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for Plutonium and Uranium
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AEC Research and Development
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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

April, May, June, 1959

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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

April, May, June, 1959

SUMMARY

I. Chemical-Metallurgical Processing (pages 16 to 69)

A direct-cycle pyrometallurgical fuel-reprocessing plant is being designed in conjunction with the EBR-II reactor. The plant complex also includes a Laboratory and Service Building, construction of which is already well under way.

A number of chemical-metallurgical methods, including refining, liquid metal extraction, and fractional crystallization processes from liquid metals, are being examined for use in this fuel-processing facility. Based on the results of these studies, process components are being designed and tested for use in the EBR-II fuel-reprocessing plant.

Bids for the complete bid package 3, of which the EBR-II Fuel Cycle Facility is part (about $\frac{2}{3}$ of cost,) were received from 11 companies. Malan Construction Company was low bidder with a base bid of \$3,440,000. The contract will be awarded after the decision of an AEC board set up to evaluate the bids.

Melt refining consists of melting discharged reactor fuel in a zirconia crucible and holding it molten for several hours. Purification occurs by volatilization and selective oxidation reactions. The new Mark-5 melt-refining furnace was put into operation in the mock-up area. Sixteen of the required 100, 10-kilogram, enriched fuel ingots for EBR-II have been prepared using this furnace. The balance of the equipment required to demonstrate remote operation of the melt-refining process is being installed and should be in operation during the next quarter.

Studies were continued on processing of melt-refining residues (crucible skull material). Oxidation of the skull material produces a powder which can be poured essentially quantitatively from a crucible. In oxygen-argon atmospheres, the oxidation progressed smoothly and was easily controllable at desired temperatures.

Skull oxide reductions in magnesium-cadmium solutions are in progress. Other reactions in liquid metal media were studied with the following results:

1. Reduction of rare earth oxides by uranium in either zinc or cadmium solutions was shown to occur readily.
2. Considerable interchange of uranium isotopes occurred when enriched metal oxide was contacted at 800 C with a zinc solution of depleted uranium.

Methods of isolation of plutonium from EBR-II blanket material are being examined. About 60 per cent of the plutonium in hydrided-dehydrided blanket material was leached into molten magnesium at 800 C within an hour. Two runs to investigate blanket processing by dissolution in cadmium followed by distillation of the cadmium in the presence of magnesium were made. Although uranium did precipitate from solution, plutonium loss from solution was excessive. Engineering techniques are being developed for the various liquid metal processes under consideration. Design is almost complete on a full-scale distillation unit capable of distilling up to 100 kg of cadmium per hour.

A liquid metal corrosion loop fabricated of mild steel has now operated for over 200 hours. Cadmium containing approximately 2 per cent uranium and 0.2 per cent magnesium is being circulated at 550 C by an electromagnetic pump. The flow rate is about 0.8 gal/min, which results in a velocity of about 2.5 ft/sec.

Additional basic data have been obtained to aid in the study of liquid metal solvents for separation processes. Solubilities of ruthenium, cerium and lanthanum in cadmium have been measured at temperatures from 325 to 625 C; the solubility of uranium in zinc has been measured at temperatures from 425 to 800 C.

A striking relationship between the position of an element in the Periodic Table and its solubility in zinc or cadmium has been observed.

The high-cadmium corners of the ternary systems cadmium-uranium-zinc and cadmium-uranium-magnesium have been investigated. A feature common to both is the disappearance of UCd_{11} as the phase of primary crystallization on the addition of relatively small amounts of zinc or magnesium.

Studies were begun on the uranium-mercury-zinc ternary system, which has aroused interest because of its especially attractive corrosion and solubility properties. Preliminary results indicate that the undesirable characteristics of uranium amalgams may be avoidable in the presence of zinc.

Results obtained by effusion experiments are presented for the vapor pressure of zinc over uranium-zinc alloys.

Emf measurements have been made with an electrochemical cell having as electrodes solid uranium and unsaturated solutions of uranium in cadmium. The purpose of these measurements was to determine the extent of departure from Henry's law of the activity of uranium in such solutions. An appreciable departure had been predicted from the nature of the phase diagram and appears to be confirmed by the preliminary measurements.

Sixteen calorimetric combustions in oxygen have been completed with natural molybdenum disulfide or an equivalent mixture of molybdenum and sulfur. The data, when finally evaluated, will yield a refined value for the heat of formation of the disulfide.

Eight successful calorimetric combustions of molybdenum in fluorine have been completed as part of a program to redetermine the heat of formation of molybdenum hexafluoride. A value which is 4 per cent lower than the most recent determination by solution calorimetry is indicated.

II. Fuel Cycle Application of Volatility and Fluidization Techniques (pages 70 to 113)

The "Fluoride Volatility Process" is used as a generic term to be applied to several schemes for processing irradiated fuels. Work is in progress on three such schemes, namely, The Fused Fluoride Volatility Process, The Aqueous Dissolution Fluorination Process, and a Direct Fluorination Process.

Increased interest in the use of ceramic fuels for reactors and the development of fluid-bed fluorination techniques have been encouraging factors in the development of a process for the direct fluorination of fuels composed of uranium oxides. Studies on the rates of fluorination of uranium oxide, as it would appear in irradiated fuels, are in progress.

Equilibrium constants are being obtained at various temperatures for the dissociation reaction of plutonium hexafluoride to fluorine and plutonium tetrafluoride. A complete knowledge of this reaction is necessary for the volatility process recovery of plutonium from spent power reactor fuels. Consistent values for the equilibrium constant have been obtained at 300 C.

A systematic study of the reaction of nickel with fluorine is in progress as a part of the study of metal reactions with fluorine. The mechanism of the nickel-fluorine reaction at elevated temperatures will be studied using several physical-chemical techniques. Preliminary experiments using "A" and "L" nickel have been made at temperatures between 500 and 700 C.

A fluid-bed volatility process for the recovery of uranium from low-uranium-Zircaloy-2 fuel alloys is under development. The major process steps include aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry fluidizable powder, and fluid-bed fluorination of the mixture to remove and recover the uranium as uranium hexafluoride.

The current series of fluid-bed fluorination experiments are part of a statistical plan devised to show the possible interaction of the fluid-bed dryer and fluorinator operating variables on uranium removal. These variables include the drying temperature, fluorination temperature, hydrofluorination pretreatment, and duration of fluorination. The best uranium removal achieved in the current tests was about 90 per cent at 600 C for materials that remained free-flowing, but greater than 99 per cent was removed at 675 C from a caked portion of a bed.

In the fused salt fluoride volatility process for the recovery of uranium from zirconium-matrix fuels, the alloy is dissolved in the fused salt at 600 C with a hydrogen fluoride sparge and then the uranium is volatilized as the hexafluoride in a fluorine sparge. Because this fused salt process environment is corrosive to metals, equipment is being developed to avoid salt-metal contact.

A graphite dissolver-hydrofluorinator has been given a shake-down test with a dummy fuel element. Operations of salt transfer, fuel element charging, and hydrogen fluoride sparging were carried out.

A series of tests has been made to examine the feasibility of drop-wise fluorination as a means of contacting fused salt (bearing uranium) with fluorine. In this scheme, molten salt is sprayed into a fluorine atmosphere. The salt is allowed to solidify before contacting the walls of the container and the uranium hexafluoride formed is recovered from the gas phase. In a series of six tests at three different temperatures, the maximum uranium removed was 29 per cent with a fluorine temperature of 200 C.

Feasibility studies on the calcination of simulated Purex process wastes were successful in providing a free-flowing, granular solid with a volume reduction factor (feed liquid to solid product) of 4.7.

Preliminary tests of a one-step, continuous fluid-bed process for the conversion of uranium hexafluoride to uranium dioxide were made in a 1½-inch-diameter Monel column. This process has potential applications both for the production of reactor-grade dioxide and for the recovery of fluoride from the large quantities of depleted uranium hexafluoride now being stored. Steam and hydrogen in the mole ratio two to one are used as fluidizing and reactant gases for the simultaneous reduction and pyrohydrolysis reactions. The experiments made at 600 C gave good conversion

(96 to 99 per cent) to uranium dioxide at feed rates of 6 to 8 g/min of uranium hexafluoride (35 lb/hr uranium per square foot of reactor cross section), using 300 to 600 per cent excess steam and hydrogen. A run made at twice this rate gave about 65 per cent conversion.

III. Reactor Safety (pages 114 to 133)

The object of the metal oxidation-kinetics program is to understand the factors which influence the pyrophoric nature of certain reactor metals. Work was initiated with studies of uranium and zirconium and will be continued with studies of plutonium and thorium. The study of ignition behavior of uranium and zirconium has been complemented with an investigation of fundamental kinetics of oxidation. In continuing studies more emphasis is being placed on the burning process.

Previous research in this program through 1958 has been summarized in ANL-5974, "Ignition Behavior and Kinetics of Oxidation of the Reactor Metals, Uranium, Zirconium, Plutonium, and Thorium, and Binary Alloys of Each."

Burning curve experiments in air have shown that etching of uranium foil with nitric acid does not cause a decrease of ignition temperature, although the burning propagation rate is increased by this treatment. The dependence of uranium ignition temperature in air on specific area has been shown to be similar to that in oxygen. Experiments in air on aggregates of powder, turnings, foils, and cubes show that ignition of the powder at a low temperature causes ignition of the turnings and foils but not of the cubes, which have a low specific area.

Study of burning propagation rates of zirconium wires and foils in oxygen have shown that there is only a minor influence of shape on the relation found between burning rate and cross-sectional area. In connection with this work reproducibility tests have shown that burning rates are reliable to about 6 per cent in air and 9 per cent in oxygen.

The amount of zirconium unconsumed during burning in air has been measured for several foil strips. Using 0.13-mm thick foils of zirconium, 4.16 atom per cent and 14.9 atom per cent titanium alloys, the fraction of unburned metal increased as the width of the foil strip increased.

Acquisition of materials and preparation of equipment necessary to conduct exploratory experiments on the burning properties of plutonium has begun.

Electron and X-ray diffraction studies of oxide films of zirconium alloys do not support a recent report that the breakaway is associated with the transformation of zirconium dioxide from the cubic to the monoclinic structure. No simple relationship between the transformation and breakaway at 700 C can be found to apply to all the alloys examined.

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. An analysis on the analog computer of the data from runs with zirconium described in the previous quarterly report, ANL-5996, page 238, was completed. The results showed that runs at temperatures up to and including the melting point could be adequately described by the parabolic rate law with constants about twice those reported by Battelle. Runs with initial temperatures exceeding the melting point and with smaller particles were apparently impeded by a diffusion process and could not be described by a simple chemical mechanism.

A series of runs with uranium was completed. Up to 6 per cent reaction occurred at temperatures of the order of 1600 C. An induction period of 5 to 20 msec was observed for the hydrogen liberation.

A second laboratory-scale method involves the rapid contact of steam with a drop or pool of molten metal. In this method a sample of molten metal in a vacuum environment receives a "pressure pulse" of water vapor. Tests with the induction heating system showed that temperatures of the order of 2600 C could be obtained.

Two experiments were performed in the CP-5 reactor to check the instrumentation and techniques to be used in TREAT. Both an unbonded strain gage and a variable reluctance pressure pickup showed negligible changes in output while subjected to a dose of 10^{14} nvt in the reactor. The average attenuation of the thermal neutron beam in passing through the walls of the autoclave was found to be 73.5 per cent.

IV. Reactor Chemistry (pages 134 to 142)

Current work being carried out on determination of nuclear constants includes the Van de Graaff neutron cross-section program applied to uranium-236 and thorium-232, instrumentation studies applied to use of an alpha pulse-height analyzer in conjunction with the 256-channel analyzer, and decay scheme studies applied to potassium-42 and tellurium-232.

Studies are being made in the Boiling Water Reactor Decontamination program for determination of contamination resulting from a fuel defect and investigation of methods of activity removal.

Work has begun on a study of the reactions of superheated steam with metals, such as zirconium, Zircalloys, and stainless steel.

V. Analytical Research and Services (page 143)

Applications of the methods of neutron activation, giving fundamental principles, limitations, and recent advances, are outlined. A gamma index of the nuclides has been prepared, arranging the nuclides by photon energy, by atomic number, and by half-life.

VI. Routine Operations (page 144)

The operation of the waste processing facility and the Gamma-irradiation Facility continued without incident.

I. CHEMICAL-METALLURGICAL PROCESSING

A direct-cycle pyrometallurgical fuel-reprocessing plant is being designed in conjunction with the EBR-II reactor. The plant complex also includes a Laboratory and Service Building, construction of which is already well under way.

A number of chemical-metallurgical methods, including melt refining, liquid metal extraction, and fractional crystallization processes from liquid metals, are being examined for use in this fuel-processing facility. Based on the results of these studies, process components are being designed and tested for use in the EBR-II fuel-reprocessing plant.

The EBR-II Fuel Cycle Facility is part of construction bid package 3, which also includes the Sodium Boiler Plant, the 200-foot high ventilation stack for the use of the entire plant, and the completion of items in the Reactor Building and Boiler House. Bids for the complete bid package 3 were received from 11 companies. Malan Construction Company was low bidder with a base bid of \$3,440,000. The contract will be awarded after the decision of an AEC board set up to evaluate the bids.

Fabrication of the five-ton cranes for the Argon and Air Cells has started. Bid specifications for the eight operating manipulators were completed and sent to manufacturers. Operation experience with the prototype manipulator in the mock-up facility has shown the need for a better lubricant than molybdenum disulfide. Radiation-resistant greases are being investigated.

The new Mark-5 melt-refining furnace was put into operation in the mock-up area. Sixteen of the required 100, 10-kilogram, enriched fuel ingots for EBR-II have been prepared using this furnace. The balance of the equipment required to demonstrate remote operation of the melt-refining process is being installed and should be in operation during the next quarter.

Magnesium-cadmium alloys were found to be effective in reducing oxide films on uranium fuel pins of the EBR-II type. Such films inhibit uranium coalescence in melt-refining. Use of such alloys, which may be contained in mild steel equipment, eliminates the container problem encountered with the effective but corrosive magnesium-zinc alloys.

Studies were continued on processing of melt-refining residues (crucible skull material). Oxidation of the skull material produces a powder which can be poured essentially quantitatively from a crucible. In oxygen-argon atmospheres, the oxidation progressed smoothly and was easily controllable at desired temperatures. Calculations indicate that,

due to fission product decay heating, skull temperatures are likely to be between 600 and 800 C. At such high temperatures, significant nitriding of the skull can occur in the cell atmosphere, which may contain up to five per cent nitrogen. "Fissium" material was readily nitrified at 850 C. It was subsequently oxidized at 850 C in an argon-oxygen atmosphere; essentially complete conversion to the oxide was effected.

Skull oxide reductions in magnesium-cadmium solutions are in progress. Other reactions in liquid metal media were studied with the following results:

- 1) Reduction of rare earth oxides by uranium in either zinc or cadmium solutions was shown to occur readily.
- 2) Considerable interchange of uranium isotopes occurred when enriched metal oxide was contacted at 800 C with a zinc solution of depleted uranium.

Methods of isolation of plutonium from EBR-II blanket material are being examined. About 60 per cent of the plutonium in hydrided-dehydrided blanket material was leached into molten magnesium at 800 C within an hour; additional contact time did not result in further plutonium extraction. Two runs to investigate blanket processing by dissolution in cadmium followed by distillation of the cadmium in the presence of magnesium were made. As the magnesium concentration increases during the distillation, uranium will precipitate as metal from solution while the plutonium should remain in solution. Although uranium did precipitate from solution, plutonium loss from solution was excessive.

Engineering techniques are being developed for the various liquid metal processes under consideration. Emphasis is now being given to design of large-scale equipment for study and demonstration of the distillation, retorting, dissolution and phase-separation operations encountered in liquid metal processes. Design is almost complete on a full-scale distillation unit capable of distilling up to 100 kg of cadmium per hour.

A liquid metal corrosion loop fabricated of mild steel was put into operation on June 3. Cadmium containing approximately two per cent uranium and 0.2 per cent magnesium is being circulated at 550 C by an electromagnetic pump at a flow rate of about 0.8 gal/min, which results in a velocity of about 2.5 ft/sec through the one-half-inch mild steel tubing. The loop has now operated over 200 hours with insignificant variations in flow or temperature.

Additional basic data have been obtained to aid in the study of liquid metal solvents for separation processes. The following solubilities have been measured and are expressed by the equations:

$$\begin{aligned}
 \text{Ru in Cd: } (627-352 \text{ C}) \quad \log (w/o \text{ Ru}) &= -2.097 - \frac{245}{T} \\
 (352-327 \text{ C}) \quad \log (w/o \text{ Ru}) &= +8.594 - \frac{6910}{T} \\
 \text{Ce in Cd: } (520-363 \text{ C}) \quad \log (w/o \text{ Ce}) &= +7.437 - \frac{5845}{T} \\
 \text{La in Cd: } (608-324 \text{ C}) \quad \log (w/o \text{ La}) &= +7.368 - \frac{5991}{T} \\
 \text{U in Zn: } (800-426 \text{ C}) \quad \log (w/o \text{ U}) &= +7.272 - \frac{6984}{T}
 \end{aligned}$$

A striking relation between the position of an element in the Periodic Table and its solubility in zinc or cadmium has been observed.

The high-cadmium corners of the ternary systems cadmium-uranium-zinc and cadmium-uranium-magnesium have been investigated and are presented in detail. A feature common to both is the disappearance of UCd_{11} as the phase of primary crystallization on the addition of relatively small amounts of zinc or magnesium. Another feature of practical interest in the cadmium-uranium-zinc system is the fact that in a solution containing more than four per cent zinc not only is the low-temperature solubility of uranium drastically lowered, but also the high-temperature solubility is significantly increased.

Studies were begun on the uranium-mercury-zinc ternary system, which has aroused interest because of its especially attractive corrosion and solubility properties. Preliminary results indicate that undesirable characteristics of uranium amalgams may be avoidable in the presence of zinc.

Results obtained by effusion experiments are presented for the vapor pressure of zinc over uranium-zinc alloys. There can be no question that the solid-phase relations in the region of U_2Zn_{17} are more complex than are shown in the published phase diagram. Although the vapor pressure plateaus appear to indicate the existence of two intermediate solid phases, it is still possible that a single intermediate phase with a wide solid solution range would fit the data. X-ray studies in progress may resolve the question.

Emf measurements have been made with an electrochemical cell having as electrodes solid uranium and unsaturated solutions of uranium in cadmium. The purpose of these measurements was to determine the extent of departure from Henry's law of the activity of uranium in such solutions. An appreciable departure had been predicted from the nature of the phase diagram and appears to be confirmed by the preliminary measurements.

Sixteen calorimetric combustions in oxygen have been completed with natural molybdenum disulfide or an equivalent mixture of molybdenum and sulfur. The data will yield a refined value for the heat of formation of the disulfide.

Eight successful calorimetric combustions of molybdenum in fluorine have been completed as part of a program to redetermine the heat of formation of molybdenum hexafluoride. The effects of fluorine purity and incomplete combustion have been assessed. A value which is four per cent lower than the most recent determination by solution calorimetry is indicated by these results.

Calorimetrically useful techniques for the combustion of zirconium and of cadmium in fluorine are being sought. New optimum conditions for zirconium have been established and it appears likely that the heat of formation of zirconium tetrafluoride can be determined experimentally by this technique.

A. EBR-II Fuel Cycle

1. Design and Construction of Process Auxiliaries and Building (J. H. Schraidt, M. Levenson)

The Fuel Cycle Facility for the processing of EBR-II fuel is described in previous quarterly reports (ANL-5789 and ANL-5820). The architect-engineer is the H. K. Ferguson Company, Cleveland, Ohio.

a. Status of Fuel Cycle Facility Design and Construction (J. O. Ludlow, E. J. Petkus)

Formal bid opening for package 3 took place at the Idaho Operations Office on May 20, 1959. Malan Construction Company was the low bidder with a base bid of \$3,440,000 and Diversified Builders was the second lowest bidder with a base bid of \$3,475,000. A total of 11 companies submitted bids and seven companies were within 10 per cent of the lowest bidder. Due to this small monetary spread the AEC has set up a board to evaluate the bids for acceptance. After receiving notice to proceed, the awardee contractor will start construction within 10 days and complete the contract within 540 calendar days.

Bid Package 3 consists mainly of the construction of the Sodium-Boiler Plant and the Fuel Cycle Facility. Other work includes Well Pump House No. 2, alarm systems, and miscellaneous work in the Reactor Building. Installation of the processing equipment will be included in Package 4. Two addenda to Bid Package 3, containing corrections and changes, have been issued.

b. Status of Laboratory and Service Building Design and Construction
(A. A. Chilenskas and G. J. Bernstein)

The construction of Bid Package 1A, which includes the Laboratory and Service Building, was 75 per cent completed as of June 30, 1959. A parts list and piping layout for the Waste Solidification Cell has been completed and a procedure for its operation is being prepared. Proposals have been received from Central Research Labs, Inc. and AMF Atomics to furnish the twelve Model 8 manipulator arms for the Junior Caves.

c. Cranes and Manipulators
(J. Graae, D. C. Hampson)

Drawings received from Paceco (Pacific Coast Engineering Company) of the five-ton cranes for the Argon Cell were reviewed and returned approved for construction. Bid specifications for the eight operating manipulators were finished and sent to a number of prospective bidders. The operating experience compiled in the mock-up facility is being incorporated in the present design. Bid specifications and drawings for crane and manipulator control systems have been completed and will shortly be out for bid. The manipulator carriage lifting beam is nearing completion. The central pivot tower for the manipulators in the Argon Cell is scheduled for completion by the end of July.

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

The nominal weight percentage of cerium oxide specified for the major glass slabs of the shielding windows has been undergoing a downward revision. The original nominal values were: 3.0, 1.8, and 1.0 per cent for the inner, intermediate and outer slabs, respectively. These have been tentatively revised to 2.4, 1.8, and 0.8 per cent. Samples have now been irradiated from the first four full-scale melts of 0.8 per cent and two of 2.4 per cent cerium oxide glasses. The results are being summarized and evaluated for the final decision on glass compositions. A total of 186 slabs, each $9\frac{1}{16}$ -inches thick, are involved.

The nine steel window liners for the Air Cell are almost ready for shipment to Idaho. The stringent leak testing procedure which will be used on each liner for the Argon Cell has been satisfactorily demonstrated by the subcontractor at his plant.

e. Material Testing
(G. J. Bernstein, L. F. Coleman, M. A. Slawecki)

Tests are continuing on two types of dc motors specified for Argon Cell manipulators - the Howard $\frac{1}{10}$ -hp and the Eemco type .

C-743-C $\frac{1}{4}$ -hp motor. The Howard motor showed negligible brush wear after 10 hours in argon containing 7 to 20 ppm water vapor. With the Eemco motor in argon containing >1000 ppm water vapor two high-altitude brushes showed high wear rates. Stackpole grade 600 brushes wore at rates from 0.118 in./hr to 0.154 in./hr after an induction period of five hours. Carbone Corp. grade P-5707 showed evidence of rapid wear after three hours.

In preliminary tests with $\frac{1}{4}$ -hp Master motors in frame type G-56 good commutation has been obtained. This has been attributed in part to the incorporation of interpoles in these motors. Such interpoles cannot be fitted into the small Eemco and Howard frames.

Interest in radiation-resistant grease has been revived as a result of failures of a number of unlubricated or molybdenum disulfide-lubricated bearings on the prototype operating manipulator. Bearings lubricated with Shell APL grease and samples of APL grease are being irradiated to levels in excess of 10^9 r (10^9 r is equivalent to about one year of continuous exposure to spent fuel elements based on the geometry of the cell).

Testing of mineral-insulated (MI) cable and rubber tape samples is continuing. MI cable samples using standard end seals have been irradiated to an accumulated dose of 2.7×10^9 rad. Substitution of fish spines (ceramic insulators) for the rubber sleeving used on the standard end seals prolonged the usable life of two of the samples to about 10^9 rad. Since then, however, all samples have broken down to the point where their use in an electrical circuit would be objectionable. Also included in the tests are MI cable samples using ceramic end seals. These samples have received a dose of 10^9 rad and still retain their original insulation resistance.

Application of high voltages to unirradiated MI cable samples has shown that those using the ceramic end seals begin arcing at 2000 volts as compared to 4000 volts for those using standard end seals. However, the former voltage is sufficiently high for a cable rated at 600 volts.

Specifications for the installation and testing of MI cable with special end seals were included in the addendum of the electrical specifications for the Fuel Cycle Facility.

2. EBR-II Fuel Processing Mock-Up Facility
(D. C. Hampson)

a. Manipulator Operation
(J. Graae, D. C. Hampson)

The prototype operating manipulator was placed on a nearly continuous running schedule to accumulate operating time in a short elapsed time. A number of the manipulator bearings have failed due to corrosion of bearing surfaces and inadequate lubrication by the lubricating method used (molybdenum disulfide coating and powder). The manipulator is now being disassembled, cleaned and lubricated with Shell APL grease, a radiation-resistant grease.

Some preliminary tests revealed that the bridge drive of the prototype operating manipulator has sufficient excess power to push an adjoining disabled manipulator along the track to a position under the blister removal hoist.

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

The new version of the melt-refining furnace (M-5) was installed. After some preliminary shakedown runs, the preparation of EBR-II fuel alloy for the first core was begun. This is made by melting approximately 10-kilogram batches of alloy materials in a crucible, equilibrating at 1400 C for three hours, and pouring into a graphite mold to form the fuel ingot. Sixteen of the required one hundred ingots have been poured. Furnace components have performed satisfactorily.

The desired nominal composition of the fuel and the results of analyses of samples taken from the ingots are listed below.

<u>Element</u>	<u>Nominal Composition, Wt Per Cent</u>	<u>Ingot Samples, Wt Per Cent</u>
Molybdenum	2.46	2.43 $\pm$ 0.11
Ruthenium	1.96	2.14 $\pm$ 0.12
Rhodium	0.28	0.273 $\pm$ 0.025
Palladium	0.19	0.194 $\pm$ 0.011
Zirconium	0.10	0.089 $\pm$ 0.018

The nominal composition is the calculated steady-state content of the element in recycled fuel. The analyses listed are the averages of the reported values for ten ingots. Isotopic analyses for the first three ingots were 48.4 ± 0.5 , 48.2 ± 0.5 and 48.2 ± 0.5 weight per cent uranium-235. The

composition desired by reactor design is 48.13 ± 0.05 weight per cent. The recoveries for the first 16 ingots were between 95 and 96 per cent. These yields are somewhat higher than should be expected for typical melt-refining runs, since rare earths are absent.

c. Auxiliary Equipment for the Operation of the Melt-Refining Furnace
(W. E. Miller, D. C. Hampson)

The Mark-5 melt-refining furnace will be integrated with auxiliary equipment to form a processing mock-up unit which will demonstrate remote operation and control of the melt-refining process. The balance of this equipment is being installed and should be in operation during the next quarter. Installed are the induction heating unit and the vacuum pumps. Piping and panelboard wiring are being installed.

d. Cell Lighting
(T. W. Eckels and L. F. Coleman)

Drawings and specifications are being prepared for the wall mounts and luminaires for the Air and Argon Cells of the Fuel Cycle Facility. The luminaire is designed to permit replacement of the 1000-watt mercury vapor lamp and/or a complete end plate assembly carrying all electrical connections. A technique has been demonstrated for performing these operations, using the heavy-duty operating manipulator.

As reported previously (ANL-5996, page 37), some experiments have been performed to evaluate the radiation stability of lamps operating in a high-gamma field. The lamps tested to date have had clear glass envelopes, whereas the specific lamp chosen for the cell lighting system is the 1000-watt mercury vapor with white fluorescent coating inside the outer envelope. With the recent introduction on the market of a 175-watt white fluorescent mercury vapor lamp, it will now be possible to test coated lamps, since this is the first such lamp small enough to fit in the irradiation urn of the Gamma-irradiation Facility.

A technique adaptable for radioactive cells has been developed for measuring the light transmittance of thick shielding windows installed in walls. This method gives results reproducible within two per cent. A voltage-stabilized 100-watt incandescent lamp and collimator rigidly mounted together on a half-meter length of optical bench comprises the light source. A Photovolt electronic photometer, battery operated, is the light-measuring instrument used. A "black box" of local manufacture is used as a light receiver. This box makes it possible to have ambient light levels in the radioactive cell and in the operating area of up to 200 foot candles without any detectable effect on the light measurements.

3. Melt Refining (L. Burris, Jr.)

The melt-refining process consists of melting discharged fuel in a zirconium oxide crucible and holding it molten for a period of several hours at a minimum temperature of 1300 C. During this time purification from fission products is effected by:

- (1) vaporization of the noble gases and other volatile elements, such as cesium, and
- (2) selective oxidation of the highly electropositive elements, such as the rare earths, and their removal in a reaction layer which forms along the crucible walls.

The noble metals are not removed except in a small side stream of material (called "drag-out"). This side stream, consisting largely of the crucible skull remaining after pouring the purified material, must be processed for removal of the noble metals and also for recovery of the fissionable materials. The noble metals will build up to steady-state concentrations which are dependent on the percentage of "drag-out" materials. The resulting alloys are called "fissium" alloys.* Studies are being made of melt refining of sodium-coated pins and of alternate materials and designs for the EBR-II melt-refining furnace. These data will be supplemented by the data from the melt-refining operations performed in the EBR-II mock-up facility (see page 22).

a. Melt Refining of Sodium-coated Pins (G. A. Bennett, L. F. Dorsey, W. A. Pehl)

The use of sodium as a bonding agent between the fuel pins of the Experimental Breeder Reactor-II and the stainless steel cladding results in the formation of an oxide film on the surface of the uranium pins due to oxygen initially present in the sodium or to exposure of the sodium-coated pins to atmospheres containing oxygen or water vapor. In the reactor, the presence of an oxide film on the uranium is desirable in order to prevent the formation of low melting point alloys with the stainless steel can. The oxide films can, however, cause difficulty in coalescence of the uranium on melt refining. Consequently, development of a standby process is currently under way on methods to effect uranium coalescence.

*The alloy composition (in weight per cent) chosen for the initial EBR-II loading is:

molybdenum	2.46	zirconium	0.10
ruthenium	1.96	niobium	0.01
rhodium	0.28	uranium	remainder
palladium	0.19		

(1) Reduction of Oxide Films by Magnesium in Zinc Solution

In the previous quarterly (ANL-5996, page 52) a series of runs, in which sodium-coated pins were dipped in 10 weight per cent magnesium-zinc solution at 625 C for contacting times varying from 30 seconds to 30 minutes, was reported. Melt refining of samples of these pins resulted in well-coalesced beads. However, these results were not completely satisfactory because the pin coatings were heavy, uneven and darkened by surface scum. Consequently, experiments during this past quarter were directed towards improving the quality of the coating.

