circulating water, increased radiation levels are observed at the crossover. The results of these surveys for Runs CL-1 and CL-2 are shown in Figure 45. The radiation level in Run CL-2 shows a maximum after 25 hours, followed by a gradual decline to the end of the run. In Run CL-1, 95 per cent of maximum was achieved at 25 hours, with the actual maximum occurring between 50 and 80 hours. The subsequent decline was less marked than in Run CL-2. Visual evidence following the run indicated that a large amount of the uranium corrosion product remained in the retaining screen and did not circulate with the water. Weights of residue recovered plus the results of chemical analyses for uranium are shown in Table 41. In Run CL-1, it will be noted that nearly 50 per cent of the

Table 40

TABULATED RESULTS FOR CONTAMINATION RUNS IN BOILING WATER LOOP

Sample Strip: SS304 preoxidized at 600 psig
 Pressure: 200 psig
 Run Length: 138 to 140 hr

	Run No.					
	CL-1		CL-2		U-1	
Steam Rate, ft/sec	0.8		1.2		0.8	
Uranium Irradiation	390 MWD/ton, cooled 3 yr		390 MWD/ton, cooled 3 yr		10.9 MWD/ton, cooled 37 days	
Liquid Level, in.	13.8 to 14.6		13.8 to 15.5		17 to 20 in.	
Time of Sampling, hr after start of run	64.5	136.5	67	90.5
Liquid level at time of sampling, in.	13.9 ^a	13.8 ^a	14.4 ^b	14.6 ^b		
Disengaging Factor (weight basis)	1.52×10^4 (γ)	8.62×10^3 (γ)	7.50×10^3 (γ)	1.85×10^4 (γ)		No Results
Disengaging Factor (volume basis)	1.76×10^6 (γ)	9.98×10^5 (γ)	8.67×10^5 (γ)	2.14×10^6 (γ)		
Counts in Liquid Phase, cpm/g	1.14×10^6 (γ)	1.12×10^6 (γ)	7.35×10^5 (γ)	8.12×10^5 (γ)		
<u>Activity Deposited on Sample Strip</u>						
a. liquid phase, cpm/sq cm	2.91×10^4 (β)		2.99×10^3 (β)		$2.1 \times 10^6(\gamma)^c$	
b. Minimum in vapor phase, cpm/sq cm	23.5 (β)		133 (β)		$3 \times 10^3(\gamma)^c$	
c. Vapor phase, max elevation, cpm/sq cm	28 (β)		150 (β)		$3 \times 10^3(\gamma)^c$	

^aAssumes void fraction of 0.31

^bAssumes void fraction of 0.36

^cValues are total counts for coupons having approximate area of 2 sq cm.

uranium was retained in the sampler screen. It appears that only small quantities, if any, of particulate uranium dioxide was in suspension in the circulating water. Complete gamma spectra are being obtained on samples of water and dissolved mud in order to determine differences in fission product distribution.

Table 41

AMOUNT OF URANIUM CORROSION PRODUCT RESIDUES
REMAINING IN SAMPLER FOLLOWING
RUNS CL-1 AND CL-2

	Run CL-1	Run CL-2
Weight of uranium charged, g	23.8	21.6
Weight of corrosion product "mud" following run, g	24.5	11
Weight of uranium in mud as determined chemically, g	11.4	4.7
Per cent uranium retained in screen	48	21

The sample strip in all runs reported was stainless steel type 304. Surface preconditioning consisted of degreasing followed by preoxidation in 600 psig steam for a period of four days. Activity deposition (total beta) on the strips in Runs CL-1 and CL-2 are shown in Figure 46. The general activity level at elevations 10 inches or more above the liquid appears to be greater by about a factor of 10 in Run CL-2 than in Run CL-1. The effect is probably due to the higher steam velocity of 1.2 ft per second in the disengaging section. Liquid-phase activity deposition (Table 40) was relatively low for Run CL-2 which suggests that increased turbulence due to the higher steam velocity may produce this effect.

FIGURE 46
BETA ACTIVITY OF STAINLESS STEEL TYPE 304 SAMPLE STRIP IN
RUNS CL-1 AND CL-2

Similar data for Runs Cs-2 and Cs-3 are shown in Figure 47. These runs were also made at steam velocities of 0.8 and 1.2 ft per second, respectively; however, the activity was tracer cesium-137. A similar factor of ten in the activity concentration above an elevation of 30 inches can be observed. It would be expected that greater entrainment would be produced at the higher steam velocity and hence yield the results indicated. However, the disengaging factors calculated from steam and water samples yielded unexpected results. Disengaging factors were at least equal if not greater in runs in which steam velocities were 1.2 feet per second.

