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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

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CHEMICAL ENGINEERING DIVISION SUMMARY REPORT

January, February, March, 1961

SUMMARY

I. Chemical-Metallurgical Processing (pages 29-128)

Pyrometallurgical processes are being developed for recovering fissionable and fertile materials from short-cooled reactor fuels. Such processes offer potential reduction in processing costs through simplicity and the ability to handle material shortly after discharge from reactors, thus making possible a reduction in fuel inventories. Processes under development are melt refining, a simple melting procedure for discharged uranium, and various schemes based on the use of liquid metal and fused salt media. Because it is the most developed process, melt refining will be the first to be used on a plant scale in the fuel-recovery cycle of the second Experimental Breeder Reactor (EBR-II). The reactor and fuel cycle facility are now under construction at Arco, Idaho.

The second laboratory demonstration of the melt-refining process with highly irradiated EBR-II-type fuel pins has been completed. A 392-gram charge of uranium-five percent fissium fuel pins irradiated to an estimated burnup of 0.4 total atom percent and cooled 28 days was melt refined for three hours at 1400 C. Analytical data have not yet been obtained on the behavior of fission products.

The effect of nitrogen concentration on the nitridation rates of un-irradiated uranium-fissium alloys in argon-nitrogen atmospheres was determined. The nitridation rate was constant with increasing nitrogen concentrations above five percent in the case of sodium-coated pins and above one percent for uncoated pins. Below these levels the nitridation rate dropped markedly with decreasing nitrogen concentration.

Experiments on the storage of fuel pins at 350 C in argon atmospheres showed that the presence of five percent nitrogen lowered product yields only slightly during subsequent melt-refining operations. Supplementary pouring techniques, such as the use of probes and mashers designed to break crusts over the melts, are moderately effective, but are a less desirable solution to the problem of maintaining high yields than the elimination of contaminants in the argon atmosphere.

Electrical heating was used to simulate the fission product decay heat generated in irradiated fuel pins. At a heat flux corresponding to

two total atom percent burnup, the temperature of the surface of a pin suspended in such a way that heat transfer occurred primarily by convection reached 128 C. The measured heat transfer coefficients were considerably larger than the theoretical values.

A liquid metal process is under development for recovery of the fissionable material contained in melt refining crucible skulls produced in the EBR-II fuel cycle. The skull-reclamation process presently involves removal of a melt-refining skull from a crucible by oxidation of the skull to convert it to a powder, selective extraction of noble metals* into zinc from a chloride flux-oxide slurry, reduction of uranium oxides by magnesium in a zinc solution, two uranium precipitations to enable removal of various fission products in supernatant solutions, and a retorting step to isolate a uranium metal product.

Demonstration runs of the skull reclamation process are in progress to pinpoint process problems. In two runs completed during the past quarter, about 60 percent of the uranium was recovered in each run as metal products of good appearance. These yields do not represent the recovery potential of the process, since the bulk of the unrecovered uranium remained in heels of various process steps from which the uranium would be recovered by repetitive plant operations. Nonrecoverable uranium losses were 7 to 8 percent but, by appropriate temperature adjustments in the precipitation step, these may be reduced considerably.

In the above runs, adequate removal (about 70 percent or more) of cerium, molybdenum, and palladium was realized, but ruthenium and zirconium removals were inadequate (about 40 percent). However, the noble metal extraction step was not employed in these runs, and its incorporation should improve the ruthenium removal. The problem of the low zirconium removal requires further study.

The following information was obtained in separate studies of the individual process steps:

- 1) Work with fissium skulls produced by melt refining irradiated uranium has shown iodine to be the major activity evolved during skull oxidation. A trace of tellurium activity was evolved, but no volatilization of ruthenium and molybdenum could be detected.

*Ruthenium, palladium, molybdenum, and technetium, whose oxides are reducible by zinc.

- 2) Over 80 percent of the ruthenium, palladium, and molybdenum was extracted into zinc from a fissium oxide-flux slurry in one hour at 750 C. Separation of phases was readily accomplished by pressure-siphoning off the liquid zinc phase after solidification of the salt. Ninety-two percent of the zinc was transferred. Analysis showed that the zinc contained only 0.4 percent of the uranium charged. This procedure is considerably more promising than transfer of the flux-oxide slurry away from the zinc phase because of the difficulty of keeping the oxide in suspension in the flux.
- 3) Further studies of reduction of uranium oxides by a dilute magnesium-zinc system in the presence of flux show that magnesium chloride is an essential ingredient of the flux for rapid and quantitative reductions of U_3O_8 . Reduction rates decreased with increase in oxide particle size and decrease in temperature, although quantitative reductions were achieved at temperatures as low as 650 C.
- 4) Zirconium oxide crucible fragments appearing in skull oxides remained largely unreduced under the conditions employed for uranium oxide reduction and would be removed in the flux phase. However, fission product zirconium may be more susceptible to reduction than the highly refractory crucible fragments.
- 5) In the skull-reclamation process, advantage is taken of the low solubility of uranium in systems with high magnesium concentrations and of the contrasting high solubility of rare earths in these systems to effect a uranium-rare earth separation. In the 46 percent magnesium-zinc eutectic system, the uranium solubility may be reduced from around 0.5 percent at 800 to around 0.1 percent by lowering the temperature to 400 C. Cerium, at process concentrations, will not be precipitated by cooling to 400 C.
- 6) Agglomeration of uranium precipitated from magnesium-rich zinc systems often occurs. This agglomeration is encouraged since it is considered advantageous in providing an easily handled retorted product. Under certain agitation and temperature conditions, the extent of agglomeration has been around 80 percent. The remaining 20 percent usually adheres firmly to the tantalum retorting crucibles.

The successful reduction of uranium oxides by zinc-magnesium systems in the presence of a halide flux has prompted application of the procedure to other compounds of interest. Quantitative reductions of uranium tetrafluoride and plutonium dioxide have been achieved.

In scouting studies, significant reduction of thorium oxide (65 percent) was also realized.

Preliminary work has been carried out on the preparation of various compounds by precipitation from liquid metal solutions. Uranium monocarbide and cerium sesquicarbide (both identified by X-ray diffraction) were precipitated respectively from cadmium-uranium and magnesium-cerium solutions by addition of finely divided carbon. This general procedure may have important applications in the preparation of fissionable or fertile ceramic reactor materials of high purity and in the processing of such materials.

In the current blanket process, the about 1 percent plutonium-uranium alloy is dissolved in zinc containing 10 to 15 weight percent magnesium. Additional magnesium is then added after the dissolution to precipitate metallic uranium. The plutonium dissolves in the magnesium-rich phase, thereby accomplishing the desired separation. The plutonium and uranium are recovered by retorting. In two experiments in which this direct dissolution procedure was tried, EBR-II blanket rods dissolved rapidly (within 2 hours). This process is simpler than those previously considered in that the uranium-zinc intermetallic compound is neither precipitated from the solution resulting from the dissolution of the blanket material nor is the intermetallic compound formed by direct reaction of uranium and zinc at low temperatures. The latter direct reaction procedure was attempted to eliminate the uranium dissolution and intermetallic compound precipitation steps. It was found that massive uranium reacts very slowly with zinc. However, by hydriding and dehydriding the uranium to convert it to a powder of large surface area, a complete reaction was effected within a few hours.

Materials evaluation studies are in progress to evaluate the compatibility of various materials with liquid metal systems of the types contemplated for reprocessing reactor fuels. Corrosion studies in the cadmium-zinc-magnesium system indicate that 1020 steel at 750 C is not appreciably corroded by cadmium containing up to 15 percent zinc. The presence of magnesium appears beneficial in reducing any attack. Testing of refractory metals (tantalum, molybdenum, tungsten, and tantalum-tungsten alloys) for containing zinc-based systems is also in progress. Uranium in 5 percent magnesium solution at 800 C reacts very slowly or not at all with grade CS graphite. However, the salt flux penetrates to some extent this relatively porous grade of graphite. Since grades of graphite of greater density are readily available, flux penetration is not regarded as a serious problem.

A pilot-plant-scale liquid metal distillation unit having a design capacity of 100 kg of cadmium per hour has been constructed and is being tested prior to operation. This unit will permit demonstration of a number of engineering operations encountered in the liquid metal processes.

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

Fuel Cycle Facility building construction was about 80 percent complete on March 7, 1961, as compared to 70 percent on December 6, 1960. The interior of the Argon Cell has been metallized with zinc and shot peened. Erection of major cell equipment, such as manipulators and cranes, has begun. Work on electrical and piping services continues.

Two melt-refining furnaces will be installed as part of the process equipment in the Argon Cell. The installation instructions for the furnace off-gas system have been completed and components are being procured. Two panelboards for furnace operation and control have been designed and are on order from a vendor. Purchase orders for the furnaces themselves have been placed.

Work continues on other equipment items for the Fuel Cycle Facility. Design of the service plug feed throughs was completed and bids for their construction are being solicited. A purchase order has been placed for the interbuilding coffin which will transport reactor fuel between the Fuel Cycle Facility and the Reactor Building. A coffin for handling scrap is also being procured. The possibility of using a glass containing cerium oxide as a gamma dosimeter is being explored. A versatile dosimeter of this type would be useful in operation of Argon Cell equipment.

Several redesigned components have been installed on the prototype manipulator. As a result of experience with this new equipment, some changes have been made in the manipulators being built by General Mills. The changes involved improvements in the bridge drive clutch mechanism, the carriage brush assembly, and the grip drive clutch mechanism.

A protective coating is required for Argon Cell equipment during the period of equipment installation. Based on the results of lengthy gamma-irradiation tests, aluminum paint appears to be a satisfactory coating for this purpose. Testing of other materials, such as MI (mineral insulated) cable and seals, and lubricants, for cell use continues. Roller bearings lubricated with irradiated greases have run successfully under loads for 300 hours.

Equipment for the oxidation of skulls from melt refining is being developed. The powder which is formed on oxidation will be poured from the crucible and stored.

Eight more ten-kilogram batches of enriched pin scrap were melted and cast into ingots suitable for production of fuel pins for EBR-II.

Fundamental studies are being made in support of the various liquid metal processes. The solubilities are being determined of those elements whose separations are being attempted. The solubilities of the rare-earth elements terbium, holmium, thulium, ytterbium, and lutetium in liquid cadmium may be represented by the empirical equations

$$\text{terbium (321 to 535 C): } \log (\text{atom percent}) = 3.296 - 2425 T^{-1}$$

$$\text{holmium (324 to 628 C): } \log (\text{atom percent}) = 3.409 - 2494 T^{-1}$$

$$\text{thulium (324 to 525 C): } \log (\text{atom percent}) = 3.488 - 2514 T^{-1}$$

$$\text{ytterbium (326 to 504 C): } \log (\text{atom percent}) = 2.992 - 1957 T^{-1}$$

$$\text{lutetium (324 to 557 C): } \log (\text{atom percent}) = 7.328 - 7630 T^{-1} \\ + 1.745 \times 10^6 T^{-2}$$

The solubilities of cobalt and chromium in liquid cadmium may be represented by the empirical equations

$$\text{cobalt (334 to 653 C): } \log (\text{atom percent}) = 3.594 - 6515 T^{-1} \\ + 1.705 \times 10^6 T^{-2}$$

$$\text{chromium (450 to 650 C): } \log (\text{atom percent}) = 0.394 - 2605 T^{-1}$$

The cadmium-rich intermetallic phase in the titanium-cadmium system has been found to have the composition TiCd and has tetragonal symmetry of the B-11 (γTiCu) structural type.

The solubility of uranium in liquid zinc above the peritectic temperature (840 C) may be represented by the empirical equation

$$\text{uranium (840 to 901 C): } \log (\text{weight percent}) = 5.87 - 5550 T^{-1}$$

Below the peritectic temperature the solubility may be represented by the empirical equation

$$\text{uranium (420 to 840 C): } \log (\text{weight percent}) = 6.946 - 6711 T^{-1}$$

A systematic study is underway to ascertain the influence of atomic size, metallic valence, and electronic configuration on the coprecipitation of various metallic elements with the cadmium-cerium intermetallic phase CeCd_{11} . The following values for the coprecipitation coefficient λ , defined by the equation

$$\log \left(\frac{\text{tracer in solution}}{\text{total tracer}} \right) = \lambda \log \left(\frac{\text{carrier in solution}}{\text{total carrier}} \right),$$

have been determined: sodium, lithium, potassium, yttrium, barium, $\lambda = 0$; lanthanum, $\lambda = 1.49$; thorium, $\lambda = 1.08$; praseodymium, $\lambda = 0.63$; gadolinium, $\lambda = 0.23$; samarium, $\lambda = 0.17$; uranium, $\lambda = 0.13$; strontium, $\lambda = 0.10$; europium, $\lambda = 0.099$; scandium, $\lambda = 0.05$; and zirconium, $\lambda = 0.04$.

The temperature dependence of the distribution coefficient of cerium and palladium when partitioned between the two partially immiscible liquids lead and zinc has been determined. The value of the coefficient (weight percent in zinc phase/weight percent in lead phase) for cerium is 24 at 650 C, 11.7 at 700 C, and 5.7 at 730 C, whereas for palladium the coefficient is 1790 at 652 C, 473 at 703 C, and 178 at 740 C.

The vapor pressure of solid uranium-cadmium alloys has been measured using the continuous-recording effusion apparatus. The vapor pressure-composition patterns observed are in complete agreement with the results previously obtained by conventional methods for phase studies.

The vapor pressure of solid cerium-zinc alloys has been measured as a function of composition by means of the effusion method. The existence of the intermetallic compounds CeZn_{11} , CeZn , Ce_2Zn , and Ce_4Zn was confirmed. The phase previously identified as CeZn_9 was shown to be $\text{Ce}_2\text{Zn}_{17}$. The existence of CeZn_2 appears highly probable. Two additional compounds $\text{CeZn}_{\sim 7}$ and a phase having a wide solid solution range between $\text{CeZn}_{\sim 3.7}$ and $\text{CeZn}_{\sim 6.4}$ were observed.

The magnetic susceptibility of the neodymium-cadmium intermetallic phase NdCd_{11} has been found to follow a Curie-Weiss relation [$\chi = C/(T - \Delta)$] with $C = 1.66_7$ and $\Delta = -8^\circ\text{K}$. The effective Bohr magneton number for this alloy is 3.67. This is in good agreement with the theoretical value of 3.68 expected for a free trivalent neodymium ion in a $^4I_{9/2}$ ground state.

A series of combustions of uranium mononitride in oxygen has been completed. The precision of the results obtained was excellent. However, insufficient proof of the exact state of some oxygen-containing impurity in the sample leaves a relatively large uncertainty in any value of the heat of formation calculable from the results. Further analytical or preparative work is necessary.

Combustions of boron nitride in fluorine are being carried out calorimetrically. These are the first combustions of a compound in fluorine and the first combustions of a spontaneously reacting material to be studied. For these studies a special combustion bomb with an attached fluorine tank is being used. This combustion bomb reaction system has been calibrated and the energy of expansion of fluorine into the bomb has been determined.

Previously reported values for the heats of formation of crystalline zirconium tetrafluoride and gaseous molybdenum hexafluoride have been

revised to $\Delta H_f^0(25\text{ C}) = -356.7_8 \pm 0.2_5$ and $-372.3_5 \pm 0.2_2$ kcal/mole, respectively.

Results of the first calorimetric combustions of uranium in fluorine were uncertain because of complications which arose in analyzing the combustion products. However, the experiments did lead to a preliminary value of $\Delta H_f^0(25\text{ C}) = -509 \pm 3$ kcal/mole for uranium hexafluoride gas. Most of the large uncertainty in the preliminary value is due to analytical uncertainties which should be capable of being resolved.

Techniques have been worked out for burning in fluorine some of the low melting metals, such as cadmium, zinc, magnesium, and aluminum. Calorimetric measurements have been started on cadmium.

Techniques somewhat similar to those used in combustion of zirconium in fluorine have been worked out for titanium, hafnium, niobium, and tantalum. Studies are being continued on thorium and vanadium.

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (pages 129-197)

A direct fluorination volatility process has been proposed for the recovery of uranium and plutonium from irradiated nuclear reactor fuels. In this process advantage is taken of the volatilities of uranium and plutonium hexafluoride and of fluidization techniques. Attempts are being made to apply this process to uranium oxide and zirconium matrix fuels.

