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SUMMARY

I. Chemical-Metallurgical Processing (pages 24 to 129)

A direct-cycle fuel reprocessing plant is being designed for pyrometallurgical processing of discharged power reactor fuel elements. Numerous chemical-metallurgical methods are being examined for use in this fuel reprocessing facility. These methods include melt-refining, liquid metal extraction, and fractional crystallation. The results of these studies are being applied to design and component testing of facilities for the EBR-II fuel reprocessing plant.

Construction of the Laboratory and Service Building is 52 per cent complete. Bids received from prospective suppliers for Model 8 manipulators are being evaluated. The design of the waste treatment evaporator was approved. Equipment drawings for items in the junior caves and solidification room are being checked.

The Fuel Cycle Facility drawings and specifications included in bid package No. 3 of the EBR-II project were issued to bidders about April 1, 1959.

The design of the 5-ton cranes for the air and argon cells is continuing. The prototype radiation-stable operating manipulator has been installed in the mock-up area and is being used for operation of prototype process equipment.

Irradiation tests on cerium-bearing glass samples for shielding windows revealed that the optimum cerium content is less than the nominal amount originally specified. Detail drawings of the shielding shutters for the windows have been completed.

A satisfactory lighting arrangement has been achieved for a prototype segment of the argon cell. The light output of gamma-irradiated mercury vapor lamps has been determined to be about 55 per cent of original after an exposure of 1.1×10^9 rads.

Analyses of the composition of 30 ten-kilogram ingots of natural uranium-5 per cent "fissium" alloy prepared in the melt-refining furnace indicate that not all of the added zirconium and molybdenum went into solution. Cerium removal from natural uranium-"fissium" alloys by oxidative dressing was demonstrated to be essentially complete (greater than 99 per cent) after four and one-half hours.

Some of the prototype melt-refining equipment has been received and assembly has started in the mock-up area. Experimentation to develop a satisfactory fume trap continued.

Tests in the melt-refining furnace to simulate the effect of heat generated by decay of fission products corresponding to one per cent fuel burn-up showed that an equilibrium temperature of 650 C was reached in four and one-half hours.

Irradiation tests have shown that natural rubber formulated with an antioxidant (Antiox 4010) is satisfactory for cable insulation at radiation levels to 2×10^8 rads.

Fabrication of the device for remote capping of sample containers was completed and it is now being tested.

Melt refining consists of melting discharged reactor fuel in a zirconia crucible and holding it molten for several hours. During this operation fission products are removed by volatilization and selective oxidation-reduction reactions. Four 2-kilogram scale runs were made to study the melt-refining characteristics of high plutonium (20 per cent)-uranium-"fissium" alloys. Preliminary results indicate insignificant plutonium enrichment in the slag relative to the concentration in the cast ingot. Cerium removal is comparable to that previously obtained with uranium "fissium". The runs were made without difficulty and with no spread of contamination.

Work was continued on study of behavior of specific fission products at full concentration levels. In agreement with earlier work, the quantitative removal of strontium and nearly complete removal of barium were demonstrated. About one per cent of each was volatilized. In a similar experiment volatilization of two per cent of the tellurium present occurred.

A further investigation was made of the possible zirconium contamination of molten uranium and its cerium alloy resulting from prolonged holding at 1400 C in stabilized zirconia crucibles. Zirconium pick-ups in five- and nine-hour tests were negligible, amounting to about 20 ± 10 ppm in each test. It seems fairly certain that the zirconia crucible will not constitute a source of zirconium contamination of a uranium melt.

The extent to which reactions may occur at high temperatures between zirconia and graphite is an important factor in design of melting assemblies for the melt-refining process. Experiments at 1700 C showed considerable evolution of carbon monoxide as a result of reaction of zirconia with graphite. Although conditions may be more extreme than in a plant furnace, the experiment indicates that care should be exercised in the choice of insulator and susceptor materials.

Reduction of oxide coatings on uranium fuel pins by magnesium in zinc solution continues to be promising. The reduction is effected by dipping the pins into a molten zinc-10 per cent magnesium alloy. Various conditions are being tried to effect both complete oxide reduction and good drainage of the molten alloy from the pins.

Studies were continued on the processing of melt-refining residues. Analyses revealed that considerable ruthenium and molybdenum were volatilized

in the course of skull pulverization by oxygen oxidation and hydrogen reduction cycles at 800 C. Kinetic studies are reported for various reactions in liquid zinc systems, major emphasis being given to uranium and cerium oxide reductions by magnesium in zinc. Several reductions of skull oxide in excess of 93 per cent have been made. One of the difficulties in achieving high recoveries of uranium by direct dissolution of skull metal and oxides in zinc-6 per cent magnesium has been indicated to be due to the formation of uranium nitrides resulting from nitrogen contamination from an as yet unidentified source.

Engineering techniques are being developed and evaluated for the various liquid metal processes under consideration. These, in general, employ various combinations of zinc, cadmium, magnesium, and perhaps other metals as solvents with various necessary separations being effected by methods such as distillation, fractional crystallization, and selective oxidation or reduction. Three successful magnesium distillations were made in a type of distillation unit being considered for remote operation. Other designs will also be tested. Preparatory to retorting intermetallic concentrates of uranium with cadmium or zinc, a fairly large-scale unit was test operated by distilling 11.6 kilograms of cadmium. Additional vapor-liquid equilibrium data were obtained for the zinc-magnesium system.

Three relatively large-scale (7- to 16-kilogram) runs were made in which supernatant zinc solution was removed from settled intermetallic crystals by pressure-siphoning through a fixed-position dip tube.

Further evidence of attack of tantalum by zinc at 800 C is reported. Metallurgical examination, microhardness determinations of various phases, and spectrographic analyses all confirm the zinc attack. The presence of magnesium inhibits the attack to a great extent.

In 100-hour tests at 550C, cadmium containing up to 10 per cent zinc did not corrode mild steel. Mild steel shows definite promise as a container material for cadmium systems of interest.

Additional basic data have been obtained to aid in the study of solutions of fuels in liquid metal solvents. The solubilities of lanthanum, palladium, zirconium, and molybdenum in liquid cadmium have been measured, and the results expressed in the equations:

$$\text{La, 400 to 600 C; } \log (w/o \text{ La}) = 7.368 - 5991/T$$

$$\text{Pd, 327 to 502 C; } \log (w/o \text{ Pd}) = 4.206 - 2869/T$$

$$\text{Zr, 327 to 461 C; } \log (w/o \text{ Zr}) = 2.870 - 2622/T$$

$$\text{Zr, 461 to 545 C; } \log (w/o \text{ Zr}) = 1.165 - 1371/T$$

$$\text{Mo, 603 C; } (w/o \text{ Mo}) = 0.00012$$

The palladium and zirconium solubilities were also examined for uranium-saturated cadmium solutions.

The solubility of uranium in various mixed solvent systems has been studied and information on the ternary phase diagrams is being gathered.

Cadmium-Zinc: The isothermal addition of zinc to uranium in cadmium solutions causes uranium to precipitate as U_2Zn_{17} . The solubility of uranium drops sharply after the addition of as little as one per cent zinc. The precipitation is at least 99.8 per cent complete after the addition of 13 per cent zinc.

Cadmium-Mercury: The addition of mercury to cadmium increases the solubility of uranium, as shown by these equations:

$$100 \text{ Cd:} \quad \log (w/o \text{ U}) = 6.148 - 4348/T$$

$$\sim 10 \text{ Hg} - 90 \text{ Cd:} \quad \log (w/o \text{ U}) = 6.387 - 4405/T$$

$$\sim 25 \text{ Hg} - 75 \text{ Cd:} \quad \log (w/o \text{ U}) = 6.715 - 4444/T$$

This effect is nearly counterbalanced by the depression of the freezing point of the solvent by mercury addition so that the maximum recovery of uranium from solution is only slightly increased by such additions.

Cadmium-Magnesium: The isothermal addition of magnesium to cadmium solutions of uranium has a complex effect. Below 475 C the solubility of UCd_{11} is increased by the initial increments. However, after the addition of 2 to 5 per cent magnesium the solid phase transforms to uranium and further magnesium additions decrease its solubility. Above 475 C, where uranium is always the saturating phase the initial increase disappears. When solid uranium is the saturating phase, the temperature coefficient of solubility is small and sometimes negative.

Zinc-Magnesium: The data for this system, previously reported in ANL-5959, have been extended by an additional isothermal solubility run. The data now show clearly that a cusped maximum solubility is attained near 33 atom per cent magnesium in the solvent, and a rounded minimum solubility occurs near 70 atom per cent magnesium. Between 34 and 52 atom per cent magnesium compositions 99.8 per cent of the uranium is precipitated as rather well developed crystals.

The Doerner-Hoskins coefficient for the coprecipitation of plutonium with uranium from cadmium solutions is 0.67. When magnesium is added so that uranium metal rather than UCd_{11} precipitates, no coprecipitation of plutonium takes place.

The activity of uranium in its saturated solutions in cadmium was measured by the emf developed versus a pure uranium electrode in a suitable electrochemical cell. As expected the corrected emf drops to zero above the temperature of the peritectic decomposition of UCd_{11} to uranium and solution. The activity and activity coefficient below this temperature are given by the equations:

$$\log a_U = 8.3893 - 6273.1/T$$

$$\text{and } \log \gamma_U = 5.1459 - 2363.7/T$$

The standard free energy of formation of UCd_{11} is small by comparison with U_2Zn_{17} ; it varies from -3.50 kcal/mole at 383 C to -0.16 kcal/mole at 475 C.

The preparation of a high-purity sample of each of two forms of molybdenum sulfide has been completed. The sulfur to molybdenum ratio for the naturally occurring hexagonal preparation is 1.997; for the synthetic rhombohedral preparation the ratio is 1.992. The techniques now being used for molybdenum sulfide combustions have been standardized.

Fluorine bomb calorimetric studies are now being carried out. Fluorine charging and discharging apparatus has been set up and a fluorine purification still has been built. A nickel bomb has been calibrated for use in the calorimetric studies.

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (Pages 130 to 198)

In connection with the reprocessing of reactor fuels by combined fluidization-volatility processes, the fluorination rates of uranium tetrafluoride by mixtures of fluorine and helium were investigated. At temperatures of 200, 300 and 375 C, maximum fluorination rates were observed at a

fluorine partial pressure of about 0.75 atm. This behavior had also been observed previously during the fluorination of plutonium tetrafluoride. Additional studies were performed on the fluorination rates of metallic titanium to determine whether or not a similar effect would be evident. In this case no maximum in the rate was found as the partial pressure of fluorine was increased. The temperature dependence of the fluorination rate of titanium corresponds to an activation energy of about 25.6 kcal/mole.

Additional studies were made of the effect of ADF process variables on the recovery of uranium from low-uranium-zirconium and Zircaloy-2 fuel alloys. This process utilizes fluid-bed drying to convert the aqueous feed solution to a dry, fluidizable powder followed by fluid-bed fluorination to volatilize and permit recovery of the uranium as the hexafluoride.

Current drying operations used synthetic feed solutions containing the equivalent of a two per cent uranium alloy. Dual nozzles were used at bed temperatures of 235 and 300 C. An auxiliary jet attrition nozzle directed into the bed has successfully retarded particle growth which had previously limited the extended operation with a particular bed. A continuous 28-hour run was made, and total combined operating time for this period was about 70 hours. The formation of nozzle agglomerates continues to give some difficulty.

Batch fluid-bed fluorinations of fluid-bed dried material were made in the 2 1/2-inch diameter unit at 500 C. The solid material representing the dried product from a two weight per cent uranium-zirconium alloy solution deposited on a zirconium oxide core. The solids contained an average of 45 per cent of core material. Velocities ranged from 0.19 ft/sec (static bed condition) to 0.95 ft/sec which is about four times the minimum fluidizing velocity for the material used. Results indicated uranium removal, during

the period where the removal rate was high, was not dependent upon fluidizing velocity but rather on the amount of fluorine passed through the bed. A high dependence of uranium removal on particle size for this type material was disclosed as a result of the analysis of separate sieved fractions. An eight-hour fluorination at 500 C showed 91 per cent uranium removal for the -100 to +200 mesh size as compared to only 72 per cent for the largest (+20) mesh size.

A fluorine recycle pump is being installed to permit the operation of the fluorinator at high fluorine concentrations without excessive fluorine consumption.

A laboratory corrosion program relative to the fluid-bed fluorination of uranium-zirconium-fluoride powders has been started. Fluorides of the elements found by spectrochemical analyses to be present in the fluid-bed dried zirconium fluoride powders were added to pure zirconium fluoride in the amount of five weight per cent. The mixtures were exposed to fluorine at temperatures near 600 C for 28 hours in the presence of the corrosion specimen, a three-eighth-inch, "A" nickel, annealed tube. Intergranular corrosion was found when lead and manganese fluorides were present. High dimensional change also occurred when lead fluoride was present.

Development work continued on a high-temperature fused-salt process for the recovery of enriched uranium from zirconium matrix fuel alloys. In this process the fuel alloy is dissolved by hydrofluorination in a fused sodium fluoride-zirconium fluoride melt at 600 C. The dissolved uranium is then volatilized by passing fluorine through the melt.

Installation of a pilot plant dissolver-hydrofluorinator constructed of graphite has been completed. Graphite is a promising material of construction for this process step. The unit has been leak tested and dissolution test runs are planned in the next quarter. Further development of salt freeze valves was carried out.

Fluorinator development continued along the lines of frozen-wall designs, in which solid salt protects the vessel wall from corrosion. Installation has started of a electrolytically coated pilot plant vessel.

Dropwise fluorination has been under study as an alternate means of contacting in the fluorination step. In this process molten salt containing uranium tetrafluoride is sprayed into fluorine and uranium removal is accomplished by the formation and volatilization of uranium hexafluoride. Results have been obtained on measurement of velocity of salt through a nozzle, the time for solidification of spray droplets, and the heat transfer coefficient for drop cooling. A series of fluorination runs is in progress.

The fused fluoride volatility process for the LMFR solution fuel was described in ANL-5820, page 35. Laboratory work was presented in ANL-5924, page 54 and ANL-5959, page 38, which demonstrated the extraction of uranium and fission products with a fused mixture of sodium fluoride and zirconium fluoride. Data are presented to show the rapid oxidation and removal of magnesium from bismuth by extraction into a fused mixture of sodium and zirconium fluoride, which was sparged with hydrogen fluoride.

The exchange of zirconium between irradiated zirconium dissolved in bismuth and molten fused fluoride salt, as well as the extent of the extraction of zirconium and niobium by the fused salt, is demonstrated.

Additional data are reported from the operation of the fluid-bed waste calciner, used to convert liquid wastes to granular solids. A run made at 400 C with an 8:1 dilution of ICPP waste gave an average ruthenium decontamination factor from feed through adsorber of 2.0×10^4 , an average non-volatile decontamination factor from feed through adsorber of 1.2×10^5 and an average decontamination factor for total activity from feed through condenser of 2×10^7 . Transfer of ruthenium from one part of the calciner system to another has been found to occur chiefly during inactive runs indicating there may be a constituent of active feed which inhibits this transfer. The use of the new filtering-blowback assembly for the waste calciner has resulted in a 20 per cent reduction in the total non-condensables leaving the system. Feasibility runs have started on fluid-bed calcining of synthetic Hanford "high-acid" and "low-acid" waste solutions. Volume reduction factors of 8 and 3.5 may be expected for the "high" and "low acid" feeds, respectively.

Feasibility studies have started on the direct continuous conversion of uranium hexafluoride to uranium dioxide by reaction with steam and hydrogen in a 1 1/2-inch diameter fluidized bed. The starting bed is uranium dioxide, which was prepared by fluid-bed pyrohydrolysis of uranium tetrafluoride at temperatures up to 650 C. Several tests with uranium hexafluoride feed with rates up to 5.7 g/min and reactant (steam and hydrogen) excesses of 300 per cent showed a dense uniform brown coating, indicative of uranium dioxide, is formed on the bed material. The tapped bulk density of material increased from 3.7 g/cc to 4.4 g/cc. A negligible quantity of fines was produced.

The planned series of experiments on the mixing of solids in straight and tapered-wall fluid-bed columns using a radioactive tracer technique has been completed. The preliminary results of mixing -20 to + 40 mesh copper

particles in the tapered bed show that mixing increases with gas velocity and decreases with bed height. A complete analysis of the data will be forthcoming in a topical report.

III. Reactor Safety (Pages 199 to 252)

A status report summarizing the previous research in this program up to and including 1958 titled, "Ignition Behavior and Kinetics of Oxidation of the Reactor Metals, Uranium, Zirconium, Plutonium, and Thorium and Binary Alloys of Each" is being issued as ANL-5974.

In the studies of the rate of propagation of burning along uranium foils, a large number of surface contaminants have been shown to have no effect or to slow the burning process in air. However, etching the uranium foil surface beforehand with concentrated nitric acid causes a significant increase of burning propagation rate. The burning propagation of zirconium and zirconium alloy foils is related in general to the ignition temperatures of the various samples. An interesting dependence of the propagation rate on both thickness and width has led to a requirement of very narrow specimens for studies in air. A correlation of propagation rate in oxygen with cross sectional area is being attempted. This relationship and a relationship established between the length of the burning zone in air and the propagation rate should lead to an understanding of the burning process by application of heat transfer principles.

Studies under the microscope in a heated cell have established that the use of induction heating influences the oxidation process of uranium. It has also been shown that the oxidation of a heated uranium sample is faster in cool oxygen than in the oxygen heated to the same temperature as the sample.

X-ray and electron diffraction studies are in progress to determine more clearly the validity of a theory which relates the breakaway phenomena during the isothermal oxidation of zirconium alloys with a transformation of the oxide film to the monoclinic form.

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 series of runs with zirconium was described in the previous quarterly report, ANL-5959, page 94. Additional zirconium runs have been made to test further the conclusions derived from the previous results. The existence of an apparent ignition temperature of 2600 C was verified. The accumulated data is under study preliminary to an analysis on an analog computer, the results of which should define the direction of further work on zirconium. A series of runs with uranium has been initiated.

A second laboratory-scale method involves the rapid contact of steam with a drop or pool of molten metal. The method, originally proposed in ANL-5896, page 109, has been modified and is now under intensive development. In this method a sample of molten metal in a vacuum environment receives a "pressure pulse" of water vapor. The rapid contact and withdrawal is accomplished by a system of electric valves.

The program to determine the reaction rates of molten fuel and cladding metals with water during nuclear transients using TREAT reactor is continuing. Progress has been made on construction, procurement, and testing of equipment. A mathematical model to predict and correlate the data on an analog computer has been set up.

IV. Reactor Chemistry (Pages 253 to 265)

The Reactor Decontamination program is a joint one with the Reactor Engineering Division. The incentive for the program results from the lack of knowledge about the consequences of a fuel rupture in a boiling water reactor and about the remedial measures necessary to place the reactor back on stream if these consequences are severe. The purpose of the program is two-fold:

- (1) to determine the types and quantity of fission product activities likely to be distributed on the internal surfaces of a boiling water reactor system,
- (2) to determine what methods of activity removal can be utilized.

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

In order to ascertain the contribution of deposited activities due to short-lived gaseous precursors, the Reactor Engineering Division conducted several fuel defect tests in the EBWR. Coupons inserted in the reactor system were evaluated by CEN personnel and reported in ANL-5959.

V. Analytical Development (Pages 266 to 268)

The analytical methods which will be used to ascertain the fate of 13 of the fission products when irradiated "fissium" is gross refined in the Chemical Engineering Division's Senior cave have been demonstrated to be satisfactory.

Mixtures of sodium carbonate and sodium hydroxide have been found to be particularly satisfactory fluxes for the fusion-dissolution of calcined aluminum oxide.

Radiochemical methods for cerium and for total rare earths in which the separations are effected by solvent extraction have been devised. No yield determinations are necessary; analysis times have been cut by a factor of three.

VI. Routine Operations (Pages 269 to 270)

The operation of the radioactive waste-processing facility and the gamma-irradiation facility continued without incident.

I. CHEMICAL-METALLURGICAL PROCESSING

A direct-cycle fuel reprocessing plant is being designed for pyrometallurgical processing of discharged power reactor fuel elements. Numerous chemical-metallurgical methods are being examined for use in this fuel reprocessing facility. These methods include melt-refining, liquid metal extraction, and fractional crystallation. The results of these studies are being applied to design and component testing of facilities for the EBR-II fuel reprocessing plant.

Construction of the Laboratory and Service Building is 52 per cent complete. Bids received from prospective suppliers for Model 8 manipulators are being evaluated. The design of the waste treatment evaporator was approved. Equipment drawings for items in the junior caves and solidification room are being checked.

The Fuel Cycle Facility drawings and specifications included in bid package No. 3 of the EBR-II project were issued to bidders about April 1, 1959.

The design of the 5-ton cranes for the air and argon cells is continuing. The prototype radiation-stable operating manipulator has been installed in the mock-up area and is being used for operation of prototype process equipment.

Irradiation tests on cerium-bearing glass samples for shielding windows revealed that the optimum cerium content is less than the nominal amount originally specified. Detail drawings of the shielding shutters for the windows have been completed.

A satisfactory lighting arrangement has been achieved for a prototype segment of the argon cell. The light output of gamma-irradiated mercury vapor lamps has been determined to be about 55 per cent of original after an exposure of 1.1×10^9 rads.

Analyses of the composition of 30 ten-kilogram ingots of natural uranium-5 per cent "fissium" alloy prepared in the melt-refining furnace indicate that not all of the added zirconium and molybdenum went into solution. Cerium removal from natural uranium-"fissium" alloys by oxidative drossing was demonstrated to be essentially complete (greater than 99 per cent) after four and one-half hours.

Some of the prototype melt-refining equipment has been received and assembly has started in the mock-up area. Experimentation to develop a satisfactory fume trap continued.

Tests in the melt-refining furnace to simulate the effect of heat generated by decay of fission products corresponding to one per cent fuel burn-up showed that an equilibrium temperature of 650 C was reached in four and one-half hours.

Irradiation tests have shown that natural rubber formulated with an antioxidant (Antiox 4010) is satisfactory for cable insulation at radiation levels to 2×10^8 rads.

Fabrication of the device for remote capping of sample containers was completed and it is now being tested.

Melt refining consists of melting discharged reactor fuel in a zirconia crucible and holding it molten for several hours. During this operation fission products are removed by volatilization and selective oxidation-reduction reactions. Four 2-kilogram scale runs were made to

study the melt refining characteristics of high plutonium (20 per cent)-uranium-fissium alloys. Preliminary results indicate insignificant plutonium enrichment in the slag relative to the concentration in the cast ingot. Cerium removal is comparable to that previously obtained with uranium "fissium". The runs were made without difficulty and with no spread of contamination.

Work was continued on study of behavior of specific fission products at full concentration levels. In agreement with earlier work, the quantitative removal of strontium and nearly complete removal of barium were demonstrated. About one per cent of each was volatilized. In a similar experiment volatilization of two per cent of the tellurium present occurred.

A further investigation was made of the possible zirconium contamination of molten uranium and its cerium alloy resulting from prolonged holding at 1400 C in stabilized zirconia crucibles. Zirconium pick-ups in five- and nine-hour tests were negligible, amounting to only 20 ± 10 ppm in each test. It seems fairly certain that the zirconia crucible will not constitute a source of zirconium contamination of a uranium melt.

The extent to which reactions may occur at high temperatures between zirconia and graphite is an important factor in design of melting assemblies for the melt-refining process. Experiments at 1700 C showed considerable evolution of carbon monoxide as a result of reaction of zirconia with graphite. Although conditions may be more extreme than in a plant furnace, the experiment indicates that care should be exercised in the choice of insulator and susceptor materials.

Reduction of oxide coatings on uranium fuel pins by magnesium in zinc solution continues to be promising. The reduction is effected by dipping the pins into a molten zinc-10 per cent magnesium alloy. Various

conditions are being tried to effect both complete oxide reduction and good drainage of the molten alloy from the pins.

Studies were continued on the processing of melt-refining residues. Analyses revealed that considerable ruthenium and molybdenum were volatilized in the course of skull pulverization by oxygen oxidation and hydrogen reduction cycles at 800 C. Kinetic studies are reported for various reactions in liquid zinc systems, major emphasis being given to uranium and cerium oxide reductions by magnesium in zinc. Several reductions of skull oxide in excess of 93 per cent have been made. One of the difficulties in achieving high recoveries of uranium by direct dissolution of skull metal and oxides in zinc-6 per cent magnesium has been indicated to be due to the formation of uranium nitrides resulting from nitrogen contamination from an as yet unidentified source.

Engineering techniques are being developed and evaluated for the various liquid metal processes under consideration. These, in general, employ various combinations of zinc, cadmium, magnesium, and perhaps other metals as solvents with various necessary separations being effected by methods such as distillation, fractional crystallization, and selective oxidation or reduction. Three successful magnesium distillations were made in a type of distillation unit being considered for remote operation. Other designs will also be tested. Preparatory to retorting intermetallic concentrates of uranium with cadmium or zinc, a fairly large-scale unit was test operated by distilling 11.5 kilograms of cadmium. Additional vapor-liquid equilibrium data were obtained for the zinc-magnesium system.

Three relatively large-scale (7 to 16-kilogram) runs were made in which supernatant zinc solution was removed from settled intermetallic crystals by pressure-siphoning through a fixed-position dip tube.

Further evidence of attack of tantalum by zinc at 800 C is reported. Metallurgical examination, microhardness determinations of various phases, and spectrographic analyses all confirm the zinc attack. The presence of magnesium inhibits the attack to a great extent.

In 100-hour tests at 550 C, cadmium containing up to 10 per cent zinc did not corrode mild steel. Mild steel shows definite promise as a container material for cadmium systems of interest.

Additional basic data have been obtained to aid in the study of solutions of fuels in liquid metal solvents. The solubilities of lanthanum, palladium, zirconium, and molybdenum in liquid cadmium have been measured, and the results expressed in the equations:

$$\text{La, 400 to 600 C; } \log (w/o \text{ La}) = 7.363 - 5991/T$$

$$\text{Pd, 327 to 502 C; } \log (w/o \text{ Pd}) = 4.206 - 2869/T$$

$$\text{Zr, 327 to 461 C; } \log (w/o \text{ Zr}) = 2.870 - 2622/T$$

$$\text{Zr, 461 to 545 C; } \log (w/o \text{ Zr}) = 1.165 - 1371/T$$

$$\text{Mo, 603 C; } (w/o \text{ Mo}) = 0.00012$$

The palladium and zirconium solubilities were also examined for uranium-saturated cadmium solutions.

The solubility of uranium in various mixed solvent systems has been studied and information on the ternary phase diagrams is being gathered.

Cadmium-Zinc: The isothermal addition of zinc to uranium in cadmium solutions causes uranium to precipitate as U_2Zn_{17} . The solubility of uranium

drops sharply after the addition of as little as one per cent zinc. The precipitation is at least 99.8 per cent complete after the addition of 13 per cent zinc.

Cadmium-Mercury: The addition of mercury to cadmium increases the solubility of uranium, as shown by these equations:

$$100 \text{ Cd:} \quad \log (w/o \text{ U}) = 6.148 - 4348/T$$

$$10 \text{ Hg} - 90 \text{ Cd:} \quad \log (w/o \text{ U}) = 6.387 - 4405/T$$

$$25 \text{ Hg} - 75 \text{ Cd:} \quad \log (w/o \text{ U}) = 6.715 - 4444/T$$

This effect is nearly counterbalanced by the depression of the freezing point of the solvent by mercury addition so that the maximum recovery of uranium from solution is only slightly increased by such additions.

Cadmium-Magnesium: The isothermal addition of magnesium to cadmium solutions of uranium has a complex effect. Below 475 C the solubility of UCd_{11} is increased by the initial increments. However, after the addition of 2 to 5 per cent magnesium the solid phase transforms to uranium and further magnesium additions decrease its solubility. Above 475 C, where uranium is always the saturating phase the initial increase disappears. When solid uranium is the saturating phase, the temperature coefficient of solubility is small and sometimes negative.

Zinc-Magnesium: The data for this system, previously reported in ANL-5959, have been extended by an additional isothermal solubility run. The data now show clearly that a cusped maximum solubility is attained near 33 atom per cent magnesium in the solvent, and a rounded minimum solubility occurs near 70 atom per cent magnesium. Between 34 and 52 atom per cent magnesium compositions 99.8 per cent of the uranium is precipitated as rather well developed crystals.

The Doerner-Hoskins coefficient for the coprecipitation of plutonium with uranium from cadmium solutions is 0.67. When magnesium is added so that uranium metal rather than UCd_{11} precipitates, no coprecipitation of plutonium takes place.

The activity of uranium in its saturated solutions in cadmium was measured by the emf developed versus a pure uranium electrode in a suitable electrochemical cell. As expected the corrected emf drops to zero above the temperature of the peritectic decomposition of UCd_{11} to uranium and solution. The activity and activity coefficient below this temperature are given by the equations:

$$\begin{aligned}\log a_U &= 8.3893 - 6273.1/T \\ \text{and } \log \gamma_U &= 5.1459 - 2363.7/T\end{aligned}$$

The standard free energy of formation of UCd_{11} is small by comparison with U_2Zn_{17} ; it varies from -3.50 kcal/mole at 383 C to -0.16 kcal/mole at 475 C.

The preparation of a high-purity sample of each of two forms of molybdenum sulfide has been completed. The sulfur to molybdenum ratio for the naturally occurring hexagonal preparation is 1.997; for the synthetic rhombohedral preparation the ratio is 1.992. The techniques now being used for molybdenum sulfide combustions have been standardized.

Fluorine bomb calorimetric studies are now being carried out. Fluorine charging and discharging apparatus has been set up and a fluorine purification still has been built. A nickel bomb has been calibrated for use in the calorimetric studies.

A. EBR-II Fuel Cycle

1. Design, Construction, and Equipment Development
of EBR-II Fuel Reprocessing Facility
(J. H. Schraidt)

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

- a. Status of Building Design and Construction
(J. O. Ludlow, E. J. Petkus)

- (1) Laboratory and Service Building

Building construction is reported by the contractor to be about half complete.

The bids for six pairs of Model 8 manipulators for the junior cave cells have been received and are being evaluated. A draft of the bid specifications for an optical "peephole" viewer was written.

The resubmitted design of the evaporator for processing liquid wastes containing low levels of radioactivity was approved.

Drawings of the 5-ton crane and the operating mechanisms for the shielding doors for the junior cave cells and the hot tank room were received for our approval.

The checking of all drawings of the Argonne-designed equipment for the junior caves and the solidification room (hot tank room), to be purchased and installed in bid package No. 4, is in process. A master list was prepared of all items to be included in this bid package. The equipment in this schedule will be fabricated either by Central Shops or by outside fabricators.

(2) Fuel Cycle Facility

Construction of the Fuel Cycle Facility will be included in bid package No. 3 of the EBR-II project. Installation of the processing equipment will be included in bid package No. 4. The drawings and specifications for bid package No. 3 have been prepared and sent to the Idaho Operations Office. Submission to prospective bidders was made around April 1 and formal bid opening is anticipated for the middle of May, 1959.

One hundred and forty-four drawings have been signed to complete the bid package for the Fuel Cycle Facility. Formal signing of the drawings was completed on March 10, 1959. Sixty main divisions of the specifications directly affecting the Fuel Cycle Facility were issued for bidding purposes on March 20, 1959. Checking of the drawings and specifications continues.

b. Fuel Cycle Facility Cranes and Manipulators
(J. Crane and D. C. Hampson)

The design drawings of the 5-ton cranes for the argon cell, revised by Pacific Coast Engineering Company to comply with our specifications, have been sent to us for our approval.

The radiation-stable operating manipulator was received from General Mills, Inc. and installed in the mock-up facility. This manipulator was fabricated as part of the development contract with General Mills, Inc., the basic conceptual design and specifications having been furnished by this Division. Bid specifications for the eight operating manipulators to be installed in the Fuel Cycle Facility have been drafted. The detailed shop drawings by General Mills are being brought up to date. Additional drawings

required for the bridges are being prepared at Argonne. Preliminary bid specifications for the control system for cranes and manipulators have been written, and the drawings to accompany the specifications are being prepared.

The newly installed prototype operating manipulator has been tested in the mock-up facility. All motions and limit switches have been checked. The manipulator is being used for operating the melt-refining equipment and other prototype equipment. The manipulator removal blister was successfully used to install the bridge drive motor and the carriage of the operating manipulator remotely.

The manipulator bridge travels on a pair of circular tracks and pivots around a central point, resulting in a polar-coordinate system of operation. Operators have experienced no difficulty in switching from the rectangular system previously used to the new system.

A new manipulator grip design promising a number of advantages over the existing General Mills, Inc grip has been developed. Drawings have been completed and parts ordered for a prototype unit to be assembled and tested.

c. Melt-Refining Furnace and Auxiliaries
(A. A. Chilenskas, L. F. Coleman, W. E. Miller,
M. A. Slawewski)

A new version (M-5) of the melt-refining furnace has been received and is being installed.

The panelboard for the remote operation of the melt-refining furnace has been completed except for the furnace power meters which will be added later. The design and construction of an enclosure to isolate the melt-refining furnace off-gas pumps from the sub-cell environment have been com-

pleted. A layout of the pressure control system for the melt-refining furnace has been prepared, equipment ordered, and installation of the system begun. The pressure control system and vacuum pump enclosure will be integrated with the Mark 5 furnace and furnace control panelboard for testing in the mock-up area.

The installation of the motor-generator set which supplies the power for the Mark 5 furnace has begun. Bus bar and MI cable are being used as power leads from the work station to the furnace. Approximately 10 feet of three-fourth-inch conductor MI cable will be used along with 10 to 15 feet of one-fourth-inch by four-inch bus bar from the work station to the furnace. This will duplicate the length of high-frequency conductor required in the Idaho plant.

Design and experimentation have continued on the development of a remotely chargeable trap for the collection of volatiles which will be evolved during the melt-refining operation. The M-2 fume trap, charged with "Molecular Sieves", was tested for collection efficiency using sodium to represent the volatile materials. A collection efficiency of about 70 per cent was obtained for both the heated-lip and unheated-lip condition. The results agree with previous experience for the unheated-lip collection but are considerably lower than the 93 per cent collection efficiency obtained in previous heated-lip experiments (see ANL-5924, page 172). These experiments demonstrated that sodium penetration of the zirconia crucible occurred, resulting in a sodium loss of 20 per cent or greater through the annulus between the crucible and the susceptor. Another fume trap (M-3) is currently being designed to improve the overall collection by supporting the fume trap on top of the susceptor. This will serve to collect the fraction which may permeate the melt-refining crucible as well as the fraction from the melt furnace itself.

d. Fission Product Heating Effect
(A. A. Chilenskas, M. A. Slawewski)

Several experiments were performed to determine the influence of fission product decay heating upon the melt-refining operation. An experiment was performed with a simulated 10-kilogram fuel charge. The simulated charge consisted of one-eighth-inch diameter steel pins (equivalent in heat capacity to 10 kilograms of fuel) and an 0.8-kilowatt resistance cartridge heater (equivalent to the heat generation expected after about one per cent burn-up of fuel). This charge was loaded into the melt-refining crucible in the furnace, covered with the fume trap, and permitted to come to equilibrium temperature. The results for this particular configuration showed that in three hours the charge reached 600 C and that in four and one-half hours it reached a steady-state temperature of 650 C. This type of experiment will be repeated with a simulated two per cent burn-up charge using the M-3 fume trap as the insulating top of the melt crucible.