The primary operating change was to increase the dipping temperature from 625 to 675 C (mp $\sim$ 575 C). Small batches of sodium-coated pins ($\sim$ 300 g) were dipped at this temperature for periods of time varying from 30 seconds to 15 minutes. The pin-dipping apparatus previously described (ANL-5996, page 52), which allows drainage of the molten alloy from the pins and removal of the pins without contacting any surface scum, was used. In all cases where the dipping time was one minute or longer, the coating was bright, tightly adherent and uniform in thickness. However, irregularities were present on the surfaces of the coatings, particularly at those points where the pins contacted each other. Melt refining at 1400 C of 1750 g of the pins, selected to avoid the coating irregularities, resulted in complete coalescence with no semblance of pin shells remaining.

Analytical results have shown a maximum uranium loss of 0.25 per cent for five different magnesium-zinc coating runs in which the dipping conditions varied from 30 minutes at 625 C to 2 minutes at 675 C.

(2) Reduction of Oxide Films by Magnesium in Cadmium Solution

To take advantage of the excellent corrosion properties of cadmium alloys, which permit fabrication of equipment from mild steel, the coating characteristics of both five and ten weight per cent magnesium-cadmium alloys were investigated. Approximately 100-gram samples of sodium-coated pins were dipped in these alloys at 675 and 700 C for periods of 5 and 15 minutes in both induction and resistance furnaces. Holding the pins at 700 C for an additional 15 minutes after withdrawal from the molten alloy increased the amount of alloy drainage from the pin surface. In all runs the pins were completely coated; however, the surface of the coating was blackened.

Melt refining of one of these samples resulted in coalescence, with a few pin shells still present. These results are comparable to those obtained in the early investigations using magnesium-zinc as the coating and reduction alloy. Work with cadmium alloys is being continued.

(3) Reduction of Oxide Films by Calcium in Cadmium Solution

Preliminary experiments were completed on the use of a four weight per cent calcium-cadmium alloy (mp ~540 C) as a coating material. Pins were contacted at 600 C for five minutes, 650 C for 15 minutes, and 690 C for 5 minutes. In no case was the alloy adherent to the pins.

b. Study of Alternate Materials and Designs for the EBR-II Melt-Refining Furnace (J. Wolkoff)

The planned use of uncooled copper coils in the EBR-II melt-refining furnace augments the need for high efficiency in the heating process. When water-cooled coils are used, large power losses in the inductor coil can be tolerated with little more than lost economy. In the absence of this large heat sink, excessive furnace power can overheat and melt uncooled copper coils. The coils at the present EBR-II prototype furnace operate at about 750 C and it is believed that this temperature can be reduced considerably. The heat generation in the uncooled copper coil can be diminished by

- (1) reducing the power consumption of the furnace by use of more effective thermal insulation, and
- (2) reducing the current in the inductor coil by using an increased number of turns and optimizing the inductor-susceptor geometry.

The compatibility of the thermal insulation with the heated susceptor will also require study. Carbon monoxide formation in the melt-refining furnace as a result of reaction between the present graphitic susceptor and zirconia powder insulation has been detected. The use of carbon susceptors at 1700 C results in carbon monoxide formation with even the most stable oxides. The use of insulating materials compatible with graphite at high temperatures, e. g., fine-grain graphite, silicon carbide, boron carbide, is to be investigated. Alternate high-temperature susceptor materials, e.g., tungsten, that are compatible with oxide insulation are also to be examined.

B. Pyrometallurgical Development (L. Burris, Jr.)

1. Studies Directed at Processing Melt-refining Skulls

The crucible skull remaining in a zirconia crucible after a melt-refining operation must be processed to recover the contained

fissionable material, which amounts to about 10 per cent of that charged to the crucible. A second objective in processing this material is removal of noble fission products which are not removed by melt refining.

a. Oxidation of "Fissium" Skulls
(R. D. Pierce, J. C. Hesson, E. F. Johnston)

The first step is removal of the skull from the crucibles in a form suitable for further processing. Oxidation of the skull to a powder which can be poured from the crucible appears to be a highly satisfactory technique and is being explored.

Several skulls from runs in the melt-refining furnace in the fuel cell mock-up have been oxidized in an oxygen-argon atmosphere. The use of diluted oxygen permitted more uniform temperature control. Skulls weighing between 300 and 1000 grams were reacted in a 40-liter stainless steel bomb. The total pressure was maintained at 800 mm of mercury and the oxygen concentration was increased from 20 to 50 per cent during each run. The reactions progressed smoothly and temperatures were easily maintained within desired limits (± 10 C at 800 C and ± 20 C at 600 C).

Typical results are presented in Table 1. These runs demonstrated that a finer product is produced at lower operating temperatures. In all oxidation runs, over 99 per cent of the skull could be poured from the crucibles.

Table 1

OXIDATION OF "FISSIUM" SKULLS

equipment: 40-liter stainless steel (304) bomb
total pressure: 800 mm Hg
oxygen conc: 20 to 50 per cent in argon
(increasing during run)

Run	Temp. (C)	Weight of Skull (g)	Duration of Oxidation (hr)	Screen Analysis (per cent)		
				+20 mesh	-20, +100 mesh	-100 mesh
1	590	515	$6\frac{1}{2}$	5	34	61
2	770	370	6	15	42	43
3	820	945	$4\frac{1}{2}$	23	49	28
4	970	900	5	33	37	30
5	720	+20 mesh from 3 & 4 above	$2\frac{1}{2}$	33	41	26

b. Decay Heating of Crucible Skulls
(R. D. Pierce)

Fission product decay heating of crucible skulls from melt-refining operations has been calculated. The temperature that these skulls may attain during storage in the fuel process cell after 15 days out of the reactor is expected to be between 600 and 800 C, as shown in Figure 1. The higher temperature can be expected if the crucibles are placed close together and the lower if they are widely spaced.

FIGURE 1
DECAY HEATING OF MELT-REFINING CRUCIBLE
SKULLS DURING EBR-II FUEL PROCESSING

BASIS:

CURVE A - ALL HEAT REMOVED BY RADIATION
OUT TOP OF CRUCIBLE.

CURVE B - HEAT REMOVED BY RADIATION OUT
TOP AND OFF SIDES AND BY NATU-
RAL CONVECTION FROM OUTSIDE WALLS.

EMISSION: SKULL = 0.5
CRUCIBLE = 0.75

CONDUCTIVITY CRUCIBLE:
0.5 Btu/(hr)(sq ft)(F)

NATURAL CONVECTION FROM
OUTSIDE CRUCIBLE WALL:
 $h_c = 2 \text{ Btu}/(\text{hr})(\text{sq ft})(F)$

At the temperatures predicted for these skulls, significant nitriding of the uranium can be expected, because the anticipated cell atmosphere may contain up to five per cent nitrogen. The extent of the nitriding will depend on the temperature and the time of exposure to the cell atmosphere. To provide material for the study of "fissium" nitride, a "fissium" skull together with some "fissium" metal was nitrided at 850 C with 50 per cent nitrogen in argon at one atmosphere total pressure. The reaction, which was complete in 13 hours, produced a finely divided product, as shown in Table 2.

A portion of the nitrided "fissium" (minus 45 mesh fraction) was oxidized in an oxygen-argon atmosphere at 850 C. Temperature measurements showed that a uniform burning rate was not attained, because nitrogen released during the reaction could not be removed continuously. Accordingly, the equipment was flushed and refilled with fresh oxygen and argon periodically. The oxidized particles are smaller than the nitride feed, as shown in Table 2. X-ray examination failed to reveal any nitride in the oxidized product, which indicates a residual nitride concentration estimated to be below two per cent.

c. Reduction of Skull Oxide by Magnesium-Cadmium Solution
(R. D. Pierce, J. C. Hesson, E. F. Johnston)

Two extractions were made to recover uranium from oxidized "fissium" with $5\frac{1}{2}$ per cent magnesium in cadmium at 700 C. These extractions were performed in the open atmosphere with a Dow 230 protective flux (55 per cent potassium chloride, 34 per cent magnesium chloride, 9 per cent barium chloride, 2 per cent calcium fluoride) on the cadmium solution. The uranium concentration in the liquid metal leveled off during

Table 2

SCREEN ANALYSES OF "FISSIUM" FROM
NITRIDATION-OXIDATION EXPERIMENTS

Screen Size		Per Cent in Indicated Size Range		
Mesh	Microns	Nitrided "Fissium" ^a	Nitride Feed for Oxidation Run	Product after Oxidation ^b
-325	< 44	7.8	16.2	37.7
-170, +325	44 to 88	9.5	19.6	26.0
-80, +170	88 to 177	15.2	31.4	24.0
-45, +80	177 to 350	15.8	32.7	11.9
-25, +45	350 to 710	21.1	-	0.6
-14, +25	710 to 1410	20.7	-	-
+14	>1410	9.7	-	-

^a nitrided at 850 C with 50% nitrogen in argon, 1 atm press.
^b oxidized at 850 C in an oxygen-argon atmosphere.

these runs after about half of it was in solution. This result is not explained by solubility, since the same effect was observed in both runs even though the uranium concentration for complete extraction in the second run was only half that of the first.

This poor uranium recovery can be explained by the reaction of uranium in the cadmium with the flux:

The measured steady-state concentration of uranium in the cadmium satisfied the equilibrium constant for this reaction as calculated from recent thermodynamic data if the balance of the uranium is assumed to be present in the flux as uranium trichloride. It appears that the reduction of uranium dioxide may have gone to completion. Extraction of uranium into the salt can be reduced by decreasing the flux-to-metal ratio. The uranium can probably be recovered by stripping the used flux with fresh magnesium-cadmium solution.

d. Reduction of Rare Earth Oxides by Uranium in Zinc or
Cadmium Solution
 (A. Schneider, T. Johnson)

Study was continued of the reduction of rare earth oxides by uranium dissolved in liquid zinc or cadmium. Although the reaction has a

large positive standard free energy change, the uranium reduces the rare earth oxide due to the low activity of the rare earth metal in the liquid metal solution.

As shown in the previous quarterly (ANL-5996, pages 59 to 65), the reaction rate is a function of uranium concentration. At low uranium concentration, the ceric oxide reduction was found to occur in two steps, which may be:

or possibly by reactions involving the solvent metal:

followed by reaction 2) and

It was determined experimentally that zinc oxide will oxidize uranium from a zinc solution.

In either zinc or cadmium solution saturated with uranium, the rate of ceric oxide reduction was rapid (see Figure 2.) With unsaturated uranium solutions, reduction rates were slower. Mixed oxides of lanthanum, praseodymium and neodymium were used in one experiment. The reduction rate appeared to be in reasonable agreement with that expected for ceric oxide at the uranium concentration employed. All runs were made in alumina crucibles, with 500 to 1000 grams of solvent metal and with similar agitation.

e. Isotopic Exchange between Solid Uranium-235 Oxide and Uranium-238 Metal Dissolved in Zinc
(J. C. Hesson, R. D. Pierce)

A possible processing scheme discussed in the previous quarterly report (ANL-5996, page 59) involves selective reduction of rare earth oxides from fission product-contaminated enriched uranium oxide using as a reducing agent depleted or natural uranium dissolved in zinc. The extent of isotopic exchange of the uranium isotopes is an important process consideration.

Considerable isotopic exchange (to 70 per cent of uniform dissolution) was shown by an experiment in which a mixture of skull oxide and $(\text{U}^{235})_3\text{O}_8$ was contacted at 800 C with zinc in which depleted uranium

FIGURE 2
REDUCTION OF RARE EARTH OXIDES
BY URANIUM IN LIQUID METAL SYSTEMS

*Concentrations shown are solubilities of U in Zn and Cd, respectively, concentrations in parentheses are based on actual amounts of U added

had been dissolved to a concentration of three per cent (see Table 3). Approximately one kilogram of the zinc phase and 40 grams of the mixed oxides were stirred (750 rpm) together at 800 C in a baffled alumina crucible. Dow 230 flux (300 g) was used as a protective cover. The U^{235}/U^{238} ratio in filtered metal samples was determined under the direction of R. P. Larsen by counting a uranium-235 gamma. The accuracy of the analysis is estimated to be ± 15 per cent.

Table 3

ISOTOPIC EXCHANGE BETWEEN SOLID URANIUM-235 OXIDE AND URANIUM-238 METAL DISSOLVED IN ZINC

Mixture of skull and enriched uranium oxides (30 g of natural uranium and 0.745 g of uranium-235 oxide) contacted at 800 C with zinc-depleted uranium solution (44 g of uranium-238) in an alumina crucible.

Time after Oxide Addition (hr)	U Conc (w/o)	U^{235}/U^{238} Ratio ^a	Time after Oxide Addition (hr)	U Conc (w/o)	U^{235}/U^{238} Ratio ^a
0	2.93	0.00154	3 $\frac{1}{2}$	0.94	0.01
1	1.92	-	5 $\frac{1}{4}$	0.45	0.01
1 $\frac{1}{2}$	1.52	-			

^aFor complete exchange the U^{235}/U^{238} ratio would be 0.0139.

Considerable uranium was being lost from solution by air oxidation. However, the data indicate that the isotopic exchange occurred.

2. Development of Processes for Recovery of Plutonium from EBR-II Blanket Material

The objective of a process for EBR-II blanket material is the isolation of plutonium in sufficient purity for reconstitution of core material. Fission product removal is not particularly important.

a. Application of a Cadmium Solution Process (I. O. Winsch, T. F. Cannon)

A proposed method of processing reactor blanket material is one in which the uranium-plutonium is first dissolved in cadmium at 550 C. Magnesium is then added to the solution, following which the mixture is heated under reduced pressure to distill away the cadmium and produce a magnesium-rich solution. Uranium will precipitate out of solution as metal because of its low solubility in the magnesium-rich solution while the plutonium should remain in solution. A separation of the uranium from the magnesium-plutonium phase would follow. A subsequent distillation of the magnesium from the magnesium-plutonium phase would enable recovery of the plutonium as pure metal.

The results of two experiments following this scheme are shown in Figures 3 and 4. In the first experiment, uranium-three weight per cent molybdenum-one weight per cent plutonium was used and in the second experiment uranium-one weight per cent plutonium alloy was the charge. In the first experiment molybdenum was included since at that time the inclusion of this element in the blanket was contemplated. Later the blanket composition was changed to unalloyed uranium. Cadmium and the alloy were charged to a baffled mild steel crucible in the tilt-pour furnace. The metals were brought up to temperature, maintained under a helium atmosphere of 5 psi, and agitated by means of a motor-driven agitator.

In the first run, about 41 per cent of the plutonium charged went into solution after 15 hours. In the second run about 0.2 per cent magnesium was added to the dissolution step, and after only 6 hours 80 per cent of the plutonium charged was in solution. It is evident that magnesium is an aid to solution of the uranium.

After addition of magnesium in the uranium precipitation step, the melt was transferred to the distillation unit shown in Figure 5. In the first run, the distillation was carried out in three steps. The final distillation was run to dryness. About four per cent of the plutonium originally in solution was found in the cadmium distillate. This might be

Figure 3

DETAILS OF RUN #1 FOR DETERMINING PLUTONIUM-URANIUM
SEPARATION IN CADMIUM-MAGNESIUM SYSTEMS

reduced, if necessary, by baffling to reduce plutonium entrainment. However, the cadmium would be recycled for the next dissolution and the plutonium content is not a loss.

During distillations, as shown in Figures 3 and 4, the plutonium concentration in the still pot decreased in both experiments. In the first experiment the plutonium concentration decreased to about 75 per cent of that originally in solution and in the second experiment the plutonium concentration decreased to about 24 per cent of that originally in solution. The temperature during distillation in the first run was about 50 C lower than in the second run. There is a possibility that plutonium interacts with the mild steel crucible and this is being checked by experiment.

The uranium concentration may be seen to decrease as the magnesium concentration increases, decreasing to 0.055 per cent at a magnesium concentration of 20 per cent and 0.014 at a magnesium

Figure 4

DETAILS OF RUN #2 FOR DETERMINING PLUTONIUM-URANIUM
SEPARATION IN CADMIUM-MAGNESIUM SYSTEMS

FIGURE 5
DISTILLATION UNIT FOR REMOVAL OF CADMIUM
FROM A CADMIUM-MAGNESIUM-URANIUM SYSTEM

concentration of 35 per cent. Because of such low uranium concentrations, final plutonium product purities of above 95 per cent should be achievable.

b. Extraction of Plutonium with Magnesium from Hydrided-Dehydrided Uranium-1 Weight Per Cent Plutonium Alloy
(I. O. Winsch, T. F. Cannon)

A method of extracting plutonium from uranium, which was previously investigated (ANL-5668, page 76), involves leaching plutonium from finely divided uranium (hydrided and then dehydrided) with molten magnesium. An advantage of this method is the relatively small quantity of magnesium required for solution of the plutonium. However, difficulty in hydriding a previously proposed three per cent molybdenum-uranium blanket alloy resulted in giving major attention to development of other methods. A recent change to an unalloyed natural or depleted uranium blanket has revived interest in the magnesium leaching process. A run has been made to test this procedure.

A one per cent plutonium-uranium alloy and 185 grams of magnesium were charged to a tantalum crucible in the tilt-pour furnace. The system was heated to 250 C and hydrogen at a pressure of 780 mm mercury was maintained in the vessel. Hydriding was completed after a reaction period of about two hours. At this point, the temperature was raised to 400 C and the system was put under vacuum until there was no further indication of gas evolution. The temperature of the furnace was then raised to 800 C and agitation of the melt was continued for a period of five hours. Filtered samples of the magnesium phase were taken periodically during the five-hour holding time.

It may be noted (Table 4) that a contact time of one hour or less was sufficient to extract 67.5 per cent of the available plutonium into the magnesium phase. After this time, no additional plutonium went into solution. The magnesium phase was separated from the uranium by decantation. A large lump of metal (uranium and plutonium) and a small quantity of magnesium remained in the crucible. It might be possible to distill the small amount of magnesium remaining in the heel and again hydride and dehydride the uranium-plutonium metal. This would be followed by another extraction with magnesium to remove the remaining plutonium. An experiment following this procedure will be attempted in the next period.

Table 4

MAGNESIUM EXTRACTION OF PLUTONIUM FROM HYDRIDED AND DEHYDRIDED URANIUM-ONE WEIGHT PER CENT PLUTONIUM ALLOY

Charge: 102.91 g U
 2×10^{-4} g Am
 1.057 g Pu
 185.5 g Mg
 Temperature: 800 C

Time (hr)	Plutonium Concentration (w/o)	Uranium Concentration (w/o $\times 10^{-2}$)	Plutonium Extracted (%)	Americium Extracted (%)
1	0.386	2.6	67.5	25
1.75	0.365	1.4	64.0	18.7
2	0.365	1.7	64.0	19.7
2.5	0.380	2.9	66.5	19.7
3.0	0.350	2.9	61.5	20
4.0	0.360	2.2	63.0	23
5.0	0.393	4.0	69.0	25

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

Development of engineering techniques and equipment must accompany the development of liquid metal processes. Investigations are therefore in progress on distillation and retorting, solid-liquid phase separations, materials handling, and corrosion.

a. Distillation and Retorting

An important operation in processing of melt-refining crucible skulls and blanket material is distillation which is employed (1) to concentrate metal solutions, (2) to remove the metal solvent from the uranium or plutonium product, and (3) to purify the metal solvents for recycle. A considerable amount of work has been done on distillation of magnesium, cadmium, and zinc on a small scale (below 10-kilogram batch sizes); accordingly, scale-up of this operation has begun.

(1) Experimental Distillation Studies (J. DeKany, I. O. Winsch, T. Cannon, J. Pavlik)

The operation of the bottom-loaded distillation unit (described in ANL-5996, Figure 9) was continued. A total of nine successful distillations, six of cadmium and three of magnesium, were performed. General observations of these runs are as follows:

1) Entrainment of plutonium during magnesium distillation will probably not pose any problems. In a simulated run with one weight per cent radioactive tin-magnesium alloy all of the tin was recovered in the still pot with no detectable entrainment in the magnesium.

2) The concentrated plutonium residue remaining in the still pot will probably coalesce into a button at the bottom of the vessel. The still pot could then be removed from the column and the plutonium melted and poured into a suitable receiver.

These conclusions were postulated on the basis of several simulated distillations using cerium in place of the plutonium. In one run 25 grams of cerium was loaded along with 515 grams of magnesium. The results of this experiment were very encouraging. The residue remaining in the still pot weighed 27.5 grams, indicating that the magnesium was almost completely distilled from the cerium. Even more significant was the fact that all the cerium collected in the bottom of the still pot in the form of a solid button. In another run, 800 grams of 5 weight per cent cerium alloy-magnesium was prepared and then distilled. As in the other run, the cerium product was coalesced in the bottom of the still pot as a nice button.

An important factor in the design of plant-scale distillation equipment will be the heat transfer characteristics of the still pot and its environment. In order to obtain a reasonable evaporation rate, sufficient heat transfer area and temperature differential driving force must be provided. In the present unit temperature drops across several gas annuli are excessive and consequently 1.5 hours are required to distill about 500 grams of magnesium.

The distillation of cadmium was much simpler than the distillation of magnesium because the cadmium could be condensed and collected in the receiver as a liquid. The high vapor pressure of magnesium at its melting point causes a slight condensation of magnesium below the receiver vessel, the cumulative effect of which could be troublesome. Thus, it seemed desirable to condense magnesium as a solid on the condenser walls and later melt the solid material and allow it to flow into the receiver. Cadmium, on the other hand, has a much lower vapor pressure at its melting point and therefore has less tendency to condense below the receiver. Cadmium also seemed to wet the condenser walls to a lesser degree, resulting in less holdup in the condenser.

Future distillations of various cadmium-magnesium alloys will be made. Ultimately, the still will be used for a distillation of plutonium-magnesium alloys.

(2) Design of Full-scale Distillation and Retorting Equipment
(P. Nelson)

A large-scale distillation station is being designed for fabrication in the near future. Information will be gained on heat transfer problems in the still pot and condenser areas, liquid level measurement and control, molten metal transfer, and corrosion. The distillation station will include a 100-liter feed tank, a 7-liter distillation unit, a 100-liter distillate receiver, and a 25-liter fission product receiver. The distillation unit, which will be continuously fed, has a design capacity of 100 kg of cadmium per hour, being inductively heated by 1000-cycle/sec current at a rate of 35 kw. The condenser will be cooled by recirculated air which will be controlled in temperature to condense the cadmium as a liquid.

Since the main constituent of the alloys to be distilled will be cadmium, the equipment will be fabricated of stainless steel. Type 405 stainless steel was chosen because it does not contain nickel (which is leached by cadmium), is non-hardening and is more easily welded than the other series 400 stainless steels. The vessels and transfer lines will be enclosed by a 40-kw furnace to maintain accurate temperature control and prevent freezing or precipitation during transfer of molten alloys.

b. Retorting of Cadmium from Uranium
(P. Nelson, R. Beck)

The processes being considered for recovery of fissionable material from the melt-refining oxide skull and recovery of plutonium from the blanket material require evaporation of cadmium from uranium or uranium intermetallic compounds. The problems which are encountered in this step are: (1) removal of the uranium from the crucible after evaporation of the solvent metals, and (2) obtaining an ingot containing little of the solvent metals or other contaminants.

Two retorting runs were made with about 3000 grams of cadmium-uranium intermetallic containing about 200 grams of uranium. The alloy was obtained by hydriding and dehydriding uranium and reacting the powdered uranium with cadmium. In the first experiment the cadmium was evaporated at 10 mm Hg pressure. The uranium was deposited as a tightly packed layer of powder at the bottom of the tantalum crucible and could not be removed easily by physical means. Five per cent magnesium was added to the cadmium-uranium alloy in the second run in the hope that the uranium precipitate would have a different form due to the high magnesium concentration at the end of the distillation. However, the uranium precipitate appeared to be of about the same character as obtained in the previous run.

Since it therefore appears to be impractical to evaporate completely the solvent metals from uranium in a metal crucible, the possibility of pouring the uranium out in a magnesium slurry after evaporating the cadmium was considered. Uranium was powdered by hydriding and dehydriding, after which magnesium was melted on the powder to simulate a slurry of precipitated uranium after evaporation of cadmium. Then the tantalum crucible was inverted and placed on a steel funnel which was supported above a graphite mold. The apparatus was heated in an inert atmosphere until the magnesium melted. Approximately 25 per cent of the uranium was not transferred to a graphite mold with the magnesium. Although some improvement may be possible, this step in the process is not very appealing because of the large number of steps involving complicated equipment which would be required to obtain the uranium as a solid ingot.

Since it is difficult to remove uranium from metal crucibles and impractical to melt uranium in metal crucibles, other crucible materials are being considered. The disadvantage of graphite is the possibility of carbon contamination of the product. However, graphite and particularly graphite crucibles with coatings of flame sprayed ceramics are being considered. Beryllia is also being considered because of its resistance to molten uranium. In an experiment with a beryllia crucible, cadmium was evaporated from a uranium-cadmium alloy made by hydriding and dehydriding

the uranium as in the above experiments. The uranium was liquated after evaporation of the cadmium at 1200 C for one hour at a pressure of less than 1 mm Hg. The 188-gram ingot was easily removed from the crucible. It appeared fairly bright and free of oxide. Spectrographic analysis indicated a cadmium content of 5 parts per million and a beryllium content of 6 parts per million. The disadvantage of beryllia is the relatively low heat transfer rate obtainable through the wall of the crucible for evaporation of the cadmium.

c. Phase Separation of Precipitated Intermetallic Compounds from Supernatant Solutions by Pressure Siphoning
(J. C. Hesson, R. D. Pierce, E. F. Johnston)

(1) Zinc-base Systems

Phase-separation work with zinc-base systems has been discontinued because of a change to cadmium-base systems. However, analytical results are now available for pressure siphoning experiments previously made with zinc systems. In these experiments U_2Zn_{17}

crystals were precipitated from solution by cooling the solution from 800 to 500 C. Separation of zinc mother liquor was effected by using pressure to force it through a dip tube and into an adjacent vessel (see Figure 6). The dip tube extended into the intermetallic bed. A thimble with $\frac{1}{32}$ -inch holes was used in most runs as a coarse filter to prevent transfer of intermetallic particles. Filtered samples of the zinc supernatant in contact with the intermetallic crystals were taken at 500 C before pressure siphoning. To determine the extent of intermetallic carry over filtered samples were taken of the decanted phase after reheating to

FIGURE 6
PHASE-SEPARATION APPARATUS

700 C to dissolve any crystals present.

The results given in Table 5 show insignificant carry over of intermetallic crystals with the supernatant solution. When no filter was used in the $\frac{5}{16}$ -inch ID siphon tube, the zinc filtrate contained about four times as much uranium as its solubility at 500 C, but this represents less than 5 per cent crystal entrainment. When a thimble drilled with

Table 5

PHASE SEPARATIONS OF U_2Zn_{17} CRYSTALS BY PRESSURE
SIPHONING AT 500 C

(See sketch of apparatus in Figure 6. The zinc solution
had a magnesium concentration of 2 to 6 per cent.)

Run No.	Separated Zinc Liquor (kg)	Filter Cake (kg)	Type of Filters	Per Cent Uranium in:	
				Saturated Solution before Siphoning	Siphoned ^a Phase
13	6.8	2.2	None	0.021	0.09
14	5.5	1.2	$\frac{1}{32}$ -inch openings	0.013	0.023, 0.028, 0.034
15	13.1	3.4	$\frac{1}{32}$ -inch openings	0.015	0.017
16	12.2 ^b	6.0 ^b	$\frac{1}{32}$ -inch openings	0.027, 0.016	0.022
17	10.1	6.2	$\frac{1}{32}$ -inch openings	0.02, 0.021	0.018
18	12.2	5.2	$\frac{1}{32}$ -inch openings	0.026	0.016, 0.018, 0.028

^a Samples taken after heating to sufficiently high temperature to dissolve any intermetallic present.

^b Approximate values; crucible leaked.

$\frac{1}{32}$ -inch-diameter openings was used as a filter, entrainment of intermetallic crystals was negligible. This indicates that a coarse filter would be adequate.

As a process example, if zinc originally contained 2 per cent uranium, the maximum theoretical recovery of uranium in the intermetallic by phase separation at 500 C would be 99.2 per cent on the basis of a uranium solubility in zinc of about 0.02 per cent at 500 C and of a 10 per cent uranium concentration in the intermetallic concentrate. In the five runs where the coarse filter was used, the uranium recovery would have averaged 99.1 per cent.

Cerium concentrations in the siphoned mother liquor were very low, <0.01 per cent, indicating complete carrying of the cerium on the U_2Zn_{17} crystals in accord with laboratory measurements.

(2) Cadmium-base Systems

The work originally begun with zinc-base systems has been continued with cadmium. Five 10-kg runs using cadmium-base solvent systems (uranium and magnesium concentrations of about 0.5 and 2 per cent, respectively) have been completed. In these runs, UCd_{11} was precipitated by cooling. As in the zinc system, pressure transfer of the mother liquor was made without difficulty. Analytical results are not available for reporting.

Work in cadmium systems will be continued by studying separation of U_2Zn_{17} precipitated by addition of a slight excess stoichiometric amount of zinc and of uranium metal which may be precipitated by addition of sufficient magnesium.

d. Corrosion Studies

(J. P. DeKany, H. W. Lavendel, J. Pavlik)

The liquid metals corrosion test program consists of three phases. In the first phase coupons of materials which show some promise are loaded along with the corrosive liquid metal media into inert containers and are kept at the test temperatures under static conditions. The materials successful in passing this screening phase of the program are then fabricated into capsules. These capsules are loaded with the corrosive media and are dynamically tested by end-over-end rotation inside of a furnace. Those materials resisting corrosion in this second stage are admitted to the final phase of testing. In this last phase the materials are fabricated into circulating loops in which the corrosive liquid metals are circulated. The loop experiments can be used to investigate the possibility of mass transfer corrosion caused by a temperature gradient.