The proposed process for recovery of uranium and plutonium from spent uranium oxide involves decladding by an appropriate reaction in a fluidized bed. Plutonium and uranium hexafluorides, which result from the reaction of the declad oxide fuel with fluorine, may be separated using a combination of the variability of the rates of fluorination of the plutonium and uranium compounds and chemical reactivities of the hexafluorides.

The decladding step of the process for uranium dioxide fuels involves gas-metal reactions in the case of elements clad either with stainless steel or Zircaloy. The gas-metal reactions are carried out with the fuel elements submerged in an inert fluidized bed (calcium fluoride or aluminum) which serves as a heat transfer medium. Dilute mixtures of hydrogen chloride in hydrogen fluoride or the separate gases have been successfully employed when zirconium decladding is necessary. In recent work, chlorine has replaced the hydrogen chloride. In the case of stainless steel cladding, chlorine appears to be a possible decladding reagent, based on results from pilot-plant studies.

The decladding reactions (referred to as primary) are being carried out in a two-zone fluid-bed reactor. Volatilization of the clad or alloying material occurs in the lower zone during the chlorination reaction.

The volatile materials pass upward into the upper zone, where hydrogen fluoride is admitted, thereby effecting conversion to solid fluorides. Where solid chlorides are formed, these will also be converted to solid fluorides, since there is solids mixing between zones. The two zones are separated by an inverted conical baffle (other types may also be suitable) which reduces back-mixing of the gases and prevents the formation of gas mixtures that have been shown to affect these reactions adversely.

In pilot-plant studies the reaction of 304 stainless steel tube sections with chlorine has been investigated in a $1\frac{1}{2}$ -inch-diameter two-zone fluid-bed reactor. The rate of chlorination has been found to decrease rapidly with time because of the formation of an adherent film comprised primarily of nickel and chromium chloride on the surface of the cladding. An average penetration rate of 4.6 mils/hr was obtained in a 4.7-hour run at 575 C using 87 percent chlorine (in nitrogen). At a higher temperature of 625 C, using the same chlorine concentration, a 35-mil tube completely reacted in 3.8 hours. The effect of chlorine dilution at 625 C was noticeable at concentrations below 48 volume percent.

After decladding has been achieved, a subsequent fluorination step is expected to provide the necessary separation of the fissile elements. The direct fluorination of dense uranium dioxide pellets is being examined in fluid-bed pilot-plant studies.

Substantial improvement in temperature control at higher reaction rates has been achieved by regulation of fluorine inlet flow in place of coolant regulation previously employed. Four runs have been made in which pellet batches of approximately 4.5 kg have been completely reacted at about 500 C; average uranium hexafluoride production rates of about 20 kg/(hr)(sq ft reactor cross section) were obtained with inert-fired pellets and approximately one-half this rate for hydrogen-fired pellets. The hydrogen-fired pellets ($\frac{1}{2}$ in. x $\frac{1}{2}$ in.) are considered more representative of reactor fuel material, and in these experiments 10 to 12 hr was required for processing a complete batch.

Fluorination runs have been made with inert fluid beds of calcium fluoride or magnesium fluoride to aid in the removal of heat. Additional runs were made to demonstrate the feasibility of operating with a pure zirconium tetrafluoride fluid bed and without an inert bed.

Since heat transfer limits the maximum practical reaction rate in the direct fluorination process, a heat transfer study is being made in a mockup system. In these tests, measurements are made of heat transfer coefficients for the surfaces of the inner heater and of the outer cooling wall, and for effective bed thermal conductivities for systems consisting of pellet beds with a fluidized medium in the pellet voids. In several experimental tests, effective thermal conductivities along the radius of the

bed of about $0.8 \text{ Btu}/(\text{hr})(\text{sq ft})(\text{F}/\text{ft})$ were found for the nonfluidized case and of 5 to 10 for fluidization. For the fluidized case, surface coefficients of about $80 \text{ Btu}/(\text{hr})(\text{sq ft})(\text{F})$ were found for the internal heating surface and 20 to 60 for the external cooling surface.

A new filter system with automatic blowback was demonstrated, in which the filters are located in chambers separated from the reactor by a length of one-inch pipe. This design promises to make filter replacement more convenient in radioactive systems.

The rate of thermal decomposition of plutonium hexafluoride has been studied at temperatures from 140 to 173 C by a static method and from 150 to 250 C by a flow method. A study of the kinetics of decomposition has established the mechanism of the reaction. The rate of the reaction has been formulated as concurrent first- and zero-order reactions with respect to plutonium hexafluoride pressure in the range between 50 and 1100 mm and of temperature from 140 to 170 C. It has been inferred that, within the aforementioned temperature and pressure ranges, the decomposition proceeds by both a homogenous and heterogeneous unimolecular decomposition and that the heterogeneous decomposition occurs on the surface of the deposited plutonium tetrafluoride. Rates of decomposition of plutonium hexafluoride obtained in the flow system approximate conditions which may be found in the fluorination reactor of the Direct Fluoride Volatility process for uranium oxide power reactor fuels. This information will be useful for plant design and future experimental work.

The physical appearance of plutonium tetrafluoride resulting from both thermal decomposition and alpha-radiation decomposition has been observed and bulk densities have been determined. The bulk density of the product of thermal decomposition was 15 to 18 times greater than the bulk density of the product of radiation decomposition.

It has been demonstrated that a large quantity (32 gm) of plutonium tetrafluoride, which had been deposited in equipment by thermal decomposition of plutonium hexafluoride, could be refluorinated to plutonium hexafluoride at about 450 C with a recovery of 98 percent of the plutonium.

The reaction of elemental bromine with plutonium hexafluoride has been investigated. The stoichiometry of the reaction has been established. Primary products of the reaction are plutonium tetrafluoride and bromine pentafluoride. The utility of the reaction for the separation of uranium and plutonium hexafluorides has been demonstrated.

In studies of fission product behavior, mixtures of uranium dioxide-ruthenium-106 were reacted with fluorine at 400 and 500 C. It was found that at both of these temperatures ruthenium was volatilized at a rate

equal to or faster than that of uranium volatilization as uranium hexafluoride. However, it was found that ruthenium pentafluoride decomposed and was deposited on a colder portion of the walls of the fluorination vessel. No alteration of the results occurred when calcium fluoride and zirconium fluoride were added to the original mixture to be fluorinated. The fluorination of uranium dioxide-niobium-95 mixtures indicated that niobium is readily fluorinated out of uranium dioxide and that there is no reaction between niobium and calcium fluoride-zirconium fluoride bed materials. Niobium differed from the ruthenium in that very little (less than one percent) deposited on the reaction boat or furnace tube, indicating that niobium can be volatilized with little or no difficulty.

In studies of reactions which might be used to separate uranium and plutonium, the reactions of gaseous sulfur tetrafluoride with uranium trioxide and uranyl fluoride to produce uranium hexafluoride were studied. Sulfur tetrafluoride has the advantage that it will not react with plutonium dioxide or plutonium tetrafluoride to produce plutonium hexafluoride. It thus can serve as a selective fluorinating reagent in fluoride volatility processes. Kinetics of the reactions of sulfur tetrafluoride with uranium dioxide and uranyl fluoride have been explored. This work serves as a classical example of the use of a thermobalance in the study of gas-solid kinetics in a reaction in which the final product is volatile.

A combined chlorination-fluorination (Direct Chlorination Process) process is being examined as an alternate to the fluorination step of the Direct Fluorination Volatility Process. The two-zone fluidized-bed concept has been employed successfully in the direct chlorination of sintered uranium dioxide pellets. The volatile uranium chlorides produced in the lower zone of the reactor are converted to solid fluorides by reaction with hydrogen fluoride in the upper zone. A charge of 20 pellets (121 g total) was 92 percent reacted at 550 C in only 2.5 hr by a gas stream containing 69 mole percent chlorine in carbon tetrachloride. An equimolar mixture of carbon tetrachloride and chlorine at 550 C has produced higher reaction rates than several other gas mixtures studied.

The reaction of sulfur tetrafluoride with uranium trioxide to form volatile uranium hexafluoride has been suggested as a basis for a possible fuel recovery scheme (ANL-6145, page 93). This reaction might also be considered an alternative for feed materials production. The overall reaction is considered to be: $\text{UO}_3 + 3\text{SF}_4 \longrightarrow \text{UF}_6 + 3\text{SOF}_2$. One exploratory two-part run was made in a 2-in.-diameter fluid-bed reactor to supplement the results gained in the laboratory (ANL-6231, page 99).

The conversion of uranium hexafluoride to uranium dioxide by a two-step fluid-bed process is being studied in order to develop a simpler method for preparation of ceramic reactor fuel. The major problem in the first step, reaction of the hexafluoride with steam to form uranyl fluoride, continues to be fines formation. Proper sizing of starting beds

assures particle growth (average particle diameter of $250\ \mu$ or coarser); however, continuous operation requires a seed particle feed stream to maintain bed fluidity. Regulation of the rate of seed particle addition to offset growth without entering the region of fines formation (average bed diameter less than $250\ \mu$) has not been successful due apparently to the continuous formation of small amounts of fines partially offsetting seed particle requirements. Runs made at hexafluoride feed rates of 100 g/min [174 lb uranium/(hr)(sq ft)] have been extended to seven hours before interruption by fines formation. The effect of starting bed particle size on fines formation was investigated in a number of short runs.

The reduction of uranyl fluoride to uranium dioxide is being studied in a series of batch fluidization runs in a 3-in.-diameter fluid-bed reactor. A mixed gas of steam and hydrogen gave much faster conversion than hydrogen alone. A typical product from a run was 3 kg of powder containing 210 ppm residual fluoride (specification grade). This was prepared in 5 hr at 650 C using a gas stream of three parts hydrogen to one part steam.

Fluid-bed calcination studies have been initiated in small-diameter columns in an attempt to reduce the overall gas requirements for these units and thus reduce the off-gas handling problems. This technique employs the atomizing and feed decomposition gases as the primary fluidizing medium by installing the spray nozzles in the apex of the cone-bottom reactors. The small-diameter aspect has application to the calcination of plutonium solutions, for which nuclear criticality considerations are necessary.

A mass transfer study using the silica gel-water system has been completed in the 6-in.-diameter multistage fluidization column designed to achieve controlled downward transport of solids without the use of internal downcomers. Murphree efficiencies of nearly 100 percent were obtained.

III. Reactor Safety (pages 198-238)

The oxidation, ignition, and combustion processes of uranium, zirconium, and plutonium are being studied to provide information to aid in minimizing the hazards associated with handling these metals.

Studies of the effect of pre-oxidation on the burning-curve ignition temperatures of uranium powders were continued. Ignition temperature, at first, decreased with extent of pre-oxidation for both a fine and a coarse powder fraction. Ignition temperatures began to rise after more than 50 percent pre-oxidation. Weight gain versus time measurements at 150 C with both powder fractions showed a two-stage reaction identical with that found in previous studies of the isothermal oxidation of uranium cubes.

The decreased ignition temperature of pre-oxidized powder may have been due to the faster reaction rates that occur in the second-stage reaction.

Ignition studies of uranium monocarbide powders are reported for powders from two sources. The powders were composed of irregular particles. An estimate of the roughness factor was obtained by the Armour Research Foundation using a Fischer Sub-Sieve Sizer. From this information, it was possible to compute the specific area of a series of powder fractions. Ignition temperatures in oxygen varied from 255 to 320 C for specific areas from 314 to 20 sq cm/g. Ignition temperatures of uranium monocarbide were 40 to 60 degrees higher than values previously reported with spherical uranium powders of corresponding specific area.

A series of measurements of burning-curve ignition temperatures in air were made with uranium foil squares of two thicknesses (one-half and five mils). Studies were made with stacks of one, two, four, and eight foil squares. Ignition temperatures decreased 45 degrees in going from one to two 5-mil foils. Only a small additional decrease occurred with four or eight foils. Studies are aimed at developing means to calculate ignition temperature decreases which are due to decreases heat loss by aggregation.

A brief study was made of uranium plates of the type used in ZPR-III blanket assemblies. Eighteen plates out of a total of 20,000 were found to be crumbling. Unaffected plates had a burning-curve ignition temperature of 480 C while deteriorated plates ignited at 115 C in either air or oxygen. The affected plates were made by powder metallurgical techniques. It appears that these plates are reverting to powder.

Studies of the rate of burning propagation along uranium and zirconium foil strips is continuing. A new instrument has been devised to measure simultaneously the propagation rate and the burning temperature. A new program was undertaken to determine the effects of halogenated hydrocarbons on propagation rates and burning temperatures. It is proposed to study several homologous series of hydrocarbons in which both R and X of a hydrocarbon RX are systematically varied. It is anticipated that this new program will shed further light on the mechanism by which the hydrocarbons inhibit burning.

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. One method involves the rapid melting and dispersion of metal wires in a water environment by a surge current from a bank of condensers. The series of runs with 60-mil zirconium wires at pressures up to 1500 psi is continuing. Runs made with water at 315 C (1500 psi) were identical in character to runs made in water from 90 to 200 C (10 to 225 psi). Explosive rates of pressure rise occurred at initial metal temperatures of 1900 C in heated water.

Results of previous studies at Battelle and Westinghouse were re-examined and shown to be consistent with rate data deduced from condenser-discharge studies of the zirconium-water reaction. The following rate law was obtained:

$$V_2 = 4.82 \times 10^8 \left(\exp - \frac{45,500}{RT} \right) t,$$

where V is cc of hydrogen at STP per sq cm of surface and t is time in min.

The lowered reactivity of zirconium in room-temperature water could be explained by a lowered rate of diffusion of water vapor through the hydrogen-steam mantle surrounding reacting particles. A diffusion rate of one-half of the value in heated water produced semiquantitative agreement with the experimental data.

The explosive reactions reported previously for zirconium at initial temperatures of 2600 C in room-temperature water and those at 1900 C in heated water could be explained by a critical particle diameter (500 μ in room-temperature water) below which rapid hydrogen evolution drives the particles through the water at high velocity. The high-speed motion results in rapid reactions. The reactions, however, are not complete because the increased velocity also increases the convective heat loss rate.

A second method involves the rapid contact of steam with heated metal. In this method, the metal receives a "pressure pulse" of water vapor. The apparatus is entirely enclosed in a box heated to 105 C. Runs with one atmosphere of water vapor reacting with molten aluminum at 1000 and 1200 C are reported. Contact times varied from 0.1 to 1000 seconds. The data can be represented approximately by the cubic rate law.

A brief study was made of the reactions occurring between aluminum or stainless steel and uranium dioxide or U_3O_8 in cermet fuel pins. The method of differential thermal analysis (DTA) was used. A very mild exothermic reaction was found to occur between aluminum and uranium dioxide or U_3O_8 at about 900 C. Reaction products included UAl_2 , UAl_3 , and UAl_4 , which were identified by X-ray diffraction. It was concluded that the reactions were not violent or dangerous.

Two series of in-pile, metal-water experiments were completed. Meltdowns were conducted on stainless steel-urania cermets, uranium wires, and on ceramic core, metal-clad fuel specimens. Cermets made of 90 weight percent stainless steel with urania showed similar behavior when submerged in water irrespective of whether the sample was in the form of pins or plates; metal temperatures greater than 1500 C were attained. The original geometry was changed into one or two large globules

together with many fine particles; the more energetic transients also produced some fine (1-mil diameter) powder. Chemical analyses indicated that a separation of the urania from the stainless steel took place during the melting-quenching cycle of the reactor burst. The larger globules were depleted in uranium (0.017 to 0.055 weight percent uranium) whereas the fine particles were more concentrated in uranium (30 to 64 weight percent uranium). The plate-type cermet elements gave only slightly more metal-water reaction than the cylindrical elements; both reacted more as the energy of the burst was increased. The stainless steel-urania cermet fuel pins gave 6.6 and 10.2 percent metal-water reaction at reactor bursts of 435 and 512 Mw-sec on a 50-ms period. The corresponding specific-energy inputs to the fuel specimen, as determined by the average from molybdenum-99 determinations, are 379 and 445 cal/gm, respectively.