The effect of fission product heating on the bed temperatures of a fume trap loaded with "Molecular Sieves" was experimentally determined. An average steady-state bed temperature of 238 C was obtained from 135 watts heat input to a resistance heater buried in the "Molecular Sieves". This represents several times the anticipated heat load from the condensed volatiles of a 10-kilogram charge of two per cent burn-up. This suggests that no special precautions due to bed temperature rise are necessary for the handling of the condensed fission products in the argon cell.

e. Irradiation Testing of Materials and Lighting
(L. F. Coleman, T. W. Eckels, P. Kelsheimer
G. J. Barnstein, M. A. Slawewski)

Radiation tests have been completed on elastomer samples submitted by several cable manufacturers. These indicate that the silicones

are very poor in radiation resistance while natural rubber compound containing to the extent of 5 parts Antiox 4010 per 100 parts of rubber is about as good as any of the synthetic compounds. Such material shows reasonable strength and flexibility after exposure to 2×10^8 r, which should be equivalent to better than 2×10^4 hours of useful life under the anticipated service conditions for manipulator cables in the argon cell. A request has been initiated to purchase a minimum quantity (250 feet) of a 54-conductor cable using a 60 per cent natural rubber with 5 pph Antiox 4010 for conductor insulation and outer sheath.

A study has been made to select end seals for MI cable which are suitable for operation in the high radiation fields in the air and argon cells. A standard end seal suffered insulation breakdown when irradiated to a gamma dose of 9×10^8 r. Ceramic end seals are considered a solution of the problem and some are being obtained for test purposes. The standard seal is suitable in the absence of radiation. Specifications are being written for testing procedures to be used on MI cable installations.

Nine prototype 1000-watt mercury lamps are now installed in the mock-up area. Light measurements have been made over the area of one complete $22\frac{1}{2}^\circ$ segment of the argon cell working area.

Illumination varies from about 400 foot-candles at 2 feet from the walls to 200 foot-candles at 6 feet from the central control room face and $6\frac{1}{2}$ feet from the annulus wall. Minimum illumination of about 100 foot-candles is found at about $7\frac{1}{2}$ feet radially from the central control room face.

To operating personnel looking through a window of approximately 10 per cent light transmittance, this means an effective illumination of from 40 foot-candles near the window to 10 foot-candles in the center of

the cell. Operating personnel have expressed satisfaction with this level of lighting for all normal operations. With only one lamp burning, various manipulator procedures around the furnace have been performed but with some eyestrain.

Three 400-watt clear glass mercury vapor lamps (General Electric Co., type H400A-1) have been tested in the Argonne Gamma Irradiation Facility. The lamps have been irradiated while burning to determine the amount of browning to be expected of a mercury vapor lamp in service in a high gamma field. The results show that light output after an integrated dose of 2.5×10^8 rads is 63 per cent of the original, and 55 per cent after 1.1×10^9 rads.

f. Ingot Preparation and Oxidative Slagging Tests
(D. Hampson, V. Thelen, R. Paul)

As previously reported (ANL-5959, page 165), the unenriched fuel pins for the test subassemblies of the EBR-II will be fabricated from the thirty 10-kilogram ingots of natural uranium-5 per cent "fissium" produced in the melt-refining furnace during the previous quarter. The analytical results from this series of thirty runs are complete. Three methods of analyses were used to determine the composition of the individual ingots, namely, wet chemical, X-ray spectrographic, and emission spectrographic. The results from these three analytical procedures are summarized in Table 1.

The results indicate that about four per cent of the molybdenum and about 15 per cent of the zirconium did not go into solution with the uranium matrix. Correction factors will be used in future alloy preparations to compensate for this.

Table 1

COMPARISON OF RESULTS FROM ANALYTICAL METHODS USED TO DETERMINE
THE COMPOSITION OF UNENRICHED "FISSION" INGOTS

<u>Element</u>	<u>Nominal Composition (w/o)</u>	<u>Per Cent of Nominal Composition</u>		
		<u>Wet Chemical</u>	<u>Emission Spec</u>	<u>X-Ray Spec</u>
Molybdenum	2.46	96.1 ± 2.5	95.9 ± 4.2	97.2 ± 2.4
Ruthenium	1.96	99.0 ± 2.5	103.7 ± 1.9	98.1 ± 1.8
Rhodium	0.28	--	97.0 ± 3.9	--
Palladium	0.19	89.0 ± 3.2	97.4 ± 3.8	--
Zirconium	0.10	86.2 ± 11.9	--	83.7 ± 9.5
Niobium	0.01	--	--	--

A series of six 10-kilogram runs was made in which cerium (~0.4 weight per cent) was removed from the "equilibrium fissium" ingots by the oxidative slagging process. These runs were conducted in the pressed zirconia crucibles at 1400 C. After one and one-half hours, 85 per cent of the cerium was removed; 95 per cent after three and one-half hours and greater than 99 per cent after four and one-half hours. These runs confirm the results obtained by the process development group (ANL-5858, page 89, Figure 19).

3. Sample Container Remote Capper (P. Fineman)

A machine for the remote capping of sample containers in the argon cell was fabricated for testing in the mock-up facility. These containers are of aluminum, and are two inches in length by 0.702-inch in ID by 0.020-inch wall. They are commercially available and are made with existing dies. For a closure, one-inch diameter inner seals, usually used with screwneck containers (e.g., varnish, turpentine cans), are being tested.

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

The melt-refining process is being developed for purification of discharged EBR-II fuel. It will be incorporated into a plant adjacent the reactor to permit the direct and undelayed recycle of fuel to the reactor. The process consists simply of melting the 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 primarily by:

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

The noble metals are not removed except in a small side stream of material (called "drag-out"). This side stream, consisting largely of the crucible skull remaining after pouring the purified material, must be processed for removal of the noble metals and also for recovery of the fissionable materials. The noble metals will build up to equilibrium concentrations which are dependent on the percentage of "drag-out" material. The resulting alloys are called "fissium" alloys.*

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

Uranium-plutonium "fissium" is an alloy of uranium containing 20 per cent plutonium and 10 per cent inactive constituents representative of fission product elements anticipated in discharged EBR-II reactor fuel. Experiments are in progress to investigate the melt-refining behavior of this alloy under conditions developed for uranium "fissium".

Four runs have been completed in which two-kilogram charges of uranium-plutonium "fissium" were liquated in lime-stabilized zirconia crucibles for periods of three to five hours at temperatures of 1300 C and 1400 C. The information sought in these experiments includes:

- (1) The degree, if any, of plutonium enrichment in the dross relative to the cast ingot of purified metal. Such enrichment would be indicative of preferential oxidation of plutonium as compared to uranium.

* The alloy composition chosen for the initial EBR-II loading is:

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

- (2) Rare earth removal. Cerium was included in the charge as representative of all rare earths present in discharged fuel. With uranium "fissium", cerium removal has been nearly quantitative after three hours at 1400 C or five hours at 1300 C. Experiments with uranium-plutonium "fissium" will show the effect, if any, of plutonium on cerium removal.
- (3) The effect of a graphite coating on plutonium losses to the dross. Appreciable removal of zirconium as the carbide from uranium "fissium" has been demonstrated by liquation in graphite-coated crucibles (ANL-5924 page 150). These experiments will show whether prohibitively large amounts of plutonium carbide will be formed. They will also show the effectiveness of carbide scavenging of zirconium from uranium-plutonium "fissium" melts.

Complete analytical data are not yet available. However, data from one run show cerium removal to be comparable to that obtained with uranium "fissium" being 90 per cent after three hours liquation at 1300 C. In the EBR-II mock-up facility six 10-kilogram runs at 1400 C have shown 95 per cent removal of cerium after three and one-half hours (see section IA, page 33). In the same run plutonium enrichment in the slag relative to the cast ingot was not significant being within the limits of the analytical accuracy of three per cent.

The appearance of crucibles and dross was not indicative of excessive losses. In the one run in which the melt was held in a graphite-coated crucible there was evidence of the formation of a somewhat heavier slag layer on the surface of the melt. However, the ingot yield was not significantly lower than that realized in uncoated crucibles.

b. Behavior of Fission Elements in Melt Refining
(W. R. Chelley, J. Schilb)

(1) Behavior of Barium and Strontium

Work was continued on determining the behavior of barium and strontium in the melt-refining process. Previously reported experiments (ANL-5959, pages 141 to 144) have indicated that about one per cent of the barium and strontium present in "fissium" alloy at EER-II levels was volatilized during a melt-refining operation conducted at 1400 C for three hours. In these experiments iodine was added as UI_3 to make possible the volatilization of barium as the iodide, since previous work showed considerable volatilization of other Group II metal solids (magnesium and calcium iodides, ANL-5959, pages 139 to 141).

Additional analytical data for the same experiments are given in Table 2, illustrating the removal of the barium and strontium from the ingot. Although the relative accuracy of presently available spectrochemical analyses for these elements is poor, the results suggest that the behavior of barium and strontium will be similar. The mechanism of removal for the elements from the ingot is believed to be preferential oxidation and incorporation into the reaction layer and/or crucible. The quantitative removal of strontium from the ingot is in accord with information obtained from a refining experiment (ANL-5560, pages 74 to 79) employing 15 per cent enriched uranium in which 0.4 per cent of the total atoms were burned.

Table 2

DISTRIBUTION OF BARIUM AND STRONTIUM BY MELT REFINING AT 1400 C

Charge^a: Run I-77# - "Fissium", 207.4 g; Barium, 0.2219 g; U₃, 0.0398 g
 Run I-80E - "Fissium", 282.6 g; Strontium, 0.2735 g; U₃, 0.0675 g
 Atmosphere: Helium
 Total Melt Time: 180 minutes
 Crucible: Lime-stabilized zirconia

<u>Fraction</u>	<u>Barium^b</u>		<u>Strontium^b</u>	
	<u>Weight (mg)</u>	<u>Per Cent of Element</u>	<u>Weight (mg)</u>	<u>Per Cent of Element</u>
Charge	221.9	100	273.5	100
Volatilized	2.7	1.2	3.1	1.1
Ingot	12	(5) ^d	0.2	0.1
Crucible Reaction Layer ^c	250	113	250	91

^aFinal weight per cent composition of charges were: Mo, 2.5; Ru, 2.0; Ce, 0.6; Zr, 0.4; Rh, 0.3; Pd, 0.2; Nb, 0.01; I, 0.013; Ba, Sr (see table); U, remainder

^bAnalytical techniques: flame-spectrophotometric for volatilized material (relative accuracy, $\pm 10\%$); spectrochemical for other fractions (relative accuracy, factor of two).

^cCrucible-metal reaction products (weighing about three per cent of charged material) physically separated from liquated ingot and combined with crucible prior to dissolution for analysis.

^dValue suspect because of possibility of sample contamination.

(2) Behavior of Tellurium

Approximately 240 ppm of tellurium will be generated when two per cent of the total atoms in EBR-II fuel, initially containing 50 per cent uranium-235, is burned. An earlier melt-refining experiment in which unenriched uranium irradiated to about one-fourth of this burn-up was heated at 1200 C (see ANL-5560, pages 74 to 79) indicated that losses by volatilization were small since all of the original tellurium was accounted for in ingot and dross fractions. A recently completed experiment was aimed at obtaining information on the volatilization of this element under refining conditions more closely approximating those envisioned for processing of spent EBR-II fuel.

Tellurium crystals, cerium metal, and uranium triiodide were placed in separate holes drilled in a "fissium" metal block to form charge material of the following composition (weight per cent): molybdenum, 2.5; ruthenium, 2.0; rhodium, 0.3; palladium, 0.2; zirconium, 0.1; niobium, 0.01; cerium, 0.6; iodine, 0.014; tellurium, 0.099; uranium, remainder. The 287-gram charge, contained in a stabilized zirconia crucible, was positioned at the bottom of a tantalum tube which was designed to collect total material that would condense above a temperature of 250 C. Melting was carried out at a temperature of 1400 C for three hours under an atmosphere of helium. After the assembly had cooled the condenser was treated with aqua regia to recover volatilized material.

Analysis for tellurium by colorimetric methods showed that 1.9 ± 0.1 per cent of the originally charged element had been volatilized. Evaporation of this small amount as an intermetallic compound was ruled out because an additional analysis (spectrochemical) revealed that only trace amounts of other "fissium" constituents were present in the condensate.

c. Zirconium Contamination of Uranium or Its Cerium Alloy
Resulting from Melting in Zirconia Crucibles
(N. R. Chelley, J. Schilb)

Studies of the zirconium contamination of molten uranium or its cerium alloy by melting in pressed lime-stabilized zirconia crucibles have been made. Earlier experiments had shown that an upper limit of 5 ppm of zirconium was introduced into uranium melted for as long as four hours in stabilized zirconia at temperatures between 1200 and 1325 C (ANL-5765, page 20); however, analytical inaccuracies at these low concentrations limited the value of these results for extrapolation to the higher temperatures (~ 1400 C) presently envisioned for melt refining of EBR-II spent fuel. Additional information on ingot contamination by crucible-metal interaction was therefore required, particularly for prolonged melt periods at 1400 C. Four experiments have been conducted in which charges were heated in previously outgassed crucibles for a maximum period of 13 hours at 1400 C.

Results for these experiments given in Table 3 indicate insignificant zirconium contamination (maximum of 13 ppm) for holding times of 13 hours. Evidently side reactions with cerium or minor amounts of carbon in charge material played a minor role in the experiments. The information indicates that the zirconia crucible will not constitute a source of zirconium contamination during the refining operation. Average rate of crucible-metal reaction product (predominantly uranium dioxide plus some adherent metal) formation during these tests was about 45 milligrams/(sq cm)(hr).

d. Interaction Between Graphite and Zirconia "H"
(N. R. Chelley, J. Schilb)

The extent to which reactions may occur at high temperatures between zirconia and graphite is an important factor in design of melting

Table 3

ZIRCONIUM PICK-UP IN MOLTEN URANIUM ALLOYS HELDAT 1400 C IN ZIRCONIA CRUCIBLES

Crucible: Pressed, lime-stabilized zirconia; Porosity, - 20 per cent;
 Area contacted by melt, 24 sq cm
 Conditions: Temperature, 1400 C; Atmosphere, helium; Average charge weight, 290 g

Element	Initial Concentrations (ppm) ^a	Concentrations (ppm) ^a after holding at 1400 C for:		
		5 hr	9 hr	13 hr
<u>Cerium-Uranium Alloy:</u>				
Zirconium	13	20	20	26
Carbon	27	31	29	21
Cerium	12,000	10	83	--
<u>Unalloyed Uranium:</u>				
Zirconium	10 ^b	--	15	
Carbon	20 ^b	--	20	

^a Estimated accuracy unless otherwise indicated (relative per cent): zirconium, ± 50 ; carbon, ± 20 ;
 cerium, ± 5 .

Results reported for alloy ingots are averages of concentration obtained in top and bottom samples.

^b Values obtained from typical sections of unalloyed uranium.

assemblies for the refining process. Lime-stabilized zirconia "H" powder (reported composition, weight per cent: calcium oxide, 5.0; silicon dioxide, 0.7; aluminum oxide, 0.5; tellurium oxide, 0.3; ferrous oxide, 0.2; hafnium oxide, 2.0; zirconium oxide, balance) is presently used as insulation in contact with a graphite susceptor. The literature reveals that a basic method for deriving carbides of several group IV and V elements is reduction of the oxides by carbon according to the general reaction:

Such reactions are usually complicated by formation of intermediate oxide phases.¹ A thermodynamic treatment of the effect of partial pressure of carbon monoxide over uranium melts² points out that a small change in pressure will result in a large change of the carbon-oxygen level in uranium solution. The exact temperature at which reaction rates become significant under melt-refining conditions is not known. Two experiments were therefore carried out in which zirconia "H" (lime-stabilized cubic crystal structure) and graphite were heated at temperatures between 1500 and 1700 C. Both reactants were separately outgassed to pressures <1 mm prior to use.

In an initial exploratory experiment 95.2 grams of the zirconia powder (-36 mesh) was charged to a graphite crucible so that 54 sq cm of crucible wall was covered by the powder. The crucible and contents were heated under less than 7 mm of helium at equilibrium temperatures of 1500 C for 2 hours and 1600 C for an additional 2.5 hours. Inspection of the assembly showed that the zirconia had darkened. No evidence of crucible undercutting or formation of an interfacial reaction layer was

¹Samsonov, G. V., "Intermediate Stages of the Reactions in Formation of Carbides of Ti, Zr, V, Nb and Ta," AEC-tr-3387, (1956).

²Roland, E. H., "Calculated Equilibrium Constants for Metal-Oxygen Reactions in Molten Uranium Alloys," Westinghouse Corporation, WAPD-TM-99, (1957).

found. However, about three grams of the initially charged materials were sublimed on a tantalum boat shield positioned at the top of the heating assembly. Analysis by X-ray diffraction indicated that the condensate contained no zirconium oxide of the form (cubic polymorph) initially charged to and retained by the crucible after heating. Spectrochemical analysis showed the constituent present in largest concentration to be aluminum. Caseous products of aluminum oxide (aluminum oxide was present at 0.5 weight per cent in the initially charged zirconia) were evidently formed during the experiment.

The high-temperature gettering properties of tantalum used in the heating assembly eliminated the possibility of obtaining good information on the extent of reaction by analyses of product gases evolved to the furnace during the first experiment. A second experiment was therefore designed primarily to follow the gas phase during the reaction. A graphite crucible-susceptor was centered in a zirconia crucible and zirconia "E" powder was added to the assembly so that the outer, bottom, and inner walls of the susceptor were contacted. The total area of graphite covered was 189 sq cm. After an initial outgassing period (maximum reactant temperature, 1300 C) purified helium was added to the furnace to a pressure of 11 mm and the graphite was heated at a new temperature of 1710 C for 55 minutes. Pressure measurements taken during the experiment indicated that 2620 cc of gas were evolved to the furnace chamber. Prior to cooling, samples of the furnace atmosphere were taken in previously evacuated bulbs for analysis of helium, carbon monoxide, nitrogen, carbon dioxide and hydrogen. A record of the results of this experiment and one in which graphite alone was heated in the same furnace is presented in Table 4.

Table 4

ANALYSES OF GAS FRACTIONS FROM GRAPHITE-ZIRCONIA INTERACTION STUDIES

Conditions: Run I-91E - Outgassed graphite susceptor heated at 1500 C for 30 min
 Run I-98E - Outgassed graphite susceptor heated in contact with zirconia powder^a (-36 mesh) at 1710 C for 55 min; total area of susceptor exposed to powder, 189 sq cm

Furnace

Atmosphere: Initial, purified helium; pressure variation, 5 to 31 mm

Experiment	Gas Volume (cc at STP)		Atmosphere Composition ^b at Completion of Experiment (volume per cent)					
	Initial	Final	He	CO	N ₂	CO ₂	O ₂	N ₂
I-91E (Blank) ^c	920	920	99.7	0.1 ^e		0.01	0.01	0.2
I-98E	2020	4640 ^d	42.5	55.3	0.7	0.2	0.1	1.2

^aReported composition of zirconia "H" powder: calcium oxide, 5.0; silicon oxide, 0.7; aluminum oxide, 0.5; tellurium oxide, 0.3; ferrous oxide, 0.2; hafnium oxide, 2.0; zirconium oxide, balance.

^bAnalyses by mass spectrometer.

^cGraphite alone, no zirconia powder.

^dIncrease in volume calculated from carbon monoxide analysis is 2570 cc giving a final volume of 4590 cc.

^eCO + N₂ combined.

The analyses reveal that the gaseous product, carbon monoxide, is evolved when zirconia powder (36 mesh or finer) is heated in contact with dense graphite at 1710 C. The quantity of evolved gas determined by pressure measurement and that calculated from analysis of carbon monoxide present in the furnace atmosphere were in good agreement. A negligible amount of carbon monoxide was produced when graphite alone was heated to 150 C in helium.

A record of the continuous evolution of carbon monoxide during the experiment at a steady temperature of 1710 C is shown in Figure 1. The total volume of gas evolved per square centimeter of graphite exposed to zirconia powder is plotted against reaction time. This record shows that the gaseous reaction product was formed at a rate decreasing with time. A probable explanation for this could be a reduction of total reactant contact area during the experiment due to progressive sintering of the zirconia powder during the experiment.

These experiments indicate that care should be exercised in the choice of insulating and susceptor materials. Further tests should be made to ascertain if these reactions are extensive under conditions in the plant melt-refining furnace. The presence of very much carbon monoxide could cause difficulties.

e. Melting of Sodium-Coated Pins
(G. A. Bennett, L. F. Dorsey)

Present investigations continue the development of chemical methods for the reduction of oxide films on Experimental Breeder Reactor-II fuel pins. The oxide films, which serve in the reactor as a diffusion barrier between the fuel pins and the stainless steel cladding,

FIGURE I
EVOLUTION OF CARBON MONOXIDE IN GRAPHITE-ZIRCONIA
REACTION AT 1710 C - RUN I- 98E
Conditions: See Table 3

probably result from the presence of oxygen in the sodium. The oxide films can create some problems in melting operation such as possible incomplete coalescence of the uranium and the presence of a number of pin shells on the melt surface which may hinder pouring of the melt. Therefore, the development of a standby process for reduction of the oxide films is of importance.

Reduction of Oxide Films by Magnesium in Zinc Solution

Previous work (ANL-5959) has indicated this problem can be overcome at least partially by reducing any oxide film present prior to melt refining by contacting with a dilute magnesium (10 weight per cent)-zinc solution at around 600 C. Problems still present were the inability to achieve complete wetting, excessive adherence or entrapment of the magnesium-zinc alloy in the array of pins after dipping, and the secondary coating of the wetted pins with surface scum material as they are raised from the molten alloy. Therefore, work this past quarter has been devoted to achieving more complete reduction of oxide films and better separation of the zinc alloy from the pins.

All experimental dipping runs made during the last quarter were carried out at 625 C in the ten weight per cent magnesium-zinc solution. Contacting time was varied from 30 seconds to 30 minutes. Comparisons were obtained between vertical stacking of the pins in the dipping basket and random arrangement. Fluxes were used in a few runs in an attempt to improve removal of the coating alloy. A pin dipping apparatus was also developed which enables both drainage of the molten alloy from the pin after dipping, and removal of the pins from the alloy without contacting either flux or surface scum. The most satisfactory result, as judged by the completeness

and uniformity of the alloy coating, was obtained without flux using the pin dipping apparatus in a run in which the pins were dipped for 30 minutes in the ten per cent magnesium alloy at 625 C. The weight of coating material on the pin was around five per cent of the pin weight. The maximum uranium loss to the alloy solution under these conditions was 0.06 weight per cent.

In order to test further the efficiency of reduction by this method, coated pins from three different dipping experiments were melt refined at 1400 C for one hour in a zirconia crucible. In all cases, well-coalesced buttons were formed; in only one case was there a trace of pin shells. This was a stringent test of the method since charge weights (pins plus alloy) were only 79.4, 36.2 and 46.7 grams.

Reduction of Oxide Films by Calcium in Zinc Solution

The removal of oxide films was also attempted by dipping the pins in a 17.5 weight per cent calcium-zinc eutectic alloy (without the newly developed pin dipping apparatus). Dipping time was about 45 minutes at 685 C (mp 633 C). The pins appeared similar to those obtained with the magnesium-zinc alloy, being partially and unevenly coated with alloy. Handling this alloy is more difficult than the magnesium-zinc alloy due to its more reactive nature.

One-Step Reduction

Because the dipping technique would involve additional processing steps, attempts were made to reduce the oxide film by addition of either the magnesium-zinc or the calcium-zinc alloy during the melt-refining operation. In these runs, the pins were first liquated at 1200 C for 30 minutes, and the temperature was then reduced to either 1050 C or

1150 C at which time the alloy was added. Liquation was continued until metal vapors were no longer visible, a period of approximately an additional half hour. In all cases, melting was incomplete and slag was excessive.

Reduction by Calcium Addition

In the last quarterly (ANL-5959) it was reported that, although calcium is an effective reducing agent for uranium oxide, no satisfactory container crucible which would hold both uranium and calcium simultaneously had yet been found. During this past period, a 2 3/4-inch ID by 6-inch high calcia crucible was tested. Although it appeared to contain calcium satisfactorily, it failed by thermal shock.

It is planned to continue the development of oxide reduction techniques and to apply the reduction method to sodium-coated pins on the two-kilogram scale.

3. EBR-II Analytical Development (J. J. McCown)

Analytical Flowsheet for EBR-II Reprocessing Cell

The EBR-II Analytical Flowsheet discussed in ANL-5820, page 45, has been revised. This revised version is shown in Figure 2. The slag recovery process and the blanket rod process are as yet undefined, and only tentative designation of these sample points on the flowsheet is given. Additional sampling points will undoubtedly be added as these process steps become more difficult.

Table 5 gives a tentative breakdown of the man-hours per determination and the determinations per week expected during normal processing operations. These estimates are for samples from the process cell only. Samples from the tentative or undefined portions of the flowsheet are not included. It is expected that the frequency of sampling at start-up will

FIGURE 2
PROPOSED ANALYTICAL FLOWSHEET FOR EBR-II REPROCESSING CELL

Table 5

ESTIMATED MAN HOURS PER DETERMINATION AND DETERMINATIONS PER WEEK
FOR EBR-II MELT REFINING SAMPLES

The estimates are for samples from the process cell only. They do not include samples from tentative or undefined steps in the process such as the slag recovery step. The frequency of sampling at start-up is expected to be higher than ordinary which will increase the numbers shown in this table.

The hours per determination numbers include only operator time for operations requiring some manipulation such as remote pipetting, titrating, extracting, etc. They do not include time spent in dissolving samples, evaporating liquids, etc.

Element	Method of Determination	Determinations Per Week ^a	Hours
U and Pu	Mass Spectrometric	16	3 to 4
U	Titrimetric	9	2
U	Colorimetric	2	2
Pu	Radiochemical	6	2
Pu	Amperometric	1	2
Burn-up	Radiochemical	2	3
Total Rare Earths	Radiochemical	2	1
Zr	Colorimetric	2	1
Mo	Colorimetric or Polarographic	2	1/2 to 1
Ru	Colorimetric	2	1
Rh	Colorimetric	2	2
Pd	Colorimetric or Polarographic	2	1/2 to 1
Np	Radiochemical	1	2
Tc	Colorimetric	2	1 1/2
Ba	Radiochemical	1	2
Sr	Flame Photometric	1	1
Cs	Flame Photometric	1	
Mg	Colorimetric	1	1

^a All analyses done in duplicate

increase the determinations per week. The man-hours per determination estimate is based only on operator time for remote operations such as pipetting, titrating, extracting, etc. It does not include time spent in sample dissolution, volume reduction, etc.

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

1. Studies Directed at Processing of Melt-Refining Skulls

The utility of the melt-refining reprocessing cycle envisioned for EBR-II type fuel elements will depend to a considerable extent on the efficiency of an auxiliary process which must accomplish:

- (1) an economic recovery of the fissionable uranium-235 and plutonium-239 present in melt-refining residues,
- (2) a fairly good purification of the uranium and plutonium from noble metals.

The presently accepted "fissium" composition for EBR-II fuel of 95 per cent uranium (45 to 50 per cent enriched) and 5 per cent alloying elements requires the removal of noble metals from a side stream ("drag-out") amounting to about 10 per cent of the charge. Yields of purified uranium by melt refining range from 90 to 95 per cent. It is, therefore, desirable to develop a recovery process for melt-refining residues which would also effect a reasonable removal of noble metal fission products.

Two processes have been contemplated for accomplishing the recovery and purification of fissionable materials from melt-refining residues. One involves a series of high-temperature oxygen-hydrogen cycles to convert the skull material to a finely divided oxide which may be poured from a crucible. Rare earth and noble metals would then be selectively reduced and removed in a zinc solution. This would be followed by reduction of

uranium and plutonium oxides by magnesium in zinc. Subsequently, inter-metallic crystals of uranium and plutonium with zinc would be precipitated, separated, and retorted to yield purified metal.

Another process scheme involves direct dissolution of melt-refining skulls in a zinc-magnesium solution followed by fractional crystallization to yield some fission product decontamination. Separated U_2Zn_{17} crystals would be treated with magnesium to decompose the U_2Zn_{17} , thereby precipitating uranium metal leaving accompanying rare earth metals in solution. The uranium metal would be then separated by distilling away any residual zinc or magnesium. This process could also handle fully oxidized skull material.

The work reported below relates to various studies on these processes. Generally, zinc has been used as the solvent metal. However, because of the more favorable corrosion situation with cadmium, attention in the future will be devoted largely to the use of this metal system.

a. Oxidation-Reduction Treatment of Melt-Refining Residues
(V. Trice, W. H. Spicer)

An oxidation-reduction cycle using oxygen and hydrogen at 800 C has been demonstrated as a satisfactory method for the in situ pulverization of melt-refining residues so that they may be poured from the crucible (ANL-5959). During this process volatile oxides of certain constituents, principally molybdenum and ruthenium, are evolved. A series of preliminary experiments has been completed which provides a measure of the amount of volatile oxides produced by the oxidation-reduction treatment.

Thin biscuits of "fissium" containing 3.9 per cent molybdenum and 2.6 per cent ruthenium were subjected to a variety of oxidation-reduction programs. With pure oxygen at 800 C, oxidation of the "fissium"

biscuits was sufficiently rapid to require control of the rate of combustion by metering of the oxygen supply. Satisfactory results were obtained using oxygen pressures of less than 100 mm. Considerable amounts of volatile oxides were evolved. The results, presented in Table 6, show that in the order of 50 per cent of the molybdenum and 90 per cent of the ruthenium may be volatilized. Hence, fuel processing schemes which include a metal oxidation step should provide for the handling of significant quantities of volatile fission product oxides.

Oxidation of "fissium" biscuits with air, Run 11, did not provide a satisfactory pulverization scheme. Exposure to air at 800 C for two hours resulted in little reaction as evidenced by a slow rate of air consumption. Subsequent exposure to oxygen at 800 C produced little additional oxidation. Examination of the product revealed that only about 25 per cent of the charge had been pulverized. Hence, it appears possible that air oxidation of "fissium" may have resulted in the formation of a protective nitride coating.

b. Oxidation-Reduction Reactions in Liquid Metal Systems
(A. Schneider, T. Johnson, I. O. Winsch, T. F. Cannon)

(1) Stability of Uranium Dioxide and Ceric Oxide in Zinc

Neither uranium dioxide nor ceric oxide was reduced by liquid zinc at 750 C. In separate experiments, filtered samples showed no uranium in zinc after four hours of sitting and no cerium after 20 hours of stirring. The cerium oxide changed from light yellow to a dark gray-green indicating a possible reduction from the ceric to the cerous state.

(2) Reduction of Ceric Oxide by Uranium in Zinc Solution

It was of interest to investigate the reduction of rare earth oxides using uranium dissolved in zinc because of the possibility

Table 6

SUMMARY OF OXIDATION-REDUCTION EXPERIMENTS WITH "FISSIUM" ALLOY

Concentration of pertinent elements in charge:
 Uranium-89 w/o; molybdenum-3.9 w/o; ruthenium-2.6 w/o

<u>Run</u>	<u>Processing Treatment</u>	<u>Per Cent of Original Mo Remaining</u>	<u>Per Cent of Original Ru Remaining</u>	<u>U Concentration in Final Product (%)</u>
10A	2 cycles of O ₂ oxidation and H ₂ reduction at 800 C	50	5	82
10B (Product from 10A)	1 cycle O ₂ oxidation and H ₂ reduction at 800 C	40	5	83
10C (Product from 10B)	O ₂ oxidation at 800 (then reduced pressure - 50μ - at 700 C for 6 hr.	44	1	80
11A ^a	Air oxidation at 800 C for 2 hours followed by 1 cycle O ₂ oxidation and H ₂ reduction at 800 C plus O ₂ oxidation at 800 C	106	62	80
12A	1 cycle O ₂ oxidation and H ₂ reduction at 800 C	45	10	84
12B (Product from 12A)	O ₂ oxidation at 800 C then reduced pressure - 50μ - at 800 C for 3 hours	50	1	79

^a Air oxidation apparently passivated surface. Pulverization incomplete. Results shown are for pulverized material.

of utilizing this selective reduction in a process. Cerium was used as a "stand-in" for all rare earth fission products. A charge consisting of 8.1 grams ceric oxide (cerium content 79.2 per cent by analysis), 7.5 grams uranium and 815 grams zinc was maintained at 750 C for four hours with constant agitation. Filtered samples were withdrawn periodically and were analyzed for uranium and cerium. Experimental results as well as calculated rates for the oxidation of uranium are shown in Figure 3. From a crossplot of rate versus concentration (Figure 3) it can be seen that, within the range studied, the rate for the oxidation of uranium was a linear function of the concentration of uranium. In a second experiment, also performed at 750 C, ceric oxide was added to a supersaturated solution of uranium in zinc (6.6 weight per cent), which ensured a constant uranium concentration throughout the experiment. The results shown in Figure 4 indicate that the reaction proceeded rapidly and was essentially completed in two hours.

The ratios between the total amounts of uranium removed from and cerium introduced in the zinc solution obtained from Figure 3, are shown in Figure 5 as a function of time. This ratio approaches the value of 1.7 which is obtained from the stoichiometry of the reaction

The much higher value of this ratio during the initial period of the experiment indicates that part of the uranium is removed by one or more reactions different from that shown above and in the course of which ceric oxide is not reduced at first to the free element. Two mechanisms are possible:

followed by:

FIGURE 3
REDUCTION OF CERIC OXIDE BY URANIUM IN ZINC SOLUTION

FIGURE 4
REDUCTION OF CERIC OXIDE BY A SATURATED SOLUTION
OF URANIUM IN ZINC

FIGURE 5
REDUCTION OF CERIC OXIDE BY URANIUM
IN ZINC SOLUTION

and the competing reactions involving the zinc solvent

It is quite likely that the reduction of ceric oxide by uranium proceeds in two steps. The reduction to cerous oxide has a very favorable free energy change. The second step has a very unfavorable free energy change but proceeds because of the very low activity coefficient of cerium in zinc.

(3) Reduction of Cerium Oxide by Magnesium-Cadmium
(A. Martin and C. Wach)

Pellets of cerium oxide, CeO_2 , were reduced by the magnesium present in a 2.1 weight per cent magnesium-cadmium alloy at 470 C with continuous stirring. The reduction was followed by taking samples periodically for chemical analysis. From the analyses, the extent of reduction was calculated, assuming that the melt never reached saturation with respect to cerium. In Figure 6, the calculated percentages of reduction are plotted versus time. The solubility of cerium in the cadmium-magnesium alloy was not known, but since the last six samples contained practically the same amount of cerium, namely, 0.22 to 0.23 weight per cent cerium, it appears possible that the solubility was reached and that consequently the final extent of the reduction might have been as high as 100 per cent rather than only 79 per cent.

In any case, it is evident that cerium oxide can be reduced by a cadmium-magnesium alloy of this composition and that the rate of reduction is fairly slow.

FIGURE 6
REDUCTION OF CERIUM OXIDE BY CADMIUM - 2 PER CENT MAGNESIUM

(4) Reduction of Plutonium Oxides with Uranium in Zinc Solution

It is important to know if plutonium oxides as well as cerium oxide will be reduced by uranium in zinc solution for "drag-out" process purposes. Results of the experiment described below show that the reduction of plutonium oxide by uranium in zinc solution occurs readily, and proper account must be taken of this reduction in design of "drag-out" processes.

