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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

July, August, September, 1959

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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

July, August, September, 1959

SUMMARY

I. Chemical-Metallurgical Processing (pages 18 to 87).

A direct-cycle pyrometallurgical plant is being designed in conjunction with the Experimental Breeder Reactor No. II (EBR-II). The plant complex also includes a Laboratory and Service Building, construction of which is nearly complete.

Chemical-metallurgical methods, including melt refining, liquid metal extraction and processes involving fractional crystallization 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" described in the previous quarterly report (ANL-6029, page 16). The contract for construction "Package 3" was awarded to Diversified Builders, Inc. of Paramount, California, on a bid of \$3 475,000. Ground was broken for the Fuel Cycle Facility on July 30, 1959.

The fabrication of the five-ton cranes for the Argon and Air Cells is being held up by a strike at Paceco's plant. A number of manufacturers have expressed interest in bidding on the eight operating manipulators to be installed in the Fuel Cycle Facility. Bids on the crane and manipulator control system have been received and are being evaluated. The search for a better lubricant than molybdenum disulfide has led to the testing of Shell APL radiation-resistant grease which shows promise. Alternate bearing materials are also being examined. The manipulator-carriage lifting beam was successfully tested in the mock-up area. This tool makes it possible to use the blister hoist to remove and replace a manipulator carriage.

Various components for the Fuel Cycle Facility process cell are being designed and tested. Window fabrication is proceeding on schedule.

In continuing tests of radiation stability, white fluorescent-type mercury vapor lamps proposed for cell lighting are demonstrating very favorable resistance to gamma darkening.

The balance of the equipment required to demonstrate remote operation of the melt-refining process has been installed and is being operated.

A study of the melt refining of 20 per cent plutonium-uranium-"fissium" alloys indicates that the process, as developed for uranium-"fissium" alloys, can be applied to alloys containing substantial amounts of plutonium without incurring excessive preferential loss of plutonium to the dross.

A further study is reported of the reaction in a melt-refining furnace between zirconia and graphite to produce carbon monoxide.

The presence of an oxide film on the surface of spent fuel pins may cause complications in melt refining, by causing incomplete uranium coalescence. Dipping of oxide-coated uranium pins in reducing alloys generally reduces or displaces the coating, but difficulties in pin drainage and in equipment design have prompted investigation of other approaches. Good pin coalescence was achieved by arc melting, but the feasibility of such a process for remote operation has not been established. With the completion of a dry-box assembly for pin decanning, runs can also now be made without exposing sodium-coated pins to air, thus enabling a more accurate assessment of this problem.

A duplicate of the melt-refining crucible-coil assembly has been constructed for thermal and material tests, the goals of which include decreasing heat losses, lowering the uncooled induction coil temperature, improvement in crucible reliability, and selection of compatible materials.

Work has been started on a demonstration of the melt-refining process at typical activity levels. Another program involves development work on a "dragout" process for the recovery of uranium from melt-refining slags.

Experiments on the nitriding rates of melt-refining slags imply that significant nitride formation will occur if they are stored in a cell atmosphere containing a few per cent nitrogen.

The slag can be removed from the zirconia crucible relatively easily by oxidizing it to U_3O_8 and the corresponding fission product oxides. The resulting material is in the form of a fine powder.

Uranium is recovered from the oxide powder by contacting it with a zinc or cadmium solution containing about 2 weight per cent magnesium. Cadmium is preferred at the present time, as it is less corrosive to common materials of construction.

Work was continued on development of processes for isolation of plutonium from EBR-II blanket material. No plutonium depletion from magnesium-rich cadmium solutions by interaction with the mild steel container occurred in 7- and 15-hour runs at 650 C.

The major areas of work connected with the development of engineering techniques and equipment for liquid metal processes are distillation and retorting, solid-liquid phase separations, materials handling, and testing of materials of construction.

Design and drafting of a full-scale distillation unit is almost complete. Having a capacity of perhaps as much as 100 kg of cadmium per hour, the unit will be used to study and demonstrate distillation operations on a practical scale.

Runs simulating recovery of plutonium (using cerium as a stand-in) from magnesium-rich cadmium solutions by distillation of the cadmium and magnesium have been very successful.

In one dragout process scheme now being considered, uranium metal is precipitated by concentrating the metal solution in magnesium. This concentration is effected by distilling cadmium away from a dilute magnesium-cadmium alloy. Several fission products, including rare earths and possibly zirconium, are expected to concentrate and be removable in the magnesium-rich supernate. In recently completed distillation experiments, essentially 100 per cent of the cerium, 80 to 90 per cent of the zirconium and less than 2.2 per cent of the uranium remained in solution. These results show the possibility of high uranium recovery and good separation from several important fission products.

In connection with the experiments described in the preceding paragraph, removal of the magnesium-rich cadmium solution from the precipitated uranium (~100 grams) was effected by pressure siphoning through porous graphite. Several ~8-kilogram-scale runs were made in which material insoluble in cadmium (magnesium and uranium oxides) was removed by pressure siphoning through porous graphite and sintered stainless steel filter media.

A mild steel loop in which was circulated a cadmium-2 per cent uranium-0.2 per cent magnesium alloy at 500 C for 1000 hours has been sectioned and is undergoing metallographic examination. No signs of significant corrosion are evident. The uranium concentration remained constant during the operation of the loop.

Thousand-hour dynamic capsule corrosion tests of 2 to 10 per cent zinc-cadmium solutions at 375 C showed readily detectable corrosion only by the 10 per cent zinc system. Closer examinations for corrosion in the other systems are being made.

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:

$$\begin{array}{ll} \text{Ba in Cd (383 to 560 C)} & \log (w/o \text{ Ba}) = 6.810 - (5635/T) \\ \text{Sr in Cd (325 to 524 C)} & \log (w/o \text{ Sr}) = 6.717 - (4873/T) \\ \text{Pd in Zn (434 to 850 C)} & \log (a/o \text{ Pd}) = 4.055 - (3226/T) \end{array}$$

The eutectic temperature in the zirconium-zinc system was found to be 419.5 ± 0.2 C.

Additional determinations of the solubility of uranium in cadmium above the peritectic temperature for UCd_{11} confirm the retrograde character of the solubility curve.

Additional data on the solubility of uranium in cadmium-zinc and in cadmium-magnesium liquid alloys have been obtained.

Preliminary results on the partition of uranium between liquid cadmium and aluminum show that uranium is almost quantitatively extracted into the aluminum.

Galvanic cell measurements on the activity of uranium in liquid cadmium solution have revealed that these solutions depart significantly from Henry's law. The quantitative relation $\log \gamma = \log \gamma_0 + AN_U$ is found to fit the data.

Combustions of molybdenum in oxygen have been carried out; these have given values for the heat of formation of MoO_3 in substantial agreement with literature data determined under less favorable conditions.

Apparatus for charging and discharging the bomb and apparatus for supporting studies in fluorine bomb calorimetry are being consolidated in a large vacuum frame hood. A few more determinations of the heat of formation of molybdenum hexafluoride and the study of the heat of formation of zirconium tetrafluoride await completion of the new bomb charging system. Preliminary studies of techniques for determining the heat of formation of boron trifluoride have been directed toward finding a suitable means of separating the boron sample from fluorine previous to intentional ignition of the sample.

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (pages 88 to 126).

The volatility of uranium hexafluoride is used as a basis for several schemes for processing irradiated fuels. Three such schemes: the Fused Fluoride Volatility Process, the Aqueous Dissolution Fluorination Process, and a Direct Fluorination Process, are being examined. Many steps of these schemes involve the use of fluidization techniques.

A process is being developed for the direct fluorination of ceramic fuels containing uranium oxide. Reaction rates, much lower than those obtained for the fluorination of UO_2 , have been obtained for the fluorination of uranium in experimental ceramic fuels of the type $\text{CaO-ZrO}_2\text{-UO}_2$.

Additional values of the equilibrium constant have been obtained for the reaction

at 200, 250 and 350 C.

Development of a fluid-bed volatility process for the recovery of uranium from low-uranium-Zircaloy-2 fuel alloys continued. The process involves aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry fluidizable powder and fluid-bed fluorination of the material to remove and recover the uranium as the volatile uranium hexafluoride. Very reliable operation of the 6-inch diameter fluid-bed dryer was achieved in runs of 36 and 54 hours using the newly designed spray nozzle. Synthetic feed solutions containing the equivalent of a 2 weight per cent uranium alloy and a high fluoride content ($\sim 14 \text{ M}$) were fed at rates up to 140 ml/min (for 18-inch bed height). Runs made at temperatures of 240, 300 and 350 C produced 4.4 lb/hr of dry zirconium-uranium fluoride powder. The use of an auxiliary attrition air jet and an oversize air annulus on the atomizing side of the feed nozzle limited particle growth during calciner operation.

Particle hardnesses of fluid-bed process materials as determined by a standardized attrition test are being investigated as a means of evaluating the particle-growth problem associated with calciner operation.

Stable zirconium fluoride feed solutions of a concentration higher than heretofore thought possible ($> 3.5 \text{ M Zr}$) have been prepared from the dissolution of both zirconium metal turnings and zirconium tetrafluoride in the proper amounts of 48 per cent hydrofluoric acid and water. The composition corresponds to 30 per cent hydrogen fluoride, 30 per cent zirconium oxide and 40 per cent water.

A study made in a $1\frac{1}{2}$ -inch diameter fluid-bed reactor of the reaction between zirconium tetrafluoride and air-steam-hydrogen fluoride mixtures simulating dryer atmospheres showed that no significant reaction occurs at 300 C with volatilized 10 M and 28 M hydrogen fluoride feeds or at 350 C with 28 M feed. The reaction at 300 C with volatilized 1 M hydrofluoric acid causes pyrohydrolysis and results eventually in the formation of zirconium oxide.

The statistical program used for fluid-bed fluorination experiments was completed. Preliminary evaluation of the data indicates reaction temperature is the most significant variable. Factors affecting uranium removal at temperatures of 600 C or below, such as pretreatments (hydrofluorination or low temperature fluorination), particle size, or zirconium matrix, become negligible at temperatures greater than 650 C, at which complete uranium removal is effected. The best removal achieved to date at 600 C with the currently produced dryer products is about 95 per cent. Previously, 98 per cent removal had been achieved at this temperature with higher (5 to 10 per cent) uranium alloy feeds.

Since corrosion of the nickel fluorinator at temperatures exceeding 600 C may be limiting, an alternative method of fluorinating involving screw-feeding the powder directly into an inert bed sustained at a high temperature (500 to 600 C) with a 100 per cent fluorine gas stream is being explored. The exothermic reactions involved should heat the feed particles to over 650 C. Preliminary runs at bed temperatures of 500 and 550 C and average residence time of 20 minutes gave results comparable to earlier six-hour batch runs, 75 and 85 per cent uranium removal, respectively.

Static corrosion experiments conducted in fluorine at 675 C in the presence of nonfluidized zirconium tetrafluoride indicate Monel is severely attacked dimensionally, while "A" nickel shows reasonable corrosion resistance. Monel showed essentially no intergranular attack. Tests on recrystallized alumina at 650 C showed no dimensional changes, but some weight gains were noted.

Further laboratory-scale studies on the fluorination of fluid-bed dried solids of high zirconium concentration indicates that temperatures in excess of 600 C are needed for complete uranium removal in less than 30 minutes from the experimental samples. Pretreatment of the solids with hydrogen fluoride prior to fluorination has a negative effect on the removal of uranium. Grinding of the solids by "ball milling" had an enhanced effect on the removal of uranium from some of the samples and little effect on others.

In studies of the Fused Fluoride Volatility Process during the present period three zirconium dummy fuel elements were dissolved in the graphite, pilot-plant dissolver. The dissolutions, carried out at 600 C,

showed the highest dissolution rate at the highest sparge rate tried: 30 lb HF/hr. The highest average dissolution rate for complete dissolution corresponded to 4.1 mils/hr or 1.1 mg/(sq cm)(min).

No difficulties with the heaters or other graphite components appeared in these operations, in which the dissolver was held at temperature continuously for a period of about 3 weeks. A partial transfer of fused salt out of the dissolver was carried out under complete control to a predetermined level. At higher salt levels and sparge rates, splashed or entrained salt deposited at the off-gas connection to the dissolver head, causing plugs. These were broken out mechanically without shutting down completely. An auxiliary heater for removing this deposited salt by melting will be installed and tested.

A preliminary test of the electrolytically heated frozen-wall fluorinator was carried out. A 38-inch deep batch of salt was initially melted with resistance heaters contained in the electrodes, and the salt was held molten continuously by electrolytic heating for over a week. The frozen salt wall thickness measured between 1 and 1.5 inches over nearly 80 per cent of the liquid depth. The salt thickness was 5 inches at the bottom in these tests.

A series of runs on the fluid-bed calcination of synthetic Purex process waste has shown that lump formation can be avoided by the use of a new nozzle design, and particle growth can be controlled by the use of an attrition jet. The addition of sugar (about 1 lb/gal) to the waste solution resulted in a more friable solid product, which was easily fractured by the attrition jet. Successful runs up to 30 hours in duration were completed. The calcined solids had bulk densities in the range from 0.9 to 1.5 g/cc.

Installation of a 3-inch diameter Monel reactor for additional studies of the one-step fluid-bed process for conversion of uranium hexafluoride to uranium dioxide with steam and hydrogen was essentially completed. The preliminary experiments performed in the 1½-inch reactor are summarized in a topical report, ANL-6023.

III. Reactor Safety (pages 127 to 158).

The investigation of the factors which influence the pyrophoricity of uranium and zirconium have been complemented with a study of fundamental kinetics of oxidation. Previous research in the 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.

In the continuing study of ignition and burning of uranium and zirconium, more emphasis is being placed on the burning process. Some effort has been devoted to establishing the relationship between rate of burning propagation and dimensions of cross section, using foil strips and wires.

The continuing study of the rates of burning propagation of zirconium has included investigations of additional alloy foils, i.e., additives of hafnium, chromium, nickel, beryllium, iron, tantalum, uranium, and vanadium. The previously reported linear relationship between length of burning zone and propagation rate also has been found to be applicable to these alloys.

A phototube pyrometer has been developed, calibrated, and used to obtain temperature traces as the ignition proceeds along the 0.13-mm thick foil strips. The maximum burning temperatures observed were as follows: for zirconium 1620 (in air) and 2900 (in oxygen); for uranium 1460 (in air) and 2150 C (in oxygen). Studies of the temperature profiles of burning zirconium foil strips with the phototube pyrometer show that the maximum burning temperature is (1) increased by additives which cause increased propagation rates, (2) decreased by increased cross-sectional area, and (3) decreased by decreased oxygen content of the gas.

From preliminary burning-propagation experiments completed on a plutonium alloy foil in air and in oxygen, it can be concluded that (1) useful data can be obtained from plutonium and plutonium alloy foils and (2) the burning behavior is similar to that of uranium. The apparatus for obtaining plutonium-burning curves and performing shielded ignitions has been partially tested, modified, and moved into the glove boxes.

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. A second laboratory-scale method involves the rapid contact of steam with a crucible containing molten metal.

An analysis on the analog computer of the data from runs with zirconium was described in the previous quarterly report, ANL-6029, page 126. Data from runs with finer zirconium wires were obtained and found to agree with the analysis provided the activation energy of the reaction is 28 kcal/mole or greater.

The experiments in CP-5 to verify the techniques to be used in the metal-water experiments in TREAT were completed; the maximum pin temperature attained was 405 C. The analog computer study of metal-water reactions initiated by nuclear reactor transients was completed. Four autoclaves were readied for the first series of tests in TREAT.

IV. Reactor Chemistry (pages 159 to 164).

The Reactor Decontamination Program is a cooperative one with the Reactor Engineering Division. It results from concern over the consequences of a fuel rupture in a boiling water reactor system and will endeavor to answer the questions: How serious is a fuel rupture? What are the magnitudes and distributions of fission products in the vapor phase of the system? What methods are available for removing such deposited activities?

A loop simulating the operation of a boiling water reactor has been installed in a shielded cell. The first run with activity (yttrium-90 tracer) has been completed, the pressure being 600 psi and the steam rate 0.36 ft per second. Activity deposited on a stainless steel sample strip was monitored with a beta-gamma probe and by direct counting. The maximum disengaging factor* between liquid and vapor was 4.4×10^3 .

Laboratory studies on the cleanup of contaminated surfaces showed that somewhat lower decontamination factors were obtained when temperatures and concentrations of reagent used in the alkaline-permanganate procedure were reduced.

V. Routine Operations (page 165)

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

*Disengaging factor is defined as the ratio of activity in the liquid phase to that in the steam phase. This factor is often called a decontamination factor in the literature but is not so called herein to avoid confusion with the "decontamination factors" reported, which are the ratios of activities on solid surfaces before and after various chemical treatments.

I. CHEMICAL-METALLURGICAL PROCESSING

A direct-cycle pyrometallurgical plant is being designed in connection with the Experimental Breeder Reactor No. II (EBR-II). The plant complex also includes a Laboratory and Service Building, construction of which is nearly complete.

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

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The fabrication of the five-ton cranes for the Argon and Air Cells is being held up by a strike at Paceco's plant. A number of manufacturers have expressed interest in bidding on the eight operating manipulators to be installed in the Fuel Cycle Facility. Complete information will be furnished to bidders sometime in October, so that they can finalize their proposals. Bids on the crane and manipulator control system have been received and are being evaluated. The search for a better lubricant than molybdenum disulfide has led to the testing of other lubricants, including Shell APL radiation-resistant grease. Alternate bearing materials are also being examined. The manipulator-carriage lifting beam was successfully tested in the mock-up area. This tool makes it possible to use the blister hoist to remove and replace a manipulator carriage.

Various components for the Fuel Cycle Facility process cell are being designed and tested. A Goodrich polyvinyl chloride gasket material type "C-2S," being substituted for Koroseal 116 in both the process cell shielding windows and in the Junior Cave windows in the Laboratory and Service Building, has shown superior radiation resistance properties. Window fabrication is proceeding on schedule.

Bid specifications and drawings for luminaires and wall mounts of cell-lighting installation are in the hands of prospective bidders. In continuing tests of radiation stability, white fluorescent-type mercury vapor lamps are demonstrating very favorable resistance to gamma darkening.

A 100-hour wear test (corresponding to about one year of operation in the Fuel Cycle Facility) on the Eemco motor was completed. Maximum brush wear was 0.116 inch, which is close to the allowable maximum.

The operating manipulator was disassembled and greased with Shell APL radiation-resistant grease. Certain changes were made in mechanisms to improve performance. The machine has now been rebuilt and is back in operation.

The balance of equipment required to demonstrate remote operation of the melt-refining process has been installed. This equipment, along with the Mark V furnace, forms the complete processing unit. The unit was tested and proved satisfactory. That part of the equipment which is within the cell area was removed and replaced remotely using the operating manipulator.

Design and procurement of equipment for the Laboratory and Service Building and the Fuel Cycle Facility continues.

A study of the melt refining of 20 per cent plutonium-uranium-"fissium" alloys indicates that the process, as developed for uranium "fissium" alloys, can be applied to alloys containing substantial amounts of plutonium without incurring excessive preferential loss of plutonium to the dross.

A further study is reported of the reaction in a melt-refining furnace between zirconia and graphite to produce carbon monoxide (first reported in ANL-5996, page 45). The purposes of the study were to determine the extent to which the reaction rate would subside with time and the magnitude of the effect on the rate of evolution of carbon monoxide of absorbed oxygen or water resulting from previous exposure of the system to air. The reaction rate at 1700 C decreased only slightly over 17 hours. Over the last 11 hours it remained essentially constant at 3.0 to 3.2 cc of carbon monoxide per sq cm of reaction area. The effect of air exposure was not significant.

The presence of an oxide film on the surface of spent fuel pins may cause complications in melt refining, by causing incomplete uranium coalescence. Dipping of oxide-coated uranium pins in reducing alloys generally reduces or displaces the coating, but difficulties in pin drainage and in equipment design have prompted investigation of other approaches. Good pin coalescence was achieved by arc melting, but the feasibility of such a process for remote operation has not been established. With the completion of a dry-box assembly for pin decanning, runs can also now be made without exposing sodium-coated pins to air, thus enabling a more accurate assessment of this problem.

A duplicate of the melt-refining crucible-coil assembly has been constructed for thermal and material tests, the goals of which include decreasing heat losses, lowering the uncooled induction coil temperature, improvement in crucible reliability, and selection of compatible materials.

A new research group has been organized to undertake the laboratory-scale development of processes aimed specifically at the EBR-II fuel cycle. Two main programs are currently being pursued by this group. One consists of reviewing the information available to date on melt refining to determine whether or not further chemical studies are necessary. Work has also been started on a demonstration of the melt-refining process at typical activity levels, using uranium-"fissium" alloy irradiated to approximately one per cent burnup. The other program involves development work on a "dragout" process for the recovery of uranium from melt-refining slags and the removal of fission products so as to maintain a suitable "fissium" composition in the recycled fuel.

Experience with the melt-refining process had indicated that the metallic uranium recovery will fall in the vicinity of 90 per cent. The remaining 10 per cent is retained in the zirconia crucible in the form of a "skull," which consists of a mixture of uranium and fission product metals and oxides. Experiments on the nitriding rates of such skulls imply that significant nitride formation will occur if they are stored in a cell atmosphere containing a few per cent nitrogen. Temperatures in excess of 500 C are anticipated during the storage of skulls, due to fission product decay heat.

The skulls can be removed from the zirconia crucible relatively easily by oxidizing them to U_3O_8 and the corresponding fission product oxides. The resulting material is in the form of a fine powder. "Fissium" skulls have been oxidized successfully using 75 per cent argon - 25 per cent oxygen atmospheres. Some fission product oxides are volatilized during this treatment.

Uranium is recovered from the skull oxide powder by contacting it with a zinc or cadmium solution containing about 2 weight per cent magnesium. Cadmium is preferred at the present time, as it is less corrosive to common materials of construction. Several laboratory experiments were performed on the reduction of molybdenum, cerium, rare earth, zirconium and barium oxides under these conditions. Complete reduction of uranium and "fissium" oxides has not been achieved for reasons which have not yet been determined.

Work was continued on development of processes for isolation of plutonium from EBR-II blanket material. A cadmium solution process, in which the blanket material is dissolved in cadmium, after which the cadmium is partially distilled away in the presence of magnesium, is promising. Plutonium should remain in the magnesium-rich solution while uranium is almost quantitatively precipitated. However, some loss of plutonium from solution did occur in a previous experiment (ANL-6029). The possibility of plutonium depletion by interaction with the mild steel now seems unlikely since 7- and 15-hour runs showed no depletion of plutonium from a 20 per cent magnesium-cadmium solution held at 650 C in mild steel.

The major areas of work connected with the development of engineering techniques and equipment for liquid metal processes are distillation and retorting, solid-liquid phase separations, materials handling, and testing of materials of construction.

Design and drafting of a full-scale distillation unit is almost complete. Having a capacity of perhaps as much as 100 kg of cadmium per hour, the unit will be used to study and demonstrate distillation operations on a practical scale.

Runs simulating recovery of plutonium (using cerium as a stand-in) from magnesium-rich cadmium solutions by distillation of the cadmium and magnesium have been very successful.

In one dragout process scheme now being considered, uranium metal is precipitated by concentrating the metal solution in magnesium. This concentration is effected by distilling cadmium away from a dilute magnesium-cadmium alloy. Several fission products, including rare earths and possibly zirconium, are expected to concentrate and be removable in the magnesium-rich supernate. In recently completed distillation experiments, essentially 100 per cent of the cerium, 80 to 90 per cent of the zirconium and less than 2.2 per cent of the uranium remained in solution. These results show the possibility of high uranium recovery and good separation from several important fission products.

In connection with the experiments described in the preceding paragraph, removal of the magnesium-rich cadmium solution from the precipitated uranium (~ 100 grams) was effected by pressure siphoning through porous graphite. Several ~ 8 -kilogram-scale runs were made in which material insoluble in cadmium (magnesium and uranium oxides) was removed by pressure siphoning through porous graphite and sintered stainless steel filter media.

A mild steel loop in which was circulated a cadmium-2 per cent uranium-0.2 per cent magnesium alloy at 550 C for 1000 hours has been sectioned and is undergoing metallographic examination. No signs of significant corrosion are evident. The uranium concentration remained constant during the operation of the loop.

Thousand-hour dynamic capsule corrosion tests of 2 to 10 per cent zinc-cadmium solutions at 375 C showed readily detectable corrosion only by the 10 per cent zinc system. Closer examinations for corrosion in the other systems are being made.

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:

Ba in Cd (383 to 560 C)	$\log (w/o \text{ Ba}) = 6.810 - (5635/T)$
Sr in Cd (325 to 524 C)	$\log (w/o \text{ Sr}) = 6.717 - (4873/T)$
Pd in Zn (434 to 850 C)	$\log (a/o \text{ Pd}) = 4.055 - (3226/T)$

The eutectic temperature in the zirconium-zinc system was found to be 419.5 ± 0.2 C.

Additional determinations of the solubility of uranium in cadmium above the peritectic temperature for UCd_{11} confirm the retrograde character of the solubility curve.

Additional data on the solubility of uranium in cadmium-zinc and in cadmium-magnesium liquid alloys have been obtained.

Preliminary results on the partition of uranium between liquid cadmium and aluminum show that uranium is almost quantitatively extracted into the aluminum.

Galvanic cell measurements on the activity of uranium in liquid cadmium solutions have revealed that these solutions depart significantly from Henry's Law. The quantitative relation $\log \gamma = \log \gamma_0 + AN_U$ is found to fit the data.

Combustions of molybdenum in oxygen have been carried out; these have given values for the heat of formation of MoO_3 in substantial agreement with literature data determined under less favorable conditions.

Apparatus for charging and discharging the bomb and apparatus for supporting studies in fluorine bomb calorimetry are being consolidated in a large vacuum frame hood. A few more determinations of the heat of formation of molybdenum hexafluoride and the study of the heat of formation of zirconium tetrafluoride await completion of the new bomb charging system. Preliminary studies of techniques for determining the heat of formation of boron trifluoride have been directed toward finding a suitable means of separating the boron sample from fluorine previous to intentional ignition of the sample.

A. EBR-II Fuel Cycle

(J. H. Schraidt and M. Levenson)

1. Design and Construction of Process Auxiliaries and Building

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

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

The contract for construction "Package 3" has been awarded to Diversified Builders, Inc. of Paramount, California, for a bid of \$3,475,000. The award for Bid "Package 3," which consists mainly of the construction of the Sodium-Boiler Plant and the Fuel Cycle Facility, was based on the decision of a board set up by the AEC to evaluate the bids. The Fuel Cycle Facility represents about 60 per cent of the total contract.

Ground was broken for the Fuel Cycle Facility on July 30, 1959. Most of the excavation for the building has been completed and is now proceeding for the footings.

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

The construction of Bid Package 1A, which includes the Laboratory and Service Building, is about 85 per cent complete. The Laboratory and Service Building is approximately 80 per cent complete.

Orders have been placed for most of the equipment components required for the Solidification Cell and Junior Caves, including a purchase order placed with AMF Atomics for 12 Model-8 manipulator arms for use in the Junior Caves.

Installation of components for the hot waste drum filling mock-up is nearly complete. A new Acid Fuming Scrubber has been designed to replace a previous unit which gave only about 50 per cent efficiency during test runs. The new unit includes an AEC filter and is expected to give improved collection efficiency.

c. Cranes and Manipulators
(J. Graae)

Although progress in fabrication of the five-ton cranes is being held up by a strike at Paceco's plant, the engineering continues. Some of Paceco's drawings are not yet complete.

Due to failure of molybdenum disulfide-lubricated mechanisms in the prototype operating manipulator, bearings, lubricants, surface preparations, and bearing and part fits are being investigated. Commercial gear sets and other mechanisms were ordered and will be given an Electrolyzing treatment to produce a hard corrosion-resistant surface which will wear well with little lubrication. The Electrolyzed parts will be tested

for friction and wear both without any lubricant and when coated with molybdenum disulfide. Alternate lubricants are discussed in section e.

Paceco has been advised to Electrolize guide pins for contact brushes and to Electrolize universal joints for the bridge drives of the five-ton cranes. Clutch mechanisms will either be Electrolized or coated with molybdenum disulfide, depending on relative costs.

Completion of work on the drawings of the eight operating manipulators to be installed in the Fuel Cycle Facility is expected in November. Among the items requiring drawing changes are bearing fits, pick-up brush assembly, and brush bars. The changes in fits will be incorporated in the design without rebuilding and retesting, but the other items will require testing on the prototype manipulator in the Processing Mock-Up.

Bids on the crane and manipulator control system have been received and are being evaluated.

d. Process-cell Windows
(T. W. Eckels)

The gasket material for the tank unit of the process-cell windows and also for the oil-laminated Junior Cave windows is being changed from Koroseal 116 to B. F. Goodrich type "C-2S" material because of demonstrated superior resistance to radiation damage when in contact with window oil, which in turn is in contact with lead.*

All the steel process-cell window liners have now been fabricated. Production-line leak testing of the liners for use in the Argon Cell has commenced. The Air Cell window liners are to be shipped to Idaho by the end of September 1959. The Junior Cave windows are scheduled for completion by November 1, 1959.

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

In a search for a suitable lubricant for use in the Fuel Cycle Facility, tests are being conducted with Shell APL grease. This grease was applied to a number of roller bearings and irradiated in the Gamma Facility in an air environment. Considerable stiffening of the grease was noted in the range from 1.3×10^9 to 1.7×10^9 rad. Several bearings were withdrawn before excessive stiffening of the grease occurred and these will be installed in the mock-up manipulator for mechanical testing.

*Tests were made by Remote Control Division

An estimate, based upon the above result, of the useful life of roller bearings lubricated with APL grease in a radiation field corresponding to that expected in the Fuel Cycle Facility (10^5 r/hr) is 1.7 to 2.3 years of operation. It is expected that this estimate will be changed as results from tests now being conducted to appraise the role of an air environment and the rate of irradiation become available. Incomplete tests suggest that grease samples irradiated in the absence of air (corresponding to an argon atmosphere) stiffen less rapidly than samples irradiated in air.

Brush wear tests on the Howard 1/10-hp dc motors and the Eemco 1/4-hp dc motors are continuing. Considerable difficulty is being encountered in obtaining low moisture content in the argon atmosphere of the test assemblies. This is due primarily to the relatively low purge rate which can be maintained using tank argon as a source. A 100-hour running test (approximately equivalent to one-year cell life) was completed on the Eemco motors using brush #P5707.* During this time, moisture in the test atmosphere varied from ~30 ppm cold and 100 ppm hot to 10 ppm cold and 30 ppm hot. Maximum brush wear was 0.116 inch, which was close to the maximum allowable. A slightly longer brush might have lasted twice as long.

Irradiation tests have shown that the rubber tape samples and MI cable samples with standard end seals have broken down to the point where their use would be objectionable. Total accumulated dose to date is 6.5×10^9 rad. The samples using ceramic end seals have been irradiated to 4.8×10^9 rad with some decrease in insulation resistance (>200 megohms to a minimum of 15 megohms). When the ceramic portion was cleaned with acetone, most of the decrease in insulation resistance was removed. Figure 1 shows MI cable terminations that will be used in the Fuel Cycle Facility.

Asbestos-covered alloy wire has been included in irradiation tests. With a total accumulated dose of 1.1×10^9 rad, all samples have retained their original insulation resistance of greater than 200 megohms.

Samples of heat-resisting aluminum paints and Steelkote, a stainless steel coating, have been irradiated to 1.1×10^9 rad. The aluminum paint samples show no visible change in properties or color, while the Steelkote samples are somewhat discolored.

*Carbone Corporation

Figure 1

TYPICAL TERMINATIONS OF ALL MI CABLES IN AND OUT OF THE ARGON OR AIR CELLS

f. Transfer of Cell Equipment
(G. Bernstein, J. Graae)

Proposals received from five companies for design and fabrication of equipment to transfer material between the air cell and Argon Cell lock are being examined, and selection of a vendor will be made shortly.

2. EBR-II Fuel Processing Mock-up

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

All bearings of the prototype operating manipulator which previously were coated (sprayed) with molybdenum disulfide have been cleaned and packed with Shell APL radiation-resistant grease. An eccentricity in the rotating tube assembly has now been corrected. The extended arm of the assembly now rotates nearly perfectly (1/16-inch off center) and can be used for screwing and unscrewing bolts, nuts, etc.

The hoist drum assemblies seized because of flaws in the design, dimensioning and mechanical execution. These have been corrected.