A Zircaloy-2 clad, ceramic core fuel pin subjected to a 648-Mw-sec pulse (606 cal/gm) on a 50 ms period gave nearly complete destruction of the specimen with 24.0 percent of the metal jacket reacting with the water. The data obtained to date from the various ceramic and cermet core fuel pins were correlated as a function of the energy of the reactor burst. The following table summarizes the results at two different energies:

Type of Fuel Pin	Percent Metal-Water Reaction		
	at 400 Mw-sec	at 500 Mw-sec	Reaction
Zr-2 clad, oxide core	8.0	13.0	Zr-H ₂ O
SS-UO ₂ cermet	5.0	9.3	SS-H ₂ O
Al-U ₃ O ₈ cermet	3.2	4.7	Al-H ₂ O
SS clad, oxide core	0.0	0.8	SS-H ₂ O
Al clad, oxide core	0.4	0.8	Al-H ₂ O

The conversion from reactor to absorbed energy for the oxide core pins is 0.935 (cal/gm)/Mw-sec and 0.87 (cal/gm)/Mw-sec for the stainless steel-urania cermets.

Transients conducted on 64-mil-diameter uranium (93 percent enriched) wires gave 33.2 and 50.2 percent molten uranium-water reaction at reactor periods of 440 and 152 ms, respectively. The average energy input to the wire was 554 cal/gm from molybdenum-99 analyses. The wires were converted into fine particles and powder. It is planned to correlate these experiments with condenser-discharge experiments which were also carried out with wires.

IV. Reactor Chemistry (pages 239-248)

The neutron-capture cross sections of neptunium-237 are being determined in the fast-neutron energy range. Work has also begun on the determination of the total neutron cross section of uranium-233. The capture-to-fission ratios in the EBR-I, Mark III are being determined for uranium isotopes 233, 235, and 238 and for plutonium isotopes 239 and 240.

The Reactor Decontamination Program is directed at determining the seriousness of fuel-element ruptures in boiling water reactors and the determination of methods of decontamination of contaminated surfaces. Several runs have been made in a stainless steel loop which simulates the action of a boiling water reactor. Current laboratory experiments on the decontamination of stainless steel 304 have been conducted with oxalic acid and citric acid-base solutions containing hydrogen peroxide.

V. Routine Operations (page 249)

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

For the convenience of the reader, appropriate parts of this summary are repeated at the beginning of each of the first four sections of this report.

I. CHEMICAL-METALLURGICAL PROCESSING

Pyrometallurgical processes are being developed for recovering fissionable and fertile materials from short-cooled reactor fuels. Such processes offer potential reduction in processing costs through simplicity and the ability to handle material shortly after discharge from reactors, thus making possible a reduction in fuel inventories. Processes under development are melt refining, a simple melting procedure for discharged uranium, and various schemes based on the use of liquid metal and fused salt media. Because it is the most developed process, melt refining will be the first to be used on a plant scale in the fuel recovery cycle of the second Experimental Breeder Reactor (EBR-II). The reactor and fuel cycle facility are now under construction at Arco, Idaho.

The second laboratory demonstration of the melt refining process with highly irradiated EBR-II-type fuel pins has been completed. A 392-gram charge of uranium-five percent fissium fuel pins irradiated to an estimated burnup of 0.4 total atom percent and cooled 28 days was melt refined for three hours at 1400 C. Analytical data have not yet been obtained on the behavior of fission products.

The effect of nitrogen concentration on the nitridation rates of un-irradiated uranium-fissium alloys in argon-nitrogen atmospheres was determined. The nitridation rate was constant with increasing nitrogen concentrations above five percent in the case of sodium-coated pins and above one percent for uncoated pins. Below these levels the nitridation rate dropped markedly with decreasing nitrogen concentration.

Experiments on the storage of fuel pins at 350 C in argon atmospheres showed that the presence of five percent nitrogen lowered product yields only slightly during subsequent melt refining operations. Supplementary pouring techniques, such as the use of probes and mashers designed to break crusts over the melts are moderately effective, but are a less desirable solution to the problem of maintaining high yields than the elimination of contaminants in the argon atmosphere.

Electrical heating was used to simulate the fission product decay heat generated in irradiated fuel pins. At a heat flux corresponding to two total atom percent burnup, the temperature of the surface of a pin suspended in such a way that heat transfer occurred primarily by convection reached 128 C. The measured heat transfer coefficients were considerably larger than the theoretical values.

A liquid metal process is under development for recovery of the fissionable material contained in melt refining crucible skulls produced in the EBR-II fuel cycle. The skull reclamation process presently involves

removal of a melt-refining skull from a crucible by oxidation of the skull to convert it to a powder, selective extraction of noble metals* into zinc from a chloride flux-oxide slurry, reduction of uranium oxides by magnesium in a zinc solution, two uranium precipitations to enable removal of various fission products in supernatant solutions, and a retorting step to isolate a uranium metal product.

Demonstration runs of the skull reclamation process are in progress to pinpoint process problems. In two runs completed during the past quarter, about 60 percent of the uranium was recovered in each run as metal products of good appearance. These yields do not represent the recovery potential of the process, since the bulk of the unrecovered uranium remained in heels of various process steps from which the uranium would be recovered by repetitive plant operations. Nonrecoverable uranium losses were 7 to 8 percent but, by appropriate temperature adjustments in the precipitation step, these may be reduced considerably.

In the above runs, adequate removal (about 70 percent or more) of cerium, molybdenum, and palladium was realized, but ruthenium and zirconium removals were inadequate (about 40 percent). However, the noble metal extraction step was not employed in these runs, and its incorporation should improve the ruthenium removal. The problem of the low zirconium removal requires further study.

The following information was obtained in separate studies of the individual process steps:

- 1) Work with fission skulls produced by melt refining irradiated uranium has shown iodine to be the major activity evolved during skull oxidation. A trace of tellurium activity was evolved, but no volatilization of ruthenium and molybdenum could be detected.
- 2) Over 80 percent of the ruthenium, palladium, and molybdenum was extracted into zinc from a fission oxide-flux slurry in one hour at 750 C. Separation of phases was readily accomplished by pressure-siphoning off the liquid zinc phase after solidification of the salt. Ninety-two percent of the zinc was transferred. Analysis showed that the zinc contained only 0.4 percent of the uranium charged. This procedure is considerably more promising than transfer of the flux-oxide slurry away from the zinc phase because of the difficulty of keeping the oxide in suspension in the flux.

*Ruthenium, palladium, molybdenum, and technetium, whose oxides are reducible by zinc.

- 3) Further studies of reduction of uranium oxides by a dilute magnesium-zinc system in the presence of flux show that magnesium chloride is an essential ingredient of the flux for rapid and quantitative reductions of U_3O_8 . Reduction rates decreased with increase in oxide particle size and decrease in temperature, although quantitative reductions were achieved at temperatures as low as 650 C.
- 4) Zirconium oxide crucible fragments appearing in skull oxides remained largely unreduced under the conditions employed for uranium oxide reduction and would be removed in the flux phase. However, fission product zirconium may be more susceptible to reduction than the highly refractory crucible fragments.
- 5) In the skull reclamation process, advantage is taken of the low solubility of uranium in systems with high magnesium concentrations and of the contrasting high solubility of rare earths in these systems to effect a uranium-rare earth separation. In the 46 percent magnesium-zinc eutectic system, the uranium solubility may be reduced from around 0.5 percent at 800 to around 0.1 percent by lowering the temperature to 400 C. Cerium, at process concentrations, will not be precipitated by cooling to 400 C.
- 6) Agglomeration of uranium precipitated from magnesium-rich zinc systems often occurs. This agglomeration is encouraged since it is considered advantageous in providing an easily handled retorted product. Under certain agitation and temperature conditions, the extent of agglomeration has been around 80 percent. The remaining 20 percent usually adheres firmly to the tantalum retorting crucibles.

The successful reduction of uranium oxides by zinc-magnesium systems in the presence of a halide flux has prompted application of the procedure to other compounds of interest. Quantitative reductions of uranium tetrafluoride and plutonium dioxide have been achieved. In scouting studies, significant reduction of thorium oxide (65 percent) was also realized.

Preliminary work has been carried out on the preparation of various compounds by precipitation from liquid metal solutions. Uranium monocarbide and cerium sesquicarbide (both identified by X-ray diffraction) were precipitated respectively from cadmium-uranium and magnesium-cerium solutions by addition of finely divided carbon. This general procedure may have important applications in the preparation of fissionable or fertile ceramic reactor materials of high purity and in the processing of such materials.

In the current blanket process, the about 1 percent plutonium-uranium alloy is dissolved in zinc containing 10 to 15 weight percent magnesium. Additional magnesium is then added after the dissolution to precipitate metallic uranium. The plutonium dissolves in the magnesium-rich phase, thereby accomplishing the desired separation. The plutonium and uranium are recovered by retorting. In two experiments in which this direct dissolution procedure was tried, EBR-II blanket rods dissolved rapidly (within 2 hours). This process is simpler than those previously considered in that the uranium-zinc intermetallic compound is neither precipitated from the solution resulting from the dissolution of the blanket material nor is the intermetallic compound formed by direct reaction of uranium and zinc at low temperatures. The latter direct reaction procedure was attempted to eliminate the uranium dissolution and intermetallic compound precipitation steps. It was found that massive uranium reacts very slowly with zinc. However, by hydriding and dehydriding the uranium to convert it to a powder of large surface area, a complete reaction was effected within a few hours.

Materials evaluation studies are in progress to evaluate the compatibility of various materials with liquid metal systems of the types contemplated for reprocessing reactor fuels. Corrosion studies in the cadmium-zinc-magnesium system indicate that 1020 steel at 750 C is not appreciably corroded by cadmium containing up to 15 percent zinc. The presence of magnesium appears beneficial in reducing any attack. Testing of refractory metals (tantalum, molybdenum, tungsten, and tantalum-tungsten alloys) for containing zinc-based systems is also in progress. Uranium in 5 percent magnesium solution at 800 C reacts very slowly or not at all with grade CS graphite. However, the salt flux penetrates to some extent this relatively porous grade of graphite. Since grades of graphite of greater density are readily available, flux penetration is not regarded as a serious problem.

A pilot-plant-scale liquid metal distillation unit having a design capacity of 100 kg of cadmium per hour has been constructed and is being tested prior to operation. This unit will permit demonstration of a number of engineering operations encountered in the liquid metal processes.

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

Fuel Cycle Facility building construction was about 80 percent complete on March 7, 1961, as compared to 70 percent on December 6, 1960. The interior of the Argon Cell has been metallized with zinc and shot peened. Erection of major cell equipment, such as manipulators and cranes, has begun. Work on electrical and piping services continues.

Two melt-refining furnaces will be installed as part of the process equipment in the Argon Cell. The installation instructions for the furnace off-gas system have been completed and components are being procured. Two panelboards for furnace operation and control have been designed and are on order from a vendor. Purchase orders for the furnaces themselves have been placed.

Work continues on other equipment items for the Fuel Cycle Facility. Design of the service plug feed throughs was completed and bids for their construction are being solicited. A purchase order has been placed for the interbuilding coffin which will transport reactor fuel between the Fuel Cycle Facility and the Reactor Building. A coffin for handling scrap is also being procured. The possibility of using a glass containing cerium oxide as a gamma dosimeter is being explored. A versatile dosimeter of this type would be useful in operation of Argon Cell equipment.

Several redesigned components have been installed on the prototype manipulator. As a result of experience with this new equipment, some changes have been made in the manipulators being built by General Mills. The changes involved improvements in the bridge drive clutch mechanism, the carriage brush assembly, and the grip drive clutch mechanism.

A protective coating is required for Argon Cell equipment during the period of equipment installation. Based on the results of lengthy gamma-irradiation tests, aluminum paint appears to be a satisfactory coating for this purpose. Testing of other materials, such as MI (mineral insulated) cable and seals, and lubricants, for cell use continues. Roller bearings lubricated with irradiated greases have run successfully under loads for 300 hours.

Equipment for the oxidation of skulls from melt refining is being developed. The powder which is formed on oxidation will be poured from the crucible and stored.

Eight more ten-kilogram batches of enriched pin scrap were melted and cast into ingots suitable for production of fuel pins for EBR-II.

Fundamental studies are being made in support of the various liquid metal processes. The solubilities are being determined of those elements whose separations are being attempted. The solubilities of the rare-earth

elements terbium, holmium, thulium, ytterbium, and lutetium in liquid cadmium may be represented by the empirical equations

$$\text{terbium (321 to 535 C): } \log (\text{atom percent}) = 3.296 - 2425 T^{-1}$$

$$\text{holmium (324 to 628 C): } \log (\text{atom percent}) = 3.409 - 2494 T^{-1}$$

$$\text{thulium (324 to 525 C): } \log (\text{atom percent}) = 3.488 - 2514 T^{-1}$$

$$\text{ytterbium (326 to 504 C): } \log (\text{atom percent}) = 2.992 - 1957 T^{-1}$$

$$\text{lutetium (324 to 557 C): } \log (\text{atom percent}) = 7.328 - 7630 T^{-1} \\ + 1.745 \times 10^6 T^{-2}$$

The solubilities of cobalt and chromium in liquid cadmium may be represented by the empirical equations

$$\text{cobalt (334 to 653 C): } \log (\text{atom percent}) = 3.594 - 6515 T^{-1} \\ + 1.705 \times 10^6 T^{-2}$$

$$\text{chromium (450 to 650 C): } \log (\text{atom percent}) = 0.394 - 2605 T^{-1}$$

The cadmium-rich intermetallic phase in the titanium-cadmium system has been found to have the composition TiCd and has tetragonal symmetry of the B-11 (γTiCu) structural type.

The solubility of uranium in liquid zinc above the peritectic temperature (840 C) may be represented by the empirical equation

$$\text{uranium (840 to 901 C): } \log (\text{weight percent}) = 5.87 - 5550 T^{-1}$$

Below the peritectic temperature the solubility may be represented by the empirical equation

$$\text{uranium (420 to 840 C): } \log (\text{weight percent}) = 6.946 - 6711 T^{-1}$$

A systematic study is underway to ascertain the influence of atomic size, metallic valence, and electronic configuration on the coprecipitation of various metallic elements with the cadmium-cerium intermetallic phase CeCd_{11} . The following values for the coprecipitation coefficient λ , defined by the equation

$$\log \left(\frac{\text{tracer in solution}}{\text{total tracer}} \right) = \lambda \log \left(\frac{\text{carrier in solution}}{\text{total carrier}} \right),$$

have been determined: sodium, lithium, potassium, yttrium, barium, $\lambda = 0$; lanthanum, $\lambda = 1.49$; thorium, $\lambda = 1.08$; praseodymium, $\lambda = 0.63$; gadolinium,

$\lambda = 0.23$; samarium, $\lambda = 0.17$; uranium, $\lambda = 0.13$; strontium, $\lambda = 0.10$; europium, $\lambda = 0.099$; scandium, $\lambda = 0.05$; and zirconium, $\lambda = 0.04$.

The temperature dependence of the distribution coefficient of cerium and palladium when partitioned between the two partially immiscible liquids lead and zinc has been determined. The value of the coefficient (weight percent in zinc phase/weight percent in lead phase) for cerium is 24 at 650 C, 11.7 at 700 C, and 5.7 at 730 C, whereas for palladium the coefficient is 1790 at 652 C, 473 at 703 C, and 178 at 740 C.

The vapor pressure of solid uranium-cadmium alloys has been measured using the continuous recording effusion apparatus. The vapor pressure-composition patterns observed are in complete agreement with the results previously obtained by conventional methods for phase studies.

The vapor pressure of solid cerium-zinc alloys has been measured as a function of composition by means of the effusion method. The existence of the intermetallic compounds CeZn_{11} , CeZn , Ce_2Zn , and Ce_4Zn was confirmed. The phase previously identified as CeZn_9 was shown to be $\text{Ce}_2\text{Zn}_{17}$. The existence of CeZn_2 appears highly probable. Two additional compounds, $\text{CeZn}_{\sim 7}$ and a phase having a wide solid solution range between $\text{CeZn}_{\sim 3.7}$ and $\text{CeZn}_{\sim 6.4}$ were observed.

The magnetic susceptibility of the neodymium-cadmium intermetallic phase NdCd_{11} has been found to follow a Curie-Weiss relation [$\chi = C/(T-\Delta)$] with $C = 1.667$ and $\Delta = -8^\circ\text{K}$. The effective Bohr magneton number for this alloy is 3.67. This is in good agreement with the theoretical value of 3.68 expected for a free trivalent neodymium ion in a $^4I_{9/2}$ ground state.

A series of combustions of uranium mononitride in oxygen has been completed. The precision of the results obtained was excellent. However, insufficient proof of the exact state of some oxygen containing impurity in the sample leaves a relatively large uncertainty in any value of the heat of formation calculable from the results. Further analytical or preparative work is necessary.