About 50.6 grams of a uranium-20 weight per cent plutonium-11 weight per cent "fissium" alloy was oxidized with oxygen at a pressure of about 100 mm at a temperature of 800 C. The oxidized metal and about 850 grams of zinc were charged to a tantalum crucible in the tilt-pour furnace. The charge was heated to 750 C and agitation was provided to the melt by means of a motor driven tantalum agitator. A filtered sample of the melt taken after seven hours indicated only about 0.02 per cent of the plutonium originally charged was present in the zinc phase.

About 25 grams of uranium metal was then charged to the melt and after an additional six hours of agitation at 750 C a filtered sample was taken. This sample indicated that about 60 per cent of the plutonium oxide charged to the melt was reduced by the uranium and was in solution in the zinc phase. After an additional seven hours mixing time at 750 C, further samples indicated a slight drop in the plutonium concentration in the zinc phase.

This experiment indicates that plutonium as well as rare earths would be put into zinc solution along with rare earths by reduction with uranium. The procedure does not, therefore, provide a plutonium-rare earth separation as was hoped.

c. Skull Oxide Reduction by Magnesium in Zinc Solution
(J. C. Hesson, R. D. Pierce, E. Johnston)

Ten runs were made at 800 C to investigate reduction of skull oxide by magnesium in zinc. The skull oxides were prepared by the oxidation-reduction treatments given in Table 6. Runs were made at 800 C both in open air under flux cover and in crucibles placed within closed vessels in which an inert argon atmosphere was maintained. The magnesium concentration employed in the zinc was five to six per cent.

Reduction rates for four runs are shown in Figure 7. Three are typical of open-air runs under flux cover in well agitated vessels. About 90 per cent reduction was realized in four or five hours. The rate of reduction was lower in the inert gas run in which agitation was poorer as a result of "drag" imposed by a stirrer gland. Whether or not a flux cover is beneficial in the uranium oxide reduction is, therefore, unknown.

The reduction rates of cerium closely paralleled, on a percentage basis, that for uranium. Molybdenum, representative of a noble metal, was also put into solution. Filtered samples, in fact, showed higher molybdenum concentrations than the reported solubility (0.06 per cent versus 0.02 per cent), which may indicate that the reduced molybdenum which was not in solution was so finely divided that it passed through the porous graphite frit in the sampling tube. In the flux runs, a small percentage of magnesium oxidation occurred as a result of oxygen diffusion from the air and by reaction with flux contaminants (hydrated water, for example).

The reaction rates shown in Figure 6 appear to be proportional to the surface of the skull oxide in contact with the zinc-magnesium melt. Mathematical expressions were developed which show that reduction

FIGURE 7
URANIUM REDUCTION OF SKULL OXIDES BY MAGNESIUM IN ZINC

curves of the type shown in Figure 7 can be a result of a reaction rate proportional to surface area. These expressions can be transformed to

$$w = 1 - \int_{w_s \text{ at } r_o = kt}^{w_s \text{ at } r_o \text{ max}} \left(1 - \frac{kt}{r_o}\right)^3 dw_s, \quad (1)$$

where w_s is the weight fraction of oxide particles which have radii less than r_o as determined by screen analysis.

Equation 1 was graphically integrated using screen analysis data of the oxide material. A value for k of approximately 0.07 millimeter per hour was obtained. A better fit of the data was obtained by assuming that k was not constant but was proportional to the square of the magnesium concentration, for which case k has the dimensions of length/(time)(Mg conc)².

d. Direct Dissolution of Crucible Skulls in Zinc-Magnesium Alloys
(R. D. Pierce, J. C. Hesson)

During the past seven months a series of runs has been made on the zinc extraction of uranium from "fissium" crucible skulls. These skulls consist of a solid button of residual metal on the bottom and an oxide-metal scale along the walls (see typical skull compositions in Table 7). Molten zinc containing up to six per cent magnesium as a reductant for uranium oxide was used to dissolve the skull material in the graphite filter crucible shown in Figure 8. After about six hours of contact at 800 C with agitation, the zinc was forced under argon pressure through a graphite filter frit into the lower collection crucible.

In most of the runs, about 20 per cent of the uranium in the skull was recovered. Failure to achieve higher recoveries has been traced to the formation of uranium nitrides, which are not reduced by the

Table 7

ANALYSIS OF MELT-REFINING SKULLS

Skull from "Fission" Run ^a	Concentration (Weight Per Cent)							
	Uranium		Cerium		Ruthenium		Molybdenum	
	Button	Scale	Button	Scale	Button	Scale	Button	Scale
HV-8	86.7 ^b	77.8 79.8	-	-	2.30 ^b 2.56	1.96 1.97	-	-
HV-9 and 10	96	81	0.194	6.8	2.76	2.16	3.5	3.5
HV-11	87	71	0.59	11.6	2.48	1.80	3.4	2.28
HV-14	79	78	3.7	4.8	2.34	1.93	3.2	2.6
HV-16	89	69	0.42	12.4	2.7	1.86	3.8	2.45
DL-13B	92	86	0.063	4.21	2.15	1.83	2.42	2.12

^a HV- designates high-vacuum furnace runs

DL- designates preliminary "dummy loadings" made in the EBR cell Mock-up.

^b Unpolished button, containing some scale; all others polished to clean metal.

FIGURE 8
EXTRACTION - FILTRATION EQUIPMENT

magnesium-zinc system. Nitrogen contamination has apparently resulted from air inleakage or from absorption or entrapment of air within the pores of the large graphite crucibles.

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

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

a. Distillation and Retorting

(1) Distillation of Magnesium
(P. Nelson, J. DeKany, R. Beck)

A bottom-loaded distillation unit with a sodium-cooled condenser has been put into operation. This unit has some features which might be employed in plant-scale apparatus for distilling magnesium from plutonium. A diagrammatic sketch of the equipment is shown in Figure 9. The condenser is between the still pot and the flanged opening to permit operating with the sealed flange in a cool zone.

Three test runs have been performed in which 450 grams of magnesium were evaporated at pressures of 5 to 10 mm of mercury. The temperature of the condenser at the inlet to the receiver was controlled at 675 C, 600 C, and 500 C, respectively, for the three runs, (melting point of magnesium: 651 C). The following conclusions were indicated by the results of these runs:

FIGURE 9
SKETCH OF MAGNESIUM DISTILLATION UNIT

- (1) It may be desirable to use induction heating to obtain a reasonable evaporation rate for large-scale distillations. Two to three hours were required to evaporate 450 grams of magnesium with a furnace temperature of 1000 C providing a temperature drop of about 300 C. The heat-transfer-area-to-magnesium-weight ratio will be smaller for full-scale apparatus.
- (2) It is possible to maintain a metal-to-metal vacuum seal in the hot still pot zone. Whether this type of seal can be used indefinitely for an opening large enough for removal of the still pot is not yet known.
- (3) The prevention of any trace of magnesium condensation beneath the receiver may require condensing the magnesium as a solid and subsequent melting at atmospheric pressure to cause the magnesium to run down into the mold.

Further tests are being performed to improve condensation techniques.

(2) Retorting of Cadmium and Zinc from Uranium Alloys
(P. Nelson, R. Beck)

A top-loaded distillation unit for large-scale retorting of uranium alloys of zinc and cadmium has been test operated by distilling of cadmium. The purpose of this equipment is to obtain data on and experience in retorting operations typical of those in the liquid metal process. A schematic sketch is shown in Figure 10. For runs in which cadmium is evaporated a steel crucible is used to contain the charge. However, tantalum or ceramic crucibles could also be used. Condensation of the vapors on the upper section of the

FIGURE 10
SKETCH OF RETORTING EQUIPMENT

crucible is prevented by insulating the crucible from the mold. The condensing section is cooled by radiation and air convection. The metal condenses as a liquid in the lower section of the condenser and runs into the mold. The metal which condenses as a solid at the upper section of the condenser is melted down after distillation is complete by induction heating the condensing section.

In the first preliminary run 11.5 kilograms of cadmium was evaporated at 10 mm of mercury pressure at which the boiling point is 484 C. An attempt was made to control the upper section of the condenser at a temperature of 300 C by adjusting the heat input to the still pot. Under these circumstances, five and one-half hours of boiling were required to evaporate the charge.

(3) Vapor-Liquid Equilibrium for Zinc-Magnesium System
(P. A. Nelson, R. A. Beck, R. C. Paul)

Some of the Pyrozinc processes which are being considered for blanket and drag-out processing require separation of zinc from magnesium by distillation. The vapor pressure of pure zinc is eight to ten times that of pure magnesium at distillation temperatures indicating easy separation of the two components. However, a departure from ideality might lower the relative volatility to the point where several distillation stages would be required to obtain sufficient separation of the components. Controllability of a remote process involving recycled streams would be facilitated by efficiency separations. Therefore, an attempt is being made to obtain vapor-liquid equilibrium data.

Two methods will be used to obtain the data. The first, by which some data have already been obtained, is dynamic (Rayleigh)

distillation of zinc-magnesium alloys. For this method the total vapor is collected in several increments and analyzed for the components. The second method is distillation of alloys in an equilibrium still which recycles the condensed vapor to the still pot until equilibrium is reached.

The dynamic still, shown in Figure 11, is constructed of tantalum and has a heavy-walled graphite secondary to provide good heat distribution. The condenser is a three-eighth-inch tantalum tube welded directly to the top of the still pot and directed downward. It is cooled by radiation and convection to the helium atmosphere but is maintained at a temperature above the melting point of the condensing vapor by resistance heating. In order to avoid condensation of the vapors anywhere except in the condenser, the wall surfaces in the still pot above the melt are superheated by adjusting the height of the induction coil.

The condenser discharges into an eight-compartment mold which rests on a rotating platform mounted on ball bearings. The position of the mold can be changed while the still is operating by changing the position of a magnet, thus rotating another compartment of the mold into position under the condenser outlet. It is possible to get eight samples of the condensed vapor during the run. The still pot composition is obtained by subtracting the amounts of magnesium and zinc distilled from the amounts charged.

A six-inch diameter quartz tube encloses the whole apparatus permitting operation at a reduced pressure with an inert atmosphere.

Two successful runs were performed with alloys having the initial compositions MgZn_2 and Mg_7Zn_3 . The magnesium and zinc were mixed in the tantalum still pot in an inert atmosphere after which the tantalum vessel was welded closed. The pressure was controlled at 100 mm mercury during

FIGURE 11
DYNAMIC DISTILLATION UNIT

the run. The temperature of the bottom of the still pot was measured by a thermocouple. However, analysis of the data revealed that this temperature indication was somewhat erratic and below the temperature of the boiling metal.

Seven samples of condensed vapor were obtained for the first run and eight samples for the second run. These samples were weighed and analyzed for zinc and magnesium. The results are given in Table 3. The unchanging vapor composition obtained at the beginning of Run II may have been caused by the presence of a light magnesium-rich phase which, it is postulated, formed on remelting the alloy.

The moles of magnesium vaporized was plotted against the total moles of metal vaporized. The slope of this curve,

$$\frac{d \text{ Mg}}{d (\text{Mg} + \text{Zn})}$$

is the atom fraction of magnesium in the vapor and by subtraction from one the atom fraction of zinc is obtained. Also the atom fraction of zinc in the liquid phase, calculated by difference, was plotted versus the moles of metal vaporized.

Equilibrium data obtained by this method are plotted in Figure 12. Except for the point corresponding to the non-equilibrium condition at the beginning of the second run, the data are in good agreement. Considerable deviation from the ideal curve based on Raoult's law is apparent except at high (greater than 0.7) atom fraction of zinc in the liquid.

Table 8

MAGNESIUM-ZINC DISTILLATION DATA

<u>Run I Vapor Samples</u>			<u>Run II Vapor Samples</u>		
<u>Sample</u>	<u>Total Weight (g)</u>	<u>Mg (w/o)</u>	<u>Sample</u>	<u>Total Weight (g)</u>	<u>Mg (w/o)</u>
A	89.60	2.38	A	49.86	38.4
B	89.77	4.77	B	38.64	38.0
C	83.22	10.0	C	44.82	37.0
D	43.59	18.2	D	49.01	46.7
E	51.15	32.6	E	26.67	55.0 ^a
F	33.39	58.6	F	24.06	58.4 ^a
G	<u>2.36</u>	72.9 ^a	G	17.65	68.3 ^a
	393.08		H	<u>12.12</u>	32.2 ^a
				262.83	

	<u>Run I</u>			<u>Run II</u>		
	<u>Mg</u>	<u>Zn</u>	<u>Total</u>	<u>Mg</u>	<u>Zn</u>	<u>Total</u>
Charged (g)	63.1	338.5	401.5	124.1	142.8	266.7
Recovered (g)	60.6	332.5	393.1	124.5	138.3	262.8
Recovered (%)	96.0	98.3	97.9	100.3	96.8	98.5

^a Obtained by subtraction from the zinc analysis.

FIGURE 12
VAPOR-LIQUID EQUILIBRIUM FOR THE ZINC-
MAGNESIUM SYSTEM AT 100 mm MERCURY

b. Phase Separation of Precipitated Zinc Intermetallic Compounds from Supernatant Solutions
(J. C. Hesson, R. D. Pierce, E. F. Johnston)

(1) Pressure Siphoning

In the previous quarterly report various methods for separating zinc intermetallic compounds from supernatant solutions were discussed. Work is being concentrated on pressure siphoning because it appears to be the most promising procedure for remote operation.

Three pressure siphoning runs (in addition to the five previously reported) were made in which the zinc was siphoned through a 5/16-inch ID tube at 500 C. In these runs zinc was siphoned

- (a) from above the crystal interface,
- (b) from below the interface,
- (c) from below the interface through a carbon filter frit (grade 20 C -- minimum particle size retained of 39 microns) inserted into the end of the tube,
- (d) from above a perforated plate which was used to compress the cake, and
- (e) from below the interface through a thimble with 1/32-inch openings, inserted into the end of the siphon tube.

In the run in which a carbon filter frit was used the frit plugged during the filtration. In all other runs phase transfers were effected without difficulty.

Charges of zinc and uranium-zinc intermetallic varying in total weights from 4 to 16 kilograms were loaded into the charge crucibles. Intermetallic crystal cakes varying in weight from 2 to 4.6 kilograms, and siphoned zinc ingots varying in weight from 2 to 13.1 kilograms were obtained.

The uranium content of the filter cakes varied from about 10 to 14 per cent. Uranium analyses of two siphoned zinc ingots were made. In the run in which the siphon tube extended into the cake the analysis was 0.058 per cent uranium. The solubility of uranium at 500 C is 0.02 per cent. When the cake was compressed by the perforated plate the analysis was 0.38 per cent uranium. It is believed that the compression of the cake broke off small intermetallic crystals which were siphoned over thus resulting in the higher uranium content.

Although some additional runs are being made on zinc-uranium phase separation, the planned future work will involve the phase separation of cadmium from uranium-zinc intermetallic and/or uranium-cadmium intermetallic crystals.

(2) Filtration

The skull dissolution runs reported on page 64 have provided experience in high-temperature zinc filtrations. Approximately 60 filtrations have been made on a kilogram-scale. Filter cakes containing as much as 22 per cent uranium were prepared by filtering zinc from the crystallized intermetallic uranium-zinc compound (30 per cent theoretical uranium). However, several difficulties which have been encountered make filtration unattractive for remote operation:

1. Equipment and lines have become clogged with condensed zinc, usually requiring cleaning after every run.
2. The high-temperature seal required to permit a pressure differential across the filter has been difficult to secure. Frequently, leaking seals

have required dismantling and resealing of the equipment. The porosity of the graphite container, in addition to the relatively poor seals, has necessitated several pressure cycles or a continuous bleed and feed of inert gas during a filtration. This has accentuated the zinc vapor deposition problem.

3. Plugging of filter frits and premature filtration have both been encountered.

Work with the filtration apparatus has been discontinued in favor of more effort on pressure siphoning experiments.

c. Corrosion in Liquid Metal Systems
(J. P. DeKany, H. W. Lavendel, I. O. Winsch, J. Pavlik)

The liquid metals corrosion test program was continued with a series of 100-hour static corrosion tests in molten zinc, zinc-magnesium, and cadmium-zinc-magnesium media. The tests were conducted with the same procedure outlined in the previous quarterly report (ANL-5959, page 160).

(1) Molten Zinc and Zinc-Magnesium Tests

A series of static corrosion tests at 750 C were conducted in pure zinc and 46 weight per cent magnesium-54 weight per cent zinc alloy. One of the purposes of these tests was to establish the resistance of tantalum to attack by these media in view of earlier evidence that this metal was corroded by zinc and zinc-magnesium alloys. In addition, other materials were investigated including molybdenum, alumina, graphite, silicon carbide, silicon nitride, Vycor, zirconia, and four high-temperature tungsten alloys developed by Armour Research Foundation.

Metallographic and spectroscopic examination of the samples disclosed the following:

- (a) Corrosion was found in the zinc-tantalum system. Spectroscopic analysis revealed the presence of tantalum in the zinc phase of nine out of ten samples containing the tantalum-zinc system. In addition a tantalum-zinc sample was forwarded to the metallographic section of the Metallurgy Division for micro-hardness determination of the corrosion phase produced by the zinc attack. Micro-photograph No. 1 (Figure 13) shows the specimen in the as mechanically polished condition and the micro-hardness indentations in the component materials at the interface. Four distinct layers were discovered. The darkest gray area is the tantalum. Adjacent to the tantalum is an entrapped zinc area; next, a border of intermetallic compound material and finally the zinc. Listed below are the Vickers micro-hardness readings in each layer, the positions reading from left to right on the micrograph:

<u>Position</u>	<u>Tantalum</u>	<u>Entrapped Zinc Layer</u>	<u>Intermetallic Compound Layer</u>	<u>Zinc</u>
1	90.8	51.2	--	28.9
2	95.8	--	342	28.1
3	104	--	292	29.3
4	--	--	363	36.7

FIGURE 13
MICRO-PHOTOGRAPHS OF TANTALUM-ZINC INTERFACE

MICRO-PHOTOGRAPH NO. 1 SHOWING MICRO-HARDNESS INDENTATIONS

MICRO-PHOTOGRAPH NO. 2 SHOWING EXTENSIVE INTERMETALLIC COMPOUND FORMATION

The very first micro-hardness indentation in the intermetallic compound was partly in the entrapped zinc area, and it was not included in the above readings. The fourth indentation in the zinc is partly in the intermetallic compound. This, no doubt, is responsible for its comparatively higher micro-hardness reading. The Vickers micro-hardness number found for the intermetallic layer is of the magnitude normally associated with intermetallic compounds.

Micrograph No. 2 is a micrograph of the cathodically etched sample and shows an area with extensive intermetallic compound particles.

There was no appearance of attack in magnesium-zinc alloys ranging in magnesium content from five weight per cent to 46 weight per cent. Lack of corrosion in the 46 weight per cent magnesium is at variance with a previous test in which a tantalum sample was observed to be attacked by this medium. However, the results of this last series of tests would seem to indicate that the presence of magnesium inhibits the attack of zinc to a great extent.

- (b) No attack on pure tungsten was observed. However, the tungsten alloys provided by Armour Research

Foundation were decomposed, with all of the phases except tungsten being dissolved in the zinc. As observed previously with other materials, the presence of 46 weight per cent magnesium inhibited the attack by zinc to a considerable extent.

- (c) While microscopic examination did not reveal a discernible attack on molybdenum by either zinc or 46 weight per cent magnesium-zinc, the spectroscopic results indicated that the molybdenum dissolved to an extent consistent with the solubility at 750 C (0.02 weight per cent).
- (d) Macroscopic and spectroscopic analysis of the ceramic materials tested in zinc and 46 weight per cent magnesium-zinc systems revealed several instances of attack by the magnesium-zinc alloy. Vycor, silicon nitride, and silicon carbide were seriously attacked by this alloy while zirconia was attacked to a lesser degree.

(2) Molten Cadmium-Zinc-Magnesium Tests

The testing of cadmium alloys in mild steel was continued. Four tests with two, four, eight, and ten weight per cent zinc-cadmium-0.2 weight per cent magnesium alloys were conducted. The spectroscopic analyses revealed no presence of iron in the corrosion media. Thus, mild steel shows a definite promise as a containment material for the cadmium system even with as much as 10 weight per cent zinc present.

(3) Future Tests

The first series of long-term dynamic corrosion tests have been planned for the mild steel-cadmium and cadmium alloy systems. An apparatus whereby capsules containing the corrosive media can be slowly rotated at 550 C has been built and installed in the Hupper resistance furnace. Mild steel will be tested in pure cadmium, two weight per cent uranium-cadmium, and eight weight per cent zinc-0.2 weight per cent magnesium-cadmium.

Another series of static corrosion tests has been planned with zinc and zinc alloys. The materials to be tested are: nitrided and cyanided steels, Thermanol, Haynes No. 25 alloy, multimet alloy, and Haynes stellite alloy No. 6B. The tests will be conducted at 750 C for 100 hours.

C. Pyrometallurgical Research
(E. M. Fader)

1. Liquid Metal Solvents Chemistry
(I. Johnson)

Fundamental data are being collected to make possible the design of separations processes based on the following scheme:

- (1) dissolution of the irradiated fuel in a solvent metal,
- (2) crystallization or precipitation of the actinide metal as an intermetallic compound, and
- (3) removal of the solvent metal from the intermetallic compound by volatilization or leaching.

This basic process may include additional steps such as hot filtration to remove insolubles or extraction of liquid metal solutions with immiscible fused salts or metals to remove fission products.

a. Phase Studies

The solubilities of various elements in liquid metal solvents are of primary importance in the separations processes under development. These solubilities need to be known as functions of temperature and solvent composition. In many cases the identity of the solid phase in equilibrium with the saturated solution is also important. Measurements of the solubilities of the major fission product elements in liquid zinc and in liquid cadmium are under way. Such measurements have been made for lanthanum, palladium, zirconium, and molybdenum in cadmium. The solubilities in cadmium of palladium and zirconium in the presence of uranium are also reported.

The recovery of uranium by crystallization or precipitation from the solvent is a basic step. With zinc as the solvent the solubility of the intermetallic compound is so low at the usual crystallization temperature

that high recoveries of uranium are obtainable. The solubility of the uranium-cadmium intermetallic in cadmium at the lowest practical crystallization temperature is too great to permit more than 95 per cent recovery of uranium. Experiments have been performed to determine the solubility of uranium in mixed solvents such as cadmium-zinc and cadmium-mercury. As reported below, zinc additions have been found to depress the solubility of uranium in cadmium enough to permit quantitative recovery.

As an alternative to volatilization the solvent metal may be removed from an intermetallic compound of uranium by a reaction which decomposes it and leaves uranium as an insoluble residue. Phase studies reported below of the systems uranium-zinc-magnesium and uranium-cadmium-magnesium show that magnesium may be used for this purpose. Because plutonium is quite soluble in magnesium this reaction has application to the separation of uranium and plutonium. The solubilities of plutonium and uranium in cadmium-magnesium mixtures are reported below.

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

The solubility of lanthanum in cadmium has not been previously studied. Measurements were made over the temperature range 350 to 600 C by taking filtered liquid samples of saturated solutions at a series of temperatures. The solubilities are shown in Figure 14. They conform to the usual straight line relation except for the lowest temperature. This point may be in error due to difficulties in the analytical method at very low lanthanum concentrations. The lower temperature range of this solubility curve will be reinvestigated using radiolanthanum. Over the temperature range of from 400 to 600 C the solubilities are given by the equation:

$$\log W = 7.368 - \frac{5991}{T} (\pm 0.02 \text{ weight per cent})$$

FIGURE 14
SOLUBILITY OF LANTHANUM IN CADMIUM

where W is the solubility in weight per cent and T , the absolute temperature in degrees Kelvin. The equilibrium solid phase over this range is believed to be LaCd_{11} , cubic and isostructural with UCd_{11} .

Palladium-Cadmium
(M. Ader and J. Pavlik)

The solubility of palladium in cadmium below 500 C has not been previously investigated. A mixture of 1300 grams cadmium, 76 grams palladium powder, and 100 grams lithium chloride-potassium chloride eutectic was melted in a covered, but not air-tight, mild steel crucible under an atmosphere of flowing argon gas. After several hours of vigorous agitation (tantalum paddle) at 514 to 430 C, sampling was begun at 397 C. Samples were drawn by suction into 2 millimeter ID quartz tubing through a press-fitted grade-60 porous graphite filter (average pore diam = 33 microns). Samples were taken only after temperature had remained constant for about an hour with the mixture being stirred continuously. Saturation was approached from both temperature directions. Temperature (± 2 C) was measured by means of a chromel-alumel thermocouple in a protection tube that dipped into the metal phase. Palladium was determined by spectrophotometry of its complex with 2-nitroso-1-naphthol in toluene (accuracy, ± 3 per cent std dev).

Solubility data are given in Table 9 and are shown (as circles) on a reciprocal temperature plot in Figure 15. A least squares analysis of the data gives the following equation for palladium solubility in cadmium in the temperature range 327 to 502 C:

$$\text{Log } w/o \text{ Pd} = 4.206 - 2869/T$$

Table 9

SOLUBILITY OF PALLADIUM IN CADMIUM

(Samples taken in order listed)

<u>Cadmium</u>		<u>Cadmium - 0.2 w/o Magnesium</u>	
<u>Temp (C)</u>	<u>w/o Pd</u>	<u>Temp (C)</u>	<u>w/o Pd</u>
397	0.80 ₇	473	2.32
355	0.42 ₉	497	3.15
327	0.29 ₂	444	1.65
380	0.60 ₀	398	0.86 ₉
420	1.10	361	0.51 ₅
473	2.36	330	0.31 ₈
502	3.34	375	0.60 ₆
442	1.58	424	1.16
		448	1.64
		480	2.50

FIGURE 15
SOLUBILITY OF PALLADIUM IN CADMIUM

The triangles in Figure 15 represent palladium solubilities in cadmium - 0.2 weight per cent magnesium. The close agreement of both sets of data indicates that low concentrations of magnesium have little, if any, effect on palladium solubility.

The solubility of palladium, as determined in the present work, is lower than would be expected by extrapolation of thermal analysis data obtained at higher palladium concentrations by previous investigators³. In this temperature range the solid phase is reported to be a body-centered cubic Hume-Rothery compound.

Palladium-Uranium-Cadmium
(M. Ader and J. Pavlik)

The effect of uranium on the solubility of palladium in cadmium solutions was determined in the same manner and equipment as previously described. Magnesium was included in the metal phase to suppress air oxidation of uranium. The mixture was stirred at 580 C for several hours prior to sampling. Uranium at concentrations greater than 0.06 weight per cent was determined spectrophotometrically as the complex with dibenzoyl methane in hexone (± 3 per cent std dev). At lower concentrations uranium was determined fluorimetrically (± 20 per cent std dev).

Palladium and uranium solubility data are shown on a reciprocal temperature plot in Figure 16. In addition, the solubility curve of uranium in pure cadmium (from ANL-5896, page 128) is included in Figure 16 for comparison. A least squares analysis of the palladium data (omitting the datum point at 600 C, 7.1 weight per cent palladium, as being unsaturated) gives the equation:

$$\log (w/o \text{ Pd}) = 4.440 - 3058/T \quad (336 \text{ to } 579 \text{ C})$$

³Hansen, M., "Constitution of Binary Alloys," McGraw-Hill Book Co., New York, 2nd Edition, 1958, page 434.

FIGURE 16
PALLADIUM-URANIUM JOINT SOLUBILITIES IN CADMIUM-RICH SOLUTIONS

Palladium solubility is only slightly depressed by the presence of uranium in cadmium-rich solutions as indicated by the close agreement (almost within experimental error) with the solubility data obtained in its absence.

Uranium solubility in liquid cadmium is decreased as much as 200-fold by saturating with palladium, as can be seen from Figure 16. This effect is somewhat similar to that described below for addition of zinc to cadmium-uranium solutions. Several points not falling on the uranium solubility curve were obtained after the mixture stood unstirred overnight at 435 C. However, these were discarded (and are not shown) since a crust or sludge of fine solid particles had formed making sampling difficult and probably non-representative. The precipitation of uranium by the addition of palladium to cadmium solutions does not appear to be of practical interest.

Zirconium-Cadmium (M. Ader and J. Pavlik)

Zirconium solubility in cadmium was determined using the same equipment and techniques previously described for determining palladium solubility. Two pieces of zirconium crystal bar weighing a total of 29 grams were suspended in 2.17 kilograms of cadmium - 0.1 weight per cent magnesium at about 485 C. The metal phase was covered with 94 grams of lithium chloride-potassium chloride eutectic flux. Magnesium metal and flux were used to suppress air oxidation of zirconium. After several hours of agitation, the crystal bar reacted completely with cadmium to form a mass of floating, inter-metallic crystals. The amount of zirconium metal used represented a nominal concentration of 1.3 weight per cent. Subsequently, it was found that the maximum solubility in the temperature range investigated, 327 to 545 C, was about 0.4 weight per cent. Thus, during the course of the solubility measurements, solid zirconium-cadmium intermetallic was always present.

Zirconium was analyzed spectrophotometrically as the complex formed with Alizarin-Red-S in perchloric acid (accuracy $\pm$ 3 per cent std dev).

Solubility data are given in Table 10 and are shown as circles on a reciprocal temperature plot in Figure 17. The circles are connected by two intersecting straight lines derived from the data by the method of least squares. Solubility measurements represented by weight per cent zirconium = 0.410, 0.216, and 0.0350, at 577 C, 423 C, and 327 C, respectively, were rejected from this analysis. The solubility equations are:

$$\text{Log w/o Zr} = 2.870 - 2622/T \quad (327 \text{ to } 461 \text{ C})$$

$$\text{Log w/o Zr} = 1.165 - 1371/T \quad (461 \text{ to } 545 \text{ C})$$

The intersection at about 461 C indicates a peritectic reaction.

Cadmium-Zirconium-Uranium
(M. Ader and J. Pavlik)

The joint solubilities of zirconium and uranium in cadmium-rich solutions were determined by adding 48 grams of uranium metal to the above-described mixture and agitating for several hours at about 475 C. Solubility data are shown on a reciprocal temperature plot in Figure 17. A previously determined solubility curve (see ANL-5896, page 128) for uranium in liquid cadmium is included in Figure 17 for comparison.

Examination of Figure 17 reveals that zirconium solubility is slightly depressed by saturating the solution with uranium and that the peritectic temperature is lowered from about 461 C to about 452 C. Likewise, the solubility of uranium in cadmium is depressed by saturating with zirconium and the peritectic temperature is lowered from about 473 C to about 467 C. Uranium solubility, above the peritectic temperature, appears to be retrograde

Table 10

SOLUBILITY OF ZIRCONIUM IN CADMIUM -- 0.1 WEIGHT
PER CENT MAGNESIUM

(Samples taken in order listed)	
Temp (C)	w/o Zr
485	0.22 ₈
423	0.21 ₆
383	0.076 ₂
345	0.043 ₂
327	0.035 ₀
369	0.059 ₀
411	0.10 ₈
456	0.18 ₉
511	0.26 ₁
577	0.41 ₀
545	0.30 ₈
580	0.22 ₀

FIGURE 17
SOLUBILITY OF ZIRCONIUM IN CADMIUM; ZIRCONIUM-URANIUM
JOINT SOLUBILITIES IN CADMIUM-RICH SOLUTIONS

as it is also in the absence of uranium. Joint solubilities of zirconium and uranium in cadmium may be expressed by the equations:

$$\text{Log (w/o Zr)} = 2.967 - 2714/T \quad (331 \text{ to } 453 \text{ C})$$

$$\text{Log (w/o Zr)} = 1.308 - 1512/T \quad (452 \text{ to } 581 \text{ C})$$

$$\text{Log (w/o U)} = 5.950 - 4202/T \quad (331 \text{ to } 467 \text{ C})$$

$$\text{Log (w/o U)} = -0.196 + 345/T \quad (467 \text{ to } 581 \text{ C})$$

Coprecipitation of zirconium with UCd_{11} has been studied (ANL-5959, page 132) and none was found.

Molybdenum-Cadmium
(A. E. Martin and C. Wach)

Molten cadmium was found to have dissolved only 0.0012 weight per cent molybdenum after 63 hours of contact with molybdenum powder with good mechanical stirring at 603 C. Our intention of measuring the solubility of molybdenum in cadmium as a function of temperature was abandoned in view of this low result.

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

The effect of zinc additions on the solubility of uranium in cadmium was studied by making two isothermal solubility runs. In each case, a cadmium melt was first saturated with uranium and then zinc was added incrementally. After each addition an hour or more was allowed for equilibrium to be reached and then a filtered liquid sample was withdrawn for chemical analysis.

The results are given in Figure 18 as a plot of log (weight per cent uranium) versus zinc concentration in solution. In both runs, a sharp drop in uranium solubility occurred at low zinc concentrations. At

FIGURE 18
EFFECT OF ZINC ON THE SOLUBILITY OF URANIUM IN CADMIUM

448 C, the solubility began to drop at about 2.5 weight per cent zinc, whereas at 325 C a solubility decrease was already evident with the first sample taken at about 1 weight per cent zinc.

In both cases, the uranium was precipitated almost quantitatively from solution. Thus at the 13.0 weight per cent zinc composition, more than 99.9 per cent of the uranium in solution had been precipitated in the run at 448 C compared to 99.8 per cent at 325 C.

The obvious explanation for this marked effect of zinc on the uranium solubility is that at the composition where the solubility begins to drop sharply, the melt composition changes from a region of primary UCd_{11} crystallization to one of primary U_2Zn_{17} crystallization. This has been confirmed by metallographic and by X-ray diffraction examination of the ingots.

Uranium-Cadmium-Mercury
(A. E. Martin and R. J. Uhle)

The effect of mercury on the solubility of uranium in cadmium was investigated by making two solubility runs by the procedure of taking filtered samples of saturated melts. In the course of the first run the mercury content decreased from 26 to 23 weight per cent as a result of selective volatilization losses, but in the second run the decrease was only from 10.4 to 10.1 weight per cent mercury. The solubility data from these runs are shown in Figure 19 in the usual log solubility versus $1/T$ form along with the data on cadmium itself as a reference. It is apparent that mercury increases the uranium solubility at a given temperature.

On the other hand, the solubility of uranium at the liquidus temperature was found to decrease with increasing mercury con-

FIGURE 19
EFFECT OF MERCURY ON SOLUBILITY OF URANIUM IN CADMIUM

tent. However, the solubility decrease observed is probably not enough to make the addition of mercury, coupled with a lowering of the temperature, an attractive technique for precipitating uranium from cadmium solutions.

Metallurgical examination of the ingots obtained from the solubility runs disclosed a bed of intermetallic crystals which appeared to be UCd_{11} .

Uranium-Cadmium-Magnesium)

(H. G. Wilsch, A. E. Martin, C. Wach, T. F. Cannon)

The effect of magnesium on the solubility of uranium in cadmium was investigated by the additions of magnesium to cadmium saturated with uranium. After each addition, an hour was allowed for equilibration and filtered liquid samples were taken. The solubility data thus obtained are shown in Figure 20. Below the peritectic decomposition temperature (475 C) the initial effect of magnesium addition is to raise the solubility; further addition of magnesium then decreases it. Metallographic examination disclosed that at 450 C uranium had been precipitated as uranium, although it had been previously established that UCd_{11} is the primary crystallizing phase in the magnesium-free system at this temperature. Thus the addition of magnesium carries the melt composition from a region of UCd_{11} crystallization to one of uranium crystallization. Above the peritectic decomposition temperature where uranium is the saturating phase in the magnesium-free system the addition of magnesium merely depresses its solubility.