On reassembly of the grip drive after cleaning and lubricating with APL grease it was found quite difficult to readjust the magnetic clutch armature. It was also unacceptably difficult to remove and replace the motor-drive unit; the unit was therefore redesigned for the eight manipulators for Idaho.

The Timken tapered roller bearings had originally been installed with no end play, since this is most advantageous for the gearing. Also, where possible, bearing races have been mounted with interference fits, according to Timken and standard handbook recommendations. However, on both counts this seems to have caused trouble. The absence of play in the bearings undoubtedly contributed to their freezing when they were lubricated with molybdenum disulfide and the interference fits have caused faulty installation of bearings. Since the bearings are oversized and rotate at low speed, slip fits are permissible. All drawings are being revised to reflect this design philosophy.

The brush assemblies which transfer the power from the bridge bus bars to the manipulator carriage were inspected. Considerable brush wear and damage were observed. Further inspection showed poor alignment of brushes and bus bars. A brush life of six months is estimated, whereas bus bar life is estimated to be 25 years. Different brush materials and designs will be tested.

A requisition has been issued to purchase a General Mills standard articulated arm only, without carriage or telescoping tubes, for attaching to the prototype manipulator. Drawings are being prepared to cover the additional controls required.

A five-ton auxiliary trolley with motorized hoist and trolley drive is being designed. This trolley will be used for general handling purposes and will be capable of lifting the manipulator carriage and lowering it to a position in front of the viewing window. The drawings have been completed and are being checked.

The manipulator-carriage lifting beam was completed and successfully tested in the mock-up area. The beam was used for lifting the carriage off the bridge, lowering it to the floor and again lifting it and placing it on the bridge (see Figure 2). Positioning of the carriage under the blister in the Argon Cell will probably require mirrors or periscopes.

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

The further production of fuel alloy ingots for EBR-II core loading was temporarily suspended because of manipulator repair work and the installation of auxiliary equipment in the furnace area. Both of these jobs have been about completed and ingot production should resume during the next quarter. Ingot production, however, is still well ahead of schedule.

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

The Mark-V furnace and auxiliary equipment will form a processing mock-up unit to demonstrate remote operation and control of the melt-refining process. Most of this equipment has now been installed and tested.

The mock-up of the Argon Cell service slot was installed in a position simulating its location in the Argon Cell. The bell jar storage rack was positioned from guides in the service slot. After initial installation, removal and replacement of the furnace base were carried out remotely with the operating manipulator. Figure 3 shows the relative positions of the service slots, service jumpers, and furnace base.

The melt-refining furnace was hooked to the new motor-generator power source through a high-frequency transmission line

Figure 2

MANIPULATOR CARRIAGE REMOVAL:
CARRIAGE LIFTED FROM BRIDGE

Figure 3

FURNACE AND SERVICE JUMPER

simulating the one to be used in the Idaho plant installation. With the furnace on, the voltage drop from the source to the furnace coil was about 40 per cent of the voltage output of the source. Two-thirds of the drop occurred in the flexible jumper system. The conductors in the jumper system are being reworked to lower the impedance of that part of the circuit.

The installation of the panelboard and pressure control system was completed. The furnace was then put into operation remotely from the panelboard. The control system performed satisfactorily. Furnace pressure was maintained within the desired limits on both the heat-up and cooling cycle. Minor changes are being made in the panel-board wiring to add safety features. When these minor jobs are finished, the unit will be used for the production of fuel alloy ingots for EBR-II.

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

Bid specifications and drawings for the luminaires and wall mounts utilizing 1000-watt mercury vapor lamps are now in the hands of prospective bidders.

Gamma radiation-stability tests on lamp bulbs of interest have continued. One 175-watt white fluorescent mercury vapor lamp has retained 80 to 85 per cent of its initial light intensity after 1×10^9 rad (water) of gamma exposure. Table 1 gives a comparison of the light outputs at various integrated gamma exposures of three lamps. The lamps were normally operated continuously while in the gamma field. Figure 4 is a photograph of the various lamps used in this test program.

Table 1

COMPARISON OF LIGHT OUTPUT AT VARIOUS INTEGRATED
GAMMA EXPOSURES FOR THREE LAMPS

	Light Output after Irradiation - % of Original Intensity		
	Lamp Type		
Gamma Exposure (Rad)(Water)	175-Watt White Fluorescent ASA Code - H22KF/W		400-Watt Clear Glass Envelope ASA Code - H25HC
	Lamp A	Lamp B	
1 x 10 ⁶	98	98 ^b	95
1 x 10 ⁷	98	98	88
1 x 10 ⁸	97	97	60 - 65
2 x 10 ⁸	97	97	60 - 65
5 x 10 ⁸	97 ^a	97	60 - 65
8 x 10 ⁸	-	85	60
1 x 10 ⁹	-	83-5	50

^aLamp A failed due to cracked outer envelope resulting from accidental rough handling at the end of this run.

^bLamp B was accidentally irradiated while turned off for two short periods near the beginning of the test.

Figure 4

MERCURY VAPOR LAMPS USED IN GAMMA RADIATION-STABILITY TESTS

Lamp A - ~40 hr irradiation after failure
 B - after 1×10^9 rad (water)
 C - control not irradiated

Lamp C-2 - after 2.6×10^8 rad (water)
 C-4 - after 1×10^9 rad (water)
 C-1 - control not irradiated

175 WATT WHITE FLUORESCENT
 MERCURY VAPOR LAMPS

400 WATT MERCURY
 VAPOR LAMPS

The 175-watt lamp uses the same materials of construction and the same fluorescent coating as the 1000-watt lamp specified for cell lighting. Operating temperature of the outer envelope varies from 370 to 400 C for all wattages, for 100 through 1000-watt sizes. It would appear that perhaps the fluorescent coating has a beneficial effect in preventing or delaying darkening of the glass. From visual inspection it appears that for Lamp B it is the quartz arc tube which is darkening.

3. Melt Refining (R. K. Steunenberg, L. Burris, Jr.)

The melt-refining process consists of melting discharge 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 vaporization and selective oxidation reactions.

a. Melt Refining of Uranium-Plutonium - "Fissium" Alloys (V. G. Trice, W. H. Spicer)

A study has been conducted on the melt refining of uranium-plutonium-fissium alloys. The purpose of this investigation was presented in ANL-5996, page 40. It was desired to determine if melt refining in zirconia crucibles of uranium alloys containing substantial (20 weight per cent) amounts of plutonium would result in prohibitively large plutonium losses. It was also desired to determine the effect, if any, of the presence of large amounts of plutonium on rare earth removals and the effect of carbide slagging for zirconium removal on plutonium losses.

The results of this work show that there was a slightly preferential retention of plutonium in the melt-refining dross. The amount of plutonium retained in the dross is sufficient to require its recovery during the processing of melt-refining skulls. The presence of plutonium had no significant adverse effect on cerium removals. The addition of carbon to promote zirconium slagging had no adverse effect on plutonium recoveries.

The nominal composition of the alloy employed was as follows:

<u>Element</u>	<u>Weight Per Cent</u>	<u>Element</u>	<u>Weight Per Cent</u>
U	70.38	Rh	0.60
Pu	20.00	Pd	1.39
Mo	3.15	Zr	0.40
Ru	3.48	Ce	0.60

Approximately 2-kg batches of alloy were melt refined by liquation at 1300 or 1400 C for 3 or 5 hours in zirconia crucibles. Melt temperatures were reduced to 1200 C before pouring into a graphite-coated copper mold. Sample chips were obtained by drilling into the side of the ingot. Carbon for carbide slagging experiments was provided by painting the interior of the crucible with an organic suspension of graphite.

The experiments were performed in two series. In each series the product from one run was used as the charge for the subsequent run. The terminal run in each series was used to study carbide slagging of zirconium. Cerium, the most reactive constituent of the alloy, was added with each charge. Six sample drillings were obtained, two each from the top, middle, and bottom of each product ingot. These samples were analyzed individually.* For a given ingot no correlation between alloy composition and sample source was evident. Therefore, for the purpose of data evaluation the ingots were presumed to be homogeneous. The variability in analyses was taken as a measure of the precision of the analytical technique. Plutonium compositions given in Table 2 reflect this variability. The methods of small-sample statistics¹ were employed to provide values at the 95 per cent confidence level.

The most important conclusion evident from the data appearing in Table 2 is that the ratio of plutonium to uranium in the oxide dross is slightly greater than that in the melt. Other conclusions are that the addition of carbon for zirconium scavenging and the choice of liquation temperature (1300 or 1400 C) have no significant effect on this ratio. Considering the overall figures for each series, the purified metal has a lower plutonium concentration than the charge material by 0.80 gram of plutonium per 100 grams of alloy after 8 hours of liquation and 0.94 gram of plutonium per 100 grams of alloy after 11 hours of liquation. The average value for the plutonium depletion of the purified metal based on the five experiments is, at the 95 per cent confidence level, 0.51 ± 0.38 per cent of the charge concentration per hour of melt refining at 1300 or 1400 C.

*Analyses performed by C. A. Seils, Jr.

¹Villars, D. S., Statistical Design and Analysis of Experiments for Development Research, Wm. C. Brown and Co., Dubuque, Iowa, 1951.

Table 2

PLUTONIUM DEPLETION IN MELT REFINING
URANIUM-PLUTONIUM "FISSION" ALLOYS

Series	Run	Conditions		Pu Conc, w/o ^a		Depletion (Difference between means)
		Time (hr)	Temp (C)	Charge	Product	
A	1	3	1300	18.97 ± 0.24	18.55 ± 0.31	0.42
A	2	5	1300	18.55 ± 0.31	18.47 ± 0.18	0.08
A ^b	3	3	1400	18.47 ± 0.18	18.03 ± 0.08	0.44
A	Overall	11	1300 or 1400	18.97 ± 0.24	18.03 ± 0.08	0.94
B	1	3	1400	19.53 ± 0.41	19.05 ± 0.24	0.48
B ^b	2	5	1400	19.05 ± 0.24	18.73 ± 0.27	0.32
B	Overall	8	1400	19.53 ± 0.41	18.73 ± 0.27	0.80

^aData are presented at the 95 per cent confidence level.

^bCarbon was added in these runs for zirconium scavenging.

Cerium removals were satisfactory, being comparable to those realized in processing uranium "fission." Cerium, as representative of rare earth constituents of irradiated fuel, was added with each charge. Samples from two runs were analyzed for cerium. Removals were 90.7 per cent in Serial A-1 and 96.4 per cent in Serial A-2.

Anomalous behavior of zirconium was noted. Carbide slagging has been demonstrated as a feasible method for reducing the zirconium concentration of uranium "fission." Carbon was added as a crucible coating in Serials A-69 and B-70. No zirconium removal was noted in the former but a 33 per cent removal was obtained in the latter. Additional experiments are indicated if future processing requirements demand an appraisal of carbide slagging.

Recoveries of purified uranium-plutonium-"fission" cast ingots were between 88.6 and 90.8 per cent. By comparison, a run in the same equipment in which uranium-10 per cent "fission" was liquated for 3 hours at 1400 C gave a recovery of cast purified metal of 90.2 per cent.

b. Carbon Monoxide Formation in Zirconia-Graphite Systems
(N. R. Chellew, J. Schilb)

A factor in the design of melt-refining equipment for processing EBR-II fuel is the amount of carbon monoxide that may form due to the high-temperature interaction of graphite susceptors with the lime-

stabilized zirconia crucible and insulation under conditions presently envisioned for the refining operation (melt temperature, 1400 C; susceptor temperature, 1600 to 1800 C; melt time, 4 hours; initial furnace gas, 1 atmosphere of argon). The strong gettering effect of molten uranium for carbon monoxide suggests that if evolution of this impurity were large, significant side reactions with the uranium-base fuel would occur. The literature reveals that the equilibrium pressure of carbon monoxide in the zirconia-carbon reaction is about 1.6 atmospheres for a reaction temperature of 1700 C [relationship: $\log p = 8.592 - (16580/T)$].²

A previously reported experiment (ANL-5996, page 45) showed that, when dense graphite was heated at 1710 C in contact with zirconia powder for 55 minutes under an initial furnace pressure of 11 mm of helium, carbon monoxide was evolved at a rate decreasing with time; however, differences in the experimental conditions from those contemplated for pilot-scale furnace operation did not permit a reasonable extrapolation of the results. The purpose of the present zirconia-graphite reaction tests was to determine the effects of extended heating time and previous exposure of the system to laboratory air (relative humidity, 40 to 50 per cent, at 27 C) upon the reaction when furnace pressures were maintained between 600 and 690 mm.

The assembly used for the experiments is shown in Figure 5. The graphite and zirconia components were outgassed separately at 1750 and 1000 C, respectively, at pressures less than one micron. They were then assembled and placed in an induction-heated, 152.2-liter vacuum-inert atmosphere furnace. An auxiliary system (described in ANL-5820, page 90) was provided for withdrawing gas samples of known volume from the furnace. Temperatures of the reaction zones were determined optically.

The reaction of graphite and zirconia powder was studied at a mean graphite temperature of 1700 C. The sequence of operations followed for a series of three heating cycles was as follows: (a) the furnace pressure was reduced to 10^{-4} mm with the graphite heated to approximately 800 C; (b) the furnace pressure was raised to 608 mm of helium, the graphite was heated at temperature for 4 hours, quenched, and retained for 16 hours in the initially charged gas containing the carbon monoxide formed; (c) the reactants were reheated in the same atmosphere for an additional reaction period of $5\frac{1}{2}$ hours, quenched, and exposed to air for 14 hours; (d) the furnace pressure was raised to 603 mm of purified helium after evacuation to less than 500 microns at room temperature, and the graphite was reheated for a third reaction period of 4 hours. For each cycle measurements of furnace pressure were taken at the beginning, end, and at selected intervals during the reaction period at 1700 C, to permit calculation of total gas evolved. Appropriate corrections were applied

²Prescott, C. H., J. Am. Chem. Soc., 48, 2534 (1926).

FIGURE 5
ASSEMBLY FOR GRAPHITE-ZIRCONIA REACTION TESTS
(Induction Heated)

REACTANTS - ZIRCONIA POWDER: NORTON COMPANY; GRADE, H; MESH, -36; REPORTED
COMPOSITION, (W/O): CaO (5.0), SiO_2 (0.7), Al_2O_3 (0.5), TeO_2
(0.3), Fe_2O_3 (0.2), HSO_2 (<2.0), ZrO_2 (BALANCE)

GRAPHITE: NATIONAL CARBON COMPANY; GRADE, Cs; APPARENT DENSITY,
1.67; AREA EXPOSED TO ZIRCONIA, 184 Sq Cm

to the observed pressure to compensate for measured furnace volumes extracted by intermittent atmosphere sampling with previously evacuated Pyrex sample bulbs. Analyses of the helium, carbon monoxide, nitrogen, oxygen, hydrogen, and carbon dioxide contents in each bulb were made by means of a mass spectrometer. The presence of significant amounts of other gaseous impurities was eliminated by sample scanning. The use of helium, rather than of argon, permitted essentially complete removal of water (~ 1 ppm, measured by dew-point techniques) from the inert gas with the use of a simple actuated charcoal trap cooled with liquid nitrogen. It is believed that this is not a significant change, although argon is to be used in the EBR-II cell atmosphere.

A record of the analytical results for the three reaction cycles is presented in Table 3. The analyses confirm the previously reported observation that carbon monoxide will be evolved if graphite susceptors are heated at 1700 C in contact with lime-stabilized zirconia powder. The source of small amounts of hydrogen in the gas samples (0.04 to 0.29 per cent) is not fully understood. If it were assumed, however, that this impurity resulted from a carbon-water reaction, most of the corrections applicable to carbon monoxide concentrations from this side reaction would fall only within the limits of the analytical precisions reported. The similarity of hydrogen concentration in the atmosphere from heats in which reactants were exposed to air (cycle III) and protected from air contamination (cycles I and II) suggests that water vapor due to the exposure was insignificant or that it was rapidly removed by evacuation of the furnace to less than 500 microns in a four-minute period. Evidence that additional side reactions with carbon and the furnace atmosphere did not occur is provided by the absence of helium impurities (other than carbon monoxide previously generated) in the initial sample of cycle II which was taken after a 16-hour reactant holding period. In addition, a comparison of carbon monoxide concentration in this sample (4.0 per cent) and that in the atmosphere prior to cooling of the reactants (4.8 per cent, cycle I) implies that preferential sorption of this gaseous product by the reactants may have occurred with cooling.

The evolution of carbon monoxide at a steady temperature of 1700 C during the three reaction periods is shown in Figure 6, where total gas evolved, determined by furnace-pressure measurement and expressed as cc of carbon monoxide per sq cm of graphite exposed to zirconia, is plotted against time. It is apparent that the reaction rate was most rapid, although slightly decreasing with time, during the initial sintering of the zirconia powder during the 5-hour cycle I. Subsequent reheats of the same reactants in cycles II and III (6 and 5 hours, respectively) indicated that the reaction proceeded at an essentially constant rate of from 3.0 to 3.2 cc per sq cm (graphite exposed to zirconia) per hr. For these reheats, analyses of a limited number of gas samples showed this rate to be about 25 per cent less. These discrepancies cannot be explained without further experimentation (e.g., complete mixing of helium and the relatively heavier carbon

Table 3

MASS SPECTROMETER ANALYSES OF GAS FRACTIONS FROM GRAPHITE-ZIRCONIA INTERACTION STUDIES

Cycle	Reactants				Initial Atmosphere					
I	Previously outgassed graphite and lime-stabilized zirconia.				High-purity helium after furnace evacuation to 8×10^{-5} mm with graphite at 800 C.					
II	Cooled assembly from Cycle I retained in furnace for 16 hr.				Gas from Cycle I (helium with ~4% CO)					
III	Cooled assembly from Cycles I and II exposed to air for 14 hr.				High-purity helium after furnace evacuation to 500 microns in 4 min; graphite at 27 C.					
Cycle	Experimental Conditions		Gas Volume Increase ^a (cc at STP)		Atmosphere Composition ^b (Volume per cent)					He (by diff)
	Sample	Sampling Time (min)	Measured	CO Analysis	CO	N ₂	O ₂	H ₂	CO ₂	
I	Initial Gas at 20 C	0	0	0	0.02 $\pm$ 0.01		<0.01	0.04	<0.03	99.9
	At 1700 C	65	0	300	0.27 $\pm$ 0.10	<0.1	<0.01	0.12	<0.03	99.6
		185	3460	3900	3.4 $\pm$ 0.2	<0.1	<0.01	0.10	<0.03	96.5
		305	5290	5550	4.8 $\pm$ 0.2	<0.1	<0.01	0.08	<0.03	95.1
	Reactants Cooled to <100 C.	362	-	-	4.5 $\pm$ 0.2	<0.1	<0.02	0.12	<0.03	95.4
II	Initial Gas at 20 C	0	0	0	4.0 $\pm$ 0.2	<0.1	<0.01	0.09	<0.03	95.9
	At 1700 C	70	0	0	4.0 $\pm$ 0.2	<0.1	<0.01	0.16	<0.03	95.8
		396	2730	2570	6.1 $\pm$ 0.2	0.4	0.09	0.24	<0.03	93.2
	Reactants Cooled to <100 C	450	-	-	6.0 $\pm$ 0.3	0.5	0.11	0.27	<0.03	93.1
III	Initial Gas at 20 C	0	0	0	0.07 $\pm$ 0.04		0.05	<0.02	<0.03	99.9
	At 1700 C	70	180	330	0.30 $\pm$ 0.10	<0.1	<0.02	0.12	<0.03	99.6
		180	1800	970	0.87 $\pm$ 0.10	<0.1	0.03	0.24	<0.03	98.9
		300	2730	1900	1.7 $\pm$ 0.2	0.07	0.03	0.24	<0.03	98.0
	Reactants Cooled to <100 C.	347	-	-	1.5 $\pm$ 0.2	0.12	0.03	0.29	<0.03	98.1

^a Volumes corrected for furnace volume reduction due to sampling with evacuated bulbs.^b Precision values were H₂, $\pm$ 0.04; O₂ (for values >0.02), $\pm$ 0.02; N₂ (for values >0.2) $\pm$ 0.2; CO in Table.

Figure 6

RELEASE OF CARBON MONOXIDE FROM ZIRCONIA-GRAPHITE REACTION AT 1700 C

CYCLE I:

Outgassed graphite and zirconia
Initial atmosphere-purified He
Pressure - 608 to 675 mm

CYCLE II:

Cooled assembly from Cycle I
Initial atmosphere-gas from
Cycle I (~4% CO in He)
Pressure - 635 to 687 mm

CYCLE III:

Cooled assembly from Cycle II,
exposed to air at 27 C for 14 hours,
then evacuated to <500 microns.
Initial atmosphere-purified He
Pressure - 603 to 653 mm

- CO evolution based on pressure rise
△ CO evolution based on mass spectrometer analysis

monoxide during the reaction periods has not been demonstrated). Results from both techniques for evolution measurement indicate, however, that solid phases formed in the reaction were not protective after the zirconia insulation had sintered. Furthermore, agreement of the rates for cycles II and III suggests that the effect of prior exposure of the reactants (cooled in inert atmosphere) to air on a subsequent reaction rate is small.

The above experiments indicate that carbon monoxide will be evolved to the argon atmosphere of the plant melt-refining furnace if graphite susceptors heated to 1700 C are employed in contact with lime-stabilized zirconia insulating material. Variations in reaction rates from those reported are likely to result primarily from changes in contact area (due to continued thermal cycling) or in the temperature of the interfacial reaction zone. Reactions of the uranium-base fuel at processing temperature with carbon monoxide could result in melt fractions of high carbon concentration and variable zirconium concentration.

c. Infrared Gas Analysis for Cell Atmospheres
(M. D. Adams, M. L. Jones)

The formation of carbon monoxide by the reaction of zirconium oxide with graphite, and possible contamination of the cell atmosphere by Freon-12 from the refrigeration system, led to a brief study on the detectability of these gases by infrared spectrophotometry.

Carbon monoxide shows an absorption maximum in the region from 4.5 to 4.9 microns, with double peaks at 4.6 and 4.72 microns. Several absorption curves in this region were determined, using 10-cm sodium chloride cell windows in a Beckman IR-4 spectrophotometer. Carbon monoxide concentrations as low as 0.7 per cent could be measured in approximately one atmosphere of argon. A one-meter cell should permit analyses in the range of 500 ppm.

Several absorption bands over the range from 4 to 12 microns can be used for the determination of Freon-12. It is estimated that this technique used with a one-meter cell should detect Freon-12 in the range of 100 ppm in an argon atmosphere.

d. Melt-refining of Sodium-coated Fuel Pins
(G. A. Bennett, W. A. Pehl)

The melting of sodium-coated fuel pins has been found, under laboratory conditions, to be more difficult than the melting of clean fuel pins. This is caused by the formation of an oxide film on the fuel pin surface due to the presence of residual oxygen in the sodium or from atmospheric contamination. Under plant conditions, such oxygen is available from oxygen in the argon cell (100 ppm oxygen) and may react with

the fuel pins in a similar manner. A standby process is currently under development for use in the event difficulties due to oxide films are encountered. This report summarizes the various approaches considered during the past quarter.

(1) Use of Reducing Alloys

In previous reports (ANL-6029, ANL-5996) experiments are summarized in which the sodium-coated fuel pins were dipped in a number of reducing alloys for removal of sodium and the oxide film. During the past quarter the type of alloys was extended to include magnesium-zinc, magnesium-cadmium, calcium-cadmium, calcium-sodium and calcium-magnesium. Under suitable conditions of time and temperature, wetting could be effected by these alloys. This, however, did not necessarily insure pin coalescence, because of the difficulty in avoiding recontamination of the pins when raised through a scum layer on the surface of the alloy, and because of the difficulty in obtaining a uniform coating, particularly at contact points between pins. These difficulties materially increase the problems in equipment design. In addition, this approach would result in the introduction of appreciable quantities of the dipping alloy into the melt-refining step. Consequently, a more effective approach is currently being sought.

(2) Coalescence Under Salt Flux

Preliminary experiments on the coalescence of sodium-coated "fissium" pins under the surface of a 55 mol per cent magnesium fluoride-45 mol per cent calcium fluoride flux show promise. The method is essentially that used at Fernald* for scrap consolidation. The salt mixture was first added to a degassed graphite or high-purity alumina crucible, and, after evacuation and argon pressurizing, was heated to melting (1100 to 1200 C). The sodium-coated "fissium" pins were then added, and the entire charge was heated to 1400 C for 30 minutes. In the two experiments performed to date, complete coalescence of ~50 grams of pins occurred within the graphite crucible, and almost complete coalescence (pin shell outlines, although incorporated into the matrix, were still visible) occurred when 200 grams of pins were melted in the alumina crucible. In both cases, oxide losses were negligible. This approach is being investigated further.

(3) Coalescence by Arc Melting

A preliminary investigation of the possibilities of arc melting sodium-coated fuel pins was made in a small, nonconsumable electrode, arc furnace. In the first experiment, individual pins, consisting

*Feed Materials Production Center, Fernald, Ohio; see F. L. Cuthbert, et al., Proc. Second UN Intl. Conf. on the Peaceful Uses of Atomic Energy, United Nations, Geneva (1958), Vol. 6, p. 384.

of clean "fissium," sodium-coated "fissium," and heavily-oxidized "fissium," were successfully coalesced. In all three cases clean beads were formed, with essentially no loss. In a second experiment, two batches of 10 short pins (each ~50 grams) were coalesced. This approach is also being investigated further.

e. Study of Alternate Materials and Designs for EBR-II
Melt-refining Furnace
(J. Wolkoff, R. P. Andres, R. Peterson)

A duplicate of the melt-refining crucible-coil assembly was constructed for purposes of thermal and material tests. The goals of the tests include:

- a. Lowering the temperature of the solid copper inductor coil. Present coil temperatures are as high as 750 C. A decrease in the furnace heat loss will effect improvement through decreased power requirements. Improvement in the coil space factor will similarly tend to lower the coil temperature.
- b. Elimination of crucible breakage. After a typical melt-refining run, the zirconia crucible contains axial and transverse cracks in the outside wall. However, metal leakage is rare and the used crucible can generally be handled in one piece by a manipulator. The bottom occasionally breaks off within the furnace on removing the crucible and is difficult to remove by remote operation. Improvement in crucible reliability by shape and dimensional modifications and by less severe temperature changes in the furnace will be tried. Improved insulation can lessen temperature shock during cooling.
- c. Use of thermal insulation compatible with the heated susceptor. It has been found that zirconia insulating grain in contact with the graphite susceptor evolves carbon monoxide (see page 38). Even the most stable oxides, e.g., ThO_2 , react with carbon at 1700 C. The use of fine grain SiC , B_4C , and graphite will be investigated. Alternatively, high-temperature susceptor materials compatible with oxide insulation will also be examined.

The goals are interrelated and efficient thermal insulation is involved in each. In the runs to date a few insulation methods have been tested, using a crucible-coil assembly of the type shown in Figure 7. In the assembly shown, which is the second to be tested, a formed rigid Fiberfrax* grain retainer was employed. In the first assembly, an Amersil retainer was used to duplicate an assembly extensively used in the melt-refining mock-up furnace and to provide a base line for evaluating changes.

*Ceramic fiber manufactured by Carborundum Company

FIGURE 7
SECOND ASSEMBLY OF MELT-REFINING TEST SYSTEM

The assembly is contained in a water-cooled vacuum furnace shell which can be vacuum purged and filled with argon. Preliminary tests have shown the Fiberfrax retainer to be free of the cracking tendency of the Amersil and considerably superior as thermal insulation.

The test assembly is equipped with thermocouples for measuring the temperature of the crucible, susceptor, insulating grain, grain retainer, copper coil, and other supporting points. The temperatures are recorded while heating the furnace at constant power input and while cooling to room temperature. Difficulty was experienced with measurement of high susceptor temperatures due to carburization of the thermocouples. For this reason tests to date have been made at less than full power. Suitable thermocouple materials are being sought.

Data pertaining to a number of the runs are shown in Table 4, and typical cooling curves at the crucible wall are shown in Figure 8. The slope of the cooling curve after it has become exponential is a function of the thermal properties of the furnace materials and their geometry and is independent of the temperature level. A low slope indicates efficient insulation or a large heat capacity. Runs 3 and 5 were made at the same conditions except temperature level and have essentially the same cooling curve slope. Run 6 was similar to Run 3 except that the crucible was covered, resulting in slower cooling.

In the first test of the rigid Fiberfrax grain retainer (Run 8), the cooling-curve slope is lower even though the heat capacity was decreased through decreased weight. Run 2 was made under vacuum for comparison and illustrates the effectiveness of vacuum for high thermal efficiency.

The low coil temperature in Run 8 (only 240 C as compared with temperatures of above 400 C in other experiments) also attests to the

Table 4

THERMAL INSULATION TEST RUNS

Insulating Grain: ZrO_2 , 25/40 mesh

Run No.	Train G Retainer	Crucible Cover	Power (kw)	Steady State	Max Crucible Wall Temp (C)	Max Copper Coil Temp (C)	Slope of Cooling Curve ^a (min^{-1})
2 ^b	Amersil	None	4.5	No	926	443	-0.00073
3	Amersil	None	4.5	Yes	880	455	-0.0032
5	Amersil	None	9.0	Yes	1105	640	-0.0033
6	Amersil	ZrO_2 brick	4.5	Yes	1047	464	-0.0026
8	Rigid Fiberfrax	ZrO_2 brick	4.5	No	1083	241	-0.0020

^aBased on $\log_{10}$ scale.^bRun 2 under vacuum; all the others under argon at one atmosphere.

FIGURE 8
CRUCIBLE COOLING CURVES FOR MELT-REFINING TEST ASSEMBLY
SLOPES IN TABLE 4

efficiency of the Fiberfrax retainer. However, final evaluation of this and other insulating materials cannot be made until they have been tested at full operating temperatures (1400 C in the crucible).

B. Pyrometallurgical Development
(L. Burris, Jr., R. K. Steunenberg)

1. Studies Directed at Processing Melt-refining Skulls

In order to recover the uranium in the crucible skulls remaining after melt refining, it is necessary to remove the skull from the crucible completely and to convert the material into a form that is amenable to further processing. These objectives must be reached through a simple operation that can be performed remotely in the EBR-II Fuel Cycle Facility. Burning the skull in oxygen produces a finely divided material that can be easily poured from the crucible. Since the skulls may be stored in the nitrogen atmosphere of the cell, partial nitridation prior to oxidation may occur. Preliminary work on liquid metal systems for uranium recovery has indicated that an oxidized skull can be processed most easily. Thus, a direct oxidation appears to be an attractive process for the preliminary treatment of melt-refining skulls.

a. Nitridation of "Fissium" Skulls
(T. R. Johnson, G. Brunzie,* R. Christensen)

In the fuel cycle for EBR-II, the bulk of the uranium from the spent fuel will be recovered by melt refining. The balance of the uranium, remaining in the crucible with the majority of the fission products, will be stored in the argon cell of the EBR-II facility for several weeks before it will be put through the liquid metal process. The temperature of the skull will probably remain above 500 C due to the fission product heat. The cell atmosphere will contain 1 to 5 volume per cent nitrogen.

As an initial portion of the skull treatment investigations, the rate of reaction between crucible skulls and nitrogen has been studied. It was found that low-pressure nitrogen will react with uranium skulls above 500 C. The rate of nitridation was studied as a function of nitrogen pressure, temperature, and time.

The skulls were prepared by melting a "fissium" alloy and cerium metal (0.6 weight per cent) in a dry-pressed, calcium oxide-stabilized zirconia crucible. The molten alloy was held at 1350 ± 25 C under 650 mm of helium. After two hours, the molten metal was poured into a copper mold. The weight of the poured ingots was 85 to 95 per cent of the original charge. This ingot was used as the "fissium" charge for the next melt. Cerium removal from the ingot averaged 97 per cent and was greater than 95 per cent in all cases in which analyses were performed.

*Resident Student Associate

The percentages of molybdenum, rhodium, and palladium remained constant throughout a series of melts, indicating no preferential removal of these metals. The residue remaining in the crucible after pouring consisted of the skull adhering to the crucible and a metallic "button."