Combustions of boron nitride in fluorine are being carried out calorimetrically. These are the first combustions of a compound in fluorine and the first combustions of a spontaneously reacting material to be studied. For these studies a special combustion bomb with an attached fluorine tank is being used. This combustion bomb reaction system has been calibrated and the energy of expansion of fluorine into the bomb has been determined.

Previously reported values for the heats of formation of crystalline zirconium tetrafluoride and gaseous molybdenum hexafluoride have been revised to $\Delta H_f^\circ (25^\circ\text{C}) = -356.7_8 \pm 0.2_5$ and $-372.3_5 \pm 0.2_2$ kcal/mole, respectively.

Results of the first calorimetric combustions of uranium in fluorine were uncertain because of complications which arose in analyzing the combustion products. However, the experiments did lead to a preliminary value of ΔH_f° (25 C) = -509 ± 3 kcal/mole for uranium hexafluoride gas. Most of the large uncertainty in the preliminary value is due to analytical uncertainties which should be capable of being resolved.

Techniques have been worked out for burning in fluorine some of the low melting metals, such as cadmium, zinc, magnesium, and aluminum. Calorimetric measurements have been started on cadmium.

Techniques somewhat similar to those used in combustion of zirconium in fluorine have been worked out for titanium, hafnium, niobium and tantalum. Studies are being continued on thorium and vanadium.

A. Pyrometallurgical Development

1. Melt Refining

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

The first core loading of EBR-II, which consists of 50 percent enriched uranium alloyed with noble metal fission product elements, will be recovered by melt refining. After the stainless steel jackets have been removed mechanically, the fuel pins are chopped and charged to a zirconia crucible, where they are melted and held at a temperature of 1400 C for three to four hours. Approximately two-thirds of the fission products are removed by this treatment through the mechanisms of volatilization and selective oxidation by the crucible. The purified product is collected in the form of an ingot by pouring the molten metal into a graphite mold. (A separate process is being developed to recover the unpoured metal and oxide remaining in the crucible as a skull.) Experimental work has been continued on (1) demonstration runs using approximately 400 gm of highly irradiated EBR-II-type fuel alloy, (2) the effect of nitrogen-containing atmospheres on the melt-refining process, (3) possible modifications of the process, and (4) the anticipated self-heating of fuel pins resulting from fission product decay energy.

a. High-activity Level Melt-refining Experiments

(V. G. Trice, W. H. Spicer)

The second melt-refining experiment with about 400 gm of highly irradiated, 10 percent enriched uranium-five percent fission alloy has been completed. The purposes of these small-scale experiments are to demonstrate the recovery and decontamination of irradiated EBR-II fuel and to observe the physical behavior of the fuel during various phases of the process. The experimental conditions and pouring yields for the experiments that have been completed to date appear in Table 1. Complete analytical results for the second experiment are not yet available.

Table 1

HIGH-ACTIVITY-LEVEL MELT-REFINING EXPERIMENTS

Item	Experiment No.		
	1	2	2A
Charge Weight (g)	387.6	392.3	398.1
Burnup (percent of total atoms)	0.56	0.2 ^a	Unirradiated
Cooling Time (days)	42	28	-
Total Activity (c/gm) ^b	6.5	2.8	-
Atmosphere	Argon	Argon	Argon
Crucible (lime-stabilized zirconia)	Norton RZ5601	Norton RZ5601	Reclaimed crucible from Expt. No. 2
Wetted Area (sq cm)	35.7	35.7	36.5
Time (hr)	3	3	3
Temperature (C)	1400	1400	1400
Yield (percent)	72.4	69.3	87.2
Yield of Reference Experiment ^c (percent)	86.7	84.0	-

^aEstimated from conditions of irradiation.

^bEstimated from fission yield data.

^cReference experiments employed unirradiated uranium-fissium alloy plus about 0.5 percent cerium added to simulate rare earth fission products.

In both experiments the fuel, irradiated to 0.56 atom percent burnup in the first experiment and to about 0.2 atom percent burnup in the second, was melt refined for three hours at 1400 C. A heavy crust which formed on the surface of the melt in the first experiment prevented pouring on the initial attempt. By allowing the melt to freeze, remelting, and pouring under vacuum, a purified metal yield of 72.4 percent was obtained in the product ingot. Somewhat similar results were obtained in the second experiment. On the first pouring attempt a metal recovery of 50 percent was realized. Freezing, remelting, and pouring under vacuum increased the final yield to 69.3 percent.

Each of the high-activity-level experiments was preceded by a reference experiment performed under identical conditions with unirradiated fuel. An average yield of 85 percent for the reference experiments compared with the 70 percent recoveries obtained in the active experiments strongly suggests the existence of a radiation effect. Analytical data from the first active experiment (see ANL-6287, page 35) showed that the lower yield was associated with a twofold greater loss of uranium as oxidized metal. Although the evidence points to an increase in the uranium oxidation rate in the case of irradiated material, no specific mechanism has been developed to explain the phenomenon.

In Experiment 2A, an attempt was made to establish the effect of a high radiation field by melt refining unirradiated fuel in the crucible used for the second active experiment. As indicated by the data from the first active experiment (ANL-6287, page 32), a substantial fraction of the fission product activity removed by melt refining is not retained in the skull. A small part of this activity is volatilized, but most of it, consisting mainly of a portion of the rare earths and the bulk of the strontium-barium, is retained in the zirconia crucible. The gamma-activity levels of the crucible and the separated skull were of about the same magnitude (about 500 r at four feet).

Before the crucible was used, the skull from the active experiment was removed by oxidation in air at 800 C, which also would be expected to restore the oxygen depleted during melt refining. In appearance the crucible closely resembled an unused crucible after degassing at high temperature. The crucible was heated to 1400 C for one hour at a pressure less than 25μ , prior to re-use. A total of 400.1 gm of metal, which consisted of 398.1 gm of unirradiated uranium-fissium fuel alloy and 2.0 gm of cerium metal, was charged to the crucible. The other conditions were identical to those of the second active experiment.

A metal recovery of 87.2 percent was obtained, with no indication of a heavy surface crust. No clear explanation for this phenomenon has been developed; however, it is possible that the type, levels, and locations of activity and fission product decay heat were not sufficiently similar to produce the increased oxidation. Perhaps the most likely cause for the lowered yields for the irradiation metal is the enhanced rate of reaction of irradiated metal with impurities in the furnace atmosphere. It is anticipated that more definitive information will be obtained as additional high-activity-level experiments are completed.

b. Nitride Formation on Sodium-coated and Uncoated Fuel Pins
(J. P. LaPlante)

The declad sodium-coated fuel pins may be stored for a period of time in the EBR-II Fuel Cycle Facility prior to melt refining. Inasmuch as the atmosphere in the facility may contain up to five percent nitrogen, an opportunity for nitridation may occur during storage and handling operations. It has been estimated that during the handling of declad pins prior to processing, the pin temperatures will be in the vicinity of 300 C as a result of fission product decay heating.

Several measurements were made to determine the effect of nitrogen concentration on the nitridation rates of uranium-5 percent fissium alloy pins with and without sodium coatings at 308 C. The sodium

coatings were prepared by subliming metallic sodium onto pins previously cleaned with a polishing wheel. The rates of nitride formation were derived from manometric measurements of the nitrogen consumed in a constant-volume system.

In Figure 1 the amount of nitrogen consumed in 24 hr per sq cm of metal surface is shown as a function of the nitrogen concentration. The nitridation rate was independent of nitrogen concentrations above about one percent for the uncoated pins and above about five percent for the coated pins. Similar results have been reported (ANL-5974, page 187) for the nitridation of uranium-fissium alloy in 100 percent nitrogen and in 5 percent nitrogen-95 percent argon atmospheres.

c. Effect of Pin Nitridation on Melt-refining Yields
(G. A. Bennett, W. A. Pehl)

Additional work has been done on the effect of nitride coatings on melt-refining yields. The results of three runs, given in Table 2, show that a slight reduction in yield occurred on melt refining after previously storing the pins at 350 C in various nitrogen-argon atmospheres. After 2-hr storage periods, the yields ranged from 94 percent in a 0.25 percent nitrogen-argon atmosphere to about 86 percent in a $5\frac{1}{2}$ percent nitrogen-argon atmosphere.

The selected storage conditions, namely, 2 hr at 350 C, represent estimates of the temperature of the spent, decanned fuel pins and the time that they will be stored in the Argon Cell before they are sealed into the melt-refining furnace.

- 2) A poker, designed to puncture the crust at its pouring edge, is effective. (A yield of 85 percent was obtained by this technique in Run No. 297 where the heavy crust prevented an initial pour.)
- 3) A masher, consisting of a cross-shaped tantalum member, is moderately effective. (A 44 percent yield was obtained in Run No. 298 in which sufficient pinshells were present to prevent an initial pour.)

Table 3

EFFECT OF SUPPLEMENTAL POURING TECHNIQUES ON
MELT-REFINING INGOT YIELD

Conditions: Charge Material: 5 percent fissium with cerium added (final cerium concentration 0.6 w/o)

Charge Quantity: ~2 kg

Atmosphere: 5% nitrogen-95% argon

Coating material: none

Run No.	Charge Shape	Storage Conditions		Initial Yield ^a (%)	Dross Appearance	Supplemental Pouring Technique	Final Yield (%)
		Temp (C)	Time (hr)				
297	Massive metal	1200	21	0	Heavy crust	(1) Vacuum applied	0
						(2) Punctured crust at edge	85.2
296	Pins	500	17.5	61.6	Some pinshells	Masher	71.3
298	Pins	500	19.5	- b	Numerous pinshells	Masher	43.7

^aYield obtained on pouring under one atmosphere of argon.

^bNo initial yield attempted

It is obvious that although these techniques are helpful, they are not comparable in effectiveness to elimination of sources of contamination.

e. Simulated Fission Product Decay Heating of EBR-II Fuel Pin
(G. A. Bennett, W. A. Pehl)

There are many operations in the reprocessing cycle, such as decladding and cutting, in which the fuel pins will be handled separately. In order to determine the temperature which a single irradiated pin will reach, a fission fuel rod (diameter = 0.144 in.) was heated electrically while suspended in such a way that heat transfer from it would occur primarily by natural convection. The measured surface temperatures under equilibrium conditions for three different heat fluxes are given in Table 4. At the heat flux corresponding to 15-day cooled 2 percent burn-up fuel (0.2 watt/gm), the surface temperature was 128 C. It is estimated that without conduction losses occurring through the electrical clamps the pin temperature would have been about 25 C higher. The measured heat transfer coefficient was 5.6 Btu/(hr)(sq ft)(F). The theoretical heat transfer coefficient for natural convection under these conditions is 3.5 Btu/(hr)(sq ft)(F)¹; this latter figure makes no allowance for radiation losses.

Table 4

SURFACE TEMPERATURE OF A FISSION FUEL ROD
UNDER FREE CONVECTION

Run No.	Power Input (watt/gm)	Measured Surface Temperature (C)	Measured Heat Transfer Coefficient [Btu/(hr)(sq ft)(F)]	Theoretical Heat Transfer Coefficient [Btu/(hr)(sq ft)(F)]
6	0.20	128	5.6	3.5
7	0.23	137	5.9	3.3
8	0.18	112	5.9	3.3

2. Development of Processes Utilizing Liquid Metal Solvents
(L. Burris, Jr., R. K. Steunenberg)

Liquid metal processes are being developed for the recovery of fissionable material contained in the melt-refining crucible skulls produced in the EBR-II fuel cycle and for the isolation of plutonium bred in blanket material. At the completion of the melt-refining operation, approximately ten percent of the charge remains behind in the zirconia crucible in the form of a skull composed of metal and oxides. An auxiliary process is required to recover partially decontaminated uranium from the skull and return it to the melt-refining process. Although complete fission product

¹McAdams, W. H., Heat Transmission, 3rd ed., McGraw-Hill Book Co., Inc., New York, N.Y. (1954), Figures 7 to 10, p. 176.

removal is not necessary, a substantial amount of each fission product element must be removed in order to maintain the proper fission composition in the recycled fuel. The objective of the blanket process is to upgrade the plutonium concentration to a point sufficient for re-enrichment of the EBR-II fuel material (from 1 percent to about 50 percent plutonium in uranium).

Work was continued on the skull-reclamation process presented in the previous quarterly report, the flowsheet for which is again given in Figure 2. Runs are in progress for demonstrating the process and for pinpointing engineering and chemical difficulties. Tests and evaluations of various possible materials for containing the liquid metal solutions of interest are reported. In support of the process work, laboratory studies were made on uranium oxide and fission skull oxide reductions in the presence of halide fluxes and on uranium and fission product behavior in various process steps.

Because of the potential application of the reduction procedures employed in the skull-reclamation process to other areas of fuel processing, reductions of uranium tetrafluoride, plutonium dioxide, and thorium oxide were demonstrated. Preliminary work has also shown that stoichiometric uranium compounds, such as uranium monocarbide, can be prepared in high purity by precipitation from liquid metal solutions.

An alternative zinc-dissolution procedure in which a small amount of magnesium is present has been applied to the processing of blanket material for the separation of contained plutonium. This procedure avoids formation of the uranium-zinc intermetallic compound and

permits, after dissolution of the blanket uranium, direct precipitation of the uranium away from the plutonium by addition of magnesium to the solution.

a. Oxidation of Radioactive Melt-refining Skulls
(R. C. Cairns and R. Nowak)

Experimental work with irradiated fissium alloy is being carried out to determine the extent of movement and methods of collection of volatile substances during the oxidation of skulls from melt-refining crucibles.

Two melt-refining oxidation runs with lightly irradiated fissium alloy (about 2×10^{13} fissions/gm) have been completed. The melt-refining yields in the runs were 92 and 89 percent using initial charges of approximately 450 gm. The skulls, which were short-cooled to allow detection of any volatilization of molybdenum-99, technetium-99, and tellurium-132, were oxidized in the equipment shown in Figure 3.

After oxidation at 800 C for three hours, essentially all the activity collected was due to iodine-131 and iodine-133. Tellurium-132 was detected in one run, but it constituted less than one percent of the activity found on a Fiberfrax* plug used to collect the volatile materials. Ruthenium, molybdenum, and technetium activities were not found.

b. Oxidation of Massive Uranium-Fissium Alloy
(T. R. Johnson, R. L. Christensen)

Oxidation has proved to be a satisfactory means of removing melt-refining skulls from zirconia crucibles for further processing in liquid metal media. The possibility of recovering molten metal spills, unpourable ingots, and certain types of scrap by a similar procedure was investigated briefly. In general, materials of this nature are considerably more massive than the relatively thin melt-refining skulls.

Two experiments were performed to study the handling of unpoured uranium-fissium ingots in zirconia crucibles. The ingots were prepared by melting about 365 gm of uranium-7.5 weight percent fissium alloy in small zirconia crucibles ($1\frac{1}{4}$ -in. ID, $3\frac{1}{2}$ -in. inside depth). The ingots in the crucibles were then oxidized by undiluted oxygen at 750 C in a $2\frac{1}{2}$ -in. stainless steel furnace tube. In the first experiment, the crucible was held in a tightly fitting stainless steel secondary container. In the second experiment, the crucible was unrestrained by the secondary container and was supported upside down over an alumina crucible.

In both cases the oxygen uptake at a constant oxygen pressure was uniform until more than 95 percent of the alloy had reacted. In both experiments the oxide expanded, thereby breaking the crucible and secondary container. At the conclusion of the experiments, the oxidized material was wedged tightly in the furnace tube. This material was removed with difficulty as large fragments which could be easily pulverized. In the first experiment, a piece of unoxidized metal weighing 18 gm was also found; in the second, no unoxidized metal remained.

These experiments indicate that the oxidation of massive uranium-fissium alloy for subsequent processing is satisfactory from a chemical standpoint. However, the mechanical problems encountered in handling an unpoured ingot in a ceramic crucible by means of this technique need study.

*A product of the Carborundum Corporation. The stated composition of the fibers is 51.2% Al_2O_3 , 47.4% SiO_2 , 0.7% B_2O_3 , 0.7% Na_2O .

c. Demonstration of Skull-recovery Process

(R. D. Pierce, T. R. Johnson, J. F. Lenc, L. F. Dorsey, K. R. Tobias, R. L. Christensen, M. A. Bowden, and J. D. Schilb)

A program is in progress to demonstrate the various steps of the proposed process for the recovery of uranium from melt-refining skulls. The objectives of the demonstrations are to determine the feasibility of the process, to investigate certain chemical aspects of the steps, and to develop process modifications and improvements. Two demonstration runs have been completed. In these, the process steps shown in Figure 4 were used. Although the present version of the process includes a preliminary step in which noble metals are removed from the skull oxide by selective reduction with magnesium-free zinc, this step was not included in these runs because it had not yet been developed when these experiments were made.