Of further interest is the fact that just as uranium has a very small, negative temperature coefficient of solubility in cadmium above 475 C, so also in the ternary system the temperature coefficient of solubility is small and sometimes negative when uranium is the saturating phase.

FIGURE 20
EFFECT OF MAGNESIUM ON THE SOLUBILITY OF URANIUM IN CADMIUM

Uranium-Zinc-Magnesium
(A. F. Martin and R. Uhle)

An isothermal solubility run was made in this system at 680 C. A zinc melt was first saturated with uranium and then magnesium was added incrementally. After each addition, several hours were allowed for equilibrium to be reached and then filtered liquid samples were withdrawn for chemical analysis. The solubility results are shown in Figure 21 in a log (atomic per cent uranium) versus atomic per cent magnesium plot. The solubility of uranium in magnesium, as reported by Chiotti, Tracy and Wilhelm⁴, is also included so that the solubility line can be extended to 100 atomic per cent magnesium.

This solubility curve confirms the shape of the isothermal curves reported for this system in ANL-5959, page 123, which had been based on the investigations of five pseudo binaries. However, the new data show the shape of the curve more exactly, particularly the inflection point near the 33 atomic per cent magnesium composition which corresponds to the $MgZn_2$ compound in the magnesium-zinc binary system. Also, the new data extend into higher magnesium concentrations and these show a uranium solubility minimum at about 70 atomic per cent magnesium. This corresponds to the compound Mg_7Zn_3 , another of the five compounds which have been reported for the magnesium-zinc system.

Metallographic examination of the ingot after the solubility run showed rather well developed uranium crystals. This indicates that the sharp drop in uranium solubility beginning at 33 atomic per cent magnesium marks a change in melt composition from a field of primary U_2Zn_{17} crystallization to one of primary uranium crystallization.

⁴ Chiotti, P., Tracy, G. A., and Wilhelm, H. A., Trans AIME 206, 562-7 (1956).

FIGURE 21
SOLUBILITY OF URANIUM IN ZINC-MAGNESIUM ALLOYS AT 680C

The solubility data show that between the 34 and 52 atomic per cent magnesium compositions, 99.8 per cent of the uranium was precipitated from solution.

b. Coprecipitation Studies

Knowledge of the coprecipitation behavior of plutonium with uranium is important process information. Blanket processes, for example, can be devised which are dependent on controlled coprecipitation of plutonium with uranium.

Plutonium with Uranium from Cadmium
(L. Wirsch and R. Paul)

About 30.3 grams of uranium-1 weight per cent plutonium-3 weight per cent molybdenum and 1737 grams of cadmium were charged to a mild steel crucible contained in the tilt-pour furnace. A helium atmosphere of about 2 psig was maintained in the furnace during this experiment. Agitation was provided to the melt and samples were taken every 50 degrees at temperatures from 550 to 326 C and every 75 degrees as the temperature was raised from 326 to 550 C.

The concentrations of uranium and plutonium in cadmium over the temperature range of 550 to 326 C are tabulated in Table 11. Analyses indicate that only about two-thirds of the alloy charged was dissolved in the cadmium so that uranium saturation was not reached until the temperature was lowered to 450 C (1.1 per cent uranium). The plutonium concentration decreased by coprecipitation with uranium from 1.15×10^{-2} per cent at 450 C to 2.4×10^{-3} per cent at 326 C.

The Doerner-Hoskins plot for the coprecipitation of plutonium with uranium is shown in Figure 22. The lambda (λ) for coprecipitation of plutonium is 0.67.

Table 11

DATA ON COPRECIPITATION BEHAVIOR OF PLUTONIUM AND AMERICIUM
DURING PRECIPITATION OF URANIUM FROM CADMIUM SOLUTION

Charge: U-3 w/o Mo-1 w/o Pu -- 30.2275 g
 Cadmium -- 1737 g

Temperature Range of Uranium Saturation: 326 to 450 C

<u>Temp,</u> <u>(C)</u>	<u>$10^4/T$</u> <u>(K)</u>	<u>Pu</u> <u>Concentration</u> <u>(w/o)</u>	<u>U</u> <u>Concentration</u> <u>(w/o)</u>	<u>Am</u> <u>Concentration</u> <u>(w/o)</u>
449	12.19	1.06×10^{-2}	1.03	1.67×10^{-6}
496	13.00	1.09×10^{-2}	1.08	1.93×10^{-6}
450	13.85	1.15×10^{-2}	1.10	2.03×10^{-6}
401	14.85	6.65×10^{-3}	0.49	1.87×10^{-6}
350	16.08	3.24×10^{-3}	0.173	1.05×10^{-6}
326	16.70	2.58×10^{-3}	0.115	1.04×10^{-6}

FIGURE 22
DOERNER-HOSKINS PLOT FOR COPRECIPITATION
OF PLUTONIUM WITH URANIUM FROM CADMIUM

Coprecipitation of Plutonium with Uranium from Magnesium-Cadmium
Solution
 L. WILSON, I. PAUL

In the zinc system, the addition of sufficient magnesium results in precipitation of uranium as metal while the plutonium remains in solution. It is of interest, therefore, to determine the effect of various concentrations of magnesium in cadmium on the coprecipitation behavior of plutonium. The cadmium solution of simulated blanket material used for the previous study of the coprecipitation behavior of plutonium was employed for this study and additions of magnesium were made to it. After each addition samples of the solutions were withdrawn for analyses at various temperatures. The uranium solubility data were given in an earlier section. In Table 12 the plutonium and americium contents are shown.

It can be readily seen that in solutions from which uranium metal precipitates (magnesium conc $\geq$ 4.47 weight per cent) there is no coprecipitation of plutonium (and probably americium). In the sample taken where UCd_{11} was precipitated -- 2.31 weight per cent magnesium at 401 C -- carrying did take place. The coprecipitation behavior of plutonium with uranium from cadmium solutions therefore checks very well with the phase study information and shows that, just as in the zinc system, plutonium coprecipitates with the intermetallic uranium compound but not with uranium metal.

c. Thermodynamic Studies

Several of the steps in the separations processes under development involve the transfer of a metallic element to or from solution in a liquid metal solvent. The wide range of values of activities found in liquid metal solutions makes knowledge of individual systems mandatory for meaningful equilibrium calculations. In this section are reported measure-

Table 12

PRECIPITATION OF VIOLICIN WITH URANIUM FROM

MAGNESIUM-CADMIUM SOLUTIONS

Charge: ~20.85 g U - 3.1 g Pu - 3 w/o Mo
 "1706" Cadmium

<u>Mg Conc</u> <u>(w/o)</u>	<u>Temp</u> <u>(C)</u>	<u>2. CONC. (w/o)</u>		<u>At conc</u> <u>(w/o)</u>
		<u>Measured</u>	<u>Calc on</u> <u>Mg-free Basis</u>	
2.31	(551	0.0121	0.0124	2.7×10^{-6}
	(401	0.0084	0.0086	1.92×10^{-6}
4.47	(553	0.0120	0.0126	2.7×10^{-6}
	(449	0.0120	0.0126	2.03×10^{-6}
	(398	0.0119	0.0125	2.38×10^{-6}
	(548	0.0116	0.0126	2.04×10^{-6}
7.45	(450	0.0116	0.0126	2.1×10^{-6}
	(400	0.0114	0.0124	2.6×10^{-6}
11.0	(548	0.0110	0.0124	1.95×10^{-6}
	(450	0.0111	0.0125	1.91×10^{-6}
15.7	(550	0.0106	0.0126	1.93×10^{-6}
	(450	0.0105	0.0124	1.94×10^{-6}

ments made on the activities and activity coefficients of uranium dissolved in cadmium.

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

To measure the activity of uranium dissolved in liquid cadmium and the free energy of formation of the uranium-cadmium intermetallic compound (which phase studies have shown to be UCd_{11} , ANL-5924, page 131) a cell of the following type was set up:

The half cell reaction at the uranium electrode is

The half cell reaction at the uranium-cadmium electrode depends on whether the cadmium solution is saturated with respect to the intermetallic compound. If the cadmium solution is not saturated the half cell reaction is:

Under these conditions the overall cell reaction is:

When, as was the case in some of the results reported below, the cadmium solution is saturated with respect to the intermetallic compound the half cell reaction is:

The corresponding cell reaction is:

Examination of the cell as written shows there is a uranium-tungsten thermal operating between the cell temperature and room temperature. Each measured emf was corrected for this thermal emf using the results obtained from a separate experiment as reported in ANL-5896, page 129. The corrected cell

emf is related to the free energy change of the cell reaction by the equation:

$$\Delta F = -nFE \quad (7)$$

In all cases this free energy change is related to the activity a_U of the uranium dissolved in the cadmium by the equation:

$$\Delta F = RT \ln a_U \quad (8)$$

when equation (6) applies to the cell reaction then the cell emf is related to the free energy of formation, ΔF_f° , of the intermetallic compound by the equation:

$$-nFE = \Delta F = \Delta F_f^\circ - RT \ln a_{Cd} \quad (9)$$

where a_{Cd} is the activity of cadmium in the saturated solution.

(9) is only valid when the cadmium solution is saturated with respect to the line compound UCd_{11} .

The data obtained for the first cell set up are given in Table 13. The corrected cell emf is shown as a function of temperature in Figure 23. The cell emf is a linear function of temperature from 280 to about 470 C. Above about 476 C the cell emf is zero.

These data are consistent with the phase diagram previously reported (ANL-5924, page 130), where at about 475 C the intermetallic compound UCd_{11} peritectically decomposes into uranium metal and saturated solution. Above this temperature a saturated solution is in equilibrium with solid uranium, hence the activity is unity. The emf would be expected to be zero as is found experimentally.

The free energy of formation of the uranium-cadmium intermetallic compound, assumed to be UCd_{11} , was computed using equation (9). It was assumed that these solutions are ideal with respect to the cadmium. This would be true if the activities of uranium in the solutions, a_U , are given

Table 13

THERMODYNAMIC QUANTITIES FOR URANIUM-CADMIUMOBTAINED FROM THE CELL

(Data in chronological order)

<u>Temperature</u> <u>(°C)</u>	<u>(volts)</u>	<u>log a_{U}</u>	<u>ΔF_f°</u> <u>(cal/mole)</u>
444.5	0.0165	-0.348	- 1239
426.6	0.0264	-0.570	- 1839
461.4	0.0056	-0.115	- 524
469.1	0.0034	-0.069	- 410
453.0	0.0109	-0.227	- 867
382.9	0.0500	-1.153	- 3488
435.7	0.0226	-0.481	- 1645
449.3	0.0150	-0.314	- 1145
418.1	0.0325	-0.712	- 2313
465.6	0.0054	-0.111	- 528
478.9	0.0000	0.000	--
520.7	0.0001	+0.002	--

FIGURE 23
EMF OF CELL

temperature, are directly proportional to the mole fraction, i.e., Henry's law is valid for the solute. This is not known to be valid for these solutions. However, in the case of the uranium-zinc system where deviations from ideal behavior were much larger, Henry's law was found to be valid (ANL-5924, page 133). It would therefore seem to be a reasonable assumption in this case. Figure 24 shows the standard free energy of formation of UCd_{11} as a function of temperature. It is seen that at the peritectic temperature 475 C, ΔF_f° is approximately -160 calories. This value is consistent with the requirements of the equilibrium:

which requires the relation

$$0 = -\Delta F_f^\circ + RT \ln a_U + 11 RT \ln a_{Cd} \quad (11)$$

to be valid. Since the solution is also in equilibrium with solid pure uranium the activity of uranium is unity, hence at the peritectic temperature:

$$\Delta F_f^\circ = 11 RT \ln a_{Cd} \quad (12)$$

The value of $11 RT \ln a_{Cd}$ is equal to about -178 cal at the peritectic temperature.

The emf of this cell below 475 C fits the straight line:

$$E = 0.4148 - 5.547 \times 10^{-4} T \quad (13)$$

to within ± 0.0009 volts. The activity of uranium a_U in the saturated solutions is given by the equation:

$$\log a_U = 8.3893 - \frac{6273.1}{T} \quad (14)$$

This equation may be combined with the equation for the solubility of uranium in cadmium, i.e.,:

$$\log K_U = 3.2434 - \frac{3909.4}{T} \quad (15)$$

to give the following equation for the activity coefficient of uranium in

FIGURE 24
STANDARD FREE ENERGY OF FORMATION OF UCd_{11}

saturated solutions:

$$\log \gamma_U = 5.1459 - \frac{2363.7}{T} \quad (16)$$

2. Calorimetry
(W. N. Hubbard)

Molybdenum Disulfide
(R. L. Nuttall, E. Greenberg, D. R. Fredrickson)

Molybdenum disulfide may be obtained in two different crystal modifications, (1) the naturally occurring compound having a hexagonal structure, and (2) a synthetic compound having a rhombohedral structure. During the last few months the preparation of a high-purity sample of each of these modifications, 100 g of natural molybdenum disulfide and 75 g of synthetic molybdenum disulfide, has been completed.

The sample of natural molybdenum disulfide was prepared by a procedure similar to that described by McBride⁵ except that (1) flotation oils were removed by washing with petroleum ether previous to the leaching with hydrochloric acid and hydrofluoric acid, and (2) surface acids, the result of possible air oxidation, were removed by washing with ammonium hydroxide after the leaching. The sample was then vacuum dried at room temperature. The starting material for this preparation was donated by Climax Molybdenum Company.

The sample of synthetic molybdenum disulfide was prepared by a procedure substantially the same as that described by Bell and Herfert.⁶ Table 14 summarizes the analyses of the two samples.

⁵ McBride, J. J., "Low Temperature Heat Capacities of Layer and Chain Type Crystal Structures," University of Michigan Doctoral Thesis (1956).

⁶ Bell, R. E. and Herfert, R. E., J. Am. Chem. Soc. 79, 3351 (1957).

Table 14

ANALYSES OF NATURAL AND SYNTHETIC MOLYBDENUM DISULFIDE SAMPLES

<u>Determination</u>	<u>Natural MoS₂</u>	<u>Synthetic MoS₂</u>	<u>Calculated from Formula</u>
Molybdenum (%) ¹	59.70	59.78	59.94
Sulfur (%) ²	39.85	39.80	40.06
S/Mo (Ratio)	1.997	1.992	2.000
Surface Acidity (% H ₂ SO ₄)	less than 0.03	less than 0.03	--
Spectroscopic Impurities	negligible ³	None detected	--

¹ Determined by precipitation from solution with α -benzoic oxime and subsequent ignition to MoO₃ at 600 C,

² Determined by combustion in oxygen, absorption of oxides of sulfur in 7% hydrogen peroxide solution, oxidation of SO₃⁼ to SO₄⁼ with Br₂ and precipitation as barium sulfate.

The deficiencies in material accounted for in the analyses, 0.45 per cent for the natural sample and 0.42 per cent for the synthetic sample, are most probably due to the presence of water. The presence of molybdenum oxide is another possibility. Samples have been submitted for water analysis, X-ray examination and oxygen determination.

The ignition and combustion techniques developed with the preliminary samples of molybdenum disulfide were not entirely satisfactory for the final preparations. The final sample of very fine natural molybdenum disulfide ignites with difficulty because it packs rather firmly. Of the kindling techniques tried, a small amount (2 to 3 mg) of sulfur on the ignition wire at the point of contact with the molybdenum disulfide pellet gives enough local added heat to ignite the pellet and seems to be an acceptable technique.

The platinum-lined bomb will be used for the calorimetric study of molybdenum disulfide. This was made necessary by the observation that a small amount (1 to 2 mg) of brownish-red precipitate remained suspended in the sodium hydroxide solution after a molybdenum disulfide combustion in the Illium bomb. Spectrographic analysis showed this to contain iron, manganese, nickel, and chromium, the main constituents of the Illium bomb.

The techniques now being used for molybdenum disulfide combustions are

- (a) the use of low oxygen pressures (6 to 8 atm),
- (b) the use of a taut platinum wire, on which the sample is formed as a pellet, as the support for the sample,
- (c) the use of a separate ignition wire with an appropriately placed bead of sulfur as kindling, and
- (d) the use of a bomb lined with platinum.

Bomb Calorimeter

(R. L. Hittell, D. Fredrickson, and J. Settle)

The rotating bomb calorimeter has been modified by replacing and/or changing certain parts which have proved to be unsatisfactory. Two series of calibration experiments, one with the Illium bomb, and one with the nickel bomb have been completed; one series with the platinum-lined bomb is under way. Recent rotational energy determinations show that the rotational energy of the system has been approximately halved by the modifications.

Most of the modifications to the calorimeter concerned the jacket motors, stirrers, and pumps. The jacket stirrer motors were replaced with ball bearing motors since this type is better adapted to operate in the vertical position. The nickel bomb is used for combustions in fluorine. The experiments with the Illium bomb were discontinued with the decision to use the platinum-lined bomb rather than the Illium bomb for molybdenum disulfide combustions in oxygen. Further experiments in the platinum-lined bomb are being done.

Fluorine Bomb Calorimetry

(J. L. Settle and L. Stein*)

Preliminary exploratory work in this field has been carried out in makeshift apparatus. Final full-scale apparatus has now been built and is being installed. An exploratory fluorine purification still has been built and a tank of fluorine has been distilled, improving the purity from 97.5 to 99.4 volume per cent. Tests have been carried out showing that no serious damage would result if the fluorine-containing bomb developed a leak while in the calorimeter. A nickel bomb has been calibrated for the calorimetric studies. A supply of pure molybdenum has been obtained for the determination of the heat of formation of molybdenum hexafluoride. Some exploratory calorimetric combustions have been carried out.

* Chemistry Division.

Apparatus. - The full-scale bomb charging and analytical apparatus have been received from Central Shops and are presently being installed in a vacuum frame hood. All lines, the ballast tank and the sodium fluoride trap are nickel. All valves, except those on the bomb are Hoke Type 341 M, or Hoke Type 1103. All pressure gauges are Helicoid with welded bourdon tubes.

Fluorine. - For the most reliable results by fluorine bomb calorimetry, high-purity fluorine should be used in the calorimetric experiments. A low-temperature fluorine purification still has been built in an attempt to remove the impurities such as oxygen, nitrogen, carbon tetrafluoride, and hydrofluoric acid in commercial tank fluorine. Oxygen (bp, -183.0°C) and nitrogen (bp, -195.9°C) are the impurities difficult to remove from fluorine (bp, -188.0°C). Argon (bp, -185.7°C) is even harder to remove but is present to a negligible extent.

A number of cylinders of tank fluorine have been analyzed by the mercury titration method; the fluorine content generally ranges from 97.5 to 99.7 per cent by volume.

One 1/2-lb cylinder of fluorine has been distilled thus far, in which the purity was improved from 97.5 to 99.4 per cent; the recovery was only 40 per cent, however. The still has been modified several times, and the operating conditions are still being investigated. Sharper separations are desired than those obtained thus far.

The still consists of a 210 cc Monel pot with a 3/8-in. ID Monel column approximately 42 in. long, packed with 1/8-in. Podbelniak nickel helices for a height of 34 in. A brass case around the pot and column is evacuated with a diffusion pump to minimize heat leakage. The valves on the commercial 1/2-lb cylinders of fluorine were found to leak at the packing, so the valves were removed from two empty cylinders and replaced by high-pressure valves

manufactured by Autoclave Engineers.

Experimental. - In an attempt to determine what degree of trouble, inconvenience or catastrophe, would occur if a leak developed after a bomb containing fluorine was installed in the calorimeter, three experiments were performed:

(a) A 1/8-in. OD copper line was connected to the bomb charging apparatus. Fluorine was run through this line and allowed to bubble through a beaker of distilled water. The flow rate was kept to less than 100 cc/minute and duration of flow was about five minutes. The only indication of reaction was that the pH of the water decreased from about 4.5 to about 2.0.

(b) The bomb was charged to 535 mm mercury pressure with fluorine which was discharged into a beaker of water at rates varying from about 50 cc/minute to over 500 cc/minute. Only at the highest flow rate was there any visible indication of reaction, which was that a small blue flame appeared at the end of the fluorine discharge tube. After the bomb had been exhausted to atmospheric pressure, it was noted that the water was warm to the touch (about 40 C) and the pH this time had decreased to about 1.0.

(c) The bomb was charged to 4850 mm mercury pressure and then discharged through a copper capillary tube, the end of which had been crimped to simulate a pin hole leak. The only indication of reaction was that the pH of the water decreased from about 4.5 to about 1.5. The conclusion reached from these experiments is that, although a leak of fluorine from the bomb into the calorimeter would spoil the experiment, no serious damage would result.

Molybdenum Hexafluoride. - A supply of 99.95 per cent pure molybdenum has been obtained from Fansteel Metallurgical Corporation in 5-mil thick sheets for use in determining the heat of formation of molybdenum hexa-

fluoride by fluorine bomb calorimetry. A spectrochemical analysis of a sample of this material showed that detectable impurities were all present to an extent less than the lower limits of detection. Specific elemental analysis showed that the sample contains 0.011 per cent carbon, 0.002 per cent silicon, 0.0042 per cent oxygen, 0.006 per cent nitrogen and 0.001 per cent hydrogen.

Preliminary to calorimetric combustions in the bomb an experiment was carried out to see whether fluorination of parts of the bomb during the initial rating period would be sufficient to cause spurious rate observations. The bomb without previous prefluorination (the worst possible circumstance) was charged with fluorine and placed in the calorimeter. No spurious rates were detected. This shows that if thermally significant fluorination of the bomb walls occurs it does so before calorimetric observations start.

The above experiment was followed by a combustion of molybdenum in fluorine in the bomb to determine the maximum extent of attack on the bomb walls that might occur during an experiment. The results showed that considerable reaction did occur. Corrections for the thermal effect might amount to as much as several per cent of the observed heat. However, inasmuch as this was done without previous prefluorination, it is expected that corrections in the future after extensive prefluorination will be much less.

Following the calorimetric combustion of molybdenum in fluorine, it was found that the bomb could not be sealed. The head gasket and the top edge of the bomb body which seats against the gasket were refaced. The bomb was then prefluorinated. This time the bomb was filled with fluorine to a pressure of 800 mm mercury and heated to 195 C for about nine hours. It is certain that this procedure will give a more protective film than prefluorination at room temperature. A series of calorimetric combustions will be carried out

to test this supposition and to get preliminary data on the heat of formation of molybdenum hexafluoride.

High Temperature (1500 C) Enthalpy Calorimeter
(R. L. Muttall and E. D. West*)

Construction of the furnace and of the calorimeter is in process by the Central Shops. A drop mechanism for suspending the sample in the furnace, allowing it to drop into the calorimeter, and then braking to prevent impact with the bottom of the calorimeter has been designed. Assembly drawings are now being made.

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II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES

In connection with the reprocessing of reactor fuels by combined fluidization-volatility processes, the fluorination rates of uranium tetrafluoride by mixtures of fluorine and helium were investigated. At temperatures of 200, 300 and 375 C, maximum fluorination rates were observed at a fluorine partial pressure of about 0.75 atm. This behavior had also been observed previously during the fluorination of plutonium tetrafluoride. Additional studies were performed on the fluorination rates of metallic titanium to determine whether or not a similar effect would be evident. In this case no maximum in the rate was found as the partial pressure of fluorine was increased. The temperature dependence of the fluorination rate of titanium corresponds to an activation energy of about 25.6 kcal/mole.

Additional studies were made of the effect of ADF process variables on the recovery of uranium from low-uranium-zirconium and Zircaloy-2 fuel alloys. This process utilizes fluid-bed drying to convert the aqueous feed solution to a dry, fluidizable powder followed by fluid-bed fluorination to volatilize and permit recovery of the uranium as the hexafluoride.

Current drying operations used synthetic feed solutions containing the equivalent of a two per cent uranium alloy. Dual nozzles were used at bed temperatures of 235 and 300 C. An auxiliary jet attrition nozzle directed into the bed has successfully retarded particle growth which had previously limited the extended operation with a particular bed. A continuous 28-hour run was made, and total combined operating time for this period was about 70 hours. The formation of nozzle agglomerates continues to give some difficulty.

Batch fluid-bed fluorinations of fluid-bed dried material were made in the 2 1/2-inch diameter unit at 500 C. The solid material represents the dried product from a two weight per cent uranium-zirconium alloy solution deposited on a zirconium oxide core. The solids contained an average of 45 per cent of core material. Velocities ranged from 0.19 ft/sec (static bed condition) to 0.95 ft/sec which is about four times the minimum fluidizing velocity for the material used. Results indicated uranium removal, during the period where the removal rate was high, was not dependent upon fluidizing velocity but rather on the amount of fluorine passed through the bed. A high dependence of uranium removal on particle size for this type material was disclosed as a result of the analysis of separate sieved fractions. An eight-hour fluorination at 500 C showed 91 per cent uranium removal for the -100 to +200 mesh size as compared to only 72 per cent for the largest (+20) mesh size.

A fluorine recycle pump is being installed to permit the operation of the fluorinator at high fluorine concentrations without excessive fluorine consumption.

A laboratory corrosion program relative to the fluid-bed fluorination of uranium-zirconium-fluoride powders has been started. Fluorides of the elements found by spectrochemical analyses to be present in the fluid-bed dried zirconium fluoride powders were added to pure zirconium fluoride in the amount of five weight per cent. The mixtures were exposed to fluorine at temperatures near 600 C for 28 hours in the presence of the corrosion specimen, a three-eighth-inch, "A" nickel, annealed tube. Intergranular corrosion was found when lead and manganese fluorides were present. High dimensional change also occurred when lead fluoride was present.

Development work continued on a high-temperature fused-salt process for the recovery of enriched uranium from zirconium matrix fuel alloys. In this process the fuel alloy is dissolved by hydrofluorination in a fused sodium fluoride-zirconium fluoride melt at 600 C. The dissolved uranium is then volatilized by passing fluorine through the melt.

Installation of a pilot plant dissolver-hydrofluorinator constructed of graphite has been completed. Graphite is a promising material of construction for this process step. The unit has been leak tested and dissolution test runs are planned in the next quarter. Further development of salt freeze valves was carried out.

Fluorinator development continued along the lines of frozen-wall designs, in which solid salt protects the vessel wall from corrosion. Installation has started of a electrolytically heated pilot-plant vessel.

Dropwise fluorination has been under study as an alternate means of contacting in the fluorination step. In this process molten salt containing uranium tetrafluoride is sprayed into fluorine and uranium removal is accomplished by the formation and volatilization of uranium hexafluoride. Results have been obtained on measurement of velocity of salt through a nozzle, the time for solidification of spray droplets, and the heat transfer coefficient for drop cooling. A series of fluorination runs is in progress.

The fused fluoride volatility process for the IMFR solution fuel was described in ANL-5820, page 35. Laboratory work was presented in ANL-5924, page 54 and ANL-5959, page 38, which demonstrated the extraction of uranium and fission products with a fused mixture of sodium fluoride and zirconium fluoride. Data are presented to show the rapid oxidation and removal of magnesium from bismuth by extraction into a fused mixture of sodium and zirconium fluoride, which was sparged with hydrogen fluoride.

The exchange of zirconium between irradiated zirconium dissolved in bismuth and molten fused fluoride salt, as well as the extent of the extraction of zirconium and niobium by the fused salt, is demonstrated.

Additional data are reported from the operation of the fluid-bed waste calciner, used to convert liquid wastes to granular solids. A run made at 400 C with an 8:1 dilution of ICPP waste gave an average ruthenium decontamination factor from feed through adsorber of 2.0×10^4 , an average non-volatile decontamination factor from feed through adsorber of 1.2×10^5 and an average decontamination factor for total activity from feed through condenser of 2×10^7 . Transfer of ruthenium from one part of the calciner system to another has been found to occur chiefly during inactive runs indicating there may be a constituent of active feed which inhibits this transfer. The use of the new filtering-blowback assembly for the waste calciner has resulted in a 20 per cent reduction in the total non-condensables leaving the system. Feasibility runs have started on fluid-bed calcining of synthetic Hanford "high-acid" and "low-acid" waste solutions. Volume reduction factors of 8 and 3.5 may be expected for the "high" and "low acid" feeds, respectively.

Feasibility studies have started on the direct continuous conversion of uranium hexafluoride to uranium dioxide by reaction with steam and hydrogen in a 1 1/2-inch diameter fluidized bed. The starting bed is uranium dioxide, which was prepared by fluid-bed pyrohydrolysis of uranium tetrafluoride at temperatures up to 650 C. Several tests with uranium hexafluoride feed with rates up to 5.7 g/min and reactant (steam and hydrogen) excesses of 300 per cent showed a dense uniform brown coating, indicative of uranium dioxide, is formed on the bed material. The tapped bulk density of material increased from 3.7 g/cc to 4.4 g/cc. A negligible quantity of fines was produced.

The planned series of experiments on the mixing of solids in straight and tapered-wall fluid-bed columns using a radioactive tracer technique has been completed. The preliminary results of mixing -20 to +40 mesh copper particles in the tapered bed show that mixing increases with gas velocity and decreases with bed height. A complete analysis of the data will be forthcoming in a topical report.

During this period work on the fluid-bed program was discussed with Messrs. Hahn, Rohde, and Stevens of Phillips Petroleum Company (ICPP) and with Mr. J. Pollack of the Idaho Operations Office, AEC.

A. Fluorine Chemistry
(R. K. Steunenberg, J. Fischer)

1. Fluorination Rates of Uranium Tetrafluoride by Mixtures of Fluorine and Helium
(M. J. Steindler, D. V. Steidl)

In connection with the development of combined fluidization-volatility processes, the fluorination rates of uranium tetrafluoride by mixtures of fluorine and helium have been investigated. The purpose of the study was two-fold. One objective was to obtain rate data which would be useful for a comparison of fluorination rates from fluidized beds with those obtained from boat experiments in the laboratory. The other purpose was to determine whether or not changes in the partial pressure of fluorine would produce the maximum rate at about 0.7 atm which was found in the plutonium tetrafluoride fluorinations (ANL-5820, page 28).

The apparatus consisted of a tube furnace connected in series with two cold traps, a bubbler and two limestone traps. Mixtures of fluorine and dry helium were made in a four-liter supply vessel by adding suitable pressures

of the two gases. The mixture was allowed to stand at least 16 hours before it was used. A solid sample of Mallinckrodt uranium tetrafluoride was placed in a hemi-cylindrical nickel reaction boat inside the furnace tube. The gas flow rate was then adjusted to produce a fluorine flow rate of approximately 50 cc/min, irrespective of the fluorine concentration. The fluorine flow rate was regulated by observing the bubbler, but the total amount used was computed from the pressure drop in the supply tank. The excess fluorine in the off-gas was consumed by the limestone traps.

The reaction rates were calculated from the initial sample weight, the amount of uranium hexafluoride collected in the cold traps, the top exposed surface area of the sample and the time of exposure. The results are presented in Figure 25. At 100 C the data scatter considerably due to the very low rates involved. At 200, 300 and 375 C, however, maxima in the rate curves are apparent with an especially pronounced effect at 300 C. The maxima at 100 and 200 C are not as obvious as those obtained with plutonium tetrafluoride, but at 300 and 375 C the effects are quite similar. The cause of the maximum rates at about 0.75 atm fluorine pressure is not understood. In the case of uranium tetrafluoride it might be attributed to the complex equilibria of intermediate compounds formed during the reaction. Such intermediates have not been observed in the plutonium system, however.

2. Fluorination Rates of Metallic Titanium (M. J. Steindler, D. V. Steidl)

A few experiments were performed on the fluorination rates of metallic titanium. The results are of interest in connection with the corrosion of titanium metal by fluorine and possibly for the preparation of titanium tetrafluoride.

FIGURE 25
FLUORINATION OF URANIUM TETRAFLUORIDE
BY MIXTURES OF FLUORINE AND HELIUM

SOURCE OF UF_4 : MALLINCKRODT
FLUORINE FLOW RATE : ~ 50 cc/min
TOTAL PRESSURE : 1 ATM

Small specimens were cut from a one-eighth-inch sheet of titanium metal. After polishing by wet grinding on 120-grit paper, the specimens were measured, rinsed in ethanol, dried, and weighed before fluorination. The apparatus and techniques used were similar to those described in the previous discussion of the fluorination of uranium tetrafluoride. The metal specimens were contained in a nickel reaction boat during the fluorination. The reaction rate was determined from the weight change of the sample during fluorination. Since the volatility of the titanium tetrafluoride product was not always sufficiently high to assure its absence in the reaction zone, the fluorinated specimen was washed with distilled water and the cleaned metal was reweighed. The initial surface area of the specimen was determined from caliper measurements.

The experimental results are listed in Table 15. The temperature coefficient of the reaction rate under condition of controlled reaction corresponds to an activation energy of about 25.6 kcal/mole. This value is considerably higher than those obtained from uranium and plutonium compounds. The activation energy is not influenced by the partial pressure of fluorine. In contrast to the data obtained with uranium and plutonium tetrafluorides, no maximum in the reaction rate at 0.7 atm fluorine pressure was observed. The effect of flow rate on the fluorination rate is small.

When certain limits of temperature and fluorine pressure were exceeded, the temperature of the titanium specimen was observed to rise above that of the furnace. The experiments in which such excursions occurred were easily distinguished from the normal runs, and the rates from these experiments were not used in computing the activation energy. An interesting correlation of temperature excursions with flow rates and fluorine pressures can be made,

Table 15

FLUORINATION OF METALLIC TITANIUM

Total Pressure: 1 atm
 Gas Mixture: fluorine and helium
 Equipment Description: see pages 134, 135, and 137

Initial Sample Weight (mg)	Initial Area (sq cm)	Weight Loss (mg Ti)	Time (min)	Temperature (C)	Gas Flow Rate (cc/min)	Partial Pressure of Fluorine (atm)	Fluorination Rate (mg Ti/(sq cm)(hr))
842.0	3.95	7.7	60	200	34	0.25	1.95
942.8	4.25	14.8	60	200	68	0.25	3.5
1109.0	4.51	16.5	60	200	111	0.25	3.7
1044.9	4.44	12.7	30	200	175	0.25	2.96
762.6	3.43	607.0	30	300	172	0.25	354.
1099.6	4.51	20.1	60	200	31	0.50	4.5
1073.8	4.44	15.1	60	200	116	0.50	3.4
1070.8	4.51	17.0	60	200	685	0.50	3.8
805.5	3.49	323.0	10	300	116	0.50	555.
1059.8	4.35	22.4	60	200	39	0.75	5.1
776.7	3.43	30.6	60	200	64	0.74	8.9
1078.7	4.39	44.7	60	200	81	0.75	10.
1012.3	4.25	1012.3	60	200 ^a	113	0.75	238.
1090.5	4.41	632.3	60	200 ^a	143	0.75	143.
1115.9	4.49	109.0	60	200 ^a	158	0.75	24.
795.4	3.38	461.6	10	300 ^a	68	0.75	142.
795.5	3.38	0.2	60	100	48	1.00	~0
760.8	3.33	8.0	30	200	32	1.00	4.8
752.8	3.33	752.8	30	300 ^a	72	1.00	456.
787.7	3.43	503.9	10	300 ^a	105	1.00	882.

^aExperiments in which temperature excursions were observed.

however. In general, the flow rate necessary for an uncontrolled reaction appears to be inversely related to the partial pressure of fluorine. The total amount of fluorine passed over the titanium sample in a given time period seems to determine the point at which an uncontrolled reaction occurs.