(1) Static Tests

The corrosion results have indicated serious difficulties in obtaining a suitable metallic container material for molten zinc solutions. Consequently, a decision was made in the past quarter to base the future processing flowsheets on cadmium-based solutions. Prior to this decision a series of static zinc corrosion tests were made at 750 C with nitrided and cyanided steels, thermanol, Haynes No. 25 alloy, multi-met alloy, and Haynes stellite alloy No. 6B, all of which were seriously corroded by zinc and zinc-magnesium eutectic alloy. As previously experienced, the presence of 46 weight per cent magnesium inhibited the attack by zinc.

A number of static tests with cadmium systems are in process and will be reported in the next quarterly.

(2) Dynamic Tests

The first of a series of long-term dynamic corrosion tests for the cadmium and cadmium alloy systems was completed. The apparatus for these tests consisted of a rectangular stainless steel box with compartments for the corrosion capsules. The box was supported on a shaft and was mounted in a large resistance furnace. During operation the box was rotated at approximately 20 rpm.

The current tests were made with mild steel capsules containing pure cadmium, cadmium-2 weight per cent uranium, cadmium-5 weight per cent magnesium, and cadmium-8 weight per cent zinc-0.2 weight per cent magnesium. These tests were run at 550 C for 963 hours. No evidence of corrosion was found in the capsules containing cadmium and cadmium-magnesium. Microscopic examination revealed a slight indication of uranium interaction with the wall in the cadmium-2 weight per cent uranium system and intergranular corrosion to a depth of not greater than 0.1 mil in the cadmium-8 weight per cent zinc-0.2 weight per cent magnesium system. Spectroscopic and metallographic examinations are being conducted to check this finding and to ascertain the extent of corrosion, if any.

Another series of capsules containing zinc-cadmium alloys is being prepared for 1000-hour dynamic tests at 350 C.

(3) Liquid Metal Corrosion Loop

Construction, installation, and startup of the first liquid metal circulating corrosion loop was completed this quarter. The material of containment is mild steel, while the liquid metal circulant is a 2 weight per cent uranium-0.2 weight per cent magnesium-cadmium alloy.

A General Electric ac electromagnetic pump (Model No. 9159849) was selected for the system. The schematic sketch of the loop appears in Figure 7. Heating of the system is accomplished by making the loop a one-turn secondary of a 10-kw power transformer. As a result a 1428-ampere current at 7 volts is induced in the loop, providing the autoresistive heating. In order to protect the loop from external air oxidation a corrosion-resistant coating of Markal SR10 was applied to all the surfaces with the exception of the pump cell. Since the cell wall is rather thin at certain places, better protection against air oxidation was considered necessary. Therefore, a chrome plate of 0.005 inch was applied to the pump cell.

FIGURE 7
SCHEMATIC SKETCH OF CADMIUM CORROSION LOOP

Prior to installation of the loop an extensive cleaning procedure was followed. First, the loop was degreased with both a detergent and acetone. It was then pickled in dilute sulfuric acid and flushed with water. This was followed by a flush with a one per cent caustic soda-one half per cent trisodium phosphate solution to remove any ferrous sulfate remaining on the surfaces. The loop was then flushed with acetone again and dried.

After installation the loop was charged with 12.88 kg of cadmium and was put into operation on June 3, 1959. After allowing it to operate for 47 hours with pure cadmium at a maximum temperature of 485 C, 25 g of magnesium and 263 g of uranium were added, making an alloy of approximately 2 weight per cent uranium-0.2 weight per cent magnesium-97.8 weight per cent cadmium composition. At this point the maximum operating temperature of the loop was raised to 550 C. To date the loop has operated very well for 205 hours. Essentially no variations in temperature and flow rate have been observed in this time.

Originally, the electromagnetic flowmeter was built and calibrated to operate in a tantalum-lined Inconel system circulating magnesium. Since the present loop is fabricated from a magnetic material (mild steel) and the circulating fluid is cadmium, the flowmeter had to be modified and recalibrated. The magnetic flux in the air gap of the flowmeter was 776 gauss. Calculations showed that this flux was below the saturation point of the mild steel and therefore very little, if any, of the flux would penetrate the steel walls of the loop. However, by placing two tapered blocks of iron in the air gap of the flowmeter, it was possible

to saturate the steel walls of the loop, thus allowing sufficient magnetic flux to pass through the molten cadmium. The actual value of the flux inside the steel tube of the flowmeter was measured by means of a gauss meter. This value of the flux was then used to calculate a plot of output emf from flowmeter versus flow rate from the following equation:

$$E = VBd \times 10^{-8} \left\{ \frac{2d/D}{1 + \left(\frac{d}{D}\right)^2 + \left(\frac{\rho_f}{\rho_w}\right) \left[1 - \left(\frac{d}{D}\right)^2\right]} \right\}$$

where

- E = flowmeter emf, volts
- B = flux, gauss
- d = inside diameter of loop, cm
- D = outside diameter of loop, cm
- ρ_f = resistivity of cadmium, ohm-cm
- ρ_w = resistivity of steel, ohm-cm
- V = velocity of cadmium, cm/sec.

The obtained plot was checked at the operating flow rate by the following method: A radiograph, employing a 2-curie iridium-192 source, was taken of the location where the loop is connected to the reservoir. A profile of the molten metal stream emptying into the reservoir is clearly discernible on the radiograph (Figure 8). By measuring the vertical and horizontal travel of the stream ejecting from the $\frac{1}{2}$ -inch steel loop, the flow rate could be calculated. Very good agreement between the flowmeter reading and the radiograph calculation was obtained. The flowmeter indicated a flow rate of 0.82 gal/min (2.45 ft/sec) while the calculated value from the radiograph was 0.85 gal/min (2.54 ft/sec).

In addition to the above application the radiographs will be used to maintain a daily check on the condition of the loop. Thief samples are also being taken every other day for spectroscopic analyses. In this way, it will be possible to obtain rate data of concentration changes (corrosion products and original constituents).

Other data concerning the operation of the loop are tabulated below:

power to heating transformer:	2.71 kw
power to EM pump:	0.515 kw
pump differential pressure (calc for measured flow)	5 psi

The typical characteristic curve supplied with the pump indicates that the developed differential pressure should be 4.5 psi.

Figure 8

RADIOGRAPH SHOWING LIQUID CADMIUM ALLOY STREAM
PROFILE USED TO COMPUTE FLOW RATE

C. Pyrometallurgical Research
(H. M. Feder)

1. Chemistry of Liquid Metal Solvents
(I. Johnson)

Fundamental data on the properties of liquid metal systems are being collected systematically to permit the design of separations processes and to furnish the basis for the evaluation of new theories of liquid metal solutions. The separations processes envisioned involve the dissolution of the irradiated fuel in a liquid solvent metal, followed by the separation of the fissile material from the fission product elements by combinations of recrystallization and extractions into immiscible liquids (either fused salts or liquid metals). Separation of the fissile metal from the solvent metal will be accomplished by either volatilization or leaching.

a. Solubilities

The solubilities of the fission product elements in liquid metal solvents are of primary importance in the separation processes under development. These solubilities need to be known as functions of temperature and solvent composition. The identity of the solid phase in equilibrium with the saturated solution is also important. The solubilities of the major metallic fission product elements in both liquid zinc and liquid cadmium have been measured. Solubilities not yet measured include those of rubidium, strontium, yttrium, niobium, technetium, rhodium, tellurium, iodine, and cesium in cadmium.

Notwithstanding some blanks in our knowledge sufficient data have been accumulated to permit the observation of certain regularities.

The most striking of these regularities is the relation of the Periodic Table to solubility in a given solvent at a given temperature. This is illustrated in Figure 9 where known solubilities* in zinc at 600 C and in cadmium at 500 C are plotted against the atomic number for the second long period. A deep minimum is observed at about technetium; a maximum (complete miscibility) when the Hume-Rothery Class II metals (to which class both solvents belong) are reached. A secondary maximum may also be observed at about zirconium. A second minimum is presumably reached at the rare gases. The solubilities in zinc of enough of the first and third long periods are known to show that a similar periodicity exists. A program has been instituted to fill some of the gaps in order that a detailed comparison may be made. Some interesting secondary structure is already known. For example, the solubility of manganese in zinc is somewhat greater than that of its neighbors,

chromium and iron; possibly technetium, when measured, will show a similar behavior.

*The value for yttrium in zinc has been kindly furnished us by J. B. Knighton, American Smelting and Refining Company, in advance of publication.

The results of recent measurements of solubility are reported below.

(1) Ruthenium-Cadmium
(I. Johnson and K. E. Anderson)

Preliminary experiments indicated that the solubility of ruthenium in liquid cadmium was less than 0.01 weight per cent. Consequently the solubility was determined using a sample of ruthenium metal containing ruthenium-106 as tracer. The ruthenium metal was prepared by reducing with magnesium metal an acidic ruthenium chloride solution containing radoruthenium. The precipitated metal was washed, dried, and treated with hydrogen at about 750 C to ensure complete reduction. The resulting metal had an activity of almost 4×10^6 cpm/mg, using a deep-well scintillation gamma counter. While ruthenium-106 is a pure beta emitter of one year half-life, secular equilibrium with the ruthenium-106 daughter of 30-second half-life allows the strong gamma of the daughter to be used for counting.

An alumina crucible (Morganite) was charged with reagent-grade cadmium metal and a small cadmium capsule containing the radioactive metal. The crucible was contained within a stainless steel furnace tube equipped with a stirrer, thermocouple, and a sampling lock. The melt was held under a high-purity argon atmosphere at all times. Temperatures were measured with a noble metal thermel which had been calibrated with NBS secondary standards. Temperature errors were less than ± 2 C.

Filtered samples of the liquid phase were taken by the usual technique of using Vycor or Pyrex sampling tubes plugged with porous carbon to remove suspended particles. The samples were dissolved in acids and aliquots taken for counting. Counting errors were less than ± 2 per cent; the over-all analysis error was estimated to be not greater than ± 10 per cent.

The low solubility (less than 50 ppm) of ruthenium in cadmium together with the slowness with which ruthenium metal dissolved or precipitated on cooling resulted in greater scatter of the experimental data than expected from the precision of the analyses. The procedure finally adopted consisted of sampling a solution at some temperature until successive samples gave a nearly constant composition, then cooling to a lower temperature and resampling. If the composition remained unchanged the solution was presumed to be unsaturated and the procedure was repeated. If the composition changed, the solution was presumed to be saturated and all points obtained during the subsequent cooling were used.

The data which were considered to be significant solubility determinations are given in Table 6. These data are shown in Figure 10 on the usual logarithmic solubility versus $1/T$ plot. The solubility curve shows two distinct segments and indicates two different solid phases in equilibrium with the solution over the temperature range involved. No attempt was made to identify these phases. From analogy to other platinum-group metals with zinc or cadmium it is likely that one of these phases is a ruthenium-cadmium intermetallic compound of the gamma-brass type. The solubility of ruthenium in cadmium may be expressed algebraically as:

$$(627 \text{ to } 352 \text{ C}) \quad \log (w/o \text{ Ru}) = -2.097 - \frac{245}{T} (\pm 0.0002 \text{ w/o});$$

and

$$(352 \text{ to } 327 \text{ C}) \quad \log (w/o \text{ Ru}) = +8.594 - \frac{6910}{T} (\pm 0.0001 \text{ w/o}).$$

Table 6

SOLUBILITY OF RUTHENIUM
IN LIQUID CADMIUM

(Data in chronological order)

Run	Temp (C)	Ru Solubility (w/o)
3	546	0.0040
	496	0.0035
	442	0.0034
	398	0.0034
	327	0.0012
4	341	0.0023
	331	0.0014
4 (remelt)	627	0.0046
	570	0.0040
	521	0.0042
	428	0.0034
	377	0.0036

FIGURE 10
SOLUBILITY OF RUTHENIUM IN CADMIUM

(2) Cerium-Cadmium

(I. Johnson and K. E. Anderson)

A preliminary experiment showed that the solubility of cerium in cadmium was about 0.55 weight per cent at 493 C and greater than 0.8 weight per cent at 596 C. A melt with a nominal concentration of 1.5 weight per cent was prepared in an argon atmosphere. This melt

was held at 600 C and sampled three times during a period of 36 hours by the usual technique of taking filtered samples of the liquid phase. The furnace temperature was then successively lowered by approximately 40 C intervals and the liquid phase was sampled after several hours at each temperature. Temperatures were measured to ± 2 C with a calibrated thermel.

The samples were analyzed for cerium spectrophotometrically by the color developed in a peroxide-ammonium tartrate solution.

The data obtained are given in Table 7 and are shown on the usual logarithmic solubility versus $1/T$ plot in Figure 11. It is seen that the points between 520 C and 363 lie on a good straight line. The data at 600 and 560 C are considered to represent unsaturated solutions because the concentrations found were just those charged. The 330 C datum point is questionable as a result of either sampling error or some difficulty in the analysis for cerium below 100 ppm. A straight line was fitted to the data; the solubility of cerium in cadmium may be expressed algebraically as

$$(520 \text{ to } 363 \text{ C}) \quad \log (w/o \text{ Ce}) = 7.437 - \frac{5845}{T}$$

Table 7

Temperature (C)	Cerium (w/o)	Remarks
600	1.55	Held over night at 600 C; soln unsat'd
601	1.58	Held over night at 600 C; soln unsat'd
560	1.54	Held over night at 600 C; soln unsat'd
520	1.18	-
480	0.46	-
441	0.172	Held over night at 441 C
441	0.180	Held over night at 441 C
401	0.058	-
363	0.0172	-
330	0.0182	-

FIGURE 11
SOLUBILITY OF CERIUM IN CADMIUM

The solid phase in equilibrium with these solutions was not specifically characterized, but Iandelli and Ferro¹ have reported that the most cadmium-rich intermetallic compound is CeCd₁₁.

(3) Lanthanum-Cadmium
(I. Johnson and K. E. Anderson)

Additional data on the solubility of lanthanum in liquid cadmium have been obtained for low concentrations of lanthanum by supplementing the chemical method of analysis by a radiochemical analysis. In the last Quarterly Report (ANL-5996, page 92) the results obtained at temperatures above 400 C by the chemical analysis were reported. The additional data were obtained at temperatures up to 457 C in order to obtain a check in the overlap interval.

A nominal three weight per cent lanthanum-cadmium melt was prepared at 720 C in an argon atmosphere. The temperature was then lowered to 608 C, the melt was stirred for about three hours and a filtered sample of the liquid phase was taken by our usual technique. The temperature was lowered by approximately 50-degree intervals and the liquid phase was sampled after a 45-minute hold. Samples were taken down to 356 C. The melt was held overnight at this temperature, the temperature was again raised to 580 C and a second series (B) was run. These samples were analyzed by titrating lanthanum with EDTA after separation of cadmium. The results obtained on samples containing less than 300 ppm are unreliable and were not used.

For the supplementary experiment (series C) pure lanthanum metal was irradiated in the Argonne CP-5 reactor in a flux of 2×10^{12} nv for a period of one-half hour. The isotope produced by neutron irradiation is lanthanum-140 with a 40-hour half-life. Beta emission is accompanied by high-energy gammas which allow ready counting with the deep-well scintillation counter. The metal had an initial specific activity of 3×10^7 cpm/mg and the samples contained sufficient activity to achieve optimum (± 2 per cent error) counting. A nominal 0.19 weight per cent lanthanum-cadmium melt was prepared by reacting the metals under an argon atmosphere at 500 C for two hours and aging overnight at 457 C. Liquid samples were taken at decreasing temperatures, the temperature being held constant for one-half hour or more prior to each sample. The samples were dissolved in 4 M nitric acid and aliquots were taken for gamma counting.

The data for all series are given in Table 8 and plotted as logarithmic solubility versus $1/T$ in Figure 12. A single line fits the data; it may be expressed by the equation

$$(608 \text{ to } 324 \text{ C}) \quad \log (w/o \text{ La}) = 7.368 - \frac{5991}{T} \quad .$$

¹ Iandelli, A. and Ferro, R., Gazz. chim. ital., 84, 463 (1954)

Table 8

SOLUBILITY OF LANTHANUM IN LIQUID CADMIUM

(Data in chronological order)

Series A and B analyzed by
chemical method.

Series C analyzed
radiochemically

Series	Temperature (C)	Lanthanum (w/o)
A	608	2.90
	552	1.24
	498	0.374
	446	0.098
	406	0.036
	356	~0.02
B	580	2.25
	532	0.82
	472	0.194
	457	0.149
C	418	0.0448
	393	0.018
	363	0.0059
	338	0.0044
	324	0.0031

FIGURE 12
SOLUBILITY OF LANTHANUM IN CADMIUM

The equilibrium solid phase was not characterized independently. It is probably the most cadmium-rich phase reported by Iandelli and Ferro,¹ LaCd_{11} .

(4) Uranium-Zinc

(A. E. Martin, R. Uhle, C. Wach)

The solubility of uranium in zinc was previously measured in this Laboratory from 800 to 500 C by Knighton (ANL-5668, Figure 37) and by Elliott (ANL-5789, page 91). With certain improvements in experimental technique the solubility of uranium in zinc has been re-measured from 750 to 425 C as a check on the earlier data and to obtain values at lower temperatures. The combined data are shown in Figure 13 in the form of log solubility versus $1/T$. Also shown in the figure for comparison is a curve (dotted line) representing the Iowa State solubility data, obtained on well-settled but unfiltered samples, as reported in the January 1959 Newsletter.

FIGURE 13
SOLUBILITY OF URANIUM IN ZINC

cadmium-zinc system are shown in Figure 14 in the form of log solubility versus $1/T$ plots. Also shown for comparison is the solubility curve of uranium in pure cadmium.

The solubility run labeled r-s was performed with a solvent containing considerably more zinc than in Run q-P₁-P₂. This is indicated by the analyzed zinc contents of the solutions which are given next to most of points. Our previous work on this system, especially isothermal precipitation experiments performed at 325 and 448 C, has indicated that the crystallization path of Run r-s would be in the field of primary crystallization of U₂Zn₁₇. This turned out to be the actual situation, as confirmed in several ways. The ingot

Although there is some undesirable scatter in the present data, particularly in the lower temperature region, they fall fairly well on a single solubility line which is best represented by the equation

$$\log(w/o \text{ U}) = 7.272 - \frac{6984}{T}$$

The lack of any inflection in this curve shows that the saturated solution does not participate in any three-phase equilibrium in this temperature range.

(5) Uranium-Cadmium-Zinc (A. E. Martin)

The data from two additional solubility runs in the uranium-

FIGURE 14
THE SOLUBILITY OF URANIUM
IN LIQUID CADMIUM-ZINC ALLOYS

resulting from the run was examined metallographically and the primary crystals were identified as U_2Zn_{17} . Further, some of these crystals were separated from the ingot by leaching with ammonium nitrate solution and submitted for chemical and X-ray diffraction examination.

The chemical analysis was reported as 29.32 weight per cent uranium, 62.0 weight per cent zinc and 6.4 weight per cent cadmium. This corresponds to a zinc/uranium atom ratio of 7.70 and a (zinc + cadmium)/uranium atom ratio of 8.16. If 1.14 weight per cent uranium is tied up as oxide in the sample (requiring only 0.23 weight per cent oxygen as uranium trioxide or 0.15 weight per cent oxygen as uranium dioxide), the (zinc + cadmium)/uranium atom ratio is brought up to 8.50 after the uranium present as oxide is subtracted.

The X-ray diffraction examination showed only the U_2Zn_{17} pattern reported by Makavov;² however, the lattice parameters were slightly larger than normal. If the cadmium present in the sample had been present as UCd_{11} , it would have been noticed in the X-ray pattern.

Thus within experimental error the chemical analysis and the X-ray data confirmed the metallographic findings as well as the supposition which had been based on prior data. However, an appreciable substitutional solubility of cadmium in U_2Zn_{17} is also indicated.

In the second solubility run, labeled q- P_1 - P_2 , an attempt was made to choose a composition such that the crystallization path would follow successively the binary eutectic troughs U_2Zn_{17} -uranium and U_2Zn_{17} - UCd_{11} . Although the location of these eutectics had been indicated by earlier experiments, this additional experiment was needed to define them more precisely. The experiment was successful in that only a few initial points, not shown, appeared not to be saturated with respect to two solid phases. The point marked P_1 was evidently about at the juncture of the two eutectic lines, i.e., at the peritectic point.

These data were combined with those previously obtained on this system to draw a tentative representation of a portion of the liquidus surface of the cadmium-zinc-uranium system which is shown in Figure 15. The fields of primary crystallization of UCd_{11} , U_2Zn_{17} , uranium and cadmium are shown together with a number of isothermal lines. The crystallization paths of the two solubility runs r-s and q- P_1 - P_2 are indicated by correspondingly labelled lines on the figure. Three additional crystallization paths in the U_2Zn_{17} field are also shown as unlabelled dotted lines. The crystallization paths of the previously reported isothermal precipitations at 325 and 448 C can also be located on this figure simply by following the corresponding isothermal lines from left to right across the diagram.

²Makavov, E. S. and Vinogradov, S. I., *Kristallografiia*, 1, 634 (1956)

FIGURE 15
PARTIAL LIQUIDUS SURFACE OF THE
URANIUM-CADMIUM-ZINC SYSTEM

Also, Figure 16 shows a schematic representation of the entire uranium-cadmium-zinc system.

A number of conclusions can be drawn from the work to date on this system, most of which can be deduced from the ternary diagrams.

1. The boundary of the UCd_{11} field on the U_2Zn_{17} side (the line P_1P_2) varies from about 1.4 to 3.6 weight per cent zinc, depending on the temperature.
2. Within the primary field of crystallization of UCd_{11} , there is relatively little effect of zinc on the uranium solubility. The solubility is only about 25 per cent less at the eutectic boundary.
3. Within the field of primary crystallization of U_2Zn_{17} , there is a sharp drop in uranium solubility as the zinc content is increased, especially at temperatures below 450 C.

Figure 1b

SCHEMATIC REPRESENTATION OF URANIUM-CADMIUM-ZINC TERNARY DIAGRAM

- In the field of primary crystallization of uranium, as zinc is added, the initial retrograde solubility changes to a normal positive coefficient. (The change-over point has not been determined.) This leads to increased uranium solubilities. For example, at 530 C, a solubility of 4.7 weight per cent uranium was observed when 4.7 weight per cent zinc was present compared to only 2.1 weight per cent uranium in the absence of zinc.
- The eutectic trough between U_2Zn_{17} and uranium probably extends at higher temperatures to the zinc-uranium binary side of the ternary diagram, there to join at the binary eutectic point e_1 between U_2Zn_{17} and uranium. This eutectic is at about

42 weight per cent uranium and 58 weight per cent zinc at a temperature of 944 C according to the zinc-uranium phase diagram of Chiotti, et al.³ If this is the case, isothermals above 475 C probably cross the eutectic trough at relatively high zinc and uranium contents. Several of these have been estimated and drawn in as dotted lines on the ternary diagram. This of course means that relatively high uranium solubilities might be attained at relatively low temperatures along this binary eutectic trough in the ternary system. This is not true in either the zinc-uranium or cadmium-uranium binary systems and the fact is likely to have practical applications.

6. The eutectic valley between cadmium and U_2Zn_{17} , the line P_2E_1 , probably approximates very closely the liquidus of the cadmium-zinc system with respect to the liquidus temperature at a given zinc content. This line probably terminates at the ternary eutectic, E_1 , with an approximate composition of 17.5 weight per cent zinc, 82.5 weight per cent cadmium, less than 0.0002 weight per cent uranium.
7. The composition triangles are shown in the schematic representation of the ternary diagram, Figure 16, which also contains a listing of the various peritectic and eutectic points with the reactions associated with them. The boundaries of the fields of primary crystallization are given and the locations of the three invariant points in the composition triangles are stated.

(6) Uranium-Cadmium-Magnesium System
(A. E. Martin)

Additional work has been carried out on the uranium-cadmium-magnesium system. Two conventional runs for measuring the solubility of uranium in liquid cadmium-magnesium alloys as a function of temperature were made, and two isothermal solubility runs in which magnesium was added incrementally to liquid cadmium saturated with uranium were made.

³ Chiotti, P., Klepfer, H. H., and Gill, K. J., Trans. AIME 209, 51-57 (1957).

The data for the two conventional solubility runs are shown in Figure 17 in the usual form of log solubility versus $1/T$. The solubility curve of uranium in cadmium itself is also shown.

The data points for isothermal runs at 450 C and 352 C are shown in Figure 18 on a ternary plot. Data points for a 448 C run, previously reported, are also shown.

These experiments combined with the phase diagram for the binary cadmium-uranium system and the binary cadmium-magnesium system yield sufficient information to locate the three fields of primary crystallization in the ternary system, and a number of isothermal lines. These are also shown in Figure 18.

The following conclusions may be drawn from this summary of experimental information:

1. The temperature range in which UCd_{11} is the primary crystallizing phase is shortened at both the high and low-temperature limits by the addition of magnesium. At magnesium contents

greater than the invariant point, at about six weight per cent magnesium, UCd_{11} cannot be formed as a primary crystallizing phase.

2. Within the UCd_{11} field of primary crystallization, the solubility of uranium increases as the magnesium concentration is raised. This is apparent from the slope of the isothermal lines in this field.
3. The limited data relating to the cadmium-magnesium field of crystallization, together with the known low contents of uranium, indicate that the liquidus temperatures are practically unaffected by the uranium content. Accordingly, liquidus temperatures along the lines DB and BC, and the extension of BC to higher magnesium contents, can be taken approximately as those indicated by the cadmium-magnesium phase diagram at the same magnesium contents.
4. The peritectic temperature of 475 C in the binary uranium-cadmium system is lowered as magnesium is added to the system and reaches its lowest point at the invariant point B at a temperature of 360 to 365 C.
5. Figure 18 shows how the solubility coefficient of uranium in cadmium above the peritectic line AB is affected by the addition of magnesium. The retrograde coefficient found in the absence of magnesium persists in the presence of magnesium, but, as the temperature increases, there appears to be a change-over to a normal, positive, but still very small, coefficient. This means that the isothermals in the uranium field of crystallization are grouped together fairly close to the line A-B-C. To avoid confusion in the diagram, only one of these lines, the 550 C isothermal, is shown. Below about six weight per cent magnesium, this isothermal appears to be in the UCd_{11} field. This is because on a two-dimensional representation the two crystallization fields partially overlap. In a three-dimensional plot part of the uranium liquidus surface overhangs the UCd_{11} liquidus surface in the low magnesium portion of the diagram and consequently its vertical projection on a two-dimensional surface falls partly within the UCd_{11} field.

6. In the field of primary crystallization of uranium the solubility of uranium in liquid cadmium-magnesium alloys decreases steadily as the magnesium content increases. This can be seen by following the 550-degree isothermal from left to right across the diagram.

(7) Uranium-Mercury-Zinc
(A. E. Martin and R. Uhle)

The effect of zinc on the solubility of uranium in mercury at 250 C was determined by making incremental additions of zinc to mercury saturated with uranium and taking filtered liquid samples after allowing several hours for equilibration following each zinc addition. The technique was the same as had previously been used in the isothermal experiments in the uranium-cadmium-zinc, uranium-zinc-magnesium and uranium-cadmium-magnesium systems.

It was supposed that at some critical zinc addition the melt composition would pass from a field of primary crystallization of

UHg_4 to that of U_2Zn_{17} , and that this would be accompanied by a sharp drop in the uranium solubility. The results of the experiment, shown in Figure 19, did indeed show a sudden drop in the uranium solubility between 1.4 and 3.4 weight per cent zinc. Preliminary microscopic examination of the solid crush formed on cooling the product of the reaction indicates that the uranium was probably precipitated as U_2Zn_{17} . This will be checked by X-ray examination of isolated crystals of the precipitate.

b. Thermodynamic Studies

A program is under way to measure activities of metallic elements dissolved in liquid metal solvents or in intermetallic compounds. These data are needed for computations of the extent of various reactions involving transfer of metals into or out of solution. Two approaches have thus far been used. In the first, free energies of transfer are computed from measured emf's of appropriate galvanic cells. In the

second, the activities are computed from vapor pressure measurements. Both methods have been used on the uranium-zinc system. Data obtained by the vapor pressure method are reported below. Results obtained by the emf method were reported in ANL-5924, page 132.

(1) Uranium-Zinc System
(C. L. Rosen, P. Bergland)

A study of the phase diagram and thermodynamics of the uranium-zinc system by means of the effusion pressure method was continued.

In the use of the continuously monitored effusion apparatus described in ANL-5959, page 125, care must be taken in the placement of the orifice of the effusion cell if one is to avoid a correction to the absolute weight of the cell due to the momentum of the effusate molecules traveling in an upward direction.^{4,5} This effect is only important for the comparison of two pressures because the correction for a given pressure is directly proportional to it. In order to eliminate the need for such corrections new cells were made with two orifices along transverse diameters.

Figure 20 shows retracings of the strip-chart recorder data for experiments conducted with the alloys at 401 C, 422 C and 455 C using the channel orifices. Figure 21 shows the vapor pressures of zinc as calculated from the initial slopes of these curves and also those obtained with zinc. For the channel orifices, pressures were calculated by the equation^{6,7}

$$P = \frac{3 g L (2 R T)^{1/2}}{8 t r^3 C (\pi M)^{1/2}} \frac{1 + 0.81 (5 r / \lambda)}{1 + (5 r / \lambda)}$$

For the knife-edged orifice at the top of the cell pressures were calculated by the equation:

$$(g / t r^2) (2 R T / \pi M)^{1/2}$$

⁴ Mayer, H., Z. Physik, 67, 240 (1931)

⁵ Margrave, J. L., J. Chem. Phys., 27, 1412 (1957)

⁶ Knudsen, M., Ann. Physik 28, 75 (1909)

⁷ Dushman, S., Scientific Foundations of Vacuum Technique, John Wiley, New York (1949)

FIGURE 20
VOLATILITY CURVES FOR ZINC IN URANIUM-ZINC ALLOYS

FIGURE 21
VAPOR PRESSURE OF ZINC

where

P = pressure, dynes

g = weight loss, g

t = effusion time, sec

R = gas constant, ergs/degree mole

M = molecular weight of effusate

L = orifice length, cm

r = orifice radius, cm

λ = mean free path of vapor, cm

C = clausius factor

T = absolute temperature, Kelvin

The negative deviation of the present results from the representative literature values⁸ for zinc above about 460 C may be interpreted as due to the fact that saturation of the vapor phase cannot be maintained with λ/r ratios (Knudsen numbers) of less than unity. Unfortunately the sensitivity of the present balance is such that the use of smaller orifices at higher temperatures is ruled out by the excessive duration of such runs.