Figure 4
FLUOWSHEET FOR TWO SKULL RECOVERY DEMONSTRATION RUNS

^aThe arc melting step is not a process step but was carried out in these runs to effect product isolation for sampling purposes.

The reduction, intermetallic precipitation, and intermetallic decomposition steps were all conducted in the furnace shown in Figure 5. This furnace was modified to make transfer by pressure possible, and it has functioned satisfactorily when operated with care. Improved equipment has been designed and ordered, but delivery is not anticipated for several months.

FIGURE 5
MODIFIED POUR FURNACE WITH PRESSURE-SIPHON
ATTACHMENT FOR DEMONSTRATION RUNS

The liquid-phase transfers were not quantitative in these runs; however, the liquid heel resulting from the treatment of a skull (or batch of skulls) can be charged to a subsequent run. Therefore, crucible heels were interchanged in these two runs in order to limit the uranium losses.

Oxidized cerium-fissium-uranium skulls were reduced (Step B) with a five weight percent magnesium-zinc solution in the presence of a salt flux (magnesium chloride, calcium chloride, and magnesium fluoride in the respective mole percentages of 47.5, 47.5, and 5.0). The composition and particle size distribution of the skull oxide are shown in Table 5. About half of the zirconium in the oxide consisted of particles from the zirconia crucible. The reductions were conducted for 5 hr at 800 C in a graphite crucible, using tantalum baffles and agitator.

After the reduction (Step B, Figure 4) in Run D-5, the metal phase was pressure-siphoned into a mold through a tantalum tube, the inlet of which was located 3 mm above the bottom of the reduction crucible. The level of the liquid metal was followed during the transfer

by means of an electrical probe, and the transfer was stopped when the metal-salt interface was about 2 mm above the tube opening. After the metal had frozen, the mold was removed and a different mold was inserted to act as a receiver for the waste salt. The furnace was tilted slightly to bring the inlet of the transfer tube into the salt phase and the salt was transferred. A heel of salt and metal was left in the reaction crucible. This crucible and the heel were used with a fresh charge for the reduction step in Run D-6. In Run D-6, a plugged argon line caused the salt to be transferred along with the metal phase after the reduction. These phases were easily separated after solidification on cooling.

Table 5

COMPOSITION OF SKULL OXIDE CHARGE

(From Skull Oxidation Run SO-50)

Skull Oxide Charge^a Weight: Run D-5, 225 g;
Run D-6, 251 g

<u>Element</u>	<u>Weight Percent</u>	<u>Element</u>	<u>Weight Percent</u>
Uranium	76.0 $\pm$ 0.4	Ruthenium	1.41 $\pm$ 0.01
Cerium	2.67 $\pm$ 0.09	Rhodium	0.25 ^b
Zirconium	1.03 $\pm$ 0.06	Palladium	0.25 ^b
Molybdenum	1.87 $\pm$ 0.09	Oxygen	16.52 ^c

^aParticle-size distribution of skull oxide in both Run D-5 and Run D-6 was as follows (expressed in weight percent): -325 mesh, 5.2; -170 +325 mesh, 15.8; -80 +170 mesh, 11.6; -45 +80 mesh, 19.7; -25 +45 mesh, 24.0; -14 +25 mesh, 23.6; and +14 mesh, none.

^bEstimate based on original metal concentration of 0.3 weight percent.

^cObtained by difference.

The uranium reductions (Step B), based on the amount of uranium appearing in solution, were 93 and 96 percent complete in Runs D-5 and D-6, respectively. The salt waste streams on the other hand, contained only 0.2 and 0.4 percent of the uranium charged. It is suspected that the 4 to 7 percent of unaccounted uranium was removed from the metal phase by reaction with the graphite crucible to form uranium carbide. Quantities of elements present in the flux before and after reduction are given in Table 6. A large fraction of the uranium in the D-6B (Run D-6, Step B) flux was probably contained in small amounts of zinc metal which were occluded by the salt when the two phases were rapidly transferred and chilled.

Table 6

COMPARISON OF URANIUM AND FISSION PRODUCT CONCENTRATIONS
IN FLUX BEFORE AND AFTER REDUCTION

Conditions: Reduction at 800 C for 5 hr in graphite crucible

Charges: 5 and 5.6 kg of 5 percent magnesium-zinc alloy in Runs D-5 and D-6, respectively, and 0.8 and 1.1 kg of flux in Runs D-5 and D-6, respectively. Flux composition: 47.5, 47.5, and 5.0 mol percent, respectively of MgCl_2 , CaCl_2 , and MgF_2

Element	Quantities in Flux (gm)			
	Run D-5		Run D-6	
	Charged	After Reduction	Charged	After Reduction
Uranium, total ^a	171	0.4	191	0.9
Cerium	6.0	0.3	6.7	0.3
Zirconium	2.3	0.07 ^b	2.6	0.07 ^b
Molybdenum	4.2	0.2	4.7	0.5
Ruthenium, Rhodium, Palladium	4.3	- ^b	4.8	- ^b
Zinc	0	Not determined	0	17
Uranium, as metal	0	Not determined	0	0.6

^aIncludes uranium present both as metal and as oxide.

^bResult is low or unavailable since the element was not completely dissolved on leaching the flux with aqua regia. Qualitative X-ray emission data show significant amounts of zirconium, ruthenium, rhodium, and tantalum (from the equipment) in the undissolved residue.

In connection with the development work on the skull reclamation process, rough determinations were made of the melting points and densities of pertinent molten salt mixtures used as fluxes. The results are shown in Table 7.

The intermetallic compound precipitation (Step C), intermetallic compound decomposition (Step D), and retorting (Step E) operations for both runs were made in the same tantalum crucible. These steps for Run D-6 were completed before they were begun in Run D-5, and the retorting heel remaining in the crucible after Step D-6E was recharged in the crucible to the precipitation step of Run D-5 (Step C).

Table 7

PROPERTIES OF SALT FLUXES

<u>Flux Composition</u>		<u>Freezing Point (C)</u>	<u>Density (g/cc)</u>		
<u>Constituent</u>	<u>Mole %</u>		<u>600 C</u>	<u>700 C</u>	<u>800 C</u>
MgCl ₂	47.5	602	2.12	2.01	1.92
CaCl ₂	47.5				
MgF ₂	5.0				
MgCl ₂	47.5	565	-	-	1.9
LiCl	47.5				
MgF ₂	5.0				
MgCl ₂	41.0	432	-	-	1.9
NaCl	54.0				
MgF ₂	5.0				

For the precipitation step, the ingots from Step B were reheated to 800 C and cooled to about 550 C to crystallize the epsilon zinc-uranium intermetallic phase. Most of the uranium-zinc solution was pressure-transferred from the crystals. The transferred metal was remelted and sampled to permit uranium analyses. The uranium concentration was only slightly higher than the solubility at the transfer temperature, as is indicated by the following data:

<u>Step</u>	<u>Transfer Temp (C)</u>	<u>Uranium Conc (w/o)</u>	
		<u>Filtered Sample Just before Transfer</u>	<u>Transferred Ingot</u>
D-5C	~560	0.17	0.19
D-6C	~550	0.10	0.11

Samples of the zinc solution in Step D-5C (intermetallic compound precipitation step) taken at 800 C before cooling indicated that about 80 percent of the retorting heel left from D-6E had redissolved.

Magnesium was added to the intermetallic compound heel from Step C to form an equal weight ratio of magnesium to zinc. The material was heated to 800 C and stirred to decompose the epsilon phase. After four hours the bulk of the magnesium-zinc was transferred from the uranium. After the transfer in Step D-5D, filtered samples were

taken from the residual solution during the cooling to help determine the lowest practicable transfer temperature for future runs. Analyses of the samples together with information on the behavior of ruthenium and cerium in approximately 50 percent magnesium-zinc solution are reported in Section e, page 57. They show that about a five-fold reduction in the uranium loss in the supernatant solution can be obtained by cooling to around 450 C in the intermetallic compound decomposition step. The uranium loss in this supernatant solution constituted the major uranium waste loss in these experiments. Cerium is retained in solution during cooling, and so the reduction in uranium loss can be achieved without jeopardizing the uranium-rare earth separation. Ruthenium largely coprecipitates with uranium even at 800 C, which further emphasizes the necessity for a noble metal extraction step, as discussed on pages 52-54.

The uranium heel in the tantalum crucible from Step D was transferred to a retort and the residual magnesium and zinc were vacuum distilled under the following conditions:

Step	Incremental Time (hr)	Temp Range (C)	Pressure (mm Hg)	Charge (gm)	Product (gm)
D-5E	1.2	540-560	0.030-0.062		
	2.5	675-770	0.018-0.010		
	2.5	790-840	0.010-0.002	290	165
D-6E	2.5	540-560	0.110-0.040		
	0.5	660-760	0.033-0.024		
	3.5	790-836	0.017-0.005	520	180

The retorted product from D-6E was largely in the form of small balls ($\frac{1}{16}$ -in. to $\frac{3}{8}$ -in. in diameter), but a portion of the product had sintered and was stuck to the crucible. This latter portion was recharged to the intermetallic compound precipitation step (D-5C) for redissolution. Most of the retorted product from Step D-5E was granular, ranging from fines to $\frac{1}{8}$ -in. balls, but again some sintered material adhered to the crucible. Both retorted products were melted in a beryllia crucible in an induction furnace. Samples of the retorted material and of the material melted in the induction furnace were analyzed.

The composition of the uranium product is compared to the composition of the skull oxide charge (expressed on an oxygen-free basis) in Table 8. In these runs, the stepwise removal of fission products was not followed, since the objective was to determine overall removals and pin-point process deficiencies. For product recycle to the melt-refining process, required fission product removals are modest, ranging between 70 and 90 percent.

Table 8

URANIUM PURIFICATION IN SKULL-RECLAMATION PROCESS RUNS

Constituent	Concentration in Starting Material (oxygen-free basis) (w/o)	Product Concentration and Decontamination			
		Run D-5		Run D-6	
		Conc (w/o)	Percent Removal	Conc (w/o)	Percent Removal
Uranium	91.0	94.3 ^b	-	95.6 ^a	-
Cerium	3.2	0.5 ^a	85	1 ^b	69
Molybdenum	2.2	0.9 ^b	59	0.6 ^{a,b}	73
Ruthenium	1.7	1.2 ^b	30	1.3 ^{a,b}	23
Zirconium	1.2	0.6 ^b	50	0.4 ^a	67
				1.0 ^b	17
Palladium	0.3	0.001 ^a	99	0.001 ^a	99
Magnesium	0	0.4 ^a	-	0.3 ^a	-
Oxygen	-	0.1 to 0.3 ^a	-	0.1 ^a	-
				0.6 ^b	

^aBased on analysis of retorted material.

^bBased on analyses of material after melting in a beryllia crucible.

No quantitative removals were anticipated, since the phase separations were deliberately incomplete. The cerium removal corresponds closely to the percent removal of the magnesium-rich supernatant solution following the decomposition of the uranium-zinc intermetallic compound. If desired, therefore, it could be increased by better phase separation or by a magnesium wash. Because of its insolubility in zinc, molybdenum probably remained as a precipitate in the metal heel of the reduction step. The removal of ruthenium is inadequate for process purposes; it is anticipated, however, that ruthenium, as well as the other noble metals, will be removed effectively in subsequent runs when the initial noble metal extraction step is added to the process. Zirconium was also inadequately removed. The reasons for this will be explored. The very good palladium removal results from its low concentration in the charge material and its high solubility in both supernatant solutions. With additional experience, it is thought that the magnesium and oxygen contents of the retorted products can be reduced.

A uranium material balance is presented in Table 9. As indicated previously, the high uranium loss in the magnesium waste stream from the intermetallic decomposition step could have been reduced significantly by lowering the temperature prior to the transfer. The heels should not be regarded as losses because they would normally be recycled in the process. Other residual uranium adhering to parts of the equipment, such

as stirrers and baffles, would not ordinarily constitute a process loss, but was dissolved in these experiments for material balance purposes. Most of the uranium losses could be avoided or reduced substantially in equipment better adapted for this purpose.

Table 9

URANIUM MATERIAL BALANCES IN
SKULL DEMONSTRATION RUNS

(See Flowsheet in Figure 4, page 46)

<u>Designation</u>	<u>Run D-5</u>		<u>Run D-6</u>	
	<u>Uranium Content (gm)</u>	<u>Percent of Charge</u>	<u>Uranium Content (gm)</u>	<u>Percent of Charge</u>
<u>Uranium Charge</u>				
Skull Oxide	171	79	191	91
Heel from Step D-6E	46	21	-	-
Heel from Step D-5B	-	-	19	9
		100		100
<u>Waste Streams</u>				
Reduction Step Flux (Step B)	0.4	0.2	0.4	0.2
Zinc-rich Supernatant (Step C)	5.4	2.5	4.1	2.0
Magnesium-rich Supernatant (Step D)	11.9	5.5	10.3	4.9
<u>Heels and Residues Available for Recycle</u>				
Reduction Step Metal Heel	19	8.8	11	5.2
Retorting Heel (Step E)	35	16	46	22
Other Residues ^a	9	4.1	6	2.8
<u>Retorted Product</u>	122	56	125	60
<u>Unaccountable Losses</u>	14	6.4	7	3.3

^aMetal on parts of the equipment such as stirrers and thermocouple walls.
This metal was dissolved for material balance purposes.

The metallic uranium product was sufficiently pure so that it could be melted satisfactorily under normal melt-refining conditions, thus indicating that it can be recycled to the melt-refining operation in the EBR-II fuel cycle.

d. Noble Metal Extraction from Fission Skull Oxides

A step currently envisioned for the melt-refining-skull-reclamation process is the selective extraction into zinc of the noble metals present in fission oxide. To facilitate this extraction and the subsequent phase separation, the fission oxide is suspended in a molten salt flux. The noble fission products whose oxides are reduced by zinc (such as molybdenum, ruthenium, rhodium, and palladium) are expected to be reduced by

and dissolved or suspended in the zinc. Uranium oxide and other stable oxides (such as the oxides of plutonium, rare earths, and zirconium) remain suspended in the flux phase. Preliminary work (ANL-6287, page 58) demonstrated that ruthenium could be transferred to a molten zinc phase from a fissium oxide-flux slurry.

In the past quarter, work on noble metal extraction with zinc was performed in two areas: (1) a further study of the extraction of noble elements, and (2) the study of the separation of the phases after the extraction. Preliminary results indicate nearly complete extraction of ruthenium, molybdenum, and palladium. The phase separation work has shown that separation by removal of the salt slurry is impractical. An alternative procedure, removal of the zinc phase after solidification of the salt, has worked well.

(1) Demonstration of Noble Metal Extraction
(J. B. Knighton, J. W. Walsh)

A run was made to study the extraction of molybdenum, ruthenium, and palladium into zinc. The conditions of this run and the distribution of the noble metals and uranium between the flux and zinc phases are shown in Table 10.

Table 10

NOBLE METAL EXTRACTION: DISTRIBUTION OF
NOBLE METALS BETWEEN ZINC AND
FLUX PHASES

Charge: 400 g of zinc, 21.9 g of -325 mesh fissium oxide from batch "SO54," 200 g of flux (47.5 m/o CaCl_2 , 47.5 m/o MgCl_2 , 5 m/o MgF_2)

Conditions: Phases contacted at 750 C for one hour in alumina crucible under an air atmosphere. The mixing rate was 400 rpm.

<u>Element</u>	<u>Percent of Total in Flux</u>	<u>Percent of Total in Zinc</u>
Uranium	100	0.001
Ruthenium	9	91
Molybdenum	16	84
Palladium	7	93

This run was of one-hour duration and -325 mesh fissium oxide was used. (Fissium oxide particles usually range from 14 mesh to 325 mesh and average about 100 mesh in size.) About 90 percent of the ruthenium, palladium, and molybdenum were found in the zinc phase. Uranium remained with the flux (only 11 ppm uranium were found in the zinc phase).

The results of this run are very promising and are indicative of the potential of this step for removing noble metals from fissium oxides. Work will continue to define process capabilities.