B. ADF Process Development for Enriched Uranium-Zirconium Fuel

ADF processes embrace a variety of anhydrous direct fluorination schemes, as well as schemes involving aqueous dissolution, drying, and fluorination. Development work is being carried out on both laboratory scale and engineering scale to apply the ADF process scheme to enriched uranium-zirconium fuel alloys. The process involves dissolution of the fuel alloy in aqueous hydrofluoric acid containing an oxidizing agent, followed by conversion of the solution to dry granular solids by spraying it into a fluidized bed of granular material. The solids are then fluorinated in a fluid-bed reactor to remove the uranium as the volatile hexafluoride.

1. Engineering-Scale Studies (A. A. Jonke)

a. Fluid-Bed Drying (J. Barghusen, N. Levitz, D. Raue, M. Jones)

Additional investigations of operating variables were performed in the six-inch Inconel fluid-bed dryer while producing material for fluid-bed fluorination studies. Operations were conducted at bed temperatures of 300 C and 235 C using dual feed nozzles. The feed for all of the runs simulated the solution resulting from dissolution of a uranium-Zircaloy-2 alloy. The use of an air jet to produce attrition of the bed particles has proved successful in reducing particle growth during the dryer operation.

(1) Operating Conditions (See Table 16)

The feed solutions used in all the runs contained about 1.4 M zirconium, 6.3 M fluoride and 0.012 M uranium as uranyl fluoride, equivalent to a two weight per cent uranium alloy. The requisite amounts of tin, nickel, chromium, and iron were added to the feed to simulate the dissolution of a uranium-Zircaloy-2 alloy*. The feed solutions were prepared either from a commercial zirconium tetrafluoride solution or by redissolving dryer products in aqueous hydrofluoric acid at 80 C.

In one case, the dissolution of dryer products resulted in an unstable solution. When the solution was cooled to room temperature, a considerable amount of crystalline solids precipitated. These solids dissolved readily upon reheating of the solution to 40 C. This solution was preheated to 50 C before being fed to the calciner in Run ZCP-61. An attempt will be made to determine the causes for this anomalous solution behavior.

The starting bed for each run was the final bed from the previous run sieved to the desired particle size. Since the particle size distribution of the starting beds was nearly the same for each run, a direct comparison of particle growth rates could be made.

Bed temperatures of 300 and 235 C were used in order to produce material which will subsequently be used to establish the effect of drying temperature on uranium removal rate during fluorination. The fluidizing gas velocity during runs ZCP-57 to 59 was maintained at two ft/sec. The velocity was lowered to 0.9 foot per second for Runs ZCP-60 and 61 in which the particle size of the bed was considerably smaller, requiring less gas for

* Zircaloy-2 contains 1.5 per cent tin, 0.15 per cent iron, 0.10 per cent chromium, and 0.05 per cent nickel, the remainder being zirconium.

Table 16

OPERATING CONDITIONS FOR RUNS MADE IN SIX-INCH FLUID-BED DRYER

Uranium Concentration in Feed: 0.012 M
 Zirconium Concentration in Feed: 1.4 M
 Fluoride-to-Zirconium mole ratio: 4.5
 Atomizing gas pressure: 30 psig
 Feed rate (two nozzles): 50 ml/min each
 Nozzle orifice diameter^a: 0.040 inch
 Starting Bed: final bed from
 previous run,
 sieved through
 20 mesh screen

<u>Run Number</u>	<u>Source Material for Feed Solution</u>	<u>Total Fluidizing Velocity^b (ft/sec)</u>	<u>Attrition Jet Bed Air Rate (cu ft/min)</u>	<u>Temp (C)</u>	<u>Run Time (hr)</u>
ZCP-57, 58	ZrF ₄ Solution	1.7	-	300	13.8
ZCP-59	Redissolved Products	1.7	-	300	12.5
ZCP-60	ZrF ₄ Solution	0.9	1.80	300	12.2
ZCP-61	Redissolved Products	0.9	1.80	235	28.0

^aDuring the first eight hours of Run ZCP-57, 58 two 0.028-inch nozzles were used. These were replaced by two 0.040-inch nozzles.

^bIncludes attrition jet air for Runs ZCP-60 and 61.

adequate fluidization. In these two runs approximately 25 per cent of the fluidizing gas was contributed by an attrition air jet which was introduced to help control the particle size distribution in the bed. The air jet consisted of a 0.047-inch orifice drilled in the wall of a one-fourth-inch tube and was located one half inch above the gas dispersion plate and one half inch from the column wall. The tube entered the column at a downward angle of 45 degrees from the vertical, and the jet was directed upward at a 45-degree angle.

The study of the effect of multiple feed points on particle growth and dryer operability was continued using two 0.040-inch liquid spray nozzles. One of the spray nozzles was redesigned for Run ZCP-61, so that the face of the nozzle projected one fourth inch into the bed. This design was intended to allow better "wiping" of the nozzle face by the fluidizing solids, thus preventing the formation of nozzle agglomerates. Preliminary results indicated no definite improvement.

(2) Operating Performance and Evaluation

Continual particle growth occurred during Runs ZCP-57, 58 and 59. The rate of growth was equivalent to that observed in previous runs. Better containment of the fines with sintered metal filters did not seem to reduce the rate of particle growth. A high percentage of the fines are probably suspended above the bed in the filter zone and evidently do not provide sufficient nuclei in the spray zones to overcome particle growth. The use of dual feed nozzles had no appreciable effect on particle growth rate.

The operation of the dryer with the auxiliary air jet was very good. The results of Runs ZCP-60 and ZCP-61 indicate that it is

possible to provide adequate attrition continuously throughout a run to maintain a desirable particle size distribution as shown in Figure 26. The dryer was operated continuously for 28 hours in Run ZCP-61 whereas all other runs were made in four- to six-hour periods on successive days. During Run ZCP-60, the amount of attrition was slightly excessive, and more fines (-200 mesh) were produced than normally desired. The final bed contained 26.6 per cent minus 200 mesh particles and could be fluidized at a minimum velocity of 0.1 foot per second. In Run ZCP-61 there was no definite trend upward or downward in particle size, although there was appreciable scatter in the amounts of coarse and fine particles in various samples, within the range indicated in Figure 26. Since the amount of attrition jet air was approximately the same in both runs, the greater rate of attrition in Run ZCP-60 may indicate a more friable product at the 300 C drying temperature than at the 235 C temperature used in Run ZCP-61. Additional runs must be made before the effect of auxiliary attrition jets on particle size control can be fully evaluated.

The formation of hard agglomerates on the face of the spray nozzles seems to be the major remaining problem associated with the operation of the fluid-bed dryer. These nozzle formations have been found in the final bed of almost every run in amounts ranging from 0.5 to 10 per cent of the final bed weight. An intensive study is being planned to determine the cause of the formations and to find means for eliminating this problem. Separate evaluation of the performance of the special nozzle which projected into the bed in ZCP-61 was not possible since at the end of the 28-hour run, evidence of malfunctioning of the dryer was found. Numerous small lumps found in the bed may have been caused by a thermowell positioned too close to the spray zone.

FIGURE 26
EFFECT OF JET ATTRITION ON PARTICLE SIZE
DISTRIBUTION DURING FLUID-BED DRYER RUNS

ATTRITION JET ORIFICE - 0.047 INCH DIA
ATTRITION AIR RATE - 1.8 CFM

(3) Jet Attrition Air Studies

Preparatory to the use of the jet attrition technique in Run ZCP-60, tests were performed in the three-inch Monel column to ascertain the amount of attrition produced by the introduction of a high-velocity air jet into a fluidized bed of dryer product. The extent of attrition was determined by calculating the mean weight diameter before and after the test. No liquid feed was used in these tests and all of the tests were of six hour duration.

Three types of air jets were evaluated:

- (1) spray nozzles ranging from 0.016 to 0.060 inches in orifice diameter,
- (2) the air annulus of a 0.040-inch spray nozzle with an area equivalent to a circular nozzle opening of 0.066 inches,
- (3) a 0.047-inch orifice drilled in the wall of a horizontal tube.

The horizontal tube was installed such that the air jet was directed vertically upward, concurrent with the fluidizing gas, rather than horizontally toward the opposite wall as in all other tests with spray nozzle orifices. This was expected to remove any target grinding effect resulting from particles colliding with the opposite wall. The annulus-type jet was tested to ascertain whether the atomizing air of the spray nozzle was adequate for the desired rate of attrition.

The results summarized in Table 17 and graphically presented in Figure 27 suggest that the rate of attrition expressed as the decrease in average particle diameter is a linear function of the mass flow rate

Table 17

ATTRITION OF FLUID-BED DRYER PRODUCT PARTICLES BY AN AIR JET

Equipment: 3-inch diameter reactor
 Bed Weight: 2.5 kilograms
 Fluidizing Gas Velocity: 2 ft/sec
 Time: 6 hours
 Temperature: 28 C (room temperature)

Type of Jet	Orifice Diameter (in)	Supply Air Pressure (psia)	Air Flow Rate $\times 10^4$ (lb/sec)	Average Rate of Change of Particle Diameter (mm/hr)
Nozzle	0.016	55	2.55	-0.010
Nozzle	0.016	95	4.29	-0.009
Nozzle	0.040	45	12.8	-0.015
Nozzle	0.060	45	28.9	-0.028
Annulus	0.066 ^a	75	33.8	-0.027
Annulus	0.066 ^a	95	38.0	-0.033
Orifice	0.047	75	30.4	-0.046

^aDiameter of a circle equal in area to the air annulus used with a 0.040-inch pneumatic spray nozzle.

FIGURE 27
ATTRITION OF FLUID-BED DRYER PARTICLES BY AN AIR JET

of air. Since in all the tests the velocity of the air from the nozzles or annuli was near the sonic velocity, the energy transferred to the particles was only a function of the mass flow rate of the air. The flow from a sharp-edged orifice however, apparently does not follow this behavior, the results indicating that the attrition produced by the orifice jet was much greater than that produced by the other types for the same air flow.

The quantity of air used in the annulus tests was equivalent to the amount used in atomizing the liquid feed in the dryer runs. Apparently most of the energy of the air fed to the spray nozzle is expended in atomizing the liquid feed. During calciner operation some attrition might be occurring but at a rate too low to be of consequence because of the relatively low friability of the zirconium fluoride particles produced. In other systems which produce a product of a more friable nature, the excess energy of the atomizing air might be sufficient to control particle size.

(4) Properties of Calcined Solids

The nature of the materials produced in the fluid-bed dryer has not been completely characterized because of a complex mixture of species is produced, some of which are unidentified. Identification of the material has been encumbered by the presence of zirconium oxide core material. Preliminary results (reported in ANL-5959, page 49) have indicated that the material is a mixture of several fluoride species, including zirconium fluoride, zirconium fluoride mono-hydrate, zirconyl fluoride, and others, the presence and relative amounts of these being dependent upon the drying temperature and the environment.

The final bed of Run ZCP-60 represents the result of 64 hours of operation at a feed rate of 100 milliliters per minute, and the

zirconium oxide starting bed has been essentially displaced. This material is thus representative of the solids formed in the dryer at 300 C. Chemical analyses show the following composition: 55 per cent zirconium, 31 per cent fluorine, 7 per cent oxygen, and 1 per cent uranium. These values indicate that the material is not entirely zirconium tetrafluoride since the fluorine to zirconium mole ratio is only 2.7. Ignition of the material at 450 C resulted in the evolution of two per cent volatile material which analyzed as approximately 75 per cent hydrogen fluoride and 25 per cent water. Other chemical analyses and X-ray diffraction studies are being made on this material.

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

Additional batch studies were made in the 2 1/2-inch diameter Monel fluid-bed fluorinator (see ANL-5789, page 39) on the removal of uranium from a uranium-zirconium fluoride powder. This material was prepared by calcining a feed solution containing the equivalent of a two weight per cent uranium-Zircaloy-2 alloy in the fluid-bed dryer at 300 C. The uranium, present as uranyl fluoride in a zirconium fluoride matrix, is reacted with fluorine gas and recovered as the volatile hexafluoride. Previous work on materials containing the equivalent of up to 10 weight per cent alloys indicated about 99 per cent uranium removal could be achieved in 12 hours of fluorination at temperatures of 500 and 600 C.

(1) Operating Conditions

Experiments were performed to determine the effect of fluidizing gas velocity and particle size (or coating thickness) on uranium removal. The solid feed material contained a core of zirconium oxide (the

starting bed material for the dryer operation). The experiments consisted of two successive four-hour fluorinations at 500 C using 15 per cent fluorine in nitrogen as the fluidizing gas stream. Tests were made over a range of gas velocities, 0.18 ft/sec (a static bed condition) to 0.95 ft/sec which is about four to five times the minimum fluidizing velocity for the material used. Uranium analysis of the various mesh size fractions in the bed was made before and after fluorination.

(2) Results and Discussion

Data indicate velocity was important only in that higher velocities introduced more fluorine for a given period of time. Uranium removal, for the period where removal rate was high, was proportional to the amount of fluorine passed through the bed (see Table 18 and Figure 28). At the low gas velocities, comparatively little uranium was removed in eight hours because of the small amount of fluorine introduced. The first four to six cubic feet of fluorine fed to the reactor were consumed with little or no release of uranium hexafluoride. Analyses of the exit gas in Runs 26 and 27 showed that no excess fluorine left the bed until about four cubic feet had been introduced and most of the fluorine was still being consumed after eight cubic feet had been fed (see Figure 28). This fluorine probably reacted with the zirconium oxide core (present to the extent of about 45 weight per cent) and with zirconium oxyfluoride and water of hydration present in the dried coating. The use of 100 per cent fluorine in place of 15 per cent fluorine will permit the introduction of larger amounts of fluorine gas in the same time.

For Run 29, made at the highest gas velocity, evaluation of the data from the sieved mesh fractions disclosed an apparent effect of

Table 18

CONDITIONS AND RESULTS OF FLUID-BED FLUORINATION EXPERIMENTS

Equipment: 2 1/2-inch dia Monel column
 Fluorination Temperature: 500 C
 Inlet Gas Composition: 15% F₂, 85% N₂
 Initial Uranium Concentration: 0.75 per cent

Fluorination (Run No.)	Gas Velocity (ft/sec)	Uranium Concentration After Quantity of Fluorine Passed			Condition of Bed ^a
		7.5 cu ft	8.8 cu ft	17.4 cu ft	
29	0.95	0.51	0.46	0.21	Slugging fluidization
25	0.57	-	-	0.24	Well fluidized
26	0.27	-	0.55	-	Upper part fluidized; velocity just above minimum for fluidization
27	0.19	0.61	-	-	Static Bed

^aAs determined in glass column with nitrogen as fluidizing gas.

FIGURE 28
EFFECT OF GAS VELOCITY ON URANIUM REMOVAL RATE

particle size on uranium removal, greater removal being observed for smaller sized particles (see Table 19 and Figure 29). After a two hour exposure at 500 C, uranium removal ranged from 51 per cent for the -20 to +40 mesh fraction to about 83 per cent for the -100 to +200 mesh fraction. Corresponding eight hour results were 76 and 91 per cent. The bed composite sample gave an average removal of 86 per cent for the eight-hour period. The data in Figure 29 show that the rate of uranium removal was rapid until about 85 per cent of the uranium had been removed from the composite bed, after which the rate decreased sharply to a low value. The rate of uranium removal was a function of particle size during the initial two-hour fluorination period, but was independent of particle size during the subsequent six-hour period of continued fluorination (as indicated by the parallel dotted lines in Figure 29).

A possible explanation for the relatively poor results may be a sintering effect as a result of the coating and core being fluorinated. The core to coating thickness ratio varies with particle size (see Table 19) due to the nature of the dryer operation. Thus the smaller particles, having a lower percentage of core material, might be subjected to less sintering. Future work will attempt to remove the core and matrix composition as variables by extending the dryer operation so that all of the core is displaced and by hydrofluorinating the dryer product, converting all of the zirconium species to the tetrafluoride. This is also expected to remove the water. Hydrofluorination will also substantially reduce fluorine consumption.

Installation of a fluorine recycle pump and auxiliaries is in progress. This equipment will permit operations at higher fluorine concen-

Table 19

ANALYSIS OF MESH SIZES FROM FLUID-BED FLUORINATION EXPERIMENTS

Fluorination Temperature: 500 C
 Inlet Gas Composition: 15% F₂, 85% H₂

Data from Run U/Zr-29

<u>Mesh Fraction</u> <u>(Size)</u>	<u>Average</u> <u>Weight</u> <u>Per Cent</u>	<u>Ratio of</u> <u>Core to Particle</u> <u>Diameter^a</u>	<u>Initial</u> <u>Uranium</u> <u>Concentration</u> <u>(%)</u>	<u>Percentage Uranium</u> <u>Removal After</u>		
				<u>2 Hours</u>	<u>4 Hours</u>	<u>8 Hours</u>
+20	1.9	0.79	0.51	-	-	72.5
-20, +40	13.1	0.78	0.53	51	-	76.5
-40, +60	37.2	0.73	0.62	64.5	71.0	82.3
-60, +100	37.7	0.62	0.79	74.8	77.2	87.4
-100, +200	9.9	0.39	1.02	83.3	-	91.2
Composite Bed Sample	100.0		0.75	68	-	85.9

^aBased on assumption of two concentric spheres, zirconium oxide core surrounded by zirconium and uranium fluorides.

FIGURE 29
EFFECT OF PARTICLE SIZE AND FLUORINATION TIME ON REMOVAL
OF URANIUM FROM URANIUM-ZIRCONIUM MIXTURES

trations with overall reduction in fluorine consumption. Other modifications to the equipment are being made to permit collection of the uranium hexafluoride.

A statistical approach may be applied to the future fluid-bed fluorination studies in an attempt to delineate the major factors affecting uranium removal.

c. Corrosion During Fluid-Bed Fluorination
(L. Hays, W. Seefeldt)

Initial runs in the fluid-bed fluorination of uranium-zirconium fluoride mixtures had revealed a severe form of dimensional attack that occurred in the vapor phase of the reactor well above the fluid-bed. This severe corrosion was not found in subsequent test specimens and the degree of corrosion appeared to decrease as the runs progressed. This behavior suggested that an impurity, possibly a volatile fluoride, might be contributing to the corrosion.

(1) Spectrochemical Analyses of Corrosion Specimen in Fluid-Bed Fluorinator

Spectrochemical analyses of a thin layer of scale scraped from sections of corrosion specimen No. 2 (see ANL-5959, pages 55 to 57, for other corrosion data on this specimen) were made. This 0.250-inch OD nickel rod was exposed to fluorine during fluid-bed operations at 500 to 600 C for 32 hours. The concentration of nearly all impurities present was found to reach a maximum about 30 to 45 inches above the gas distributor plate. This compares with a fluidized-bed height of 11 inches, and with a maximum corrosion found at an elevation of 20 inches. This maximum corrosion did not occur at the point of maximum impurity concentration. The magnitude of the peaking varied with the impurity—manganese, copper, and tin having the most pronounced concentration peaks.

(2) Corrosion Tests

A series of bench-scale tests was made to evaluate the corrosion of nickel by fluorine gas flowing through a fixed bed of zirconium tetrafluoride containing various metallic inorganic fluorides. The basic test unit is shown in Figure 30; the inner of the two tubes is the test specimen and the annular space is filled with zirconium fluoride plus additive. A decreasing temperature gradient was intentionally provided to enable possible volatile materials to escape the bed and condense in higher portions of the equipment. The tubing specimens were annealed "A" nickel, all from the same heat of material.

The addition of lead fluoride accelerates both dimensional change and sub-surface corrosion, while manganese fluoride was found to increase intergranular corrosion. Additions of the fluorides of cobalt, chromium, tin, and titanium had no accelerating effect.

In future work, it is planned to study the effects of fluorine impurities on the degree of intergranular attack occurring in nickel.

(3) Evaluation of Fluid-Bed Specimen No. 4.

Specimen No. 4 consisted of a strip of nickel 0.032 inch by 0.75 inch and was in the fluid-bed during runs U/Zr-21 to U/Zr-24. Total exposure was 32 hours at 600 C. Shallow pitting 1 to 1.5 mils deep was observed on the bottom 32 inches of the strip. No sub-surface attack was noted in any of 20 cross-sections taken from the specimen; this is not consistent with prior observations.

FIGURE 30
EXPERIMENTAL APPARATUS FOR DETERMINING EFFECT
OF ADDITIVES TO ZrF_4 ON THE CORROSION
OF NICKEL IN FLUORINE

2. Laboratory Fluidization Studies
(R. K. Steunenberg)

a. Fluorination of Calcined Fuel Solutions
(C. Johnson, G. Redding and M. Jones)

Work has begun on the problem of uranium removal from calcined solutions of enriched uranium-zirconium alloys. Variables being investigated are the effects of time and temperature on uranium removal from pilot-plant materials containing approximately one per cent uranium.

C. Fused Salt Process Development
(W. Mechem)

In the fused-salt process enriched uranium in a zirconium matrix fuel alloy is dissolved by hydrofluorination in a fused sodium fluoride-zirconium fluoride melt at 600 C. The dissolved uranium is then fluorinated by passing fluorine or its equivalent through the melt. Fractional distillation provides the final purification and decontamination of the uranium hexafluoride.

1. Graphite Dissolver Installations
(R. W. Kessie, W. Murphy, A. Rashinskas, W. Mechem)

Graphite is a promising material of construction for the hydro-fluorination step, and a pilot plant graphite dissolver unit has been installed for process run studies. Leak testing has been completed and component checks are under way. Dissolution tests are scheduled in the next quarter. The basic features of the unit have been described in previous reports.

Further development of salt freeze valves was carried out. The sealing of transfer lines by means of freeze valves has the advantage of avoiding mechanical operation in a molten salt environment. Since freezing of the salt involves a shrinkage in volume by about 25 per cent, a reasonably long salt path must be provided to allow any cracks initially formed to be sealed before solidification is complete. Re-melting must be accomplished by

heating uniformly to provide a path for escape of the lower density liquid. A freeze valve consisting of a loop of autoresistively heated pipe is well-suited to these requirements.

To avoid mechanical complications, the transfer of molten salt from one vessel to another is accomplished by differences in liquid head and gas pressure in the vessels. A loop in the transfer line constitutes the main portion of the freeze valve in which a salt seal is provided upon cooling. The freeze valve is vented to prevent siphoning-out of the seal loop and to allow the transfer lines to drain to both vessels. The chief problem with this arrangement occurs when the vessel from which the transfer is being made becomes completely empty. The high gas pressure in the vessel causes a mixture of gas and salt to blow into the vent riser with hazard of carrying salt into the gas valves.

To avoid this problem an unvented freeze valve has been designed and tested. This valve contains a trap which holds a small volume of the molten salt during transfer. When the transfer is completed the salt in the trap is permitted to drain into the seal loop to provide the necessary frozen salt seal. Syphon-breaking is accomplished by introduction of inert gas under pressure. In this system large vent lines are not required and there is no salt entrainment problem. This valve has been successfully tested in a transparent model using air and water. A metal unit is being fabricated for tests with molten salt.

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

By cooling the wall of the fluorination vessel a protective layer of solid salt can be formed. In such designs a method of internal heating of the salt is required. Tests in mock-up equipment described in the previous

report indicated the feasibility of either induction or electrolytic heating in such a unit, and design studies are continuing. An electrolytically heated pilot plant unit is being assembled for testing. Heat is to be generated directly in the molten salt by current passing between two electrodes.

3. Dropwise Fluorination Studies
(J. D. Gabor)

Because of high corrosion rates of containers in which molten salt is sparged with fluorine, an alternate means of contacting fused salt and fluorine is being investigated. In this dropwise fluorination scheme, molten salt containing uranium tetrafluoride is sprayed into a fluorinating atmosphere, and the vessel walls are kept below the melting point of salt. Uranium removal is accomplished by fluorination and volatilization of uranium from the salt spray droplets.

a. Velocity of Fused Salt Discharged from Nozzle

Spray tests of the sodium fluoride-zirconium fluoride fused salt were made from a nozzle in order to determine the volumetric discharge rate and the linear velocity of droplets at the nozzle. In two tests with a solid cone spray nozzle under 40 psig gas pressure, the salt collected during a measured portion of the spray period was weighed. The volumetric flow rate for the 0.026-inch orifice was 242 ml/min. For comparison the discharge rate of tetrabromoethane was measured under the same conditions. The density of tetrabromoethane is about 10 per cent lower than the 200 lb/cu ft density of the salt. Also for reference, the theoretical velocity was calculated assuming complete conversion of the gas pressure head (40 psig) into salt velocity head (neglecting friction). These results, given in Table 20, show that the discharge velocity is approximately 40 ft/sec.

Table 20

VELOCITY OF LIQUID DISCHARGE FROM A SPRAY NOZZLE

(Solid Cone Spray Nozzle, 0.026-inch orifice,
40 psig pressure head)

<u>Basis</u>	<u>Discharge Velocity</u> <u>(ft/sec)</u>
NaF-ZrF ₄ molten salt	38.8
Tetrabromoethane	41
Calculated from pressure head	43

b. Determination of Droplet Size and Solidification Point

Three spray tests were made in which droplets at various distances from the nozzle were collected and sizes measured. The salt at 650 C was sprayed through the solid cone nozzle previously used. Size measurements were made by observation with a microscope. The results of these tests are presented in Figure 31, in which relative frequency of drop sizes in per cent is plotted against drop size in microns for six distances from the nozzle, ranging from 15 to 40 inches. The number of droplets measured for each distance ranged from 100 to 393 as shown in the figure.

Not all material collected in the one and one-eighth inch diameter copper collection cups was in the form of discrete droplets. This indicated that a substantial portion of the salt had not solidified at the point of collection. Since droplet measurements were made only on solidified material, the droplet size distribution in Figure 31 show a rapid falling-off in relative numbers for the larger size droplets, which require more time to solidify. The largest or critical size droplets solidified at the various distances are indicated on the figure as the largest size at which 90 per cent of the droplets were solid. At 15 inches from the nozzle, droplets smaller than 100 microns are solid, while at 40 inches, droplets of over 200 microns have solidified. The size distributions in the figure also show a fairly flat distribution of droplet sizes with this solid-cone nozzle, from about 30 microns to over 200 microns diameter.

c. Cooling Time and Heat Transfer Coefficients for Spray Droplets

For the conditions in these spray tests calculations were made of the time for droplets to cool to the freezing point and the corresponding

FIGURE 31
EFFECT OF DISTANCE FROM NOZZLE
ON DROP SIZE DISTRIBUTION
(Solidified droplets of molten salt sprayed at 650 C)

heat transfer coefficient. For droplets slowed by air resistance the equation relating time (t) and distance (y) is:

$$y = \frac{1}{\alpha^2} \left(-\frac{g}{2} - \frac{V_0}{\alpha} \right) + 1/\alpha \left(gt - \frac{g}{\alpha} + V_0 \right)$$

where:

$$\alpha = C N_{Re}^{-3/4} \frac{\mu}{D^2 \rho}$$

N_{Re} = Reynolds number

C = drag coefficient

g = gravity constant

μ = viscosity of air

ρ = density of salt

D = diameter of drop

V_0 = initial velocity = 38.8 ft/sec

Since the drag coefficient is a function of the Reynolds number, α changes with decreasing drop velocity. The equation was therefore solved by an incremental method.

The heat transfer coefficient from drop to air was calculated for the two stages of heat removal, i.e., cooling to the melting point and removal of the heat of fusion. For the first stage, cooling from 650 C to the salt melting point (505 C), the following equation applies:

$$h = \frac{1}{t_1} \frac{\rho C_p r}{3} \ln \frac{T_1 - T_s}{T_2 - T_s}$$

where

h = heat transfer coefficient, BTU/(hr)(sq ft)(°F)

t_1 = time for the first stage

r = drop radius, ft

C_p = heat capacity, BTU/(lb)(°F)

T = temperature, (1) initial, (2) final, (s) surroundings

For the second stage, removal of the heat of fusion at 505 C, the following equation applies:

$$h = \frac{1}{t_2} \frac{\rho \Delta H r}{3} \left(\frac{1}{T - T_s} \right)$$

where

ΔH = heat of fusion

It was assumed that the heat transfer coefficients for both stages were equal and that the total solidification time, determined by the time for the drop to traverse the distance from the nozzle to the cup, was equal to t_1 plus t_2 .

The results are summarized in Table 21. The calculated heat transfer coefficients range from 72 to 144 BTU/(hr)(sq ft)(F). The Nusselt number ($\frac{hD}{k}$) compares favorably with that predicted from the correlation⁷

$$\frac{hD}{k} = 0.37 (N_{Re})^{0.6}$$

Figure 32 shows how these heat transfer data compare with a correlation of data by other workers. The fused salt data extend the range of the previous data to smaller size spheres than used in any previous study.

d. Fluorination Tests

Two runs were made in which fused salt was sprayed into a fluorine atmosphere. The salt consisted of a 40 mole per cent zirconium fluoride, 60 mole per cent sodium fluoride mixture, to which was added one weight per cent uranium tetrafluoride. The salt temperature was brought up to 760 C for spraying, and the fluorine in the vessel was at room temperature. Helium at 40 psig was used to force the molten salt through a single-phase hollow-cone nozzle (Spraying Systems Co. #1/4 LN3). The overall uranium removal in the first run (SY-1) was eight per cent, as determined by an X-ray

⁷McAdams, W. H., Heat Transmission, 3rd Edition, McGraw-Hill Book Company, New York, (1954), p. 266.

Table 21

SOLIDIFICATION TIME AND HEAT TRANSFER COEFFICIENTS

FOR FUSED SALT DROPLETS

Initial velocity: 38.8 ft/sec
 Initial temp: 650 C (T_1)
 Final temp: (mp): 505 C (T_2)
 Room temp: 20 C (T_s)

Distance from Nozzle (inches)	Drop Size (microns)	Ave Velocity (ft/sec)	Ave N_{Re}	Predicted $\frac{hD^2}{k}$	Calculated $\frac{hD}{k}$	Solidification Time (sec)	h (BTU/(hr)(sq ft)(°F))
15	100	15.5	32.2	2.9	2.2	0.08	95
18	133	20.4	56.0	4.1	4.5	0.07	104
21	133	17.6	47.3	3.8	3.2	0.10	101
24	133	14.1	38.7	3.3	2.4	0.133	76
27	142	14.7	43.1	3.5	2.4	0.15	72
40	217	20.2	90.4	5.5	5.1	0.165	100

^aBased on correlation shown in Figure .

FIGURE 32
CORRELATION OF DATA ON HEAT TRANSFER FROM SPHERICAL PARTICLES TO GAS

spectral analysis. It is planned to obtain analyses of screened fractions of this sprayed material to determine the effect of drop diameter on uranium removal.

Based on previous experience, it was assumed that a sponge pretreatment of the salt before spraying mixed the fluorides and fluorinated the oxides. The spray gas was a mixture of helium, hydrogen and hydrofluoric acid. It was thought that the oxides present might react initially with the fluorine and delay the formation of uranium hexafluoride from the uranium tetrafluoride.

Two mechanical means were used to keep the nozzle free of salt. A nickel stopper rod was inserted from above into the nozzle coupling on the salt side of the nozzle, and a nichrome wire was inserted into the nozzle orifice on the fluorine side of the nozzles. Both of those devices were operated through gas seals. In addition, to prevent oxidation the air was evacuated from the vessel before the pretreatment step, and the vessel was then filled with nitrogen to 3 psig. The nitrogen was then subsequently evacuated, and fluorine was introduced into the vessel.

Future plans are to alter the spray conditions by heating the fluorine to 200 C and thus extend the time of the spray droplet in the fluorine atmosphere before solidification.

D. Liquid Metal Fuel Reprocessing
(J. Fischer, M. Adams, H. Phillips*)

Magnesium is added to the LMFR solution feed as an antioxidant to prevent the loss of uranium. In the initial phase of the fluoride volatility process

*Special Scientific Employee from the Babcock and Wilcox Company.

for the EMF the reaction of the fuel with the fused fluoride results in the oxidation of the magnesium. The results presented here indicate that the extraction of magnesium by the fused salt is rapid and goes to completion upon adding hydrogen fluoride to the system. The experiments also indicate the behavior of zirconium and niobium in the fuel.

The "stirring-extraction-liquid sampling" apparatus and procedure for the extraction experiments, the data for which are shown in Tables 22 and 24, were described in ANL-5959, page 39. The "shaking experiments", the data for which are shown in Table 23, were described in ANL-5924, page 54.

Bismuth alloys used in the experiments shown in Tables 22 and 24 were made in a molybdenum crucible in the stirring apparatus. The alloy used in the shaking experiment shown in Table 23 was prepared by the method described in ANL-5896, page 43. The fused salt was 55 mole per cent sodium fluoride and 45 mole per cent zirconium fluoride (see ANL-5924, page 55 for analysis).

Uranium in all of the samples was determined polarographically using the amalgam leach procedure described in ANL-5853, page 127. Magnesium, for the experiment shown in Tables 22 and 23, was determined with ethylene-diamine-tetra-acetic acid (EDTA), using eriochrome black T as an indicator. The magnesium determinations of the samples shown in Table 24 were done spectrographically.*

It is evident from the data shown in Tables 22 and 23 that magnesium is oxidized and extracted rapidly by the fused salt even before hydrogen fluoride is added. Upon sparging hydrogen fluoride through the melt, at approximately 0.4 to 0.6 gram per minute, the magnesium concentration in the bismuth is lowered below the minimum limit of detection. It is assumed that all of the magnesium is converted to magnesium fluoride and extracted by the salt phase.

*The magnesium determinations shown in Table 22 were done at the Alliance Research Center of Babcock and Wilcox Company.

Table 22

EXTRACTION OF URANIUM AND MAGNESIUM FROM BISMUTH USING
SODIUM FLUORIDE-ZIRCONIUM FLUORIDE AND HYDROGEN FLUORIDE

Stirring Extraction-Liquid Sampling Equipment^a

	Temperature: 550 C	
	Salt: 90 g	
	Bi alloy: 400 g	
	Uranium Concentration ^b ppm	Magnesium Concentration ppm
Original Bi Alloy	1400	1960
Alloy after contact with molten salt at 500 C	1480	265
Alloy after 15 minutes stirring and sparging ^c with HF	None	less than 15 ^d
Alloy after 105 minutes stirring and sparging with HF	None	less than 15

^aEquipment and procedure described in ANL-5959, page 39.

^bAverage blank uranium value of 15 ppm was subtracted.

^cHF sparge rate approximately 0.6 gram per minute.

^dMinimum limit of detection.

Table 23

RADIOCHEMICAL EXCHANGE OF ZIRCONIUM BETWEEN IRRADIATED ZIRCONIUM DISSOLVED IN
BISMUTH AND MOLTEN ZIRCONIUM FLUORIDE-SODIUM FLUORIDE-- NIOBIUM EXTRACTION

Shaking Experiment^a

Temperature: 600 C
Salt: 15 g
Bi Alloy: 50 g

	<u>Magnesium (ppm)</u>	<u>Zirconium^b (ppm)</u>	<u>Zirconium cpm/gram metal</u>	<u>Niobium cpm/gram metal</u>
Bismuth Alloy Before extraction	1580	300	7.31×10^4	8×10^4
Alloy after one hour of extraction	34	1100	1.03×10^3	4.3×10^3

^aDescribed in ANL-5959, page 38.

^bANL spectrographic determination.