In our compiled results for the alloys, shown in Figure 22, only those points with Knudsen numbers greater than unity have been included.

The existence of two apparent pressure plateaus in the isothermal volatility curves of the alloys in addition to that of zinc indicates either (a) that there are two intermediate compounds in the system, or (b) that there is only one intermediate compound with a solution range. In the latter case the apparent second break in the volatility curves would be spurious, and the two apparent plateau pressures would represent the vapor pressures of the zinc-saturated and uranium-saturated intermediate compound.

FIGURE 22
VAPOR PRESSURE PLATEAUS FOR URANIUM-ZINC ALLOYS

⁸Darken, L. S., and Gurry, R. W., Physical Chemistry of Metals, Mc Graw-Hill Book Co., 1953, page 228. ff.

The alternatives interpretations are subject to elucidation by means of X-ray analysis. Therefore, certain effusion experiments were terminated by cooling when the samples contained less than 25 weight per cent uranium (i.e., before the first volatility break) and others when they contained more than 30 weight per cent of the uranium (i.e., after the second volatility break). There exists in the literature two X-ray patterns for "the" zinc-uranium intermetallic compound.^{9, 10} X-ray patterns of these samples* show that the sample containing less than 25 weight per cent uranium exhibits a pattern similar to that found by Vold,⁹ whereas the sample containing more than 30 weight per cent uranium exhibited a pattern similar to that of Makarov.¹⁰ This work is being continued and will be supplemented by examination of annealed alloys in the intermediate range.

The reliability of the continuously monitored effusion apparatus as a tool for determining phase diagrams is being tested by investigating the location of the volatility breaks in the known copper sulfate-hydrate system. This system affords a severe test because hydration equilibrium is obtained quite slowly.

(2) Activity of Uranium in Liquid Cadmium
(I. Johnson and R. M. Yonco)

The uranium-cadmium system is being studied using the emf method. Preliminary data were reported in the last quarterly (ANL-5996) for the emf's of the cell

After correction for the uranium-tungsten thermal emf, the cell reaction may be written as

when the liquid cadmium solution is saturated with respect to the intermetallic compound UCd_{11} . Whether the cadmium is saturated or not the cell emf $\mathcal{E}$, after correction for the uranium-tungsten thermal emf, is related to the activity of the uranium, a_{U} , in the solution by the equation:

$$\mathcal{E} = -\frac{RT}{nF} \ln a_{\text{U}} \quad (3)$$

Thus measurements of cell emf may be used to compute activities, and these, when combined with the known uranium contents of solutions, may be used to compute the activity coefficients.

⁹Peterson, D., and Vold, C. L., ISC-1050, p. 76 (1959)

¹⁰Makarov, E. S., and Vinogradov, S. I., Kristallografiia, 1, 634 (1956)

*Work done by D. S. Flikkema of this division.

The utility of activity coefficients depends upon whether they are, at any given temperature, simple functions of concentration. In the case of dilute solutions of uranium in zinc, Henry's law was found to be obeyed, i.e., the activity coefficients of uranium were constant at a given temperature. For solutions of uranium in cadmium, consideration of the phase diagram, especially the retrograde portion above the peritectic temperature, made it seem highly unlikely that Henry's law was obeyed. A second uranium-cadmium cell was therefore set up to determine whether deviations from Henry's law could be determined. The results of preliminary experiments show that significant deviations do occur. Sufficiently accurate data are not yet available to determine the relationship between the activity coefficient and the solution concentration quantitatively. Qualitatively, the results indicate that the activity coefficient decreases as the solution concentration is decreased.

(3) Calorimetric Research
(W. N. Hubbard)

(a) Heat of Formation of Molybdenum Disulfide
(R. L. Nuttall and D. R. Fredrickson)

A series of eight combustions in oxygen has been carried out on a natural sample of molybdenum disulfide using the platinum-lined bomb in the rotating bomb calorimeter. Calculations of the heat of combustion values for the idealized combustion reaction are in progress. Also, a series of eight combustions in oxygen has been carried out with molybdenum metal and sulfur in the stoichiometric proportion found in molybdenum disulfide. A comparison of the heats of combustion for the two series will provide a more accurate value for the heat of formation of the compound.

The platinum-lined bomb used for these combustions shows two pronounced differences from previous combustions in an Illium bomb:

- (1) A reddish precipitate suspended in the bomb solution (evidence of attack on the Illium) is no longer formed.
- (2) The platinum catalyzes a more complete conversion of the sulfur to the +6 oxidation state.

A suspended wire technique for burning natural molybdenum disulfide worked well and gave conversion of more than 99.9 per cent of the molybdenum to molybdenum trioxide and of more than 81 per cent of the sulfur to the +6 oxidation state. The pellet of molybdenum disulfide was cast on a one-inch length of iridium wire with 6-mil platinum wire welded at each end for attaching to a support. A separate 6-mil platinum

wire was used as a fuse. At the point of contact of fuse wire and pellet, there was attached a 5 to 10-mg bead of sulfur which acted as a kindler. The molybdenum disulfide was burned in 6 atmospheres of oxygen pressure. When burning was complete, the bomb was rotated to dissolve the MoO_3 in a solution of sodium hydroxide placed in the bomb at the start of the experiment. The heat of combustion thus determined is for the reaction

In order to determine the heat of formation of molybdenum disulfide the heats of formation of MoO_4^- and SO_4^- in a sodium hydroxide solution must be known. In order to lessen the effects of uncertainties in these values, a series of combustions of molybdenum-sulfur mixtures has been completed. The measured heat is for the reaction

Equation (2) has the same products as equation (1) and the heat of formation of molybdenum disulfide is just the difference between the two heats of combustion experimentally measured in the same calorimeter.

A crucible-and-disc technique was used for the combustions of molybdenum and sulfur. More than 99.5 per cent of the molybdenum was burned to molybdenum trioxide and the rest to molybdenum oxide. More than 98.5 per cent of the sulfur was converted to the +6 oxidation state. The sulfur was placed in a thin quartz crucible having arms for suspension from a gimbal. The molybdenum foil, triply crimped into the form of a "W," was placed on a thin quartz disc supported near the top of the crucible on indentations. A cotton thread, attached to the platinum fuse wire, ignited the sulfur. Another cotton thread ignited a molybdenum wire which was attached to either end of the molybdenum foil. Thus, the molybdenum and sulfur burned independently. Fifteen atmospheres of oxygen were used in the bomb. When the combustion was over, the bomb was rotated to dissolve the molybdenum trioxide in a sodium hydroxide solution. Bomb washings were filtered to determine the amount of residue. The solutions were titrated with standard iodine to determine the amount of sulfur in the +4 oxidation state. Calculations to reduce the experimental data to standard-state conditions are in progress.

(b) Fluorine Bomb Calorimetry
(J. L. Settle, E. Greenberg, E. Rudzitis, L. Stein*)

Molybdenum

A series of seventeen calorimetric combustions has been carried out to determine the heat of formation of molybdenum hexafluoride vapor according to the equation

*Cooperating Chemist, Chemistry Division

Two of these combustions were discarded because some nickel fittings contained in the bomb were ignited and produced excess energy. Three combustions were discarded because too large a sample was used and the excess hexafluoride condensed to the liquid state. Four combustions were discarded because of uncertainties in one or more of the measurements taken. Table 9 gives a summary of the remaining eight calorimetric combustions. The corrected temperature rise of the calorimeter is ΔT . The heat capacity of the bomb, used to convert the temperature rise to energetic quantities, is preliminary; hence the results to be discussed are not absolute. The weight gain of the bomb is the weight, in milligrams, of material fixed on the bomb surface during the reaction. The observed heat of combustion of molybdenum in fluorine, with all corrections applied except that for the weight gain, is $-\Delta E_c/M$ on a gram basis.

There is an apparent heat effect associated with the weight of material fixed on the bomb surfaces during a combustion. Figure 23 is a large-scale plot of the observed heat of combustion in calories per gram vs the weight gain of the bomb for the experiment. Extrapolation to zero weight gain gives a value of -3883.6 calories per gram (372.63 kcal/mole) of molybdenum as the standard heat of formation of molybdenum hexafluoride. Scrapings taken from the nickel liners used in the combustion bomb have been submitted for X-ray diffraction analysis in an effort to establish the state in which part of the molybdenum is deposited on the bomb surfaces.

Table 9

MOLYBDENUM COMBUSTIONS IN FLUORINE

Combustion Number	Mass Sample Reacted (g)	ΔT (C)	Wt Gain of Bomb (mg)	$-\Delta E_c/M$ (cal/g of Mo)
8	0.73774	0.79743	25.1	3877.6
10	0.74724	0.80727	25.0	3875.2
11	0.74305	0.80339	24.7	3878.3
12	0.73875	0.79947	13.4	3882.2
14	0.74715	0.80547	51.7	3867.1
15	0.72253	0.78194	6.7	3882.0
16	0.73254	0.79195	1.2	3878.2
18	0.72445	0.78002	70.7	3862.5

FIGURE 23
OBSERVED HEAT OF COMBUSTION
OF MOLYBDENUM IN FLUORINE
AS A FUNCTION OF THE WEIGHT
GAIN OF THE BOMB

Of the combustions listed in Table 9, numbers 8 through 13 were performed with 98.9 per cent pure fluorine; the chief impurities were oxygen, nitrogen, CF_4 , C_2F_6 , C_3F_8 , NF_3 , SiF_4 , SF_6 , and HF . The remaining combustions were done with 99.9 per cent pure fluorine containing only oxygen and nitrogen as impurities. The average corrected $-\Delta E_C$ of combustions 8 through 12 was 372.78 ± 0.02 kcal/mole. The average corrected $-\Delta E_C$ of combustions 14 through 18 was 372.54 ± 0.13 kcal/mole. Although it appeared that the less pure fluorine gave an average energy 0.06 per cent higher than the average energy from combustions with fluorine of higher purity, the difference was judged to be of borderline significance.

Another series of combustions is being carried out in an attempt to shed more light on the problem of the weight gain of the bomb. In this series the mass of sample reacted is only 0.375 g, about one-half of that of the previous studies. Consequently, the temperature of the reaction zone should be lower. It would be expected that if side reactions occur during the reaction period their extent should be a function of the temperature.

The results reported here are of a preliminary nature only and contain certain inconsistencies and errors. However, it is apparent that the heat of formation of molybdenum hexafluoride is about four per cent lower than the value recently obtained by Brady¹¹ and about seven per cent lower than estimates appearing in the literature.¹²

Zirconium

Exploratory work to establish a technique for calorimetric combustions of zirconium in fluorine has begun. A variety of shapes and sizes of zirconium were burned in both fluorine and fluorine-helium mixtures. The major difficulty in burning zirconium to the tetrafluoride quantitatively arises from melting of the metal. When molten metal falls to the bottom of the bomb it is quenched. Efforts were therefore directed toward lowering the burning temperature of the sample, and, in the more successful experiments, up to 85 per cent of the zirconium has been burned.

A glass bomb was used for these experiments in order to observe the ignition and burning characteristics of zirconium. The need for a crucible was eliminated by suspension of samples of sheet zirconium from one end and ignition of the other end with an electrical fuse wire. The samples varied in thickness from 0.0003 inch to 0.020 inch. In every case melting occurred and incomplete combustion resulted. A one-inch-diameter coil of 0.030-inch wire was burned with similar results. It was noted, however, that thicker samples and samples ignited at the top

¹¹Brady, A. P., Clauss, J. K., and Myers, O. E., WADC-TR-56-4.

¹²Glassner, A., ANL-5750

rather than at the bottom burned at an appreciably slower rate. Pellets of zirconium ($\frac{1}{4}$ inch $\times$ $\frac{1}{4}$ inch) were burned with somewhat greater success, but this introduced the problem of a suitable crucible or support plaque. Zirconium rods about $\frac{1}{8}$ -inch diameter by one inch long, supported in an upright position and ignited at the top, were then used in a number of successful experiments in which up to 85 per cent of the sample was burned. A combustion technique of this kind may be used for calorimetric measurements provided the amount of unburned zirconium is accurately determined.

In some of these experiments the burning temperature of the sample was reduced, and its melting was prevented, by diluting the fluorine with helium. There appears to be a rather narrow range of gas compositions which will prevent the sample from burning at too high a temperature and still be high enough to give complete combustion. When excessive helium diluent is used the electrically ignited fuse wire does not get hot enough to ignite the main sample. Because the glass bomb can only sustain approximately four atmospheres, recent combustions have been carried out in a trial nickel bomb. A glass-nickel bomb which will safely permit the use of pressures up to 10 atmospheres is being fabricated.

Cadmium

Techniques are being studied for the combustion of cadmium in fluorine.

(3) High-temperature (1500 C) Enthalpy Calorimeter (R. L. Nuttall and E. D. West*)

Construction of the high-temperature enthalpy calorimeter is in progress in the Central Shops. The furnace is nearly complete and the work on the auxiliary apparatus is proceeding satisfactorily.

*Consultant, National Bureau of Standards, Washington, D. C.

II. FUEL CYCLE APPLICATION OF VOLATILITY AND FLUIDIZATION TECHNIQUES

The "Fluoride Volatility Process" is used as a generic term to be applied to several schemes for processing irradiated fuels. Work is in progress on three such schemes, namely, the Fused Fluoride Volatility Process, the Aqueous Dissolution Fluorination Process, and a Direct Fluorination Process. The first is in the pilot plant stage of development, the second in both pilot and laboratory phases of development, and the third is in the initial stages of laboratory research and development. The diversified approach to volatility processing has become necessary due to the variability in fuels in current and proposed reactors.

Increased interest in the use of ceramic fuels for reactors and the development of fluid-bed fluorination techniques have been encouraging factors in the development of a process for the direct fluorination of fuels composed of uranium oxides. Studies on the rates of fluorination of uranium oxide, sintered in a manner to simulate an irradiated fuel, are in progress.

Equilibrium constants are being obtained at various temperatures for the dissociation reaction of plutonium hexafluoride to fluorine and plutonium tetrafluoride. A complete knowledge of this reaction is necessary for the volatility process recovery of plutonium from spent power reactor fuels. Consistent values for the equilibrium constant have been obtained at 300 C.

Fluorination of plutonium compounds in laboratory and pilot plant operations requires an efficient and safe means of disposal of unreacted fluorine. Experiments with several substances indicate that activated alumina will serve as a chemical trap reactant.

A systematic study of the reaction of nickel with fluorine is in progress as a part of the study of metal reactions with fluorine. The mechanism of the nickel-fluorine reaction at elevated temperatures will be studied using several physical-chemical techniques. Preliminary experiments using "A" and "L" nickel have been made at temperatures between 500 and 700 C.

A fluid-bed volatility process for the recovery of uranium from low-uranium-Zircaloy-2 fuel alloys is under development. The major process steps include aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry fluidizable powder, and fluid-bed fluorination of the mixture to remove and recover the uranium as uranium hexafluoride. Drying operations were conducted in the six-inch-diameter Inconel reactor, using synthetic feed solutions containing the equivalent of a two weight per cent uranium alloy. The use of a high fluoride concentration in the feed solution (16 M)

is being investigated in an effort to minimize the formation of hydrated zirconium tetrafluoride and zirconyl fluoride, two species that consume fluorine during the subsequent fluid-bed fluorination operation. The dryer was operated for approximately 45 hours at 240 C with single and dual nozzles at rates of 50 to 70 ml/min per nozzle. Nozzle agglomerate formation disrupted several runs, but such formation was later virtually eliminated by the use of a newly designed nozzle. Control of particle size during cal-ciner operation by utilizing an auxiliary attrition air jet continues to be successful.

X-ray diffraction analyses of dryer product made at 240 C with the 6.3 M fluoride feed show the major constituents to be anhydrous and monohydrated zirconium tetrafluoride. Material made at a drying temperature of 300 C consists primarily of zirconyl fluoride. Hydrofluorination of these materials at 450 C as a pretreatment to fluorination substantially reduced both their oxygen and water contents.

The current series of fluid-bed fluorination experiments are part of a statistical plan devised to show the possible interaction of the fluid-bed dryer and fluorinator operating variables on uranium removal. These variables include the drying temperature, fluorination temperature, hydrofluorination pretreatment, and duration of fluorination. Preliminary results may be summarized as follows: Hydrofluorination pretreatment (450 C for five hours) improved the uranium removal for material dried at 240 C but not for material dried at 300 C; increasing the fluorination temperature from 450 to 525 C had a large beneficial effect on uranium removal for 300 C drier product but a smaller effect on 240 C dryer product; increasing the duration of fluorination had little effect since the major fraction of uranium was removed in the first few hours. The best uranium removal achieved in the current tests was about 90 per cent at 600 C for materials that remained free-flowing, but greater than 99 per cent was removed at 675 C from a caked portion of a bed.

Laboratory fluorinations of high zirconium content fuel solution have been performed. The effects of particle size, additives and temperature on uranium removal have been investigated.

In the fused salt fluoride volatility process for the recovery of uranium from zirconium-matrix fuels, the alloy is dissolved in the fused salt at 600 C with a hydrogen fluoride sparge and then the uranium is volatilized as the hexafluoride in a fluorine sparge. Because this fused salt process environment is corrosive to metals, equipment is being developed to avoid salt-metal contact.

A graphite dissolver-hydrofluorinator has been given a shake-down test with a dummy fuel element. Operations of salt transfer, fuel element charging, and hydrogen fluoride sparging were carried out. Several additions and modifications were called for on the basis of this test, the primary change being a revamping of the top portion of the graphite pipe which carried sparge gas from the dissolver head to the gas distributor plate.

A series of tests has been made to examine the feasibility of drop-wise fluorination as a means of contacting fused salt (bearing uranium) with fluorine. In this scheme, molten salt is sprayed into a fluorine atmosphere. The salt is allowed to solidify before contacting the walls of the container and the uranium hexafluoride formed is recovered from the gas phase. In a series of six tests at three different temperatures, the uranium removal was found to depend strongly on droplet size and less strongly on fluorine temperature: small droplets and high temperatures favor better uranium removal. The maximum amount of uranium removed was 29 per cent with a fluorine temperature of 200 C. Two additional runs made with a highly purified and prefluorinated salt did not show substantially higher uranium removals under the same conditions. Calculations based on the experimental results indicate that multistage operation would be required for a uranium recovery of 99 per cent by this method.

Feasibility studies on the calcination of simulated Purex process wastes were successful in providing a free-flowing, granular solid with a volume reduction factor (feed liquid to solid product) of 4.7. Some difficulties resulting from the formation of about five per cent of the product as small aggregates or lumps have not yet been overcome. The use of an alternative nozzle design and a high-velocity attrition air jet did not offer much improvement. No corrosion problems have been encountered despite the presence of high concentrations of sulfate in the feed.

Preliminary tests of a one-step, continuous fluid-bed process for the conversion of uranium hexafluoride to uranium dioxide were made in a $1\frac{1}{2}$ -inch-diameter Monel column. This process has potential applications both for the production of reactor-grade dioxide and for the recovery of fluoride from the large quantities of depleted uranium hexafluoride now being stored. Steam and hydrogen in the mole ratio two to one are used as fluidizing and reactant gases for the simultaneous reduction and pyrohydrolysis reactions. The experiments made at 600 C produced a dense coating of dioxide on the surface of the starting dioxide powder. Good conversion (96 to 99 per cent) to uranium dioxide was achieved at feed rates of 6 to 8 g/min of uranium hexafluoride using 300 to 600 per cent excess steam and hydrogen. These rates are equivalent to over 50 lb/hr per cubic foot static bed volume or 35 lb/hr uranium per square foot of reactor cross section. A run made at twice this rate gave about 65 per cent conversion.

Discussions on various fluidization and fluoride volatility topics were held during this quarter with representatives from Hanford, ORNL, Aeroprojects Inc., General American Transportation, and National Committee of Nuclear Research in Rome, Italy.

A. Fluorine Chemistry
(J. Fischer)

1. Fluorination of Uranium Dioxide
(M. Steindler, D. Steidl)

Considerable interest has developed in the use of ceramic fuels for power reactors. It is possible that fuels containing uranium oxide can be reprocessed in a simple and economic manner by a direct fluorination process, involving removal of the oxide fuel from the cladding, followed by treatment of the oxide by a fluorinating agent. Uranium and plutonium oxides are converted ultimately to the hexafluorides and volatilized. Separation and additional purification of the hexafluorides is followed by such chemical reactions as are necessary to convert the uranium and plutonium hexafluorides to the desired compounds. The pyrohydrolysis of uranium hexafluoride (ANL-5996, page 184) serves as a simple means of converting the uranium back to the oxide for use in the fuel.

Fluorination in boat experiments of uranium dioxide powder, formed by reduction of the trioxide at modest temperatures in a fluidized bed, has been reported previously (ANL-5924, pages 28 to 33). Uranium dioxide pellets are fabricated under high temperature and pressure with the result that the density of the material is high and the chemical reactivity is relatively low. On occasion uranium dioxide pellets have melted internally while under irradiation, producing an even more refractory material.

Exploratory experiments have been carried out to determine the rates of fluorination of uranium dioxide samples with thermal histories similar to those anticipated for reactor fuel pellets. The equipment and procedures used in these experiments are similar to those used previously (ANL-5924, page 28). Samples of uranium dioxide were fluorinated, with a stream of fluorine, in a heated tube furnace. Uranium hexafluoride formed in the reaction was removed from the gas stream by two cold traps. Rate data for the fluorination of powdered samples were based on the amount of uranium converted to the hexafluoride, the time of fluorination, and the average exposed sample area.

Several types of samples were fluorinated and results are shown in Tables 10 and 11. Although the data scatter more than those obtained from material prepared by the fluidized-bed method, it is likely that no basic difference exists in the mode of fluorination. Conversion to both uranyl fluoride and uranium tetrafluoride was shown by X-ray analysis

Table 10

FLUORINATION OF FUSED AND GROUND URANIUM DIOXIDE

Source of UO_2 : Fluor Corp arc fused and ground^a
 Fluorine Pressure: one atmosphere, 100% F_2
 Flow Rates: 45 to 70 cc/min; constant for each experiment

Expt	Initial Weight (mg)	Weight Loss (mg)	Time (min)	Uranium Collected ^b (mg)	Area ^c (sq cm)	Temp (C)	Rate [mg U/(sq cm)(hr)]
119	758.7	-2.5	60	0.67	2.23	200	0.30
122	665.4	-2.8	120	0.069	2.14	300	0.016
120	761.2	47.0	60	53	2.21	300	24
123	738.1	363.5	120	330	2.02	300	82 ^d
125	709.1	90.2	60	91	2.14	300	42
117	467.5	461.2	60	380	1.53	375	235
118	1079.8	1056.7	60	880	2.02	375	435
121	764.0	202.3	15	186	2.14	375	348
124	1539.8	1522.0	30	1250	2.25	375	1100

^a Bulk density; 6.0 g. cc.

Sieve Analysis: +60 15 w/o
 -60, +140 28 w/o
 -140, +230 25 w/o
 -230, +325 9 w/o
 -325 23 w/o

^b Collected as UF_6

^c Top exposed area of powder.

^d Sample of the residue from this experiment submitted for X-ray analysis.
 Results: major phase - UO_2F_2 ; minor phase - UO_2 ; no UF_4 detected.

Table 11

FLUORINATION OF FUSED AND SINTERED URANIUM DIOXIDE PELLETS

Fluorine Pressure: one atmosphere, 100% F_2
 Flow Rates: 50 to 70 cc/min; constant for each experiment

Expt	Initial Weight (mg)	Initial Area (sq cm)	Temp (C)	Rate ^a [mg U/(sq cm)(hr)]
112	669.3	1.06	375	58.5 ^b
113	1458.0	1.66	600	2820 ^b
114	1132.1	1.51	500	2280 ^b
115	1762.0	1.87	500	3190 ^c
116	2015.2	2.59	500	2500 ^d

^a The rates are expressed in terms of milligrams uranium collected as UF_6 per hour and per INITIAL geometric area of the sample. The final areas of the fluorinated samples were not measurable. [1 mg U (hr)(sq cm) = 10^{-4} cm/hr penetration for samples of density 10 g/cc]

^b These samples were pieces of arc fused UO_2 having smooth faces.

^c Pressed and sintered UO_2 pellet, fuel grade, hydrogen fired at 1825 C for 12.5 hours, 78% of the theoretical density.

^d Pressed and sintered UO_2 pellet, fuel grade, hydrogen fired at 1340 to 1400 C for 16 hours, 63% of theoretical density.

of the residue. The rates of fluorination of the fused and ground uranium dioxide were appreciably less than that found for material produced at lower temperatures. Data from experiments shown in Table 11 are not directly comparable to data obtained from powdered samples. The effective surface areas of the solid materials used in Experiments 112 to 116, Table 11, were probably less than that of powdered uranium dioxide. This reduction is reflected in the observed decrease in fluorination rate. The fluorination rate at 375 C of uranium dioxide produced in a fluidized bed is approximately the same as the fluorination rate of fused uranium dioxide at 600 C. From the preliminary data it appears that undiluted uranium dioxide fuels will react with elemental fluorine at rates acceptable for process use, although such a decision can probably not be made on the basis of laboratory experiments alone. It is recognized that particle size distribution from irradiated material may be different from that available in the powders fluorinated in the present experiments. Attempts will be made to exercise a more accurate control over particle size distribution in experimental samples. The fluorination of ceramic fuels containing additives will also be studied.

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

A complete knowledge of the reaction $\text{PuF}_4(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$ is needed for the development of the fluoride volatility process for the recovery of fissile materials from fuels containing plutonium. It is important to obtain the equilibrium constant for the reaction at several temperatures. Reported here are measurements at 300 C.

The equilibrium constants of this reaction have been measured at several temperatures from 167 to 600 C by A. E. Florin et al.¹³ They found that the dependence of the equilibrium constant on temperature changed abruptly at about 308 C and suggested that this was the result of a change in the reacting material.

Weinstock and Malm¹⁴ also measured the equilibrium constant at 220 C.

One difficulty involved in measurement of the equilibrium constant of the reaction is the rather small ratio of plutonium hexafluoride to fluorine in the equilibrium gas phase. In the present work the equilibrium gas mixture was analyzed by determining the total amounts of plutonium hexafluoride and fluorine present in the system. In order to have a large

¹³Florin, A. E., Tannenbaum, I. R., and Lemons, J. F., J. Inorg. and Nuclear Chem. 2, 368 (1956).

¹⁴Weinstock, B. and Malm, J. G., J. Inorg. and Nuclear Chem. 2, 380 (1956).

amount of plutonium hexafluoride in the equilibrium mixture, both the volume of the vessel used to contain the mixture and the equilibrium fluorine pressure were made as large as conveniently possible.

The equilibrium mixture was made up in a three-inch-diameter vessel of about 1 liter volume. A three-eighths-inch-diameter gas take-off

FIGURE 24
APPARATUS USED IN DETERMINATION
OF EQUILIBRIUM CONSTANT OF THE REACTION
 $\text{PuF}_4(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$

tube and a thermocouple well extended down into the center of the vessel (see Figure 24). The gas take-off tube was closed by a Hoke diaphragm valve. The vessel was housed in a cylindrical stainless steel heater shell. The shell was flanged, and circular end plates were bolted onto it. One end plate was designed with appropriate openings for the gas take-off tube and the thermocouple well. Another opening permitted operation of the diaphragm valve on the vessel by an extension handle.

Two "U" traps, constructed from 20-inch lengths of one-fourth-inch-diameter nickel tubing, were joined at one end to the gas take-off tube, and at the other end to the vacuum line. The ends of the traps were fitted with Hoke No. 1103 bellows valves and flare connectors. Each trap weighed about 170 g and therefore could be weighed on the 200-g capacity analytical balance. The equipment was tested with a helium leak detector prior to use. Temperatures were measured with a Chromel-Alumel thermocouple and a recording potentiometer. Pressures were measured with a mercury manometer in conjunction with a Booth-Cromer pressure transmitter and self-balancing relay.

The large nickel vessel was charged with sufficient plutonium tetrafluoride for several experiments by filling the vessel with plutonium hexafluoride vapor and decomposing it at 200 to 300 C. The preparation and purification of plutonium hexafluoride in this laboratory has been discussed previously (ANL-5924, pages 33 to 39). At the start of an experiment fluorine was added to plutonium tetrafluoride in the vessel at room temperature, and the pressure and temperature measured. The volume of the vessel was known, and the amount of fluorine was calculated using the ideal gas equation. The equilibrium temperatures were approached from both higher and lower starting temperatures. After equilibration, the diaphragm valve was opened slightly, and the equilibrium gas mixture was allowed to stream slowly from the vessel. The gas stream was passed through the traps which were cooled in dry ice-trichloroethylene mixture

to condense the plutonium hexafluoride. After the vessel had been emptied, the traps were evacuated, allowed to warm to room temperature, and weighed to obtain the amount of plutonium hexafluoride present in the vessel at equilibrium. The experiments that established the stoichiometry of the decomposition reaction (ANL-5924) had shown that the ratio of plutonium hexafluoride to fluorine would not change with a change in total pressure, and therefore no shift in the equilibrium ratio was expected as the total pressure decreased during the removal of the equilibrium gas mixture from the vessel. The gas mixture was allowed to stream from the vessel at a rate of about 15 to 30 ml per minute. Doubling the flow did not produce a significant change in the results.

The results of several experiments at 300 C are shown in Table 12. The ratios of $(\text{PuF}_6)/(\text{F}_2)$ observed at 300 C are all slightly higher than the value of 0.0021 reported by Florin et al.¹³ All of the experiments reported here were done at the same fluorine pressure of about 1900 mm at 300 C. Experiments are planned for other fluorine pressures and for several other temperatures.

Table 12

EQUILIBRIUM CONSTANT FOR THE REACTION

Temperature: 300 C

~1900 mm F_2 pressure

Equipment Description: See Figure 24

No.	Initial Temp (C)	Equilibrium Temp (C)	Time at Equilibrium Temp (hr)	Equilibrium Constant ^a
1	25	302 ± 1	3	0.00263
2	25	303 ± 0.5	1½	0.00263
5	340	301 ± 2	1	0.00288
6	345	302 ± 0.5	2	0.00244
7	348	301 ± 0.2	2	0.00258
10	25	302 ± 0.5	2½	0.00278
11	330	300 ± 0.5	24½	0.00260

$$^a K_p = K_c = (\text{PuF}_6)/(\text{F}_2)$$

3. Chemical Traps for Fluorine (G. J. Vogel, H. Griffin)

Experiments will be done in which plutonium and plutonium-uranium mixtures will be reacted with elemental fluorine. Any unreacted fluorine coming from the reactor must be trapped for disposal, since dilution with hood ventilation air is not permissible. Since a minimum of liquid is desired in the hoods, only solid reactants were considered. A survey indicated that limestone, soda-lime, alumina, carbon and a two-stage method involving sodium chloride followed by soda-lime have been used for trapping fluorine. The two-stage method was not considered because no outstanding advantages were noted. Although carbon has been used in large-scale applications, a potential explosion hazard exists due to possible formation of $(CF)_x$ compound. Since no comparative reaction data were found for the other solids, simple fixed-bed experiments were performed.