For nitriding, the crucible containing the residue was placed in a resistance-heated stainless steel furnace tube. The furnace was evacuated and brought to temperature. The furnace pressure was raised and kept at the desired value by adding nitrogen from a tank of known volume. The quantity of nitrogen added to the furnace was calculated from the decrease in pressure of the calibrated tank. The compositions of the two "fissium" alloys used are shown in the following table:

COMPOSITION OF "FISSIUM" ALLOYS

	High Zirconium Alloy		Low Zirconium
	Nominal (w/o)	From Analyses (w/o)	Alloy Nominal (w/o)
Zr	3.6	2.8 $\pm$ 0.1	0.1
Mo	2.6	2.6 $\pm$ 0.1	2.6
Ru	2.6	2.6 $\pm$ 0.2	2.0
Pd	0.6	0.60 $\pm$ 0.03	0.5
Ce	0.6	-	0.6

After nitridation, a majority of the skulls were pyrophoric; the skulls had been partially pulverized and the button could be removed intact. The metallic button reacted only to a very small extent even at the highest temperatures. The quantity of the metallic uranium in the skulls was estimated as 70 per cent of the skull weight (not including the button weight). The ratios of nitrogen absorbed to uranium in the skull are plotted as a function of time, temperature, nitrogen pressure, and alloy type in Figures 9, 10, and 11.

The rate of reaction was very rapid at first and became much slower after about 20 minutes. Neither the crucible itself nor the furnace tube absorbed a significant quantity of nitrogen over the temperature and pressure range used. In order to learn more of the nature of the initial reaction, the rate of nitrogen absorption at 500 C and 76 mm was followed for 10 minutes. The furnace was then evacuated quickly and repressurized with nitrogen for another 10 minutes. These cycles were repeated several times. The measured amount and rate of nitrogen adsorption were essentially the same for each cycle.

The rate of nitridation was a direct function of temperature and pressure. The high-zirconium alloy skulls reacted faster and to

FIGURE 9

REACTION OF NITROGEN WITH URANIUM SKULLS AT A NITROGEN PRESSURE OF 38 mm Hg

FIGURE 10

REACTION OF NITROGEN WITH URANIUM SKULLS AT A NITROGEN PRESSURE OF 38 mm Hg

FIGURE II
REACTION OF NITROGEN WITH URANIUM SKULLS AT
A NITROGEN PRESSURE OF 8mm Hg.

a greater extent than did the low-zirconium skulls. The results at 8 mm pressure all fall essentially on the same curve, except for the one run at 700 C.

On the basis of these preliminary data, it appears that a melt-refining skull above 500 C and exposed to the atmosphere of the EBR-II Argon Cell will form nitrides. The extent of nitridation will depend greatly on the manner in which the skull is stored, the duration of storage, and the nitrogen content of the atmosphere. All of these factors will not be known until the EBR-II Fuel Cycle Facility is in actual operation. Since it appears certain that the skull will be at least partially nitrided, a subsequent skull treatment step must be designed to handle uranium nitrides.

b. Oxidation of "Fissium" Skulls
(R. D. Pierce, L. F. Dorsey)

Skulls can be removed from melt-refining crucibles by oxidizing them to a fine powder which may be easily and essentially completely poured from the crucible. This procedure appears attractive for use with EBR-II skulls if the resultant oxides prove suitable for further processing for uranium recovery and fission product removal. Two approaches to the skull oxidation are under consideration - complete combustion of the residue to a fine powder, and just sufficient burning to free

the skull from the crucible. The latter approach may have a process advantage in that the bulk of the uranium in the skull is present in a button of fuel alloy, most of which would not be oxidized and therefore would not need to be reduced to metal during later processing.

The oxidation runs to date have all been aimed to complete oxidation of the skulls. Table 5 presents analytical results obtained on the blended oxide from three runs. The higher cerium and lower molybdenum concentrations of the fine oxide indicate that the scale material, which comprises reaction products of the melt-refining run, tends to oxidize to a finer material than the button, which is unpoured "fissium" alloy. As indicated in the footnote of Table 5, the fate of ruthenium needs further analytical work. In addition to the "fissium" elements the oxidized skulls always contain about 5 per cent of fine zirconia from the melt-refining crucible. The fate of this material must be considered in subsequent processing steps.

Table 5

ANALYSIS OF OXIDIZED "FISSIUM" SKULLS

(A blend of 3 skulls which were oxidized at 770, 820, and 970 C, respectively, in approximately 25 per cent oxygen-argon atmosphere)

Mesh	Weight (g)	Concentration (per cent) ^a		
		U	Ce	Mo
-325	247.7	71.5	12.7	1.16
+325, -170	405.7	67.6	11.2	1.36
+170, -80	370.3	73.1	6.6	1.66
+80, -45	472.3	75.4	5.7	1.75
+45, -25	489.7	79.4	3.4	1.96
+25, -20	128.9	81.8	2.9	1.90
+20	697.3	— — — Not analyzed — — —		

^a Appreciable ruthenium removal by volatilization of the tetroxide occurred. However, analytical difficulties have been encountered, which prevents giving values of the percentage removed at this time.

c. Reduction of Oxides in Liquid Metal Solutions
(A. Schneider, T. R. Johnson, J. D. Schilb)

The scheme under consideration for the recovery of uranium from melt-refining slags consists of oxidizing the slag to form U_3O_8 and fission product oxides. This mixture is then reduced by a suitable solution of liquid metals. Zinc alloys were considered originally, but the emphasis has shifted to cadmium, which is a less corrosive medium. The following studies were conducted to determine the behavior of uranium and fission product oxides contacted with reducing solutions of liquid metals.

Reduction of Molybdenum and Rare Earth Oxides by Uranium in Liquid Zinc

Reagent grade molybdenum oxide, which is considered to be a typical noble metal oxide, was contacted with liquid zinc at 750 C. After 16 hours uranium was added, and agitation was continued for another 3.4 hours. Analyses of the zinc phase before and after the uranium addition indicated that no molybdenum had been reduced and dissolved. Examination of the ingot showed that the oxide had not been wet by the liquid metal.

A mixed rare earth oxide (Lindsay No. 420 "didymium oxide") was contacted with a zinc solution containing 1.7 weight per cent uranium at 750 C. This material contains mostly lanthanum, praseodymium, and neodymium oxides. The initial rate of oxide reduction was faster than a previously observed rate of ceric oxide reduction under similar conditions. After two hours the rate became slow, and after six hours only 60 percent of the mixed oxides had been reduced.

Reduction of Ceric Oxide by Uranium in Liquid Cadmium

Uranium metal, finely divided by hydriding and dehydriding, was dissolved in liquid cadmium at 570 C. The uranium concentration reached saturation, 2.2 weight per cent, within one hour. Ceric oxide was then added. The oxide was reduced rapidly to cerium metal, the reaction being 95 per cent complete within one hour. A similar rapid reduction occurs in liquid zinc saturated with uranium. The final cerium concentration was 1.4 weight per cent, which is well below the saturation concentration of about 2 weight per cent at 570 C. Since excess uranium was present, the solution remained saturated with uranium during the reduction.

Reduction of Zirconium and Barium Oxides by Magnesium in Liquid Cadmium

Zirconium oxide was reduced at 556 C by a liquid cadmium solution containing 2 weight per cent magnesium. After three hours, approximately 22 per cent of the zirconium oxide had been reduced. The extent of ZrO_2 reduction could not be followed beyond a zirconium content of 0.34 weight per cent, which corresponds to the saturation value at this temperature. However, based on magnesium analyses of samples taken at several points, the reduction of zirconium oxide was complete within 20 hours.

Barium oxide was reduced very rapidly by a cadmium melt containing 2 weight per cent magnesium at 520 C. A maximum concentration of barium, about 1.45 weight per cent, was reached in less than two hours. This concentration is close to the solubility of barium at this temperature. The ingot from this experiment was remelted and heated to 700 C. The barium content of a filtered sample taken at this temperature showed that quantitative reduction had occurred. The magnesium balance also indicated complete reduction of the oxide within two hours.

Reduction of U_3O_8 by Magnesium in Liquid Cadmium

A systematic investigation was started on the rates of U_3O_8 reduction by magnesium in liquid cadmium, examining variables such as temperature, magnesium and uranium concentrations, agitation, particle size of the oxide and salt fluxes. The oxide was prepared by oxidizing natural uranium metal in oxygen, followed by two reduction-oxidation cycles with hydrogen and oxygen, respectively, for size reduction. The weight change of the solid showed that U_3O_8 was produced during the oxidation.

The results of the experiments are summarized in Table 6. In no case did the reduction proceed beyond a yield of about 60 per cent. These results are in agreement with similar experiments by the Pilot Plant Group. The cause of the incomplete reduction has not yet been determined.

The reduction rate was relatively rapid during the initial three hours, but it levelled off after four to six hours at less than 60 per cent completion. In Experiment 4, the initial uranium level was raised by the addition of a cadmium-uranium alloy. Both the reaction rate and the extent of reduction were reduced somewhat, but the difference was not sufficiently large to attribute the levelling-off phenomenon to an equilibrium condition.

Table 6

U₃O₈ REDUCTION EXPERIMENTS

Reducing media: 3 w/o Mg in liquid Cd

All crucibles equipped with baffle

Accessories: Type 304 stainless steel

Temperature: 660 C

Stirrer Speed: 300 rpm Run 1; 450 rpm Runs 2,3,4

Expt	Crucible Material	Maximum U Content ^a (w/o)	Time Stirred (hr)	Uranium Content ^b (w/o)	U ₃ O ₈ Reduced (%)
1	Al ₂ O ₃	0.486	0.5	0.019	4
			1.0	0.081	17
			2.0	0.180	37
			3.0	0.248	51
			4.2	0.267	55
			20.4	0.222	46
2	SS-304	0.491	0.5	0.025	5
			1.5	0.227	46
			2.3	0.279	57
			18.3	0.269	55
			18.6	0.266	54
3	SS-304	0.476	0.5	0.036	8
			1.5	0.131	28
			2.5	(0.474) ^c	(100) ^c
			19.0	0.298	63
4	SS-304	0.726 ^d	0.2	0.138	-
			0.7	0.255	1
			1.7	0.346	20
			2.7	0.412	34
			3.7	0.430	38
			4.7	0.434	39
			5.7	0.470	46
			6.0	0.458	44

^aTotal amount of uranium added to the system as U₃O₈^bBased on chemical analysis of filtered samples of the liquid metal^cUnfiltered sample (accidentally)^dIncludes uranium metal added initially and equivalent to 0.25 w/o.

In view of these results it was concluded that simple changes in the operating variables would be unlikely to produce satisfactory yields. Effort is therefore being devoted to an examination of the chemistry of the system in an attempt to establish the cause of the incomplete reduction and to eliminate the effect.

d. Reduction of Oxidized Skull Material in Cadmium-Magnesium Alloys
(R. D. Pierce, L. F. Dorsey)

Runs are being made to gain experience and information on reducing oxidized "fissium" in liquid cadmium-magnesium alloys. The effect of temperature on the reduction rate for a given set of experimental conditions (constant agitation, same material and equipment) is shown in Figure 12. A pronounced effect of temperature on initial reduction rates is apparent, higher rates being achieved at higher temperatures. A temperature of 650 C has been chosen for future runs in order to avoid the excessive volatilization of cadmium which occurs at 700 C.

FIGURE 12
RECOVERY OF URANIUM FROM OXIDIZED SKULLS BY REDUCTION
WITH LIQUID CADMIUM-2 WEIGHT PER CENT MAGNESIUM ALLOY
Baffled SS Crucible, 5-in diam
Agitated by Stirrer

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

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. Cadmium Solution Process

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 the cadmium away 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 metallic plutonium.

As reported in ANL-6029, the plutonium concentration in the still pot decreased during the distillation of cadmium from a solution of plutonium in magnesium-cadmium. Interaction of plutonium and the mild steel container was considered a possible mechanism for this loss. In an experiment made to check this possibility, a solution of plutonium in a 20 per cent magnesium-80 per cent cadmium alloy was held in a mild steel crucible at a temperature of 650 C for 15 hours with constant agitation. Analyses of melt samples taken periodically in 7- and 15-hour runs showed no decrease in the plutonium concentration, thus indicating no interaction of this particular solution with the mild steel crucible.

Previous experiments, ANL-5996, page 114, have indicated that coprecipitation of plutonium with uranium does not occur in the cadmium-magnesium system. The decrease in plutonium concentration observed during distillation may have resulted from spattering onto the still pot walls during distillation. This possibility will be investigated.

b. Extraction of Plutonium with Magnesium from
Hydrided-Dehydrided Uranium-1 w/o Plutonium
Alloy

Leaching of plutonium into magnesium from finely divided (hydrided-dehydrided) uranium has previously resulted in solution of about two-thirds of the plutonium (ANL-5668 and 6029). For additional plutonium removal it has been proposed that, after removal of the bulk of the plutonium-bearing magnesium phase, the residual magnesium be vaporized and a second hydriding-dehydriding operation be conducted. This would be followed by another magnesium-leaching step.

An experiment following this scheme was tried and proved unsuccessful due to the disintegration of the tantalum equipment during the second hydriding step. Fifty per cent of the plutonium was removed by the first magnesium-leaching operation, which is somewhat lower than that realized in a previous experiment (68 per cent removal).

While the above procedure has a potential advantage in requiring small quantities of magnesium, the equipment difficulties encountered will delay further work on this process. Emphasis will be given to the cadmium solution process described above.

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

Development of engineering techniques and equipment, which are necessary to the success of liquid metal processes, are in progress on distillation and retorting, solid-liquid phase separations, materials handling, and corrosion of materials of construction.

a. Distillation and Retorting

(1) Experimental Distillation Studies

In some of the flowsheets being considered for processing of melt-refining skulls or EBR-II blanket material, a solution which contains cadmium, magnesium, uranium, plutonium, rare earths, and zirconium must be distilled. In a melt-refining skull process, the object of this operation is to precipitate the uranium by increasing the magnesium concentration by distillation of cadmium and to permit separation of the rare earths and zirconium from the uranium by drawing off the magnesium-rich phase containing the dissolved rare earths and zirconium. In a blanket process, the object is to provide for separation of uranium and plutonium, the plutonium being removed in the magnesium-rich phase (see page 58 of this report)

(a) Distillation Studies Relative to Skull Processing (P. A. Nelson, J. F. Lenc, R. Zeman)

Experiments were performed to determine 1) the fate of zirconium and cerium during evaporation of the cadmium to produce a magnesium-rich phase and 2) whether the magnesium-rich phase could be drawn off from the uranium-rich phase by transfer through a tube. Data on the fate of zirconium and cerium are available for an experiment in which the initial charge alloy had the composition shown in Table 7 for zero time. Concentrations of uranium, cerium, and zirconium were near or even exceeded those which are expected to be encountered in processes under consideration. The zirconium concentration employed was representative of a fuel containing 2 to 3 per cent in zirconium, a concentration which would be reached only after many fuel passes, if present plans of using initially a zirconium concentration of 0.1 per cent prevail.

Samples were taken after dissolving the materials before distillation of the cadmium and after various intervals of the distillation, which was conducted at a fairly constant rate of 650 C. Before

Table 7

FATE OF ZIRCONIUM AND CERIUM DURING CADMIUM DISTILLATION
RUNS SIMULATING PROCESSING OF MELT-REFINING SKULLS

(Initial charge weight was 9.32 kg. Composition is shown for zero time, with balance being cadmium. Equipment used was described in ANL-5996, page 75)

Analysis of Liquid Remaining in Still Crucible									
Distillation Time (min)	Temp (C)	Magnesium		Uranium		Cerium		Zirconium	
		(w/o)	(% of Mg ^a Charged)	(w/o)	(% of U Charged)	(w/o)	(% of Ce Charged)	(w/o)	(% of Zr Charged)
0	664	1.65	100.0	1.55	92	0.162	95	0.0476	84
34	666	1.86	100.0	1.18	78	0.188	98	0.051	80
124	647	15.1	98.6	0.35	2.2	1.6	102	0.43	82

^aCalculated from Rayleigh distillation equation.

taking a sample, the heat input was stopped, the secondary crucible was allowed to cool to 700 C, and argon was added until atmospheric pressure was attained. The total amount of solution left in the distillation crucible after each interval was calculated from the magnesium concentration assuming that the amount of magnesium lost was that amount calculated from the Rayleigh distillation equation.

The results, summarized in Table 7, indicate essentially complete retention of the cerium in the magnesium-rich supernatant solution. In terms of that initially present in solution, the zirconium retention was essentially 100 per cent at a final magnesium concentration of 15 per cent. Thus, adequate zirconium decontamination should be possible if conditions are properly selected.

In two runs, the magnesium-rich phase was successfully drawn into a vacuum receiver through a 0.180-inch ID stainless steel tube. A small amount of uranium precipitate was drawn off in one of these. In the other, a porous graphite filter employed in the end of the transfer tube eliminated transfer of uranium.

Full-scale Distillation and Retorting Equipment

Design and drafting for the full-scale distillation equipment (previously described in ANL-6029) is almost complete. The purpose of this equipment will be to study distillation operations on a practical scale and, more specifically, to study the distillation and retorting operations in the recovery process for melt-refining skulls. This equipment is designed to (1) evaporate cadmium from a solution of cadmium, magnesium, uranium, and magnesium-soluble fission products, (2) draw off the magnesium phase containing the fission products from the precipitated uranium phase, and (3) evaporate the remaining magnesium to recover the uranium decontaminated from fission products. The equipment is expected to be capable of processing a batch containing 10 kg of uranium.

An order has been placed for a 100-kilowatt, 960-cycle/sec motor generator. This equipment will be used to provide the heat for distillation. An order has been placed for a furnace to enclose the vessels and transfer lines.

(b) Distillation Studies Relative to Blanket Processing
(I. O. Winsch, T. F. Cannon)

Several distillation experiments using cadmium-magnesium-cerium alloys have been completed in the sodium-jacketed distillation unit (ANL-5996, page 73). These runs simulated recovery of plutonium from a magnesium-rich cadmium solution, cerium being used as a substitute for plutonium (see process description on page 56). About 100 per cent of the cerium initially charged to the unit was present in the still pot after distillation of the cadmium and magnesium.

In the first run, the cadmium and magnesium were condensed as a liquid, and it was observed that some vapors condensed below the receiver crucible. Over a long period of time a large band of metal would build up and prevent removal of the receiver from the unit. In the second run, the metal vapors were condensed as solids, and at the end of the run the condensate was melted from the condenser wall and collected in the receiver. In this procedure, there were no indications of metal vapors around or below the receiver.

The distillation unit is to be hooded in order to perform final demonstration runs with plutonium.

A second distillation unit, which will be used in experiments on the cadmium solution blanket process (see page 56), has been vacuum and pressure tested. A sketch of this unit is shown in Figure 13. The unit has been heated inductively to the temperatures required in actual distillation operations. Cadmium vapors will be condensed as a solid on the condenser walls. At the end of the distillation run, helium under a pressure of about 5 psig will be introduced to the system. The condensed metal will be melted and will flow into the distillate trough, after which it will be pressure siphoned into the receiver vessel. The transfer line is heated by autoresistance using a low voltage-high amperage transformer.

About 10 kg of cadmium which was melted in the distillate trough was transferred easily to the receiver crucible by pressure siphoning. A distillation of about 14 kg of cadmium has been successfully demonstrated. The unit is to be installed in a hood to enable work with plutonium systems.

FIGURE 13
CADMIUM DISTILLATION UNIT

b. Retorting of Uranium Concentrates
(J. F. Lenc, P. A. Nelson, R. Zeman)

An important step in the processes using metal solvents is the final retorting step for uranium recovery, which must be conducted in such a fashion that the uranium can be removed in a form suitable for subsequent handling and use. A number of retorting operations have been conducted to ascertain the characteristics and form of the uranium product. Of particular interest was whether or not the uranium product might be granular or similarly disposed for easy removal and handling. No such characteristic was found in three retorting experiments conducted with 1 to 2 kilograms of a cadmium-7 per cent zinc-1 per cent magnesium-5 per cent uranium master alloy. In all cases the uranium had sintered together or plated out along the crucible walls. Maximum final retorting temperatures ranged between 712 and 924 C. Final pressures were less than 1 mm (generally around 200 microns).

The above type of experimentation will be continued by retorting at lower temperatures. The scale of operation is also being increased to one kilogram of uranium. The crucible material and the retorting temperature will be the main variables considered.

c. Phase-separation Studies
(J. C. Hesson, K. Tobias)

(1) Separation of Cadmium-Uranium Intermetallic from Cadmium Supernatant Solution

Phase-separation work on the separation of UCd_{11} crystals from cadmium by pressure siphoning has been continued. In these experiments UCd_{11} crystals were precipitated from solution by cooling the solution from about 550 C to 335 C. Separation of the cadmium mother liquor was effected by using pressure to force it through a dip tube into an adjacent vessel (see Figure 6, ANL-6029). The dip tube extended into the intermetallic bed. A thimble with $\frac{1}{32}$ -inch holes was used as a coarse filter to prevent transfer of intermetallic particles. Filtered samples of the cadmium solution were taken before cooling, after cooling but before siphoning, and after siphoning and reheating to about 450 C to dissolve any crystals carried over. Analytical results are shown in Table 8.

Table 8

ANALYTICAL RESULTS IN PHASE SEPARATION OF
CADMIUM-URANIUM INTERMETALLIC FROM CADMIUM SOLUTION

Run	Total Charge Wt ^a (kg)	Total U in Solution (%)	Wt of Solution Trans (kg)	Temp (C)	U Conc in Filtered Sample (%)	Measured U Sol at Ind Temp (%)	% U in Product Cake ^b	Wt of Siphoned Liquor (kg)	Total U Conc in Siphoned Mat'l (%)
27	11.70	0.32	11.02	335	0.20	0.10	8.1	10.74	0.12
28	9.25	0.26	8.30	335	0.08	0.10	3.5	7.86	0.08
32	12.96	0.52	8.40	322	0.20	0.08	5.9	7.66	0.11
33	13.98	0.61	12.32	370		0.24	9.2	11.81	0.24
36	10.65	2.91 ^c	8.12	335	0.07 ^d	0.10	8.2	5.25	0.09 ^d
41	8.82	1.26	8.11	340	0.30	0.11	11.5	7.14	0.15

^a Excluding samples

^c 4.3% zinc by material balance

^b By material balance

^d 2.0% zinc by material balance

Uranium concentrations after separation are in good agreement with solubility values at the separation temperature, indicating essentially complete separation. The difference in uranium concentrations

in the filtered samples before and after filtration is difficult to explain. The samples prior to siphoning may have included intermetallic particles fine enough to pass through the sample filter. Because of the small amounts of uranium involved in many experiments, the product cake uranium concentrations are sometimes rather low. The theoretical maximum uranium concentration in this cake is 16.1 per cent.

It appears from the above that cadmium can be siphoned from UCd_{11} crystals through a coarse filter with essentially no crystal carryover.

(2) Phase Separation of Insoluble Material from Cadmium

Phase-separation work on the removal of magnesium and uranium oxides and other insoluble oxides and slags from molten cadmium has been started. The material used in these experiments consisted of the ingots from skull oxide dissolution runs in which the oxides are dispersed.* Runs utilizing charges of from 7 to 14 kilograms have been made.

Some runs were made in which a thimble with $\frac{1}{32}$ -inch openings was inserted in the end of the dip tube. In these runs the thimble was kept about $\frac{1}{2}$ inch above the bottom of the crucible and the transfer was stopped when the liquid level was about $\frac{1}{2}$ inch above the thimble, in order to avoid transferring settled or floating oxides. A liquid-level gauge was used to enable transfer of cadmium solutions to predetermined levels. Oxide material was found in the siphoned ingots, indicating inadequate separation and that some of the oxide is dispersed in the cadmium.

Several grades of porous graphite, $\frac{1}{4}$ inch thick, and sintered porous metal, $\frac{1}{8}$ inch thick, have been employed as filtration media. Discs of these materials were fastened in holders $\frac{7}{8}$ and $1\frac{3}{8}$ inches in diameter. The holders were in turn attached to the end of the dip tube through which the molten cadmium alloy was transferred. Porous graphite, grades 20C, 40C, and 60C (average pore sizes of 140, 69, and 33 microns, respectively), and sintered metal filters (grade S-340 stainless steel) of 20-micron and 200-micron pore openings were used. The runs are summarized in Table 9. In Runs 40 and 41, material was siphoned to the dip tube level; in Runs 42 to 47, material transfer was stopped when the liquid level had lowered to about $\frac{1}{2}$ inch above the filter. In all cases, the desired filtration of metal was effected, but, as would be expected, transfer was slow and more difficult with the fine-porosity graphite (60C). In one run (Run PhS-46), it was necessary to back flush twice and to increase the pressure from 10 to 20 psi to achieve filtration in 68 minutes. In this run, there was a considerable amount of oxides in the charged material. An important factor in filtration rate was the amount of oxides present.

*An attempt was made to disperse magnesium oxide powder and skull oxide in molten cadmium by stirring to provide material of controlled composition for use in phase separation studies. This was unsuccessful because the magnesium oxide did not stay dispersed in the cadmium and floated to the top as a dry powder.

Table 9

TESTS OF VARIOUS FILTER MEDIA FOR SEPARATING
INSOLUBLE OXIDES FROM CADMIUM SOLUTIONS

Run No.	Filter Media	Charge (kg)	Amount Transferred (kg)	Temp of Transfer (C)	Pressure Used (psi)	Time Required (min)
PhS-40	None	9.1	8.4	556	10	3½
PhS-41	20 C Graphite (7/8 in. D)	9.0	8.3	550	19	33
PhS-42	Filter of Run 41 reused	7.9	5.0	575	10 to 18	20
PhS-43	40 C Graphite (1 3/8 in. D)	7.9	5.4	635	11	8½
PhS-44	Filter of Run 43 reused	7.8	5.2	600	10	14
PhS-45	60 C Graphite (1 3/8 in. D)	7.8	5.3	580	10	28
PhS-46	Filter of Run 45 reused	7.0	4.2	565	10 to 20	68
PhS-47	Sintered SS (S-430) (7/8 in. D)	6.9	4.3	565	10	9½

From the appearance of transferred and residual material, good separation of insoluble material appears to have been effected. The ability to transfer the above quantities of material through the small filter discs is somewhat encouraging. It appears important to avoid the siphoning of floating insoluble material, since the frequency of replacement or reconditioning of plugged filters would be proportional to the amount of material removed by the filters. The use of a second settling vessel might have merit.

Equipment for testing filters of considerably larger diameter in a portion of the line outside the tank is now being installed. Various types of valves and unions are also incorporated in this equipment. A major consideration in the design has been the eventual need for remote installation and replacement of the various items.

d. Corrosion in Liquid Metal Systems
(J. P. DeKany, H. W. Lavendel, J. Pavlik)

The liquid metals corrosion test program was continued with the completion of several static and dynamic tests on mild steel and 410 stainless steel in various molten cadmium-alloy media. Among the

dynamic tests completed was a 1000-hour test in which a cadmium-uranium alloy was circulated at 550 C in a mild steel loop. The corrosion program was conducted with the same procedure outlined in the previous quarterly report (ANL-6029, page 44).

(1) Dynamic Tests

(a) Liquid Metal Corrosion Loop

The loop circulating molten cadmium-1.49 weight per cent uranium-0.2 weight per cent magnesium alloy at 550 C with an electromagnetic pump (ANL-6029, pages 43 to 46) continued to operate without incident for a total elapsed time of 1021 hours. At this time the loop was shut down because the scheduled operating time of 1000 hours had elapsed. The loop was then dismantled, sectioned, polished, and etched with 2 per cent nitric acid-ethyl alcohol for metallographic examination.

Radiographs taken periodically of the loop during operation did not indicate significant corrosion. This was substantiated in most part by metallographic examination. Only in three locations were there indications of slight interaction with the mild steel loop: the bottom of the reservoir, the electromagnetic pump cell, and at the loop exit to the reservoir. The interaction at these points consisted of a double reaction layer on the steel wall accompanied by the presence of various intermetallic compound particles in the near vicinity of the layer. Spark spectroscopy, Vickers hardness determinations, and X-ray examination are being used to identify the nature of the interaction products.

One possible explanation of the localized interactions is indicated by an examination of the results of the chemical analyses of periodic thief samples, which are tabulated in Table 10. Initially enough uranium in the form of rods was charged into the loop to make an alloy of 2 nominal weight per cent composition. However, the chemical analyses show that the composition of the uranium remained nearly constant at a value of around 1.5 weight per cent.

This would seem to indicate that not all of the uranium charged remained in solution and that some of it precipitated at cold spots in the loop as alpha uranium or cadmium-uranium intermetallic. The highly localized interactions might then be attributed to the presence of precipitated uranium or intermetallic in contact with the steel walls at cold regions. All three of the locations where attack occurred are points of high heat loss and consequently are cold spots. The pump cell, which had the thickest interaction layer, was the coldest point in the loop because of massive bus bars which conducted away a large amount of heat.

Table 10

PERIODIC URANIUM AND IRON CONCENTRATIONS IN
CADMIUM ALLOY CIRCULATED FOR 1000 HOURS
IN MILD STEEL CORROSION LOOP

Alloy Composition: Cadmium-0.2 w/o magnesium-U as shown
Temp of Circulation: 550 C

(Loop details are given in ANL-6029, page 44)

Sample No.	Elapsed Time (hr)	Temp (C)	Concentrations	
			Uranium (wt per cent)	Iron (ppm) ^a
1	113	480	1.47	-
2	209	548	1.58	-
3	283	552	1.55	-
4	621	555	1.42	5.6
5	669	542	1.47	4.3
6	717	560	1.45	4.1
7	837	555	1.47	3.8

^aThe solubility of iron in cadmium has been reported to be about 2 to 3 ppm at 400 C and 700 C (Hansen, M., Constitution of Binary Alloys, McGraw-Hill Book Co., New York (1958), 2nd Ed., p 417)

From an overall evaluation of the loop, it seems likely that, since the interactions are both highly localized and slight, mild steel is a satisfactory material of containment for the cadmium-uranium system. However, further checking is certainly indicated.

The construction of another mild steel loop is near completion. This loop will again circulate the cadmium-uranium system at 550 C, but in this experiment fission elements will also be present at concentrations present in a dragout process solution.

(b) Rotating Capsule Tests

A number of mild steel and 410 stainless steel capsules holding molten cadmium-zinc alloys (containing up to 10 weight per cent zinc) were rotated end over end for 1000 hours at 350 C. Preliminary examination disclosed corrosion in the mild steel-cadmium-10 weight per cent zinc (highest zinc weight per cent alloy tested) system. While the other capsules appeared to be uncorroded, further metallographic examinations are being performed.

(2) Static Tests

(a) Molten Cadmium and Cadmium-Zinc Tests

A series of mild steel and 410 stainless steel capsules containing cadmium and cadmium-10 weight per cent zinc was tested at 700 C under static conditions for 100 hours. The samples were polished and etched with 2 per cent nitric acid-ethyl alcohol for metallographic examination. The examination showed that both the mild steel and 410 stainless steel capsules containing pure cadmium were intergranularly attacked slightly to an average depth of 0.2 mil. Both the mild steel and 410 stainless steel capsules were attacked by the 10 weight per cent zinc-0.2 weight per cent magnesium-cadmium alloy to an average corrosion depth of 0.5 mil.

(b) Molten Zinc and Zinc-Magnesium Tests

Although current work is with cadmium systems because of their less corrosive nature as compared with zinc systems, a number of tests started in zinc systems have been completed. Several Rokide refractory coatings on mild steel were tested in zinc and 46 weight per cent magnesium-zinc. Coatings of Rokide "A" (aluminum oxide), Rokide "ZS" (zirconium silicate), Rokide "Z" (stabilized zirconia), Rokide "C" (silicon carbide), and CrB_2 applied to mild steel coupons were tested in the two media at 750 C for 100 hours. None of the refractory coatings prevented the pure zinc from penetrating through and attacking the mild steel. With the exception of Rokide "Z", the zinc-magnesium alloy also penetrated the coatings and attacked the mild steel. However, the zinc-magnesium alloy did not attack the samples as severely as did the pure zinc. The Rokide "Z" successfully protected the mild steel from the zinc-magnesium alloy.

C. Pyrometallurgical Research (H. M. Feder)

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

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 theories of liquid metal solutions. The separations processes envisioned involve dissolution of the spent reactor fuel in an appropriate liquid metal, separation of the fissile material(s) from the fission product or other extraneous elements by crystallizations and/or extractions into immiscible liquids (either fused salts or liquid metals), and recovery of the fissile metal(s) from its mother liquor by volatilization of the latter.

a. Solubilities in Liquid Metals

The solubilities of the fission product elements in liquid metal solvents are of primary importance in the separation processes under development. The solubilities must be known as functions of temperature and solvent composition. For a better understanding of the phenomena involved it is useful to characterize the solid phase whose solubility has been measured.

The general method which has been employed in all the solubility determinations reported from this laboratory consists of the preparation of a saturated solution at a given temperature, sampling this solution through an appropriate filter and analysis of this sample. This procedure is repeated at several different temperatures in order to characterize the temperature dependence of the solubility. The experimental technique has been described in part in ANL-5820.