(2) Separation of Phases

(R. D. Pierce, K. R. Tobias, D. Armstrong)

Exploratory runs were made to investigate the separation of phases after a noble metal extraction. Several alternative separation procedures are possible. These include removal of either of the liquid phases, or pouring of both and subsequent separation of the solidified materials. Work to date has involved removal of one of the liquid phases by pressure siphoning.

Removal of Flux-Oxide Slurry

In the first runs, pressure siphoning of the molten flux and suspended fissium oxide was attempted. This method appeared advantageous because it would permit reuse of the zinc for a large number of runs. Accumulation of noble metals in the zinc phase in amounts considerably in excess of their solubilities is considered practical.

A diagram of the apparatus is presented in Figure 6. Several runs were made to determine the settling characteristics of fissium skull oxide in the salt phase and to determine practical fissium oxide loadings. Successive transfers of a series of flux and skull oxide charges from the same zinc melt were also made to determine if a steady-state concentration of uranium in the salt-phase heel was realized.

It was possible to achieve a uniform dispersion of 12 weight percent skull oxide in molten salt with fine fissium oxide (-170 +325 mesh). However, it seems certain that rapid settling of this fine oxide slurry will occur. Experimental information on this point is shown in Figure 7 for a 5 per-

cent skull oxide slurry. The experimental results show that in 15 min the uranium concentration near the bottom of the flux was more than twice the nearly uniform concentration of the remainder of the flux. Considerably greater difficulty was encountered in suspending larger particles of skull oxide (-14 +25 mesh). Although wetted with flux, these coarse particles settled through the zinc phase and accumulated on the side and bottom of the crucible. However, none of the particles could be found within the zinc phase.

The suspension became thick and noticeably more difficult to transfer at oxide concentrations of about three percent for the -14 +25 mesh particles and at about ten percent for the -170 +325 mesh particles. These concentrations are both lower than the uranium oxide loadings of about 15 percent, which are considered attractive from a volume standpoint for the subsequent reduction step.

Although these studies illustrated that quantitative suspension of skull oxide in flux is difficult, a few runs (see Table 11) were made to see whether successive contacts of salt-oxide with zinc would result in a constant heel of oxide after each salt transfer.

TABLE 11									
Successive Transfers of Skull Oxide to Molten Salt and Then to Molten Zinc									
Run	Transfer	From	To	Weight of Skull Oxide (g)	Weight of Salt (g)	Weight of Zinc (g)	Weight of Residue (g)	Weight of Residue (%)	Weight of Residue (g)
1	Initial	Skull Oxide	Salt	20.0	400.0	600.0	1.5	0.75	1.5
2	1st	Salt	Zinc	1.5	1.5	1.5	0.5	33.3	0.5
3	2nd	Zinc	Salt	0.5	0.5	0.5	0.2	40.0	0.2
4	3rd	Salt	Zinc	0.2	0.2	0.2	0.1	50.0	0.1
5	4th	Zinc	Salt	0.1	0.1	0.1	0.05	50.0	0.05
6	5th	Salt	Zinc	0.05	0.05	0.05	0.02	40.0	0.02
7	6th	Zinc	Salt	0.02	0.02	0.02	0.01	50.0	0.01
8	7th	Salt	Zinc	0.01	0.01	0.01	0.005	50.0	0.005
9	8th	Zinc	Salt	0.005	0.005	0.005	0.002	40.0	0.002
10	9th	Salt	Zinc	0.002	0.002	0.002	0.001	50.0	0.001
11	10th	Zinc	Salt	0.001	0.001	0.001	0.0005	50.0	0.0005

This heel might then be recovered by washing the zinc with additional flux. The greater difficulty with the coarser material is evident in Run KT-9, but all runs resulted in a fairly large loss of uranium, even after two flux washes. Removal of the flux slurry is therefore regarded as an unattractive procedure for the skull recovery process.

Removal of Zinc Phase

Because of the difficulty in making quantitative transfers of flux-oxide slurries, studies were directed to the removal of the zinc phase, thereby leaving the oxide and flux to be subsequently reduced with magnesium-zinc in the same crucible. This separation has been successfully performed by pressure-siphoning away the zinc phase after cooling to freeze the salt. An opening was maintained in the salt by running the agitator while the salt was freezing. Analysis of the transferred zinc showed only 0.4 percent transfer of uranium with the zinc. Since this method of transfer appears satisfactory, it will be exploited further.

- e. Uranium and Fission Product Solubilities in High Magnesium-Zinc Systems
(I. O. Winsch, R. D. Pierce, T. Johnson, T. Cannon, and K. Tobias)

The changes in uranium, fission product, and plutonium solubilities as magnesium is added to zinc systems are utilized in both the blanket- and skull-reclamation processes. For example, uranium solubility at 800 C first decreases as magnesium is added to zinc (to a minimum of about 5 percent at a magnesium concentration of about 5 percent), then increases to about 20 percent at a magnesium concentration of 12 percent, and thereafter decreases sharply as further magnesium is added. The insolubility of uranium in the systems of high magnesium concentrations is exploited in the blanket process to effect a plutonium-uranium separation and in the skull-reclamation process to effect a uranium-rare earth separation.

Uranium solubility data at several high magnesium concentrations have been obtained (see Figure 8). Both magnesium concentration and temperature have pronounced effects on the uranium solubility and can be varied to provide low uranium solubilities (e.g., 0.1 percent at 405 C in the 46 weight percent magnesium-zinc eutectic). In the experiment at a 50 percent magnesium concentration, the cerium concentration remained unchanged at 0.2 percent as the temperature was lowered from 800 C to 405 C.

The behavior of ruthenium and cerium on the decomposition by magnesium of an intermetallic uranium-zinc compound formed by direct interaction of a uranium-ruthenium-cerium alloy with the zinc is shown in Table 12.

FIGURE 8
URANIUM SOLUBILITIES IN VARIOUS HIGH MAGNESIUM-ZINC SYSTEMS

Table 12

BEHAVIOR OF URANIUM, RUTHENIUM, AND CERIUM ON
DECOMPOSITION OF URANIUM-ZINC INTERMETALLIC
COMPOUND WITH MAGNESIUM

Charge: 1800 g Zinc	} To Form U-Zn Inter-metallic Phase
372.7 g Uranium	
5.75 g Cerium	
7.55 g Ruthenium	
1540 g Magnesium	

Concentrations in Zinc-Magnesium Phase

Time (hr)	Temp (C)	Uranium		Cerium		Ruthenium	
		(g)	(% of Charge)	(g)	(% of Charge)	(g)	(% of Charge)
1.5	710	4.47	1.2	5.23	91	0.685	9.1
3.5	710	6.70	1.8	4.85	84.5	0.638	8.5
5.5	405	3.73	1.0	5.57	97.0	0.037	0.53

Addition of magnesium to a concentration of 46 percent precipitated over 98 percent of the uranium and over 90 percent of the ruthenium, the latter possibly by coprecipitation. Most of the cerium (85 percent or over) remained in solution.

f. Pyrometallurgical Reduction Studies

(1) Reduction of Fission Skull Oxides

(J. B. Knighton, T. R. Johnson, R. L. Christensen,
J. W. Walsh)

When melt-refining skulls are oxidized for further treatment in the liquid metal skull-recovery process, the principal product is U_3O_8 . This material is accompanied by the various fission product oxides and fragments of the melt-refining crucible which ordinarily represent about one percent of the total skull oxide. Since the liquid metal process involves reduction of this oxide mixture by a zinc-magnesium alloy in the presence of a flux, reduction studies were conducted on a product obtained by oxidizing unirradiated uranium-fission melt-refining skulls.

Several experiments were performed in an air atmosphere (see Figure 9). In Runs 78 and 79 fission oxide was reduced rapidly and quantitatively, with rates similar to those found for U_3O_8 . The material used in Run 78 was reconstituted from proportional amounts of the various screen fractions of the oxide, whereas in Run 79 only the -325 mesh material was used.

FIGURE 9
REDUCTION OF FISSION OXIDE BY ZINC-5 PERCENT MAGNESIUM

FLUX: $CaCl_2$ - $MgCl_2$ - MgF_2 (47.5, 47.5, 50 m/o)
METAL: 392g Zn-5 w/o Mg
ATMOSPHERE: AIR
STIRRING: PROPELLER, 800 rpm
U CONC'N IN METAL PHASE AT 100% REDUCTION: RUNS
74, 81-3.46 w/o U RUNS 78, 79-0.87 w/o

In Run 74 an attempt was made to increase the final uranium concentration in the metal phase by initially adding more uranium-fissium skull oxide to the system. As indicated in Figure 9, the system was unstable, the uranium concentration in the metal phase decreasing with time. When the amount of flux was increased from 200 gm in Run 74 to 300 gm in Run 81, but with the same amounts of skull oxide charged, the reaction proceeded to completion and no instability was evident. This effect is believed to result from an increased viscosity of the flux caused by the higher concentration of suspended magnesium oxide when less flux is used. This, in turn, alters the ability of the flux to protect the metal phase from oxidation by the air atmosphere.

It is expected that zirconium will be present in the skull oxide in two forms: as finely divided fission product zirconium oxide and as zirconia fragments produced by degradation of the crucible during the skull oxidation. The melt-refining crucibles also contain about five percent calcium oxide as a stabilizing agent and small amounts of other impurities, chiefly silicon and iron oxides. Several experiments were conducted to investigate the behavior of zirconium oxide from these two sources during the reduction of fissium oxide.

The crucible fragments do not appear to be reduced readily, possibly because they are a refractory, high-fired type of material. With a sodium chloride-magnesium chloride-magnesium fluoride flux (54.2, 41.1, 4.7 mole percent, respectively), a zinc-6 weight percent magnesium solution, crushed zirconium oxide (<60 mesh) from the reaction zone of a used melt-refining crucible was reduced relatively slowly at 800 C and there appeared to be an induction period (see Figure 10).

FIGURE 10
BEHAVIOR OF ZIRCONIA CRUCIBLE FRAGMENTS
DURING THE REDUCTION OF SKULL OXIDE

In Run 81 a water-insoluble flux residue from a skull oxide reduction showed a strong $K\alpha$ line upon examination by X-ray fluorescence, which indicated retention of zirconium in the flux. Chemical analysis of the residue showed 1.47 weight percent zirconium; this corresponds to 87 percent of the total zirconium originally present in the oxide mixture.

It is believed that the fission product zirconium may be present in the skull oxide in a form somewhat similar to reagent zirconium oxide powder. The reduction of this powder by zinc-magnesium in the presence of the calcium chloride-magnesium chloride-magnesium fluoride flux was nearly 60 percent complete after 120 min. Complete reduction was not anticipated, since solution instability has been observed with zirconium systems. It appears, therefore, that the fission product zirconium oxide in a skull oxide mixture may undergo significant reduction, but that the crucible fragments may be expected to remain largely in the flux phase.

In another experiment, the zirconium concentration in the metal phase was followed as a skull oxide (which contained both forms of zirconium oxide) was being reduced by zinc-five weight percent magnesium in the presence of a calcium chloride-magnesium chloride-magnesium fluoride flux (47.5, 47.5, 5.0 mole percent, respectively) in an air atmosphere. The zirconium concentration in the metal phase was 0.01 weight percent, compared to a theoretical value of 0.167 weight percent based on complete reduction of zirconium oxide. The flux contained 0.287 weight percent zirconium, which accounts for 94.4 percent of the total zirconium present in the system as the oxide.

(2) Reduction of Uranium Oxide by a Magnesium-Zinc System (J. B. Knighton, J. W. Walsh)

Effect of Flux Composition

Previously reported work (ANL-6287, page 51) has shown that group II cations (Mg^{++} , Ca^{++} , Ba^{++} , and Sr^{++}) are beneficial in promoting rapid and quantitative reduction of U_3O_8 by zinc-magnesium-molten halide systems. An additional survey experiment was performed, in which the conditions of the previous study were used, to determine the effect of a molten salt containing only Ca^{++} on the rate and extent of U_3O_8 reduction. A eutectic salt, 80 mole percent calcium chloride-20 mole percent calcium fluoride (mp 650 C), was used. After 120 min at 800 C, only 17 percent reduction had taken place, thus indicating that this flux performed poorly compared with those containing significant amounts of Mg^{++} . Based on the results of this and previous experiments, it has been concluded that Mg^{++} is an essential ingredient of the flux for rapid and quantitative reductions of U_3O_8 by zinc-low magnesium alloys.

Temperature Effect

Studies were made to determine the effect of temperature on the reduction rate of U_3O_8 by zinc-5 weight percent magnesium in the presence of two different fluxes (calcium chloride-magnesium chloride-magnesium fluoride, 47.5, 47.5, 5.0 mole percent, respectively, and lithium chloride-magnesium chloride-magnesium fluoride, 47.5, 47.5, 5.0 mole percent, respectively). The results are indicated in Table 13. As would be expected, the reduction rate decreased as the temperature was lowered. These data also indicate that quantitative reduction of U_3O_8 can be achieved at temperatures as low as 650 C.

Table 13

EFFECT OF TEMPERATURE ON THE REDUCTION RATE OF U_3O_8

Oxide:	U_3O_8 , -325 mesh			
Flux:	200 g, composition as indicated			
Metal:	400 g zinc-5 w/o magnesium			
Stirring:	800 rpm			
Atmosphere:	Air			
U Concentration in Metal at 100% Reduction:	1.00 w/o			
	<u>Percent Reduction</u>			
Temp (C)	<u>(10 min)</u>	<u>(20 min)</u>	<u>(30 min)</u>	<u>(60 min)</u>
<u>Flux: 47.5 m/o LiCl - 47.5 m/o $MgCl_2$ - 5.0 m/o MgF_2</u>				
600	80	95	95	96
650	79	90	94	99+
700	97	99+	99+	99+
750	99+	99+	99+	99+
<u>Flux: 47.5 m/o $CaCl_2$ - 47.5 m/o $MgCl_2$ - 5.0 m/o MgF_2</u>				
650	77	94	99	99
700	94	97	99	99
750	97	99+	99+	99+

Particle Size Effect

The effect of particle size on the reduction rate of U_3O_8 by zinc-5 weight percent magnesium was investigated. A calcium chloride-magnesium chloride-magnesium fluoride flux (47.5, 47.5, 5.0 mole percent) was used. The results of this study, shown in Table 14, indicate that the reduction rate decreases as the particle size is increased.

Status of Systematic Reduction Studies

The overall objectives of this program have been (1) to define flux systems that produce rapid and complete reduction of uranium oxide by zinc-magnesium solutions, (2) to define the effects of process variables on the reduction, and (3) to apply the findings of these studies to the fissium oxide reduction step of the melt-refining skull-recovery process.

Table 14

EFFECT OF PARTICLE SIZE ON THE REDUCTION RATE OF U_3O_8

Oxide: U_3O_8
 Flux: 47.5 m/o $CaCl_2$ - 47.5 m/o $MgCl_2$ - 5.0 m/o MgF_2 ,
 200 g
 Metal: 400 g zinc-5 w/o magnesium
 Stirring: 800 rpm
 Temperature: 750 C
 Atmosphere: Air
 U Concentration in Metal at 100% Reduction: 1.00 w/o

Particle Size (Mesh No.)	Percent Reduction			
	(10 min)	(20 min)	(30 min)	(60 min)
-12, +25	55	76	79	80
-25, +45	75	81	79	84
-80, +170	87	97	97+	99
-325	97	99+	99+	99+

The present status of this work is summarized as follows:

- (1) Flux systems which promote rapid, complete reduction of U_3O_8 have been defined. Magnesium chloride is an essential component of fluxes for this purpose.
- (2) The effect of temperature has been investigated. Complete reductions have been achieved at temperatures as low as 650 C, the rate increasing as the temperature is raised.
- (3) The effect of particle size has been studied. As expected, smaller particles of the oxide are reduced more rapidly than large ones.

Work on the following aspects of uranium oxide reductions in the presence of fluxes is in progress:

- (1) The concentration of Mg^{++} in the flux required for satisfactory reduction.
- (2) The effect of MgF_2 in the flux.
- (3) The magnesium concentration in the metal phase.
- (4) The effect of flux-to-metal ratio.
- (5) Chemical studies of the species and mechanisms involved in the reduction.