Grade F-1, four to eight-mesh activated alumina was obtained from the Aluminum Company of America. Four to eight-mesh soda-lime was supplied by Daigger and Company. Eight to twenty-mesh crushed limestone was obtained from Mississippi Lime Company. Fluorine was received from General Chemical Company in six-pound cylinders.

The solid reactant being tested was contained in a brass reactor, $1\frac{29}{32}$ inches in diameter and 12 inches long. Reaction temperatures were measured using four thermocouples tied to the outside wall of the reactor and evenly spaced axially. After the solid reactant had been loaded into the reactor, fluorine or a fluorine-nitrogen mixture was passed through the solid until fluorine could be detected in the exit gas with starch-iodide paper. The trapping capacity was considered to be the amount of fluorine entering the trap divided by the grams of solid originally placed in the reactor. The fluorine flow rate was calculated using the time interval over which a pressure drop occurred in a tank of known volume and assuming that the perfect gas law applied. Nitrogen, when used, was metered by a rotameter.

Alumina, dried soda-lime, undried soda-lime and limestone in decreasing order were effective in trapping fluorine. Fluorine was detected almost immediately when passed through approximately 700 grams of crushed limestone at a flow rate of 13 cc/min.

Soda-lime, dried overnight at 100 C was an effective reactant for fluorine (see Table 13). Undried soda-lime was unsatisfactory, not only because the capacity was low, but also because liquid was found in the inlet lines after the trap had cooled.

Table 13

CONDITIONS AND RESULTS OF REACTING FLUORINE WITH SODA-LIME

Trap Diameter: $1\frac{29}{32}$ inches
 Bed Height: As indicated
 Inlet Gas: 100 per cent fluorine at room temperature
 Sorbent: Daigger and Company, Soda-lime, 4 to 8 mesh

Run No.	Bed Material	Approximate Bed Height (in.)	Flow Rate (cc/min) ^a	Weight of Bed (g)	Capacity, Vol of Fluorine per Gram of Bed Material (cc/g)
1	Soda-lime as received	11.5	100	393	204
2	" " " "	7.5	100	263	52
3	" " " "	3.5	100	130	36
4	4 to 8-mesh soda-lime dried overnight at 100 C	8.5	100	230	197

^a At room temperature.

With undiluted fluorine the capacity of the alumina trap increased with increasing fluorine flow rates due to the higher temperature of the

alumina bed resulting from the heat of reaction. Increasingly higher maximum bed temperatures, 100, 160, and 800 C, were recorded for fluorine flow rates of 100, 300, and 1000 cc/min, respectively. In a single experiment (see Figure 25) it was demonstrated that heating the solid prior to and during the experiment increased the amount of fluorine that could be passed through the solid before fluorine was detected in the exit gas.

Dilution of fluorine with equal parts of nitrogen did not affect the capacity of the alumina. However, dilution with two parts nitrogen decreased the capacity. Capacities were 420 cc fluorine per gram alumina for no dilution and one part dilution and 371 for two parts dilution. Starting solid weight was 189 grams and the fluorine rate was 200 cc/min.

The fluorine appears to have reacted with the alumina, since attempts to desorb fluorine by heating plus vacuum pumping were unsuccessful. In one case, 189 grams of alumina after fluorination weighed

262 grams. This material was heated to 115 C and held at this temperature for four hours, followed by four hours at 300 C. A one gram loss in weight was recorded.

From the above capacity data the amount of fluorine that can be safely passed through the alumina reactant can be calculated. In addition, by means of an external thermocouple the movement of the reaction zone up the trap can be observed. The latter will serve as a check on the calculated capacity.

The fluorinated alumina, except in the 1000-cc/min experiment, was easily removed from the container. The 1000-cc/min experiment was performed only to demonstrate that a flow of fluorine five times that required during normal operations could be safely trapped.

4. Metal Fluorination Studies

(R. L. Jarry, W. H. Gunther, L. Seiden)

This program has as its objectives a study of the rates and mechanisms of the reactions of fluorine with various metals, such as nickel, uranium, zirconium and the nickel alloys. Information as to the extent of the fluorination reaction under varying conditions and the nature of the film formed is of interest to many current and projected processes. For example, the protective nature of the film formed on nickel is important for process equipment used to handle plutonium and uranium hexafluorides, and the direct fluorination of uranium metal is pertinent to reactor fuel processing. Although a considerable amount of information is already available on these reactions, it has been for the most part short-range work designed for specific problems. There has remained a need for a systematic study designed to obtain data over a wide range of conditions.

Calculation of the reaction rate as a function of temperature, time, pressure and surface conditions will be based on weight gain for adherent films and/or the weight loss following chemical or physical stripping of the fluoride films. To determine the mechanisms of the reactions, information derived by means of such techniques as X-ray and neutron diffraction, autoradiography, single-crystal work, film conduction and light and electron microscopy will be used.

The apparatus used for the fluorination of nickel consists of a nickel tube reactor, 2 inches in diameter, an associated nickel manifold, a source of fluorine, and a tube furnace and the necessary measuring and control devices.

The nickel specimens were coupons, 1 cm by 5 cm. Surface preparation was either by acid dipping in nitric acid containing a small amount of sodium chloride or by mechanically polishing with 600 grit.

Assays of the tank fluorine used in these experiments gave an average value of 98.1 volume per cent for the purity. The assays were made by reaction of a known volume of fluorine with mercury, followed by measurement of the residual pressure.

Coupons were weighed, placed in the tube reactor, which was then evacuated and heated. When the reactor and contents had reached the desired temperature, fluorine was admitted to a pressure of one atmosphere. The admission of the fluorine took several minutes, after which the reactor was closed with a valve for the static experiments, or the flow was adjusted to 50 ml/min for the dynamic experiments. Termination of an experiment was accomplished by rapidly evacuating the reactor after which the sample coupons were removed and reweighed.

Preliminary experiments have been conducted and the results are shown in Tables 14 to 18. The effects of variation in temperature, time of exposure, condition of surface, pretreatment with fluorine and static and flow conditions have been explored.

Table 14

FLUORINATION OF L-NICKEL: EFFECT OF
TEMPERATURE AND SURFACE PREPARATION

Flow: 50 ml/min
Time: 5 hr
Pressure: 1 atm

(The composition of "L" nickel in w/o is C 0.02;
Mn 0.26; Fe 0.23; Si 0.04; Cu 0.06.)

Temp (C)	Surface Preparation	Average Weight Gain (mg)	Film Thickness ($\text{\AA} \times 10^{-3}$)
500	acid dip	1.4 ± 0.1	6.9
500	polished	1.5 ± 0.1	7.8
600	acid dip	4.6 ± 0.1	25
600	polished	3.7 ± 0.1	19
700	acid dip	8.9 ± 0.4	47
700	polished	8.6 ± 0.5	42

Table 15

FLUORINATION OF L-NICKEL AT 700 C: EFFECT OF
TIME OF EXPOSURE AND SURFACE PREPARATION

Flow: 50 ml/min

Pressure: 1 atm

<u>Time (hr)</u>	<u>Preparation of Surface</u>	<u>Average Weight Gain (mg)</u>	<u>Film Thickness ($\text{\AA} \times 10^{-3}$)</u>
0.25	acid dip	3.8 ± 0.1	20
	polished	3.4 ± 0.1	18
0.50	acid dip	5.3 ± 0.6	28
	polished	4.0 ± 0.1	22
1.00	acid dip	8.1 ± 0.4	43
	polished	7.4 ± 0.4	39
4.00	acid dip	8.1	41
	polished	9.3	50
5.00	acid dip	8.9 ± 0.4	47
	polished	8.6 ± 0.5	42

Table 16

FLUORINATION OF L-NICKEL
UNDER STATIC CONDITIONS

Initial Pressure: 1 atm

<u>Time (hr)</u>	<u>Temp (C)</u>	<u>Surface Preparation</u>	<u>Average Weight Gain (mg)</u>	<u>Film Thickness ($\text{\AA} \times 10^{-3}$)</u>
5	500	acid dip	1.9 ± 0.2	10
5		polished	1.8 ± 0.0	9.1
17	500	acid dip	1.6 ± 0.1	8.4
		polished	1.9 ± 0.1	10
5	600	acid dip	3.3 ± 0.2	18
		polished	3.2 ± 0.2	17
17	600	acid dip	5.0 ± 0.1	28
		polished	5.1 ± 0.1	26

Table 17

COMPARISON OF THE FLUORINATION OF
"A" AND "L" NICKEL

Flow: 50 ml/min
Time: 5 hr
Pressure: 1 atm

Temp (C)	Type Nickel ^a	Surface Preparation	Average Weight Gain (mg)	Film Thickness (Å x 10 ⁻³)
500	L	acid dip	1.4 ± 0.1	6.9
	A	acid dip	2.1 ± 0.3	9.9
600	L	acid dip	4.6 ± 0.7	25.1
	A	acid dip	12.5 ± 1.2	61
700	L	acid dip	8.9 ± 0.4	47
		polished	8.6 ± 0.5	42
700	A	acid dip	113 ± 7	560 ^b
		polished	100 ± 3	500 ^b

^a The compositions of the "A" and "L" nickel used are as follows. "L" nickel contains, in w/o, C 0.02; Mn 0.26; Fe 0.23; Si 0.04; Cu 0.06. "A" nickel contains C 0.07; Mn 0.28; Fe 0.10; Si 0.08; Cu 0.05.

^b Calculated from weight loss of coupons after film had been completely removed.

Table 18

CALCULATED AND MEASURED FILM
THICKNESSES OF FLUORIDE FILMS
ON "L"-NICKEL

Temp: 700 C
Time: 64.5 hr
Flow: 50 ml/min
Pressure: 1 atm
Surface Prep: polish

Weight Gain (mg)	Film Thickness (Å x 10 ⁻³)	
	Calc	Measured
61.9	319	404
57.1	298	270

Calculations of film thicknesses from weight gain data were based on the assumptions of uniform density of the film and a value of 4.63 g/cc for the density of nickel fluoride (the crystal density). The following equation was used:

$$\text{Film Thickness } (\text{\AA}) = \frac{(\text{weight gain, g}) \left(\frac{\text{mole wt, NiF}_2}{\text{mole wt, F}_2} \right) (10^8 \text{ \AA/cm})}{(\text{coupon area, sq cm})(\text{crystal density NiF}_2 \text{ g/cc})}$$

Duplicate coupons of each type of surface preparation were used in these experiments. The weight gain data given in the tables are average values. In the cases where no deviation is indicated only one coupon was fluorinated.

Table 14 lists data over a range of temperatures for a constant exposure time, while Table 15 lists data for a range of exposure times at constant temperature. The data of these tables indicate that surface conditions are important.

From microscopic examination of the coupons before exposure, it appears that the acid-dipped samples have a greater surface area. Examination of the coupons after reaction showed a correspondingly greater surface roughness for the acid-dipped samples. This effect tended to diminish with increasing film thickness. Small areas of film spalling were noted at corners of the coupons having the thicker films.

Table 16 lists the results of static condition runs. Comparison of the static runs at five hours with those in Table 14 shows no large difference. There appears to be less effect due to surface preparation in these static runs. At 700 C under static conditions there was extensive film spalling and a weight change could not be obtained.

Comparative data for the fluorination of "L" and "A" nickel are shown in Table 17. The "A" nickel appears to react to a greater extent and film spalling was more pronounced. For the 700 C run with "A" nickel, large areas of the fluoride film had flaked from the metal and the remaining film was easily removed. The metal surface was bright and showed no trace of film. This could be interpreted to mean that the film had separated from the base metal during the cooling period. The weight of nickel reacted for these coupons was calculated from the weight loss data.

The calculation of film thickness by the use of weight gain data can be in error due to nonuniformity of the film, variation in density and other causes. To check the accuracy of the calculation, film thicknesses were obtained on two L-nickel coupons by microscopic examination. These coupons were run for a longer than usual period to insure a film

of sufficient thickness for mounting and sectioning. The results are shown in Table 18. The agreement between these values and their averages is good, considering the assumptions made in deriving them.

A few experiments were carried out using INOR-1 (a nickel-molybdenum alloy containing 15 to 20 weight per cent molybdenum) instead of nickel. This alloy has shown superior resistance to fluoride action in fused salt work. Tests were run to compare its passivation to the action of fluorine with that of nickel.

Several runs were made at 400 C under the same flow conditions as were used for the nickel tests. The weight gain of the INOR-1 averaged 0.5 mg/sq cm. This was greater by a factor of two than the corresponding value for nickel at 500 C. Therefore, it can be said that INOR-1 is less resistant to attack than nickel and presents no advantage as a material of construction for service with fluorine gas.

B. ADF Process Development for Enriched Uranium-Zirconium Fuel

The ADF process for zirconium-based fuels consists of dissolution in hydrofluoric acid containing an oxidant, conversion to dry granular solids in a fluid-bed dryer, and fluorination in a fluid-bed reactor to separate uranium hexafluoride. Development work on all steps of the process is being carried out on an engineering scale, and work on the fluorination step is also being performed on a laboratory scale.

1. Engineering-scale Studies (A. A. Jonke, N. Levitz)

a. Fluid-bed Drying (J. Barghusen, D. Raue, M. Jones)

Additional investigations of operating variables were performed in the six-inch fluid-bed dryer while preparing material for fluid-bed fluorination studies. Two different nozzle designs were evaluated in attempts to avoid the formation of nozzle agglomerates during the drying operation. Two hydrofluorination runs were made to pretreat fluid-bed dryer products prior to fluorination.

(1) Operating Conditions for the Six-inch Fluid-bed Dryer (See Table 19)

All of the runs were made at a bed temperature of 240 C. The feed solutions contained about 1.4 M zirconium, 0.012 M uranium as uranyl fluoride, and the requisite amounts of tin, nickel, chromium, and iron simulating the dissolution of a two weight per cent uranium-Zircaloy-2 alloy. Zircaloy-2 contains 1.5 per cent tin, 0.15 per cent iron,

0.10 per cent chromium, and 0.05 per cent nickel, the remainder being zirconium. Total fluoride concentrations of 6.3 M and 16 M were used. The higher concentration is being tested in an effort to reduce the formation of hydrated zirconium tetrafluoride and zirconyl fluoride. A previous run (see ANL-5924, page 66) using the high fluoride feed at 300 C gave a product consisting primarily of anhydrous zirconium tetrafluoride. The feed solutions were prepared by dissolving dryer products from previous runs in aqueous hydrofluoric acid at 80 C.

Table 19

SUMMARY OF RUNS MADE IN SIX-INCH FLUID-BED DRYER

Uranium Concentration in Feed	0.012 <u>M</u>
Zirconium Concentration in Feed	1.4 <u>M</u>
Fluoride to Zirconium Mole Ratio	4.5 and 11 (for ZCP-67 only)
Atomizing Gas Pressure	30 psig
Liquid Nozzle Diameter	0.040 inch
Bed Temperature	240 C

Run No.	No. of Nozzles	Feed Rate [ml/(min)(nozzle)]	Total Fluidizing Velocity (ft/sec)	Attrition Air Rate (cu ft/min)	Run Time (hr)
ZCP-62	2	70	1.0	2.0	3.7
ZCP-63	2	50	1.0	2.0	7 4
ZCP-64	1	55	1.0	2.0	3.2
ZCP-65	1	52	1.2	2.5	5.3
ZCP-66	1	55	1.2	2.5	3.3
ZCP-67	1	60	1.2	0.8	22.3

NOTE: The feed solution for Runs 62 to 66 was preheated to 55 C before being fed to the calciner.

The starting bed for each run was the final bed from the previous run. A high-velocity air jet directed into the fluidized bed was used to control the particle size. The total fluidizing velocity, expressed as the sum of the fluidizing and attrition air velocities, was maintained between 1.0 and 1.2 ft/sec at column conditions. Up to 25 per cent of the fluidizing gas was contributed by the attrition air jet.

Two different spray-nozzle designs were tested during these runs in an effort to discover the cause for and prevention of agglomerate formation on the nozzle. Runs ZCP-62 to 66 were made with a Spraying Systems Company nozzle which was mounted to project $\frac{1}{4}$ -inch from the vessel wall into the fluidized bed. This differed from the previous

mounting arrangement in which the nozzle face was flush with the inner wall of the vessel. The second nozzle variation, used in Run ZCP-67, involved a design in which the liquid nozzle portion of the two-fluid nozzle extended $\frac{3}{16}$ inch beyond the atomizing air annulus, which was mounted flush with the column wall.

(2) Operating Performance of the Fluid-bed Dryer

All of the runs except ZCP-67 were terminated prematurely due to either the formation of agglomerates on the nozzle or to a plug in the liquid feed line. The plug in the feed line was always found upstream from the nozzle and was undoubtedly caused by precipitation of solid material from the unstable feed solution. This instability has been observed only with feeds prepared by redissolution of certain dryer products and does not constitute a process problem for feed prepared by fuel element dissolution. The "wiping" action of fluidized particles on the surface of the air cap of the protruding nozzle did not keep the cap free from adhering material. Consequently, use of this nozzle mounting has been discontinued. The operation of the dryer during Run ZCP-67 (22.3 hours accumulated over four days) with the extended liquid nozzle was very encouraging, there being no indication of any agglomerate formation, either on the nozzle or in the bed. Use of this nozzle will be continued.

FIGURE 26
PARTICLE SIZE DISTRIBUTION DURING
FLUID-BED DRYER OPERATION

Due to the presence of agglomerates in Runs ZCP-62 to 66 no quantitative evaluation of the attrition jet with respect to particle size control could be made; however, on the basis of qualitative observations, the use of attrition air seemed to halt particle growth. During Run ZCP-67 the particle size distribution remained essentially constant (see Figure 26). Since the larger air annulus of the new nozzle required a much larger amount of atomizing air than that used in previous runs, and this excess air was effecting some attrition, only a small amount of auxiliary attrition jet air (0.8 cfm) was required in this run to control particle growth.

(3) Hydrofluorination of Fluid-bed Dryer Products

Since both oxygen and water, found in fluid-bed dryer products, have been suspected of inhibiting uranium removal during fluorination, the possibility of removing these species by a hydrofluorination prior to fluorination was investigated.

Two-kilogram quantities, each of 300 and 240 C dryer product, were hydrofluorinated at approximately 435 C in the three-inch-diameter Monel fluid-bed reactor. The operating conditions and results of the runs are presented in Table 20. The concentration of hydrogen fluoride in the fluidizing gas stream (primarily nitrogen at the start) was gradually increased during the first three hours. The remainder of the run was made with essentially 100 per cent anhydrous hydrogen fluoride.

Table 20

OPERATING CONDITIONS AND RESULTS OF HYDROFLUORINATION RUNS ON FLUID-BED DRYER PRODUCTS

Equipment	3-inch-diameter Monel reactor
Bed Weight	2 kilograms
Feed Material	300 C dryer product-ZCP-60 240 C dryer product-ZCP-66
Fluidizing Velocity	0.7 ft/sec at column conditions
Bed Temperature	435 C
Duration of Runs	5 hours
Amount of HF used	9.5 lb/run

Material	Chemical Analyses			Material Volatile at 450 C		
	Zirconium (%)	Fluoride (%)	Oxygen (%)	HF (%)	H ₂ O (%)	F/Zr Mol Ratio
Dryer product, ZCP-60	54.8	30.9	6.5	1.5	0.4	2.71
Same, after hydro- fluorination	49	41.3	1.70	3.6	0.11	4.05
Dryer product, ZCP-66	47	40.6	4.03	3.4	1.8	4.15
Same, after hydro- fluorination	46	43.4	1.03	3.3	0.43	4.53

There was a slight temperature rise when the hydrogen fluoride was introduced into the bed of 300 C dryer material from ZCP-60, indicating a chemical reaction, probably the conversion of zirconyl fluoride to the tetrafluoride, had occurred. No such indication was noticed with 240 C dryer product (ZCP-66), because in this case the change which occurred was primarily a dehydration of the zirconium tetrafluoride monohydrate.

The chemical analyses of the feed materials and products (see Table 20) indicate that the oxygen and water content of both 300 C and 240 C dryer products were significantly decreased during the hydrofluorination. The fluoride contents of both materials were increased; the greatest increase occurred with the 300 C dryer product. The high fluoride/zirconium mole ratio (4.53) for ZCP-66 may be due to sorption of hydrogen fluoride by the solid.

(4) Chemical Analysis of Fluid-bed Dryer Products

Results from X-ray analyses indicate that the material made in the fluid-bed dryer at 300 C (ZCP-60) with a feed solution containing a fluoride/zirconium mole ratio of 4.5 is a mixture of three zirconium fluoride species: zirconyl fluoride, anhydrous zirconium tetrafluoride, and zirconium tetrafluoride monohydrate. The major component is zirconyl fluoride. Zirconium oxide was not detected. Chemical analyses of the material show 30.9 per cent fluoride, 54.8 per cent zirconium, 6.5 per cent oxygen, and 1.9 per cent volatile material at 450 C. A possible composition calculated from the chemical analyses, and assuming only the species identified by X rays to be present, is 57 per cent zirconyl fluoride, 28 per cent anhydrous zirconium tetrafluoride, and 9 per cent zirconium tetrafluoride monohydrate. Operation of the dryer at 300 C with a feed solution containing a fluoride/zirconium mole ratio of 10 (instead of the normal 4.5) produced a product essentially free of zirconyl fluoride (see ANL-5924, page 66).

Chemical and X-ray analyses of 240 C dryer product (ZCP-66) indicate that the major fraction is anhydrous zirconium tetrafluoride. Monohydrated zirconium tetrafluoride, the only other species identified, is present as a minor constituent.

Several runs are planned to study the solid-vapor reaction between zirconium tetrafluoride and several concentrations of hydrogen fluoride and steam. The atmospheres will simulate those in the dryer when low and high hydrofluoric acid feeds are used. Additional testing of the new feed nozzle and the attrition jet are planned.

b. Recovery of Uranium from Uranium-Zirconium Mixtures by Fluorination in a Fluid-bed Reactor (E. Carls, G. J. Vogel, J. Wehrle, L. Marek)

Batch fluid-bed fluorinations were carried out in the $2\frac{1}{2}$ -inch-diameter reactor on uranium-zirconium powders prepared in the fluid-bed dryer at 240 C and 300 C. The majority of runs made this period are part of a statistical experiment designed to show possible interaction of operating variables on uranium removal.

A fluorine recycle pump and automatic gas bleed-off system were installed and are operating satisfactorily. This installation has substantially reduced the over-all fluorine consumption.

(1) Operating Conditions

FIGURE 27
STATISTICAL PLAN FOR SCHEDULED FLUORINATION RUNS

FLUORINATION TEMPERATURE	NO PRETREATMENT		450 C HYDROFLUORINATION		300 C FLUORINATION	
	240 C	300 C	240 C	300 C	240 C	300 C
600 C	B		C		C	B
525 C		C	C	A	A	
450 C	C	A		A		C

BLANK SPACES INDICATE THAT RUN IS LEFT OUT INITIALLY. THE LETTERS A,B,C INDICATE THE SAMPLING PROCEDURE TO BE FOLLOWED DURING FLUORINATION RUNS:

A 0 - 2 - 6 HOUR SAMPLES
B 0 - 3 - 6 HOUR SAMPLES
C 0 - 4 - 6 HOUR SAMPLES

The statistical experiment outlined in Figure 27 prescribes the operating temperature, type of feed (dryer temperature), feed pretreatment and sampling schedule to be followed for each run. The feed for these runs was prepared by extended running of the fluid-bed dryer to displace the starting bed material (refractory zirconium oxide) and thus eliminate this as one of the variables in the fluorination step. About 900 grams of material was used for each six-hour fluorination run, which was conducted at a temperature ranging between 450 and

600 C. The pretreatments (intended to eliminate the residual oxygen and water content of the dryer products and produce anhydrous zirconium tetrafluoride) involved either hydrofluorination at 450 C or fluorination at 300 C.

The fluorine concentration in the fluidizing gas stream (initially nitrogen) was increased from 0 to 100 per cent during the first two hours after the desired operating temperature was reached. The gas velocity was about 0.5 ft/sec at column conditions.

(2) Results and Discussion

The current statistical program requires 18 runs; however, the number of runs can be cut to 12 without affecting the reliability of the results, if the interaction among the variables is a predictable function. Twelve runs are planned at the outset and the others will be made later, if necessary. The results of the experiment are to be evaluated on the computer at the Data Processing Section of the Accounting Department. Preliminary results of the effect of individual operating variables on uranium removal are discussed below.

Fluorination Temperature (see Table 21)

The 300 C dryer product (with no pretreatment) showed a somewhat greater increase in uranium removal with temperature than the 240 C material. The effect may be related to the composition of these materials

which is described on page 88. In one experiment, more than 99 per cent uranium was removed from a caked portion of the bed, which reached a temperature of 675 C. Caking occurred in all of the experiments with 240 C dried material at a fluorination temperature of 600 C. Quantitative uranium removal at these extreme temperatures may be related to sublimation of the zirconium tetrafluoride, which has a vapor pressure of about 2.5 mm at 675 C. These conditions are too severe for existing metal equipment and means of protecting the metal wall from exposure to the high-temperature fluorine atmosphere are being considered.

Table 21

EFFECT OF FLUORINATION TEMPERATURE ON
URANIUM REMOVAL

Equipment		2½-inch-diameter fluorinator		
Inlet gas composition		100 per cent F ₂		
Gas velocity		0.5 ft/sec		
Run No.	Starting Material	Fluorination Temperature	Uranium Concentration	
			Initial (w/o)	Final (w/o)
31	300 C Dryer Product	450	1.0	0.58
33	300 C Dryer Product	525	1.0	0.18
35	240 C Dryer Product	450	0.8	0.34
36	240 C Dryer Product	600	0.8	0.25
34 ^a	240 C Dryer Product	675	0.8	0.008

^a Caked portion of bed.

Hydrofluorination Pretreatment

The hydrofluorination pretreatment (see Table 22) of material dried at 240 C had an apparent beneficial effect on uranium removal during fluorination, the removal going from 68 per cent without pretreatment to about 90 per cent with pretreatment under the same fluorination conditions (600 C). On the other hand, the same hydrofluorination treatment applied to material dried at 300 C had a deleterious effect on subsequent uranium removal during fluorination. Thus no firm conclusions can be reached from these experiments.

Duration of Fluorination (see Table 23)

The rate of removal of uranium is high during the initial period (first few hours) and tends to plateau as the run proceeds. This is true for material made at both drying temperatures (240 C and 300 C) and for

untreated or prehydrofluorinated material. The uranium concentrations in all samples were virtually the same within experimental error as that of the first sample from the run. Thus it appears possible that quantitative uranium removal may depend on rapid, high-temperature fluorination to separate the uranium hexafluoride in a short time.

Table 22

EFFECT OF HYDROFLUORINATION PRETREATMENT
PRIOR TO FLUORINATION ON URANIUM REMOVAL

Equipment		2½-inch-diameter fluorinator		
Gas composition		100 per cent F ₂		
Gas velocity		0.5 ft/sec		
Run duration		6 hours		
Run No.	Starting Material	Fluorination Temperature (C)	Uranium Concentration	
			Initial (w/o)	Final (w/o)
33	300 C Dryer Product	525	1.0	0.22
38	Same after hydro-fluorination	525	1.0	0.45
36	240 C Dryer Product	600	0.8	0.25
41	Same after hydro-fluorination	600	0.8	0.09
37	Same as Run 41	525	0.8	0.11

Table 23

EFFECT OF FLUORINATION PERIOD ON URANIUM REMOVAL

Equipment		2½-inch-diameter fluorinator			
Gas composition		100 per cent F ₂			
Gas velocity		0.5 ft/sec			
Run No.	Starting Material	Fluorination Temperature (C)	Time of Fluorination (hr)	Uranium Concentration	
				Initial (w/o)	Final (w/o)
33	300 C Dryer Product	525	6	1.0	0.22
			12	1.0	0.20
38	Same after hydro-fluorination	525	2	1.0	0.41
			4	1.0	0.34
			5	1.0	0.45
35	240 C Dryer Product	450	4.5	0.8	0.38
			6.0	0.8	0.34
36	240 C Dryer Product	600	4.0	0.8	0.23
			6.0	0.8	0.25
37	Same after hydro-fluorination	525	3.0	0.8	0.13
			5.0	0.8	0.11

Analysis of several size fractions are being made to determine the effect of particle size on uranium removal in this series of experiments.

(3) Future Studies

An early completion of the statistical series of experiments is planned, following which an alternate method of fluorinating the uranium will be tried. The powder will be screw fed into an inert fluidized bed maintained with a high fluorine concentration at a high temperature. It is hoped that the elimination of both the relatively long heat-up period and the reactions taking place initially in dilute fluorine atmospheres will prove advantageous. Methods of introducing heat directly into the bed (instead of through the metal walls) are being considered in the event temperatures in excess of 600 C are required. A replacement reactor of three-inch, schedule 80, "A" nickel pipe will be fabricated.

2. Laboratory Studies (J. Fischer)

a. Fluorination of Calcined, High Zirconium Content, Fuel Solutions (C. Johnson, J. Stockbar)

The laboratory group is making a systematic study of the variables involved in uranium removal from calcined solutions of uranium-zirconium alloys. This is part of the research program aimed at the development of the Aqueous Dissolution Fluorination Process. The experimental procedure is as follows: about 15 grams of calcined material is weighed into a tared nickel boat (0.8 x 4 x 0.2 inches), which is placed in a one-inch nickel tube furnace. Helium is allowed to pass over the sample while the furnace is brought to temperature. Fluorine is then passed over the sample and any uranium hexafluoride that is formed is condensed from the gas stream in a cold trap. Uranium analyses* are obtained on the initial and final residues in the boat.