Run Cs-4 was conducted with cesium-137 tracer to clarify the effect of liquid level on the increase in the count rate in the disengaging section or measured by the scintillation detector and single-channel analyzer. The increase in count rate was determined at six different liquid levels, each of which was maintained for a period of 20 hours or more to achieve equilibrium conditions. The results are shown in Figure 48. The most significant result was the rapid change in count-rate increase occurring in the range of liquid levels between 14 and 15 inches. It appears that this level of water is necessary to dissipate the kinetic energy resulting from the high velocity of the steam-water mixture as it enters the disengaging section from the riser. It should be noted that this curve was obtained at a steam velocity of 0.8 feet per second at 200 psig pressure. Presumably the curve would be altered by changes in either the steam-generation rate or pressure.

FIGURE 47
BETA ACTIVITY OF STAINLESS STEEL TYPE 304 SAMPLE STRIP IN
RUNS Cs-2 AND Cs-3

FIGURE 48
COUNT RATE INCREASE AT LOOP DISENGAGING SECTION AS
INFLUENCED BY LIQUID LEVEL

The short cooling time of the uranium used in Run U-1 affords an opportunity to observe the behavior of shorter lived fission products. The liquid level throughout the run was maintained above the critical 14- to 15-inch transition region (see Figure 48). Three kinds of gamma activity measurements were made: 1) total gamma counts from the sample strip removed from the equipment after the run, 2) 256-channel gamma scintillation spectrometer scans on the same sample strip, and 3) single-channel gamma-ray spectrometer scans of the disengaging section obtained during the run. Most of the results of gamma-ray spectrometer scans on the sample strips for this run are not yet available. Total gamma counts on the sample strip as a function of elevation have been obtained. Typical liquid-phase deposition is of the order of 2×10^6 cpm per sq cm while vapor-phase deposition above an elevation of 30 inches is 3×10^3 cpm per sq cm. The decrease is very rapid from an elevation of 22 inches (probably the liquid level) to 30 inches, followed by a lower rate of decrease to an elevation of 68 inches.

Gamma-energy scans of the disengaging section were obtained with the single-channel analyzer throughout the run. The 0.662-Mev peak of cesium-137 was the only one observed. Integrated count rates indicated the presence of other fission products, but in amounts too low to be detected by gamma scanning because of the high background level.

Following Run U-1, the vapor-phase section of the loop was decontaminated with the two-step alkaline permanganate procedure. Gamma-energy spectra were obtained during the first step, in which 3 per cent potassium permanganate-10 per cent sodium hydroxide was circulated at about 90 C. It should be noted that during the decontamination procedure, the radiation detector sees not only the activities deposited on the disengaging section sidewall, but also the dissolved activities in the circulating liquid. During the first half hour, the cesium-137 peak previously observed was the only one in evidence. After one hour, peaks of 0.49 Mev and 0.75 Mev appeared. These are probably associated with zirconium-niobium-95 and ruthenium-103 activities. When the loop was drained, the latter two peaks disappeared, which indicated that these activities were associated with the solution rather than sidewall plate-out. The cesium-137 peak remained. It appears that the decontaminating solution effectively removed zirconium and ruthenium activities.

D. Structural Materials for Nuclear Superheaters (E. H. Dewell)

As the plans for nuclear superheaters develop, the need for a continual flow of basic and applied data on the nature of reactions between the various chemical entities making up such systems becomes increasingly important. This program is intended to supply a part of that need. At the present time three separate systems of apparatus are under construction. A brief discussion of their purposes and current status follows.

1. Corrosion-testing Apparatus

This unit and its auxiliary equipment will provide a test facility in which samples of metals and alloys can be subjected to conditions simulating those of a nuclear superheater. Test temperatures up to 575 C are planned, and provisions are being made for controlled additions of hydrogen and oxygen to simulate the effects of radiolytic decomposition. The apparatus, primarily a circulating autoclave, has been described and its operating principles have been discussed (ANL-6029, page 141). Many of the conditions which have been anticipated for nuclear superheaters can be reproduced in the testing apparatus, except the extremely high steam velocities and radiation fields. Thus such factors as steam erosion and the effects of radiolytic free radicals must be studied in other equipment. The chemical effects of molecular hydrogen and oxygen can be observed, however, and an evaluation of their practical importance is a major objective of the program.

The corrosion-testing apparatus is being installed in a testing cell constructed specifically for it. Installation of the pressure vessel and heaters is complete. The control panel has also been set in place and will shortly be ready for service. Two major items remain - the hydrogen and oxygen-injection equipment and the analytical apparatus. Neither of these can be fully designed and built until more is known of the rates at which hydrogen and oxygen react with each other in steam at temperatures of interest to this program. This information will be obtained from the other equipment which is under construction. Meanwhile, the test apparatus will be pressurized and operated with a pure steam environment to check out the operating controls and recording equipment, and to establish a basis for comparing samples exposed to pure steam with those exposed to steam-hydrogen-oxygen mixtures.