Saturated solutions are prepared by vigorously stirring a mixture of the molten solvent metal and a quantity of solute in excess of its solubility for an extended period of time (up to several days in some cases) at a constant temperature. Successive samples are taken and analyzed until constancy of sample composition is reached, or, if analytical results are not available, until sufficient time has elapsed to achieve saturation as indicated by prior experiences. The temperature is then raised by increments and the procedure is repeated at each higher temperature. Values for the solubility so obtained are designated by "heating."

In the alternative method all of the added solute is dissolved at some high temperature where the solubility exceeds the amount of solute added. The solution is then cooled to successively lower temperatures, held for several hours at each temperature, and sampled. Only those samples which have a solute content less than the nominal starting alloy are considered as saturated. Values for the solubility obtained by this method are designated by "cooling."

These methods ideally yield solubility-temperature curves which are identical, but this is not always observed in practice, owing to nonequilibrium situations. For example, in the "heating" method, if the equilibrium solid is an intermetallic phase but the solute was added as the pure solid metal, one may encounter an abnormally slow approach to saturation due to a diffusion-controlled reaction at the solid surface. Vigorous stirring and a finely divided solute mitigate this tendency. It is also sometimes expedient to prepare a master alloy near the composition of the expected equilibrium solid prior to attempting the solubility measurement. This expedient is particularly useful with metals, such as the alkali and alkaline earth metals, which are very reactive to the atmosphere or react with the solute very exothermically.

The "cooling" method may give high values due to one or both of two principal causes. The first is the tendency of crystallizing systems to supersaturate. Such residual supersaturation³ is reduced by lowering the temperature by moderately large increments and by digestion prior to sampling. This effect may be expected to be particularly serious in systems exhibiting very small solubilities or very small temperature coefficients, since even a moderately large lowering of the temperature may produce only a small absolute change in the amount of solute in solution. Moreover, such conditions also lead to the formation of fine crystals which may pass through the filters used. Under these conditions a sequence of heating (to dissolve the finest crystals) and cooling has proved to be effective in removing the causes which contribute to high results.

The second cause is the accidental nucleation and precipitation of a metastable phase. This may be revealed by large discrepancies between independent runs and is cured only by ensuring adequate digestion time.

Solubilities reported for some of the systems have been determined by both "heating" and "cooling" methods. In no case was a significant difference found after the special features of a particular system were taken into account.

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

The solubility of barium in cadmium was measured by the "cooling" method. Barium was added to the liquid cadmium in the form of a barium-cadmium master alloy. The samples were analyzed for barium by flame spectrophotometry. The results of these experiments are shown on the usual logarithmic solubility versus $1/T$ plot in Figure 14. The points between 560 and 383 C lie on a straight line which may be expressed algebraically as

$$\log (w/o \text{ Ba}) = 6.810 - (5635/T).$$

The solid phase in equilibrium with these saturated solutions was not separately characterized. Sanderson and Baenziger⁴ have reported the most cadmium-rich compound (which is presumed to be the solid phase present) to be BaCd_{11} .

³Amiard, G., *Experientia* 15, 38 (1959).

⁴Sanderson, M. J. and Baenziger, N. C., *Acta Cryst.* 6, 627 (1953).

(2) Strontium-Cadmium
(I. Johnson and K. E. Anderson)

The solubility of strontium in cadmium was measured in a manner entirely similar to that discussed for barium. Two runs were made. In the first run the lower temperature range was studied. In the second run the master alloy which contained a slight excess of cadmium above the formula SrCd_{11} was melted without dilution. The results of the two experiments are shown on the usual logarithmic solubility vs $1/T$ plot in Figure 14. It is seen that the points between 524 C and 325 C lie on a straight line which may be represented algebraically as

$$\log (w/o \text{ Sr}) = 6.717 - (4873/T).$$

The solid phase in equilibrium with the saturated solution was not separately characterized but Sanderson and Baenziger⁴ have reported that the most cadmium-rich compound is SrCd_{11} . The strontium-cadmium system has been studied by Hodge and co-workers⁵ by an admittedly not precise method. Their thermal analyses show the melting point of the first compound to be about 375 C, whereas if the present solubility equation is extrapolated a short distance to the composition of the SrCd_{11} compound (i.e., 6.62 weight per cent strontium) the predicted melting point is 553 C. In addition, the present data indicate the first eutectic composition is about 0.03 weight per cent strontium; Hodge interpreted photomicrographs of the alloy as indicating this eutectic at 0.9 weight per cent. It has been shown in our previous reports that dilute eutectic compositions are grossly overestimated by the metallographic technique.

(3) Cadmium-Uranium System (A.E. Martin, C. Wach)

The case of a metal having a retrograde solubility in another liquid metal is unusual; it may present some difficult experimental problems. The retrograde solubility (ANL-5896, page 128) of uranium in liquid cadmium above the peritectic temperature of 475 C was established more firmly by an additional solubility run using alternate heating and cooling periods. In this experiment the holding periods were of at least two hours duration at each temperature, during which the mixtures were vigorously mechanically stirred, and quiescent settling periods of twenty minutes were allowed before sampling.

The data from this run are shown in Figure 15 in a log solubility versus $1/T$ plot. They confirm the retrograde character of the solubility curve and indicate that it may be nonlinear on this plot. From these data the composition of the saturated liquid at the peritectic temperature is about 2.5 weight per cent uranium. The earlier estimate was 2.2 to 2.3 weight per cent uranium.

(4) The Palladium-Zinc System (A. E. Martin, C. G. Wach and C. Wade)

The solubility of palladium in zinc has been measured by both the heating and cooling methods. The results are shown in Figure 16 in a log atom per cent solubility versus $1/T$ plot. Also shown are two points obtained by Knighton (ANL 5668, page 94) by a similar technique but using shorter equilibration periods, and thermal analysis data reported by Nowotny et al.⁶ The latter data were obtained for the most part at higher

⁵Hodge, H.C., et al., *Metals and Alloys*, 2, 355 (1931); summarized by M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill Book Co., New York (1958), 2nd Edition, page 443.

⁶Nowotny, H., Bauer, E., Stemfl, A., *Monatsch. Chem.* 82, 1086-1083 (1951).

FIGURE 15
SOLUBILITY OF URANIUM IN CADMIUM ABOVE THE PERITECTIC
DECOMPOSITION TEMPERATURE OF UCd_{11}

FIGURE 16
SOLUBILITY OF PALLADIUM IN LIQUID ZINC

temperatures and palladium concentrations, but there is some overlap with the present study. It is gratifying to find that the combined data fall on a common line (within their probable precisions) which can be represented by the equation

$$\log (a/o \text{ Pd}) = 4.005 - (3226/T)$$

Thermal analysis measurements were made on the melt which had been used in this solubility run. They showed a good thermal arrest on heating at 434 C. This appears to be a more accurate determination of a peritectic reaction in this system which had been previously reported as at 425 and ~430 C.⁷

(5) Zinc-Zirconium System
(A. E. Martin and C. G. Wach)

As previously reported (ANL-5959, pages 116 and 117), measurements of the solubility of zirconium in liquid zinc made in this Laboratory were in agreement with those made at Iowa State College above the peritectic temperature of 545 C but disagreed at lower temperatures. A possible source of error in our measurements is the scavenging of small amounts of zirconium by porous graphite during the short time that the solution passes through the filter. As a further check on our data both unfiltered and filtered samples of a zirconium-saturated melt were withdrawn at 425 C after a holding period of 17 hours. The analyses of each of the five samples taken checked our earlier data within the experimental error, but all were lower by a factor of ten than the Iowa State data for this temperature. Furthermore, the analyses of the unfiltered and filtered samples checked with each other; the three unfiltered samples had an average content of 0.031 weight per cent zirconium, and the two filtered samples had an average content of 0.028 weight per cent. Thus, the possibility that an appreciable amount of the zirconium is extracted by passage through a graphite filter is eliminated.* The thermal arrest temperature corresponding to the eutectic in this system was also remeasured and a value of 419.5 ± 0.2 C was obtained. This value is consistent only with the composition of the eutectic indicated by our solubility data.

(6) Zinc-Ruthenium
(A. E. Martin, C. G. Wach, and C. Wade)

In obtaining data for solubility of ruthenium in liquid zinc (ANL-5759, page 120) filtered samples were taken on cooling after holding periods of from 10 minutes to 40 minutes. Activated ruthenium was used for analyses by counting. Difficulties and inconsistencies which have been encountered with these data led to a decision to attempt additional

⁷Hansen, M., Constitution of Binary Alloys, McGraw-Hill Book Co., New York, (1958), 2nd Ed. page 1130.

*A. Schneider, of this Laboratory, also reports good agreement of zirconium analyses between filtered and unfiltered samples of unsaturated solutions of zirconium in cadmium at concentrations of 0.13 and 0.29 weight per cent zirconium in two separate tests.

work. These additional solubility data were obtained by both heating and cooling cycles after holding periods of from 1.5 to 18 hours. The samples were analyzed by chemical separation and spectrophotometry. There appear to be consistent differences between the two sets of data beyond their analytical errors.

A thermal analysis was made on the melt from this study and weak thermal arrests on heating were obtained at 555 C and 635 C; these are thus indicated as probable peritectic temperatures in this system. Further studies will be made to elucidate this region of the phase diagram.

(7) Cadmium-Zinc-Uranium System

(A. E. Martin, C. G. Wach, and R. J. Uhle)

An isothermal solubility run was made in this system at 548 C using the technique described in ANL-5996, page 104. The results of this and two earlier runs are shown in Figure 17 in a ternary plot.

A sharp cusp is apparent in the 548 C curve. The sample at this point analyzed 4.3 weight per cent uranium, 5.9 weight per cent zinc, and 89.8 weight per cent cadmium (by difference). From other observations, it is apparent that this point marks the transition from a field of primary crystallization of alpha uranium to that of primary crystallization of U_2Zn_{17} . In the uranium field of crystallization at 548 C there is a uniform increase in uranium solubility as the zinc content of the melt is increased. In the U_2Zn_{17} field, however, the effect of zinc is not so simple. The first zinc additions in this region precipitated uranium as U_2Zn_{17} and also, somewhat anomalously, caused a slight drop in the zinc content

of the melt. The explanation of this apparent anomaly is that the zinc added to the melt was precipitated as U_2Zn_{17} , and, in addition, some previously dissolved zinc was also precipitated as the same compound, thus lowering the zinc content of the melt. This explanation is more easily visualized by reference to the conventional ternary diagram which is nearing completion.

Regular uranium solubility runs in two cadmium-zinc alloys have been made over the temperature range in which alpha uranium is the primary crystallizing phase. These data are shown in Figure 18 in a log solubility versus $1/T$ plot, along with the curve for cadmium alone. The data show that the retrograde solubility persists at the 1.5 weight per cent zinc composition. The data are too scattered to show whether this is also true at the 5 weight per cent zinc level. The temperature coefficient of solubility is certainly very small in this solvent.

FIGURE 18
SOLUBILITY OF URANIUM IN CADMIUM AND IN CADMIUM-ZINC
ALLOYS IN THE TEMPERATURE RANGE OF PRIMARY CRYSTALLIZATION
OF ALPHA URANIUM

(8) Cadmium-Magnesium-Uranium System
(A. E. Martin, C. G. Wach and R. Uhle)

The solubility of uranium in two additional cadmium-magnesium alloys was measured by the usual filtered liquid sampling technique. The data for these two runs are shown in Figure 19 in a log solubility versus $1/T$ plot. Earlier solubility runs at lower magnesium contents are included for comparison. The data for the run at 40 weight per cent magnesium scatter considerably. This may be due to analytical difficulties at very small uranium contents or to inadvertent contamination of the melt with silicon from reaction with the sampling tubes. An isothermal plot of the same data at 600 C is shown in Figure 20. Because of the low temperature coefficients of solubility in this region, the data for other temperatures would fall on nearly the same line.

FIGURE 19
SOLUBILITY OF URANIUM IN CADMIUM AND
IN CADMIUM-MAGNESIUM ALLOYS IN THE TEMPERATURE
RANGE IN WHICH URANIUM IS THE PRIMARY CRYSTALLIZING PHASE

FIGURE 20
SOLUBILITY OF URANIUM IN LIQUID CADMIUM-MAGNESIUM
ALLOYS AT 600 C

b. Liquid-Liquid Partition Studies

(1) Uranium between Aluminum and Cadmium (F. Cafasso)

Partition of a substance between two immiscible or partially immiscible liquid phases is a separation technique that has proven useful in the past. The aluminum-cadmium system was chosen as a model system in which to study the partition of various fissile elements and fission products. An additional stimulus for this study is the fact that partition data may be made to yield thermodynamic data for the various elements dissolved in aluminum.

The apparatus used in this study is shown schematically in Figure 21. It consisted of a flanged cylindrical stainless steel tube, 4.5 inches in internal diameter and 21.5 inches long, which was provided with a side arm for connection to a vacuum line. The assembly was heated by a resistance furnace. Water-cooled coils, located near the flanged surface, served to protect the rubber "O"-ring. Melts were contained in alumina crucibles which rested in secondary graphite crucibles. A graphite block was used to support and to position the latter, laterally and longitudinally, within the tube. The upper flange was provided with fittings and valves to permit stirring, temperature measurements, and sampling operations to be performed. A tantalum paddle driven by an electric motor was used for mechanical stirring. Temperature measurements were made with an immersed chromel-alumel thermocouple in an alumina protection tube. Two ports were provided for simultaneous sampling of both phases. Samples were taken by pressurizing the assembly after 3-mm quartz tubes, fitted with graphite filters, had been lowered into each phase.

Several preliminary experiments were necessary to establish the best operating conditions with uranium as the solute. These experiments showed that equilibrium was established after one hour of stirring at a rate of 500 rpm. They also served to establish approximate mutual solubility of the liquid metals. At 682 C, the mutual solubilities determined by spectrographic analysis were: cadmium in aluminum, 8.0 weight per cent; aluminum in cadmium, 1.2 weight per cent. The concentration of tantalum in each phase was less than the detectable limit, 0.1 weight per cent.

The partition of uranium between the phases was determined in an equimolar mixture of aluminum and cadmium. Sufficient uranium was added to correspond to a nominal concentration of 1.89 weight per cent if dissolved completely in the cadmium layer, or 6.9 weight per cent if dissolved entirely in the aluminum phase. The temperature was 682 C. Samples of each layer were taken at intervals over a 21-hour period. Analyses of samples from each phase indicated that uranium was

FIGURE 2I
APPARATUS FOR DISTRIBUTION EXPERIMENTS

extracted into the aluminum layer almost quantitatively. After one hour of stirring, the uranium concentrations were 6.8 weight per cent in aluminum and 1.2×10^{-2} weight per cent in cadmium. Subsequent samples showed small decreases in uranium concentration which were ascribed to accidental oxidation. On the basis of these preliminary results the tentative value of the molar partition coefficient is 570.

c. Thermodynamic Studies

Thermodynamic functions for certain metallic elements of special interest in liquid alloys or in solid intermetallic phases are being measured. Two methods are in use: in one the desired quantities are determined from the measured emf of an appropriate galvanic cell; in another they are determined from measurements of the vapor pressure of a volatile constituent.

(1) Uranium-Cadmium (I. Johnson and R. M. Yonco)

The thermodynamic activity of uranium metal dissolved in liquid cadmium has been measured by means of the following cell:

where N is the atom fraction of uranium in liquid cadmium solution. The emf, E , of this cell is given by the equation

$$E = -\frac{RT}{nF} \ln a = -\frac{RT}{nF} \ln N - \frac{RT}{nF} \ln \gamma \quad , \quad (1)$$

where a is the activity of uranium in solution, γ its activity coefficient, and the other symbols have their usual meanings. The reference state is solid uranium.

Measurements have been reported (ANL-5996, page 116) for a cell in which the liquid electrode was saturated with respect to uranium at each temperature. Additional measurements have now been made for this cell with an unsaturated liquid electrode. Unsaturated liquid electrodes were prepared by electrolyzing uranium from solution in cadmium to the solid uranium electrode by application of a back emf. The determination of the exact composition of the resulting solution could not be reliably made from knowledge of its original composition and the total current passed. Instead, it was determined by measuring the cell emf for a fixed composition at various temperatures and extrapolating to the temperatures at which the emf's of both saturated and unsaturated cells were equal. The emf's of both saturated and unsaturated cells were found to be linear functions of

their temperatures within the precision of measurement; these extrapolations were therefore readily accomplished algebraically. The compositions were then computed from the known saturation temperatures and the solubility-temperature relation for uranium in cadmium (ANL-5896, page 128).

The results of applying equation (1) to the data obtained are shown in Table 11. In this table values for four different compositions were computed at 459.6 C. At this temperature the activity coefficient of uranium decreases appreciably with decreasing concentration and the Henry's Law approximation is not valid in this range.

Table 11

ACTIVITY AND ACTIVITY COEFFICIENT OF URANIUM
DISSOLVED IN CADMIUM AS A FUNCTION OF URANIUM
CONCENTRATION OF THE SOLUTION

$t = 459.6 \text{ C}$

Series	Atom fraction Uranium (N)	E (mv)	$\frac{dE}{dt},$ (mv/C x 10^2)	log a	log γ
A	1.476×10^{-3}	47.80	4.10	-0.9864	1.845
B	4.861×10^{-3}	19.80	3.89	-0.4087	1.905
C	7.018×10^{-3}	10.16	3.96	-0.2097	1.944
D	7.863×10^{-3}	7.06	3.48	-0.1458	1.959

The temperature coefficient of the emf of a saturated cell reflects both the effect of composition change with temperature required by the solubility equilibrium, and the dependence of the activity coefficient of the solution on composition and temperature. The temperature coefficient of the constant composition cell reflects only the dependence of the activity coefficient on temperature. Thus by combining data from the saturated cell, the constant composition cell and the solubility-temperature relationship, it is possible to calculate the dependence of the activity coefficient on composition. The quantitative relation required may be calculated in the following manner. The rate of change of emf, E, with temperature of a cell whose composition is also changing is given by

$$\frac{dE}{dT} = \left(\frac{\partial E}{\partial T} \right)_N + \left(\frac{\partial E}{\partial N} \right)_T \left(\frac{dN}{dT} \right) \quad (2)$$

Making use of equation (1) one then derives

$$\frac{dE}{dT} = \frac{E}{T} - \frac{RT}{nF} \left(\frac{\partial \ln \gamma}{\partial T} \right)_N - \frac{RT}{nF} \left(\frac{\partial \ln \gamma}{\partial N} \right)_T \left(\frac{dN}{dT} \right) - \frac{RT}{nF} \left(\frac{d \ln N}{dT} \right) \quad (3)$$

For a constant composition this equation reduces to:

$$\left(\frac{dE}{dT} \right)_N = \frac{E}{T} - \frac{RT}{nF} \left(\frac{\partial \ln \gamma}{\partial T} \right)_N$$

The difference between the temperature coefficients of cells with saturated (denoted by subscript S) and unsaturated constant composition liquid electrodes is therefore

$$\left(\frac{dE}{dT} \right)_S - \left(\frac{dE}{dT} \right)_N = -\frac{RT}{nF} \left(\frac{\partial \ln \gamma}{\partial N} \right)_T \frac{dN_S}{dT} + \frac{d \ln N_S}{dT} \quad (4)$$

This relation may be further simplified by substitution of the equation which expresses the temperature dependence of the solubility, viz.,

$$\ln N_S = A - (B/T) \quad ,$$

to obtain

$$\left(\frac{dE}{dT} \right)_S - \left(\frac{dE}{dT} \right)_N = -\frac{RB}{nFT} \left[\left(\frac{\partial \ln \gamma}{\partial N} \right)_T N_S + 1 \right] \quad (5)$$

The experimental emf's as functions of temperature for the saturated liquid electrode and for a liquid electrode of constant composition (Series C) are shown in Figure 22. Also shown is the temperature dependence of the emf for the same composition, computed on the assumption that the Henry's Law approximation is valid, i.e., that the activity coefficient remains constant below saturation. The marked deviation from the Henry's Law approximation is readily seen.

The quantitative relation between the activity coefficient of a dilute solute and its concentration may be expressed in different ways which may apparently fit the observed data equally well. The reason for this apparent ambiguity usually lies in the small range of concentrations available for experimental study and the consequent great demands on accuracy and precision. The simplest relation which is consistent with all the data obtained in this study has the form suggested by Lumsden⁸ for moderately dilute solutions.

$$\log \gamma = \log \gamma_0 + AN \quad , \quad (6)$$

⁸Lumsden, John, Thermodynamics of Alloys, Institute of Metals (London), 1952, page 183.

FIGURE 22
COMPARISON OF TEMPERATURE DEPENDANCE OF EMF FOR CELL
WITH SATURATED LIQUID ELECTRODE AND CONSTANT
COMPOSITION LIQUID ELECTRODE
(CELL $U|UCl_3 \text{ KCl-LiCl (eutectic)}| \text{Liquid Cd-U Soln}$)

where γ_0 is the activity coefficient in the infinitely dilute solution and A is a constant. Both constants are temperature dependent. A typical plot is shown in Figure 23. The slope of this line, A , is in satisfactory agreement with the value of $\left(\frac{\partial \log \gamma}{\partial N}\right)_T$ computed from equation (5).

FIGURE 23
EFFECT OF URANIUM CONCENTRATION ON THE ACTIVITY
COEFFICIENT OF URANIUM IN LIQUID CADMIUM

2. Calorimetric Research (W. N. Hubbard)

a. Instrument Calibration

Platinum-lined Bomb

(R. L. Nuttall and D. R. Fredrickson)

The platinum-lined bomb calorimetric system was recalibrated this quarter in accordance with a predetermined schedule for maintaining all the instrumentation of this laboratory. The results of this recalibration are given in Table 12.

Nickel Bomb

(E. Greenberg and J. Settle)

A new nickel bomb calorimetric system was calibrated by benzoic acid combustions. The results obtained are given in Table 13. Since the two series of runs, one with half-gram samples and one with one-gram samples, gave calibration factors in substantial agreement, the grand mean will be used. This bomb is being prefluorinated prior to calorimetric combustions in fluorine.

Tabel 12

CALIBRATION OF PLATINUM-LINED BOMB
CALORIMETRIC SYSTEM

(ANL-R1-Pt-1)

$\alpha \times 10^4$ (sec ⁻¹)	Mass of Benzoic Acid (g)	Temperature Rise, ΔT (C)	$\epsilon_{\text{calorimeter}}$ (cal/deg)
0.3358	0.50110	0.88545	3578.9
0.3332	0.50206	0.88753	3577.6
0.3322	0.50042	0.88426	3578.6
0.3328	0.50003	0.88416	3576.8
0.3340	0.50031	0.88446	3577.5
0.3340	0.49982	0.88344	3577.2
0.3318	0.49979	0.88307	3579.1

Mean = 3578.0

Std Dev of mean = 0.3₄ or 0.01%

Table 13

CALIBRATION OF NICKEL BOMB CALORIMETRIC SYSTEM

(ANL-R1-Ni-T)

Series I (0.5-gram samples)

$\alpha \times 10^4$ (sec ⁻¹)	Mass of Benzoic Acid (g)	Temperature Rise, ΔT (C)	$\epsilon_{\text{calorimeter}}$ (cal/deg)
0.3349	0.50027	0.88650	3568.1
0.3360	0.49995	0.88617	3567.1
0.3363	0.50006	0.88556	3570.3
0.3421	0.49963	0.88564	3567.0
0.3361	0.49969	0.88516	3568.7
0.3378	0.50000	0.88618	3566.7

Mean = 3568.0

Std Dev of mean = 0.56 or 0.01₆%

Series II (1.0-gram samples)

0.3377	1.00017	1.76977	3568.37
0.3383	1.00021	1.76946	3568.64
0.3370	1.00023	1.76992	3568.47
0.3393	1.00057	1.77029	3568.88
0.3360	0.99996	1.76936	3568.10

Mean = 3568.49

Std Dev of mean = 0.13 or 0.003₆%

Grand mean (11 runs) = 3568.2

Std Dev of mean (11 runs) = 0.31 or 0.008₇%

b. Heat of Formation of Molybdenum Trioxide
(R. L. Nuttall and D. R. Fredrickson)

The most recent literature⁹ reports a value for the standard heat of formation of molybdenum trioxide based on combustions of 20-mil molybdenum wire in oxygen which were only 70 to 80 per cent complete. A technique was devised for obtaining more nearly quantitative combustions in order to confirm the accepted value.

Pure molybdenum foil, 2.5 mils thick, $\frac{3}{8}$ inch wide and 3 inches long, was crimped into the form of a "W" (for minimal contact) and placed on a 0.5-mm thick quartz disc, supported by indentations near the top of a thin quartz crucible. The crucible, in turn, was supported by arms hung in a gimbal. A cotton thread ignited a molybdenum wire attached to both ends of the molybdenum foil. The combustion was run in a dry bomb with a pressure of 16 atmospheres of oxygen. The heat produced was due to the reaction

The degree of completeness of combustion was determined by dissolving the bomb contents in 4 N NaOH, filtering, drying, and weighing the residue. This residue was ignited to 900 C and the weight loss was attributed to MoO₂ being oxidized to MoO₃ and vaporized. The results of four experiments in which greater than 99 per cent combustion to the trioxide took place are given in Table 14. The mean standard heat of formation, -177.66 ± 0.07 kcal/mole, does not differ greatly from the best literature value, -177.99 ± 0.10 kcal/mole.

Table 14

COMBUSTION OF MOLYBDENUM IN OXYGEN

Mass Mo Reacted (g)	Mass MoO ₂ Formed (mg)	Correction ^a for MoO ₂ (cal)	Standard Heat of Formation, $-\Delta H_f$	
			(cal/g)	(kcal/mole)
0.49777	3.86	1.12	1852.12	177.71
0.49735	3.02	0.88	1852.08	177.71
0.50285	1.55	0.45	1851.37	177.64
0.50700	0.28	0.08	1850.65	177.57
Mean			1851.56 ± 0.72	177.66 ± 0.07

^a Based on the value, -37.12 kcal/mole, as the standard heat of formation of MoO₂ to MoO₃.

⁹Staskiewicz, B. A., Tucker, J. R., Snyder, P. E., The Heat of Formation of MoO₂ and MoO₃, J. Am. Chem. Soc., 77, 2987 (1955)

c. Heat of Formation of Molybdenum Hexafluoride
(J. Settle)

Preliminary determinations of the heat of formation of molybdenum hexafluoride have been reported (ANL-6029). Experiments with both commercial fluorine and fluorine purified by low temperature fractionation were included. Further experimentation has shown that the heat obtained with commercial fluorine were 7 cal/gram sample too large and should be discarded. Table 15 is a tabulation of all the runs that have been carried out to date with purified fluorine. In the last three experiments only one half the usual sample was used in order to gain confidence in the results obtained or reveal systematic errors. The weight gain in the bomb has been attributed to the formation of nonvolatile lower fluorides or oxyfluorides during the combustion process. This series is being continued with some modifications in techniques in an attempt to minimize the side reactions occurring in the bomb.

Table 15

COMBUSTION OF MOLYBDENUM IN FLUORINE

Combustion No.	Mass Molybdenum Reacted (g)	Weight Gain of Bomb (mg)	Observed Heat of Combustion (cal/g)	Empirical Correction for Weight Gain (cal/g)	Corrected Heat of Combustion (cal/g)
14	0.74722	49.2	-3865.10	-17.09	-3882.19
15	0.72260	12.8	-3880.56	- 4.60	-3884.16
16	0.73261	-1.0	-3878.24	+ 0.36	-3877.88
18	0.72452	59.8	-3862.63	-21.43	-3884.06
19	0.37431	27.8	-3858.25	-19.30	-3877.55
20	0.36254	19.6	-3869.20	-14.06	-3883.26
22	0.37149	36.4	-3854.45	-25.46	-3879.91

d. Heat of Formation of Zirconium Tetrafluoride
(E. Greenberg)

A technique for burning zirconium metal in fluorine to a high degree of completion without side reactions was required. A glass bomb with nickel heads, capable of sustaining internal pressures up to 10 atmospheres, was used for exploratory runs. These exploratory experiments revealed that combustions in pure fluorine were unsatisfactory because the zirconium specimens melted and reacted with their supports or quenched the combustion. Dilution of the fluorine with helium proved to be a solution to this problem. Successful combustions were achieved

using zirconium rod specimens, approximately $\frac{1}{8}$ -inch diameter and $\frac{1}{2}$ to 2 inches long, supported vertically in a relatively massive nickel base. Samples were ignited at the top with a zirconium fuse wire and a small piece (about $\frac{1}{4}$ inch $\times$ $\frac{1}{4}$ inch) of 5-mil zirconium sheet which acted as a kindler. Sample weights varied from 0.5 to 2.0 grams and the combustion mixture consisted of 2.7 atmospheres of fluorine with helium added to bring the total pressure up to 9 atmospheres. (In a typical calorimetric run, fluorine will be in approximately 50 per cent to 200 per cent excess of that required for stoichiometric combustion of the zirconium to zirconium tetrafluoride.) In these experiments the combustions lasted for several minutes and the product sublimed away rapidly from the glowing zirconium rod. At the end of successful combustions small, spear-shaped pieces were left unconsumed at the bottom where the sample was supported in the nickel base. The fraction of zirconium burned averaged about 95 per cent. The nickel block acted as a good thermal sink and there did not appear to be any attack on the nickel or interaction of the nickel with the zirconium.

In calorimetric runs to be performed in the nickel bomb, the extent of combustion will be determined by recovering and weighing the unburned zirconium after dissolving any adhering zirconium tetrafluoride with 4 molar sulfuric acid. X-ray examination of the product obtained in a trial combustion showed an unidentified phase present in addition to β -ZrF₄. This result will be checked on the product obtained from a calorimetric combustion with pure fluorine.

e. Heat of Formation of Boron Trifluoride
(S. Wise)

Work has begun on the determination of the heat of reaction of boron with fluorine. Since boron burns spontaneously in fluorine, it is necessary to find some method for keeping the two separated in the bomb until the reaction is desired. Thus far effort has been devoted to finding a method for encapsulating the boron. Kel-F bags, thin quartz capsules, and gold foil bags have been tried. Kel-F proved unsatisfactory since it tended to burn spontaneously. Quartz ampoules satisfactorily contained the boron and burned completely in fluorine. However, the heat of combustion of the capsule is comparable to that of the boron sample. Therefore, quartz may not be satisfactory. Gold foil (1 mil thick) capsules were made. These melted partially without burning and trapped significant amounts of boron.

A nickel capsule which could be sealed with a foil over the top was designed. A guillotine was fixed in the bomb so that the foil could be punctured by a plunger released either by firing a fuse or by rotating the bomb. Nickel and gold foils could be sealed satisfactorily to the capsule; aluminum foil could not. However, both the nickel and gold melted, burned, and splattered after being punctured and exposed to the burning boron. The combination of aluminized mylar film with aluminum foil appears promising.

Another design which will be tried is that of a capsule with a spring-loaded lid. If mechanically successful, this design will eliminate the necessity for burning materials other than a small length of fuse wire.

The gaseous products of combustion of boron in commercial fluorine were examined by infrared absorptiometry. The only absorption peaks observed were those of boron trifluoride and silicon tetrafluoride. Silicon is a known impurity in the boron which is being used in these preliminary investigations.

The possibility that gaseous boron trifluoride may be adsorbed on the nickel fluoride film which coats the inside of the calorimetric bomb is being examined.

The combustion of various compounds of boron in fluorine is being examined as a possible means of determining their heats of formation after that of boron trifluoride is known with some exactness. It has been found that boron nitride burns spontaneously in fluorine. Infrared analysis of the gaseous products showed the presence of boron trifluoride and silicone tetrafluoride. No nitrogen fluorides were detected and it is presumed that the main reaction is

An interesting phenomenon was observed in the course of this reaction. When an excess of fluorine gas was admitted the combustion gave off an intense white light, but when the supply of fluorine was limited the reaction was accompanied by a deep blue glow. This glow was reminiscent of that created by the recombination of activated nitrogen atoms.

f. Heat of Formation of Tungsten Disulfide
(E. Greenberg)

A 30-gram sample of tungsten disulfide was prepared in accordance with the procedure described by Bell and Herfert¹⁰ for synthesizing molybdenum disulfide. Preliminary noncalorimetric oxygen combustion studies are currently being carried out on this sample. A second preparation of tungsten disulfide to be used as the calorimetric and analytical sample, is almost complete.