Two types of samples have been used in these experiments. The first, given the code designation L, is obtained by converting to solids a zirconium fluoride solution containing about 0.012 M uranium. This was accomplished by feeding the solution dropwise into a Monel beaker heated on a hot plate at a temperature of about 300 C. The resulting solids were ground in a mortar before fluorination. The other type of sample used was obtained from the pilot plant group. Because of the varied complexity of the pilot plant drier products, their make-up and history are summarized in Table 24.

*Uranium analysis by X-ray spectrochemical method.

Table 24

SUMMARY OF CONDITIONS USED FOR PREPARATION OF VARIOUS MATERIALS IN PILOT PLANTS

Run No.	Bed Temp ^a (C)	Starting Bed Material	Feed Composition		Feed Preparation	Total Run Time (hr)	Uranium Concentration (w/o alloy equiv)	Remarks
			Zr (M)	F (M)				
ZCP-38	300	CaF ₂	1.5	6.8	Dissolve UO ₂ F ₂ and ZrF ₄ in aq HF at 75 C. Add SnCl ₂ to reduce U ⁺⁶ to U ⁺⁴ .	70	3.5	During spray drying an HF side stream boosted F/Zr mole ratio to 10.
ZCP-44	240	ZrO ₂ pre-coated with ZrF ₄	1.4	6.6	Dissolve UO ₂ F ₂ and ZrF ₄ in aq HF at 75 C. 1% SnF ₄ added.	8	5.0	----
ZCP-47	300	CaF ₂	1.4	6.5	Dissolve UO ₂ F ₂ and ZrF ₄ in aq HF at 75 C. 1% SnF ₄ added.	11	5.0	Bed material only thinly coated with uranium.
ZCP-50	300	ZrO ₂ pre-coated with ZrF ₄	1.5	6.5	Feed soln from General Chemical Company.	40	5.0	----
ZCP-59	300	ZrO ₂	1.4	6.5	Dissolve UO ₂ F ₂ and ZrF ₄ in aq HF at 75 C. 1.5% Sn ⁺⁴ and small amounts Ni, Cr, Fe added.	60	2.0	----
ZCP-60	300	ZCP-59 final bed	1.4	6.5	Feed soln from General Chemical Company	12	2.0	Jet attrition used to reduce particle size (total run - 72 hr)
ZCP-66	240	ZCP-60 final bed	1.4	6.4	Dissolved 300 C drier products in proper amount of aqueous HF.	51	2.0	Solids separated from feed at room temperature. Feed temperature, 55 C

^a Temperature of fluid bed during calcination.

Results from experiments on the effect of particle size on uranium removal are given in Table 25. For material ZCP-44 the per cent uranium removed increased markedly as particle size decreased. The L-materials showed essentially the same uranium removal regardless of the particle size. This probably occurs because this material was a more "homogeneously" dried material, with the uranium being equally distributed throughout the zirconium salt matrix.

Table 25

EFFECT OF PARTICLE SIZE ON URANIUM REMOVAL

	Reactor Temp:		600 C	
	Time for Run:		2 hr	
	Fluorine Flow Rate:		11 g/hr	
	Uranium Concentration (w/o)		Particle Size	Uranium Removed
<u>Material</u>	<u>Initial</u>	<u>Final</u>	<u>(μ)</u>	<u>(%)</u>
ZCP-44	1.47	0.16	420 to 840	89.3
ZCP-44	1.82	0.27	250 to 420	85.2
ZCP-44	2.15	0.23	177 to 250	89.3
ZCP-44	2.44	0.13	149	94.6
ZCP-47	0.53	0.015	250 to 420	97
ZCP-47	0.76	0.016	150 to 149	98
ZCP-47	0.84	0.037	62 to 105	95.7
L-1	1.10	0.12	All sizes	89.1
L-1	1.13	0.12	250 to 420	89.4
L-1	1.30	0.106	105 to 149	90.9
L-2	1.16	0.075	177 to 250	93.5

In recent work at Brookhaven¹⁵ on the removal of protactinium from thorium fluoride, inert metals were added to induce defects in the thorium matrix so as to facilitate uranium removal. A somewhat similar technique has been applied here, more importance being placed on the fluorinating ability of the metal additive. It was hoped that the added metal fluoride would serve not only to induce defects in the zirconium matrix, but also would act as an internal fluorinating agent or catalyst. The metal fluorides were added to the feed solution before drying; concentrations of the metals were equal to that of the uranium in weight per cent.

¹⁵Miles, F. T., Heus, R. J., and Wiswall, R. H., "Removal of Protactinium from Solid Thorium Fluoride," BNL-482, (November 1954).

Results of these experiments are shown in Table 26. In general, the additives do not appear to have appreciably affected the removal of uranium. The one exception to this is the lead-containing material, but here corrosion of the nickel boat was so severe that its use appears impractical.

Results of the effect of temperature on uranium removal are given in Table 27. It appears that a temperature of 650 C is needed for complete uranium removal. Solid ZCP-66 is an exception to this, for it gave poor uranium removal at all temperatures. The solids ZCP-59 and ZCP-60 show excellent uranium removal. The fluorinated solids were lower in uranium content than the lowest concentration standard used by the X-ray spectral group.

X-ray diffraction analyses indicate that the materials ZCP-59 and ZCP-60 have zirconyl fluoride as the major species present, with zirconium tetrafluoride and zirconium tetrafluoride monohydrate being there in minor amounts. ZCP-66 was shown to have zirconium tetrafluoride as the major species present, with zirconium tetrafluoride monohydrate being there in a minor amount. Analytical results, shown in Table 20, indicate that ZCP-66 has a larger amount of water than previous drier products. The possibility exists that the presence of this larger amount of water may act to inhibit uranium removal.

Experiments have tested the effect of time on uranium removal (see Table 28). In all cases a plateau was reached beyond which additional uranium was not removed. At higher temperatures greater amounts of uranium were removed, but the plateau effect was still present.

Mixtures of calcium fluoride-uranium tetrafluoride and calcium fluoride-uranyl fluoride were prepared to test uranium removal from mixed solids. These materials were mixed in a ball mill, screened and then mechanically tumbled. Total mixing time was about eight hours. The solids were then fluorinated in a boat in the conventional manner. Data from experiments on the effect of temperature on uranium removal are given in Table 29. These data indicate that at higher temperatures some of the uranium appears to be "unavailable" for fluorination. Attempts at verification of complex formation, uranium hexafluoride or solid-solid interaction are planned.

C. Zirconium-matrix Fused Salt Process Development (W. J. Mechem, A. A. Jonke)

In the fused salt fluoride volatility process for the recovery of uranium from zirconium-matrix fuels, the alloy is dissolved in the fused salt at 600 C with a hydrogen fluoride sparge and then the uranium is

Table 26

EFFECT OF ADDITIVES ON URANIUM REMOVAL

Reactor Temp:		600 C		
Time for Run:		2 hr		
Fluorine Flow Rate:		11 g/hr		
Material	Uranium Concentration (w/o)		Additive	Uranium Removed (%)
	Initial	Final		
L-1	1.10	0.12	--	89.1
L-1	1.11	0.09	Co ⁺⁺ a	92.0
L-1	1.07	0.04	Pb ⁺⁺ a	96.3
L-2	1.16	0.075	--	93.5
L-2	1.14	0.070	Sn ⁺⁺ a	93.8

a Weight per cent of added metal approximately equal to the initial uranium concentration.

Table 27

EFFECT OF TEMPERATURE ON
URANIUM REMOVAL

Time for Run: 2 hr
Fluorine Flow Rate: 12 g/hr

Material	Uranium Concentration (w/o)		Temp (C)	Uranium Removed (%)
	Initial	Final		
ZCP-38	1.69	1.42	450	16.0
ZCP-38	1.69	0.27	600	84.0
ZCP-47	0.63	0.086	450	86.3
ZCP-47	0.63	0.027	600	95.7
ZCP-50	2.60	0.39	450	84.0
ZCP-50	2.60	0.033	600	98.7
ZCP-50	2.60	0.014	650	99.5
ZCP-59	0.76	0.64	300	15.7
ZCP-59	0.76	0.54	400	29.0
ZCP-59	0.76	0.30	500	60.5
ZCP-59	0.76	0.069	600	90.9
ZCP-59	0.76	<0.008	650	>99.2
ZCP-60	1.02	0.92	300	10.0
ZCP-60	1.02	0.50	450	51.0
ZCP-60	1.02	0.28	525	72.6
ZCP-60	1.02	0.048	600	95.3
ZCP-60	1.02	<0.008	650	>99.2
ZCP-66	0.77	0.59	300	23.4
ZCP-66	0.77	0.55	400	29.6
ZCP-66	0.77	0.47	500	38.8
ZCP-66	0.77	0.37	600	49.4

Table 28

EFFECT OF TIME ON URANIUM REMOVAL

Fluorine Flow Rate: 12 g/hr

Material	Uranium Concentration (w/o)		Time (hr)	Temp (C)	Uranium Removed (%)
	Initial	Final			
ZCP-44 ^a	1.39	1.02	1.0	450	26.7
ZCP-44 ^a	1.39	0.73	2.0	450	47.5
ZCP-44 ^a	1.39	0.74	3.0	450	46.7
ZCP-44 ^a	1.82	0.98	5.0	450	46.2
ZCP-59	0.76	0.705	1.0	300	7.2
ZCP-59	0.76	0.64	2.0	300	15.7
ZCP-59	0.76	0.66	3.0	300	13.1
ZCP-59	0.76	0.66	4.0	300	13.1
ZCP-60	1.02	0.85	1.0	525	16.8
ZCP-60	1.02	0.28	2.0	525	72.6
ZCP-60	1.02	0.30	4.0	525	70.4
ZCP-60	1.02	0.21	6.0	525	79.4
ZCP-60 ^a	1.02	0.27	2.0	525	73.6
ZCP-60 ^a	1.02	0.20	6.0	525	80.4

^a 50% fluorine was used for these experiments;
approximately 6 g/hr, diluted with nitrogen.

Table 29

URANIUM REMOVAL FROM CALCIUM-URANIUM
MIXTURES

Time for Run: 2 hr
Fluorine Flow Rate: 12 g/hr

Material	Uranium Concentration (w/o)		Temp (C)	Uranium Removed (%)
	Initial	Final		
CaF ₂ - UF ₄	0.96	0.0052	450	99.5
CaF ₂ - UF ₄	0.96	0.011	525	98.8
CaF ₂ - UF ₄	0.96	0.035	600	96.4
CaF ₂ - UO ₂ F ₂	0.92	0.0072	450	99.3
CaF ₂ - UO ₂ F ₂	0.92	0.033	525	96.4
CaF ₂ - UO ₂ F ₂	0.92	0.057	600	93.8

volatilized as the hexafluoride in a fluorine sparge. Because this fused salt process environment is corrosive to metals, equipment is being developed to avoid salt-metal contact.

1. Graphite-dissolver Tests

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

After completing the installation of the graphite dissolver-hydrofluorinator, one shakedown run was made with a dummy fuel element. Operations of salt transfer, fuel element charging, and hydrogen fluoride sparging were carried out. Several minor additions and modifications were called for on the basis of this test. The only major alteration was the replacement of the top portion of the graphite pipe which carried sparge gas from the dissolver head to the gas distributor plate. This graphite pipe broke off at the upper threaded connection, thus forming an internal leak preventing normal contact of the salt and fuel element with the sparge gas. The break was apparently due to seizing of a slip joint designed to relieve tensile stresses arising from temperature changes. An improved connection will be made and the dissolution runs will be continued.

Measurement of heat losses from the dissolver at 600 C were made. The results given in Table 30 show that about 70 per cent of the heat was lost through the water-cooled top (including process lines, etc.) and 30 per cent was lost through the sides and bottom.

Table 30

HEAT LOSSES FROM GRAPHITE DISSOLVER

Conditions: empty (no metal and no molten salt), no gas flow, 20 psia inert gas pressure

Temperature: 600 C at 24 inches from bottom
567 C at 48 inches from bottom

<u>Electrical Power Input:</u>	<u>kw</u>	<u>% Power</u>
24.3 v, 482 a	11.7	100.0

Heat Output

Upper body flange	2.74	23.2
Head Flange	2.37	20.1
Packing Glands ^a	0.23	1.1
Heaters (two)	3.08	26.1
Sides and Bottom ^b	3.3	29.5

^a For thermowell, electrodes, and sparge line.

^b Values for sides and bottom were obtained by difference; other values obtained by cooling water temperature measurements.

The inner graphite crucible is composed of $1\frac{1}{2}$ -inch thick slabs and is surrounded by $1\frac{1}{2}$ inches of lampblack packed to a density of 55 lb/cu ft and contained in a nickel shell. The outside temperature of this metal shell measured at several points was 150 ± 25 C during the 33-hour run. Cooling was by natural air convection only. The melting point of the salt was 500 to 550 C. Calculation of the average thermal conductivity of the lampblack layer from over-all temperature and heat loss data yielded a value close to the initial value for the lampblack, viz., 0.075 Btu/(hr)(sq ft)(F)/(ft). This result indicates that no major penetration of salt into the lampblack has occurred in operations thus far.

Monitoring of the dissolution was carried out by measurement (by difference) of the hydrogen fluoride consumed and by measurement of the hydrogen produced by the reaction. The hydrogen fluoride was measured by remote-reading weigh tanks, one serving as a boiler and the other as a condensate receiver. The hydrogen evolution was determined by measurement of the total noncondensable gas evolved by a wet-test meter and by measurement of the concentration of hydrogen by a thermal conductivity cell. Argon was used as the purge and diluent gas. The determination of zirconium dissolved was lower for the hydrogen measurement by about a factor of two, 9.5 lb as compared to 20.5 lb from the hydrogen fluoride measurement. The reason for this discrepancy will be investigated further.

2. Frozen-wall Fluorinator Development (J. D. Gabor, R. W. Kessie, W. J. Mecham)

In order to provide long process life for a fused salt fluorinator, vessel designs employing frozen salt walls have been developed. In this scheme internal heating is provided, and a layer of solid salt is maintained on the cooled inner wall of the container. Both electrolytic and induction heating of the fused salt are feasible, but only the former method

is currently being developed. A pilot plant fluorinator vessel using electrolytic heating is ready for testing. A schematic of the vessel is shown in Figure 28. Power is brought into the bottom of the electrodes to minimize the shorting-out effect of salt at the surface and thereby allow heat to be introduced more uniformly throughout the salt volume. Thermowells, a sparge line, and resistance heaters for startup are also contained in the well of each heater.

FIGURE 28
MARK II ELECTRODE DESIGN
ELECTROLYTICALLY HEATED FROZEN-WALL FLUORINATOR

3. Dropwise Fluorination (J. D. Gabor, R. Peterson*)

A series of tests have been made to examine the feasibility of dropwise fluorination as a means of contacting fused salt (bearing uranium) with fluorine. In this scheme, molten salt is sprayed into a fluorine atmosphere. The salt is allowed to solidify before contacting the walls of the container and the uranium hexafluoride formed is recovered from the gas phase.

In a series of six tests at three different temperatures, the uranium removal was found to depend strongly on droplet size and less strongly on fluorine temperature. Small droplets and high temperatures favor better uranium removal. The maximum uranium removed was 29 per cent with a fluorine temperature of 200 C. Two additional runs made with a highly purified and prefluorinated salt did not show substantially higher uranium removals under the same conditions.

Equipment and Procedure

The fused salt was sprayed into the top of a vessel approximately three feet in diameter and four feet high. The vessel was heated by tubular electrical resistance heaters on the outside. The vessel used in these tests was stainless steel, which fact limited the maximum temperature of the fluorine atmosphere to 200 C. A nickel or Monel vessel could be used for higher temperatures.

The salt was melted in a small nickel vessel attached directly to a Monel spray nozzle, and this unit was mounted on top of the larger vessel containing fluorine at one atmosphere. The nozzle was a single-fluid hollow cone nozzle, Spraying Systems Company 1/4 LN3.

The sodium fluoride-zirconium fluoride salt mixture containing one weight per cent uranium tetrafluoride was melted and sparged with helium. The salt temperature was raised to nearly 800 C and sprayed under a head of 50 psig of helium. When the spraying was completed, the vessel was cooled and purged with nitrogen. The solidified salt particles collected on a nickel tray in the vessel were removed and screened into fractions. Analyses were made of the uranium content of the salt before and after spraying by measuring X-ray fluorescence intensity of the uranium.

*Student Aide from Northwestern University.

Results of the First Six Runs

In this series a 40 mol per cent zirconium tetrafluoride-60 mol per cent sodium fluoride was used. It was supplied by the General Chemical Company and contained less than 2000 ppm metal impurities other than alkali metals. Major impurities in the salt as received were potassium (about one atom per cent) and oxygen (equivalent to about five per cent of the zirconium as zirconium dioxide). This salt was melted and given a $\frac{1}{2}$ -hour sparge pretreatment with hydrogen fluoride before spraying. The results of these runs are given in Table 31.

Table 31

RESULTS OF DROP FLUORINATION RUNS

Salt Composition: Approx 40 m/o ZrF_4 - 60 m/o NaF
with one w/o UF_4 added.

Conditions	Mean Drop Diam of Fraction (microns)	Spray Parameters				Measured Per Cent U Removed		
		Y avg ^a	$\frac{hd^b}{K}$	h^c	Cooling Time (sec)	1	2	Avg
Gas temp 200 C (T_s)	62.13	7.70	2.00	154	0.037	11.8	9.8	10.8
mp 505 C (T_2)	118.2	7.57	2.13	86.3	0.13	8.5	8.7	8.6
Salt temp 765 C (T_1)	157.7	8.57	2.71	82.5	0.18	6.9	7.5	7.2
	215.2	9.83	3.56	79.0	0.25	6.7	5.7	6.2
	307.9	11.5	4.84	75.0	0.38	6.7	3.8	5.3
Gas temp 100 C (T_s)	62.13	6.96	2.00	187	0.036	16.4	26.4	21.4
mp 505 C (T_2)	118.2	7.02	2.00	98.2	0.13	12.9	18.5	15.7
Salt temp 765 C (T_1)	157.7	7.13	2.00	73.4	0.23	9.4	14.8	12.2
	215.2	7.74	2.24	60.5	0.39	5.7	10.9	8.3
	307.9	10.2	3.28	61.8	0.54	2.3	8.3	5.3
Gas temp 200 C (T_s)	62.13	6.22	2.00	224	0.039	21.0	29.3	25.2
mp 505 C (T_2)	118.2	6.20	2.00	118	0.14	7.6	15.0	11.3
Salt temp 765 C (T_1)	157.7	6.25	2.00	86.2	0.26	5.7	10.7	8.2
	215.2	6.73	2.00	64.8	0.47	3.9	8.5	6.2
	307.9	8.98	2.25	51.0	0.85	2.0	3.1	2.6
Purified	62.13	6.22	2.00	224	0.038	18.7	11.7	-
Salt	118.2	6.20	2.00	118	0.14	18.6	5.8	-
Gas temp 200 C (T_s)	157.7	6.40	2.00	86.2	0.25	29.3	8.2	-
mp 523 C (T_2)	215.2	6.78	2.00	64.8	0.46	25.7	-	-
Salt temp 800 C (T_1)	307.9	9.03	2.25	51.0	0.83	24.4	-	-

^a Mean droplet velocity, ft/sec.

^b Nusselt number, dimensionless.

^c Heat transfer coefficient, Btu/(hr)(sq ft)(F).

The uranium removal was higher for smaller drop sizes and also higher for higher temperatures of fluorine gas. Under the most favorable conditions tested, 62-micron diameter drops and 200 C fluorine temperature, the average removal (two runs) was 25 per cent.

Results of Prefluorination Runs

Two runs were made with the fluorine temperature at 200 C and a fluorine sparge pretreatment of the salt. The fluorine was sparged at one bubble per second for a half hour. After the fluorine sparge, uranium tetrafluoride was added to the molten salt and mixed with a helium sparge. High-purity salt made by the Kawecky Chemical Company and containing only 1 ppm oxygen was used. The salt composition was 44.2 mol per cent zirconium tetrafluoride-55.8 mol per cent sodium fluoride, and the melting point was 523 C.

In the first fluorine pretreatment run with the high-purity salt, a maximum uranium removal of 29.3 per cent was indicated, which is the same maximum value as that for the previous hydrogen fluoride-pretreated salt at the same temperature. However, unlike the previous runs, the per cent removal was about the same for various drop sizes. This behavior is consistent with the condition of kinetics as the rate-controlling step. The absence of impurities might be used to account for better uranium removal in the larger droplet sizes, but the fact that no fraction showed maximum removal higher than in the previous runs leaves the issue somewhat in doubt as to the over-all effect of impurities at this level.

The second fluorine pretreatment run failed to duplicate the first, as can be seen from Table 31. These differences may have been associated with operating difficulties encountered in these last two runs, particularly with respect to satisfactory operation of the spray nozzle. This problem did not appear in the first series of six runs.

Spray Parameters

Also shown in Table 31 are the spray parameters: (1) mean droplet velocity, (2) drop-to-gas heat transfer coefficient, and (3) cooling time for complete solidification of the droplets from their original high temperatures. Calculations of these parameters were made from the Nusselt equation for heat transfer from spheres. (In the previous quarterly report (ANL-5996, page 168) experimental data were given showing the applicability of this equation.) Velocities were obtained by integration of the frictional drag equation for spheres. These calculations show the short time available for liquid phase reaction of the salt phase with fluorine before solidification, but no correlation with uranium removal was found.

Mechanism of Uranium Removal

In general the uranium removal process involves

- (1) liquid diffusion of dissolved uranium tetrafluoride to the surface of the drop,
- (2) chemical reaction of fluorine with the tetrafluoride at the drop surface, and
- (3) gas-film diffusion of uranium hexafluoride from the surface.

Assuming one of these three operations is the rate-controlling step, the extent of uranium removal in the processes is the product of the rate of this controlling step and the drop-solidification time. Since the time factor depends inversely on the heat transfer rate, the effect of drop size tends to cancel out for all mechanisms except liquid diffusion. In the case that liquid diffusion is controlling, the extent of removal would be expected to be inversely proportional to drop size.

Predicted values of uranium removed were calculated as follows:

- (1) The gas diffusion rates were calculated from standard correlations of K_G and diffusivity.^{16,17} The diffusivity used was 0.07 sq cm/sec (20 C).
- (2) The uranium tetrafluoride liquid diffusion rate was calculated using the standard unsteady-state diffusion equations for spheres. The diffusion coefficient used was 6.5×10^{-5} sq cm/sec. This value was based on a limited amount of experimental data and is regarded as correct with respect to order of magnitude.

The calculations showed that uranium removal for all of the experimental runs would be 100 per cent if gas-film resistance was controlling, and between 85 and 96 per cent if the uranium tetrafluoride diffusion in the liquid was the controlling step.

Since the actual removals were less than those predicted if mass transfer were controlling, this is considered to be an indication that the overall process is complex and probably controlled by chemical kinetics.

¹⁶ Sherwood, T. K., and Pigford, R. L., Absorption and Extraction, McGraw-Hill Book Company (1952).

¹⁷ Reid, R. C. and Sherwood, T. K., Properties of Gases and Liquids, McGraw-Hill, New York (1958).

Empirical Correlation of Data

In an attempt to form an empirical correlation of these data for purposes of process design, a least-squares analysis of the data was made. In Figure 29 the results are plotted as the per cent uranium removed vs the parameter $1/r \ln [(T_1 - T_S)/(T_2 - T_S)]$ and in Figure 30 for $\ln C_0/C$ vs the same parameter. This parameter combines the effect of drop size (r = radius in microns) and time for the drop to cool from its initial high temperature, T_1 , to its melting point, $T_2 = T_{mp}$. The constant temperature of the fluorine gas environment is given by T_S . The time effect is thus represented by a log mean temperature difference.

FIGURE 29
CORRELATION OF DROP FLUORINATION DATA

FIGURE 30
CORRELATION OF DROP FLUORINATION DATA

While both correlations fit the data about equally well, there is a theoretical preference for the representation of the uranium removal, in terms of the ratio of initial to final uranium concentration, C_0/C , since concentrations would be expected to be the driving forces in kinetic or diffusion operations. The concentration ratio is also the more conservative parameter for design purposes, since it involves an asymptotic approach to complete removal of uranium.

FIGURE 31
DESIGN PARAMETERS - DROPWISE FLUORINATION

small, a longer tower is required. The column height in the figure is calculated for the case of $r = 50$ microns; for the case of $r = 25$ microns, the equivalent minimum height is about 42 per cent that shown.

From this figure it appears that impractically high towers are required for uranium removals of as high as 95 per cent in a single pass. If four passes were used, each with a 10-foot tower, the removal in each pass for a 100-micron-diameter drop would be 67 per cent. The uranium remaining after four passes is then given by $C_4 = (0.33)^4 C_0 = 0.012 C_0$, or 1 per cent remaining. The removal is thus 99 per cent. Temperature control to within 5 C of the salt melting point is required for each stage, as well as salt nozzles delivering 100 per cent of the spray drops of less than 100 microns in diameter. For such a process to work, adequate means of recycle of fluorine and salt are also required. The fluorine system would require pumps and uranium hexafluoride cold traps. The solid separation and transfer system would require cyclones and filters. While these steps are technically feasible, it appears that the process might be more complicated than a fused salt sparge system because of the multistage operation.

No further work on the dropwise fluorination scheme is planned.

D. Calcination of Reactor Fuel Processing Wastes

(L. J. Anastasia, J. W. Loeding, A. A. Jonke, C. Schoffstoll, L. J. Marek)

A heated, fluidized-bed technique is used for the calcination of aqueous wastes resulting from certain solvent extraction processes. Spray injection of the liquid wastes into the fluidized bed results in their conversion to a free-flowing granular solid reduced substantially in volume. The past quarter was spent in the calcination of synthetic Purex low-acid waste.

1. Calcination of Synthetic Purex Process Wastes

The feasibility studies on the calcination of synthetic Purex wastes were successful in providing a free-flowing granular solid. The product had a bulk density of 1.35 g/cc (untapped) and of 1.55 g/cc (tapped), and had been

Process Application

For purposes of design-evaluation a plot has been made of per cent removal of uranium as a function of the temperature of the surroundings, T_S (see Figure 31). Since, to prevent fused salt from contacting the wall, T_S must be always less than T_{mp} , the length of the tower must then be sufficient to allow the drop to fall freely for a long enough time to cool to the solidification point. Where the temperature difference $T_2 - T_S$ is

reduced in volume by a factor of 4.7. Nominal operating conditions were determined during the feasibility studies performed earlier. A bed temperature of 500 C, a fluidizing air rate of about 1.4 ft/sec, an atomizing air rate of 0.72 cfm and a feed rate of about 80 ml/min were selected as the most satisfactory operating conditions. The automatic blowback of the off-gas filters has been established at a frequency of one fractional second burst of compressed air each 90 sec. Recent emphasis has been directed to processing the low-acid wastes which results from treatment of high-acid wastes with formaldehyde before storage. The compositions of these waste solutions were given in ANL-5996, Table 27.

Under these conditions, some 20 runs of varying duration (i.e., 4 hours to 14 hours) were made to develop a suitable operating technique and to provide calcined material for study by Hanford personnel.

2. Results of Waste Calcination Runs

Screen analyses of the product from the runs indicate a particle size distribution of essentially 20 to 50 mesh. By using the final bed from one run as the starting bed for the next run, it was determined that in approximately 16 hours of operation, the -20, +40 mesh fraction accounted for 80 to 95 per cent of the product, the -40, +50 mesh fraction accounting for most of the remainder. Although this particle size is suitable for calciner operation, sieve analyses of samples taken during the run indicate that particle growth would continue with longer operation. While on a percentage basis the amount of +20 mesh particles were small (~5 per cent average), they were nevertheless troublesome, as they were comprised almost entirely of small aggregates about $\frac{3}{16}$ in. in diameter.

Because it was known from previous experience (with aluminum oxide beds) and again observed with this calcine that a high-velocity air jet would cause attrition, several runs were made with attrition air introduced through a nozzle in an effort to break up the aggregate particles. Results thus far have not been entirely successful, but the use of larger amounts of attrition air will be investigated in subsequent runs.

In addition to the small aggregates mentioned above, occasional larger lumps have been formed at the spray nozzle. In an effort to avoid formation of these agglomerates, alternate spray nozzle designs are being tested. The most recent calciner runs have been made with a conical nozzle (60° cone tip) which extends into the bed about $\frac{3}{8}$ in. Previously used nozzles had a flat face and were flush with the inner wall of the calciner. Use of a conical nozzle resulted in smooth operation, but nozzle lumps were observed after five or six hours of operation. Other nozzles are being designed and will be tried.

Upon standing for short periods the Purex low-acid feed crystallized and precipitated to a large extent. A technique was evolved whereby a stock solution containing all constituents but sodium sulfate was prepared. This solution proved to be sufficiently stable for extended storage. The addition of sodium sulfate was made immediately preceding the synthetic feed use. Prepared in this manner the feed remained stable for periods up to two weeks.

Because these wastes contain larger amounts of sulfate ion, some concern was felt that the stainless steel equipment might be subjected to undue corrosion caused by the presence of sulfur compounds in the off-gas. Laboratory-scale experiments were performed to determine whether sulfur is present in the off-gas resulting from calcination of low-acid feed. The gases were passed into a six per cent hydrogen peroxide solution to which barium nitrate was added. These tests qualitatively indicated the presence of some sulfur dioxide or sulfur trioxide at feed sulfate concentrations of 1.5 to 2.0 M. However, full-scale calciner experiments at 1.5 M sulfate showed only 35 ppm sulfate in the off-gas condensate. No corrosion of off-gas or condensed off-gas piping has been observed.

E. Conversion of Uranium Hexafluoride to Uranium Dioxide in Fluidized Beds

(I. E. Knudsen, N. M. Levitz, A. A. Jonke, R. Finley)

Preliminary tests of a one-step, continuous, fluid-bed process for the conversion of uranium hexafluoride to uranium dioxide were completed. Hydrogen and steam were used for simultaneous reduction and pyrohydrolysis reactions carried out at 600 C, resulting in the formation of a dense coating on the starting bed of uranium dioxide. The tests were made in a $1\frac{1}{2}$ -inch-diameter Monel column; scale-up of operations to a 3-inch-diameter column is planned for further study of operating variables. The primary objective is a process for the preparation of reactor-grade uranium dioxide, but these studies should also be useful for a process to recover fluoride from stored, depleted uranium hexafluoride.