2. Static Autoclaves

The data obtained through extended exposure of samples in the corrosion testing apparatus will be supplemented by information from much shorter tests carried out in small static autoclaves. As the experimental work proceeds, many different autoclave designs will be used according to the nature of the particular tests, and in some cases the simplest procedure will be the alteration of available commercial equipment. Radical changes are likely to result in operation beyond the maximum safe operating pressures or temperatures; hence there is a possibility that an autoclave could rupture in these experiments. Accordingly, all the static autoclave tests will be carried out behind heavy barricades and with remotely operated equipment. This shielded area is currently in the design stage. Two small autoclaves built by Autoclave Engineers, Inc., are being modified for service at temperatures around 540 C. When the autoclaves are ready for service, they will be used first for heating a series of sealed ampoules to be used in studying the hydrogen-oxygen reaction.

3. Ampoule Filling and Analysis Equipment

The hydrogen-oxygen reaction will be studied by heating small ampoules containing measured amounts of these gases with water for extended periods and then analyzing the residual gas. For work at the lower temperature ranges, glass ampoules will be used; at the higher temperatures near the critical region of water, it may become necessary to use fused quartz or metal ampoules, since some components of glass are slowly leached by high-temperature steam and water. At the present time the ampoule-charging apparatus is nearly complete; but construction of the gas-analysis apparatus to determine the residual gases has just begun. The latter has been designed along the lines of the micro gas apparatus described by Kenty and Reuter.¹⁹

¹⁹Kenty, C. and Reuter, F. W., Jr., Rev. Sci. Instruments, 18, 918-24 (1947).

V. ANALYTICAL RESEARCH AND DEVELOPMENT (R. P. Larsen)

A fusion technique has been developed for dissolution of plutonium oxide. It involves fusion of the plutonium oxide with ammonium bifluoride, followed by dissolution of the resulting plutonium (IV) fluoride in an acid aluminum-containing solution.

Two analytical methods have been developed for determination of plutonium. One is a spectrophotometric determination of plutonium (IV) with arsenazo, the other is an amperometric titration of plutonium (VI).

The Dissolution of Plutonium Oxide (C. A. Seils)

Plutonium oxide, particularly if it has been fired at a high temperature, is notably difficult to dissolve. Fluoride-catalyzed nitric acid dissolutions require hours of refluxing and may introduce undesirable contaminants as a result of attack upon glass containers. Refluxing with concentrated hydrobromic acid has also been used, but it too is a protracted method. Neither method can be regarded as dependable. Fusions are generally unsatisfactory since they must be carried out at relatively high temperatures and introduce excessive amounts of salt when the melt is dissolved.

Fusion with ammonium bifluoride provides a rapid and effective means of solubilizing plutonium oxide. The sample is covered with a tenfold excess of ammonium bifluoride in a nickel or platinum crucible and the reaction carried out for 15 minutes on a hot plate just above the melting point of the fluoride (245 C). The excess ammonium bifluoride is fumed off by raising the temperature to about 300 C, and plutonium (IV) fluoride dissolved with acid and a fluoride complexant such as aluminum.

This procedure has worked equally well with zirconium oxide, uranium (IV) oxide and thorium oxide.

A recently declassified report²⁰ states that this fusion technique has been studied as a means of converting plutonium oxide to fluoride in the metal production process.

²⁰ Tolley, W. B., The Preparation of Plutonium (IV) Ammonium Fluoride and Its Decomposition to Plutonium Tetrafluoride for Its Subsequent Reduction to Metal, HW-31211 (March 1954).

Spectrophotometric Determination of Plutonium with Arsenazo (L. E. Ross, D. E. Kudera)

A spectrophotometric determination of plutonium (IV), which uses arsenazo [3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalene disulfonic acid] as the chromogenic reagent, is under development. With this method it would appear that 25 to 100 μ g of plutonium in 25 ml will be determinable with a coefficient of variation of 1 per cent. By using 5-cm cells, the sensitivity of the method will be increased to within a factor of 10 of that for the radiochemical determination.

After separation from interferences and adjustment of the oxidation state, color development is carried out at a pH of 1.0 ± 0.1 . Since plutonium samples are invariably quite acid, and there are no satisfactory buffers for attaining a pH of 1.0, a suitable acid adjustment step had to be found. Coprecipitations with either lanthanum hydroxide or lanthanum fluoride, followed by dissolution in a known amount of nitric acid or nitric acid-aluminum nitrate, are equally satisfactory. The lanthanum fluoride precipitation also serves to separate plutonium from such common interferences as uranium and iron. By using sodium hydroxide to precipitate lanthanum hydroxide, amphoteric hydroxides are separated; by using ammonium hydroxide, such interferences as cadmium, magnesium, and zinc are separated.