¹⁰Bell, R. E., and Hervert, R. E., J. Am. Chem. Soc., 79, 3351 (1957).

g. Auxiliary Equipment

Fluorine Purification, Handling, and Analysis
(E. Rudzitis, J. Settle, and L. Stein*)

Calorimetric work with fluorine has been delayed while the auxiliary equipment is being reconstructed. The system for charging bombs with pure fluorine was formerly located in the Chemistry Building. All the apparatus used for this work is now being rebuilt and consolidated in a large vacuum frame hood in this laboratory. The fluorine purification still, which is in the final design stage, will be incorporated into a high-pressure system. Apparatus for combustions at elevated fluorine pressures has been designed and will also be installed. This apparatus will be used to obtain information on conditions of combustion of less reactive substances.

Glass Bombs
(D. R. Fredrickson)

In three preliminary combustions of molybdenum in oxygen, the Pyrex glass pipe parts of the trial bombs shattered with explosive force. These experiments showed that the shielding provided, which consisted of a stainless steel screen and three concentric Lucite shields, was entirely adequate. The stainless steel screen contained all of the initial force of the breaking glass. The first plastic shield was only slightly scarred by powdered glass. Observations made in the course of these failures indicate that spattering of molten metal on to the glass initiates its fracture and the subsequent failure.

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II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES

The volatility of uranium hexafluoride is used as a basis for several schemes for processing irradiated fuels. Three such schemes: the Fused Fluoride Volatility Process, the Aqueous Dissolution Fluorination Process, and a Direct Fluorination Process, are being examined. Many steps of these schemes involve the use of fluidization techniques.

A process is being developed for the direct fluorination of ceramic fuels containing uranium oxide. Reaction rates, much lower than those obtained for the fluorination of UO_2 , have been obtained for the fluorination of uranium in experimental ceramic fuels of the type $\text{CaO-ZrO}_2\text{-UO}_2$.

Additional values of the equilibrium constant have been obtained for the reaction

at 200, 250 and 350 C.

Development of a fluid-bed volatility process for the recovery of uranium from low-uranium-Zircaloy-2 fuel alloys continued. The process involves aqueous dissolution of the fuel, fluid-bed drying of the solution to a dry fluidizable powder and fluid-bed fluorination of the material to remove and recover the uranium as the volatile uranium hexafluoride. Very reliable operation of the 6-inch diameter fluid-bed dryer was achieved in runs of 36 and 54 hours using the newly designed spray nozzle. Synthetic feed solutions containing the equivalent of a 2 weight per cent uranium alloy and a high fluoride content ($\sim 14 \text{ M}$) were fed at rates up to 140 ml/min (for 18-inch bed height). Runs made at temperatures of 240, 300 and 350 C produced 4.4 lb/hr of dry zirconium-uranium fluoride powder. The use of an auxiliary attrition air jet and an oversize air annulus on the atomizing side of the feed nozzle limited particle growth during calciner operation.

Particle hardnesses of fluid-bed process materials as determined by a standardized attrition test are being investigated as a means of evaluating the particle growth problem associated with calciner operation. Attrition indices, the amount of attrition produced in a one-hour period under standardized conditions, were found to vary with dryer conditions.

Stable zirconium fluoride feed solutions of a concentration higher than heretofore thought possible ($> 3.5 \text{ M Zr}$) have been prepared from the dissolution of both zirconium metal turnings and zirconium tetrafluoride in the proper amounts of 48 per cent hydrofluoric acid and water. The composition corresponds to 30 per cent hydrogen fluoride, 30 per cent zirconium oxide and 40 per cent water.

A study made in a $1\frac{1}{2}$ -inch diameter fluid-bed reactor of the reaction between zirconium tetrafluoride and air-steam-hydrogen fluoride mixtures simulating dryer atmospheres showed that no significant reaction occurs at 300 C with volatilized 10 M and 28 M hydrogen fluoride feeds or at 350 C with 28 M feed. The reaction at 300 C with volatilized 1 M hydrofluoric acid causes pyrohydrolysis and results eventually in the formation of zirconium oxide.

The statistical plan used for fluid-bed fluorination experiments was completed. Preliminary evaluation of the data indicates reaction temperature is the most significant variable. Factors affecting uranium removal at temperature of 600 C or below, such as pretreatments (hydrofluorination or low temperature fluorination), particle size, or zirconium matrix, become negligible at temperatures greater than 650 C, at which complete uranium removal is effected. The best removal achieved to date at 600 C with the currently produced dryer products is about 95 per cent. Previously, 98 per cent removal had been achieved with higher (5 to 10 per cent) uranium alloy feeds at this temperature.

Since corrosion of the nickel fluorinator at temperatures exceeding 600 C may be limiting, an alternative method of fluorinating involving screw-feeding the powder directly into an inert bed sustained at a high temperature (500 to 600 C) with a 100 per cent fluorine gas stream is being explored. The exothermic reactions involved should heat the feed particles to over 650 C. Preliminary runs at bed temperatures of 500 and 550 C and average residence time of 20 minutes gave results comparable to earlier six-hour batch runs, 75 and 85 per cent uranium removal, respectively. The powders were not preheated before being fed to the unit.

Static corrosion experiments conducted in fluorine at 675 C in the presence of nonfluidized zirconium tetrafluoride indicate Monel is severely attacked dimensionally while "A" nickel shows reasonable corrosion resistance. Monel showed essentially no intergranular attack. Tests on recrystallized alumina at 650 C showed no dimensional changes, but some weight gains were noted.

Further laboratory-scale studies on the fluorination of fluid-bed dried solids of high zirconium concentration indicate that temperatures in excess of 600 C are needed for complete uranium removal in less than 30 minutes from the experimental samples. Pretreatment of the solids with hydrogen fluoride prior to fluorination has a negative effect on the removal of uranium. Grinding of the solids by "ball milling" had an enhanced effect on the removal of uranium from some of the samples and little effect on others

In studies of the Fused Fluoride Volatility Process during the present period three zirconium dummy fuel elements were dissolved in the graphite, pilot plant dissolver. The dissolutions, carried out at 600 C, showed the highest dissolution rate at the highest sparge rate tried: 30 lb HF/hr. The dummy elements weighed approximately 42 lb and were 10-plate units, 48 inches long. The spacing between plates was 0.09 inch. No significant variation in dissolution rate occurred, until most of the metal was dissolved. The highest average dissolution rate for complete dissolution corresponded to 4.1 mils/hr or 1.1 mg/(sq cm)(min).

No difficulties with the heaters or other graphite components appeared in these operations, in which the dissolver was held at temperature continuously for a period of about 3 weeks. A partial transfer of fused salt out of the dissolver was carried out under complete control to a predetermined level. At higher salt levels and sparge rates, splashed or entrained salt deposited at the off-gas connection to the dissolver head, causing plugs. These were broken out mechanically without shutting down completely. An auxiliary heater for removing this deposited salt by melting will be installed and tested.

A preliminary testing of the electrolytically heated frozen-wall fluorinator was carried out. A 38-inch deep batch of salt was initially melted with resistance heaters contained in the electrodes, and the salt was held molten continuously by electrolytic heating for over a week. The frozen salt wall thickness measured between 1 and 1.5 inches over nearly 80 per cent of the liquid depth. The salt thickness was 5 inches at the bottom in these tests. Measurement of electrical resistance across the salt wall was used to control the power to the electrodes. Additional refinements of the system are being made to reduce the bottom salt thickness and to determine the stability of the frozen wall.

A series of runs on the fluid-bed calcination of synthetic Purex process waste has shown that lump formation can be avoided by the use of a new nozzle design, and particle growth can be controlled by the use of an attrition jet. The addition of sugar (about 1 lb/gal) to the waste solution resulted in a more friable solid product, which was easily fractured by the attrition jet. Production of fines was not excessive when the proper amount of attrition air was used. Successful runs up to 30 hours in duration were completed. The calcined solids had bulk densities in the range from 0.9 to 1.5 g/cc.

Installation of a 3-inch diameter Monel reactor for additional studies of the one-step fluid-bed process for conversion of uranium hexafluoride to uranium dioxide with steam and hydrogen was essentially completed. The preliminary experiments performed in the $1\frac{1}{2}$ -inch reactor are summarized in a topical report, ANL-6023.

Visitors during the current report period included representatives of Hanford Atomic Power Operations, the United Kingdom, Argentina and the French AEC.

A. Fluorine Chemistry (J. Fischer)

1. The Reaction of UO_2 - ZrO_2 - CaO Mixtures and Elemental Fluorine (M. J. Steindler and D. V. Steidl)

The possibility that power reactor fuels containing uranium dioxide can be processed in a simple manner by direct fluorination was mentioned previously (ANL-6029). Various types of ceramic fuels containing uranium dioxide have been proposed and some of them have been tested in existing reactors. Samples of fused UO_2 - ZrO_2 - CaO , obtained from the ANL Ceramics Group, were ground and fluorinated in equipment described previously (ANL-5924, page 29). Samples of the ground oxide mixture were first fluorinated at 375 C. A part of the resulting solid residue was analyzed and the remainder refluorinated at 500 C. Uranium present in the unfluorinated sample, the residues from each of the experiments, and the material volatilized during the fluorinations were analyzed fluorophotometrically and colorimetrically. Properties of the untreated samples are shown in Table 16. The results of the experiments are summarized in Table 17.

These experiments indicate that, although ceramic fuels of this type can be fluorinated to remove uranium as the hexafluoride, the rate of reaction is considerably lower than that previously observed for pure uranium dioxide, even when correction of the observed rate is made for dilution due to zirconium and calcium oxides. For example, fused and ground samples of pure uranium dioxide fluorinated at 375 C showed rates of fluorination varying from 200 to 1000 mg U/(hr)(sq cm).

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

Work has continued on the determination of equilibrium constants of the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$ at several temperatures. The experimental techniques used and results obtained at 300 C were described in ANL-6029. Additional results obtained at 200, 250, and 350 C are reported in Table 18.

The equilibrium constants measured below 300 C are higher than those reported by Florin.¹¹ This suggests that there is no sharp change in the relation between equilibrium constant and temperature at 308 C as reported by Florin. It is planned to obtain additional data at 100, 150, and 400 C.

¹¹Florin, A. E., et al., J. Inorg. Nucl. Chem., 2, 368 (1956).

Table 16

PROPERTIES OF UO_2 - ZrO_2 - CaO EXPERIMENTAL FUEL

Sample	Nominal Composition			Firing Conditions		Bulk density ^a (g/cc)
	UO_2 (w/o)	ZrO_2 (w/o)	CaO (w/o)	Temp (C)	Atmos- phere	
1	10	81	9	1450	Air	2.2
2	30	63	7	1450	Air	2.5
3	20	80	-	1450	Air	2.5
4	30	63	7	1700	H_2	2.6
5	10	81	9	1750	Air	2.5
6	10	81	9	1700	H_2	2.5
7	20	72	8	1450	Air	2.8

^a Experimental bulk density of ground samples

Table 17

FLUORINATION OF URANIA-ZIRCONIA-CALCIA MIXTURES

Fluorine Reserve	One atmosphere, 100% fluorine
Flow Rate	50 cc/min
Time of Fluorination	One hour
Source of Oxide	As indicated

Exp.	Sample	Initial Uranium (w/o)	Final Uranium (w/o)	Temp (C)	Rate of formation of UF_6 ^a	
					Observed Rate [mg U/(hr)(sq cm)]	Corrected Rate ^b [mg U/(hr)(sq cm)]
126	1	9	8.4	375	1.6	18
127	Residue 1 ^c	8.4	5.4	500	7.2	86
128	2	24.4	24.4	375	1.4	5.7
129	Residue 2	24.4	22.2	500	8.1	33
130	3	18.0	17.0	375	1.7	9.4
131	Residue 3	17.0	13.6	500	10	59
132	4	27.2	25.6	375	1.6	5.9
133	Residue 4	25.6	18.2	500	32	125
134	5	8.6	8.6	375	0.6	7
135	Residue 5	8.6	8.4	500	1.8	21
136	6	9.2	8.2	375	0.5	5.4
137	Residue 6	8.2	7.8	500	1.7	21
138	7	26.4	25.4	375	4.5	17
139	Residue 7	25.4	16.2	500	23.5	92

^a Calculated from mg U in the UF_6 , and the top exposed sample area of the powder.^b The rates of formation of UF_6 were corrected for dilution by ZrO_2 and CaO by dividing the Observed Rate by the fraction of uranium in the powder.^c Residues obtained from the initial sample after fluorination at 375 C.

Table 18

EQUILIBRIUM CONSTANTS FOR THE REACTION

No.	Initial Temperature (C)	Time at Equilibrium Temp (hr)	Total Pressure at Equilibrium (mm Hg)	Equilibrium Temperature (C)	Equilibrium Constant ^a
8	25	25	6230	199 ± 0.5	0.000708
9	25	24½	6270	202 ± 0.5	0.000620
12	300	23	6250	200 ± 0.5	0.000818
15	25	47½	6230	200 ± 0.8	0.000667
16	25	18½	5020	251 ± 0.3	0.00164
17	300	66	3690	251 ± 0.5	0.00151
18	25	18	3140	342 ± 0.3	0.00380
19	387	17	2320	336 ± 0.3	0.00334

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

B. ADF Process Development for Enriched Uranium-Zirconium Fuel

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

1. Engineering-scale Studies
(N. Levitz, A. A. Jonke)a. Fluid-bed Drying
(J. Barghusen, D. Raue, D. Busch*)

In the fluid-bed drying step of the ADF process, simulated fuel solutions are fed in the form of fine spray droplets into a heated fluidized bed where the water is flash evaporated and the metal salts (fluorides) are deposited and dried on the particles in the bed. Satisfactory operation of the dryer has been demonstrated in previous work (ANL-6029, page 87) using a newly designed nozzle (see Figure 24), which has eliminated the tendency for nozzle agglomerates to form, using air jet grinding (attrition) to help control particle size in the bed.

During this quarter, runs of extended duration made under several operating conditions provided continued testing of the reliability of the new nozzle and techniques for controlling particle size while preparing solids for additional fluorination studies. By variations in drying

*Student aide, Michigan College of Mining and Technology.

conditions two types of powders were produced, one containing a high percentage of zirconium tetrafluoride and the other consisting primarily of zirconyl fluoride.

FIGURE 24
TWO FLUID SPRAY NOZZLE
(JJB-TYPE)

(1) Operating Conditions (see Table 19)

The nominal composition of the feed solutions, prepared in several batches by dissolution of dryer products from previous runs, was 1.4 M zirconium, 0.012 M uranyl fluoride and contained the requisite amounts of tin, nickel, chromium and iron to simulate the dissolution of a 2 weight per cent uranium-Zircaloy-2 alloy. The solutions were made high in free acid, about 9 M (F/Zr mole ratio about 10), as compared to previous runs with 1 M free acid. At a bed temperature of 240 C, the high acid content feed yielded a product consisting primarily of zirconium tetrafluoride, while at 350 C the product contained zirconyl fluoride. A short run at 300 C was also made. Run periods ranged from 4 to 54.5 hours. The starting bed for each run was the final bed from the previous run. Total inlet fluidizing air velocities (fluidizing air plus jet attrition air) ranged from 0.9 to 1.7 ft/sec. The newly designed feed nozzles were each 0.040 inch in diameter on the liquid side, while either of two sizes of air annuli was used: 0.118-inch OD by 0.100 ID, or 0.154-inch OD by 0.100 ID.

The larger one required a high air rate which probably provided appreciable attrition of the bed and helped counteract particle growth. The atomizing air pressure was 30 psig, except for the last half of Run ZCP-71, where it was increased to 60 psig. The attrition jet air orifice was 0.047 inch in diameter.

Table 19

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

		Uranium Concentration in Feed		0.012 M			
		Zirconium Concentration in Feed		1.0 to 1.4 M			
		Fluoride to Zirconium Mol Ratio in Feed		10			
		Liquid Nozzle Diameter		0.040 inch			
		Atomizing Air Pressure		30 and 60 psig			
		Attrition Air Jet Orifice Diameter		0.047 inch			
Run No.	Bed Temp (C)	Average Feed Rate (ml/min)	Attrition Jet Air Rate (scfm)	Total Inlet Fluidizing Air Velocity ^a (ft/sec)	Atomizing Air Annulus OD ^d (inch)	Atomizing Air Rate (scfm)	Run Time (hr)
ZCP-68	240	60 and 92	0.84 ^b	1.00 ^b	0.154	5.5	36.3
ZCP-69	240	140	none	0.90	0.154	5.7	5.2
ZCP-70	300	94	none	1.13	0.118	2.2	4.0
ZCP-71	350	72	1.8	1.36 ^c	0.118	2.2 and 3.3	54.5

^a Sum of fluidizing gas and attrition jet air.

^b Attrition jet air not used during first 23 hours; total velocity 0.90 ft/sec.

^c Fluidizing air rate increased so that effective velocity was 1.7 ft/sec during time interval of 29 to 47 hours.

^d The ID of the annulus in each case was 0.100 inch.

(2) Operating Performance and Evaluation

The operation of the fluid-bed dryer throughout all of the runs was excellent. Spray nozzle operation was completely trouble-free as evidenced by the absence of nozzle agglomerate formations. Evidently, the new nozzle design, by eliminating the nozzle cap adjacent to the liquid nozzle opening, has solved this problem. The increase in atomizing air pressure from 30 to 60 psig during Run ZCP-71 apparently caused the deposition of feed material on the wall opposite the nozzle. Evidence of these deposits in the form of a few elongated, characteristically shaped agglomerates was found in the final bed.

Premature shutdown on Run ZCP-68 after 36 hours was caused by a plug in the liquid feed line upstream from the nozzle, undoubtedly the result of precipitation of solid material from a batch of unstable feed solution. This instability results from redissolution of

previously dried solids and would not occur in feed prepared by fuel dissolution. At this time the Monel feed line was also found to be severely corroded, possibly due to the presence of air in the line, and was replaced with a nickel line.

The high-acid feed coupled with the low dryer temperature (240 C) produced material containing a predominance of zirconium tetrafluoride and some monohydrate (total fluoride 42.4%), while the high-temperature (350 C) run produced a large fraction of zirconyl fluoride (total fluoride 34.0%).

The primary evaluation of a dryer run is made on the basis of the change in the distribution of particle sizes in the bed. Since particle growth occurs continuously, a means of providing particle attrition must be employed to counteract the growth. During the runs of extended duration, ZCP-68 and 71, the effects of some of the variables which affect particle growth, such as feed rate, auxiliary attrition jet air rate, atomizing air rate, and relative hardness of the particles, were noted. These variables are interrelated and are difficult to separate without performing a large number of experiments; therefore only qualitative observations can be made.

(a) Effect of Particle Hardness

Attrition air requirements for control of particle size are a function of the relative hardness of the dryer products, which in turn appear to be a function of the type of feed and operating temperature. This was proved in a series of attrition tests described in a later section of this report (page 102). Material produced in Run ZCP-71 was very hard and had a low rate of attrition, whereas material produced in previous runs from feeds having a low (4.5/1) fluoride-to-zirconium ratio had attrition rates two to five times as great. For this reason larger volumes of attrition air were required in the current series of runs that had been used in the past.

(b) Effect of Total Gas Velocity and Feed Rate

The total gas velocity -- the sum of fluidizing air, atomizing air, attrition air and vapors from evaporation of feed -- affects the concentration of fine particles in the fluidized bed by effecting a certain elutriation rate¹² for a given gas rate. The fines produced in the bed by attrition, as well as those returned to the bed from the filters during blow-backs, are constantly being entrained by the gas; however, a steady-state concentration of fines probably exists under a given set of conditions. The

¹²Othmer, D. F., Fluidization, The Waverly Press, Inc., Baltimore (1956), page 16.

feed rate probably also affects fines concentration in the bed (besides contributing to the gas velocity effect) due to the amount of spray which wets bed particles and effects agglomeration. Higher gas velocities and higher feed rates thus tend to cause a similar effect, namely, a reduction in the steady-state concentration of fines in the bed. Overall effects of this type are notable in Run ZCP-68, where a high rate of production of fines (-200 mesh size) during the first 14 hours was curtailed by an increase in the feed rate from 60 to 92 ml/min (see Figure 25). An apparent steady-state concentration (about 26 per cent) of fines resulted. The seemingly abrupt change in fines concentration (with a corresponding change in the coarse, +60, fraction) accompanying this feed rate change is not readily explained, since one would expect a more gradual change before reaching a steady-state condition. An increase in total air flow due to introduction of jet attrition air after 23 hours lowered the steady-state value somewhat from 26 to 17 per cent.

FIGURE 25
PARTICLE-SIZE DISTRIBUTION DURING FLUID-BED DRYER OPERATION

The sharp increase in fines concentration noted near the start of Run 69 (made several days later as a continuation of Run 68) was due to excessive attrition caused by the use of full atomizing air flow (from the large annulus) during start-up. The concentration of fines (-200 mesh) rapidly decreased during the 5-hour run but did not reach steady state. This run was made at a feed rate of 140 ml/min.

(c) Effect of Atomizing Air and Jet Attrition Air

Both the atomizing air and fluidizing air rates were varied in Run ZCP-71 as a result of changes which occurred in the particle-size distribution (see Figure 26). Since the atomizing nozzle used during this run used the smaller air annulus, the amount of attrition resulting from the atomizing air was correspondingly decreased. Particle growth occurred, and it was necessary to increase the air rate after 24 hours of operation to obtain the desired attrition rate. A considerable time lag was noted before the effect of the increased attrition started to decrease the particle size, but by the end of the 55-hour run the particle size had returned to approximately the same value as in the original bed.

Because of the particle growth, it was necessary to increase the fluidizing gas velocity from 1.4 to 1.7 ft/sec during the run to insure that the bed was adequately fluidized. In contrast with Run ZCP-68, neither this increase nor the increase in atomizing air rate had any noticeable effect on the concentration of fine particles in the bed, probably because the concentration of fines at the time these changes were made was very small (less than 10 per cent below 100 mesh).

The results of these runs indicate a steady state in fluid-bed dryer operation may be achieved under a given set of operating conditions. Also, it may not be necessary to isolate the effects of individual variables to achieve satisfactory performance of this type of unit.

(3) Preparation of a Concentrated Zirconium Fluoride Feed Solution

Since the rate of processing nuclear fuel element solutions in the drying step of the ADF process is dependent in part on the concentration of the metal salt solution that can be prepared, it would be desirable to process more concentrated feeds. According to Tananayev et al.,¹³ zirconium exhibits a maximum solubility in aqueous hydrogen

¹³Tananayev, I. V., Nikolayev, N. S. and Buslayev, I. A., Investigation of the System HF-ZrF₄-H₂O by the Isothermic Solubility Method (Isotherm 0.5°). Zhurnal Neorganicheskoi Khimii, 1, 274-281 (1956).

fluoride at a composition corresponding to 30 per cent zirconium oxide, 30 per cent hydrogen fluoride, and 40 per cent water. This solution contains over twice the concentration of zirconium as the feed now being used. Several experiments were performed to prepare concentrated solutions and to evaluate their stability.

FIGURE 26
PARTICLE-SIZE DISTRIBUTION DURING RUN ZCP-71

FEED RATE 72 ml/min

BED TEMPERATURE 350 C

ATTRITION JET AIR RATE 1.8 SCFM

ATOMIZING AIR ANNULUS THICKNESS 0.009 inch

F/ZR MOL RATIO IN FEED-10

ATOMIZING AIR RATE 2.2 SCFM 0-24 hours

3.3 SCFM 24-54.5 hours

A dissolution of zirconium metal turnings was made by slowly adding 250 grams of 48 per cent hydrofluoric acid to 88.8 grams of metal in 71.2 grams of water. After the acid was added, the mixture was heated at 65 C for 12 hours under continuous reflux and then cooled to room temperature. No undissolved metal or precipitated zirconium fluoride salt was evident. The solution had a density of 1.59 g/cc and chemical analyses (see Table 20) showed a zirconium molarity of 3.6. The solution has been stable for 65 days with only trace amounts of a very fine precipitate having formed.

Table 20

CHEMICAL ANALYSES OF CONCENTRATED
ZIRCONIUM FLUORIDE SOLUTIONS

Analysis	Zirconium Metal Dissolution	Zirconium Tetrafluoride Dissolution
Zirconium	3.6 <u>M</u>	3.8 <u>M</u>
Total Fluoride	23.3 <u>M</u>	24.8 <u>M</u>
Acidity	8.27 <u>N</u>	9.28 <u>N</u>
Density	1.59 g/cc	1.63 g/cc

Since synthetic feed solutions prepared by dissolution of zirconium fluoride are being used in the ADF process development work, a similar solution was prepared by dissolving 326 grams of zirconium tetrafluoride in 192 grams of 48 per cent hydrofluoric acid and 283 grams water. The major fraction of salt dissolved in the first 12 hours; however, after 40 hours of heating under reflux at 65 C about 5 to 10 per cent of the material remained undissolved. The filtered solution had a density of 1.63 g/cc and zirconium concentration of 3.8 M (see Table 20). The clear solution has remained stable for 35 days. The experiment was repeated to determine if zirconium tetrafluoride could be dissolved without leaving an insoluble residue. The quantities of ingredients were adjusted so that less zirconium tetrafluoride and more water were used. However, an insoluble residue still remained after the materials were heated and mixed for 40 hours.

It is planned to operate the fluid-bed dryer with concentrated feed solutions. The dryer product that is produced will also be fluorinated, to determine whether there is any unusual effect of the feed solution concentration on subsequent uranium removal.

(4) Reaction between Zirconium Tetrafluoride and Air-Steam-Hydrogen Fluoride Mixtures

Several runs have been made to study the solid-vapor reaction between zirconium tetrafluoride and gaseous mixtures of air, hydrogen fluoride, and water vapor simulating fluid-bed dryer conditions. The purpose of the study was to determine if the reaction leads to a zirconium fluoride composition in equilibrium with the gas.

The experiments were conducted in a $1\frac{1}{2}$ -inch Monel fluid-bed column at 300 and 350 C, using pure zirconium tetrafluoride and volatilized 1 M, 10 M, and 28 M hydrofluoric acid solutions. The vaporization of 1 M and 10 M hydrofluoric acid yields vapors approximating the composition of those produced in the drying of feed solutions having fluoride to zirconium mole rates of 4.5/1 and 10/1, respectively. Approximately 300 grams of pure zirconium tetrafluoride were charged to the column and heated to the desired temperature. The feed solution was pumped into a preheater where it vaporized and mixed with the fluidizing air. The mixture then passed into the column. The liquid feed rate was 5.5 ml/min and the fluidizing gas rate was 0.26 scfm. Several intermediate samples and the initial and final beds were analyzed for fluoride content. The results are shown in Figure 27.

FIGURE 27

The reaction of zirconium tetrafluoride with 1 M hydrofluoric acid vapor at 300 C will eventually produce zirconium oxide. Even though zirconyl fluoride may be formed as an intermediate, this species is not in equilibrium with the gases and undergoes further reaction to the oxide. For all the other conditions presented in Figure 27 (10 M and 28 M HF), no significant reaction occurred between zirconium tetrafluoride and the environmental gases. Data are pending for the reaction at 350 C between zirconium tetrafluoride and 10 M hydrofluoric acid feed.

(5) Attrition Tests on Fluid-bed Process Materials

The use of attrition jets to regulate particle growth has helped make possible runs of extended duration in the fluid-bed calciner operations with zirconium fluoride solutions. In order to evaluate more carefully the problem of particle growth as related to any of the fluid-bed operations, the attrition test apparatus, in which attrition is obtained by the collision of particles accelerated by an air jet, was installed. Various powder samples were tested under standardized conditions¹⁴ and compared in terms of an attrition index.

The apparatus consists of a 3-ft section of 1-inch ID glass pipe topped by a 3-inch ID section which contains a porous metal bayonet filter for the retaining of entrained solids in the exit gas stream. The attrition air enters the column through a 0.016-inch hole drilled in the center of a $\frac{1}{16}$ -inch aluminum disc which is bolted to the bottom of the column. High-pressure supply air is reduced to 62 psig with a pressure-reducing valve and is metered by a needle valve through a rotameter. For target-grinding tests (as opposed to jet-grinding) a small plate is affixed about $\frac{1}{2}$ inch above the orifice to serve as a target.

A 100-gram sample of a particular size range (usually 60 to 100-mesh) is charged to the column. An air rate of 0.26 scfm is used, which gives a pressure upstream of the orifice of 60 psig. The test is run for 1 hour and the material (including filter fines) is then removed and screened. Recovery is normally better than 99 per cent of the charge. Screening is done with a Tyler Ro-Tap and Tyler standard series screens.

The results shown in Table 21 are reported in terms of an attrition index (referred to as AI), which is expressed as the per cent of minus 100 mesh material produced in a "standard" test. Studies showed that, with some powders, the fraction 60 to 100-mesh gave more consistent results than powders of full-range particle-size distribution. The attrition index for zirconium fluoride powders prepared in a fluid-bed dryer ranged from about 5 to 30, with the materials prepared at

¹⁴Forsythe, W. L., and Hertwig, W. R., Attrition Studies of Fluid Cracking Catalysts, Ind. and Eng. Chem., 41, 1200 (1949).

Table 21

CONDITIONS AND RESULTS OF ATTRITION TESTS

Duration of test	1 hr
Sample weight	100 g
Attrition orifice size	0.016 in.
Attrition air rate	0.26 scfm

Test Materials

- A. Zirconium fluorides from fluid-bed dryer.
- B. Product from fluid-bed calcination of synthetic Hanford Purex low-acid type waste (see page 121).
- C. UO_2 produced from UF_6 by direct conversion in fluid-bed (see page 126).

Material	Mesh Size	Attrition Index (AI) ^a
A, Run ZCP-48 (450 C, F/Zr-4.5)	<div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;">{</div> <div style="display: inline-block; vertical-align: middle;">20 thru 325 20 thru 325 60 to 100</div> </div>	8.4, 12.4, 10.5 15.6, ^b 16.0, ^b 15.8 ^b 14.0, 12.6, 14.4, 14.6, 13.1
A, Run ZCP-60 (300 C, F/Zr-4.5)	<div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;">{</div> <div style="display: inline-block; vertical-align: middle;">60 to 100 60 to 100</div> </div>	32.8, 29.8 79.5, ^c 79.5, ^c 76.9 ^c
A, Run ZCP-71 (350 C, F/Zr-10)	60 to 100	6.4, 4.2, 6.2
B, Run HWC-117	60 to 100	24.6, 23.6, 23.6
C, Run PY-17	<div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;">{</div> <div style="display: inline-block; vertical-align: middle;">40 to 60 60 to 100</div> </div>	13.9 16.0, 15.3
C, Run PY-18	<div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;">{</div> <div style="display: inline-block; vertical-align: middle;">40 to 60 60 to 100 100 to 200</div> </div>	46.7, 45.0 28.6, 29.0, 27.5 26.9

^a Numbers denote results of replicate tests.

^b These tests were 2 hours long.

^c Target-grinding used.

higher temperature (350 and 450 C) having lower values of AI than material prepared at 300 C. The zirconium fluoride prepared from feed having a fluoride to zirconium mole ratio of 10 (Run ZCP-71) had the lowest rate of attrition of all the materials tested (AI of 4 to 6). The target-attrition tests gave AI values greater than twice those of the jet attrition test, 80 as compared to 30. As noted in Table 21, attrition tests were also run on

products from the calcination of waste and from the conversion of uranium hexafluoride to uranium dioxide to obtain an indication of the relative effectiveness of jet grinding in these operations. The standard test appears to have good reproducibility and is considered to be a useful tool in fluidization process development.

b. Recovery of Uranium from Uranium-zirconium Mixtures by Fluorination in a Fluid-bed Reactor
(E. Carls, J. Wehrle, M. Jones, D. Busch*)

Fluorinations of uranium-zirconium fluoride powders to effect uranium removal were carried out in the 2½-inch diameter fluid-bed reactor. The powders were prepared in the fluid-bed dryer at 240 and 300 C. Four batch experiments using pretreated (prehydrofluorinated or prefluorinated) material concluded the statistical program outlined in ANL-6029, page 146. Studies have been started on an alternate method of fluorinating the uranium, using the technique of screw-feeding the powder into an inert fluidized bed sustained with a high fluorine concentration at a high temperature. Further studies will be made in a replacement fluid-bed fluorinator (3-inch, Schedule 80, "A" nickel pipe) now being installed.

(1) Operating Conditions

The final fluorination runs of the statistical experiment were conducted at 450 and 600 C using fluid-bed dryer products pretreated either by hydrofluorination at 450 C or by fluorination at 300 C. The pretreatments removed water and oxygen, producing powders consisting primarily of zirconium tetrafluoride.

The fluidizing velocity was maintained near 0.5 ft/sec. The fluorine concentration in the fluidizing gas stream (initially nitrogen) was raised from 0 to 100 per cent within two hours after the operating temperature was reached. The fluorine was recycled by a Lapp pump after it passed through a condenser to remove the uranium hexafluoride and other volatiles. All runs were of six-hour duration, with intermediate samples being taken after 2, 3, or 4 hours.