(3) Reduction of U_3O_8 by Liquid Magnesium
(A. Schneider, G. L. Rogers)

In earlier studies of the reduction of uranium oxides by liquid magnesium (ANL-6183, pages 46 to 51), it was shown that this reaction can be carried to completion. The uranium product was found to be associated with the magnesium oxide formed during this reaction, and any practical use of this procedure would require the separation of the uranium metal from magnesium oxide as well as unreacted magnesium. In the preceding report (ANL-6287, page 65) it was shown that this separation can be accomplished by contacting the magnesium melt with molten chlorides following the reduction step. It was found that the magnesium oxide transferred to the flux, while two separate metal ingots were present, one near the top and one at the bottom of the flux phase (Figure 11). The upper metal phase consisted of pure magnesium metal, whereas the heavier metal ingot contained the bulk of the reduced uranium metal and was surrounded by a thin magnesium envelope.

FIGURE 11
METAL INGOTS RESULTING FROM THE
REDUCTION OF URANIUM OXIDE WITH
LIQUID MAGNESIUM

Several additional experiments were performed to determine whether the reduction of uranium oxides by liquid magnesium proceeds satisfactorily in the presence of a flux. If so, this would enable the transfer of magnesium oxide to the flux to proceed simultaneously with the reduction. The experimental conditions and results are shown in Table 15. It was found that the presence of the flux greatly enhanced the rate and yield of the reductions. Moreover, the extraction of magnesium oxide into the flux was fairly complete, thus permitting the separation of a uranium-rich metal product. A metallographic examination of this ingot (Figure 12) revealed a highly porous network of small uranium particles embedded in magnesium.

Table 15

REDUCTION OF U_3O_8 BY LIQUID MAGNESIUM-FUSED SALT SYSTEMS

All reductions performed at 725 to 730 C; alumina (Morganite)
crucibles; tantalum accessories.
 U_3O_8 : 100% through 200 mesh

Expt. No.	Flux Type ^a	Duration (hr)	Uranium (% of Charge)		Overall (%)	Material Balances	
			Recovered as Metal	In Flux Phase		Total Metal (U plus Mg) ^c (%)	Flux and Magnesium Oxide ^c (%)
12-7-0	A	4	103	2.7	99.2	102.0	97.0
12-15-0	B	4	97	6.6	99.5	100.3	97.5
12-27-0	C	3	87	10.1	99.4	99.0	96.7
1-3-1	B	4 ^b	Not recovered	17.1	99.6	100.1	95.8
1-5-1	B	4	93	8.5	100.0	100.0	100.0
1-9-1	B	0.5	Not recovered	6.7	97.3	95.1	99.5

^aFlux types: A: NaCl - 69.3; MgCl₂ - 26.8; NaF - 3.9 w/o; freezing temp, 700 C.

B: NaCl - 56.7; MgCl₂ - 39.5; NaF - 3.8 w/o; freezing temp, 600 C.

C: KCl - 57.1; CaCl₂ - 38.0; MgF₂ - 4.9 w/o; freezing temp, 625 C.

^bBaffles not used in this experiment.

^cMaterial balances for metal and flux phases are referred to the quantities calculated for complete reduction, in accordance with the equation

Although the reduction of uranium oxide with liquid magnesium appears to be a feasible procedure, zinc-magnesium solutions are preferred for the skull-recovery process. The metallic uranium product is soluble in the zinc-magnesium solution, and the higher density of the liquid metal phase permits an easier separation of the metal and salt.

(4) Reduction of Uranium Tetrafluoride (J. B. Knighton, J. W. Walsh)

The reduction of uranium tetrafluoride by zinc-5 weight percent magnesium in the presence of a halide flux was demonstrated. The flux consisted of calcium chloride, magnesium chloride, and magnesium fluoride (47.5, 47.5, and 5.0 mole percent, respectively). The zinc, magnesium, flux, and uranium tetrafluoride were charged to an alumina crucible prior to heating. Upon heating rapidly to 750 C, the metal phase was

sampled immediately. Subsequent samples were taken after 10, 20, 30, 60, and 120 min of stirring at 750 C. All samples including the one taken initially, indicated complete reduction of the uranium tetrafluoride. This experiment was conducted in an air atmosphere.

FIGURE 12
URANIUM METAL PRODUCED BY THE REDUCTION OF
 U_3O_8 BY LIQUID MAGNESIUM
Magnification: 250X

Although not directly related to the reprocessing of EBR-II fuel, the reduction of uranium tetrafluoride is of general interest and may represent a useful extension of zinc-magnesium reductions in the presence of fluxes to the processing of feed materials.

(5) Plutonium Oxide Reduction by Liquid Magnesium
(I. O. Winsch, T. F. Cannon)

In the previous quarterly report, quantitative reduction of plutonium dioxide by a five percent magnesium-zinc solution in the presence of a halide flux was reported (ANL-6287, page 57). Results are

now available of a reduction of plutonium oxide by pure magnesium in the absence of a flux. Eighty-seven percent of a 21-gm charge of plutonium dioxide was reduced in 4 hr in pure magnesium (500 gm) at 800 C. The constituents were mixed in a baffled tantalum crucible under a helium atmosphere. Since plutonium is soluble in magnesium, the reduction was followed by means of samples of the magnesium phase.

This exploratory experiment shows the possibility of employing pure magnesium for the reduction of plutonium dioxide. As has been found for other reductions, it is expected that the use of a molten flux would be beneficial in providing nearly complete reductions and for suspension and removal of the magnesium oxide byproduct.

The reduction of plutonium oxide is not a part of the present skull-recovery process. It may prove useful, however, in a process for future core loadings of EBR-II, and has potential application in the direct production of plutonium metal from the oxide.

(6) Reduction of Thorium Oxide
(J. B. Knighton, J. W. Walsh)

Although it is not related directly to the reprocessing of EBR-II fuel, the reduction of thorium is of chemical interest and may represent a potential extension of flux reductions to thorium breeder reactor fuels. Survey experiments were conducted on the reduction of thorium dioxide by zinc-5 weight percent magnesium alloy in the presence of fluxes. The present status of this survey is shown in Table 16.

Table 16

REDUCTION OF THORIUM OXIDE BY ZINC-MAGNESIUM ALLOY

Oxide: 4.55 g ThO₂ powder
Flux: 200 g, composition as indicated
Metal: 400 g zinc-5 w/o magnesium
Stirring: 800 rpm
Temperature: 750 C
Atmosphere: Air
Thorium concentration in metal at 100% reduction: 1.0 w/o

Flux Composition (mole %)	Percent Reduction									
	5 min	10 min	15 min	20 min	25 min	30 min	35 min	60 min	90 min	120 min
CaCl ₂ (47.5), MgCl ₂ (47.5), MgF ₂ (5.0)	4	-	12	-	23	-	30	49	53	-
CaCl ₂ (47.5), LiCl (47.5), MgF ₂ (5.0)	3	-	8	-	13	-	18	29	37	-
NaCl (47.5), LiCl (47.5), MgF ₂ (5.0)	3	-	2	-	3	-	3	3	5	-
NaCl (47.5), KCl (47.5), MgF ₂ (5.0)	1	-	2	-	7	-	1	5	4	-
MgCl ₂ (95.0), MgF ₂ (5.0)	-	11	-	21	-	27	-	44	-	65
CaCl ₂ (80.0), CaF ₂ (20.0)	-	5	-	6	-	6	-	8	-	14

As in the reduction of uranium oxides, fluxes containing group II cations (Mg⁺⁺, Ca⁺⁺) produced better reductions than those containing group I cations (Li⁺, Na⁺; K⁺). Fluxes containing only Mg⁺⁺ as cation

(95 mole percent magnesium chloride-5 mole percent magnesium fluoride) gave better reductions than those containing only Ca^{++} as cation (80 mole percent calcium chloride-20 mole percent calcium fluoride). Magnesium chloride appears to be essential for significant reduction of thorium oxide.

Complete reductions of thorium oxide in this system have not yet been achieved. It is believed, however, that with magnesium chloride present and with the proper choice of variables (such as stirring, temperature, magnesium concentration, flux-to-metal ratio, and time) complete reductions may be possible.

(7) Possible Processing of Uranium Carbide Fuels
(T. R. Johnson, R. L. Christensen)

Uranium carbide has been suggested as a potential fuel for future loadings of EBR-II as well as other fast breeder reactors. It is possible to convert uranium carbide to the oxide by treatment with oxygen and to reduce the oxide to the metal with a zinc-magnesium solution. This sequence of reactions, which has been demonstrated in a laboratory experiment, suggests the possibility of applying to these fuels a liquid metal separation procedure similar to the skull oxide-recovery process.

g. Retorting of Uranium Concentrates
(J. F. Lenc, M. A. Bowden)

In the current skull-reclamation process (see Figure 3, page 44), a final retorting step is required to isolate the precipitated uranium solid phase from the zinc-magnesium liquid metal phase. The retorted uranium must be recovered in high yield from a suitable crucible in a form adaptable to remote handling. In addition, it must be sufficiently free of impurities that would inhibit its incorporation with other fuel material upon recycle to melt refining. Partial success in obtaining a uranium product meeting the above requirements has been achieved in experiments in which the retorted product was readily recovered in the form of compact, irregular-shaped masses (see Figure 13, ANL-6287, page 68). The yield of these sphere-shaped products (about 70 to 80 percent), however, has been lower than desired. In an effort to improve this yield, retorting studies have been directed toward the determination of the mechanism responsible for the formation of the sphere-shaped masses.

In these studies, 200-gm batches of uranium were processed through the last three steps of the skull-reclamation process, namely, (1) precipitation of the uranium-zinc intermetallic compound, (2) decomposition of this compound with magnesium, and (3) retorting

of the precipitated uranium. An initial charge of 4 kg zinc-5 percent magnesium-5 percent uranium was used in each experiment. Precipitation of the uranium-zinc intermetallic phase was accomplished by dissolving the uranium in the liquid zinc-5 percent magnesium at 800 C with agitation (400 to 700 rpm) for about 4 hr followed by slow cooling without agitation to 525 to 575 C. The bulk of the zinc-rich liquid phase was then poured from the precipitated uranium-zinc compound.

Sufficient magnesium was subsequently added (to approximately a 50 percent concentration) to decompose the intermetallic compound and precipitate uranium as metal. The mixture was heated to 800 C with agitation (400 to 700 rpm) for about 4 hr followed by slow cooling without agitation to 550 C. The bulk of the liquid phase was then poured from the precipitated uranium. Final retorting of the residual zinc-magnesium was conducted at 550 to 850 C at a pressure of less than 1 mm Hg to recover the precipitated uranium.

Seven experiments, in which the above procedure was used, were made during the past quarter. Three experiments were carried out in graphite crucibles and four in a seamless tantalum crucible. One CS-grade and two ATJ-grade graphite crucibles were used. In all three tests the graphite crucibles cracked during cooling to room temperature. The cracking very likely resulted from the wetting of the graphite by the metal and the contraction stresses that occurred on cooling.

Because of the crucible failures experienced with graphite, subsequent experiments were made in a seamless tantalum crucible. Various time and agitation conditions (see Table 17) were studied to determine the optimum conditions for the production of agglomerates.

Table 17

EFFECT OF AGITATION ON FORMATION OF URANIUM AGGLOMERATES

Run No.	Agitator Design	Conditions of Agitation			Yield of Uranium Agglomerates ^a	
		Time (hr)	Temp (C)	Speed Range (rpm)	(g)	(w/o) ^b
A-60	Flat Blade	4.5	800-750	300-700	140.8	80.8
A-62	Flat Blade	5	800	400-600	126.3	70.5
A-64	Propeller Blade	4	800	400-600	143.7	82.3
A-66	Propeller Blade	1	800	600	0	0

^aReadily removed after final retorting.

^bWeight percent of total retorted product.

In Table 17 it may be seen that the best yield obtained was about 80 percent. The remainder of the uranium adhered to the tantalum crucible and could not be removed by mechanical means. In one run (A-66) in which the time was reduced from 4 or 5 hr to 1 hr, the entire retorted product adhered to the crucible in a porous, spongelike form.

Further work on this problem is required. Additional experiments are planned to investigate the effects of time, temperature, and various agitation variables (such as type of stirrer and speed) on the formation in high yield of well-coalesced masses of uranium during the intermetallic decomposition step of the skull-reclamation process. The effect of other variables (such as the presence of fission products, the method of magnesium addition, the nature of the intermetallic compound prior to decomposition, and the crucible material) will also be evaluated.

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

In the EBR-II reactor, plutonium will be allowed to build up in the depleted uranium blanket material to a concentration of about one percent before discharge of the blanket material. The liquid metal process under consideration for separation of the plutonium from uranium is based on the relatively high solubility of plutonium in magnesium-rich zinc alloys and the contrasting low solubilities of uranium in these alloys. Processes investigated previously have involved formation of a uranium-zinc intermetallic compound (approximately $\text{UZn}_{11.5}$, designated as the epsilon phase) and subsequent decomposition of this compound by addition of magnesium to precipitate the uranium while retaining the plutonium in solution. After removal of the plutonium solution, the plutonium may be recovered by the vaporization of the magnesium and zinc.

In the previous work, the uranium-zinc intermetallic compound was formed and isolated by dissolution of the uranium in zinc, precipitation of the intermetallic compound by cooling, and withdrawal of the zinc supernatant. Two simplifications of this procedure were investigated during the past quarter: (1) reaction of uranium and zinc in approximately a stoichiometric ratio to form the intermetallic compound directly, and (2) dissolution of the uranium to a concentration of about 14 percent in a 12 percent magnesium-zinc solution. In this latter direct dissolution procedure, a further addition of magnesium to a concentration of about 50 percent precipitates the uranium as metal, thus avoiding the formation of the intermetallic compound. This dissolution procedure is based on information obtained in the Division which shows remarkably high solubilities of uranium in zinc systems containing around 12 percent magnesium (up to 20 percent at 800 C as compared to about 6 percent in pure zinc).

(1) Direct Formation of Uranium-Zinc Intermetallic Compound

A possible simplification of the blanket process is the direct reaction of blanket uranium material with a quantity of zinc which is only slightly in excess of the stoichiometric amount required in the formation of the intermetallic compound $\text{UZn}_{11.5}$, designated as the epsilon phase. Previous runs to produce the intermetallic compound directly were made by treating EBR-II uranium blanket rods (0.43 in. in diameter) with zinc alone or with zinc-0.15 weight percent magnesium alloys at 430 C (ANL-6287, page 69). Reactions were 90 to 100 percent complete in 100 hr. Agitation was not possible after a period of about 8 to 10 hr because of the high viscosity of the slurry.

Eight additional runs have been completed during the past quarter to explore various methods of reducing the reaction time. These included (1) addition of a small quantity of magnesium to the zinc, (2) use of zinc in considerable excess over the stoichiometric quantity based on formation of $\text{UZn}_{11.5}$, and (3) increase of the uranium surface area by previously hydriding and dehydriding the blanket uranium to produce fine particles.

The results of these runs are shown in Table 18. In Run 7, a zinc-2 weight percent magnesium alloy (melting point 395 C) was allowed to react with the uranium for a period of 96 hr at 410 C. About 85 percent of the blanket rods charged had reacted with the zinc-magnesium alloy at the completion of the run. At a two percent concentration, magnesium was not helpful in reducing reaction time.

Table 18

DIRECT REACTION OF URANIUM BLANKET RODS AND HYDRIDED-
DEHYDRIDED BLANKET RODS WITH ZINC TO FORM THE
URANIUM-ZINC INTERMETALLIC COMPOUND

Run No.	Time (hr)	Temp (C)	Charge		Uranium:Zinc Ratio	% of Zinc in Excess of Stoichiometric ^a	Uranium Reacted (%)
			Uranium (g)	Zinc (g)			
7 ^b	96	410	455	1810	0.25	28	85
8	96	420-430	400	1800	0.22	45	77
9	60	430	504	2520	0.20	60	40
10	48	430	500	3125	0.16	100	42
11 ^c	12	430-450	400	1250	0.32	0	~96
12 ^c	10	430	503	1770	0.28	11	~98
13 ^c	7.5	430-800	503	2621	0.19	66	100
14 ^c	10	430-860	504	3150	0.16	100	100

^aThe stoichiometric ratio for formation of $\text{UZn}_{11.5}$ is 0.32.

^b36 g of magnesium in charge to form Zn-2 wt % Mg.