1. Operating Conditions

The tests were all made at 600 C with steam and hydrogen in a 2/1 mole ratio as the fluidizing gases; the superficial gas velocity at column conditions was increased from 0.5 to 0.75 ft/sec as denser oxide and larger particles were produced. Uranium hexafluoride feed rates ranged from 5.2 to 10.9 g/min. The flow was metered manually with a needle valve, using a thermal flow meter to indicate the flow rate. The uranium hexafluoride inlet orifice was an open $\frac{1}{4}$ -inch OD tube. Runs of $2\frac{1}{2}$ to $4\frac{3}{4}$ -hour duration were made with steam and hydrogen excess ranging from 230 to 600 per cent. Operating conditions and analytical results are summarized in Table 32; analytical results for earlier runs (ANL-5996, pages 187 to 188) are also included.

Table 32

SUMMARY OF OPERATING CONDITIONS AND RESULTS OF
FLUID-BED CONVERSION OF URANIUM HEXAFLUORIDE
TO URANIUM DIOXIDE

Equipment: $1\frac{1}{2}$ -inch-diameter Monel column
 Bed Temperature: 575 - 625 C
 Fluidizing Gas Velocity: 0.5 - 0.75 ft/sec
 Starting Bed: ~1000 g UO_2 (static height ~8 in.)

Run No.	UF_6 Rate (g/min)	Run Duration (min)	Reactants Excess (%)	Results	
				Conversion ^a (%)	Residual Fluoride (%)
7A	5.7	120	300	99.4	0.08
8	1.4	180	1500	99.3	0.09
13	5.2	150	600	97.6	0.29
14	6.2	165	450	97.6	0.29
15	6.7	165	375 ^b	78.3 ^c	0.05 ^c
16	8.2	255	335	95.9	0.50
17	10.9	190	230 ^b	62.6	4.61
18	7.2	285	240 ^b	57.0	5.30

^a Conversion is based on the $\text{U}^{(+4)}$, $\text{U}(\text{total})$, and residual fluoride analyses assuming the constituents are only UO_2F_2 and UO_2 .

^b Some fines formation.

^c These analyses indicate U_3O_8 was formed.

2. Results

Good conversion (96 to 99 per cent) to uranium dioxide was achieved at feed rates of 6 to 8 g/min of uranium hexafluoride using 300 to 600 per cent excesses of steam and hydrogen. The feed rate at the highest conversion (99.4 per cent) was equivalent to a rate of 50 lb uranium/(hr) (cu ft static bed volume) or about 35 lb uranium/(hr)(sq ft of reactor cross section). The residual fluoride in this material was 0.08 per cent.

The run made at the highest feed rate, 10.9 g/min (equivalent to a uranium rate of 103 lb/(hr)(cu ft of static bed volume), was operationally smooth and only a run of extended length would determine whether the rates used were near maximum for this system for "hex" to solids conversion; conversion to dioxide was about 65 per cent complete. Additional contact time or an additional stage would probably permit achieving complete

conversion. The analytical results of Run 15, indicating the formation of U_3O_8 with a low residual fluoride content, were rechecked and verified; inadequate fluidization during the latter part of the run may have resulted in abnormal conditions producing U_3O_8 . Negligible amounts of uranium were found in the off-gas condensate trap in all experiments.

During the first few runs there was little evidence of particle growth in the bed; however, in the following runs particle growth occurred to the extent that the minimum velocity for the bed exceeded the fluidizing velocity used (0.75 ft/sec). In these cases, part of the reaction took place in the gas phase (rather than on the surface of the fluidized particles), as evidenced by the fraction of fines (-200 mesh) sustained in the bed. Previously, this fraction disappeared after about an hour of operation. Two premature shutdowns were necessary in runs made before increasing the gas superficial velocity; lumps formed due, perhaps, to the insertion of a thermowell in the area of the uranium hexafluoride inlet or to the near minimum fluidizing velocity. The thermowell was subsequently removed.

The surface areas and densities of the uranium dioxide products are listed in Table 33. The dioxide bed for the initial runs prepared by

Table 33

PHYSICAL PROPERTIES OF PROCESS MATERIALS FROM
FLUID-BED CONVERSION OF URANIUM HEXAFLUORIDE
TO URANIUM DIOXIDE

Run No.	Material	Conversion (% UO_2)	Density (g/cc)		Surface Area ^a (sq m/g)
			Xylene Displacement	Bulk Untapped Tapped	
-	Starting UF_4 ^b	-	6.4	3.0/3.2	0.39
1	UO_2 Pyrohydrolysis Product ^b	49.5	7.9	3.3/3.6	-
5	UO_2 Pyrohydrolysis Product ^b	99.3	-	3.5/3.9	0.98
8	UO_2 from UF_6 Conversion	99.3	-	4.2/4.4	0.59
14	UO_2 from UF_6 Conversion	97.6	9.9	4.4/4.5	0.90
18	UO_2 from UF_6 Conversion	57.0	7.5	4.0/4.3	-

^a -60, +100 mesh fraction.

^b The original uranium dioxide bed was prepared by pyrohydrolysis of uranium tetrafluoride. The materials from Runs 1 and 5 are products of this operation.

steam pyrohydrolysis of uranium tetrafluoride had a bulk density of 3.9 g/cc and a surface area of 0.98 sq m/g. As new material was made and deposited on the original particles by conversion of "hex," the bulk density increased and leveled off near 4.5 g/cc. The products of some runs have shown densities as high as 5.0 g/cc. A xylene-displacement density determination of the product of Run 14 gave 9.9 g/cc, which is about 90 per cent of theoretical density. The surface area of the dioxide product has shown only a slight decrease (0.59 to 0.90 sq m/g) despite the expectation that the particle pores would be filled by the reaction product. However, Figure 32 shows the growth rings on the particles and also a raspberry-like surface appearance which may be associated with high feed rates. The hollow spaces probably result from the specimen-polishing operation.

A single sintering experiment (1700 C in hydrogen for 15 hours) performed by the Metallurgy Division (Ceramics) on the product of Run 13 gave pellets with a density near 8 g/cc. Additional sintering experiments are planned.

3. Corrosion

Spectrochemical analysis of the product from one of the early runs (7A) showed little contamination from the Monel in the bed reaction zone, as indicated by contents of 50 ppm nickel and 30 ppm copper. Other metallic impurities were of the same order of magnitude, implying little corrosion in this zone. Additional analyses are being made to confirm this.

4. Scale-up

Scale-up of operations to a three-inch-diameter column is planned for further process demonstration and for further study of operating variables. It is hoped that increased bed depth will permit higher production rates. The ultimate use of the process, uranium dioxide production or hydrogen fluoride recovery from depleted uranium hexafluoride, would determine the specifications upon which to optimize operating variables.

Figure 32

PHOTOMICROGRAPHS OF URANIUM DIOXIDE PARTICLES
PREPARED IN FLUID-BED CONVERSION OF
URANIUM HEXAFLUORIDE

32a Run 14, -60, +100 mesh size, 45X

Figure 32 Cont'd.

32b Run 14, -40, +60 mesh size, 45X

III. REACTOR SAFETY

The object of this program is to understand the factors which influence the pyrophoric nature of certain reactor metals. Work was initiated with studies of uranium and zirconium and will be continued with studies of plutonium and thorium. The study of ignition behavior on uranium and zirconium has been complemented with an investigation of fundamental kinetics of oxidation. In continuing studies more emphasis is being placed on the burning process.

Previous research in this program through 1958 has been summarized in ANL-5974, "Ignition Behavior and Kinetics of Oxidation of the Reactor Metals, Uranium, Zirconium, Plutonium, and Thorium, and Binary Alloys of Each."

Burning curve experiments in air have shown that etching of uranium foil with nitric acid does not cause a decrease of ignition temperature, although the burning propagation rate is increased by this treatment. The dependence of uranium ignition temperature in air on specific area has been shown to be similar to that in oxygen. Experiments in air on aggregates of powder, turnings, foils, and cubes show that ignition of the powder at a low temperature causes ignition of the turnings and foils but not the cubes which have a low specific area.

Study of burning propagation rates of zirconium wires and foils in oxygen have shown that there is only a minor influence of shape on the relation found between burning rate and cross-sectional area. In connection with this work reproducibility tests have shown that burning rates are reliable to about six per cent in air and nine per cent in oxygen.

The amount of zirconium unconsumed during burning in air has been measured for several foil strips. Using 0.13-mm thick foils of zirconium, 4.16 atom per cent and 14.9 atom per cent titanium alloys, the fraction of unburned metal increased as the width of the foil strip increased.

Acquisition of materials and preparation of equipment necessary to conduct exploratory experiments on the burning properties of plutonium has begun.

Electron and X-ray diffraction studies of oxide films of zirconium alloys do not support a recent report that the breakaway is associated with the transformation of zirconium dioxide from the cubic to monoclinic structure. No simple relationship between the transformation and breakaway at 700 C can be found to apply to all the alloys examined.

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. An analysis on the analog computer of the data from runs with zirconium described in the previous quarterly report, ANL-5996, page 238 was completed. The results showed that runs at temperatures up to and including the melting point could be adequately described by the parabolic rate law with constants about twice those reported by Battelle. Runs with initial temperatures exceeding the melting point and with smaller particles were apparently impeded by a diffusion process and could not be described by a simple chemical mechanism.

A series of runs with uranium was completed. Up to six per cent reaction occurred at temperatures of the order of 1600 C. An induction period of 5 to 20 msec was observed for the hydrogen liberation.

A second laboratory-scale method involves the rapid contact of steam with a drop or pool of molten metal. In this method a sample of molten metal in a vacuum environment receives a "pressure pulse" of water vapor. Solenoid valves for these experiments were modified to provide an open time as short as 10 msec. Tests with the induction heating system showed that temperatures of the order of 2600 C could be obtained.

Two experiments were performed in the CP-5 reactor to check the instrumentation and techniques to be used in TREAT. Both an unbonded strain gage and a variable reluctance pressure pickup showed negligible changes in output while subjected to a dose of 10^{14} nvt in the reactor. The average attenuation of the thermal neutron beam in passing through the walls of the autoclave was found to be 73.5 per cent.

A. Metal Ignition-Oxidation Kinetics Studies (J. G. Schnizlein, and R. C. Vogel)

1. Uranium Ignition Studies (J. G. Schnizlein, L. Leibowitz, J. D. Bingle, and M. Cusick*)

a. Specific Area Dependence of Ignition in Air

The ignition of uranium specimens in air has been shown (ANL-5924, page 93) to be a somewhat different phenomenon than ignition of similar specimens in oxygen. This seems to be associated with the thermocyclic burning and the difference in maximum burning temperatures (ANL-5959, page 69) achieved in the two media. The observation has also been made repeatedly in uranium ignition and propagation studies that metallic uranium remains after foil specimens have been ignited in air.

* Cooperative Institution Student from Detroit University

The ignition temperatures in air and oxygen of uranium powder, turnings, 0.5, 1, 5, and 10-mil foils,* and 3.5, 5, and 10-mm cubes were determined and are reported in Table 34. The specific area dependence in air is compared with that in oxygen in Figure 33. Because the ignition temperatures are 20 to 50 degrees higher in air than in oxygen, the relationships are slightly different in the two gases:

$$\text{in Air: } T_{\text{ign}} = \frac{4190}{4.89 + \log (A/m)}$$

$$\text{in O}_2 : T_{\text{ign}} = \frac{4190}{5.23 + \log (A/m)}$$

where A/m is the specific area, $\frac{\text{sq cm}}{\text{g}}$

Table 34

IGNITION TEMPERATURES OF VARIOUS URANIUM SPECIMENS

(Ignition temperatures determined by burning curve technique)

Sample	Approximate Specific Area (sq cm/g)	Ignition Temperature (C)	
		Air	Oxygen
Powder	1200 ^a	-	125
0.01-mm (0.5-mil) foil	120	315	315
0.03-mm (1-mil) foil	50	350	335
0.13-mm (5-mil) foil (SMF-5) ^b (BMI) ^b	8	410	-
		390	380
0.25-mm (10-mil) foil (BMI)	5	385	385
3.5-mm cube (BMI)	1	-	530
8.5-mm cube (ANL)	0.4	650	595

^a Calculated on the basis of ideal spheres using a microscopic estimation of particle diameter of 2.5 microns.

^b Fabricated from reactor-grade uranium from two sources, with similar total impurities but different individual concentrations (see ANL-5996, page 201).

* Foils prepared by the Metallurgy Division, Argonne National Laboratory.

b. Effect of Nitric Acid Etch on Ignition Temperatures

During the study of the effect of surface and gas contaminants on the burning propagation rates (ANL-5996, pages 206 through 213), it was found that etching the surface of uranium foils caused an increase in burning rate. Since nitric acid is a common pickling agent and had caused the greatest effect, further investigation of the effect of nitric acid etches on the ignition temperature of uranium specimens was undertaken.

Samples of both 1- and 5-mil uranium foils were used in burning curve experiments in air after undergoing nitric acid etches. The 1-mil foil had an ignition tem-

perature of 350 C both when polished with 600 grit SiC paper and when etched for one minute in concentrated nitric acid until 2.1 mg or 1.7 per cent weight was lost. The 5-mil foil had an ignition temperature of 410 C both when polished and when etched for three minutes in concentrated nitric acid (4.4 mg or 0.5 per cent loss in etch).

Despite the fact that the etch treatment would be expected to cause an increase in surface area, no effect on the ignition temperature is observed with burning curve experiments. It should be remembered that samples are rather extensively oxidized before ignition when the burning curve technique is used. It may be that any increase in surface area of the sample due to etching may not be very noticeable after this heavy oxidation had taken place. Regrettably, shielded ignition tests on foils in air do not give a clear indication of ignition temperature (see ANL-5959, pages 64 through 66). When air is admitted, the foil would heat up somewhat and then immediately the temperature would drop back to its original value even when the experiment was initiated at a high temperature.

c. Ignition of Uranium Aggregates in Air

Most of the incidents involving uranium have not been violent and the principal hazard was the toxicity of the broadcasted radioactive particulate and fission products. The ignition and burning of machining chips is by far the more common incident but anticipation and good housekeeping seems

to prevent these from assuming very dangerous proportions. On most of the occasions in which bulk uranium has burned, the metal has frequently been at an elevated temperature before ignition, such as during rolling, biscuit discharging, or reactor operation, or because of fission product heat.

Another source of sufficient heat to cause burning of massive uranium would be ignition of powder or machine chips in an aggregate or accumulation of various size pieces of metal.

To date, the factor causing the greatest decrease in ignition temperatures and also the greatest increase in burning propagation rates of uranium has been specific area. In fact, a sample of high specific area has been shown to trigger the ignition in oxygen of a more massive specimen about 200 degrees C below the usual ignition temperature of the massive sample (see ANL-5858, page 57). Therefore, burning curve type experiments in air have been designed, using an aggregate of various sizes of samples, in which ignition of the smallest particles would be expected to ignite larger ones and so on in an ignition cascade.

In the aggregate experiments various amounts of the different uranium samples were mixed together in a small crucible containing a thermocouple well and then subjected to the usual burning curve procedure. A typical aggregate was composed of:

	<u>grams</u>
Uranium powder	0.485
Uranium turnings	5.643
0.03-mm (1-mil) uranium foil	0.235
0.13-mm (5-mil) SMF-5 foil	0.389
3.5-mm BMI cube	0.693
5-mm BMI cube	1.805
Total	<u>9.249</u>

In the experiments conducted to date, several observations have been made. Perhaps the most important is that the uranium powder will readily ignite the foil and turnings at a temperature around 150 C. More massive samples, i.e., the cubes, apparently were not ignited in turn by the foils and turnings. This may be simply because ignition of samples above a certain size is not self-sustaining in air. Burning propagation rate experiments have shown (ANL-5959, page 72) that strips greater than 1.7 x 3 mm would not continue to burn in air. Perhaps the relative amounts of the various sized samples were such that not enough heat was produced to ignite them. The particular conditions of the experiment, i.e., apparatus, sample geometry, etc., may also be a factor. Additional experiments of this type are planned with zirconium to elucidate further the factors involved in the spontaneous ignition.

2. Zirconium-ignition Studies

(L. Leibowitz, D. F. Fischer, J. D. Bingle, and M. Cusick)

Incidents involving zirconium rarely involve bulk metal but usually have involved powder and machine chips, which may react very violently. The ease of ignition of lathe turnings is common knowledge among fabricators.

In addition to understanding the factors influencing the ignition temperature of a metal, it would be useful to understand the factors influencing and controlling the rate of burning propagation. It may be possible to predict or anticipate the violence or the ease of control of a potential incident when the controlling factors of the burning process are known.

The apparatus and studies of burning uranium foils were presented in ANL-5959, pages 71 through 75, and ANL-5996, pages 201 through 213. The effects of varied purities, some additives, varied foil thickness, surface and gas contaminants, and surface etching on the burning propagation rate of uranium foils have been studied. Similar studies on zirconium foils have shown (ANL-5996, pages 222 through 231) that alloy additives which cause lower ignition temperatures cause increased burning rates and that variation of the width as well as the thickness of the foil strips affects the propagation rate. A linear relationship was shown between the length of the burning zone and the propagation rate for various alloys. Additional data are reported below, and planned studies include determination of effects of surface and gas contaminants, surface etches, and additional additives.* Noteworthy effects will be verified, wherever possible, with studies on lathe turnings, which in normal machining operations, although very irregular, have cross-sectional areas of the same magnitude as the foils studied.

a. Reproducibility of Burning Propagation Rate in Air

Seven runs have been completed in air using 0.13×0.6 -mm pure zirconium foil strips to check the reproducibility of the burning propagation rates. These rates ranged from 0.416 to 0.511 cm per sec with the average being 0.463 ± 0.027 cm per sec, or 5.8 per cent average deviation. The average length of the burning zone in air was 1.3 ± 0.1 cm. For comparison, in oxygen, the rate was 30.6 cm per sec for similarly sized samples. The average deviation has previously been reported (ANL-5996, page 223) to be approximately nine per cent from a value of 11.1 cm per sec for 0.13×3.0 -mm pure zirconium foil strips in oxygen.

b. Completeness of Combustion in Air

Exploratory experiments were carried out to determine whether or not unreacted metal remained after a strip of zirconium foil had been burned in air. Various metal strips were polished, weighed, burned in

* If mechanical properties permit, foils have been and are being prepared by cold rolling arc melted alloys (see ANL-5974, page 88) by the Metallurgy Division, Argonne National Laboratory.

air, and re-weighed. Samples of zirconium foil and of the 4.16 and 14.9 atom per cent titanium alloy foils, 0.13-mm thick, were used. In addition, a few experiments were performed using 0.02-mm thick zirconium foils. In general, only in cases for which the samples were relatively narrow was the metal completely oxidized. With the thin 0.02-mm foil virtually

complete combustion was observed up to a width of 3.9 mm, the widest sample used. For the others distinctly incomplete consumptions, varying with the sample width, were found. The results are presented in Figure 34. Thus, any development of the nature of the thermal processes involved in these ignitions will have to account for this experimental fact.

c. Influence of Cross-sectional Area on Propagation Rates in Oxygen

As has been previously reported (ANL-5996, page 226), the cross-sectional area of zirconium foils has a marked effect on burning propagation rates in oxygen. In order to explore this effect further, several additional measurements have been carried out with both foil strips and wires. All of the results obtained to date are given in Table 35 and Figure 35. It is interesting to note that the values for wires fall on the same curve as those for foils, thus supporting the notion that an area effect is being observed regardless of shape. However, as the foil thickness is decreased, the effect of varied width gradually diminishes (see family of dashed lines with varying slope on Figure 35). For 0.007-mm thick zirconium foil, the propagation rate is independent of the width. For thicker specimens and wires the propagation rate is roughly described (see solid line on Figure 35) by the relation $V = 5.3 A^{2/3}$, where V is the propagation rate in cm per sec and A is the cross-sectional area in sq mm.

Further studies to determine the relationship in air are under way.

Table 35

DEPENDENCE OF PROPAGATION RATES
IN OXYGEN ON CROSS-SECTIONAL AREA
FOR PURE ZIRCONIUM FOILS AND WIRES

Thickness (mm)	Width (mm)	Diameter (mm)	Cross-sectional Area (sq mm)	Propagation Rate (cm/sec)
0.007	~0.9		0.006	167.
0.007	4.2		0.029	177.
0.02	0.90	-	0.02	53.0
0.02	3.0	-	0.06	42.8
0.13	0.55	-	0.072	30.6
0.13	0.56	-	0.073	22.9
0.13	0.58	-	0.075	20.7
0.13	1.5	-	0.20	17.8
0.13	1.0	-	0.13	17.3
0.13	2.9	-	0.38	12.3
0.13	2.9	-	0.38	11.8
0.13	3.1	-	0.40	10.5
0.13	2.9	-	0.38	9.64
0.13	6.2	-	0.81	8.52
0.27	3.0	-	0.81	8.24
0.27	6.0	-	1.62	6.99
0.27	2.1	-	0.57	6.63
0.27	4.5	-	1.22	5.08
-	-	0.39	0.12	16.4
-	-	0.77	0.47	6.36
-	-	1.53	1.84	4.62
-	-	2.54	5.07	1.10

3. Zirconium Isothermal Studies
(H. A. Porte and D. F. Fischer)

To test a recent hypothesis and to obtain a better understanding of the mechanism of oxide film growth on zirconium alloys, additional electron diffraction analyses* have been obtained on oxidized zirconium alloy samples. It has been proposed¹⁸ that the breakaway was associated with the transformation of face-centered cubic zirconium dioxide, formed during the initial portion of the run, to monoclinic zirconium dioxide formed after the breakaway.

* Electron diffraction by glancing from oxidized sample surface. Interpretation by H. Knott and M. Mueller, Metallurgy Division.

¹⁸ Korobkov, I. I. et al., "Electron Diffraction and Kinetic Investigations of the Reactions of Oxidation of Zirconium and Some of Its Alloys" Second United Nations International Conference on Peaceful Uses of Atomic Energy, A/Conf. 15/P/2054 (1958).

The oxide structures observed on 16 different alloys after oxidation to selected extents are presented with the oxidation data in Table 36.

Table 36

OXIDE PHASES ON OXIDIZED ZIRCONIUM ALLOYS

(Oxidized at 700 C in 200 mm oxygen to extent tabulated, evacuated, cooled, and examined)

Alloy (atom per cent)	Extent of Oxidation ($\mu\text{g}/\text{sq cm}$)	Breakaway Weight ^a ($\mu\text{g}/\text{sq cm}$)	Observed Oxide Phase ^b
Oxidation Terminated Prior to Breakaway			
Pure Zr	2832	- ^c	fcc
1.96 W	5787	- ^c	fcc
4.22 Pt	1128	1763	fcc
1.42 Al	1071	1467	fcc
3.72 C	783	1076 p	fcc
2.12 Ti	2508	9468	fcc ^d
4.16 Ti	3957	15975 p	fcc plus unknown
3.60 Cu	2385	- ^c	fcc plus unknown ^d
1.78 Ta	11688	- ^c p	fcc plus unknown
3.52 U	1398	2645	unknown bcc ^d
1.82 Nb	1894	5625 p	unknown bcc plus unknown ^d
3.88 V	3392	- ^c p	monoclinic ^d
3.88 V	14392	- ^c p	monoclinic ^e
4.08 Hf	2634	-	monoclinic
Alloys Oxidized Beyond Breakaway			
4.22 Pt	3292	1763	fcc
2.12 Ti	14770	9468	fcc plus unknown
4.16 Ti	23402	15975 p	fcc plus unknown
3.60 Sn	1343	521	fcc
3.60 Sn	13404	521	monoclinic ^e
3.52 U	4139	2645	monoclinic ^e
1.94 Si	22435	1650 p	monoclinic
1.64 C	10845	1225	monoclinic ^e
1.42 Al	24780	1467	monoclinic ^e
3.54 Ta	15727	7830	monoclinic ^e

^a Determined in previous oxidation studies at 700 C in 200 mm oxygen (see ANL-5924, page 101). Initial oxidation followed the cubic rate law unless indicated as parabolic rate law by the letter p.

^b fcc = face-centered cubic ZrO_2 structure; a_0 between 5.37 and 5.61 Å (a_0 for fcc ZrO_2 = 5.07 Å).

-bcc = body-centered cubic structure; a_0 = 3.16 Å.

Electron diffraction by glancing from oxidized surface; interpretation by H. Knott and M. Mueller, Metallurgy Division.

^c No breakaway observed for 1400-min oxidation

^d Electron diffraction patterns presented in Figure 36.

^e Determined by X-ray diffraction of powder removed from surface; interpretation by D. S. Flikkema, CEN Division.

Typical electron diffraction patterns are presented in Figure 36 for five cases that were oxidized to an extent less than breakaway weight (A: face-centered cubic structure on 2.12 atom per cent titanium alloy; B: face-centered cubic structure plus an unknown phase on 3.60 atom per cent copper alloy; C: unknown body-centered cubic structure on 3.52 atom per cent uranium alloy; D: unknown body-centered cubic structure plus unknown phase on 1.82 atom per cent niobium alloy; and E: monoclinic structure on 3.88 atom per cent vanadium alloy).

FIGURE 36

**ELECTRON DIFFRACTION PATTERNS FROM SELECTED
OXIDES ON ZIRCONIUM ALLOYS**

Of the 14 samples examined after oxidation to an extent less than breakaway weight, nine showed the face-centered cubic structures (3 of which had another unknown phase), two showed an unknown body-centered cubic structure, and three showed the monoclinic structure.

Of the 10 samples oxidized beyond breakaway, four showed the face-centered cubic structure (two of which had another unknown phase) and six showed the monoclinic structure.

Although a majority of the alloys showed a relationship between the oxidation kinetics and the change of structure of the oxide film, careful consideration of the data shows enough exceptions to the predicted sequence of polymorphic transformations to make it clear that there is no rule which is applicable a priori to all zirconium alloy systems. Some of the unidentified phases found may be secondary or ternary compounds with the alloying element. To identify the unknown phases would involve an extended research program beyond the scope of this investigation.

These results show that the predicted sequence of phase transformation in the zirconium dioxide film and the relationship to the oxidation kinetics as reported in the Russian publication¹⁸ is probably an oversimplified explanation which may be applicable for pure zirconium and some zirconium alloys but cannot be extended to include all zirconium alloys.

In an earlier report (ANL-5996, page 232) it was stated that possibly the reason for the exceptions to the predicted theory was due to an initial parabolic oxidation. However, these additional results refute that statement since there were as many exceptions to the theory with samples that oxidized according to the cubic rate law as those following the parabolic rate law. The 4.08 atom per cent hafnium (cubic rate) and the 3.88 atom per cent vanadium (parabolic rate) both produced monoclinic zirconium dioxide even though neither had shown a breakaway; a 2.12 atom per cent titanium (cubic rate) and a 4.16 atom per cent titanium (parabolic rate) alloy both showed some fcc zirconium dioxide, although both of these alloys were oxidizing at a rapid rate well beyond the breakaway when the runs were terminated.

4. Plutonium-ignition Studies

(J. G. Schnizlein, P. J. Pizzolato, and D. F. Fischer)

The increasing use and handling of plutonium make it imperative that the factors leading to its pyrophoricity be more clearly understood. Negotiations have been completed to prepare various plutonium samples and a series of alloys.

Prior to completion of a well-equipped laboratory for handling metallic plutonium, exploratory experiments are going to be performed in an existing glove box. Equipment has been constructed and is being tested and installed in the glove box train. Despite the added difficulties and slowness of the work in glove boxes it is expected that preliminary burning curve and shielded ignition experiments and burning propagation rate studies will be completed in the next quarter.

B. Metal-Water Reactions

(L. Baker, R. C. Liimatainen, M. Kilpatrick*, W. A. Rodger)

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

In this study 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 indicates reaction 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. Further runs with 60-mil uranium wires are reported. Results of an analog computer study of the previous zirconium data are reported.

Table 37

URANIUM-WATER REACTION DATA:
CONDENSER-DISCHARGE METHOD
USING 60-MIL WIRES

Run	Energy Input (Cal/g)	Calc Temp (C) and Phys State	% Reaction	Appearance of Residue
48	29.6	750, solid (β)	0.61	Intact
50	39.2	850, solid (γ)	0.86	Intact
47	42.5	1000, solid (γ)	1.05	4 pieces
51	53.4	1130, 35% liq	2.4	Large particles
49	55.9	1130, 60% liq	3.7	Large particles
46	67.1	1300, liq	6.1	Some fine chips
45	78.9	1600, liq	4.8	Some fine chips

a. Runs with Uranium

The experimental procedure used has been described in previous Quarterly Reports in connection with zirconium runs. The uranium data obtained to date are summarized in Table 37. The total extent of reaction, as determined from measurements of the total hydrogen liberated, is plotted in Figure 37. The higher energy runs represent the maximum capability of the present discharge apparatus. These runs used 60-mil wires; runs at higher initial temperatures will be made using 30-mil wires. Uranium appears to be considerably more reactive than zirconium at similar temperatures. Both metals show a significant reaction in the region of their melting points.

Oscillograms of pressure as a function of time were obtained for the runs. The pressure-time traces are reproduced in Figure 38.

*

Consultant from Illinois Institute of Technology.