Other runs, not a part of the statistical experiment, were made in which the powder was continuously fed into the reactor by means of a screw feeder. The bed was preheated to the desired temperature and maintained with essentially a 100 per cent fluorine stream at velocities near 0.7 ft/sec. About 400 g of powder was fed into the 800-g starting bed in a 40-minute period. The starting beds in these tests were fluorinated residues from previous runs. The preliminary runs in this study were made over a temperature range 500 to 600 C.

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(2) Results and Discussion (see Table 22)

Evaluation of the completed statistical experiment now has confirmed previous conclusions regarding factors affecting removal of uranium by fluorination from the types of powders prepared in the fluid-bed dryer. The following is a summary of the conclusions reached from these experiments.

1. Removal increases with fluorination temperature. Complete (greater than 99 per cent) removal is achieved near 675 C.
2. Removal is affected by the type of zirconium matrix with which the uranium is associated, that is, better removal is achieved from material containing a large fraction of zirconyl fluoride than from those containing a large fraction of zirconium tetrafluoride.
3. The hydrofluorination pretreatment is deleterious to removal of uranium from zirconyl fluoride powders, although it seems to improve uranium removal from zirconium tetrafluoride powders.
4. Prefluorination at 300 C had a marked beneficial effect on uranium removal, especially for zirconium tetrafluoride powders fluorinated at the higher temperatures (>525 C).
5. Major uranium removal occurs rapidly (two hours or less) and little additional removal is achieved with prolonged fluorination. The amount of fluorine passed through the bed is unimportant as long as reasonable excesses are used.
6. Uranium removal is enhanced with decreasing particle size at temperatures above 500 C except for prehydrofluorinated materials.

Statistical interpretation of the data is being carried out by the Data Processing Section of the Accounting Department to determine possible interaction of the variables. Among the questions still unanswered are the effects on uranium removal of such things as water (in the zirconium tetrafluoride monohydrate dryer product), possible complexes or solid solutions of uranium and zirconium fluoride, and effects of sintering and sublimation of the tetrafluoride. The best removal achieved to date with the 2 per cent alloy-equivalent powders at temperatures up to 600 C is about 95 per cent. Results of laboratory tests indicate most of the above effects are unimportant at temperatures over 650 C, at which complete uranium removal is effected.

Table 22

COMPLETE ANALYTICAL RESULTS OF STATISTICAL
FLUID-BED FLUORINATION EXPERIMENTS

Equipment: $2\frac{1}{2}$ -inch diam Monel column
 Inlet Fluorine Composition: 0 to 100%
 Initial Uranium Concentration: 1% for 300 C dryer product
 0.8% for 240 C dryer product
 Run Duration: 6 hours except where noted

Fluorination Temperature (C)	Dryer Temperature (C)	Final Uranium Concentration (w/o)		
		Pretreatment		
		None	450 C Hydrofluorination	300 C Pre-fluorination
450	240	0.35	-	-
	300	0.58	0.75	0.53
525	240	-	0.11	0.08
	300	0.20	0.45	-
600	240	0.25, 0.49	0.10	0.06, <0.01 ^b
	300	-	-	0.09
~ 675 ^a	240	0.02, < 0.01	-	-
	300	-	-	0.01 ^c

^a Caked portion of bed only

^b Caked portion of bed; temperature excursion not detected on thermocouples

^c Result of a static fluorination experiment (20-min contact) on a residue (100 g) previously fluorinated at 600 C. Initial uranium concentration, 0.22 per cent.

(a) Screw Feeding of Powder

Since it has not been possible to achieve complete uranium removal at low temperatures and since high bed temperatures result in severe corrosion, an attempt was made to produce very high individual particle temperatures while maintaining a relatively low overall bed temperature. The uranium-zirconium powder was screw-fed at a rate of approximately 10 g/min into a 900-g bed (fluorinated residues) fluidized with fluorine. Results obtained at bed temperatures of 500 and 550 C of samples taken immediately after the 40-minute feeding period (average residence times are thus only 20 minutes) are comparable to those for previous 6-hour

batch runs - uranium removal of 75 and 85 per cent, respectively. An attempt to operate at 600 C with screw-feed powders resulted in serious caking difficulties in the bed, which prevented reliable determination of uranium removal.

It is planned to continue these studies using relatively inert material such as nickel powder for the starting bed. The powder-feed system is also being modified so that the material will be more dispersed as it enters the reactor. This will be achieved by a nitrogen-conveyor stream coupled to the screw feeder. The length of time at which the particles are at the required temperature may be increased to insure uranium removal by feeding preheated powder rather than room temperature powder as is now done.

A new fluid-bed fluorinator (3-inch "A" nickel, Schedule 80 pipe) designed to give somewhat more flexibility than the existing unit is presently being installed.

(b) Fluorination in a Static Bed

All the results to date indicate that temperatures in excess of 600 C are required for quantitative removal of uranium. Since corrosion of presently used materials of construction (nickel and nickel alloys) is severe at these temperatures, only short-term contact of fluorine and solids in the bed would be tolerable. A static-bed experiment on a 100-g sample of powder previously fluorinated at 600 C showed overall uranium removal near 99 per cent with only an additional 20 minutes of exposure to static fluorine at 665 C. The residue, although severely caked, was readily removed from the reactor tube in one piece. For high-temperature work the use of a protective liner for the metal wall is conceivable. Static-bed experiments will be continued on a somewhat larger scale to determine the minimum fluorination time required and to determine whether the solid cake can be readily removed from the reactor.

c. Fluorination Corrosion (L. Hays, W. Seefeldt)

A series of bench-scale experiments, in which efforts were made to clarify corrosive effects observed earlier in the fluid-bed fluorinator, has been concluded. In addition, several experiments were performed at a higher temperature, 675 instead of 600 C, to determine whether either nickel or Monel have useful resistance to fluorine in the presence of zirconium fluoride at this temperature.

The tests were conducted in the same apparatus described in ANL-5996, pages 156 to 158. The corrosion specimens (tubes) were in contact with zirconium fluoride in a fluorine atmosphere; a temperature

gradient along the metal provided information relative to the temperature parameter. All nickel used for the experiment was "A" nickel and came from the same heat of material. It was fine grained and annealed. Results are shown in Table 23.

Table 23

SUMMARY OF STATIC CORROSION EXPERIMENTS IN FIXED BEDS OF
ZIRCONIUM TETRAFLUORIDE IN A FLUORINE ATMOSPHERE

Material	Bed	Exposure Time (hr)	Treated Fluorine ^b	Max Bed Temp (C)	Max Dimensional Change (mils)	Intergranular Attack (mils)	
						Typical	Maximum
Nickel ^c	None	70	Yes	600	0.1	0.4	0.5
Nickel ^c	ZrF ₄	70	No	600	1.5	2.7	5.9
Nickel ^c	ZrF ₄ + 5% AlF ₃	28	No	600	0.1	1.2	1.6
Monel	ZrF ₄	70	No	675	>62 ^a	0	0
Monel	ZrF ₄	49	Yes	675	>62 ^a	0	0
Nickel ^c	ZrF ₄	70	No	675	4.4	5.6	5.9
Nickel ^c	ZrF ₄	70	Yes	675	4.0	5.7	7.0
Recrystal- lized Al ₂ O ₃	ZrF ₄	7	No	650	0 ^a	-	-

^a Metal perforated through wall.

^b Fluorine is treated by passing it through a bed of porous sodium fluoride.

^c Nickel was "A" nickel, fine grained and annealed.

The data at 600 C indicate that the presence of zirconium tetrafluoride accelerates the rate of attack on "A" nickel in fluorine - dimensional change and intergranular attack both show an increase. Additions of aluminum fluoride to the zirconium fluoride had no pronounced effect. The effect of additions of tin, manganese, cobalt, chromium, lead and titanium, as their respective fluorides, were reported previously in ANL-5996, pages 156 to 158.

The four runs made at 675 C show that Monel has little usefulness in a fluorinated static bed of zirconium fluoride. With both treated* and untreated fluorine, the Monel was perforated badly in the zone of highest temperature. No intergranular attack was noted, even in the areas where perforation occurred. The nickel specimens were well intact following the runs. The maximum dimensional change of 4 mils is greater than that observed in the same experiment at 600 C (1.5 mils); intergranular attack was also somewhat greater. No significant difference

*Fluorine is treated by passing it through a bed of porous sodium fluoride.

appeared between the two tests in which treated and untreated fluorine was used. This is at variance with 600 C data previously obtained where fluorine pretreatment reduced intergranular attack.

This series of experiments indicates that under the conditions used, nickel is more useful than Monel, particularly in the laboratory, where the intergranular degradation of nickel is not likely to be objectionable. It has not been established whether this is equally true for a fluid bed; no Monel specimen removed from the fluid-bed fluorinator has shown the degree of perforation observed in the static test. The corrosion rate of nickel in a static bed was not so high as to preclude its use under some conditions.

Two samples of recrystallized alumina were exposed to fluorine at 650 C for 7 hours. No dimensional changes were observed; weight gains were 0.9 and 2.0 mg/sq cm.

2. Laboratory Studies (J. Fischer)

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

Work is continuing on the systematic study of the variables involved in uranium removal from calcined solutions of uranium-zirconium alloys. Two additional lots of pilot-plant, drier products (ZCP-69 and ZCP-71) have been tested for uranium removal by fluorination. The history of these materials is summarized in Table 24.

Results indicating the effect of temperature on uranium removal are given in Table 25. These data are very similar to those obtained from previous experiments on pilot-plant drier products. The data indicate that under present experimental conditions, temperatures in excess of 600 C (~650 C) are needed for complete uranium removal from the dried solids.

The effect of time on uranium removal has been studied at 650 C for solid ZCP-59. Experiments were designed to maintain a constant ratio of sample weight to time of exposure to fluorine (at a flow rate of 12 g/hr): (3.9 g/0.5 hr; 7.7 g/1.0 hr, 14.9 g/2.0 hr). In all cases the final uranium content was less than 0.008 weight per cent, which is the lowest concentration of analytical standard used by the X-ray group. At 650 C, it appears that less than 30 minutes are required for complete uranium removal.

Some effort has been given to evaluating the effect on uranium removal of various pretreatments made prior to fluorination. The experimental procedure used in pretreating the solids with anhydrous hydrogen fluoride is as follows. About 15 grams of calcined material are

Table 24

PROPERTIES OF PILOT-PLANT DRIER PRODUCTS TESTED FOR
URANIUM REMOVAL BY FLUORINATION

Run No.	ZCP-69	ZCP-71
Bed Temperature (C) ^a	240	350
Starting Bed Material	Material previously calcined at 240 C (ZCP-66)	ZCP-69
Feed Composition	1.4 <u>M</u> Zr 15 <u>M</u> F	1.4 <u>M</u> Zr 14 <u>M</u> F
Feed Preparation	Material previously calcined at 240 C dissolved in hydro- fluoric acid	Material previously calcined at 300 C dissolved in hydro- fluoric acid
Total Run Time (hr)	41.5	54.5
Uranium Concentration w/o Alloy Equivalent	1.2	1.2
Remarks	-	Starting bed was heated slowly from 240 to 350 C to minimize agglomeration

^aTemperature of fluid bed during calcination.

Table 25

EFFECT OF TEMPERATURE ON URANIUM REMOVAL

	Time for Run	2 hr	
	Fluorine Flow Rate	12 g/hr	
	Initial Uranium Concentration	0.55 w/o	
	Final Uranium Concentration		
Material	(w/o)	Temp (C)	Removed (%)
ZCP-69	0.34	450	28.2
ZCP-69	0.27	525	51.0
ZCP-69	0.067	600	87.8
ZCP-71	0.38	450	31.0
ZCP-71	0.19	525	65.5
ZCP-71	0.045	600	91.0

weighed into a tared nickel boat, which is then placed in a one-inch nickel tube furnace. Helium is passed over the sample while the furnace is brought to a temperature of 450 C. Anhydrous hydrogen fluoride is then passed over the sample for a two-hour period, after which helium is again passed over the sample. After the hydrogen fluoride has been removed the sample is ready for fluorination

Data on the effect of hydrofluorination pretreatment are given in Table 26. The only solid whose behavior on fluorination was improved by this pretreatment was ZCP-66. If one refers to Table 20 of ANL-6029, it is noticed that water content of solid ZCP-66 was appreciably changed by treatment with hydrogen fluoride. From these data it appears that this pretreated material would undergo little or no oxide formation on heating prior to fluorination. The oxide of ZCP-44 (about 30 per cent ZrO_2) and the oxyfluoride of ZCP-60 (about 60 per cent ZrOF_2) appear to have been changed in an unsatisfactory manner by hydrogen fluoride pretreatment.

Table 26

EFFECT OF HYDROFLUORIC ACID PRETREATMENT
ON URANIUM REMOVAL

Time for Run		2 hr	
Temperature of Hydrofluorination		450 C	
Temperature of Fluorination		600 C	
		Final Uranium Concentration (w/o)	
Material	Initial Uranium Concentration (w/o)		
		No Pretreatment	After Hydrofluorination
ZCP-44	1.82	0.27	0.58
ZCP-60	1.02	0.04	0.13
ZCP-66	0.77	0.39	0.23

Because the pretreatment of calcined uranium-zirconium solutions with anhydrous hydrogen fluoride has an apparently detrimental effect on the uranium removal from these solids, other more suitable pretreatments were sought. Previous experiments had shown that higher uranium removal was obtained from small particles. Therefore, calcined materials were ground in a ball mill for 24 hours and then fluorinated at two temperatures. The results of these experiments are shown in Table 27.

Table 27

EFFECT OF BALL MILLING ON URANIUM REMOVAL

Fluorine Flow: 12 g/hr for 2 hr

Material ^a	Temperature (C)	% Uranium Remaining After Fluorination	
		Original (Mesh Size ~100)	Ball Milled (Mesh Size ~325)
ZCP-38	450	84.0	77.3
	600	16.0	15.7
ZCP-59	450 ^b	59.5	21.0
	600	9.1	3.8
ZCP-66	450 ^b	65.5	56.3
	600	50.7	6.3
ZCP-69 ^c	450	61.8	50.0
	600	12.2	9.5

^a For composition of materials see Table 24, page 94, ANL-6029.

^b Interpolated value.

^c For composition, see Table 24.

Ball milling appears to be ineffective on material ZCP-38, somewhat effective on ZCP-59 and ZCP-69, and very effective on ZCP-66. Due to a wide variation in drier conditions it is difficult to say exactly why the solids differ so markedly on fluorination.

C. Zirconium Matrix Fused Salt Process Development (W. J. Mecham, 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 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, W. Murphy, A. Rashinskas)

During the present period, three zirconium dummy fuel element subassemblies were dissolved completely in the sodium fluoride-zirconium fluoride fused salt in the graphite, pilot-plant dissolver. Dissolver operation and dissolution data are reported in detail.

The first of the present series of runs, A-1, was a partial dissolution reported previously. Of the three total dissolution runs made to date, two, Runs A-2 and A-3, have been analyzed and are reported here. In Run A-4 the off-gas monitoring equipment was not functioning during the whole run and data analysis is not complete.

The dummy subassemblies used in these tests were 10-plate assemblies of reactor-grade zirconium plates. The plates were 2.5 inches wide and 48 inches long, welded together with spacers to form 0.087-inch channels between plates. The thickness of the plates varied between 0.137 and 0.145 inch, with the average about 0.140 inch. These plates are thus about 60 per cent thicker than a typical reactor fuel plate. The total surface area of the plates was 2400 square inches or 15,460 sq cm. The total weight of each assembly was about 41 lb.

Results of Dissolver Runs A-2 and A-3

At the beginning of Run A-2, 641 lb of salt of 38 mole per cent zirconium tetrafluoride was charged to the dissolver. The fuel elements were loaded through the air lock with a claw-type slug charger. The dissolution was monitored (1) by weighing hydrogen fluoride entering as sparge and recovered from the off-gas condenser and (2) by measuring the volume of uncondensed off-gas, which included hydrogen produced in the reaction. The course of the dissolution was indicated by the rate of off-gas evolution and by the rate of apparent hydrogen fluoride consumption. The uncorrected rate data for Runs A-2 and A-3 are plotted in Figures 28 and 29, respectively. The actual rate of hydrogen evolution was lower by the amount of argon purge and hydrogen fluoride passing through the condenser. The actual amount of hydrogen fluoride reacted was lower by an amount equal to the losses through the condenser.

The data in Figures 28 and 29 show relative rates of zirconium dissolution during the run and indicate the time for complete dissolution. The data show little, if any, progressive variation of dissolution rate from the beginning to the approximate point indicating 90 per cent dissolved. At the point of complete dissolution, the two monitoring methods are in agreement.

FIGURE 28
ZIRCONIUM DISSOLUTION RATE-GRAPHITE DISSOLVER RUN A-2

FIGURE 29
ZIRCONIUM DISSOLUTION RATE-GRAPHITE DISSOLVER RUN A-3

The chief results of the runs are summarized in Table 28.

Table 28

SUMMARY OF DISSOLUTION RUNS A-2 AND A-3

Run Conditions:

Salt Composition: 38 to 45 mol per cent

ZrF₄; balance NaF.

Salt Temperature: 600 C

Fuel Elements Completely Submerged.

Run Data	A-2	A-3
Avg HF Sparge	19 lb/hr	32 lb/hr
Time for complete dissolution of 0.140-inch thick plates	21 hr	18 hr
Overall average rate	1.9 lb Zr/hr 3.4 mil/hr 0.9 mg/(sq cm)(min)	2.3 lb Zr/hr 4.1 mil/hr 1.1 mg/(sq cm)(min)
Overall HF efficiency	8.4%	6.1%
Estimation of Processing Time (hr)		
For 90% dissolution of plates 0.087-inch thick	10.5	8.8

The cumulative amount of dissolution during the runs is shown in Figure 30. Based on the dissolution rates shown in Table 28, the time required for 90 per cent dissolution of fuel plates 0.087 inch thick (a typical size) would range from 9 to 11 hours, depending on the hydrogen fluoride sparge rate. The dissolution rate of 1 mg/(sq cm)(min) is comparable with our semi-works data and with ORNL data

Operating Experience

A new taper joint connection of the graphite sparge pipe to the metal pipe extending through the dissolver head was made before the start of Run A-2. The joint was kept under compression by a spring support outside the packing gland. This joint has remained tight in all subsequent operations.

In Run A-4 a partial transfer of fused salt out of the dissolver was carried out in a completely controlled manner to a predetermined level. Telegage and electrode readings agreed closely in this operation. Argon pressure was used to transport molten salt through autoresistively heated Inconel pipe lines.

FIGURE 30
ZIRCONIUM DISSOLVED DURING RUNS A-2 AND A-3 AS INDICATED
BY HF CONSUMPTION AND HYDROGEN EVOLUTION

The graphite heaters have operated without difficulty for a period of about 4 weeks with molten salt during the time the dissolution runs were made. The calculated resistance in operation has remained at 0.042 ohm.

No pressure increase due to plugging of the sodium fluoride desublimation bed or of the carbon filters has been observed in operations through Run A-4. However, at high salt levels and hydrogen fluoride sparge rates, plugging at the dissolver head has occurred due to splashed or entrained salt. The plug formed in the bottom few inches of the six-inch diameter Monel pipe which serves as slug chute and off-gas line connection. During the runs, once in A-3 and several times in A-4, this plug was broken out mechanically through the fuel-charging lock without shutting down completely. Since the mechanical method is not suited to remote operation, other solutions to this problem are being considered. Current approaches are (1) use of a heater to melt down such salt deposits, and (2) operation at lower salt levels to allow more heated freeboard. Operation at a 36-inch salt level appears promising from experience to date.

The thermal conductivity cell for hydrogen analysis and the wet test meter for measurement of gas volume have both failed, due to attack by residual hydrogen fluoride passing through the condenser. No problem in principle is involved in obtaining hydrogen fluoride-resistant units and new equipment has been ordered.

2. Electrolytically Heated Frozen-wall Vessel Tests (J. D. Gabor, B. Bydal,* J. Gates, W. Mecham)

Preliminary tests were made on the electrolytically heated frozen-wall fluorinator vessel. The objective of these tests was to obtain data on power requirements and frozen-wall control. The data are summarized and improvements made for further tests are described below.

Apparatus and Procedure

The dished-bottom vessel is made of Monel. The inside diameter is 17.4 inches and the total inside height is 52.6 inches. Five external cooling zones are provided, each consisting of windings of approximately 10 turns of 3/8-inch OD copper tubing bonded to the tank wall with copper spray metal. The heights of the zones are approximately 10 inches. Circulating distilled water at a constant temperature is used as coolant. The electrodes are of well-type design with a 2-inch schedule-40 nickel pipe as the outer shell. Inside this pipe a 3/4-inch diameter copper power lead brings the current to the closed bottom of the electrode. A 1/4-inch nickel sparge line is connected inside the electrode so that it discharges directly from the bottom. Internal, electric, tubular resistance heaters for start up are also located in the electrode well. The two resistance heaters in each electrode are each rated at 3 kw at 230 v. Thermocouples are provided in the well to measure electrode temperature. The electrodes are mounted vertically, 4 inches from the wall and 4 inches above the bottom of the vessel.

Solid sodium fluoride-zirconium fluoride salt was charged to the vessel. Initial melting was done with the internal resistance heaters to obtain a molten salt bridge between the electrodes. From this point, electrolytic heating was used to complete the melting. The composition of the salt was 40 mol per cent zirconium tetrafluoride.

Argon sparging was provided through the electrode sparge lines and, in some cases, through a centrally located tube sparger. Cooling water flow was individually controlled and measured and temperatures were recorded. Measurement of the frozen salt thickness was taken with a large caliper.

The electrode power was controlled by a saturable reactor initially operated by a West pyrometer with a temperature set-point. An alternate control system providing control by measurement of the overall resistance of the salt wall was designed. A schematic diagram of the control system is shown in Figure 31. The controller consists of a low dc electronic bridge circuit that balances the wall resistance with any of eight fixed resistance points. The output of the controller is dc matched to the saturable reactor circuit. This controller provides an

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accurate measurement of wall resistance under operating conditions and gives automatic protection against removal of the salt wall or any other cause of a short circuit.

FIGURE 31
SCHEMATIC DIAGRAM OF POWER CONTROL SYSTEM FOR FROZEN-WALL VESSEL

Operating Performance

A general summary of operating performance is given below.

1. In the start-up with indirect resistance heaters inside electrodes, approximately 19 hours was required to melt an initial 480-lb salt charge, with 2.5 kw in the heaters.
2. The maximum temperature of resistance heater cladding during start-up was 729 C.
3. The total time that the salt was held in a fused state by electrolytic heating was 8 days (continuously).

4. The indicated electrode temperature with resistance heaters on was approximately 660 C at steady state.

5. The indicated electrode temperature at steady state with heaters off was approximately 520 C (mp of salt about 510 C).

6. The electrode power requirement at near steady state was between 9 and 11 kw for a total salt charge of 980 lb. Electric current requirement was approximately 720 amperes at this 38-inch salt depth.

Removal of Heat by Coolant

The 980-lb salt charge filled the vessel to a depth of 38 inches. Removal of heat in the five cooling zones for three separate equilibrium periods is shown in Table 29. The heat removal varied widely among the

Table 29

HEAT REMOVED BY COOLING WATER IN THE VARIOUS ZONES OF A FROZEN-WALL VESSEL AT STEADY STATE

Notes:

1. The zone elevations were measured from the inside bottom of the vessel.
2. The salt interface location was 38 inches from the bottom.
3. Approximately 50 per cent of the heat was lost to the surroundings. The vessel was uninsulated.
4. A small argon sparge was used in these tests.
5. An additional 1.6 kw was introduced by the left electrode heater only.
6. Heat removed by the copper lead amounted to about 150 watts for both electrodes.
7. Heat generated by the current in the copper lead amounted to about 75 watts for both electrodes.

Equilibrium Period		1	2	3
Electrode Power, kva		8.9	10.1	10.1
Volts		13.3	13.8	13.8
Amps		668	735	735
		Heat Pickup in Water (kw)		
Zone	Side Elevation (in.)			
5(top)	41 to 53	0.26	1.42	1.21
4	29 to 41	2.11	3.44	3.26
3	17 to 29	1.76	0.43	0.22
2	3 to 17	0.97	0.73	0.73
1(bottom)	0 to 3	0	0	0
		5.10	6.02	5.42

zones, most heat being removed in the zone corresponding to the upper 10 to 12 inches of the fused salt. Essentially no heat was picked up by the water in the bottom zone, indicating that low losses here were taken care of by ambient air convection.

Frozen-wall Measurement

Near the end of the operation a wall traverse was made to determine frozen-wall thickness. A plot of the profile is shown in Figure 32.

Figure 32
FROZEN-WALL PROFILE

<u>Conditions</u>	
Electrode Power, kva	10.6
Volts	13.1
Amps	810
Wall Resistance, ohm	2000
Salt Temperature, C	520
Inlet Water Temp, C	72
Water Temp. Rise, C	4.5 to 13.6

The frozen-wall thickness was between 1 and 1.5 inches for 80 per cent of the liquid depth (32 inches). The heavier wall at the bottom was 5.0 inches thick and extended slightly above the bottom of the electrodes.

Observation of Attack on Electrodes

After about eight days of continuous operation the vessel was shut down and the salt removed. The dimensional changes of the electrodes were measured. Attack consisted of surface irregularities or shallow pits concentrated on the surfaces of the electrodes that faced each other. The left electrode had pits ranging up to 40 mils in depth and the right electrode had a few pits as deep as 80 mils. The absence of interface attack was probably due to a surface crust at the electrode, which was cooled at the top. Considerably more attack was noted for the right electrode. No certain reason can be given for this. The role of current arcing as a possible cause of this attack will be investigated in future runs.

Modifications of the test equipment are being made for further operational tests, and a fluorine system is being installed for use with the vessel.

D. Calcination of Reactor Fuel-processing Wastes

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

The calcination of aqueous wastes resulting from certain solvent extraction processes is accomplished by the use of a heated, fluidized bed. The technique involves the spray injection of the liquid waste into the fluidized bed with the resultant conversion of the liquid to a freely flowing granular solid, reduced considerably in volume. Studies of the calcination of synthetic Purex low-acid waste continued during the current quarter.

1. Operating Conditions (see Table 30)

Calcination of two synthetic Purex low-acid wastes, one with the concentrations given in ANL-5996, Table 27, and the other having the same composition except diluted by the addition of sugar (to act as a reductant and to supply heat of reaction in the reaction zone), have been successfully demonstrated in a 6-in. fluidized bed. The calcine in either case is a free-flowing granular material differing superficially only in color and bulk density. Earlier work (ANL-5996, page 181) had shown that a temperature of 500 C yielded the most satisfactory results; therefore all runs were made at this temperature. Using the tabulated conditions, three runs were made for the purpose of establishing optimum operating conditions for the synthetic feed, and ten runs were made to determine the feasibility of and optimum conditions for calcining sugared feed. In addition to these runs, several runs were made with alternate nozzles in the search for a satisfactory nozzle which would avoid the formation of lumps and agglomerates with the Purex waste. Conical nozzles, porous cap nozzles and pressure nozzles were tried without notable success. The nozzle currently employed (JJB-type) has proved to be the best yet tested and has virtually eliminated lumps and agglomerates.

This nozzle is the same as that found to be optimum for the drying of zirconium fluoride solutions (see Figure 24, page 94). The results of recent runs using this nozzle are given in Table 31.

Table 30

OPERATING CONDITIONS FOR CALCINATION OF
SYNTHETIC LOW-ACID PUREX WASTE

Bed Temperature: 500 C
Calciner Pressure: 0.76 atm abs
Nozzle: Projecting tip ("JJB") type

Run	Avg Feed Rate (ml/min)	Attrition Air (scfm)	Fluidizing Air (scfm)	Total Fluid- izing Gas Velocity (ft/sec)	Starting Bed Mesh	Sugar Content (lb/gal waste)	Run Duration (hr)
127	69	-	4.62	1.5	Screened (-20+200)	-	21
128	71	2.0	2.62	1.5	"	-	30
130	75	-	4.62	1.5	"	2.08	5.5
131	75	1.0	3.62	1.5	Residual	2.08	5.5
132	81	0.75	3.88	1.5	Screened	0.52	5.6
133	78	-	3.78	1.24	"	1.04	5.7
134	73	-	3.78	1.24	Residual	1.04	6.0
135	75	-	3.78	1.24	"	1.04	5.2
136	60	-	3.78	1.24	Screened	1.04	5.8
137	70	-	3.78	1.24	Residual	1.04	5.7
138	70	-	3.78	1.24	"	1.04	5.7
139	65	0.36 to 0.60	3.42 to 3.18	1.24	Screened	1.04	30

Table 31

RESULTS OF WASTE CALCINATION RUNS HWC-127-139
USING PUREX LOW-ACID FEED

Bed Temperature 500 C,
Nozzle - Projecting Tip ("JJB") Type

Run No.	Volume Reduction Factor	Bulk Density (g/cc)		Remarks
		Untapped	Tapped	
HWC-127	-	1.37	1.49	Extended length run - involuntarily shut down. Excessive lumps led to caked bed after 21 hr.
HWC-128	4.93	1.38	1.55	Duplicate of HWC-127, except attrition air used. Voluntary shut-down. Some lumps in bed; less growth evident.
HWC-130	3.91	1.07	1.17	2.08 lb/gal sugar added. Heat effect in bed. Very soft product. Some particle growth.
HWC-131	3.91	1.02	1.12	2.08 lb/gal sugar added. Good run operationally. Many fines found at conclusion of Run HWC-131. Decrease in particle size.
HWC-132	5.35	0.82	0.94	0.52 lb/gal sugar. Attrition air used. Many fines produced. Not much improvement.
HWC-133	5.01	1.06	1.13	1.04 lb/gal sugar added. No attrition air. Reduced fluidizing air. Few fines or agglomerates.
HWC-134- 138	3.3	0.83	0.90	Duplicates of Run HWC-133. Some particle growth. Side-arm overflow pipe.
HWC-139	3.9	0.84	0.90	30-hr run. Very good generally. Growth noticed after ~ 10 hours. Controlled by attrition air.

2. Results

a. Synthetic Purex Waste

The first of these runs, HWC-127, was made using synthetic Purex low-acid waste as feed at a bed temperature of 500 C and was intended to be a run of extended duration. Particle size gradually increased during the run to the extent that, after 20.5 hours of operation, over half of the particles were larger than 20 mesh. Shortly after this condition was reached, the bed caked due to the excessive growth and consequent insufficient flow of fluidizing air.

Run HWC-128 duplicated the preceding run except that attrition air was used as a means of control over particle growth. The attrition air (2 cfm) was introduced at the bottom of the bed through a 0.055-in. orifice. Results were quite gratifying, with only 5 per cent of the bed particles being retained on a 20-mesh screen after 25.5 hours of operation. The run was voluntarily terminated. Although an inspection of the residual bed disclosed some agglomerates, a study of the screen analyses (Figure 33) indicated a definite ability to reduce the rate of particle growth. The presence of small agglomerates is not considered detrimental unless the amount becomes excessive.

FIGURE 33
PARTICLE SIZE DISTRIBUTION
(RUN HWC-128)

b. Synthetic Purex Waste with Sugar Added

The addition of sugar to Purex waste before calcination has been tried at Hanford in spray calcination experiment. It was decided to investigate the effect of sugar additions on the product obtained from the fluid-bed calciner to determine if a softer, more friable product would be obtained. A secondary objective was the generation of internal heat by the chemical reaction of sugar with the feed or decomposition gases.

The first run (HWC-130) of a series of short (6-hr) runs using sugar addition to the feed yielded promising results. Sugar was added to the extent of 2.08 lb/gal of waste. The results did show an absence of agglomerates and a decided heat effect - a reduction of 33 per cent in input power while maintaining a bed temperature of 500 C. The product was much lighter both in color and in density and proved to be considerably softer than the previous products. Despite the softer product, considerable particle growth was observed. Accordingly, the next run, HWC-131, was made under similar conditions with the addition of 1 cfm attrition air (and corresponding decrease in fluidizing air). Although particle growth was halted, the amount of attrition air proved to be excessive and numerous fines resulted. An average volume reduction factor of 3.9 was realized for the two runs.

Run HWC-132 employed a lesser amount of attrition air (0.75 cfm), which also proved to be more than adequate, with numerous fines resulting. The feed for this run contained 0.5 lb/gal of sugar. Although no nozzle lumps were found, some agglomerates were found which appeared to have been formed on the wall opposite the feed nozzle. These would be absent in a larger calciner.