RADIOCHEMICAL EXCHANGE OF ZIRCONIUM AND THE EXTRACTION OF ZIRCONIUM
AND NIOBIUM WITH FUSED SODIUM FLUORIDE-ZIRCONIUM FLUORIDE

Stirring Extraction - Liquid Sampling Experiment^a

Temperature: 550 C
 Bismuth: 400 g
 Salt: 90 g

	Uranium ^b (ppm)	Magnesium ^c (ppm)	Zirconium ^c (ppm)	Zirconium γ (cpm/g of metal) ^d	B/A	Niobium γ (cpm/g of metal)
Original alloy	1520	2300	245	5.8×10^4	2.4×10^2	4.2×10^4
Alloy after contact with salt at 550 C	925	570	2300	4.0×10^4	1.7×10	2.2×10^4
Alloy after 5 minutes stirring and sparging ^e with HF	85	25 ^d	2500	6.5×10^3	2.6	1.9×10^4
Alloy after 10 minutes stirring and sparging with HF	57	25	1800	4.2×10^3	2.3	1.9×10^4
Alloy after 15 minutes stirring and sparging with HF	17	25	1400	3.4×10^3	2.4	1.9×10^4
Alloy after 30 minutes stirring and sparging with HF	14	25	480	$(2.15 \times 10^3)^f$	4.5	1.9×10^4

^a Described in ANL-5959, page 39.

^b Corrected for 15 ppm blank value uranium value.

^c Analysis made at the Alliance Research Center of the Babcock and Wilcox Co.

^d Limit of detection for spectrographic standard curves in use.

^e HF sparge rate approximately 0.4 gram per minute.

^f Value most likely in error.

The redicchemical exchange of zirconium and the extraction of zirconium and niobium were demonstrated in two experiments. The first experiment (Table 23) was performed as a shaking experiment and was done with the equipment and procedure described in ANL-5959, page 38. The second experiment (Table 24) was performed with the stirring apparatus and procedure also described in ANL-5959, page 39.

Zirconium, used in these experiments, was irradiated in CP-5. Approximately half of the gamma activity was due to zirconium-95 and the rest to niobium-95. The absence of any other activity was ascertained by gamma ray spectroscopy.

The alloy of bismuth, magnesium and zirconium used in the experiments shown in Table 23 was prepared according to the method described in ANL-5896, page 43. A 50-gram portion of the alloy was placed in a graphite tube with 15 grams of sodium-zirconium fluoride salt and rocked at 600 C for one hour. Samples were taken of the metal phase before and after extraction.

The alloy of bismuth, magnesium, uranium and irradiated zirconium used in the experiments described in Table 24 was prepared in the stirring apparatus. The equipment and procedure were described in ANL-5959, page 39.

Samples were analyzed polarographically for uranium. Zirconium was determined spectrographically. The magnesium determinations in Table 23 were determined by titration with EDTA. The magnesium analyses shown in Table 24 were done spectrographically. The spectrographic analyses for magnesium and zirconium shown on Table 24 were done at the Alliance Research Center of Babcock and Wilcox Company.

Active zirconium and niobium were determined by counting gamma activity. The difference between total gamma and zirconium gamma, after separation from niobium, was attributed to the niobium-95, daughter of zirconium-95. The niobium activity is present only in tracer amounts.

It can be seen in Tables 23 and 24 that the rapid oxidation of magnesium in the bismuth, contacted by the fused salt, is accompanied by the reduction of zirconium in the fused salt and its extraction by the metal phase. Simultaneously the zirconium activity decreases in the metal phase. This decrease in zirconium activity in the metal is due to the exchange of zirconium with the zirconium present in a very much higher concentration in the salt phase. The exchange is rapid as seen in Table 24. The ratio of zirconium γ activity in the metal to zirconium concentration in the metal remains constant after five minutes of hydrogen fluoride sparging. It is evident from Table 23 that there is no extraction of zirconium from the bismuth phase in the absence of hydrogen fluoride.

In order to extract zirconium from bismuth with the fused salt it is necessary to add hydrogen fluoride. The zirconium concentration, as seen in Table 24, was reduced from 2500 ppm to 480 ppm after sparging the melt with hydrogen fluoride.

The concentration of 2300 ppm zirconium in the bismuth phase after contact with the fused salt (Table 24) represents about two-thirds of the zirconium that would have been reduced to metal by the uranium and magnesium oxidized at this point. Perhaps the zirconium in the salt is reduced to a lower oxidation state producing a bifluoride of zirconium.

The activity of the niobium in the bismuth is reduced to a constant level in the experiment shown in Table 24 and to a lower value in the shaking experiment in Table 23. Since the niobium is present in an amount which is a very small fraction of the amount in an IMFR fuel, it is difficult to say much about its practical extraction.

E. Calcination of Reactor Fuel Processing Wastes
(J. W. Loeding, L. Anastasia, A. A. Jonke, C. Schoffstoll, W. D. Turner)

The waste calcination process utilizes a heated fluidized-bed technique for the conversion of atomized liquid wastes to solids. The resultant calcine, a free-flowing, granular solid is reduced in volume over the starting waste by a factor of eight. The off-gases from this process are treated to remove volatile and entrained fission products prior to atmospheric discharge. During the past quarter, additional runs on the calcination of acidic aluminum nitrate wastes were made, and exploratory runs on the calcination of synthetic Purex "high" and "low acid" wastes were started.

1. Calcination of Acidic Aluminum Nitrate Wastes

Since it was felt that the analyzing of too few actual counts in the condensate and off-gas streams imposed a superficial limit on the decontamination factors previously reported, a spike run containing a higher level of activity in the feed than had been used previously was made. The run (HWC-72) was made at 400 C and the feed consisted of an 8:1 dilution of ICPP waste with non-radioactive solution. A summary of the results of this run is given in Table 25. An average ruthenium decontamination factor from feed through adsorber of 2.0×10^4 was achieved for this run as compared to an average of 10^3 for a previous 100:1 dilution run at 400 C (HWC-66). The average non-volatile decontamination factor from feed through adsorber was 1.2×10^5 and the average decontamination factor for total activity from feed through condenser was 2×10^7 . These figures are slightly higher, but essentially comparable to those from previous runs.

The silica gel adsorber was backwashed after HWC-72 with a 2.2 bed volume of warm water (55 to 60 C). Approximately 83 per cent of the re-

Table 25

SUMMARY OF WASTE CALCINATION RUN HWC-72

Temperature:	400 C
Length of Run:	6 Hours
Feed Rate:	95 ml/min
Feed Composition:	8:1 dilution of ICPP waste
	Total γ - 2.78×10^7 cpm/ml
	Ru γ - 9.80×10^5 cpm/ml

Average Decontamination Factors For

Ruthenium from feed through adsorber	2.0×10^4
Non-volatile activity from feed through adsorber	1.2×10^5
Total activity from feed through condenser	2.3×10^7

Venturi Scrubber Solution

Percentage of feed ruthenium collected over entire run	15.5
Percentage of feed non-volatile activity removed over entire run	2.1
Particulate removal efficiency (%)	93.9

Silica Gel Adsorber

Percentage of feed ruthenium recovered during regeneration	57
Percentage of feed non-volatile activity recovered during regeneration	0.16

movable ruthenium was eluted with the first 0.45 bed volume of wash. The amount of ruthenium recovered in the adsorber was equal to 57 per cent of the ruthenium fed to the calciner. Sixteen per cent was recovered in the scrub recycle stream and five per cent in the product, giving a ruthenium material balance of 78 per cent for this run.

One deviation from previous results was the amount of non-volatile activity found in the scrub stream. During this run, 2.1 per cent of the non-volatile activity of the feed was found in the venturi scrubber solution as compared to 14 per cent for the last previous spike run (HWC-69). The scrubber is in series with the sintered metal filters in the off-gas purification system. Since it was felt that the calciner filters were in an increasing state of decay, it was expected that the percentage of feed non-volatile activity would be at least as high, if not higher, for run HWC-72. A possible explanation might be partial self-sealing of defects in the filters.

2. Ruthenium Carryover During Runs with Inactive Feed

On many occasions it has been noted that an unusually large amount of ruthenium activity appeared in the condensate stream during the start up of a run, generally during the period in which non-radioactive feed was being introduced prior to the start of active feed. A series of runs has been made in an attempt to understand and evaluate better the importance of these data. The results of some of these runs made with inactive feed following active Run HWC-72 are summarized in Table 26. The amount of ruthenium carried over into the condensate in the four inactive runs was greater than that carried over in the run with active feed (Run HWC-72). In each case the ruthenium in the initial condensate sample was 30 to 50 times as high as in the final sample for the same run. The initial sample ruthenium was at least tenfold higher than the final

Table 26

RUTHENIUM CARRYOVER INTO CONDENSATE DURING RUNSWITH INACTIVE FEED FOLLOWING AN ACTIVE RUN

Run	Ruthenium in Condensate γ cpm/ml	Run Sample	Remarks
72	0.7×10^2	Final	Active Feed, 8:1 Dilution, 400 C
74	1.7×10^4 4.7×10^2	Initial Final	New Bed, Inactive Feed, 400 C
75	1.0×10^4 1.9×10^2	Initial Final	Same as Run 74, Inactive Feed, 500 C
76	2.4×10^3 0.9×10^2	Initial Final	Same bed as Run 75, Inactive Feed, 400 C
77	5.4×10^3 1.0×10^2	Initial Final	Same bed as Run 76, Inactive Feed, 400 C

sample from the previous run. This high carryover of ruthenium occurred despite the replacement of the radioactive bed with a bed of inactive aluminum oxide.

These data indicate that the source of the ruthenium collected during the operation with inactive feed is probably not that present in the calciner bed, but more likely that deposited in the off-gas piping or some other part of the off-gas system. This ruthenium is probably not transferred in the form of ruthenium tetroxide since it is not removed by the silica gel adsorber. The transfer of ruthenium is apparently affected by the thermal cycling of the equipment occasioned by the shut-down and start-up between runs. There is also some indication that there may be a constituent in the active feed (not present in the inactive feed) which inhibits the transfer of ruthenium into the condensate. On the basis of these data, it is expected that in continuous plant operation the ruthenium decontamination factor may be higher than that experienced in intermittent operations.

3. Equipment Changes

The filtering and venturi blowback assembly (described in ANL-5858, page 45) has been tested and installed in the waste calciner. Ten sintered stainless steel bayonet filters are employed each of which is blown back in regularly spaced, fractional second bursts of 80 psig air. Frequency of blowback is one burst per filter per minute. Operations to date (84 hours) have been highly satisfactory. Use of this head assembly has resulted in about a 20 per cent reduction in the total non-condensable gases leaving the system due to the reduction in volume of blowback gas required.

4. Calcination of Concentrated Purex Process Waste

Feasibility runs were conducted to examine the suitability of the fluid-bed calcination process for the conversion of Hanford Purex process

wastes into solids. Two waste solutions have been tested. One represents waste concentrated by evaporation, and the second represents waste which has been concentrated and treated with formaldehyde to destroy part of the nitric acid. The composition of these solutions is given in Table 27. These feeds were spray-injected at about 100 ml/min into a starting bed of aluminum oxide particles at elevated temperatures. The alumina was displaced as runs progressed leaving a rust-colored bed of undetermined composition, but probably containing primarily sodium sulfate and iron oxide. Runs were made with the high-acid feed at temperatures of 350 C, 400 C, and 500 C. At the lower temperatures a large percentage of agglomerates about one fourth-inch in diameter were formed. The amount of agglomeration decreased considerably at the higher temperature. With the low-acid feed at 500 C, the amount of agglomeration was still further reduced, and operation of the calciner appeared to be fairly satisfactory. Only a small amount of fine dust particles, comparable with that produced in calcination of aluminum nitrate solutions, was obtained in these runs. Preliminary data indicates the volume reduction factors will be about eight for the high-acid waste and about 3.5 for the low-acid waste.

It is conjectured that the cause of the agglomeration is the presence of sodium nitrate in the solid product. Sodium nitrate would be molten at these calcination temperatures. The low-acid feed, having a higher ratio of sulfate to sodium, might tend to produce a solid containing less sodium nitrate. The addition of small amounts of extra sulfate to these feeds may result in further operational improvement by displacing nitrate from the product. Chemical analyses for nitrate and other components of the solid have not yet been completed.

Runs with inactive feed solution will be continued, and one or more runs with radioactive feed will be made to compare the distribution of radioactivity with that obtained in the calcination of acid aluminum nitrate waste.

Table 27

COMPOSITION OF HAMFORD PUL-X PROCESS WASTES

<u>Ion</u>	<u>High-Acid Waste</u>	<u>Low-Acid Waste</u>
H^{+}	6.2 <u>M</u>	0.5 <u>M</u>
Fe^{+++}	0.25	0.6
Al^{+++}	0.17	0.3
Na^{+}	0.40	3.0
Cr^{+++}	0.006	0.03
Ni^{++}	0.006	0.018
$SiO_2^{=}$	0.15	1.50
$PO_4^{=}$	0.015	0.06
NO_3^{-}	7.10	3.21

F. Conversion of Uranium Hexafluoride to Uranium Dioxide in Fluidized Beds
(I. Knudsen, N. Levitz, A. A. Jonke, R. Finley)

Feasibility studies on the direct continuous conversion of uranium hexafluoride to uranium dioxide by reaction with steam and hydrogen in a fluidized-bed reactor have started. A starting bed of uranium dioxide is used. Experiments are planned in 1 1/2 and 3-inch diameter Monel reactors to determine operating conditions and reagent excess requirements for adequate conversion.

1. Introduction

The interest in uranium dioxide as a reactor fuel has grown because of its comparative stability under irradiation and ease of preparation as compared to the problems associated with the use of uranium metal as fuel. Consequently, a more economical process for large-scale production of enriched uranium dioxide from uranium hexafluoride is needed. A "dry" process using the fluid-bed technique with gas-solids reactions appears to have economic advantages over the "wet" process now being used. The "wet" process⁸ includes hydrolysis of uranium hexafluoride with water, precipitation of the uranium as the diuranate using ammonium hydroxide, filtration, drying and calcination of the diuranate to uranium oxide and finally reduction of uranium oxide to uranium dioxide with hydrogen.

Dry processes⁹ using "hot" and "cold" wall reactors have been developed at K-25 for the hydrogen-reduction of uranium hexafluoride to the tetrafluoride and are in use at Y-12 for enriched material and at Fernald

⁸Murray, J. P., et al, "Economics of Unirradiated Processing Phases of Uranium Fuel Cycles," Paper A/Conf. 15/P/439, Second International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, June, 1958, p. 8.

⁹Smiley, S. H., and Brater, D. C., "Continuous Processes for the Direct Reduction of Uranium Hexafluoride to Uranium Tetrafluoride of High Purity and Density," Paper A/Conf. 15/P/523, Second International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, June, 1958.

and Paduch for depleted material. The tetrafluoride has been converted mainly to metal and little or no uranium dioxide has been made by pyrohydrolysis of the tetrafluoride even though horizontal rotary furnaces are in use at feed materials plants for "reverting" high-fluoride feeds to oxides prior to solvent extraction processing.

A one-step fluid-bed process using a bed of uranium dioxide for simultaneous adsorption of uranium hexafluoride and reaction with steam and hydrogen to uranium dioxide is being tested. The overall reaction is assumed to be as follows:

2. Equipment

A one and one-half-inch diameter Monel column two and one-half feet high, has been installed in a vacuum-frame hood. The upper 16-inch section is an expanded three-inch diameter disengaging section containing two porous Monel bayonet filters. The fluidizing gas enters at the apex of the sixty-degree cone bottom. The fluidizing gases are preheated in a fluidized bed of sand in a one-inch tube mounted in a furnace. A schematic diagram of the equipment is shown in Figure 33. Separate feed systems were installed for the steam, hydrogen, nitrogen, and uranium hexafluoride as well as an exhaust gas condenser, scrubber, and a hydrogen leak detector.

3. Results

a. Uranium Tetrafluoride Pyrohydrolysis

A number of uranium tetrafluoride-steam pyrohydrolysis runs were made as an operating shakedown of the equipment and, also, because of some interest in the particular process application itself. Good operation was demonstrated after a number of minor modifications of the equipment were

FIGURE 33
SCHEMATIC DIAGRAM OF EQUIPMENT FOR FLUID-BED CONVERSION
OF URANIUM HEXAFLUORIDE TO URANIUM DIOXIDE

made. The operating conditions and analytical results of the runs appear in Table 28. The uranium tetrafluoride was a mixture of products from the fluid-bed hydrofluorination of refined uranium dioxide. Runs were of such duration as to permit four stoichiometric equivalents of steam to contact the fluoride. Intermediate bed samples were taken half way through the run.

A pronounced increase in rate of reaction was observed at higher temperatures. Residual fluoride contents of 0.30 and 0.18 per cent were obtained at temperatures of 600 and 650 to 675 C, respectively. However, intermediate samples showed the initial removal of fluoride to be much more rapid at the higher temperature. The difference in the results of the two runs at 500 C is probably due primarily to the different reaction times required for the 300 per cent steam excess. The uranium dioxide products did not appear to be very reactive, e.g., in discharging the bed, no temperature rise was noted due to reaction with air.

b. Conversion of Uranium Hexafluoride to Uranium Dioxide

Preliminary tests of the direct conversion of uranium hexafluoride to uranium dioxide in fluidized beds were made with steam and hydrogen in a 2/1 mole ratio as the fluidizing gases. The starting bed was 1000 grams of uranium dioxide which gave a static bed height of about eight inches. The superficial gas velocity at column operating conditions was about 0.5 ft/sec. The uranium hexafluoride was introduced directly into the bed through a heated line at a point about two inches above the bottom of the bed.

At temperatures of 575 to 625 C with reactant excesses as low as 300 per cent, virtually complete conversion of the hexafluoride to solids was obtained with negligible fines formation (see Tables 29 and 30). Analytical data on the products have not been completed as yet; the products

Table 28

FLUID-BED PYROHYDROLYSIS OF URANIUM TETRAFLUORIDE

Equipment: 1 1/2 inch dia Monel column
 Bed Material: UF_4 from fluid-bed hydro-
 fluorination of refined UO_2
 Fluidizing Gas Velocity: ~ 0.75 ft/sec
 Steam Excess: 300 %

<u>Run No.</u>	<u>Charge (g)</u>	<u>Temp (C)</u>	<u>Duration of Run (hr)</u>	<u>Residual Fluoride</u>	
				<u>Intermediate^a Sample (w/o)</u>	<u>Final Sample (w/o)</u>
1	500	500-550	0.67	-	12.2
4	750	500	1.25	15.4	2.65
3	750	600	1.75	9.66	0.30 ^b
5	800	650-675	1.50	3.26	0.18 ^b

^a After steam excess of 100 per cent.

^b Colorimetric measurement of HF obtained from pyrohydrolysis of product at 1000 C.

Table 29

CONVERSION OF URANIUM HEXAFLUORIDE TO URANIUM DIOXIDEIN FLUIDIZED BEDS

Equipment: 1 1/2 in. dia Monel column
 Starting Bed: 1000 grams UO_2
 Fluidizing Gas Velocity: 0.5 ft/sec
 Estimated Bed Temperature: 575 to 625 C

Run No.	UF_6 Rate (g/min)	Run Duration (min)	Reactants Excess (%)	Recovery ^a (w/o)
6B	0.89	90	2400	91.3
7A	5.7	120	300	100.6
8	1.4	180	1500	92.6

^aAssuming all solids recovered to be 100 per cent uranium dioxide.

Table 30

PARTICLE SIZE DISTRIBUTION AND BULK DENSITY OF INITIAL AND FINAL BEDS

Mesh Size Range	RUN 7A		RUN 8	
	Initial (w/o)	Final (w/o)	Initial (w/o)	Final (w/o)
+20	0	0	0	0
-20+40	0	0	0	0.4
-40+60	22.2	22.0	22.0	24.6
-60+100	59.3	67.8	67.8	67.4
-100+200	18.5	9.9	9.9	7.2
-200+325	0	0.3	0.3	0.4
-325	0	0	0	0
Tapped Bulk Density, g/cc	3.7	4.3	4.3	4.5

appear to be primarily brown uranium dioxide although some yellow solid (probably uranyl fluoride) was noted in the small amounts of fines (10 to 25 grams) retained on the filters. Microscopic comparison of the particles of the initial and final beds show a uniform, dense coating; the thickness was about 10 per cent of the diameter of the particle. The tapped bulk density of the beds increased from 3.7 g/cc at the start of Run 7A to 4.5 g/cc at the end of Run 8.

Some plugging was encountered in feeding the uranium hexafluoride through the 0.020-inch diameter hole in the end of the feed tube in spite of a nitrogen purge on the line. Also a faulty bed thermocouple necessitated estimating the bed temperature from the sheath temperature. Additional minor modifications of the unit (a second bed thermocouple, temperature and feed rate controls) and further work on the introduction of the uranium hexafluoride should permit determining the effects of temperature and reactant excess on completeness of reduction and residual fluoride content.

G. Solids Mixing in Straight and Tapered Fluidized Beds
(H. Littman, A. A. Jonke)

The planned series of experiments on solids mixing in straight and tapered-wall fluid-bed columns (see ANL-5858, pages 51 to 53) has been completed. A radioactive tracer technique was used with two sizes of copper spheres, -20 to +40 mesh and -140 to +200 mesh, using dry air at room temperature as the fluidizing medium. Several bed heights and gas velocities were tested for each mesh size and each type of column.

The aluminum column is 50 inches high with a two-inch square inlet. The taper is calculated to compensate for the expansion of the gas due to pressure drop as it flows upward through the bed, i.e., the column is designed for a uniform superficial gas velocity at all points in the bed. The required taper is calculated from the equation:

$$\tan \theta = \frac{a_1}{P_i} \frac{B}{2}$$

where θ = taper angle

a_1 = inlet opening, length on tapered side

P_i = inlet pressure

B = bulk density of solids in the bed.

An increase in gas velocity decreases the bulk density and reduces the required angle. Increasing the bed height also lowers the required angle. Since the required taper varied depending on run conditions, an intermediate value of 0.509 degrees was chosen.

The experimental procedure is to fluidize the bed, drop in the tracer (a few grams of irradiated bed material -- 12.8-hour half-life) at the top and with the counter fixed at some distance from the top of the bed, obtain a time-activity trace for a given set of conditions. Scans along

the bed length are also made with the probe to ascertain when steady state was reached. A complete analysis of the data will be forthcoming in a summary report. A preliminary evaluation of one set of experiments is described below.

The results of mixing of -20 to +40 mesh copper particles in the tapered bed are shown in Table 31. The data show that bed mixing increases with gas velocity and decreased with bed height. Two beds with unfluidized bed heights of 16.5 and 26.6 inches were used. For the shorter bed, the rate of mixing as represented by the time needed for the tracer activity front to travel a given distance below the top of the bed is shown in Figure 34 for superficial gas velocities of 1.86 and 2.30 feet per second (6.9 and 30.9 per cent above the minimum). The activity front travels faster at the higher gas velocity. The activity penetrates the bed faster at the top than at the bottom of the column.

The time required for the activity to reach 50 per cent of the steady state value at various distances below the top of the bed is shown in Figure 35. The curves show the same behavior as those of the activity front. A constant activity reading was reached earlier in the center of the column than at the extremities. The bottom of the column did not reach its steady state value for nearly 27 minutes. The peak to steady state activity ratios were slightly higher than those predicted by the diffusion equation, indicating that mixing behind the activity front is moderate.

For the taller bed, the gas velocity must be raised considerably above the minimum before mixing takes place at a reasonable rate. At gas velocities of 1.82 and 2.02 feet per second (4.0 and 15.4 per cent above the minimum) mixing was extremely slow and a homogeneous steady state was

SUMMARY OF RESULTS OF -20 to +40 SOLIDS MIXING IN A TAPERED FLUIDIZED BED

Bed Material: -20, +40 mesh copper spheres

Superficial Gas Velocity u (ft/sec)	Counter Distance Below Top of Bed x (in.)	Fluidized Bed Height L (in.)	$\frac{x}{L}$	Activity Front ^a (sec)	50% of Steady State (sec)	Peak (sec)	Steady State (sec)	Peak Steady State Activity Ratio
---	--	--	---------------	---	------------------------------------	---------------	--------------------------	---

Series A - Static Bed Height - 16.5 inches

1.86	5.40	17.4	0.310	37	51	137	1807	2.24
1.86	9.65	17.4	0.550	113	252	-	687	1.00
1.86	13.50	17.4	0.776	280	660	-	1587	1.00
2.30	3.40	19.4	0.175	13	15	28	1800	3.32
2.30	7.40	19.4	0.381	54	78	283	1612	1.72
2.30	11.65	19.4	0.601	88	319	-	651	1.00
2.30	15.50	19.4	0.799	249	750	-	1613	1.00

Series B - Static Bed Height - 26.6 inches

1.82	9.3	27.3	0.341	539	-	14700	-	-
2.02	5.4	29.4	0.184	72	-	296	-	-
2.02	11.4	29.4	0.388	148	-	1950	-	-
2.02	17.4	29.4	0.592	-	-	4320	-	-
2.02	23.4	29.4	0.796	960	-	8820	-	-
2.28	13.0	31.0	0.419	81	-	880	-	-

^a Time for a detectable change of activity to occur after radioactive particles have been charged to the bed.

FIGURE 34
MIXING STUDIES: MOVEMENT OF ACTIVITY FRONT IN TAPERED
FLUIDIZED-BED COLUMN

FIGURE 35
TIME REQUIRED FOR ACTIVITY TO REACH 50 PER CENT OF STEADY STATE
VALUE AT ANY DISTANCE BELOW TOP OF BED

not reached in 24 hours. The results of two runs made under identical conditions are combined in Figure 36 to show the activity-time curves at 5.4, 11.4, 17.4 and 23.4 inches below the top of the bed for a gas velocity of 2.02 feet per second (15.4 per cent above the minimum). A homogeneous steady state was not reached in the column. The activity appeared to be concentrating in the top of the column and to be depleted in the bottom after three hours. No explanation for this behavior has yet been found.

Figure 37 shows the activity-time curves for a gas velocity of 1.82 feet per second (4.0 per cent above the minimum). The mixing is clearly slower than for the 2.02 feet per second gas velocity and appears to show similar trends. A homogeneous steady state was not reached in 24 hours.

A final run was made at a gas velocity of 2.28 feet per second (30.3 per cent above the minimum) and it is readily observed in Table 30 that the rate of mixing increased over runs made at lower gas velocities. It can also be seen in Table 31 that mixing in the taller bed is much slower than that in the shorter bed for corresponding gas velocities. An interesting explanation of this is that the short bed is undertapered while the deep bed is overtapered (see Table 32), except for the lowest gas velocity which is very close to the minimum.

FIGURE 36
MIXING STUDIES: ACTIVITY-TIME CURVES FOR TAPERED FLUIDIZED-BED COLUMN;
2.02 FT/SEC GAS VELOCITY

FIGURE 37
MIXING STUDIES: ACTIVITY-TIME CURVES FOR TAPERED
FLUIDIZED-BED COLUMN; 1.82 FT/SEC GAS VELOCITY

Table 32

SUMMARY OF PROPERTIES OF TAPERED FLUIDIZED BEDS USED IN MIXING STUDIES

Particle Size (mesh)	Gas Velocity		Bed Weight (g)	Bed Height (in.)	Bed Density (g/cc)	Volume Change (%)	Bed Taper (Actual) (deg)	Bed Taper Required (Calculated) (deg)
	(ft/sec)	Per Cent Above Minimum						
-20 +40 ↓	0	0	6336.3	16.5	5.50	0	0.509	-
	1.86	6.9	6315.8	17.4	5.18	5.8	↓	0.573
	2.30	30.9	6366.7	19.4	4.64	19.0		0.538
-20 +40 ↓	0	0	10538.0	26.6	5.44	0	0.509	-
	1.82	4.0	10527.8	27.3	5.28	2.9	↓	0.547
	2.02	15.4	10538.0	29.4	4.87	11.8		0.505
	2.28	30.3	10548.0	31.0	4.60	19.1		0.488

III. REACTOR SAFETY

A status report summarizing the previous research in this program up to and including 1958 titled, "Ignition Behavior and Kinetics of Oxidation of the Reactor Metals, Uranium, Zirconium, Plutonium, and Thorium and Binary Alloys of Each" is being issued as ANL-5974.

In the studies of the rate of propagation of burning along uranium foils, a large number of surface contaminants have been shown to have no effect or to slow the burning process in air. However, etching the uranium foil surface beforehand with concentrated nitric acid causes a significant increase of burning propagation rate. The burning propagation of zirconium and zirconium alloy foils is related in general to the ignition temperatures of the various samples. An interesting dependence of the propagation rate on both thickness and width has led to a requirement of very narrow specimens for studies in air. A correlation of propagation rate in oxygen with cross sectional area is being attempted. This relationship and a relationship established between the length of the burning zone in air and the propagation rate should lead to an understanding of the burning process by application of heat transfer principles.

Studies under the microscope in a heated cell have established that the use of induction heating influences the oxidation process of uranium. It has also been shown that the oxidation of a heated uranium sample is faster in cool oxygen than in the oxygen heated to the same temperature as the sample.

X-ray and electron diffraction studies are in progress to determine more clearly the validity of a theory which relates the breakaway phenomena during the isothermal oxidation of zirconium alloys with a transformation of the oxide film to the monoclinic form.

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 series of runs with zirconium was described in the previous quarterly report, ANL-5959, page 94. Additional zirconium runs have been made to test further the conclusions derived from the previous results. The existence of an apparent ignition temperature of 2600 C was verified. The accumulated data is under study preliminary to an analysis on an analog computer, the results of which should define the direction of further work on zirconium. A series of runs with uranium has been initiated.

A second laboratory-scale method involves the rapid contact of steam with a drop or pool of molten metal. The method, originally proposed in ANL-5396, page 109, has been modified and is now under intensive development. In this method a sample of molten metal in a vacuum environment receives a "pressure pulse" of water vapor. The rapid contact and withdrawal is accomplished by a system of electric valves.

The program to determine the reaction rates of molten fuel and cladding metals with water during nuclear transients using the TREAT reactor is continuing. Progress has been made on construction, procurement, and testing of equipment. A mathematical model to predict and correlate the data on an analog computer has been set up.

A. Metal Oxidation and Ignition

(J. G. Schnitzlein, H. A. Porte, P. J. Pizzolato, L. Leibowitz, J. D. Bingle, D. F. Fischer, L. W. Mishler, M. Cusik,* and R. C. Vogel)

1. Uranium Ignition Studies

a. Uranium Burning Propagation Rate Studies

As previously reported in ANL-5959, page 71, a program has been

*Cooperating Institution Student from Detroit University.

established to understand more fully the factors influencing and controlling the rate of burning propagation of uranium and zirconium. The apparatus and procedure used in this study have been fully described in that report. In addition, preliminary data obtained using various uranium foils were presented.

In order to have a sufficient amount of uranium foil of uniform quality with which to study all the variables of interest to the propagation rate studies, 150 square inches of a 0.13-mm (5-mil) thick uranium foil were obtained from Special Materials. This foil has been given the designation SMF-5. Table compares an analysis of this metal with analyses previously reported for ANL- and BMT-base metal uranium. The significant differences seen to be in the increased amounts of carbon, oxygen, silicon, and magnesium present in the SMF-5 metal.

(1) Measurement of Reproducibility

Five samples of the SMF-5 foil have been run in air and three in oxygen under identical conditions in an effort to establish the reproducibility which can be expected from these experiments. The results are reported in Table . It can be seen from this table that the average deviation from the mean burning propagation rate for the SMF-5 foil is only 4.3 per cent in air, while it is about 7.8 per cent in oxygen. The average deviation of the distance between fronts for the air runs is somewhat greater than that of the propagation rates, however. It should be mentioned here that the sample oscillations which give trouble in the zirconium propagation studies reported herein are only very occasionally observed for uranium specimens, undoubtedly because the uranium foil is not as flexible.

Comparisons of these average burning propagation rates for the 0.13-mm SMF-5 foil were made with rates previously reported (ANL-5959,

Table 33

URANIUM ANALYSES COMPARISON

(parts per million)

Chemical analysis for O, C, H, N; all other elements determined by spectrographic analysis

<u>Element</u>	<u>ANL Base Metal</u>	<u>BMI-Base Metal</u>	<u>SMF-5</u>
O	12	19	60
H	5.0	0.54	2
C	21	69	240
N	56	22	45
Al	7 (15) ^a	10 (34) ^a	6
Cr	5	30	8
Cu	2	3	1
Fe	45	50	60
Mg	2	2	20
Ni	15	30	10
Si	30	20	100
Mn	2	4	5
Ag	<1	<1	5

^aSpecial wet chemical analysis.

REPRODUCIBILITY OF URANIUM BURNING PROPAGATION EXPERIMENTS

(Samples were 3 mm wide, 0.13 mm thick, and 6 mm long, and were wet polished with 600-grit SiC paper)

Table 34

Run		Metal		Burning Propagation Rate		Avg Distance Between Fronts			
In Air				(cm/sec)		(cm)			
33	SMT-5	0.553	0.549	0.558 ± 0.024	0.519	0.48 ± 0.05	0.53		
34	SMT-5	0.585	0.571						
37	SMT-5	0.512	0.506						
61	SMT-5	0.592	0.594						
70	SMT-5	0.548	0.545						
Avg		0.558 ± 0.024		0.553 ± 0.024		0.48 ± 0.05			
8	BMI	0.509		0.519		0.53			
In Oxygen									
36	SMT-5	6.04		6.04 ± 0.47	5.78	6.04 ± 0.47	5.78		
42	SMT-5	5.33							
87	SMT-5	6.74							
Avg		6.04 ± 0.47							
13	BMI	5.78		5.78		5.78			

page 74) for the 0.13-mm foil of BMI-base metal uranium. These data, which are also included in Table 34, show relatively good agreement. The propagation rate in oxygen of 5.78 cm per sec for the BMI foil compares favorably with the average rate of 6.04 ± 0.47 cm per sec observed with the SMF-5 foil in oxygen. And, while the propagation rates in air for the BMI foil are about seven per cent lower than the average rates for the SMF-5 foil in air, the rates for one of the individual SMF-5 foil specimens are even lower than those for the BMI foil. Thus, the impurity content differences between BMI base metal uranium and SMF-5 uranium, as reported in Table 32, apparently have no significant effect on the burning propagation rates, either in air or in oxygen.

In conjunction with these reproducibility experiments, tests were made to see whether the clamping arrangement that supports the foil specimens causes any heat losses from the sample and thus possibly affects the propagation rate. It was established that the heat loss during that portion of a run that is used to determine the burning propagation rate is insignificant.

(2) Sample Width or Cross Sectional Area Dependence

In ANL-5959, page 75, were presented the relationships between sample thickness and burning propagation rates in oxygen and air for uranium. On page 74 of the same document, it was also reported that a wedge-shaped 0.25-mm (10-mil) thick foil varying in width from 2.0 to 7.6 mm gave a linear burning propagation rate in air. In a further effort to examine the effect of sample width on the propagation rates, 1, 2, and 4 mm-wide strips of SMF-5 foil were run in both air and oxygen. These are compared in Table 35 with the usual 3-mm wide strips used in the majority of the uranium burning propagation investigations.

Table 35

WIDTH DEPENDENCE OF URANIUMBURNING PROPAGATION EXPERIMENTS

(SMF-5 foil samples were 0.13 mm thick and 6 cm long,
and were wet polished with 600-grit SiC paper)

<u>Run</u>	<u>Width of Sample (mm)</u>	<u>Burning Propagation Rate</u>		<u>Avg Distance Between Fronts (cm)</u>
		<u>Oxidation Front (cm/sec)</u>	<u>Ignition Front (cm/sec)</u>	
<u>In Air</u>				
54	1	-- ^a	0.748	-- ^a
64	2	0.582	0.577	0.38
-- ^b	3	0.558 ± 0.024 ^b	0.553 ± 0.024 ^b	0.48 ± 0.05 ^b
65	4	0.534	0.518	0.56
<u>In Oxygen</u>				
55	1		9.60	
66	2		6.58	
-- ^c	3		6.04 ± 0.047 ^c	
67	4		7.34	

^aThe oxidation front is not clearly discernible on the film of the event.