FIGURE 37
URANIUM-WATER REACTION:
PER CENT REACTION AS A FUNCTION OF
ENERGY INPUT AND INITIAL TEMPERATURE

FIGURE 38
PRESSURE-TIME TRACES FOR URANIUM-WATER REACTION
(Pressure at 4.5 sec is denoted by the horizontal lines)

An induction period ranging from 5 to 20 msec was observed for the hydrogen evolution. No such induction period was observed with zirconium. The residue did not consist of spherical particles as was the case with zirconium; but rather had the appearance of flakes or chips. Preliminary runs with 3-mil platinum wire did give the characteristic spherical particles. The failure of the uranium to yield spherical particles and the presence of the induction period are under intensive study.

b. Analysis of Zirconium Data

Equations were presented in ANL-5896, page 108, to describe the process whereby hot spherical particles simultaneously

react, undergo self-heating and eventually cool to room temperature. It was assumed that the original metal wire is heated and formed into spherical particles of radius r_0 instantaneously. The reaction at the surface was assumed to follow the parabolic rate law. This law was found to apply approximately to the Zircaloy-steam reaction by A. W. Lemmon, Jr.,¹⁹ and his associates. The following equations were derived and programmed on the Pace Analog Computer:

$$(1) \quad W^2 = \rho^2(r_0 - r)^2 = k_0 t \exp(-\Delta E/RT)$$

$$(2) \quad -\frac{dr}{dt} = \frac{k_0}{2\rho^2} \frac{1}{(r_0 - r)} \exp(-\Delta E/RT)$$

$$(3) \quad \frac{dT}{dt} = \frac{3Qk_0}{2\rho^2 C_p r_0^3} \frac{r^2}{(r_0 - r)} \exp(-\Delta E/RT)$$

$$- \frac{3h}{C_p \rho r_0} (T - T_W) - \frac{3\sigma \epsilon}{C_p \rho r_0} T^4$$

¹⁹ Lemmon, A. W., Jr., "Studies Relating to the Reaction Between Zirconium and Water at High Temperatures," BMI-1154 (January 3, 1957).

$$(3A) \quad \frac{L}{C_p} \frac{dF}{dt} = \frac{3Qk_0}{2\rho^2 C_p r_0} \frac{r^2}{(r_0-r)} \exp(-\Delta E/RT_M) \\ - \frac{3h}{C_p \rho r_0} (T_M - T_W) - \frac{3\sigma\epsilon}{C_p \rho r_0} T_M^4$$

$$(4) \quad \text{Per Cent Reaction} = 1 - (r/r_0)^3$$

The symbols are defined as follows:

Variables:

- F is the fraction of original metal in the solid state
- r is radius of unreacted metal (liquid or solid), cm
- t is time, sec
- T is average temperature of sphere, K
- W is weight of metal oxidized, g/sq cm

Adjustable Constants:

- ΔE is activation energy, kcal/mole
- ϵ is total emissivity of oxide surface
- h is convective heat transfer coefficient, cal/(sq cm)(sec)(K)
- k_0 is pre-exponential factor in parabolic rate law, $\text{g}^2/(\text{cm}^4)(\text{sec})$
- r_0 is initial radius of sphere, cm

Fixed Constants:

- C_p is specific heat of Zr, 8.0 cal/(mole)(K)
- L is heat of fusion of Zr, 4.9 kcal/mole
- Q is heat of reaction of $\text{Zr} + 2 \text{H}_2\text{O}$, 140.5 kcal/mole
- R is gas constant, 1.987 cal/(mole)(K)
- ρ is density of Zr, 6.5 g/cu cm
- σ is Stefan Boltzman constant, 1.37×10^{-12} cal/(sec)(K)(sq cm)
- T_M is melting point of Zr, 2125 K
- T_W is water temperature, 298 K

Equation (1) is the parabolic rate law. Equation (2) is the derivative of the rate law and represents the rate of reaction. Equations (3) and (3A) are heat balances. The first term on the right hand side of

equations (3) and (3A) represents self-heating of the particle due to reaction; the second and third terms of the equation are the convective and radiative heat loss terms, respectively. Equation (3A) replaces (3) when the metal either heats or cools through the melting point. Heat is then absorbed or liberated without a change in temperature.

One particular piece of experimental data was chosen for analysis by means of the derived equations. Experimentally, it was found that eight per cent total reaction occurred when the condenser discharge supplied just enough energy to liquefy fully the metal but not heat it beyond the melting temperature of 2125 K. Experimentally, the area of the original 60-mil wire was not increased by the melting process. A sphere of 0.105-cm radius was taken as an average value for all of the experiments at the melting temperature and below.

Further experimental information was required in order to verify the trial values of the heat transfer coefficient, h . The high-speed motion pictures showed that the residue remained luminous (above ca. 1500 K) for at most 1.1 sec for fully liquefied metal at the melting point. No data were available that would verify a value of the emissivity, ϵ , independently of the heat transfer coefficient. Two values of ϵ were arbitrarily

used: 0.67 and 1.00. These represented minimum and maximum values.¹⁸

FIGURE 39
TIME REQUIRED FOR FULLY LIQUEFIED ZIRCONIUM
SPHERES AT 2125 K TO COOL TO 1500 K
FOR VARIOUS ASSUMED CONSTANTS

Cooling times taken from computed results are shown in Figure 39 as a function of the assumed heat transfer coefficient, h , and emissivity, ϵ . The results show that values of $h = 0.0125$ and $\epsilon = 1.00$ will yield reasonably correct values of the cooling time as based on the motion picture study. The effect of changes in h and ϵ on the parabolic rate constants required for eight per cent reaction is shown in Table 38.

Using values of h and ϵ obtained from the above analysis, the extent of reaction was calculated for various experimental conditions. A comparison of the computed results with the experimental data is shown in Figure 40. The computed curves agree with the experimental points for initial temperatures in the melting point region and below, although the data are not sufficiently accurate to define an activation energy.

Table 38

VALUES OF $k_0 e^{-\Delta E/RT}$ AT 2125 K REQUIRED TO GIVE
EIGHT PER CENT REACTION FOR LIQUID ZIRCONIUM
DROPLETS OF 0.105-CM RADIUS

Activation Energy, ΔE (kcal/mole)	Emissivity, ϵ	Heat Transfer Coefficient, h [cal/(sec)(sq cm)(K)]	$k_0 e^{-\Delta E/RT}$ [g ² /(cm ⁴)(sec)]
35	0.67	0.0100	0.00025
	0.67	0.0125	0.00027
	0.67	0.0250	0.00034
	1.00	0.0125	0.00029
30	0.67	0.1000	0.00022
	0.67	0.0125	0.00025
	1.00	0.0125	0.00033
25	1.00	0.0125	0.00035
34 ^a	-	-	0.00015 ^a

^a Experimental values calculated from data correlation in Ref. 19.

FIGURE 40
COMPARISON OF COMPUTED AND
EXPERIMENTAL RESULTS FOR ZIRCONIUM-WATER
REACTION BY CONDENSER DISCHARGE METHOD

The experimental particle radii are also given on Figure 40. Runs at initial temperatures above the melting point had smaller particle radii than the lower temperature runs. The computed results for decreased radii indicate much greater reaction than is observed. This suggests that some other effect is impeding the reaction at high temperature and/or small particle size. It is likely that the low results are due to a diffusion barrier set up by the liberated hydrogen which prevents free access of the water to the surface.

The computed rates of reaction, i.e., pressure-rise rates, are compared in Figure 41 to experimental pressure-time curves obtained with the pressure pick-up. The experimental curves are somewhat scattered because of various instrumental difficulties which have been resolved in more recent runs. The initial reaction rates show general agreement with the computed curves. The initial rates are very sensitive to deviations of several of the assumptions involved in the theoretical treatment. Some of the assumptions implicit in the treatment are as follows:

1. The theoretical initial rate is infinite. Actually this rate must be limited by either a transport or a chemical mechanism.
2. Independent particles formed in the liquid range are formed instantaneously and all have the same radius. These assumptions are only approximately true. Although heating occurs in less than 0.3 msec, the wire break-up may require up to 5 msec as shown by high-speed motion pictures.
3. The assumed convective heat transfer model is also an approximation for the early stages of the process.

The theoretical treatment does not account for the explosive pressure-rise rates reported at temperatures above 2900 K (2600 C). The rapid rates are apparently due to a mechanism change possibly involving melting of the oxide and a corresponding breakdown of the parabolic law.

The results of the analysis show that turns through the melting point region can be represented by a parabolic rate law and a simple heat transfer model. A convective heat transfer coefficient of 0.0125 cal/(sec)(sq cm)(K) [92 BTU/(hr)(sq ft)(F)] was found to be consistent with the experimental data and with correlations presented in standard texts on heat transfer. The analysis has shown that more data are required to obtain an accurate value of the activation energy and to justify further the theoretical treatment. Studies are under way using finer wires. The tentative rate constants are approximately twice those reported by previous investigators as shown in the following summary.

ΔE (kcal/mole)	$k_0 e^{-\Delta E/2125 R}$ [g ² /(cm ⁴)(sec)]
35	0.00029
30	0.00033
25	0.00035
34 ^a	0.00015 ^a

^aRef. 19

Special thanks are due Messrs. L. Just and N. Morehouse of the Applied Mathematics Division who carried out the analog computer program.

2. Laboratory Studies - Pressure-pulse Method (D. Mason, P. Martin)

The pressure-pulse method involves the momentary contact of water vapor with molten metal contained in a crucible. The method permits careful control over the reaction time and surface area of metal exposed to reaction.

Temperatures high enough to melt zirconia (2680 C) have been obtained by induction heating of platinum in zirconia crucibles in air. Attempts to melt zirconium in thoria crucibles in vacuum are under way. Thoria has been found to have poor thermal shock characteristics, but minor cracks in the crucible may not seriously affect the experiments.

Commercial solenoid valves have been successfully modified to provide very rapid operation. These will be used for rapid contact and withdrawal of water vapor. Effective open-time intervals as low as 10 msec have been obtained by discharging a condenser through the solenoid. Variations of the condenser capacity and charging voltage and the return spring characteristics provide control over the operation of the valves.

3. In-pile Testing in the TREAT Reactor

(R. C. Liimatainen, R. O. Ivins, W. A. Rodger, M. Deerwester)

Since TREAT will not be available for experimentation until some time in the fall, it was decided to conduct some initial experiments in CP-5. For these experiments, the autoclave described in ANL-5996, page 249, was inserted into CP-5 while the reactor was shutdown. No secondary container was used. The two purposes for these tests were (a) to determine the influence of neutron and gamma radiations on the pressure transducer, and (b) to determine the attenuation of the neutron beam and to obtain the integrated dose inside of the vessel.

The conditions for the first experiment in which the autoclave contained no uranium were as follows:

1. Reactor flux dose: (a) 1.03×10^{14} observed thermal neutrons per sq cm, (b) 1.0×10^{10} fast neutrons per sq cm, (c) 0.2×10^6 roentgens gamma.
2. Time: (a) 9.3 minutes to rise to full power on 40-sec period; (b) 10.0 minutes at 2-Mw reactor power.
3. Ambient temperature of cooling air in reactor: ~ 30 C.
4. Pressure: 20 psia of helium in autoclave.

A gold-foil activation method was used to obtain data on neutron attenuation and dose. For two foils attached to the outside surface of the vessel, an average value of 1.026×10^{14} neutrons/sq cm (nvt) was obtained. For the foil inside the autoclave the dose was 0.239×10^{14} . From these values the attenuation of the neutron beam by the autoclave wall was calculated to be 76.7 per cent.

Observations on the performance of the Consolidated Engineering Company unbonded strain gage pressure transducer showed no change in output. However, during the last minute of the test the pressure trace showed a slight increase in the noise level equivalent to ± 2 psi. The full-scale deflection on the oscillograph was approximately 100 psi. It is concluded that the strain gage shows considerable promise for pressure measurements in radiation fields. It is of interest to compare the stability of the strain gage in the neutron-gamma field to previous tests on a quartz crystal transducer in a gamma field of the same intensity ($\sim 10^6$ r/hr). The output of the quartz crystal changed markedly whereas the strain gage output remained constant.

After removal from the reactor the activity levels resulting from activation of the autoclave were as follows:

time after end of test (hr)	gamma activity at 2 inches (r/hr)
0.3	675.
3.9	75.
29.3	0.4
47.0	0.12
150.0	0.02

The main contribution to the activity one day after the test was from the gold foils; the external foils showed a gamma level of about 4.5 r/hr at two inches.

In the second experiment, the autoclave contained a 4.743-gram natural uranium pin. The Wiancko variable reluctance pressure pickup was used. The results may be summarized as follows:

From gold-foil activation data the attenuation of the neutron beam (0.60×10^{14} nvt inside of autoclave) through the wall of vessel was 70.2 per cent. No change in output of the variable reluctance transducer was observed. The pressure of 20 psia of helium remained constant. The activity levels of the autoclave with gold foils after removal from reactor were:

time after end of test (hr)	gamma activity at 2 inches (r/hr)
0.3	2000
5	500
24	1.5

Forty-eight hours after the test a survey meter showed only 25 mr/hr at two inches from the uranium pin itself.

The observed temperature rise of the metal was 26 C. From the two in-pile tests, it was concluded that both the unbonded strain gage and variable reluctance pressure pickups will be acceptable for use in TREAT experiments since neither was appreciably influenced by the radiation.

The next experiments will be conducted in a similar manner but enriched pins will be used. This will simulate as nearly as possible the conditions to be expected in TREAT experiments.

IV. REACTOR CHEMISTRY

Current work being carried out on determination of nuclear constants includes the Van de Graaff neutron cross-section program applied to U^{236} and Th^{232} , instrumentation studies applied to use of an alpha pulse-height analyzer in conjunction with the 256-channel analyzer, and decay scheme studies applied to K^{42} and Th^{232} .

Studies are being made in the Boiling Water Reactor Decontamination program for determination of contamination resulting from a fuel defect and investigation of methods of activity removal.

Work has begun on a study of the reactions of superheated steam with metals such as zirconium, Zircaloy, and stainless steel.

A. Determination of Nuclear Constants (C. E. Crouthamel)

1. Van de Graaff Neutron Cross-section Program (D. Stupegia and R. Heinrich)

This work consists of the measurement of the neutron-capture cross section of uranium-236 and thorium-232, using neutrons produced by the bombardment of lithium targets with protons from the Van de Graaff generator of the Reactor Engineering Division. The neutron energy range is from 0.4 to 1.5 Mev.

Uranium-236. The starting material for the uranium-236 work is uranium oxide containing about 95 per cent uranium-236. A method has been found to form the uranium-236 into discs of uranium dioxide 1 cm in diameter and about 0.022 inch in thickness. These target discs each weigh about 0.25 g and are strong enough to stand handling. The activation product, uranium-237, of the bombardment, will be determined by 4π beta counting in the original standardization. Thereafter following the actual bombardments, the whole target will be gamma-counted with the scintillation counter, which will have been calibrated against the 4π beta count.

Thorium-232. Thorium-233, the neutron-activation product of thorium-232, has been determined by 4π beta counting. An end-window beta counter and the gamma scintillation counter will be calibrated against the 4π beta counter for use in these measurements.

2. Instrumentation (R. Heinrich)

The alpha pulse-height analyzer has been used successfully in conjunction with the 256-channel analyzer. The instrument has been calibrated to cover an alpha-particle energy range of 2.25 to 7.95 Mev, using the following standards: uranium-233 (4.82 Mev); plutonium-239 (5.15 Mev); curium-244 (5.80 Mev). Resolution of alpha peaks is about 1.5 per cent (full width of peak at half-maximum height).

3. Decay-Scheme Studies: Decay Characteristics of K^{42} and Te^{132} (C. Gatrousis and C. E. Crouthamel)

During our recent compilation of gamma-ray spectra it became evident that a number of details concerning the gamma transitions of several radioactive nuclides were uncertain. For example, the low-intensity potassium-42 gamma transitions are difficult to observe because of the intense and very energetic beta emission. Also, the tellurium-132 gamma transitions are difficult to examine because of the rapid growth of the harder iodine-132 daughter activities. In the present investigation the main features of the gamma transitions associated with the decay of potassium-42 and tellurium-132 have been characterized by using a large thallium-activated sodium iodide crystal, a multichannel analyzer and a simple coincident summing technique at high geometry.

The potassium-42 used was prepared by a short thermal neutron bombardment of natural potassium in the Argonne CP-5 reactor. The gamma spectrum observed with the scintillation spectrometer showed gamma rays at 1.52 Mev and 0.320 Mev, which subsequently decayed with a 12.5-hour half-life. At a source geometry of 40 per cent, a sum peak at 1.84 Mev was observed. This clearly indicates that the 1.53-Mev and 0.320-Mev gamma rays are in cascade.

The tellurium-132 was prepared by a thermal neutron irradiation of natural uranium oxide followed by chemical purification and isolation of tellurium from the other fission products. The gamma-ray spectrum of tellurium-132 showed the 0.230-Mev gamma ray which had been previously established. In addition, however, a highly converted 0.052-Mev gamma transition was observed. Coincident summing in a single sodium iodide crystal has revealed that the 0.230-Mev gamma transition is in cascade with the 0.053-Mev transition. At a high geometry, the 0.230-Mev gamma peak appeared extremely distorted, which indicates summing with the 0.053-Mev gamma ray and the 28-Mev iodine KX-ray. A simple decay scheme of tellurium-132, based on the results of this experiment, is shown as follows:

A paper summarizing the results of this investigation has been accepted for publication in the Journal of Inorganic and Nuclear Chemistry.

B. Reactor Decontamination (W. B. Seefeldt)

The Reactor Decontamination program is a joint one with the Reactor Engineering Division. The incentive for the program results from the existing concern for the consequences of a fuel rupture in a boiling water reactor and the need to know what remedial measures may be taken to place the reactor back on stream if these consequences are severe. The purposes of the program are: 1) to determine the types and quantities of fission product activities likely to be distributed on the internal surfaces of a boiling water reactor system, and 2) to determine what methods of activity removal can be utilized.

A loop simulating the operation of a boiling water reactor has been completed and is expected to provide answers for the first objective for longer-lived activities, and in addition will furnish metallic specimens for bench-scale decontamination studies. The decontamination studies made to date were done in laboratory autoclaves.

1. Laboratory Studies (S. Vogler and H. Tyler)

Laboratory studies are under investigation to evaluate reagents for decontaminating Type 304 stainless steel. To produce contaminated specimens, a stainless steel liner containing approximately two grams of irradiated natural uranium and 100 ml of deionized water is placed inside

an autoclave and heated for six days at 600 psi and 486 F. At the completion of an experiment, the contents are removed, and the liner is rinsed with distilled water and cut into one-inch squares for use in decontamination experiments. Each liner is preoxidized with 600 psi steam for one week prior to use.

Results reported in the last quarterly (ANL-5996, pages 255 to 258) indicated that alkaline permanganate solutions followed by ammonium citrate were effective decontaminating reagents. Early experiments utilized the alkaline permanganate solution at ~90 C. Later experiments at reduced temperatures and concentrations for the alkaline permanganate solution were found to produce nearly as effective results.

a. Alkaline Permanganate Decontamination

A series of experiments was planned to evaluate the effect of potassium permanganate concentration, sodium hydroxide concentration, and time of contact on decontamination. The potassium permanganate was varied from 0.1 to 3 per cent, the sodium hydroxide from 1 to 10 per cent, and the time from 4 hours to 3 days. The variables for the ammonium citrate second step were held constant - 10 per cent solution for 15 minutes at 85 C.

(1) Effect of Solution Concentration at Room Temperature

The results showing the effect of reagent concentrations are given in Table 39. The exposure at 90 C is included for reference and indicates that room-temperature treatments for step one are nearly as effective as the high-temperature treatments if exposure times are extended. The decontamination results are all within a factor of 2 or 3 of each other. A casual inspection reveals no obvious pattern of the variation of decontamination with solution composition. A significant effect on the decontamination may be noticed with more dilute solutions.

Table 39

DECONTAMINATION OF TYPE 304 STAINLESS STEEL: EFFECT OF CONCENTRATION OF POTASSIUM PERMANGANATE

Conditions: Plates, ~1 inch square, contaminated at 600 psi
Activity $\sim 5 \times 10^5$ γ cpm
KMnO₄-NaOH: 25 C for 4 hours
10% Ammonium Citrate: 85 C for 15 minutes

Expt. No.	Potassium Permanganate (per cent)	Sodium Hydroxide (per cent)	<u>Decontamination</u>	
			Beta	Gamma
2	3.0	1	740	460
3	0.5	1	1050	860
1	0.1	1	420	290
6	0.1	3	1100	850
4	0.1	10	530	350
5	3.0	10	870	620
Refer- ence ^a	3.0	2	-	1300

^a 90 C for 30 minutes

Table 40

DECONTAMINATION OF TYPE 304 STAINLESS STEEL:
EFFECT OF EXPOSURE TIME ON DECONTAMINATION

Conditions: Plates, ~1 inch square, contaminated
 at 600 psi
 Activity: $\sim 2 \times 10^5$ γ cpm
 $\left. \begin{array}{l} \text{KMnO}_4: 0.5\% \\ \text{NaOH: } 1\% \end{array} \right\}$ at room temperature
 Ammonium citrate: 10% at 85 C for
 15 minutes

Time (hr)	Decontamination	
	Beta	Gamma
4	1140	710
	720	590
24	370	190
	310	170

(2) Effect of Exposure Time
at Room Temperature

An experiment was performed to measure the effect of an increased exposure time to the caustic-permanganate reagent, the results of which are given in Table 40.

These data apparently indicate that longer exposure times to the alkaline-permanganate reagent result in poorer decontamination. These first results need verification by additional experiments.

(3) Effect of Initial Activity Level on the Decontamination

No effort was made to test this factor in a specific group of experiments in which activity level was the only variable. However, examination of several experiments indicates that with higher original activity levels, a higher decontamination is obtained. This effect has also been noticed in other types of decontamination experiments.

b. Stability of Alkaline Permanganate Solutions

(1) Stability to Gamma Radiation

Solutions used for decontamination purposes should be reasonably stable in the presence of radiation fields. Preliminary measurements of the radiation stability of potassium permanganate in sodium hydroxide solution were made by exposing such solutions to gamma radiation from a cobalt-60 source.

Three different solutions were prepared, using deionized water. The compositions are listed below.

Potassium Permanganate		Sodium Hydroxide	
Per Cent	M	Per Cent	M
0.1	0.0063	1	0.25
1.0	0.063	1	0.25
0.1	0.0063	3	0.75

These solutions were placed in 10-ml glass ampoules with a capillary stem at either end; no attempt was made to remove dissolved air. These solutions were then exposed to a cobalt-60 gamma field of 10^{21} ev/(1) (min) (equivalent to 10^6 rads per hour). Changes in the permanganate concentrations were determined by measuring changes in absorption spectra with a Cary recording spectrophotometer. A blank was run with each sample to compensate for any changes in the absorption of the solution because of reduction of the permanganate ion to manganate ion. The results are given in Table 41. G values of 2 and 3.7 were obtained for one-hour irradiations; this is in fair agreement with data of other investigators.* A single value of 1.2 was obtained for a 20-hour exposure.

Table 41

EFFECT OF GAMMA RADIATION ON
POTASSIUM PERMANGANATE SOLUTIONS

Sample Volume: 10 ml

Dose Rate : 10^{21} ev/(1)(min)($\sim 10^6$ rads/hr)

Time of Irradiation (hr)	KMnO ₄ Concentration, <u>M</u>		
	NaOH 0.25 <u>M</u>	NaOH 0.25 <u>M</u>	NaOH 0.75 <u>M</u>
0	6.25×10^{-3}	7.0×10^{-2}	5.75×10^{-3}
1	-	6.63×10^{-2} (3.7) ^b	3.81×10^{-3} (2.0) ^b
20	a	4.63×10^{-2} (1.2) ^b	a

^a In these samples the color was completely discharged and a light brown precipitate was observed.

^b The numbers in parentheses are calculated G values for the disappearance of potassium permanganate. The G value is defined as the number of molecules undergoing change per 100 ev absorbed.

A qualitative test run on the precipitate which formed in the 0.1 per cent permanganate solutions confirmed the presence of manganese. No precipitate was detected in the 1.0 per cent permanganate solution.

* Malcolm Daniel, ANL Chemistry Division - Private Communication.

These results indicate that some care in the selection of permanganate and caustic concentrations would be necessary to avoid precipitation on long exposure in high-level radiation fields. Continuous additions of permanganate to the decontaminating solution might be possible to replace that lost by decomposition. Some additional radiation stability experiments will be required after a decontamination procedure is more firmly established.

(2) Stability in Alkaline Solution

Previous experiments of a scouting nature had indicated that potassium permanganate was unstable in concentrated (20%) caustic solutions. These changes were confirmed by spectrophotometric data. Also observed in the spectra was absorption typical of the manganate ion.

Solutions of lower caustic concentrations (1 to 3%) which had been prepared for the radiation stability tests were examined. The solutions had been prepared by mixing aliquots of an aqueous potassium permanganate solution and a sodium hydroxide solution to give the desired composition. Samples of these solutions after standing for various lengths of time were removed and diluted to 25 ml in a volumetric flask. These diluted samples were scanned in the spectrophotometer. The results shown in Table 42 indicate little or no change in the potassium permanganate concentration under the conditions of the test.

Table 42

STABILITY OF POTASSIUM PERMANGANATE IN SODIUM HYDROXIDE SOLUTION

Temperature: Ambient ($\sim 25^\circ\text{C}$)

Optical densities measured with a Cary
Recording Spectrophotometer

KMnO ₄ %	0.1	1.0	0.1
NaOH %	1.0	1.0	3.0
Time	<u>Optical Density (547 mμ)</u>		
40 min	1.12	1.25	1.02
5 $\frac{1}{4}$ hr	-	1.25	1.03
23 hr	-	1.28	-
48 d	1.05	1.22	1.0

C. Steam-Metal Reactions at High Temperatures (J. Fischer, R. L. Jarry, N. Phillips,* T. Gerding)

An apparatus is being built to study the reactions of metals with superheated steam. Information concerning the kinetics and mechanism of the reactions will be useful in evaluating materials of construction for a nuclear superheat reactor. A study will be made of the reactions of zirconium, Zircalloys, stainless steel and other metals with steam between 425 and 565 C and between 540 and 1400 psi.

This program is concerned with the mechanism and rate of formation of corrosion films on various metals by the action of superheated steam. In order to simulate conditions resulting from the radiation action in in-pile operation, oxygen and hydrogen will be added to the superheated steam. A level of approximately 70 cc of oxygen and hydrogen (in the ratio of 2:1, respectively, at STP) per liter of condensed steam will be used, based on EBWR operating experience. Included among the metals tested will be stainless steels, carbon steels, zirconium and zirconium alloys. The range of pressure and temperature over which the experiments will be conducted are up to 1500 psi and 427 to 565 C (800 to 1050 F).

While our program will approximate some of the conditions of the EBWR superheat test, which are 454 to 565 C (850 to 1050 F), 540 to 1400 psi and 250 to 350 ft/sec, the flow will be negligible by comparison. Therefore, the effect of erosion will not be evaluated. Moreover, it is not the intention of this project to obtain corrosion data in a narrow range specifically designed for one set of conditions.

A schematic drawing of the test apparatus is shown in Figure 42. It consists essentially of a loop comprising a boiler, superheater and condenser. The specimens to be evaluated are suspended on hangers attached to a thermocouple well in the superheat section.

*Special Scientific Employee from Babcock and Wilcox Company, Alliance, Ohio

Control and safety devices for the system include the following:

- (1) pressure switch and gage to control the boiler heater and system pressure,
- (2) pyrometer temperature controls for the superheat section furnaces, and
- (3) a rupture disc for safety pressure release.

Auxiliary items of equipment are: (1) a gas analysis system (to assay the quantity of hydrogen and oxygen in the superheated steam), (2) a water feed pump, and (3) an electrolysis system to produce hydrogen and oxygen by means of the dissociation of a portion of the water in the boiler.

Some dimensions and specifications of the apparatus are: over-all height, 51 inches; boiler section, 5 inches OD by 18 inches long, wall 0.4 inch; superheat section, $2\frac{1}{2}$ -inch schedule 160 pipe $27\frac{1}{4}$ inches long; maximum operating pressure, 1500 psi, with a cold hydrostatic test to 2500 psi; maximum operating temperatures of 315 C and 565 C for the boiler and superheat sections, respectively.

While not a part of the present design, consideration is being given to the addition of a balance to sense the weight change continuously as a function of time. The nature of the apparatus would require a totally enclosed sensing system and several designs of that type are now under consideration.

V. ANALYTICAL RESEARCH AND SERVICES

Applications of the methods of neutron activation, giving fundamental principles, limitations, and recent advances, are outlined. A gamma index of the nuclides has been prepared, arranging the nuclides by photon energy, by atomic number, and by half-life.

A. Analytical Research and Development (C. E. Crouthamel)

1. Activation Analysis (C. Gatrousis and C. Crouthamel)

A review article describing the fundamental principles, limitations, recent advances, and applications of the method of neutron activation analysis has been completed. Special emphasis has been placed on combining the method with scintillation spectrometry, thus eliminating the tedious, time-consuming chemical separations. A number of techniques based upon the formation of short-lived induced activities are being examined in order to characterize and measure the constituents of several matrix materials.

This article will be submitted to an appropriate journal for publication.

2. Gamma Index (A. Madson)

A gamma index of the nuclides has been printed and a limited number of copies are being distributed prior to publication. The index consists of three sequences: by photon energy, by atomic number, and by half-life. Each entry may contain

- (1) the half-life,
- (2) the characteristic X ray of the decay product,
- (3) up to six photon energies with their respective intensities or conversion ratio, and
- (4) the active daughter.

In the sequence by photon energy, a nuclide with six gamma rays appears at six different locations with a different energy value in the sorted column of photon energies. It is expected that this index will be useful as an aid in the rapid identification of the nuclides using scintillation counters.

VI. ROUTINE OPERATIONS (H. G. Swope)

A. Waste Processing

(H. G. Swope, J. Harast, B. Kullen, K. Bremer, R. Juvinall, C. Ryberg)

Radioactive liquid wastes processed from April through June, 1959, were as follows:

<u>Processing Method</u>	<u>Material Processed (gel)</u>
Evaporation and Concentration	21,500
Filtration	2,700
Cation Exchange	2,700
Absorption on Vermiculite	450
Neutralization	200
Total	<u>27,550</u>

B. High-level Gamma-Irradiation Facility

(H. G. Swope, J. Harast, J. Gates, N. Ondracek, and F. Testa)

Data for samples irradiated in Rack M-1 during April, May, and June, 1959 are given in Table 43. In addition there were 24 dosimetry samples or one dosimetry urn unit in Rack M-2 during this quarter.

The special problem of rotating an urn in the field was solved by a method in which a submersible pump was used to form a jet which turned an urn on a roller-bearing base.

Rack M-1 was brought up for repair in May. The assembly was repaired, cleaned, and returned to use.

Table 43

SUMMARY OF IRRADIATIONS PERFORMED IN RACK M-1 DURING APRIL, MAY, AND JUNE, 1959

<u>Month</u>	<u>No. of Samples ^a</u>	<u>No. of Special Dosimetry Samples</u>	<u>Total Urn Units ^b</u>		<u>Special Handling, Man-hours</u>
			<u>Day</u>	<u>Night</u>	
April	687	457	1154	1835	21.5
May	308	262	598	1087	19.0
June	<u>796</u>	<u>392</u>	<u>1536</u>	<u>2926</u>	<u>21.0</u>
Totals	1791	1111	3288	5848	61.5

^a Equivalent to a No. 2 ($3\frac{7}{16}$ inch diam x $4\frac{9}{16}$ inch high) can.

^b One urn unit = 2×10^6 r.