To reduce the quantity of fines produced, Run HWC-133 was made with no attrition air and a sugar content of about 1 lb/gal of the feed. Because of the smaller particle size, the superficial velocity of the fluidizing air was reduced from 1.5 ft/sec to 1.24 ft/sec. The product from this run was very good in appearance with few fines and agglomerates found. A 14 per cent input power reduction was noted for this run.

In order to accumulate operational data over an extended period, Runs HWC-134 to 138 were made under essentially the same operating conditions as Run HWC-133. Product appearance from these runs was uniformly good. Although some particle growth was noted in each run, the growth was not detrimental to calciner operations. Similarly, an accumulation of fines in the disengaging section was noted to some extent in one run but was not sufficiently harmful to cause run failure. The fines accumulation was minimized in a subsequent run by furnishing a periodic impact to the top flange of the calciner. These fines apparently fail to drop back into the bed when the filters are blown back. Installation of a vibrator to assist in dislodging the dust cake is planned.

Because small agglomerates were found in the final beds from many of the runs and because no agglomerates were detected in the continuously removed product, it was felt that the agglomerates might result from the water used in the shut-down or start-up steps. Accordingly, after thoroughly cleaning the calciner, a dummy run was performed in which the normal start-up and shut-down procedures were followed. This consisted of heating a fluidized bed, introducing atomized water for a brief period, then cutting off the heat and water feed and reintroducing purge air through the liquid nozzle. Upon removal, the bed was found to contain agglomerates very similar to those found in actual runs.

Following these experiments, Run HWC-139 was made to observe the effect of an extended-duration (30-hr) synthetic feed run without the periodic water start-up and shut-down steps. The product from this run was uniformly good, except for the last hour, during which pumping difficulties (due to a plugged strainer) were encountered. Particle growth was observed and attrition air was employed after 10 hours of operation. To minimize fines production, attrition air was introduced at a very low rate (0.36 cfm) and was gradually raised to 0.5 cfm. The fluidizing air was correspondingly lowered to maintain a superficial velocity of 1.24 ft/sec. Screen analyses (Figure 34) indicated that the attrition air had stopped the particle growth, and lumps or agglomerates were virtually absent. Although some fines accumulated in the disengaging section over the 30-hour period, the amount was not excessive.

Sample analyses of the condensate from the sugared feed (2 lb/gal) indicated a considerably higher sulfate content than that found from the unsweetened feed, 0.3 mg/ml as compared to 0.03 mg/ml. Analyses of the calcined solid showed that sulfate content of the product from the sweetened feed was essentially the same as that of the unsweetened feed, 50 per cent as compared to 51.6 per cent. Residual nitrate was less than 10^{-4} per cent in both cases.

To conclude the studies on Purex waste, two short runs, with solutions spiked with radioactive waste to determine whether the distribution of fission products is appreciably different from that observed with Idaho Chemical Processing Plant waste, are planned. Additional studies on fluid-bed calcination of Purex waste are planned at Hanford where an 8-inch diameter calciner has been installed.

Figure 34

PARTICLE SIZE DISTRIBUTION
(Run HWC-139)

"JBB" Nozzle

500 C - low acid purex feed with sugar added (125 g/l)

Attrition air introduced after 15 hours.

The 17 hour sample represents the point of maximum growth of particles.

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

(I. Knudsen, N. Levitz, R. Finley)

A series of preliminary experiments on the one-step fluid-bed process for conversion of uranium hexafluoride to uranium dioxide with steam and hydrogen made in a $1\frac{1}{2}$ -inch diameter Monel reactor was completed and reported in topical report ANL-6023. A 3-inch diameter reactor for additional studies of the process was installed. The addition of automatic controls for the uranium hexafluoride rate, product withdrawal and filter blowback should permit improved operation. Particle-size control by means of jet grinding is being considered. A preliminary shake-down run was made with steam and hydrogen to remove residual fluoride from previous uranium dioxide products to be used as the starting bed for the current studies. No uranium hexafluoride was fed to the unit. Operation of the unit is planned for the next quarter.

III. REACTOR SAFETY

The investigation of the factors which influence the pyrophoricity of uranium and zirconium have been complemented with a study of fundamental kinetics of oxidation. Previous research in the 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.

In the continuing study of ignition and burning of uranium and zirconium, more emphasis is being placed on the burning process. Studies of rates of burning propagation provide a useful tool to observe the effects of many variables. Some effort has been devoted to establishing the relationship between rate of burning propagation and dimensions of cross section, using foil strips and wires. Future studies will include typical machine turnings and chips. For both uranium and zirconium foil strips, the dependence on thickness is greater than on width and cannot be totally explained by cross-sectional area.

The continuing study of the rates of burning propagation of zirconium has included investigations of additional alloy foils prepared by the Metallurgy Division. The effects of additives of hafnium, chromium, nickel, beryllium, iron, tantalum, uranium, and vanadium have been determined. The previously reported linear relationship between length of burning zone and propagation rate has been found to be applicable for these alloys also.

A phototube pyrometer has been developed, calibrated, and used to obtain temperature traces as the ignition proceeds along the 0.13-mm thick foil strips. The maximum burning temperatures observed were as follows: for zirconium 1620 (in air) and 2900 (in oxygen); for uranium 1460 (in air) and 2150 C (in oxygen). Studies of the temperature profiles of burning zirconium foil strips with the phototube pyrometer show that the maximum burning temperature is (1) increased by additives which cause increased propagation rates, (2) decreased by increased cross-sectional area, and (3) decreased by decreased oxygen content of the gas. Studies in nitrogen-oxygen and helium-oxygen mixtures indicate that both heat transfer and diffusional processes are important to the overall reaction in different regions of oxygen content.

From preliminary burning-propagation experiments completed on a plutonium alloy foil in air and in oxygen, it can be concluded that (1) useful data can be obtained from plutonium and plutonium alloy foils and (2) the burning behavior is similar to that of uranium. The apparatus for obtaining plutonium-burning curves and performing shielded ignitions has been partially tested, modified, and moved into the glove boxes. Determination of ignition characteristics of several samples of varied purity and a few alloys will be undertaken after additional tests of procedure.

Experiments have been performed to appraise the damage to neoprene gloves by contacting hot objects. Although contacting the gloves with a zirconia tube heated to 500 C for periods of time up to 60 seconds or to 600 C for periods of time up to 20 seconds causes damage to the rubber, the glove was not penetrated. Another significant observation was that, if an operator should accidentally grasp a hot object, he will be very much aware of the heat before the integrity of the glove is impaired.

In the microscopic study of the oxidizing surface of uranium it has been clearly demonstrated that the nucleation and growth of mounds is markedly different on differently oriented grains if the surface was mechanically polished.

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.

A second laboratory-scale method involves the rapid contact of steam with a crucible containing molten metal.

An analysis on the analog computer of the data from runs with zirconium was described in the previous quarterly report, ANL-6029, page 126. Data from runs with finer zirconium wires were obtained and found to agree with the analysis provided the activation energy of the reaction is 28 kcal/mole or greater.

The experiments in CP-5 to verify the techniques to be used in the metal-water experiments in TREAT were completed; the maximum pin temperature attained was 405 C. The analog computer study of metal-water reactions initiated by nuclear reactor transients was completed. Four autoclaves were readied for the first series of tests in TREAT.

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

1. Uranium Ignition Studies (L. Leibowitz, J. D. Bingle, D. R. Armstrong,* M. Cusick**)

a. Studies of Burning Propagation

Most of the incidents involving uranium have not been violent and the principal hazard has been the toxicity of the broadcast radioactive particulate material and fission products when present. The ignition

*Student Aide from Iowa State University with the group for the summer.

**Cooperating Institution student from Detroit University with the group during the spring quarter.

and burning of chips from machining operations is by far the more common incident, but anticipation and good housekeeping seems to prevent these incidents from assuming very dangerous proportions. However, they constitute a constant hazard and considerable inconvenience in a shop operation.

Because chips from machining operations usually have irregular cross sections and are not uniform along their length, a more careful study of the burning process can be performed on foil strips or wires. Attention has been directed to the rate of propagation of a burning region along the metal. This rate of burning propagation is readily measured photographically, using the device previously described (ANL-5959, page 71). A high-speed motion picture is taken of the metal strip burning above a steel rule. Rates of burning propagation are readily obtained from the resulting film. Studies of various thicknesses of uranium foils have shown that strips greater than 1.5 mm thick will not continue to burn in air when the heat from the igniter is removed. Previous studies have also shown (ANL-5996, page 203) the limited effects of surface contaminants and gas contaminants. However, etching the surface in nitric acid pickling solution caused an increase in the rates of burning propagation. The burning-propagation experiments are attractive as a simple means of studying a large number of varied factors. In addition, the possibility of application of steady-state principles to the burning process seems inviting.

(1) Dependence on Cross-sectional Area

A solution of a model of heat transfer in an idealized system which may be analogous to burning propagation has been given by Jakob¹⁵ as follows:

$$V = q/A\rho c_p (T - T_0) \quad ,$$

where V = rate of movement of heat source,

q = rate of heat generation,

A = cross-sectional area

ρ = density

c_p = specific heat [cal/(gm)(deg)], and

$(T - T_0)$ = temperature difference from original.

Because of the marked effect of varied thicknesses of foils on the propagation rate, and as a test of the above relationship to cross-sectional area, the study has been extended to determine the effects of varied diameters of uranium wires.

¹⁵Jakob, M., Heat Transfer, Vol. 1, John Wiley and Sons, Inc., New York(1956), page 343.

A summary of all the values measured, as well as the data previously reported, is given in Table 32.

Table 32

BURNING-PROPAGATION RATES OF URANIUM IN AIR AND OXYGEN

Metal ^a	Thickness (mm)	Width (mm)	Diameter (mm)	Cross-sectional Area (sq mm)	Burning-propagation Rates	
					in Air ^b (cm/sec)	in O ₂ (cm/sec)
SMF-5	0.01	1.0		0.01	3.39	42.9
SMF-5	0.01	3.0		0.03	3.04	60.6
-- ^c	0.03	3.0		0.09	1.71	24.5
SMF-5	0.13	1.0		0.13	0.748	9.60
-- ^d			0.48	0.18	0.545	5.96
SMF-5	0.13	2.0		0.26	0.580	6.58
SMF-5	0.13	3.0		0.39	0.555 ^e	6.04 ^f
BMI	0.13	3.0		0.39	0.514	5.78
-- ^d			0.78	0.48	0.347	3.51
SMF-5	0.13	4.0		0.52	0.526	7.34
ANL	0.23	3.0		0.69	0.355	2.99
BMI	0.25	3.0		0.75	0.352 ^g	3.10
-- ^c	0.25	3.0		0.75	0.386	3.75
ANL	0.48	3.0		1.44	0.239	1.46
-- ^d			1.57	1.94	-- ^h	0.712
-- ^d	1.00	3.0		3.00	0.125	0.972
-- ^c	1.73	3.0		5.19	-- ^h	0.634
-- ^d			2.59	5.27	-- ^h	0.541
-- ^c	3.40	3.0		10.2	-- ^h	0.293

^aDetailed analyses of the SMF-5, BMI, and ANL uranium metal are given in ANL-5996, page 202.

^bAverage of propagation rates of oxidation and ignition fronts (see ANL-5959, page 72.)

^cUranium foil not further characterized.

^dUranium of purity equivalent to ANL metal.

^eAverage of 5 runs.

^fAverage of 3 runs.

^gAverage of 2 runs.

^hBurning would not propagate in air.

In Figure 35 is shown the relationship between cross-sectional area and rates of burning propagation for these samples. It is clear that there is a general decrease in burning-propagation rate with increasing cross-sectional area, but there are also other factors involved. This is clear

FIGURE 35
RELATIONSHIP BETWEEN BURNING-PROPAGATION RATES
IN AIR AND OXYGEN AND CROSS-SECTIONAL
AREA FOR URANIUM FOILS AND WIRES.

since the wires do not burn at the same rate as foils of identical cross section. Moreover, even for foil strips a cross-sectional area dependence is not the only factor involved, since, in the cases of samples which had the same thickness but varying width, burning-propagation rates did not fall on the same line as the other samples which had identical widths but varying thickness. It is evident that the effect of thickness is very much greater than that of width for these foil samples.

(2) Effect of Ozone on Burning-propagation Rates

Limited effects on the propagation rates were found when a series of surface and gas contaminants were tested using the 0.13-mm SMF-5 uranium foil (ANL-5996, page 203). It has been suggested that ozone might be a possible gas contaminant that would warrant investigation. Therefore, propagation tests were run on the SMF-5 foil in air containing 1% ozone (by analysis of the gas stream) from a Welsbach ozonator. Rates of 0.575 and 0.564 cm/sec for the oxidation front and ignition front, respectively, were found. These experiments are included in Table 33, from which it is possible to compare the effects of all of the gas contaminants so far studied. None of these gas contaminants has a great effect on the burning-propagation rates of uranium.

Table 33

EFFECT OF GAS CONTAMINANTS ON THE RATES OF PROPAGATION
OF BURNING OF URANIUM IN AIR

(SMF-5 foil samples, 0.13 x 3.0 x 60 mm)

Gas Composition	Avg Distance Between Fronts (cm)	Burning-propagation Rate	
		Oxidation Front (cm/sec)	Ignition Front (cm/sec)
No contaminant (dry Air)	0.48 ± 0.05	0.558 ± 0.024	0.553 ± 0.024
Air saturated with H ₂ O vapor (25 C)	0.42	0.546	0.558
Air with 5% CO ₂ added	0.46	0.514	0.518
Air with 1% O ₃ added	0.55	0.575	0.564

b. Burning-temperature Studies

The burning temperature is important because it is probably a major factor in the rate of burning propagation. Let us assume that a spontaneous fire begins in a small localized area of a scrap pile of metal. The likelihood of the fire to spread will depend in part on whether the burning temperature of this localized "hot spot" is high enough to heat the surrounding metal to its ignition point. If the burning temperature is low, the burning will not be propagated. This study was undertaken to determine the burning temperature of a metal foil under various conditions.

(1) Experimental Method and Calibration

The accurate measurement of the surface temperature of burning metal foil strips was accomplished by means of a photoelectric pyrometer. The apparatus for mounting and igniting the foil strips is illustrated in Figure 36. One end of a foil was securely clamped and the other

FIGURE 36
APPARATUS FOR IGNITING FOIL SPECIMENS

was connected to a fine leaf spring. The spring was required to prevent the sample from swinging out of the view of optical system. Magnesium turnings were ignited in the cup below the foil and the magnesium fire in turn ignited the foil.

A schematic diagram of the photoelectric pyrometer is illustrated in Figure 37. The foil and ignition system are placed in the controlled atmosphere box and the foil is viewed through an enclosure window. The image of the foil, magnified 12X by a double convex lens, passes through an adjustable slit and two filters, and is focused on a vacuum phototube. As the foil burns past the observed area, a small current is developed in the phototube. The phototube current is amplified by a cathode follower and impressed on the vertical plates of a cathode-ray oscilloscope. A linear sweep, which is triggered manually as the ignition front nears the observed area, is applied to the horizontal plates.

FIGURE 37
APPARATUS FOR PHOTOELECTRIC PYROMETER

The optical measurement of temperatures is based on Planck's law of radiation, which, for a black body, is

$$W_{B,\lambda} = \frac{C_1}{\lambda^5} \cdot \frac{1}{e^{C_2/\lambda T} - 1} \quad (1)$$

where $W_{B,\lambda}$ is the radiant energy, λ is wavelength in cm, T is temperature (K), and C_1 and C_2 are constants [$C_2 = 1.4384 \text{ (cm)(deg K)}$].

Most surfaces, however, cannot be assumed to be perfect radiators. The fraction of the theoretical radiation actually emitted at a particular wavelength is called the spectral emissivity, ϵ . The apparent temperature of an imperfect radiator is called the brightness temperature, T_B . Thus, the energy received by the detector is

$$E \propto \left[e^{(C_2/\lambda T_B)} - 1 \right] = \frac{1}{e^{C_2/\lambda T_B} - 1} \quad (2)$$

For the temperature range of interest, the exponential term is much greater than unity and

$$E \propto e^{-C_2/\lambda T} = e^{-C_2/\lambda T_B} \quad (3)$$

The oscilloscope deflection, D , for a particular gain setting and slit width should be proportional to the emitted energy, E :

$$\log D \propto \log \epsilon - \frac{C_2}{2.303 \lambda T} = - \frac{C_2}{2.303 \lambda T_B} \quad (4)$$

The relationship between the true temperature, T , and the brightness temperature, T_B , is thus

$$1/T = (1/T_B) + \frac{2.303 \lambda \log \epsilon}{C_2} \quad (5)$$

A tungsten ribbon-filament light bulb was used as a calibration source. Brightness temperatures were obtained using a Leeds and Northrup optical pyrometer as a function of lamp current. The brightness temperatures were at the wavelength used in the instrument ($6500 \text{ \AA}$). These values were converted to yield the true temperature of oxide surfaces that would have the same radiant emission. The conversion involved the repeated use of equation (5) using the following data for various surfaces:

Surface	Wavelength ($\text{\AA}$)	Emissivity ϵ
Tungsten	6500	0.45
Tungsten	8000	0.43
Oxides	8000	0.80

Oscilloscope deflections were then determined for two slit widths as a function of lamp current. The phototube, using the smaller slit, viewed an area of foil of approximately $0.2 \times 0.2 \text{ mm}$. The phototube, using the larger slit, viewed an area of foil of approximately $0.8 \times 0.2 \text{ mm}$. Plots of log deflection vs reciprocal oxide temperature should then yield straight lines according to equation (4). The calibration plots, which demonstrate good agreement with the theoretical slope of $-C_2/2.303 \lambda$, are shown in Figure 38 for the temperature range from 1100 to 1800 C obtainable with the lamp. Higher temperatures can be determined by extrapolation.

FIGURE 38
AGREEMENT OF CALIBRATION DATA WITH PLANCK'S LAW

(2) Results

Burning temperatures for uranium were obtained in air and in oxygen; the temperature-time plots are shown in Figures 39 and 40 which also contain plots of zirconium data. The maximum burning temperatures of uranium foils as compared to cubes (ANL-5959 , page 69) are:

	Max Foil Temp (C) Photoelectric Pyrometer	Max Cube Temp (C) Burning-curve Experiments, Rhenium-Tungsten Thermocouple
Uranium, Air	1460	1400
Uranium, Oxygen	2670	≥ 2150

FIGURE 39
BURNING-PROPAGATION TEMPERATURES
OF URANIUM AND ZIRCONIUM IN AIR

FIGURE 40
BURNING PROPAGATION TEMPERATURES
OF URANIUM AND ZIRCONIUM IN OXYGEN

The maximum burning temperature of uranium foil in air (1460 C) is in good agreement with the temperature obtained with a cube during a burning-curve experiment (1400 C). Both temperatures were above the melting point of uranium (1133 C). In oxygen no valid comparison can be made, since the rhenium-tungsten thermocouple is only useful up to about 2200 C, and even then only for a brief period in an oxidizing medium before failure. The maximum temperature observed for the foil, 2670 C, is below the melting point of uranium dioxide, 2880 C. The halt at 2520 in the cooling portion of the temperature trace has not yet been explained satisfactorily because of the lack of knowledge of the uranium-oxygen system.

2. Zirconium Ignition Studies

(L. Leibowitz, J. D. Bingle, H. A. Porte, M. Cusick)

a. Burning-propagation Rates of New Alloy Foils and Their Burning-zone Lengths in Air

Incidents involving zirconium rarely involve bulk metal but usually have involved powder and chips from machining operations 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.

Burning-propagation studies, similar to those on uranium, have been reported for various zirconium and zirconium alloy foils (ANL-5996, page 222 and ANL-6029, page 119). Some additional measurements have been carried out in air and in oxygen, using a series of new alloy foils, and these results are listed in Table 34, along with those previously reported. In the case of zirconium burning in air, it is observed that there is a burning zone of fixed length which progresses along the foil strip. The relationship between the length of this burning zone (Z) and the burning-propagation rate, $\text{Rate} = 0.17 + 0.24 Z$, which has been presented previously (ANL-5996, page 227), is also applicable to the data for the new alloys. This may be closely connected with the rate of cooling of the metal once the oxidation rate has diminished to the point at which combustion is not self-sustaining.

b. Influence of Cross-sectional Area on Propagation Rates in Air

The marked effect of cross-sectional area on the burning-propagation rates in oxygen of zirconium foils and wires has previously been reported (ANL-6029, page 120). It was noted in that report that the

Table 34

BURNING-PROPAGATION AND IGNITION DATA OF ZIRCONIUM AND ZIRCONIUM ALLOYS IN OXYGEN AND IN AIR

Alloy Composition (a/o)	Propagation Rate		Maximum Burning Temperature in Air (C)	Burning Zone Length in Air (cm)	Shielded Ignition Temperature		Oxygen Weight Gained First Minute ^c ($\mu\text{g}/\text{sq cm}$)
	Oxygen ^a (cm/sec)	Air ^b (cm/sec)			O ₂ (C)	Air (C)	
3.60 Cu	13.2	0.393		1.1	784	800	195
4.08 Hf	10.2	0.444		1.2			199
0.91 Ni	10.5	0.562	1575	1.7	792	794	218
3.61 Cr	10.3	0.545		1.4			230
4.22 Ni	11.3	--d		--d	818		233
3.60 Sn	14.3	0.498		1.2	759	767	233
Pure Zr	11.1 $\pm$ 1.0	0.463 $\pm$ 0.027	1620	1.3 $\pm$ 0.1	786	784	256
4.23 Be	9.09	0.447		1.3			266
3.72 C	9.13	0.477	1660	1.2	803		272
1.76 U	13.6	0.608	1735	2.0	765	766	276
3.95 Fe	9.71	0.554		1.8	763		317
3.54 Ta	11.6	0.614		1.9			318
1.04 Ta	12.0	0.647	1660	1.8			320
1.84 V	11.8	0.654	1680	2.0	763	764	323
3.52 U	9.96	0.667		2.2			331
2.15 Al	14.6	0.585	1645	1.6	739	740	452
3.62 Al	13.4	0.452	1670	1.0	753	754	549
1.08 Ti	14.3	0.762	1730	2.3	694	698	624
2.12 Ti	17.6	0.835 $\pm$ 0.014		2.6	634	632	840
3.88 V	9.18	0.591		1.8	766		961
4.16 Ti	13.3	0.882		3.3	529	531	1424
14.9 Ti	17.1	1.06	1760	3.7	372	374	-

^aSamples were 0.13-mm thick and 3.0-mm wide.

^bSamples were 0.13-mm thick and 0.6-mm wide.

^cObtained from isothermal studies of bulk samples at 700 C in 200 mm oxygen.

^dA 0.6-mm wide sample did not propagate. However, a 0.44-mm wide sample exhibited a propagation rate of 0.503 cm/sec with a burning-zone length of 1.2 cm.

values for the wires fell on the same line as those for the foils, thus supporting the notion that an area effect was being observed, regardless of shape. However, as the foil thickness was decreased, the effect of varied width gradually diminishes, until for the 0.007-mm thick zirconium foil the propagation rate is independent of the width.

Similar studies have now been completed to determine this relationship in air. Table 35 summarizes all of the experiments conducted in this medium, while Figure 41 graphically compares the relationship previously observed in oxygen with the air data (two new oxygen data points are also included). It is apparent that in air the dependence of the propagation rate on cross-sectional area follows a very similar pattern to the oxygen data for the thinner foils. However, the wires and thicker foils do not propagate in air and therefore no data are available in the larger cross-sectional area region.

Table 35

DEPENDENCE OF PROPAGATION RATES IN AIR ON
CROSS-SECTIONAL AREA FOR PURE ZIRCONIUM FOILS

Thickness (mm)	Width (mm)	Burning-zone Length (cm)	Cross-sectional Area (sq mm)	Propagation Rate (cm/sec)
0.007	0.9	-	0.006	19.5
0.007	1.6	-	0.011	21.4
0.007	3.7	-	0.026	21.7
0.020	0.48	1.30	0.010	3.25
0.020	0.90	-	0.018	3.23
0.020	1.0	2.10	0.020	2.34
0.020	2.4	2.60	0.048	2.29
0.020	5.2	3.70	0.104	1.50
0.050	0.63	2.10	0.032	1.28
0.050	2.2	2.00	0.109	0.755
0.13	0.38	1.70	0.049	0.742
0.13	0.60	1.50	0.078	0.511
0.13	0.61	1.35	0.079	0.416
0.13	0.61	1.15	0.079	0.438
0.13	0.60	1.25	0.078	0.495
0.13	0.61	1.20	0.079	0.456
0.13	0.59	1.30	0.077	0.481
0.13	0.60	1.25	0.078	0.444

FIGURE 4I

RELATIONSHIP BETWEEN BURNING-PROPAGATION RATES
IN AIR AND OXYGEN AND CROSS-SECTIONAL
AREA FOR PURE ZIRCONIUM FOILS AND WIRES

c. Burning-temperature Studies on Zirconium

The procedures described earlier (page 132) for obtaining maximum burning temperatures of uranium were also applied to zirconium and some zirconium alloys. The temperature-time plots for zirconium in air and oxygen were shown in Figures 39 and 40. The maximum burning temperatures as read off the plots were 1620 C in air and 2900 C in oxygen. In the cooling portion of the oxygen curve a slight halt was observed at 2670 C, which could be interpreted as the melting point of zirconium dioxide (2690 C). However, the similarity to the unexplained halt in the uranium curve causes this interpretation to be doubted.

A number of zirconium alloys were burned in air. Maximum burning temperatures are reported in Table 36. Except for nickel, all of the alloying agents raised the burning temperature. The temperature-time plots for the alloys were very similar to those of the pure metal (see Figure 39). The highest burning temperature in air (1760 C) was obtained for the 14.9 atom per cent titanium alloy, but even this is below the melting point of zirconium (1845 C).

Table 36

MAXIMUM BURNING TEMPERATURES OF ZIRCONIUM AND ZIRCONIUM ALLOYS IN AIR

(Foil 0.6 x 0.13 mm cross section)

Foil	Maximum Burning Temperature, C	Foil	Maximum Burning Temperature, C
Pure Zr	1620	3.62 a/o Al	1670
14.9 a/o Ti	1760	1.04 a/o Ta	1660
1.76 a/o U	1735	3.72 a/o C	1660
1.08 a/o Ti	1730	2.15 a/o Al	1645
1.84 a/o V	1680	0.91 a/o Ni	1575

Previous experiments have shown a definite dependence of rate of burning propagation on the cross-sectional area of foils. Therefore, temperature studies were undertaken on a 14.9 atom per cent titanium-zirconium alloy because this alloy burns in air at relatively large cross-sectional areas, whereas pure zirconium and most zirconium alloys do not. The width of the alloy strips was varied from 0.6 to 6.6 mm (the thickness of all foils was 0.13 mm). As the width was increased the maximum burning temperature decreased from 1760 to 1350 C in the manner shown in Figure 42.

FIGURE 42
RELATIONSHIP BETWEEN MAXIMUM BURNING
TEMPERATURE IN AIR AND SAMPLE WIDTH FOR
14.9 % Ti ALLOY OF ZIRCONIUM (0.13mm THICK)

The effects of oxygen concentration and the nature of the diluent on the burning temperatures of foils were investigated. Pure zirconium foils were burned in both nitrogen-oxygen and helium-oxygen mixtures. The results are shown in Figure 43 for varying oxygen concentration. In both the helium-oxygen and nitrogen-oxygen mixtures the burning temperatures increased with increasing per cent oxygen.

At oxygen concentrations of approximately 20 to 50 per cent, the helium mixtures burned at higher temperatures than the corresponding nitrogen mixtures; however, at high oxygen concentrations the opposite effect was observed (see Figure 43). This would indicate that the burning of the foil is dependent upon two factors: (a) diffusion of oxygen through the diluent and (b) loss of heat to the diluent. At the lower oxygen concentrations the burning must be diffusion-dependent, since diffusion of oxygen is much faster through helium than through nitrogen. But helium has a much higher thermal conductivity than nitrogen and therefore at high oxygen concentrations the diffusion effect is counterbalanced by increased heat losses in the helium mixtures. This results in higher burning temperatures in the nitrogen mixtures than in the corresponding helium mixtures.

FIGURE 43
EFFECT OF OXYGEN CONCENTRATION AND NATURE OF DILUENT
ON THE MAXIMUM BURNING TEMPERATURE OF ZIRCONIUM FOIL
(0.6x0.13 mm CROSS SECTION)

d. Burning-propagation Rates in Gases of Varied Oxygen Content

The studies of the burning temperatures of metal foils, presented in the previous section, have shown the relationships between the maximum burning temperature and the oxygen content of gas mixtures. It was of considerable interest to see whether or not burning-propagation rates would parallel the temperature changes. Measurements were made of rates of burning propagation of strips of zirconium foils with a cross section of 0.6 x 0.13 mm. Mixtures containing 20 and 80 per cent oxygen were obtained by suitable adjustment of flow rates. Tank gases without further purification were used. The burning-propagation rates from these experiments are compared with temperatures from Figure 43 in the table below.

	20 Per Cent Oxygen		80 Per Cent Oxygen	
	Rate, cm/sec	Temp, C	Rate, cm/sec	Temp, C
Helium diluent	1.0	1800	16.	2400
Nitrogen diluent	0.46	1600	19.	2700

It is interesting to note a reversal of rates of burning propagation which parallels the reversal in maximum burning temperatures. There appears to be a close connection between burning-propagation rate and the maximum burning temperature.

3. Plutonium Ignition Studies

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

The potential use of plutonium in nuclear reactors and concomitant handling of the metal in various forms makes it imperative that knowledge of the ignition behavior be obtained. A survey of the available literature (ANL-5974, page 131) has shown relatively little information on the oxidation or ignition characteristics.

A program of study similar to that described (ANL-5974) for zirconium and uranium has been initiated. Arrangements for preparation of special plutonium samples and alloys have been made with Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

a. Apparatus and Facilities

Prior to the completion of an adequate glove-box facility for handling metallic plutonium, exploratory experiments are being performed in a glove box used for analyses of plutonium-bearing samples. Apparatus for performing burning-propagation rate studies and ignition experiments (burning curve and shielded ignitions) has been built, tested, and installed in the glove box.

The apparatus has been designed so that it is not necessary to have one's hands in the boxes during the ignition or burning experiment. Solenoid valves, controlled from outside the box, permit rapid switching from helium to air (or oxygen) and back to helium. This arrangement is essential for shielded ignitions and will be an added safety feature to permit extinguishing fires in either apparatus quickly. The system for gas (oxygen, air, and helium) supply has pressure-relief valves to avoid overpressurizing the apparatus, in addition to regulators, gages, flowmeters, and sampling valves for operational purposes. Filters (gas mask canisters) are incorporated in the input lines to prevent contamination of lines and other equipment outside the box.

b. Damage to Neoprene Gloves by Hot Objects

Because of the importance of the gloves in glove-box operations and the susceptibility of such gloves to damage, it was suggested that tests be done to appraise the damage resulting from direct contact of the neoprene gloves with hot objects.

Several experiments in which the $\frac{3}{4}$ -inch diameter zirconia liner tube from the ignition apparatus was heated to 500 or 600 C, removed from the furnace and immediately placed against a glove for various periods of time up to 60 seconds, were completed.

The results are summarized in Table 37. With the tube initially at 500 C and in contact with the glove for 10, 30, and 60 seconds, some smoke was observed. Examination of the glove indicated rubber had melted and charred on the outside surface. The interior surface of the glove showed no damage. With the tube at 600 C and in contact for approximately 5 and 20 seconds, more smoking, melting, and charring were observed, but the interior of the glove was still intact. Contact for 30 seconds caused heavy smoke, considerable charring and considerable penetration of the glove.

Table 37

DAMAGE TO NEOPRENE GLOVE-BOX GLOVES BY HOT OBJECTS

$\frac{3}{4}$ -inch zirconia tube was heated to temperature, removed from furnace and immediately held against glove for indicated time.

Tube Temperature (C)	Portion of Glove Contacted	Duration of Contact (sec)	Surface Damage Observed		
			Melting	Charring	Penetration
500	Back of thumb	5 to 10	Some	Slight	None
500	Back of hand	30	yes	yes	None
500	Little and ring finger	60	yes	yes	None
600	Thumb, index and middle finger ^a	~5	None	Slight	None
600	Palm	20	yes	yes	None
600	Back of index and middle finger	30	yes	Extensive	yes

^a The tube was grasped until heat was felt and then dropped. A small blister appeared on the operator's hand the next day.