The British worker Ockenden²¹ has recently reported on the use of arsenazo as a reagent for plutonium. However, the precision of his work is somewhat poorer, and he has applied the method only to plutonium solutions of known acidity which contain no interferences.

Amperometric Titration of Plutonium (C. A. Seils)

An amperometric titration of plutonium (VI) with iron (II) is under development. It would appear that the coefficient of variation for 10 to 20 mg of plutonium will be about 0.05 per cent and for 0.1 to 0.2 mg about 0.5 per cent. After the plutonium has been oxidized to the hexavalent state with argentic oxide in a dilute sulfuric acid medium and the excess oxidant destroyed by heating, the plutonium is titrated with standardized ferrous sulfate, using a constant-speed rotating platinum electrode to determine the end point. The platinum electrode is operated at +0.6 volt vs. a standard mercurous sulfate electrode.

²¹Ockenden, D. W., Complexes of Plutonium (IV) with Phenylarsenic Acid Derivatives, IGO-R/W-2, Part II (1959).

In an accuracy and precision check, 10 solution aliquots containing from 10 to 20 mg of plutonium were analyzed. (The solution was prepared by electropolishing and dissolving metal, the reported purity of which was 99.98 per cent.) The mean of the results was 99.97 per cent, with a coefficient of variation of 0.05 per cent.

An article describing the method is being prepared for publication.

VI. ROUTINE OPERATIONS (H. G. Swope)

A. Waste Processing

(H. G. Swope, J. Harast, K. Bremer, B. Kullen and R. Jarrett)

During April, May, and June, 1960 there were 33,070 gallons of liquid radioactive wastes processed as follows:

Process	Gallons
Evaporation and Concentration	23,640
Filtration	7,220
Flocculation	1,360
Ion-exchange (Cation only)	400
Absorption onto Vermiculite	450
Total	33,070

B. High-level Gamma Irradiation Facility

(H. G. Swope, J. Harast, N. Ondracek, G. Teats, R. Juvinal and C. Ryberg)

Data for samples irradiated in Rack M-1 during April, May, and June, 1960 are summarized in Table 42. The large rack (M-2) was used this period with dosages of 18 day units and 34 night units.

Table 42

SUMMARY OF IRRADIATIONS PERFORMED IN RACK M-1 DURING APRIL, MAY, JUNE, 1960

Month	No. of Samples	No. of Special Dosimetry Samples	Total Urn Units	
			Day	Night
April	678	220	1311	2119
May	1067	333	1858	1872
June	1015	329	1720	3201
Total	2760	882	4889	7192

In the main rack, M-1, of the High-level Gamma Irradiation Facility, five No. 2 cans may be loaded on top of one another for irradiation. Because the spent fuel rods have the highest intensity in the center 12 to 15 inches of their 27-inch length, the dose distribution in each can, except the center one, varies considerably.

In Rack M-1 there are twelve sample ports capable of irradiating 60 No. 2 sized cans ($3\frac{7}{16}$ in. diam $\times$ $4\frac{9}{16}$ in. high) at one time. The dose variation between cans in each urn location is shown in Table 43. The dosimetry was determined in the vertical center of a No. 2 sized can and the results have been expressed as per cent of position 3, the middle can, in each group of five. Actual dose distribution in No. 2 cans in position B-2 as a function of six horizontal dosimetry cells per urn is shown in Figure 49.

Table 43

PER CENT OF IRRADIATION RECEIVED IN THE DIFFERENT POSITIONS IN RACK M-1 OF ARGONNE'S HIGH-LEVEL GAMMA IRRADIATION FACILITY

M-1 Rack Position	No. of Fuel Elements Around Sample Urn	Per Cent Dose Received in Can Position Shown (Compared to 3rd Position = 100%)				
		1B	2	3	4	5T
B-2	4	62.1	89.9	100.0	88.0	52.9
B-3	4	66.4	93.6	100.0	84.2	49.7
B-4	4	72.2	98.4	100.0	80.3	45.6
C-1	4	64.1	91.8	100.0	84.9	50.0
C-2	4	68.2	94.6	100.0	83.1	48.6
C-3	4	75.1	100.0	100.0	79.1	44.7
A-1	2	66.1	93.3	100.0	84.2	52.0
A-2	2	63.1	90.8	100.0	85.6	53.0
A-3	2	59.1	88.0	100.0	88.7	55.5
B-1	2	56.4	86.4	100.0	92.8	60.3
B-5	2	70.0	95.7	100.0	82.5	49.1
D-1	2	65.9	92.9	100.0	86.2	53.4

FIGURE 49
TYPICAL VARIATION OF DOSIMETRY FROM
TOP TO BOTTOM IN IRRADIATION URN

COMPARISON OF SINGLE VERTICAL
CELL VS. SIX HORIZONTAL CELLS