^bAverage of five runs (see Table 34, page 203).

^cAverage of three runs (see Table 34, page 203).

In air the 1-mm wide strip burns significantly faster, but, while the 2, 3, and 4-mm wide strips show a trend of slightly decreasing rates, both the 2 and 4-mm strips give rates that are within the range of the average deviation of the 3-mm strip. On the other hand, the average distance between fronts seems to be quite clearly dependent on the sample width. One can easily surmise, nevertheless, that sample width from 2 to 4 mm is a relatively unimportant consideration for foils of this thickness burning in air. This then eliminates the necessity of having extremely accurate sample widths for these propagation rate studies.

In oxygen the pattern is not quite so clear. Again the 1-mm wide strip gives the fastest propagation rate. However, the next fastest rate was observed using the 4-mm wide strip and no trend is apparent. Possibly one could state that in oxygen sample width from 2 to 4 mm is again not very important, but that the range in rates is somewhat greater than in air.

In considering both thickness and width variations together, there appears to be no cross sectional area dependence in either oxygen or air.

(3) Effects of Surface and Gas Contaminants

To determine their effect on the uranium burning propagation rate, a series of surface and gas contaminants has been tried on the 0.13-mm (5-mil) SMF-5 foil in air. The experimental results are summarized in Table 36. Similar experiments on 0.25-mm (10-mil) uranium foils gave comparable results. In comparing the propagation rates with those of the uncontaminated foil also listed in Table 36, it is quite apparent that water, long suspected as a source of trouble as far as uranium ignitions are concerned, seems to have no effect whatever on the burning propagation rate either as a surface contaminant or as

Table 35

EFFECT OF CONTAMINANTS ON THE URANIUM BURNINGPROPAGATION RATE IN AIR

(SMF-5 foil samples, 0.13 mm thick, 3 mm wide, and 6 cm long)

	<u>Burning Propagation Rate</u>		<u>Avg Distance Between Fronts (cm)</u>
	<u>Oxidation Front (cm/sec)</u>	<u>Ignition Front (cm/sec)</u>	
Polished Uranium	0.558 ± 0.024	0.553 ± 0.024	0.48 ± 0.05
<u>Surface Contaminants</u>			
Water corroded ^a	0.569	0.563	0.39
γ alumina	--b	0.558	--b
Aluminum dust	--b	0.538	--b
Water	0.533	0.526	0.41
Ethyl alcohol	0.517	0.521	0.40
Cutting oil	0.492	0.490	0.41
Silicon carbide	--b	0.454	--b
Oxide coated ^c	--b	0.444	--b
Boron nitride	0.417	--b	--b
30% H ₂ O ₂	0.394	0.392	0.47
Sea sand	--b	0.392	--b
Graphite	0.387	--b	--b
Magnesia	--b	0.358	--b
<u>Gas Contaminants</u>			
Air saturated with water	0.546	0.558	0.42
Air with 5% CO ₂ added	0.514	0.518	0.46

^aIn distilled water for 336 hours (2 weeks); then allowed to dry.^bThe front is not clearly discernible on the film of the event.^cAs received.

a gas contaminant. In addition, water corrosion products, which significantly change the appearance of the sample (bright yellow with black splotches), also do not affect the propagation rate. It may be recalled that water vapor also showed no effect on uranium ignition temperatures either in oxygen or air during the burning curve investigations (see ANL-5896, page 83).

(4) Effects of Surface Etches

In addition to surface and gas contaminants the effect of etching the foil surface was examined. Three minute etches in bromine tri-fluoride or concentrated nitric acid followed by rinsing and drying caused increases in the burning propagation rate in air to 0.65 and 0.68 cm per sec, respectively. Since nitric acid is a common pickling agent and had caused the greatest effect, further investigation of the effect of nitric acid etch was undertaken. Propagation rates were measured for samples after treatment in various concentrations of the acid and for various lengths of time.

Three concentrations of nitric acid were used in this study, 1, 7.7, and 15.4 N. The 15.4 N acid is concentrated nitric and the 7.7 N acid is that most commonly used for pickling uranium. Eight-centimeter long polished strips of 3-mm wide and 0.13-mm thick SMF-5 foil were weighed and immersed in the various concentrations of acid for times of one, three, ten, and thirty minutes. They were then rinsed, dried, and reweighed. A 1.7-cm length was next cut from the end of each specimen for purposes of mounting for microscopic observation of the surface. The samples were then subjected to the regular burning propagation test. The data, summarized in Table 37, show a trend toward faster propagation rates for samples undergoing the increasingly severe etches. A graphic presentation of these data is given in Figure 38. Very short contact with the 15.4 N nitric acid resulted in more of an increase

Table 37

EFFECT OF NITRIC ACID ETCHES ON THE URANIUM BURNING PROPAGATION RATES IN AIR

SMF-5 foil samples 0.13 mm thick, 3 mm wide, and 8 cm long
(1.7 cm removed after etching for microscopic examination)

HNO ₃ Concentration (N)	Etch Time (min)	Weight Lost (%)	Burning Propagation Rate		Avg Distance Between Fronts (cm)
			Oxidation Front (cm/sec)	Ignition Front (cm/sec)	
0	0	0 ^a	0.558 ± 0.024	0.553 ± 0.025	0.48 ± 0.05
1	3	0.003 ^{a, b}	0.553	0.545	0.58
1	10	0.011 ^b	0.596	0.597	0.56
1	30	0.012 ^b	0.539	0.527	0.57
7.7	1	0.079 ^b	0.614	0.611	0.64
7.7	3	0.12 ^a	0.610	0.615	0.61
7.7	10	0.34 ^a	0.598	0.592	0.69
7.7	30	0.97	0.679	0.665	0.65
15.4	1	0.16	0.651	0.654	0.62
15.4	3	0.39	0.683	0.679	0.56
15.4	10	1.68	0.685	0.682	0.59
15.4	30	8.38 ^a	0.738	0.738	0.59

^aThese samples were examined microscopically at 550 X after mounting and normal sectioning (see Figure 39).

^bThe weight lost was based on analysis of etchant solution because the analytical balance was not sufficiently sensitive to determine accurately the weight loss of the sample.

FIGURE 38
EFFECT OF NITRIC ACID ETCHING ON BURNING
PROPAGATION RATES OF URANIUM IN AIR
(SMF-5 foil samples originally 0.13 X 3 X 80-mm)

in the propagation rate than did considerably longer contact with the other two concentrations of the acid, indicating that the strength of the acid is of more importance than the time of contact. The maximum rate increase of one-third was observed after undergoing a 30-minute etch in the 15.4 N nitric acid.

Profiles of cross sections of selected specimens as observed at 550 X are illustrated in Figure 39. It can be seen that the surface is increasingly roughened after subjection to the more rigorous etchant conditions. No indication of intergranular attack was observed.

There is a trend between the propagation rate and the average penetration or the weight of sample lost in the etch solutions (see Figure 40). However, the increase in propagation rates is much greater than can possibly be accounted for (see ANL-5959, Figure 23, page 75) by decreases in foil thickness corresponding to the weight loss. The roughening of the foil surfaces may be the explanation for these increases in uranium burning propagation rates. It is postulated that the ignition temperature of the uranium foil may be lowered as a result of the increase in specific area of the sample caused by the nitric acid etch. The corresponding lowering of the ignition temperature with increased specific area, as illustrated in Figure 21, ANL-5896, page 81, could well cause an increase in the propagation rate. A comparison of propagation rates reported in ANL-5959, page 74, with the ignition temperatures observed for similar sized samples (see ANL-5858, page 55) shows that there may be a relationship between the two.

It is presently planned to investigate the effect of nitric acid etches on the ignition temperature of uranium specimens. If the ignition temperatures are indeed lowered as a result, then this relationship between propagation rate and ignition temperature may well be established.

FIGURE 39

CROSS-SECTIONAL PROFILES OF FOIL SURFACE
AFTER ETCHING WITH NITRIC ACID

(Examined microscopically after
mounting and normal sectioning)

FIGURE 40
 RELATIONSHIP BETWEEN URANIUM BURNING PROPAGATION RATE IN AIR
 AND PENETRATION IN NITRIC ACID ETCH
 (SMF-5 foil samples originally 0.13 X 3 X 80 mm)

2. Isothermal Oxidation of Uranium

a. Microscopic Observation

(1) Effect of Light and Heating Method on Oxidation Behavior

Very early in the hot-stage studies it was observed that the results obtained with this experimental arrangement (ANL-5896, page 84) differed in certain respects from those obtained using the isothermal apparatus. There was no real first stage observed in the hot-stage runs and the oxide produced had a rougher, less uniform appearance characterized by the presence of very large nodules. Although it appeared likely from the second stage rates of three of the initial five hot-stage runs that the actual sample temperatures were higher than intended, the variations in break weights and times still seemed to be greater than could be satisfactorily explained by temperature difference alone. The data in Table 38 show that except in one case the hot-stage oxidations were characterized by first stages so brief that it was not possible to calculate satisfactory linear rates. The oxidation curve for a typical hot-stage run at 200 C in 200 mm of oxygen is compared in Figure 41 with that for a typical run carried out in the isothermal apparatus under similar conditions.

Possible sources of the observed variations originally considered were the two most obvious differences in the experimental arrangements used. These had to do with the methods of heating employed and the shielding of the uranium sample from light sources during oxidation. In the isothermal apparatus the sample is maintained at the desired operating temperature by resistance heating, while in hot-stage studies induction heating is used. Samples oxidized in the isothermal apparatus are almost completely shielded from light during the experiment, while in the hot-stage study the

Table 38

COMPARISONS OF OXIDATION OF URANIUM IN 200 mm OF OXYGEN IN HOT STAGECELL AND ISOTHERMAL APPARATUS

<u>Apparatus</u>	<u>1st Stage Rate</u> <u>[($\mu\text{g/sq cm}$)/min]]</u>	<u>Break Time^a</u> <u>(min)</u>	<u>Break Weight^a</u> <u>($\mu\text{g/sq cm}$)</u>	<u>2nd Stage Rate</u> <u>[($\mu\text{g/sq cm}$)/min]]</u>
<u>Argonne-Base Uranium</u>				
Isothermal (200 C) ^b	0.49 $\pm$ 0.03	121 $\pm$ 30	57 $\pm$ 16	6.6 $\pm$ 0.6
Hot Stage ^c	1.0	52	52	18
Hot Stage ^c	-- ^d	(16)	(12)	15
Hot Stage	-- ^d	(25)	(13)	7.0
Hot Stage	-- ^d	(20)	(15)	8.0
Isothermal (225 C) ^b	1.1 $\pm$ 0.1	46 $\pm$ 10	58 $\pm$ 6	13 $\pm$ 2
<u>High-Purity Uranium</u>				
Isothermal (200 C)	0.4	265	123	4.3
Hot Stage ^c	-- ^d	(18)	(5)	9.2
Isothermal (250 C)	4.5	34	160	21

^aData in parentheses are estimates because of uncertainty in initial rates.

^bBase-line data.

^cActual sample temperature probably higher than 200 C.

^dNo clearly defined first stage.

FIGURE 4I
EFFECT OF HEATING METHOD ON OXIDATION BEHAVIOR OF URANIUM
AT 200 C IN 200 mm OXYGEN

specimen is exposed to room light for the duration of the run. Also, the small area of the specimen surface under observation is exposed to the microscope illuminator sources (the tungsten filament lamp or carbon arc lamp) for shorter periods during which the specimen is being examined or photographed.

The influence of light on the kinetics of oxidation and the appearance of the oxide surface was studied by exposing uranium specimens to light from a tungsten filament lamp during oxidation experiments carried out in the isothermal apparatus. No marked acceleration of the initial oxidation or unusual changes in the surface appearance was noted. Also, results of an oxidation run carried out in the hot-stage cell with nearly complete shielding from room light were about the same as for earlier runs carried out without shielding.

The most significant difference between the two types of experiment becomes more apparent when one considers the two different heating methods for the specimen. In the use of induction heating there is very likely a considerable difference in temperature between the uranium metal surface and the surrounding oxygen, while in the case of resistance heating both reactants are at the same temperature. It is impossible to separate the effects of reversing the thermal gradient through the oxide and the difference of temperature between the gas and the specimen. Using an isothermal reactor modified for induction heating of the specimen and resistance heating of the gas phase, it was possible to study the effect of the oxygen temperature on the kinetics of the reaction. Reaction rates were first measured with the specimen heated to 200 C by means of induction and with no effort made to heat the gas phase directly. In later experiments a resistance winding was added to the reactor and rates were measured with the gas phase heated to approximately

the same temperature as the induction-heated specimen. Finally, control runs were made with the resistance winding relocated on the reactor so that both specimen and gas phase were heated by the resistance method. Results of the series of experiments just described are compared in Table 39. It can be seen that with induction heating only, i.e., no direct heating of the gas phase, the rate behavior was similar to that described earlier for runs carried out in the hot-stage cell. No real first stage was observed. When the gas phase surrounding the sample was heated to a temperature approaching that of the sample, the oxidation behavior was intermediate in character between that observed for induction heating alone and that for resistance heating of both sample and gas phase. There was a definite first stage observed with the latter arrangement, although the initial rates were appreciably higher than the baseline data. It would appear, therefore, that when the temperature of the reacting oxygen is considerably lower than that of the uranium metal, the first stage rate tends to be accelerated and the duration of the first stage reduced. Also, there is some indication in the data that there may be an effect due to the induction heating itself.

(2) Effect of Oxide Surface Roughness on Oxidation Kinetics

The possibility that the rate controlling step in the oxidation takes place at the oxygen-oxide interface is suggested by,

- (1) the observations of nodule growth on the oxide surface,
- (2) the absence of significant effects of additives to the metal,
- (3) the existence of a pressure dependence.

The first stage of the reaction could conceivably correspond to the formation

Table 39

OXIDATION OF URANIUM AT 200 C IN 200 mm OXYGEN

<u>Run No.</u>	<u>Sample</u>	<u>Gas Phase</u>	<u>1st Stage Rate</u> <u> (μg/sq cm)/min </u>	<u>Break Time</u> <u>(min)</u>	<u>Break Weight</u> <u>(μg/sq cm)</u>	<u>2nd Stage Rate</u> <u> (μg/sq cm)/min </u>
Base Line Average	Resistance	Resistance	0.49 ± .03	121 ± 30	57 ± 16	6.6 ± .6
176	Induction	--	-- ^a	--	--	12.4
183	Induction	--	-- ^a	--	--	13.3
179	Induction	Resistance	1.13	51	47	6.33
180	Induction	Resistance	1.17	49	45	6.63
184	Resistance ^b	Resistance	0.37	185	68	4.75
185	Resistance ^b	Resistance	0.41	183	90	5.67

^aNo real first stage, rate accelerated initially until second stage is reached.

^bResistance winding of Runs 179 and 180 was relocated so that both sample and gas phase were heated by the same source.

of an oxide layer of relatively uniform thickness with little change in the external surface area of the oxide as the reaction proceeds. Transition to the faster second-stage rate might then be correlated with a gradual roughening of the surface as oxidation begins to accelerate at discrete sites on the base film, giving rise to nodular growths of oxide. If the number of nodules increases steadily and each continues to grow the surface area could be expected to increase exponentially, and if the rate controlling step takes place at the oxide surface, the rate of the reaction should increase in a similar manner. However, as the spreading oxide nodules coalesce, a limiting surface condition would eventually be reached and there would be no further increase in surface area accompanying the reaction. Oxidation beyond this point would be linear and correspond to the observed second stage.

From the above line of reasoning it follows that a sample of initially roughened surface should show a smaller ratio of second to first-stage rate than a polished sample. This hypothesis was tested in a series of experiments with polished and abraded samples at 125 and 150 C in 22 mm of oxygen. Changes in surface appearance during oxidation were followed visually in similar experiments in the hot-stage cell to provide for a qualitative estimation of the extent of surface roughening during reaction. Results obtained at 150 C for samples with finishes produced by grinding with 240- and 600-grit silicon carbide paper are compared in Figure 42 with those for an electropolished sample oxidized at the same temperature.

The curves show that there are considerable differences in the initial rates as might be expected from the increased sample area produced by the coarser finishes. However, the rate data at longer times show good agreement. The curves for the abraded specimens show a much more gradual approach to this fast linear rate than is typical of electropolished specimens.

FIGURE 42
EFFECT OF INITIAL SURFACE ROUGHNESS ON
THE OXIDATION BEHAVIOR OF URANIUM
AT 200 C IN 200 mm OXYGEN

The transition was so gradual for the samples with the 240-grit finish that the first stage rates, break weights, and break times could only be roughly estimated. These estimates are considerably different from those for electro-polished specimens. The decrease in ratio of second to first stage rates with increasing initial surface roughness is shown in Table 40. It would appear, therefore, that these results are consistent with a reaction mechanism having its rate controlling step occurring at the surface of the oxide. It would also appear, therefore, that this may be a reasonable explanation for the slow first stage rate and the break to a faster second stage rate.

3. Zirconium Ignition Studies

a. Zirconium Burning Propagation Rate Studies

Burning propagation rate studies on zirconium and zirconium alloy foil specimens in air and in oxygen have been continued. The apparatus and procedure have been described previously (ANL-5959, page 71). A new foil specimen, wet polished with 600-grit silicon carbide paper, was used for each run. The only modification in the previously described procedure was to place small pieces of the 14.9 atom per cent titanium alloy between the heating wire and the samples in order to obtain rapid and reproducible ignitions.

(1) Burning Propagation Studies in Air

When zirconium samples burn in air they maintain their original shape and a narrow oxidation front is observed preceding the ignition front. The burning propagation rates of several zirconium alloys in air are presented in Table 41. The copper alloy had the slowest propagation rate and the titanium alloys propagated faster than pure zirconium.

Most of the specimens used in these experiments were 0.6 x 70 mm strips of 0.13-mm foil. It was necessary to use narrow (0.6 mm wide)

Table 40

EFFECT OF INITIAL SURFACE ROUGHNESS ON
OXIDATION BEHAVIOR OF URANIUM AT 150 C IN 200 mm OXYGEN

<u>Surface Finish</u>	<u>1st Stage Rate ($\mu\text{g}/\text{sq cm}$)/min</u>	<u>Break Time (min)</u>	<u>Break Weight ($\mu\text{g}/\text{sq cm}$)</u>	<u>2nd Stage Rate ($\mu\text{g}/\text{sq cm}$)/min</u>	<u>Ratio of 2nd to 1st Stage Rate</u>
Electropolished	0.11	360	41	0.60	5.4
600 grit SiC paper	0.18	540	96	0.74	4.1
600 grit SiC paper	0.18	616	112	0.56	3.1
240 grit SiC paper	0.3 ^a	500 ^a	150 ^a	0.67	2 ^a
240 grit SiC paper	0.4 ^a	430 ^a	200 ^a	0.66	2 ^a

^aRough estimates. First stage not well defined.

Table 41

BURNING PROPAGATION RATES OF ZIRCONIUM ALLOYS IN AIR

Foil Dimensions: Thickness, 0.13 mm; Length, 70 mm; Width as Specified

Alloy Composition (Atom Per Cent)	Ignition Temperature (C)	0.6 mm Wide Foil		1 mm Wide Foil	
		Propagation Rate (cm/sec)	Burning Zone Length (cm)	Propagation Rate (cm/sec)	Burning Zone Length (cm)
3.60 Cu	800	0.39	1.1	Would not propagate	
0.91 Ni	794	0.56	1.7	Would not propagate	
Pure Zr ^a	784	0.44	1.2	Would not propagate	
3.60 Sn	767	0.50	1.2	Would not propagate	
1.76 U	766	0.61	2.0	Would not propagate	
1.84 V	764	0.65	2.0	0.44	1.3
3.62 Al	754	0.45	1.0	Would not propagate	
2.15 Al	740	0.58	1.6	Would not propagate	
1.08 Ti	698	0.76	2.2	0.58	1.8
2.12 Ti	632	0.84 ^b	2.6	0.59	2.0
4.16 Ti	551	0.88	3.3	0.66	2.6
14.9 Ti	374	1.06	3.7	0.77	3.3

^aThickness of pure zirconium foil was 0.14 mm.^bAverage of two experimental rates which only differed by 0.03 cm/sec.

samples in order that all of the alloys would propagate since at a width of 1 mm only the 1.84 atom per cent vanadium and the 1.08, 2.12, 4.16, and 14.9 atom per cent titanium alloys would propagate in air. The propagation rates of the 1 mm wide foils are included in Table 40 to show the decrease in propagation rates for the increased width.

(a) Effect of Moisture on Propagation Rate

Two runs were made on the 2.12 atom per cent titanium alloy with moist air and the average propagation rate was found to be 0.81 cm per sec. The rate is slightly lower than the rate in dry air (0.84 cm per sec) indicating that moisture in air shows an insignificant effect on the burning rate.

(b) Correlation Between Propagation Rate and Ignition Temperature

A plot of propagation rate versus ignition temperature for various 0.13-mm thick alloy foils is presented in Figure 43. A fairly sharp increase of propagation rate with decreasing ignition temperature occurs for ignition temperatures down to 700 C. However, the propagation rates do not increase as markedly for ignition temperatures below 700 C. Instead, it appears that a limiting propagation rate is being approached.

(c) The Burning Zone and Its Relationship to Propagation Rates

While each specimen burns in air, the burning area behind the ignition front maintains a relatively constant length. It was observed that the length of this "burning zone" was different for each alloy and was directly related to the propagation rate. The burning zone lengths for the various specimens are included in Table 41. Their relationship to the propagation rate is illustrated in Figure 44. This relationship may be of fundamental importance to the burning process. Continuing study of the relationships between sample size, propagation rates, and burning temperatures will include considerations of heat transfer principles.

FIGURE 43
RELATIONSHIP BETWEEN PROPAGATION RATES
IN AIR AND AIR IGNITION TEMPERATURE
FOR ZIRCONIUM ALLOYS

FIGURE 44
RELATIONSHIP BETWEEN BURNING ZONE
LENGTH AND PROPAGATION RATE IN
AIR FOR ZIRCONIUM ALLOYS

(2) Propagation Rate Studies in Oxygen

When samples burn in oxygen they are completely converted to the oxide. As the burning propagates globules of molten metal an oxide drop from the foil strip. The propagation rates are much faster (approximately 20 times) in oxygen than in air as can be seen by comparing the rates for the alloys listed in Table 42 to those in Table 41. In oxygen the nickel alloy is the only alloy for which burning propagation is slower than the base metal. The titanium alloys propagate fastest of all the alloys in oxygen, as they did in air. Specimens $3.0 \times 70 \times 0.13$ mm were used in propagation experiments in oxygen.

(a) Reproducibility of Propagation Rates

The average deviation of four runs on zirconium base metal was nine per cent. Because runs in oxygen are complicated by sample oscillations and molten metal dropping off the specimens, this may be considered good reproducibility. The propagation rate does not seem to be dependent on surface preparation. An experiment conducted on an "as received" specimen gave a propagation rate of 11.2 cm per sec as compared with the average of four runs on 600-grit wet polished specimens, 11.1 cm per sec.

(b) Correlation Between Propagation Rate and Ignition Temperature

The relation between propagation rates and ignition temperatures in oxygen is similar to that which was found in air. A plot of propagation rate versus ignition temperature is shown in Figure 45.

(c) Dependence of Propagation Rate on Cross-Sectional Area

Since foil strips with greater variations of width and thickness could be burned in oxygen than in air, the study of these variables was continued with pure zirconium foils in oxygen. The propagation rates for

Table 42

BURNING PROPAGATION RATES OF ZIRCONIUM ALLOYS IN OXYGEN

Foil Dimensions: Thickness 0.13 mm, Length 70 mm, Width 3.0 mm

<u>Alloy Composition</u> <u>(Atom Per Cent)</u>	<u>Ignition Temperature</u> <u>(C)</u>	<u>Propagation Rate</u> <u>(cm/sec)</u>
0.91 Ni	792	10.5
Pure Zr ^a	786	11.1 ^b
3.60 Cu	784	13.2
1.76 U	765	13.6
1.84 V	763	11.8
3.60 Sn	759	14.3
3.62 Al	753	13.8
2.15 Al	739	14.6
1.08 Ti	694	14.3
2.12 Ti	634	17.6
4.16 Ti	529	15.0
14.9 Ti	372	17.1

^aThickness of pure zirconium foil was 0.14 mm.^bAverage of four runs with an average deviation from the mean of 1.0 cm/sec.

FIGURE 45
RELATIONSHIP BETWEEN PROPAGATION RATES
IN OXYGEN AND OXYGEN IGNITION TEMPERATURE
FOR ZIRCONIUM ALLOYS
(3.0 X 0.13-mm Foils)

various sizes of pure zirconium foil are listed in Table 45. The data show that the propagation rate is dependent on both thickness and width and that a correlation of rate with cross sectional area is better than with either thickness or width alone. A plot of propagation rate versus cross-sectional area is given in Figure 46. It can be seen that relatively large decreases in cross sectional area produce only small increases in propagation rates for larger cross sectional areas. However, in the region of small cross-sectional area small decreases produce large increases in propagation rates.

Study is continuing on samples with different geometry and cross-sectional area in an attempt to establish a relationship involving known heat transfer principles.

b. Shielded Ignition Experiments

(1) Effect of Moisture on Ignition Temperature

It has often been postulated that moisture may be an important factor in the ignition of zirconium. Accordingly, ignition temperatures were determined for the 0.13 mm zirconium foil in both moist air and moist oxygen. When the gas was passed through a water bubbler at room temperature before contact with the sample, the ignition temperatures were 841 C in air and 813 C in oxygen. Because these ignition temperatures are higher than those determined in the dry gases (784 and 786 C, respectively), moisture is not expected to be an important factor in the ignition of bulk zirconium. However, adding liquid water to burning metal is a different situation and is extremely hazardous since the water acts as an additional supply of oxygen.

Table 43

DEPENDENCE OF PROPAGATION RATES IN OXYGEN ON CROSS SECTIONAL AREAFOR PURE ZIRCONIUM

Point No. ^a	Thickness (mm)	Width (mm)	Cross-Sectional Area (sq mm)	Propagation Rate in Oxygen (cm/sec)
1	0.008	0.9	0.007	167.
2	0.023	0.9	0.021	53.0
3	0.020	3.0	0.060	42.8
4	0.14	1.0	0.14	17.3
5	0.14	1.5	0.21	17.8
6	0.14	2.9	0.41	11.1 ± 1.0
7	0.14	6.2	0.87	8.52
8	0.27	2.1	0.57	6.63
9	0.28	3.0	0.84	8.24
10	0.27	4.5	1.22	5.08
11	0.27	6.0	1.62	6.99

^aNumber corresponds to points on Figure 46.

FIGURE 46
RELATIONSHIP BETWEEN PROPAGATION RATES
IN OXYGEN AND CROSS-SECTIONAL AREA
FOR PURE ZIRCONIUM FOILS

(2) Effect of Surface Preparation on Ignition Temperature

The effect of surface preparation on the ignition temperature of 0.27-mm (11-mil) zirconium foil in oxygen has been determined. The results are listed in Table 44. A small effect was observed. The chemically polished samples had an ignition temperature of 842 C, while the dry polished samples had an ignition temperature of 838 C. Both the wet polished and as received samples gave an ignition temperature of 833 C.

The effect of different surface preparations on the ignition temperature in air of the 0.13-mm foil of 14.9 atom per cent titanium alloy has previously been reported (ANL-5959, page 80). It was found that wet polishing with 600-grit silicon carbide paper produced the lowest ignition temperature, 374 C, and that the "as received" condition produced the highest ignition temperature, 406 C. Dry polishing with 600-grit paper yielded an intermediate ignition temperature of 388 C. Obviously, the effect of surface preparation on the ignition temperature of the titanium alloy is much greater than and considerably different from the effect on pure zirconium ignition temperature. Although these experiments do not define whether the difference is due to alloy effects, thickness of foil, or the oxidizing gas, they have demonstrated that wet polishing with 600-grit paper produces the lowest ignition temperature. Therefore, this method of polishing will continue to be used as the standard method of preparing samples for ignition tests, and the problem of surface preparation will not be pursued further.

4. Zirconium Isothermal Oxidation Studies

In a recent study¹⁰ on the kinetics of oxidation of zirconium

¹⁰Korobkov, I.I., Ignatov, D. V., Yevstyukhin, A.I., and Yemelyanov, V.S., "Electron Diffraction and Kinetic Investigations of the Reactions of Oxidation of Zirconium and Some of Its Alloys," Second United Nations International Conference on Peaceful Uses of Atomic Energy, A/Conf. 15/P/2054, Geneva, Switzerland (1958).

Table 4.1

EFFECT OF SURFACE PREPARATION ON THE IGNITION TEMPERATURE
OF ZIRCONIUM AND 14.9 ATOM PER CENT TITANIUM-ZIRCONIUM ALLOY

Flow rates for oxygen ignitions: Helium, 5200 cc/min; followed by oxygen, 3050 cc/min
 Flow rates for air ignitions: Helium, 1900 cc/min; followed by air, 4660 cc/min
 For conversion to linear flow rates: 1 cc/min = 0.20 cm/min

<u>Surface Preparation</u>	<u>Ignition Temperature ($\pm 5^\circ\text{C}$)</u>	
	<u>0.27-mm Zr Foil in Oxygen</u>	<u>0.13-mm 14.9 a/o Ti Alloy Foil in Air</u>
Chemical Polish ^a	842	-
Dry Polish (600 grit SiC paper)	838	388
Wet Polish (600 grit SiC paper)	833	374
As Received	833	406

^aComposition of chemical polishing solution: 45 parts H_2O , 45 parts HNO_3 (conc.), and 10 parts HF (48%).

and zirconium alloys in air the following explanation of the relationship between kinetic breakaway and polymorphic transformation of the oxide film was given. In the initial oxidation process a thin film of cubic zirconium dioxide is formed. As the oxidation progresses the cubic zirconium dioxide transforms to tetragonal zirconium dioxide. Up to this point the oxidation rate is relatively slow. When the oxide film reached a critical thickness, tetragonal zirconium dioxide transforms to monoclinic zirconium dioxide. Simultaneous with this last transformation a faster oxidation is observed. Thus, the transformation from tetragonal zirconium dioxide to monoclinic zirconium dioxide coincides with what is commonly described as the break-away.

Further evidence is considered necessary to determine the validity of this theory. Therefore, oxidized samples (oxidations performed at 700 C in 200 mm oxygen) of a number of zirconium alloy specimens were submitted for X-ray and electron diffraction analyses. A summary of the results obtained is presented in Table . Some of these oxidations were terminated before kinetic breakaway was observed. The column titled "Breakaway Weight" indicated the weight gain at which breakaways are normally observed. Fifteen samples were submitted for analyses. Ten agreed with the theory, four disagreed, and for one sample (3.88 atom per cent vanadium) the oxide could not be identified.

One sample which disagreed (3.60 atom per cent tin) was in a run which was terminated very shortly after the breakaway, and it is possible that the top layer of oxide was only partially transformed. The other three samples which disagreed were alloys which oxidized initially according to the parabolic rate law rather than the usual cubic rate law. This would indicate that alloys,

Table 45

PREDICTION OF POLYMORPHIC FORM OF ZIRCONIUM DIOXIDE FROM KINETIC DATA

Monoclinic form predicted after kinetic breakaway observed

<u>Alloy Composition</u> (Atom a/o, Balance Zr)	<u>Weight Gain^a</u> ($\mu\text{g}/\text{sq cm}$)	<u>Breakaway Wt^a</u> ($\mu\text{g}/\text{sq cm}$)	<u>Polymorphic</u> <u>Predicted</u>	<u>Form of ZrO₂</u> <u>Found</u>	<u>Agreement with</u> <u>Theory</u>
Pure Zr	2,832	No Breakaway	Cubic	Cubic ^b	Yes
3.60 Sn	431	521	Cubic	Cubic ^b	Yes
3.60 Sn	1,343	521	Monoclinic	Cubic ^b	No
3.60 Sn	13,404	521	Monoclinic	Monoclinic ^b	Yes
1.42 Al	1,071	1,467	Cubic	Cubic ^b	Yes
1.42 Al	24,780	1,467	Monoclinic	Monoclinic ^c	Yes
3.60 Cu	2,385	No Breakaway	Cubic	Cubic ^b	Yes
1.96 W	5,787	No Breakaway	Cubic	Cubic ^b	Yes
1.64 C ^d	10,845	1,225	Monoclinic	Monoclinic ^c	Yes
1.78 Ta ^d	11,668	No Breakaway	Cubic	Monoclinic ^b	No
3.54 Ta ^d	15,727	7,380	Monoclinic	Monoclinic ^c	Yes
3.52 U	4,139	2,645	Monoclinic	Monoclinic ^c	Yes
4.16 Ti ^d	3,957	15,975	Cubic	Monoclinic ^c	No
3.88 V ^d	4,492	No Breakaway	Cubic	Not Identified	--
3.88 V ^d	14,392	No Breakaway	Cubic	Monoclinic ^c	No

^aIsothermal oxidation data at 700 C and 200 mm oxygen.^bElectron diffraction analyses by H. Knott and M. W. Mueller, Metallurgy Division.^cX-ray diffraction analyses by D. S. Flikkema, Chemical Engineering Division.^dOxidized initially according to the parabolic rate law.

which do not oxidize initially according to the cubic rate law, do not follow the predicted sequence of transformations. These three cases had not shown the kinetic breakaway and yet the monoclinic form of zirconium dioxide was found in each case. This would suggest that alloys, which initially oxidize according to the parabolic rate law, form monoclinic zirconium dioxide very early in the oxidation, perhaps from the beginning. The association of oxidation behavior with the oxide transformation will be studied further.

B. Metal-Water Reactions

(L. Baker, M. Kilpatrick*, R.C. Liimatainen, D.F. Mason, C.H. Smith, D. Martin, R. Warchal, W.A. Rodger, R.C. Vogel)

1. Laboratory Studies -- Condenser Discharge Method

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; hydrogen generated gives extent of reaction; and particle size of residue indicates the surface area exposed to reaction. Further runs with 60-mil zirconium wires are reported. Measurement of the particle sizes of residue are described. The accumulated zirconium data are under study preliminary to an analysis on the Pace analog computer. A series of runs with 60-mil uranium wires has been started.

a. Zirconium Experiments

The experimental procedure used has been described in the previous quarterly report, ANL-5959, page 94. The zirconium data obtained to date are summarized in Table 46. The total extent of reaction, as determined from measurements of the total hydrogen liberated according to Equation 1, is plotted in Figure 47.