In the most significant experiment, the operator, wearing the usual arrangement of a surgical glove inside the neoprene glove, grasped the zirconia tube with his thumb and first two fingers immediately after its removal from the furnace at 600 C. It took a moment before any heat was felt. As soon as the heat was felt, it was intense and the zirconia tube was dropped. No smoke was observed. The operator's thumb and fingers stung for quite a while after removal of the gloves. On the following day a narrow $\frac{1}{4}$ -inch long blister appeared on his middle finger.

Some evidence of melting and charring of the rubber surface was observed. There is no indication of damage to the inside of the glove fingers and only a narrow indentation was seen on the inside of the thumb.

This test clearly shows that the operator would be very much aware of the heat before the integrity of the glove is impaired.

c. Burning-propagation Rate Studies

Preliminary studies of the burning-propagation behavior of a plutonium alloy in air and oxygen are being carried out. The principal objectives of this work are: (a) to gain experience in handling metallic plutonium and in glove-box operations; (b) to develop suitable apparatus and techniques for carrying out the measurements within the limitations imposed by glove-box operation; (c) to determine whether useful burning-propagation rate data can be obtained for plutonium and its alloys; and (d) to obtain data needed for establishing the specifications for the pure metal and alloy specimens.

A cell has been prepared for enclosing the sample in a controlled atmosphere during studies of propagation rates similar to those used for studies on uranium and zirconium. It consists of a 6-inch length of 4-inch ID Pyrex pipe closed at one end by a circular window of $\frac{1}{4}$ inch plate glass and at the other by a metal plate fitted with supports for the sample, gas inlet and outlet tubes, and insulated electrical leads. The apparatus is easily dismantled, and the sample supports and other parts are such that sample mounting and alignment can be accomplished readily. Experiments using the apparatus have been performed on zirconium foil strips prior to the transfer to the glove boxes.

Foil specimens are cut to the desired small uniform width on a bench shear having a 3-inch blade which was modified for this application before being introduced into the glove-box. A quick-clamp has been attached to the shear platform for holding the foil in place during the cutting operation.

Specimens of a 1 weight per cent aluminum-plutonium alloy in thicknesses of 0.11 and 0.82 mm were obtained from the Metallurgy Division.

The rate of burning propagation across the plutonium-aluminum alloy foil strips was demonstrated to be constant, as has already been observed for uranium and zirconium (ANL-5959, page 72). The rates for various sample sizes presented in Table 38 are compared, where possible, with data obtained using uranium foils. The propagation rates of plutonium strips are dependent on both width and thickness.

Table 38

BURNING-PROPAGATION RATES OF 1 w/o ALUMINUM-PLUTONIUM ALLOY
FOIL IN AIR AND OXYGEN

Thickness (mm)	Width (mm)	Cross-sectional Area (sq mm)	Avg Distance between Fronts (cm)	Burning-propagation Rate	
				Oxidation Front (cm/sec)	Ignition Front (cm/sec)
In Air					
0.11	1.0	0.11	0.24	0.74	0.74 ^a
0.11	1.2	0.13	0.27	0.69	0.69
0.11	1.2	0.13	0.25	0.68	0.68
0.11	1.2	0.13	0.12	0.67	0.67
0.11	3.3	0.36	0.43	0.54	0.53 ^b
0.23	3.1	0.71	0.20	0.29	0.29
0.23	3.1	0.71	0.19	0.25	0.24
0.82	1.2	0.98	0.29	0.20	0.20
0.82	2.9	0.38	--	--	0.15 ^c
In Oxygen					
0.11	1.1	0.12	--	--	16. d
0.23	2.9	0.67	--	--	5.5 ^e

^a Compares to burning-propagation rate of 0.75 cm/sec for 0.13 x 1 mm uranium foil in air.

^b Compares to burning-propagation rate of 0.55 cm/sec for 0.13 x 3 mm uranium foil in air.

^c Since neither the oxidation nor the ignition front was readily observed, the rate is based on the advance of the swollen oxide along the edge.

^d Compares to burning-propagation rate of 9.6 cm/sec for 0.13 x 1 mm uranium foil in oxygen.

^e Compares to burning-propagation rate of 3.1 cm/sec for 0.25 x 3 mm uranium foil in oxygen.

From the runs on burning propagation in air of the 0.82 mm thick specimens, it has been observed that, for a cross-sectional area greater than approximately one square millimeter, it is very difficult to obtain burning-rate data in air because of the relatively low burning temperature. The ignition front is not clearly discernible on the film because of the low intensity of light from the burning compared to that of the floodlights. The rate of burning propagation was based on the advance of the swollen oxide along the edge. Because the rate is so low, a visual measurement without the flood lamps, which are needed for photography, may be more satisfactory.

These data demonstrate that useful propagation rate data can be obtained for plutonium and its alloys. The burning-propagation rates measured for the 1 weight per cent aluminum-plutonium alloy were found to be linear and satisfactorily reproducible. From the limited amount of data obtained thus far the burning-propagation behavior of plutonium appears to be similar to that of uranium.

4. Uranium Isothermal Studies (L. Leibowitz, P. Pizzolato, L. Mishler)

The use of a metallographic microscope in conjunction with a vacuum hot cell has been of considerable help in advancing our understanding of the nature of the oxidation process. It has been possible by this means to photograph the surface of a uranium sample during the course of the oxidation.

Previous work using an induction heater (ANL-5996, page 214) revealed the complication caused by this heating method. A new resistance-heated hot cell, shown schematically in Figure 44, has therefore been constructed. The lower brass plate is so constructed as to permit attachment of the Leitz Panphot used in this work. Connection to the constant-pressure volumetric system is made by means of the 18/7 semiball joint through a Pyrex glass spring which allows ample motion for focusing.

FIGURE 44
RESISTANCE-HEATED HOT CELL FOR MICROSCOPIC EXAMINATION

From an examination of photographs taken during some preliminary runs it was clear that the mound formation and growth previously reported (ANL-5924, page 95) was still in evidence. It seemed that some areas of the sample did not become covered with nodules as fast as others, and there also appeared to be a rough correspondence of these regions with certain grains observed before the oxidation was begun. In order to explore this aspect of the process more carefully, a sample of grain-coarsened uranium was obtained. This metal contains grains many times larger than those normally found. The surface of this sample was mechanically polished

with $0.1\text{-}\mu$ alumina; the sample was mounted in the microscopic cell and oxidized at 200 C in 200 mm oxygen while photographs were taken of the surface. Figure 45 shows the appearance of the metal after some three hundred minutes of oxidation and indicates the marked difference in nucleation rates shown on two grains. Similar differences in nodule formation on various grains have been observed by other workers, as has the general formation of oxide nuclei during the course of metal oxidations.¹⁶⁻¹⁹

Figure 45

PHOTOMICROGRAPH OF THE SURFACE OF TWO GRAINS OF A URANIUM
SAMPLE AFTER 300 MINUTES OF OXIDATION AT 200 C
IN AN OXYGEN PRESSURE OF 200 MM

¹⁶Bardolle, J., and Benard, J., Compt. rend. 232, 231 (1951); 239, 706 (1954).

¹⁷Cathcart, J. V., Campbell, J. J., and Smith, G. P., J. Electrochem. Soc., 105, 442 (1958).

¹⁸Young, Jr., F. W., and Jenkins, L. H., ORNL-2614.

¹⁹Gulbransen, E. A., and Andrew, K. F., J. Electrochem. Soc., 106, 511 (1959).

B. Metal-Water Reactions

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

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

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

In the condenser-discharge experiment, metal wires are rapidly melted and dispersed in a water-filled cell by a surge current from a bank of condensers. The energy input to the wire 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.

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

a. Analysis of Zirconium Data

An analysis of the results of condenser-discharge runs using nominal 60-mil zirconium wires was presented in the previous quarterly report, ANL-6029, page 126. The condenser-discharge experiment was simulated on the analog computer by the parabolic law of oxidation and a simple model of heat transfer. A possible source of confusion in the differentiation of the parabolic law was brought to our attention. Equations (1) and (2) are repeated below (symbols in ANL-6029, page 127):

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

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

*Consultant from Illinois Institute of Technology.

Equation (2) was stated to be the derivative of equation (1), which is true only when temperature, T , is independent of time. Equation (2) was used in the computer program and is believed to be the more fundamental form of the parabolic rate equation. Equation (1) is then an integrated form of (2) which applies only under isothermal conditions. A simple development of the parabolic rate law from first principles is given in Kubaschewski,²⁰ where it is shown that the differential form, equation (2), is obtained initially. Ample justification for the Arrhenius form of the temperature dependence is also provided in Kubaschewski. It should also be pointed out that equation (2) is an approximation when applied to a curved surface. Runs below 2600 C showed a maximum of 20 per cent reaction, so that the principal metal-oxide interface receded no more than 8 per cent of the radius into the metal sphere.

b. Runs with Zirconium

The analysis of the results of runs using nominal 60-mil wires showed that reasonable agreement with computed results was obtained for runs having initial temperatures through the melting point. Experimentally, no significant increase in ratio of surface to volume occurred until the initial temperature exceeded the melting point, where progressively finer particles were produced. The runs that could be described adequately by the computer curves were thus confined to a single ratio of surface to volume, i.e., to cylinders of 0.07-cm radius or to equivalent spheres of 0.105-cm radius. It was therefore of interest to study the reaction using finer wires having greater ratios of surface to volume.

Partial results of runs with nominal 30-mil zirconium wires are given in Table 39. The experimental procedure was identical to that used for studies of the 60-mil specimens, except for the method of energy measurement, which is described later. The data for total extent of reaction are plotted in Figure 46 along with 60-mil wire data and the computed curves. The computer study was not carried out for initial temperatures in the melting point range or below for the fine wires, since the experiments were not available at that time. The data for 30-mil specimens at the upper end of the melting point range agree with the computed results if the reaction has an activation energy of roughly 28 kcal/mole. This must be considered as a minimum value, however, because of the likely limitation of a diffusion barrier (transport of the water through the hydrogen envelope surrounding the particles). Many of the 30-mil runs produced more reaction than very high-temperature fine particles derived from 60-mil specimens. This behavior is not presently understood. It is anticipated that the inclusion of diffusion terms into the theoretical equations will shed some light on the problem.

²⁰Kubaschewski, O. and Hopkins, B. E., Oxidation of Metals and Alloys, Butterworths Scientific Publications, London (1953), p. 41 ff.

Table 39

METAL-WATER REACTION DATA: CONDENSER DISCHARGE
METHOD USING 30-mil WIRES

Run	Energy Input (cal/g)	Calc Temp (C) and Phys State	Per Cent Reaction	Appearance of Residue
<u>Runs with Zirconium</u>				
85	124	1460, Solid	5.9	Intact
86	146	1720, Solid	10.0	2 pieces
71	149	1760, Solid	8.6	4 pieces
88	160	1840, 10% Liq.	13.7	Elliptical
89	163	1840, 15% Liq.	12.3	Elliptical
87	165	1840, 15% Liq.	15.6	Elliptical
75	180	1840, 40% Liq.	12.6	Elliptical
76	182	1840, 45% Liq.	16.4	Elliptical
72	190	1840, 60% Liq.	11.8	Coarse Spheres
82	214	1840, 100% Liq.	18.5	Coarse Spheres
90	214	1840, 100% Liq.	19.7	Coarse Spheres
83	241	2180, Liq.	14.8	Coarse Spheres
74	270	2550 ^a , Liq.	23.9	Fine Spheres
73	324	3220 ^a , Liq.	44.9	Powder
<u>Runs with Platinum</u>				
91	39.7	1150, Solid	-	Intact
92	42.6	1200, Solid	-	Intact
93	54.3	1500, Solid	-	Intact
102	71.3	1773, 20% Liq.	-	Intact
94	73.4	1773, 30% Liq.	-	Intact
96	76.5	1773, 40% Liq.	-	Intact (mottled)
103	81.5	1773, 60% Liq.	-	Intact (Bent, expanded)
104	84.1	1773, 70% Liq.	-	Coarse Spheres
100	88.2	1773, 85% Liq.	-	Coarse Spheres
101	92.1	1773, 100% Liq.	-	Coarse Spheres
98	92.6	1800, Liq.	-	Coarse Spheres
99	94.3	1800, Liq.	-	Coarse Spheres
97	114	2250, Liq.	-	Some fine Spheres
105	136	2600, Liq.	-	Some fine Spheres
95	183	3750, Liq.	-	Fine Spheres

^a Runs had explosive pressure rise.

FIGURE 46
COMPARISON OF COMPUTED AND
EXPERIMENTAL RESULTS FOR ZIRCONIUM-WATER
REACTION BY CONDENSER-DISCHARGE METHOD

Only two 30-mil runs were made with initial temperatures of the order of 2600 C and higher. Oscillographic pressure traces for these runs showed the characteristic explosive pressure rises. In all other runs uniform gas evolution occurred for several tenths of a second.

c. Runs with Platinum

A series of runs was made with 30-mil platinum wires, principally to test the procedure for energy measurement. The method described in ANL-5896, page 103, has been improved through the use of two "calorimetric cells" consisting of short lengths of constantan wires

with fine thermocouples attached. The revised method has a parallel path shunting the specimen, arranged to minimize stray inductance. One of the thermocouple elements is located in the parallel path. Calculations show that the temperature rise of the parallel path element is somewhat analogous to a voltmeter reading, while the second element, in series with the specimen, is analogous to an ammeter. The method greatly increases the accuracy of energy measurement for conductive metals such as platinum and particularly aluminum.

The data for the platinum runs are included in Table 39. The behavior of platinum specimens in the melting region is somewhat different from zirconium in that elliptical distortion of the wire does not occur. It, therefore, is not possible to compare the calculated temperature and physical state quantitatively in terms of the appearance of the residue. Platinum forms spheres sharply at a calculated energy input corresponding to 70 per cent melting, while zirconium forms spheres at 50 per cent melting under identical experimental conditions. Runs with aluminum will be made to test the accuracy of energy measurement with a third metal.

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

The pressure-pulse method is an attempt to study the reaction of molten metals with water vapor under nearly isothermal conditions at very high temperatures. The method involves the momentary contact of water vapor with molten metal contained in a crucible, followed by an analysis for hydrogen generated by reaction. The presence of an initially clean surface provides for measurement of the fastest possible reaction.

Isothermal rate data obtained by this method should provide a comprehensive check on the results of both the condenser-discharge method and the in-pile studies. The method should give the best determination of the form of the rate law to be used to interpret the results of the other methods.

Apparatus construction and preliminary testing were completed during the last few months.

a. Apparatus and Procedure

A diagram of the apparatus is shown in Figure 47. The metal sample, contained in a crucible, is heated in a high-vacuum glass cell, C, to the desired temperature by an induction heater. The solenoid valve, A, is then opened and closed rapidly to allow water vapor from the reservoir, D, to contact the sample in C. Following a preset delay, valve B is opened and closed rapidly to expand most of the water vapor and product hydrogen from the cell into the large evacuated bulb, E. Water vapor is condensed in the cold trap and the hydrogen transferred from bulb E to a manifold of calibrated volume by the Toepler pump. The quantity of hydrogen is then determined by a pressure measurement using a mercury manometer.

FIGURE 47
DIAGRAM OF COMPLETED PRESSURE-PULSE SYSTEM

b. Instrumentation

The operations of valves A and B are controlled automatically by an electronic timer. Condensers are discharged through the solenoids of the valves by the sequenced firing of thyratrons. The time interval between valve firings is variable in steps from 0.01 to 20 sec and can be extended indefinitely by manual operation.

A rapid-response pressure pick-up located in the reaction cell records the pressure pulse on an oscilloscope camera. The oscillogram is a record of both the contact time and the pressure.

Initial temperature measurements are made with an optical pyrometer. Temperature fluctuations during the course of a run are sensed by a photoelectric pyrometer and recorded on the oscilloscope camera simultaneously with the pressure pulse.

c. Preliminary Results

Initial tests of valve firing showed an effective open time of 0.010 sec for each valve. The pressure in the reaction cell under these conditions reached only about one-third of the reservoir pressure. A more serious result of the short open time was that only about one-third of the gas in the reaction cell was removed for analysis. Valve open time was

then increased by increasing the inductance and capacitance of the condenser discharge circuit. Open times of 0.03 and 0.07 sec for the inlet and outlet valves, respectively, were found to be satisfactory. Approximately 90 per cent of the water vapor-hydrogen mixture in the reaction cell is then removed for analysis. An oscillogram of the pressure inside the reaction cell is shown in Figure 48 for a firing interval of 0.05 sec. The upper trace shows the current pulses received by the valves.

FIGURE 48
OSCILLOGRAM SHOWING OPERATION OF
PRESSURE-PULSE APPARATUS

Two preliminary runs, one with aluminum at 1000 C in a zirconia crucible and one with zirconium at 1900 C in a thoria crucible, were successfully completed. Apparatus calibration and further refinement of the procedure are required to interpret the results quantitatively.

3. In-Pile Testing in TREAT

(R. C. Liimatainen, R. O. Ivins, W. A. Rodger, M. Deerwester, H. Bates,* E. Regnier*)

The program of conducting experiments in CP-5 (described in ANL-6029, page 132) preliminary to the TREAT tests was concluded. To achieve a greater temperature rise in the final experiment an enriched, insulated uranium pin was used. The conditions for the test were as follows:

*Cooperating summer employees from Kansas State University.

1. autoclave in reactor for 5 minutes at 2000 kw;
2. initial pin temperature of 25 C;
3. initial pressure of 20 psia of helium;
4. 93 per cent enriched uranium pin; and
5. thermal neutron dose inside of autoclave of 9.8×10^{12} nvt.

The temperature was measured by a chromel-alumel thermocouple attached to the center of the pin by "thermon" (graphite) cement. The resulting temperature-time data are shown in Figure 49. The final equilibrium temperature was 405 C.

The tests in CP-5 have served to verify the experimental techniques to be used in the forthcoming transient tests in TREAT. The rate of energy input to the specimen was obtained by dissolving the pin after the irradiation and analyzing for Ba^{140} fission product. By equating the rate of energy production to the rate of heat dissipation to the surroundings at the steady-state temperature of 405 C, an overall heat transfer coefficient of 11.4 Btu/(hr)(sq ft)(F) was obtained, based on the surface area of the pin. For comparison, by integrating the expression for the unsteady-state cooling of the pin following the reactor shutdown, an overall film coefficient of 7.5 Btu/(hr)(sq ft)(F) was computed. The next phase of the experimental program will be metal-water meltdown tests in TREAT. Four experiments were prepared for the first series.

A program* of calculations on metal-water reactions initiated by reactor transients was completed to the extent feasible until experimental data become available. The method used was to divide the pin into five elements of volume, thus obtaining temperature as a function of both time and position. The solutions of differential difference equations describing the model were solved on a PACE analog computer. The results are being summarized in a topical report; however, a brief discussion will be given herein. For each of the five zones the equations of energy balance were of the form

$$\frac{dT_i}{dt} = \bar{B} f(t) - \frac{\bar{M}r_{i-1} (T_i - T_{i-1})}{(r_i^2 - r_{i-1}^2)r} + \frac{\bar{N}r_i (T_{i+1} - T_i)}{(r_i^2 - r_{i-1}^2)r} - \frac{\bar{I}x}{(r_i^2 - r_{i-1}^2)} \frac{dx}{dt}$$

where

T = temperature
 t = time
 f(t) = time-dependent neutron flux
 r = radial position in pin
 sub i = ith element of volume
 $\bar{I}, \bar{N}, \bar{B}, \bar{M}$ = constants involving physical properties.

The chemical rate equation was

$$-\frac{dx}{dt} = \frac{F}{(x_0 - x) \exp(G/T)}$$

where

F, G = constants
 x = distance to metal-oxide interface.

Figures 50 and 51 show typical results obtained from the computer solutions. The temperature gradients within the pin are illustrated in Figure 50. The strong dependence of the center temperature on the magnitude of the chemical kinetic coefficient is shown in Figure 51.

*Cooperative with the Applied Mathematics Division.

FIGURE 50
TEMPERATURE - TIME REACTION FOR
CASE OF NO CHEMICAL REACTION

FIGURE 51
VARIATION OF CENTER-PIN TEMPERATURE WITH TIME
(CHEMICAL RATE CONSTANT F A PARAMETER)

IV. REACTOR CHEMISTRY

The Reactor Decontamination Program is a cooperative one with the Reactor Engineering Division. It results from concern over the consequences of a fuel rupture in a boiling water reactor system, and will endeavor to answer the questions: How serious is a fuel rupture? What are the magnitudes and distributions of fission products in the vapor phase of the system? What methods are available for removing such deposited activities?

A loop simulating the operation of a boiling water reactor has been installed in a shielded cell. The first run with activity (yttrium-90 tracer) has been completed, the pressure being 600 psi and the steam rate 0.36 ft/sec. Activity deposited on a stainless steel sample strip was monitored with a beta-gamma probe and by direct counting. The maximum disengaging factor* between liquid and vapor was 4.4×10^3 .

Laboratory studies on the cleanup of contaminated surfaces showed that somewhat lower decontamination factors were obtained when temperatures and concentrations of reagents used in the alkaline-permanganate procedure were reduced.

A. Reactor Decontamination

1. Loop Operations

(D. Grosvenor, C. Bally, W. B. Seefeldt)

A loop (see ANL-5858, page 66) which simulates the action of a boiling water reactor has been installed in a shielded cell and given preliminary checks for its operational characteristics. The unit is designed primarily to study the deposition characteristics of mixed fission products from the steam phase onto metallic sample strips. Of secondary interest is the procurement of de-entrainment or disengaging data between liquid and vapor phases. These data are obtained as a function of elevation in the disengaging section of the loop.

In the first run involving activity, 25 millicuries of yttrium-90 tracer, together with one gram of yttrium as carrier, were introduced into the loop. The purposes of the run were as follows: (1) to determine de-entrainment characteristics of the loop as measured by disengaging

*Disengaging factor is defined as the ratio of activity in the liquid phase to that in the steam phase. This factor is often called a decontamination factor in the literature but is not so called herein to avoid confusion with the "decontamination factors" reported which are the ratios of activities on solid surfaces before and after various chemical treatments.

decontamination factor, (2) to determine yttrium-90 plate-out characteristics on a stainless steel type 304 sample strip, and (3) to check for points of leakage by monitoring the escaped beta activity following the run. The yttrium-90 activity has two desirable characteristics relative to the above objectives: the beta activity reduces shielding problems, and its short half-life of 64 hours makes it attractive for leak testing.

The power input during the run was 24.7 kw. Of this amount, 12.4 kw were removed in the main condenser. This corresponds to a net steam velocity of 0.36 ft/sec, or a weight flow rate of 58 lb/hr. The loop was uninsulated and the operating pressure was 600 psi. The water level in the disengaging section was 10 inches above the riser exit.

The quantity of yttrium-90 inserted into the loop was predicated on obtaining a count level in the steam phase in excess of 100 cpm/g. The samples taken one hour after the start of operation met this requirement; those taken after 20 hours did not because of precipitation of yttrium in the liquid phase of the loop. The steam activities plus calculated disengaging factors for the one-hour samples are shown in Table 40 as a function of elevation in the disengaging section. The maximum disengaging factor obtained was 4.4×10^3 .

Table 40

DISENGAGING FACTOR BETWEEN
STEAM AND LIQUID PHASES
(One hr after introduction of activity)

Phase	Elevation ^a (inches)	Sample Activity ^b (cpm/g)	Disengaging Factor
Liquid	0	1.38×10^6	-
Vapor	$6\frac{1}{2}$	6.81×10^2	2.03×10^3
Vapor	$27\frac{1}{2}$	3.50×10^2	3.94×10^3
Vapor	$48\frac{1}{2}$	3.12×10^2	4.42×10^3

^a Relative to estimated liquid level

^b All values corrected to common time

At the conclusion of the run, the type 304 stainless steel sample strip was removed and checked for activity. The strip had been thoroughly pre-oxidized with 600 psi steam prior to exposure to activity. The strip was monitored in two ways: (1) an inch-by-inch survey with a portable beta-gamma monitor, and (2) direct assay for beta activity in a proportional counter. The results obtained are shown in Figures 52 and 53 respectively. Both methods appear to be useful. It is intended to use a single-channel analyzer in assaying the activities deposited from later runs involving mixed fission product activities.

FIGURE 52
RADIATION SURVEY OF SS304 SAMPLE
STRIP FROM DISENGAGING SECTION

PRESSURE 600 psi
STEAM VELOCITY 0.36 ft/sec min
ACTIVITY γ^{90} (Beta)
RUN LENGTH 21 hours
REFERENCE ELEVATION Bottom of Sample Holder

FIGURE 53
VARIATION OF BETA ACTIVITY OF SS304 SAMPLE STRIP WITH ELEVATION

PRESSURE 600 psi
STEAM VELOCITY 0.36 ft/sec min
ACTIVITY γ^{90} (Beta)
RUN LENGTH 21 hours
REFERENCE ELEVATION Bottom of Sample Holder

Additional runs using yttrium-90 and cesium-137 tracers will be made prior to the use of irradiated uranium and portions of irradiated EBWR fuel plates.

2. Laboratory Studies (S. Vogler, H. Tyler)

Laboratory studies are being made to evaluate decontamination methods that have potential usefulness in boiling water reactor systems. Present efforts are being made on stainless steel type 304 with liquid reagents. 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 contamination.

Treatment with a solution of potassium permanganate in sodium hydroxide followed by a solution of ammonium citrate was shown to be an effective decontamination procedure. Successful results were obtained at temperatures of 80 to 90 C for both solutions. Efforts during the last quarter directed at lowering the temperature of the permanganate solution were successful, and it was indicated that one-half per cent potassium permanganate in one per cent sodium hydroxide at room temperature was a satisfactory conditioning reagent for ammonium citrate applied at 85 C. Current effort is directed primarily at reducing the temperature of the ammonium citrate step. Lower temperatures and concentrations are desirable in a boiling water reactor system because of (1) the potential difficulty in heating the large volumes of solutions required, and (2) waste-handling difficulties associated with liquids having high solid contents.

a. Alkaline-Permanganate Decontamination

An additional comparison was made of the alkaline-permanganate solution at room temperature and at 85 C. The contaminated plates were different from those used previously in that the decay time was much shorter and larger amounts of iodine-131 were present. The uranium used as a source of contamination had been irradiated for one day and cooled for 20 days.

In the first test, the contaminated specimen was placed in a stirred solution of three per cent potassium permanganate in twenty per cent sodium hydroxide at 90 C for 30 minutes. In the second test, the contaminated specimen was placed in 0.5 per cent potassium permanganate in 1 per cent sodium hydroxide and the solution was stirred for four hours at room temperature. After a distilled water rinse, both specimens were treated separately with 10 per cent ammonium citrate for 15 minutes at 85 C. Beta activity was determined with a proportional counter and the gamma activity was determined with a single-channel scintillation counter using a four-inch sodium iodide crystal. The iodine counting rate was determined by summing the counting rates under the 0.34-Mev peak as indicated by the 256-channel gamma scintillation spectrometer. Results are shown in Table 41. In these samples the most pronounced peak was that of iodine-131 at 0.34 Mev. These results indicate that somewhat better decontamination was obtained for the potassium permanganate reagent at the elevated temperature.

Additional experiments were carried out in a manner similar to those reported just above to determine the effectiveness of ammonium citrate and citric acid at various temperatures. The results are indicated in Table 42. Gamma-decontamination factors of approximately 20 were obtained for a fifteen-minute exposure with either ammonium citrate or citric acid at room temperature. An additional exposure of one hour increased the decontamination by a factor of two; further exposure of 18 hours had only a slight effect.

Table 41

ALKALINE-PERMANGANATE DECONTAMINATION
OF TYPE-304 STAINLESS STEEL: EFFECT
OF STEP ONE PARAMETERS

Activity: $\sim 2 \times 10^5$ cpm (20 days cooled)
 Step One Reagent: As indicated
 Step Two Reagent: 10 per cent ammonium citrate
 15 minutes at 85 C

Activity	Decontamination Factor ^a	
	3% KMnO ₄	0.5% KMnO ₄
	20% NaOH	1.0% NaOH
	0.5 hr, 90 C	4 hr, 25 C
β	290	70
γ	230	120
I ₂	120	65

^a Ratio of counting rates before and after
decontamination

Table 42

ALKALINE-PERMANGANATE DECONTAMINATION
OF TYPE-304 STAINLESS STEEL: EFFECT
OF STEP TWO PARAMETERS

Activity: $\sim 2 \times 10^5$ cpm (approximately 7 weeks cooled)
 Step One Reagent: 0.5 per cent potassium permanganate plus
 1.0 per cent sodium hydroxide at room
 temperature for 4 and 24 hours with
 stirring
 Step Two Reagent: Ammonium citrate and citric acid;
 15 minutes at the indicated temperature

Step 2 Reagent	Decontamination Factor							
	Step 1 - 4 hr				Step 1 - 24 hr			
	Step 2 -		Step 2 -		Step 2 -		Step 2 -	
	85C		25C		85C		25C	
	β	γ	β	γ	β	γ	β	γ
10% ammonium citrate	65	38	21	18	143	97	25	32
1% ammonium citrate	9	7	13	19	-	-	-	-
10% citric acid	97	175	10	20	50	84	29	27
1% citric acid	64	38	68	55	-	-	-	-

As might be expected, the use of higher temperatures for the citric acid or ammonium citrate reagent results in a higher decontamination, although the decontamination obtained at room temperature appears to be useful.

Several experiments were performed in which one per cent Versene was added to the second step solution for the purpose of complexing fission product cations in the aqueous phase. These results indicate that little or no advantage is obtained by adding Versene to the second reagent.

The high-temperature permanganate, high-temperature ammonium citrate procedure yields the best results. With a change to the low-temperature permanganate there is a modest decrease in the decontamination obtained. With the change to room-temperature ammonium citrate a further decrease in decontamination is noted. Based on this information, the proper procedure to be selected may be determined by the decontamination required, and the physical facilities available at the reactor where decontamination is needed.

b. Corrosion of Stainless Steel

Previous experience with the alkaline permanganate and ammonium citrate reagents had indicated that the test specimens showed a weight loss of one to two mg per test specimen (one-inch square). This corresponds to a penetration of $4 \text{ to } 8 \times 10^{-3}$ mil per exposure. In the current tests the substitution of citric acid for the ammonium citrate did not affect the corrosion rates previously observed.

c. Rate of Activity Removal

In order to establish some correlation between laboratory beaker tests and projected loop-decontamination tests and to measure the rate of activity removal from contaminated specimens, a small glass loop has been set up. The design is such that the activity on a metal specimen may be monitored continuously by means of a two-inch sodium iodide (thallium-activated) crystal connected to a single-channel pulse analyzer. The glass tubing is $\frac{9}{16}$ inch in diameter and the liquid is circulated by means of a gas lift. In the first experiment 3 per cent potassium permanganate in 20 per cent sodium hydroxide at 90 C was circulated through the loop for 60 minutes. After a water rinse, 10 per cent ammonium citrate at 85 C was circulated through the loop for an hour and a half. The total gamma decontamination was 50.

During the circulation of the potassium permanganate solution, periodic measurements of the gamma activity indicated a very slight reduction in the activity on the metal sample. Upon the addition of the hot ammonium citrate solution there was a sudden sharp drop in the gamma activity by a factor of about five. Thus it is indicated that the bulk of the activity is removed when the ammonium citrate solution first comes in contact with the contaminated metal.

V. ROUTINE OPERATIONS

(H. G. Swope)

A. Waste Processing

(H. G. Swope, J. Harast, K. Bremer, G. Teats, A. Sanders, E. Schap, R. Juvinall, C. Ryberg, R. Williams, T. Baker)

Volumes of liquid radioactive wastes processed from July through September, 1959, were as follows:

Method of Processing	Volume (Gallons)
Evaporation and Concentration	14,510
Filtration	1,360
Cation Exchange	1,360
Neutralization	100
Absorption on Vermiculite	410
Total	17,740

B. High-level Gamma-irradiation Facility

(H. G. Swope, J. Harast, B. Kullen, R. Jarrett, N. Ondracek and T. Kinsella)

Data for samples irradiated in Rack M-1 during July, August, and September, 1959, are given in Table 43. In addition, Rack M-2 was used for one day unit and 27 night units.

Table 43

SUMMARY OF IRRADIATIONS PERFORMED IN RACK M-1 DURING JULY, AUGUST AND SEPTEMBER, 1959

Month	No. of Samples	No. of Special Dosimetry Samples	Total Urn Units ^a		Special Handling Man-hours
			Day	Night	
July	960	489	1696	1081	56.0
August	357	204	806	1145	26.0
Sept.	1059	215	1524	2847	49.5
Totals	2376	908	4026	5073	131.5

^a One urn unit = 2×10^6 rads

The M-1 rack was brought up for repairs on August 14 to replace a cadmium strip that had fallen off.