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Table 46

ZIRCONIUM-WATER REACTION DATA -- CONDENSER DISCHARGE METHOD

Run	Energy Input (cal/g)	Calc Temp, C and Comp	% Reaction	Pressure Rise Rate ^a	Mean Particle Diameter ^b (μ)	Appearance of Residue
32	100	1150, solid	0.70	Slow	2140	Intact
23 ^c	127	1500, solid	1.2	Slow	2180	Intact
13	137	1600, solid	3.9	Slow	2160	Intact
22	150	1800, solid	4.2	Slow	2170	Intact
24	158	1840, 5% liq	5.9	Slow	2060	Elliptical
28 ^c	174	1840, 30% liq	-	Slow	2180	Elliptical
27 ^c	183	1840, 50% liq	-	Slow	2240	Elliptical
25	190	1840, 60% liq	8.9	Slow	2280	Large Particles
26	203	1840, 80% liq	7.9	Slow	2100	Large Particles
29	208	1840, 90% liq	7.9	Slow	1500	Coarse Particles
14	217	1900, liq	8.2	Slow	1960	Elliptical
15	218	1900, liq	9.0	Slow	2040	Large Particles
18	233	2100, liq	12.1	Slow	1500	Large Particles
30	235	2100, liq	12.6	Slow	940	Coarse Particles
31	258	2400, liq	18.3	Slow	680	Coarse Particles
42	269	2550, liq	10.9	Slow	740	Fine Particles
33 ^d	271	2550, liq	-	Slow	1300	Coarse Particles
20	275	2600, liq	24.	Rapid	440	Coarse Particles
19	276	2600, liq	43.	Rapid	340	Fine Particles
16	284	2700, liq	17.1	Slow	980	Coarse Particles
40	290	2800, liq	39.	Rapid	160	Powder
41	294	2850, liq	45.	Rapid	110	Powder
17	296	2900, liq	71.	Rapid	340	Fine Particles
39	300	2900, liq	50.	Rapid	240	Powder
21	313	3100, liq	37.	Rapid	240	Fine Particles
37	332	3300, liq	52.	Rapid	180	Powder
35	361	3700, liq	60.	Rapid	200	Powder
34	388	3900, 1% vap	71.	Rapid	270	Powder
36	393	3900, 1% vap	50.	Rapid	480	Powder
11	501	3900, 10% vap	67.	Rapid	70	Powder

^aSlow runs require 50 to several hundred milliseconds to reach a final pressure; the pressure rise is completed in a fraction of a millisecond in rapid runs.

^bA "mean particle" is one that has the same surface to volume ratio in the entire sample, i.e., $d_{\text{mean}} = 6n D^3 / nD^2$

^cArgon gas present to the extent of 3 atm.

^dWire was pre-oxidized (run 32) before discharge.

FIGURE 47
ZIRCONIUM WATER REACTIONS: EFFECT
OF ENERGY INPUT ON HYDROGEN YIELD

The results show considerable scatter for high energy runs. It is considered likely that some of this variance is due to variations in particle sizes produced by the discharge.

Oscillograms of pressure as a function of time were obtained for most of the runs. Again, it was found that very fast, explosive pressure rises occurred for runs with an initial temperature exceeding 2600 C. This is indicated in Table 45 as a rapid pressure rise rate. Relatively slow pressure rise rates occurred for runs whose initial temperatures were less than 2600 C.

b. Measurement of Particle Sizes

A method for estimating the total surface area and particle size of residue from runs was developed using a specially constructed slide projector. Preliminary attempts using photomicrographs showed that a great number of separate photographs and an intricate sampling procedure would be required. A magnification suitable for large particles would not allow diameter measurements of the smaller particles. It was necessary to have a very large blow-up of the sample residue which could best be done by projection over a long optical arm followed by tracing the image on large pieces of paper. All particles were generally spherical in shape. It was necessary to assume that they were ideally spherical. A summary of the particle diameters is included in Table 46. Five different procedures were required to obtain particle size data for the different types of residue.

1. High energy runs produced fine particles. Residue from a run was carefully mixed and divided until a small representative quantity remained. This was sprinkled on microscope slides coated with a thin film of Glyptal varnish and allowed to dry. They were then projected at 100 X using a high quality, achromatic lens from a

motion picture camera. Over 100 particle tracings were made for each run. Only a negligible quantity of particles as small as 10μ were found; these measured 0.1 cm on the enlargement and represented the lower limit of the method. Larger particles could be measured with progressively greater accuracy.

2. Runs of somewhat lower energy produced a few large particles ($> 500\mu$) and a number of smaller particles. All of the larger particles were mounted on slides using forceps. The total surface area and volume were then computed from diameter measurements made at 50 X. The volume obtained was subtracted from the calculated initial wire volume and the difference assumed to be in the form of fine particles. The finer material was separately treated as for the high-energy runs. The total areas for both coarse and fine material were added together to give the total. In this way sampling errors were greatly reduced because the larger particles did not have to be sampled.
3. Runs of intermediate energy produced a limited number of large particles (generally larger than the original wire diameter). The entire residue from each run could then be mounted and projected at about 30 X. Diameter measurements of every particle allowed the calculation of total surface and volume. The volume calculation agreed with the original wire volume within 20 per cent.

4. Energy input values which resulted in between 0 and 50 per cent melting produced wires of elliptical rather than circular cross-section. Although these specimens were somewhat irregular, it was possible to measure the major and minor axes of the cross-section and approximate the surface area. Increases in area over the original wire of 3 to 7 per cent were obtained.
5. Low energy runs left the wire intact so that only a knowledge of the diameter and sample weight were required to calculate surface area.

Surface area data were converted to mean particle diameter as follows:

$$D_{\text{mean}} = \frac{6V}{S} \quad (2)$$

where V is the total volume of sample and S is the total surface area. In the case of wires that remained intact, the diameter given in Table 45 is an equivalent diameter of spheres having the same surface to volume ratio as the cylindrical wire.

The log of the mean particle diameters is plotted as a function of reciprocal initial temperature in Figure 48. The results can be represented approximately as two straight lines. The first corresponds to the region below the melting point. The second indicates that there is a regular decrease in particle size with increasing temperature beyond the melting point. The apparent activation energy for the process is 24 kcal/mole. Numbers representing per cent reaction are indicated on Figure 48. Variations in particle size will account for some of the variance in the extent of reaction for runs made at similar initial temperature.

FIGURE 48
ZIRCONIUM WATER REACTIONS: EFFECT
OF TEMPERATURE ON MEAN PARTICLE SIZE
(Condenser Discharge Heating Method)

c. Analysis of Zirconium Data

Equations were derived in ANL-5896, page 108, to describe the overall reaction process following the instantaneous heating and dispersion of metal by the condenser discharge. Preparations are under way to obtain graphical solutions to the equations on an analog computer. A solution for a single set of assumed constants was obtained by hand computation. The results are shown in Figure 49. The calculated transient pressure curve is very similar in form to those observed experimentally and reported previously for runs made at lower temperatures. Although the initial conditions border the ignition region of Figure 48, the results show that the equations do not predict an ignition. The tentative conclusion is that a mechanism change must occur (melting of oxide at 2700 C or other effect) to account for the explosive pressure rise.

The constants in the equations which involve the rate constant, activation energy, radiative and convective heat loss coefficients, and physical properties will be adjusted until semi-quantitative agreement is obtained between calculated results and the experimental data. The results will guide future experimental work with the zirconium-water system.

d. Uranium Experiments

Three runs have been completed using 60-mil uranium wires.

The following results were obtained:

<u>Run</u>	<u>Energy Input (cal/g)</u>	<u>Calc Temp, C and Comp</u>	<u>% Reaction (Based on UO₂)</u>	<u>Appearance of Residue</u>
47	42.5	1000 γ, solid	1.05	4 pieces
46	67.1	1300 liq	6.1	Coarse Particles
45	78.9	1600 liq	4.8	Coarse Particles

FIGURE 49
CALCULATED TEMPERATURE-TIME AND PER CENT
REACTION-TIME CURVES FOR ZIRCONIUM WATER
REACTION WITH ASSUMED CONSTANTS

A pressure-time curve taken from the oscillogram from Run 46 shows an apparent induction period of 5 milliseconds followed by a pressure rise of about 0.01 atm/msecond. Runs 45 and 46 were made using the maximum energy of the present apparatus. Higher temperatures were not obtained because of the lower electrical resistivity of uranium compared to zirconium. High temperature runs will be made using 30-mil wires.

Particles were obtained in Run 47 even though the calculated temperature was below the melting point. It appeared that the uranium was broken up by the rapid heating even though melting temperatures were not attained. It was also observed that the particles resulting from higher temperature runs were not spherical in shape. This also implies that break-up occurred before melting. Particles from runs involving zirconium were generally observed to be spherical in shape, indicating that particles were formed from liquid metal. The mechanism of wire break-up will be studied further.

2. Laboratory Studies -- Pressure-Pulse Method

The pressure-pulse method involves the momentary contact of water vapor with molten metal contained in a crucible. The objective of this experiment is to study the steam-metal reaction under conditions designed to give the upper extreme conditions of rate. This will arise since the metal surface will be oxide free. The method permits careful control over the reaction time and the surface area of metal exposed to reaction.

Experiments preliminary to the final apparatus design are under way. Indications are that thoria crucibles will be satisfactory for containing molten zirconium for the short times involved. The other metals to be studied, uranium, aluminum, and stainless steel, should not be as difficult to contain as zirconium. A 4-KW induction heating unit has been ordered. Tests with a

more powerful unit have indicated that 4 KW will be adequate to reach temperatures of the order of 2500 K. Tests with rapid-acting solenoid valves have shown that rapid contact and withdrawal of the water vapor will be feasible. Design of a controller to sequence valve operation has begun. The apparatus is designed to allow studies up to 2500 K and 1 atm. Apparatus for studies at higher pressure will be built if necessary. Estimates of the rate of reaction of zirconium and water vapor at 2500 K can be made by extrapolating the data of Crooks et al.,¹¹ for molten Zircaloy-2 between 1900 and 2050 C.

Crooks gives the following equation:

$$V^2 = 0.1132 \times 10^6 \cdot (\exp - 34,000/RT) t \quad (3)$$

where V is ml H₂ formed per sq cm of surface, t is time in seconds.

If samples to be used have an exposed surface area of about 0.7 sq cm, the following table indicates extrapolated values of the hydrogen yield for various exposure times at 2500 K:

<u>Time</u>	<u>Hydrogen Yield (ml STP)</u>
10 msec	0.77
100 msec	2.43
1 msec	7.7

These gas volumes will be well within the measurement range of the proposed analytical system.

A possible complicating factor is the possibility that the reaction rate may become controlled by gas transport processes at the high temperatures proposed for this study. If the true oxidation rate is very rapid it is possible that the observed rates will be controlled by the rate of inward diffusion of water vapor through a protective layer of product hydrogen. The presence of this can be detected by a departure of the data from a simple power law and the presence of a spuriously low activation energy.

¹¹Lemmon, A.W., "Studies Relating to the Reaction Between Zirconium and Water at High Temperatures," BMI-1154 (1957).

3. In-Pile Testing in the TREAT Reactor

A second autoclave, made of type 316 stainless steel and weighing 11 kilograms, has been modified from the design previously described (see ANL-5924, page 107). Its construction is one-half completed. This autoclave is designed to withstand an internal static pressure of 7600 psia at 750 F (the maximum design core temperature for the TREAT reactor) as determined from the Unfired Pressure Vessel Code. The maximum static pressure expected will be 4000 psia at 750 F.

A dummy TREAT fuel can is being modified to permit insertion of the autoclave inside the element which will act as a secondary container. Graphite reflector blocks will support the autoclave within the element.

Experiments are being conducted on a liquid metal (NaK_2)-water reaction inside the autoclaves to test the instrumentation that will be used in TREAT. These experiments give an indication of the type of temperature and pressure traces to be expected, a verification of the experimental technique, and a check-out of the instrumentation under dynamic conditions. The temperature and pressure data obtained on an oscillograph for an experiment in autoclave Number 1 (304 stainless steel) are plotted in Figure 50. The small wiggle throughout the temperature trace is due to 60-cycle AC which was picked up by the leads. The three pronounced temperature and pressure rises in the range of 80 to 170 milliseconds could be due to large drops of NaK_2 hitting the water. Larger and more severe tests in both autoclaves are planned. The pertinent conditions for this experiment are listed in Table 47 along with a comparison of the conditions to be expected in the first series of experiments planned for TREAT.

A program to predict and correlate the TREAT metal-water reaction data on the PACE analog computer (Applied Mathematics Division, Argonne National

FIGURE 50
REACTION OF NaK_2 WITH WATER

Table 47

DATA OF NaK₂-WATER REACTION AND COMPARISON
TO A PLANNED TREAT EXPERIMENT

	<u>NaK₂</u>	<u>TREAT (1 pin)</u>
Natural frequencies of galvanometers: (cps)		
Thermocouple	200	--
Pressure transducer	400	--
Metal (grams)	2.3	9.63 (uranium)
Water (grams)	25	33
Volume of Vessel (cc)	230	230
Heat evolved for complete reaction (gram calories)	6120	4840
Hydrogen liberated for complete reaction (liters at STP)	0.76	1.81

Laboratory) has been initiated. A set of four simultaneous differential equations considering the temperature of the unreacted metal, temperature of the oxide, amount reacted, and the pressure in the vessel was derived which should describe the transient, physical, and chemical factors as functions of time. The constants will be refined as experimental data become available and the results of the temperatures, pressure, and the extent of reaction predicted from the equations can be matched to the results of the TREAT data. This work is approximately three-quarters complete and will be reported on in detail upon its completion.

IV. REACTOR CHEMISTRY

The Reactor Decontamination program is a joint one with the Reactor Engineering Division. The incentive for the program results from the lack of knowledge about the consequences of a fuel rupture in a boiling water reactor and about the remedial measures necessary to place the reactor back on stream if these consequences are severe. The purpose of the program is two-fold:

- (1) to determine the types and quantity of fission product activities likely to be distributed on the internal surfaces of a boiling water reactor system,
- (2) to determine what methods of activity removal can be utilized.

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

In order to ascertain the contribution of deposited activities due to short-lived gaseous precursors, the Reactor Engineering Division conducted several fuel defect tests in the EBWR. Coupons inserted in the reactor system were evaluated by CEN personnel and reported in ANL-5959.

A. Reactor Decontamination (W. B. Seefeldt)

1. Laboratory Investigations (S. Vogler, H. Tyler)

In autoclave experiments fission product activity is introduced onto Type 304 stainless steel. To achieve this, a stainless steel crucible-shaped liner containing approximately two grams of irradiated natural uranium

and 100 ml of deionized water is placed inside an autoclave and heated for approximately six days at 600 psi and 486 F. At the completion of an experiment the contents are removed and the liner rinsed with distilled water. The liner is then cut into one-inch squares for use in experiments which measure the effectiveness of various decontaminating reagents.

Results reported in the last quarterly (ANL-5959, page 99) had indicated that despite various pretreatments, including etching of the crucible before use, the activity deposition was always very spotty. The decontamination results indicated a trend towards better decontamination with an etched liner or one that had been preoxidized in saturated steam at 600 psi for six days. The preoxidizing procedure has been chosen as the reference pretreatment for all contamination experiments. This is consistent with reactor operation, as all reactor surfaces will be thoroughly oxidized prior to exposure to fission product activity.

a. Liquid Phase Decontamination Experiments

Many reagents have been tested as decontaminants for Type 304 stainless steel contaminated with fission products at pressures of 600 psi. Selected results are shown in Table 4.6. None of these reagents except for the ammonium persulfate-hydrofluoric acid appears to be as effective as the treatment with alkaline permanganate followed by ammonium citrate. The ammonium persulfate-hydrofluoric acid is extremely corrosive to mild steel, expected to be present in some reactor systems.

In addition to these reagents the decontamination procedure advanced by the Turco Products Company has been investigated. The procedure utilizes a series of three reagents:

- (1) Turco 4501 of undisclosed composition used at 130 to 140 C,

Table 48

DECONTAMINATION OF 304 STAINLESS STEEL

Cooling Time: Approximately 3 months
 Activity: β and γ $\sim 5 \times 10^3$ cpm
 Coupon Size: ~ 1 in. square
 Activity Determination:
 Beta : Proportional counter
 Gamma : Scintillation spectrometer

Reagent	Time (min)	Temp (C)	Decontamination		Wt Loss (mg)
			Beta	Gamma	
1. 3% KMnO_4 -20% NaOH 10% Ammonium Citrate	30 15	95 85	67	46	2.1
2. Water	30	95	2	2	0.3
3. 10% HNO_3	30	60	11	12	0.8
4. Conc HNO_3	30	60	10	9	0.1
5. Conc HNO_3	30	90-95	25	45	1.0
6. 10% Sulfamic Acid 0.3% Mercaptobenzothiazole	30	85	13	11	1.2
7. 5% $(\text{NH}_4)_2 \text{S}_2\text{O}_8$ 2% HF	30	60	109	40	0.8
8. 5% $(\text{NH}_4)_2 \text{S}_2\text{O}_8$ 2% HF 10% $\text{Al}(\text{NO}_3)_3$	30	60	13	11	0.5
9. 5% $(\text{NH}_4)_2 \text{S}_2\text{O}_8$ 2% HF 10% $\text{Al}(\text{NO}_3)_3$	30	90-95	9	13	+0.7
10. 10% NaOH 2.5% Sodium Tartrate 2.5% H_2O_2	30	60	15) ^a 5)	11 4	0.1
11. 10% Phenol	30		3	3	0.9
12. Rubbed with Damp Kleenex	--	--	3	3	--
13. Rubbed with Cleanser			10	13	--

^aThis reagent decontaminates zirconium-niobium very well. At the completion of the decontamination step in both cases the zirconium-niobium peak and the cerium peak were almost missing. Thus the presence of more zirconium-niobium originally in the one case may result in the higher decontamination.

2. Turco 4502, which is believed to be alkaline

permanganate, at 100 to 105 C,

3. 25 per cent nitric acid at ambient temperatures.

A recent change replaces the third reagent with inhibited phosphoric acid for mild steel surfaces. When each of these reagents was used in the reference manner for one-half-hour exposure per reagent, beta and gamma decontaminations of approximately 30 were obtained. When the contact times were increased to two hours for Turco 4501 and to one hour for Turco 4502, the decontamination improved to a value of 150 for beta and 110 for gamma. Although this is a good decontamination, little advantage over the alkaline-permanganate procedure is apparent. In addition the cost of using large volumes of these proprietary reagents might be prohibitive.

5. Decontamination of Stainless Steel with Alkaline Permanganate

The alkaline permanganate procedure for the decontamination of stainless steel surfaces appears to have considerable usefulness. The results shown in Table 49 indicate the reproducibility of the decontamination obtained when two separately contaminated crucibles were tested.

Additional data obtained with this reagent are summarized in Table 50. These results indicate that increasing the time of treatment with the permanganate solution results in an increase in the decontamination obtained. The data also indicate that a decrease in the sodium hydroxide concentration adversely affects the decontamination obtained.

Because of the attractiveness of the alkaline-permanganate decontamination procedure, a further investigation of some of the pertinent variables was initiated. The second step of the procedure (ammonium citrate treatment) was not varied. Longer exposure times (on the order of 24 hours) would be reasonable if lower temperatures and/or reduced solution concentra-

Table 49

DECONTAMINATION OF STAINLESS STEEL WITH ALKALINE PERMANGANATE

Pretreatment of Crucible: Preoxidized
 Time of Heating with Uranium: 6 days
 Cooling Time of Uranium: approximately 3 months

Run No.	Decontamination ^a	
	β	γ
6	61	38
	73	53
8	141	44
	91	32

Procedure: The sample is treated with a solution of three per cent potassium permanganate in 20 per cent sodium hydroxide for one-half hour at 90 C. The sample is then treated with 10 per cent ammonium citrate for 15 minutes at 85 C. The sample is then rinsed and dried before counting.

^aEach number represents a single determination on a fresh coupon.

Table 50

DECONTAMINATION OF 304 STAINLESS STEEL WITH ALKALINE PERMANGANATE

Pretreatment of Crucible: Preoxidized
 Cooling Time: Approximately 3 months
 Activity: β and γ $\sim 5 \times 10^3$ cpm

Reagent	Time (min)	Temp (C)	Decontamination		Wt Loss ^a (mg)
			Beta	Gamma	
1. 3% KMnO ₄ 20% NaOH 10% Ammonium Citrate	30 15	90-95 85	67	46	2.1
2. Duplicate of 1			116	38	1.0
3. 3% KMnO ₄ 2% NaOH 10% Ammonium Citrate	30 15	90-95 85	22	15	0.4
4. 3% KMnO ₄ 20% NaOH 10% Ammonium Citrate	60 15	90-95 85	22	15	0.4
5. 3% KMnO ₄ 20% NaOH 10% Ammonium Citrate	120 60	90-95 85	329	234	1.3

^aA weight loss of one mg is equivalent to a penetration of 4×10^{-3} mils.

tions could be utilized. Several preliminary experiments of 24-hour duration were tried. These results indicated that three per cent potassium permanganate in 20 per cent sodium hydroxide at room temperature for 24 hours gave a decontamination comparable to that obtained at 90 C for 30 minutes. An increase in the exposure time to three days at ambient temperatures did not produce any significant increase in the decontamination. A subsequent experiment with one-half per cent potassium permanganate in three per cent sodium hydroxide also produced a comparable decontamination. The ammonium citrate treatment in all cases was the same as in earlier tests, namely 10 per cent ammonium citrate at 85 C for 15 minutes. For these exploratory experiments, the results indicated gamma decontamination factors of approximately 100. Additional experiments to study the effect of solution composition, temperature, and time of exposure of both the permanganate and ammonium citrate reagents are planned.

c. Stability of Potassium Permanganate in Sodium Hydroxide

During the long-term tests previously mentioned, it was noticed that after 24 hours the potassium permanganate solution color changed from purple to a deep blue-green since potassium permanganate is unstable in strong caustic. In order to obtain a qualitative idea of the degree of reaction of potassium permanganate with sodium hydroxide, a series of four solutions were prepared with the following composition:

<u>Solution</u>	<u>Concentration, Weight Per Cent</u>	
	<u>KMnO₄</u>	<u>NaOH</u>
1	3	20
2	0.5	20
3	3	3
4	0.5	3

The spectra of these solutions were obtained by diluting with water and scanning with a Cary recording spectrophotometer. The potassium permanganate spectrum consists of twin peaks at 527 and 548 mμ with a small shoulder on either side.

Examination of the spectra 20 hours after solution preparation indicated that in 20 per cent sodium hydroxide there was a great change. With the three per cent potassium permanganate, the peaks of maximum absorption were still visible but somewhat distorted. The characteristic absorption of the manganate ion was observable.* In the 0.5 per cent permanganate solution, only the very slightest traces of the permanganate peaks were visible; the absorption spectra was that of the manganate ion. In the three per cent sodium hydroxide, there was less distortion of the permanganate absorption peaks. However, in all cases the maximum absorbance was depressed from that obtained with a potassium permanganate solution in water.

Several of these solutions were studied with and without metal present to determine the effect, if any, of the stainless steel on permanganate stability. Spectra were obtained after one and three days of stirring. No effect was observed.

One experiment was done to determine whether the low concentrations of caustic (0.05 M max) in the final solution affected the absorbance. A series of solutions were prepared using 0.5 per cent potassium permanganate in water and pipetting this into sodium hydroxide solutions of 0.01, 0.1 and 1 M. The samples were prepared and examined one hour after preparation. The results are given in Table 51. These results indicate that even in dilute caustic the reduction of permanganate is progressing slowly. In fact in one hour the dilute solutions of potassium permanganate ($\sim 3 \times 10^{-4}$ M) in 1 M sodium hydroxide were completely discharged. The main purpose of these last experiments was to determine the extent of the permanganate reduction while dilutions were being prepared for spectrophotometry.

*Private communication - Malcolm Daniel - ANL Chemistry Division.

Table 51

EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON STABILITY
OF PERMANGANATE ION

Initial MnO_4^- Conc: $3 \times 10^{-4} \text{ M}$

<u>NaOH (M)</u>	<u>Absorbance (Max)</u>	
	<u>1 Hr</u>	<u>5 Hr</u>
0	1.53	1.53
0.01	1.46	1.32
0.1	1.15	--
1.0	Color Completely Gone	

These results may be summarized as follows:

- (1) Potassium permanganate is reduced to the manganate ion in sodium hydroxide solution, the extent of the reduction being determined by the sodium hydroxide concentration.
- (2) Apparently the presence of stainless steel does not affect the stability of permanganate solutions. The amount of the corrosion (~ 1 mg) should not measurably affect the permanganate concentration.
- (3) Most of the reduction occurs during the first day, with little change occurring the next two days.

The effect that this instability may have on the decontamination procedure will require further study.

d. Corrosion of Mild Steel

Since most reactor systems include mild steel as well as stainless steel, several corrosion tests were made on mild steel with some of the promising decontaminating reagents for stainless steel. The tests consisted of using the same procedure as was used for the decontamination experiments except that mild steel was substituted for stainless steel. The results are tabulated in Table 52.

These results indicate that the alkaline permanganate procedure is compatible with mild steel. The corrosion appears to taper off with time, so that if long contact periods are necessary, the corrosion should be lower than that indicating by extrapolation from the table. The corrosion rate of mild steel in the fluoride containing reagents is excessive.

Table 52

CORROSION OF MILD STEEL IN DECONTAMINATION REAGENTS

Coupon Size 1 x 1 x 0.017 in.

Procedure	Time (min)	Temp (C)	Wt Loss (mg)	Penetration (mils)
1. 3% KMnO_4 ^a 20% NaOH 10% Ammonium Citrate	30 15	90 85	8.6	0.05
2. 3% KMnO_4 2% NaOH 10% Ammonium Citrate	30 15	90 85	4.3	0.02
3. 3% KMnO_4 20% NaOH 10% Ammonium Citrate	240 90	90 85	21.0	0.08
4. 5% $(\text{NH}_4)_2 \text{S}_2\text{O}_8$ 2% HF	30	60	1150	4.6
5. 5% $(\text{NH}_4)_2 \text{S}_2\text{O}_8$ 2% HF 10% Al $(\text{NO}_3)_3$	30	60	1070	4.3
6. 10% Sulfamic Acid 0.3% Mercaptobenzothiazole	90	30	3.6	0.01

^aIn this case the coupon size was 1 x 5/8 x 0.017 in.

e. Decontamination of Mild Steel

The efficiency of the alkaline permanganate procedure in decontaminating mild steel from fission products was measured. The experiments were carried out in the same manner as the stainless steel experiments. In the first experiment the coupon was immersed in three per cent potassium permanganate-20 per cent sodium hydroxide at 90 C for one-half hour. After rinsing with water, the coupon was immersed in 10 per cent ammonium citrate at 85 C for 15 minutes. The measured decontamination (average of two results) was approximately 1.7×10^3 for beta and approximately 700 for gamma which is approximately five-to ten-fold higher than the results obtained with stainless steel.

A second experiment was made using a more dilute permanganate solution at room temperature. In this experiment the coupon was allowed to remain in 0.5 per cent potassium permanganate-3 per cent sodium hydroxide at room temperature with stirring for 24 hours. After rinsing with water the same ammonium citrate treatment was employed as described in the previous paragraph. In this case the measured decontamination (average of two results) was about 10^3 for beta and 550 for gamma. The weight losses in both cases were approximately 10 mg which represents a penetration of 0.04 mils.

f. Vapor Phase Decontamination

Additional experiments were made using the vapor phase decontamination technique (ANL-5959). The specimens were obtained from a liner which had been preoxidized for six days at 600 psi and were contaminated in the usual manner. For these experiments the cooling time of the irradiated uranium was approximately four months. The reagents investigated were concentrated nitric acid (mainly to check some previous results on a different

specimen), inhibited hydrochloric acid (with formaldehyde), and acetic and formic acids. The apparatus for these experiments was arranged so that the liquid whose vapor was to be tested was to boil, with the rising vapors passing over the metallic specimens. These vapors were condensed and returned to the boiler. It was also observed that vapor condensed on the metallic specimens.

From the large weight loss of the stainless steel coupon and observation of the experiment, it was obvious that the inhibited hydrochloric acid reagent reacted with the metal. No attempt was made to determine the activity on the metal at the end of this experiment. The results of the other experiments are given in Table 53. The individual fission product activity was obtained by measuring the area under the appropriate scintillation spectrometer peak before and after the experiment. The decontamination was then calculated in the usual manner. The weight loss was determined for each of these experiments and averaged 0.3 mg, which represents a penetration of 3×10^{-3} mils.

The nitric acid apparently removes the ruthenium and cerium much more readily than the zirconium-niobium. For the acetic and formic acids the cerium decontamination appears to be somewhat higher than the ruthenium or zirconium-niobium decontamination.

Based on the results gathered to date vapor phase decontamination does not appear as favorable as decontamination with liquid reagents.

2. Loop Tests

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

The installation of the loop and all associated instrumentation has been completed. Leak testing of the equipment is being done and faulty components replaced. The operational characteristics of the loop together with the control system are being determined. Calibration of instrumentation is in progress.

Table 53

REMOVAL OF FISSION PRODUCT ACTIVITY FROM
STAINLESS STEEL BY VAPOR PHASE REACTION

Activity: Deposited at 600 psi
Cooling Time: 4 Months
Time of Treatment: 1 Hour
Procedure: See Text

<u>Reagent</u>	<u>BP (C)</u>	<u>Decontamination Factor</u>				
		<u>β</u>	<u>γ</u>	<u>Ru</u>	<u>Zr-Nb</u>	<u>Ce</u>
Conc HNO_3	120	30	10	a	3.5	a
20% $\text{CH}_3\text{CO}_2\text{H}$	~110	1.4	1.3	1.4	1.2	1.6
20% HCO_2H	~110	2.6	2.2	2.4	2.5	5.8
100% $\text{CH}_3\text{CO}_2\text{H}$	118	3.5	2.5	2.7	2.8	4.2
90% HCO_2H	100	7.8	4.0	4.6	3.5	7.5

^a Both the cerium and ruthenium peaks were absent after the nitric acid experiment.

V. ANALYTICAL DEVELOPMENT
(R. P. Larsen)

The analytical methods which will be used to ascertain the fate of 13 of the fission products when irradiated "fissium" is dross refined in the Chemical Engineering Division's Senior cave have been demonstrated to be satisfactory.

Mixtures of sodium carbonate and sodium hydroxide have been found to be particularly satisfactory fluxes for the fusion-dissolution of calcined aluminum oxide.

Radiochemical methods for cerium and for total rare earths in which the separations are effected by solvent extraction have been devised. No yield determinations are necessary; analysis times have been cut by a factor of three.

1. Irradiated Materials Processing Analytical Development
(J. J. McCown, W. Sovereign)

To verify laboratory findings and extend the knowledge of the fate of other fission products in the EBR-II melt-refining process, one-kg batches of highly irradiated fuel (up to one per cent burn-up) will be processed in the Chemical Engineering Division's senior cave. This program has been previously discussed in ANL-5959, page 146.

Since the analytical work in support of this program will in many ways be the same as that which will be required for the EBR-II Processing Facility, the opportunity of confirming the methods and techniques to be used in the attendant analytical facility is being exploited. Short-cooled irradiated "fissium" was used for testing the required methods. Standard radio-

chemical methods for tellurium, iodine, barium-strontium, and the rare earths can be used without modification. The high concentrations of inert fission elements made it necessary to modify the radiochemical methods for cesium¹² and neptunium¹³. The colorimetric methods which have been used to determine zirconium, molybdenum, ruthenium, rhodium, and palladium in inactive samples work equally well with the active ones. Technicium will be determined by a modified thiocyanate procedure¹⁴ after separating it from the other "fission" constituents with a sulfuric acid distillation.

2. Dissolution of Calcined Aluminum Oxide (L. E. Ross, R. Kilboy)

To solubilize samples of active calcined aluminum oxide prior to radiochemical analyses, the practice has been to fuse the oxide in potassium carbonate and dissolve the melt in dilute sulfuric acid. The method has not been highly satisfactory. Some ruthenium activity is lost by volatilization during the fusion and in the small insoluble residue which remains after the bulk of the melt has been dissolved in the acid. Potassium added in the fusion step interferes in the chloroplatinic acid determination of cesium in low level samples.

Mixtures of sodium hydroxide, carbonate and nitrate in a 1:1:2 ratio and sodium hydroxide and carbonate a 1:2 ratio both give fusions of aluminum oxide which dissolve completely in 6 N sulfuric acid. However, gamma scans taken before and after fusion show that as much as 25 per cent of the cesium activity can be lost when sodium nitrate is present during the fusion. Small cesium losses, 5 to 10 per cent, also occur during the carbonate-hydroxide fusion but this appears to be unavoidable, as the carbonate, oxide and hydroxide of cesium are unstable at the temperature at which this fusion must be carried out.

¹²Fix, R. C. and Irvine, J. W., Jr., Mass. Inst. Tech. Lab. Nuclear Science Progress Report, Nov. 30, 1955.

¹³Moore, F. L., Anal. Chem. 29, 941, (1957).

¹⁴Crouthamel, C. E., Anal. Chem., 29, 1756, (1957).

The following procedure has been adopted: after grinding several grams of the aluminum oxide, a 0.2-g sample is fused with 2 g of sodium carbonate and 1 g of sodium hydroxide in a gold crucible. Heating is carried out cautiously at first and then after fusion at a red heat for about five minutes. The melt is dissolved in 6 N sulfuric acid, evaporated to dryness, again taken up in 6 N acid, and diluted to volume.

3. Radiochemical Methods for Cerium and Total Rare-Earths
(J. J. McCown)

Two new methods, one for the determination of fission product cerium and the other for fission product rare earths, have been developed. These methods are based on Peppard's¹⁵ studies of rare earth extraction with solutions of dioctylphosphoric acid. The cerium is extracted from 10 M nitric acid - 1 M potassium bromate solution, scrubbed with more nitric acid - potassium bromate solution, and stripped with 10 M nitric acid - 1 M hydrogen peroxide solution. The total rare earths are extracted from a 0.01 M hydrochloric acid solution, scrubbed with more 0.01 M hydrochloric acid, and stripped with 8 M hydrochloric acid. Each of the strip solutions is fumed with perchloric acid to remove ruthenium activity.

Each of these methods is a factor of three faster than the precipitation methods used previously. The decontaminations from other activities are comparable with less than 0.5 per cent other activities in the final product solutions. Recoveries are 100 per cent and therefore yield determinations are unnecessary. Papers discussing these methods in detail are being prepared for publication.

¹⁵Peppard, D. E., Mason, G. W., Moline, S. W., J. Inorg. and Nucl. Chem., 5, 141, (1957).

VI. ROUTINE OPERATIONS
(H. G. Swope)

A. Waste Processing

(H. G. Swope, J. Harast, B. Kullen, R. Juvinall, C. Ryberg)

Radioactive liquid wastes processed from January through March 1959

were as follows:

<u>Processing Method</u>	<u>Material Processed (gal)</u>
Evaporation and Concentration	24,940
Filtration	14,760
Cation Exchange	12,870
Flocculation	960
Absorption on Vermiculite	10
Neutralization	170
Allowed to Decay	<u>4,220</u>
Total	<u>57,930</u>

B. High-Level Gamma Irradiation Facility

(H. G. Swope, J. Harast, R. Juvinall, J. Gates,
N. Ondracek and F. Testa)

Data for samples irradiated during January, February and March are shown in Table 54.

Table 54

SUMMARY OF IRRADIATIONS PERFORMED IN RACK M-1
OF THE HIGH-LEVEL GAMMA IRRADIATION FACILITY
DURING JANUARY, FEBRUARY AND MARCH, 1959

	<u>No. of Samples^a</u>	<u>No. of Special Dosimetry Samples</u>	<u>Total Urn Units^b in Rads</u>	
			<u>Day</u>	<u>Night</u>
January	462	12	699	1500
February	535	253	845	2082
March	<u>984</u>	<u>332</u>	<u>1821</u>	<u>3390</u>
Totals	<u>1981</u>	<u>597</u>	<u>3365</u>	<u>6972</u>

^aEquivalent to a No. 2 sized can.

^b1 Unit = 2×10^6 r.