^cUranium hydrided and dehydrided before reaction with zinc

The use of 45, 60, and 100 percent excess zinc (Runs 8, 9, 10, respectively) produced no significant reduction in reaction time. A heavy vibrator employed in Run 8 also was ineffective. Radiographs of the ingots from Runs 9 and 10 clearly revealed the shapes of the unreacted rods. This technique will be valuable in future runs to indicate the percent of uranium reacted.

Hydriding and dehydriding of the uranium was carried out in Runs 11 through 14 prior to melting the zinc to permit the formation of the intermetallic compound at desired temperatures. In Runs 11 and 12, near-stoichiometric quantities of zinc were employed and appreciable reaction (about 90 percent and 98 percent, respectively) took place in the 12- and 10-hr reaction times. No agitation was employed. In both of these runs, a slight amount of unreacted uranium which was present on the surface of the intermetallic ingot ignited when exposed to air.

A combination of hydriding-dehydriding, excess zinc, and higher temperatures was employed in Runs 13 and 14 in an attempt to realize sufficient fluidity for employment of stirrers. In these runs, excess zinc (60 and 100 percent, respectively) was used, but it was not possible to stir the melt until a temperature of 800 C was reached. However, in Run 14, the temperature was raised to 860 C (about 15 C above the peritectic decomposition temperature of $\text{UZn}_{11.5}$ to $\text{UZn}_{8.5}$), and because of the consequent release of zinc, it was possible to agitate fairly easily. Cross sections of the ingots from Runs 13 and 14 indicated complete formation of the uranium-zinc intermetallic compound. X-ray diffraction studies of a number of the intermetallic compound ingots indicated that the major components were the uranium-zinc epsilon phase and zinc.

The direct reaction of uranium and zinc as a first step in a blanket process has been demonstrated. With hydrided-dehydrided material, the reaction time is probably only a matter of minutes, since a solid mass was formed shortly after the zinc melted. However, hydriding and dehydriding of the blanket material would prohibit the use of tantalum as a crucible material in this step. Molybdenum or aluminum oxide crucibles may be satisfactory alternatives. If a uranium-3 weight percent molybdenum alloy is used for the blanket in the future, it would probably be quite difficult to use the hydriding and dehydriding procedure. Previous experimentation has shown that hydriding of this type alloy was extremely slow under the experimental conditions employed (temperature of 250 C and a hydrogen pressure of 800 mm).

(2) Dissolution of EBR-II Blanket Material in Zinc-14 Weight Percent Magnesium

The solubility data of uranium in zinc-magnesium solutions suggests another possible simplification for the blanket process. The zinc-magnesium-uranium phase diagram indicates that at about 800 C it

would be possible to produce a ternary system of 14 weight percent uranium-12 weight percent magnesium-74 weight percent zinc. It is convenient to bypass the usual uranium-zinc intermetallic precipitation step entirely and simply to add additional magnesium to precipitate the uranium.

Two experiments with EBR-II uranium blanket rods (of 0.433-in. diameter) have been completed to investigate uranium dissolution in the 14 percent magnesium-zinc system. In Run 1 (Table 19), the results indicate that after about 8 hr dissolution time the entire uranium charge was in solution. The uranium rods in this run were charged into a perforated tantalum basket-type agitator which rotated through the solvent metal at a speed of 250 rpm.

Table 19

URANIUM DISSOLUTION IN ZINC-14 WEIGHT
PERCENT MAGNESIUM AT 800 C

Charge: Run No. 1: 504.3 g uranium, 2665 g zinc,
432 g magnesium
Run No. 2: 493.0 g uranium, 2665 g zinc,
432 g magnesium
Tantalum agitator, crucible, and
sampling tubes^a

Run No.	Time (hr)	% of Uranium Charged in Solution	Run No.	Time (hr)	% of Uranium Charged in Solution
1	4.3	96.5	2	1.0	79.0
	7.2	97		2.5	96.5
	8.2	100		3.5	96.0
	8.3	100		4.7	97.0
				6.7	94.0
				7.7	92.0
				8.7	88.0

^aFirst and second samples were "thief" samples in Run 1. Subsequent samples in both runs were "bucket" type.

In Run 2, the uranium blanket rods were charged directly into the crucible with the zinc and magnesium and a conventional type of paddle agitator was used. The results indicate that after about 5 hr 97 percent of the uranium charge was in solution. However, with increased holding time there was a decrease in the uranium concentration. At present, an explanation for this decrease is not apparent. No graphite

was present in the equipment; graphite filter frits were not employed in sampling; instead dip-type samples were obtained. The amount of carbon introduced with charge materials is not significant in comparison to the concentration decrease that occurred. It is believed that improvements in sampling and sample-handling techniques may resolve this problem.

i. Preparation of Compounds by Precipitation from Liquid Metal Solutions
(A. Schneider, G. L. Rogers)

The formation of various compounds in liquid metals has been observed in the past in the course of studies directed toward the development of recovery and decontamination processes for fissionable and fertile materials. For example, compounds such as uranium carbide or uranium silicide were precipitated from uranium-cadmium solutions by reaction with carbon or silicon present as impurities in the solution. Interest has now developed in exploiting such reactions for preparative purposes, either to synthesize nuclear feed materials or to recover decontaminated nuclear fuel materials in a form suitable for recycling to a reactor. Evidence is now available which shows that this method of preparation is applicable to the synthesis of uranium carbide, uranium silicide, and plutonium carbide.

This method of preparation of compounds such as uranium carbide can also be integrated with present liquid metal processes for conversion of an oxide to a carbide or for purification of irradiated material. The following reaction is an example of the first possibility:

The Preparation of Uranium Monocarbide

Several methods are available for the preparation of uranium carbides.² Carried out at high temperatures (above 1000 C), these methods generally involve: (1) the direct reaction of uranium and carbon, (2) the reduction of uranium oxides with carbon, resulting in the formation of either the monocarbide or dicarbide and carbon monoxide, and (3) the reaction of hot uranium with an organic compound such as methane. For use as a reactor fuel, the uranium monocarbide is desired. The general difficulty encountered in the preparation of the monocarbide is in the achievement of high purity. Even with careful precautions, free uranium or uranium dicarbide is usually present in the product.

²Bowman, F. E., The Carbides of Uranium - An Annotated Bibliography, NYO-2686 (March 1960).

It has been found possible to prepare uranium monocarbide at temperatures below 700 C by precipitating uranium dissolved in an appropriate metal solvent with carbon. In experiments conducted to date in alumina crucibles, uranium, which was dissolved in cadmium to a concentration of nearly 2 percent, was precipitated from the cadmium solution by addition of finely divided activated carbon (-230 mesh). In the first experiment, at 550 C, 64 percent of the uranium precipitated with stirring in 8 hr. In a second experiment, nearly complete precipitation was realized within $\frac{1}{2}$ hr at 700 C. After distilling away the cadmium, the product of the second experiment was identified as uranium monocarbide by X-ray diffraction. However, free carbon is not detectable by X-ray diffraction. Chemical analyses are in progress to obtain carbon-to-uranium ratios. In both experiments an excess of carbon was employed, but the product did not contain any dicarbide. Segregation of the uranium carbide and unreacted carbon was observed in a cross section of the solidified ingot. The uranium carbide settled to the bottom while the unreacted carbon concentrated near the surface of the melt.

In a similar experiment uranium was precipitated from a 5 percent magnesium-95 percent zinc solution at 800 C. Again the product was identified as uranium monocarbide. The reaction rate in this system was found to be lower than in cadmium, but over 85 percent of the uranium had reacted after 3 hr of stirring.

The Preparation of Cerium Carbide

In many pyrometallurgical experiments it has been found that cerium behaves quite similarly to plutonium. The preparation of cerium carbide was investigated to gain familiarity with procedures before attempting the synthesis of plutonium carbide.

Cerium carbide (Ce_2C_3) was precipitated from magnesium solutions in which it was present initially at a concentration of 21.5 percent. At 695 C, 58 percent of the cerium was precipitated in $3\frac{1}{2}$ hr. The product was identified by X-ray diffraction as Ce_2C_3 with an indication that traces of CeC_2 and $\alpha\text{-Ce}$ may have been present. This result also supports the findings of Spedding and coworkers³ that Ce_2C_3 is the lowest stable carbide.

j. Materials and Equipment Evaluation

Materials evaluation studies are in progress to evaluate the compatibility of various materials with liquid metal systems of the types contemplated for reprocessing reactor fuels. Much of the effort is being concentrated on determining which construction materials will be most suitable for EBR-II processing equipment. However, the conditions chosen for some of the tests extend beyond the conditions for processes of immediate interest in order to obtain data from which predictions of the effects of process changes can be made.

³Spedding, F. H., et al., J. Am. Chem. Soc. 80, 4499-4503 (1958).

Three main types of tests are being used to evaluate materials: 1) corrosion testing of metal coupons with solvent metals and molten salts, 2) solution-stability tests in which solutions of uranium in solvent metals are contained in agitated vessels made of the test material and sampled at intervals for uranium concentration, and 3) materials demonstration runs in which operations such as skull oxide reduction are carried out repeatedly or for long periods of time after which the effects on the container materials are determined.

(1) Corrosion Studies
(P. Nelson, M. Kyle, A. Sanders)

A program is underway to determine the corrosion resistance of the refractory metals, graphite, and ceramics to molten metals, particularly to zinc and zinc-magnesium solutions. It is also of interest to test the corrosion resistance of the same materials to flux systems, especially to those containing alkali and alkali earth chlorides and fluorides.

Several means of determining attack by liquid metals are available. Some of the methods are enumerated below:

- 1) weight and size change of metal coupons exposed to liquid metals for a determined time;
- 2) metallographic examination of the material before and after exposure;
- 3) comparison of physical properties before and after exposure to the liquid metal environment.

None of these methods has been found to be entirely satisfactory by itself, thus indicating that a combination of these methods is probably desirable.

Preliminary tests have been completed to determine the corrosion rates of three flux systems on tantalum, tungsten, molybdenum, and tantalum-10 percent tungsten alloy. The tests were conducted in tantalum capsules for 100 hr in the rocking furnace described in ANL-6287, page 74. An attempt was made to use weight and size changes to determine liquid metal attack.

The results indicated that changes in weight and size are not precise measures of the extent of corrosion, since the changes noted in nearly all cases were too small to be significant. However, hardness testing, in conjunction with ductility tests and metallographic examinations, does look promising as one means of evaluation.

Metallographic examination of corrosion specimens is the most important means of determining the extent of corrosion on tantalum, tantalum-tungsten, and tungsten by molten salts and zinc-magnesium solutions. This is true because the attack is intergranular and cannot be detected by weight or thickness change. Physical testing of the samples will indicate the effect of intergranular corrosion on the metal properties, but the depth of corrosion can only be determined metallographically. Metallographic investigation of material adhering to the surface of the specimen is a separate technique that may indicate the mechanics of corrosion, but will not be useful in determining the depth of corrosion.

The following technique has been found to be the most satisfactory to date for examining tantalum:

- 1) Mount sample in Bakelite.
- 2) Abrade on 180, 240, 320, and 600-grit abrasive paper.
- 3) Polish with 15-micron diamond paste followed by one-micron diamond paste charged on a silk cloth wheel backed with lens cloth (Hyprez oil lubricated).
- 4) Final polish on a microcloth-covered wheel charged with 0.1-micron particle size alumina in distilled water.
- 5) Electroetch in a solution containing 60 ml of 85 percent lactic acid, 20 ml of 70 percent nitric acid, and 20 ml of 49 percent hydrofluoric acid at 0.02 amp per sq cm for 2 to 15 sec.

This procedure has been used successfully to examine tantalum corrosion specimens. Figure 13 is a photomicrograph of a 0.030-in. tantalum agitator blade which failed due to embrittlement after an 8-hr exposure at 800 C to a mixture of skull oxide, 5 weight percent magnesium-zinc alloy, and halide flux (47.5 mole percent magnesium chloride, 47.5 mole percent calcium chloride, and 5 mole percent magnesium fluoride). Studies to correlate changes in microscopic structure with the degree of corrosion evidenced by physical testing are in progress.

Corrosion of Mild Steels in the Zinc-Cadmium-Magnesium Systems

Results of additional tests to determine the corrosion resistance of mild steels to zinc-cadmium-magnesium systems are presented in Table 20. Results previously reported in ANL-6243 indicated little or no corrosion of mild steel at temperatures up to 550 C and zinc concentrations of 0 to 10 percent. The new results extend the range of

conditions to 750 C and 15 percent magnesium. These tests show the capability of the large-scale cadmium distillation unit now nearing completion of construction to handle cadmium solutions containing moderate concentrations of zinc.

FIGURE 13
CORROSION OF TANTALUM AGITATOR BLADE

System: Skull oxide, 5 w/o magnesium-zinc alloy;
47.5 m/o magnesium chloride-47.5 m/o
calcium chloride-5 m/o magnesium fluo-
ride flux.
Exposure: 8 hr at 800 C
Magnification: 250X

At 750 C some corrosion of the steel was noted when the corrosive material was cadmium-15 percent zinc-1 percent magnesium. It appears that the addition of magnesium in high concentrations (15 percent) to the zinc-cadmium system inhibits zinc corrosion. A similar inhibition of zinc corrosion by magnesium was found in previous studies on the corrosion of tantalum (see ANL-6243; also see ANL-6287, page 76).

Table 20

CORROSION OF 1020 STEEL BY CADMIUM SOLUTIONS
CONTAINING ZINC AND MAGNESIUM

Conditions: 500 hr, 1-in. x 2-in. x 0.120-in. coupons
 in tantalum capsules with 20 to 40 gm of
 solvent metal of indicated composition.
 Capsules were rotated 180° at 2 cycles
 per minute.

Temp (C)	Magnesium Conc (w/o)	Observed Corrosion Effects ^{a,b} Zinc Conc (w/o)				
		0	2	5	10	15
500	1	-	NC	-	NC	-
500	15	-	-	-	NC	-
750	1	NC	NC	NC	-	SC
750	15	NC	NC	-	NC	NC

^aNC indicates corrosion less than 0.001 in.

^bSC indicates slight corrosion, less than 0.002 in.

It should be noted that in Table 20 the concentrations are given in weight percent. Because of the low atomic weight of magnesium, as compared with cadmium, relatively small weight percentage substitutions of magnesium for cadmium would be expected to reduce considerably the chemical activity of the zinc.

(2) Solution Stability and Materials Demonstration Tests
 (P. Nelson, J. Wolkoff, and J. Pavlik)

Experiments to determine the stability of uranium in various metal solvents and container systems, and tests to demonstrate the suitability of container and accessory combinations under process conditions are in progress. The main differences in the two types of tests are that in the former the effect of the container, metal solvents, and impurities on solution stability is studied and in the latter the attack by the solution on the container is studied. Both types of experiments are conducted in crucibles of about one-liter capacity fabricated of the test material. Agitation and means of sampling are provided in order that the uranium concentration may be followed over the course of the run (25 to 300 hr).

The materials demonstration runs have been conducted in a tilt-pouring furnace which permits pouring off the charge at the end of the run. Subsequently, the crucible and accessory parts are examined metallographically and by physical testing. The temperature and solvent composition are held as nearly constant as possible during materials demonstration runs so that the degree of attack on the materials may be associated with particular processing conditions.

Solution-stability runs are conducted in a deep furnace to provide precise temperature control and even temperature distribution. The control temperature and the solvent concentration may be changed during the run to study the effect of these variables on the stability of dissolved uranium.

Equipment designed for both types of experiments has only recently been completed. However, a few exploratory experiments have been completed with available equipment.

In one exploratory experiment conducted under conditions simulating those present in the reduction step of the skull-reclamation process, flux and a metal solution were contained in a Grade CS graphite crucible for about 100 hr. The conditions under which the run was made and the results obtained are shown in Table 21. Seventeen samples of the metal phase were taken at intervals throughout the run. The uranium content varied from 92.7 percent to 106.8 percent of the concentration calculated from the amounts of materials added. The average uranium analysis was 98.6 percent of the calculated value, with a standard deviation of 3.5 percent. However, approximately 3 to 5 percent of the zinc was evaporated during the course of the experiment, which would indicate a like percentage of uranium lost even if the uranium concentration remained at the calculated initial concentration. Deposits of uranium which were removed from the tantalum baffles above the flux level contained 22.4 percent uranium. The deposition and redissolution of this material during the run could account for the large standard deviation in the uranium content.

Microscopic examination of the crucible after the run indicated a flux penetration depth of about $\frac{1}{4}$ in. The tantalum baffles were somewhat embrittled during the run but not to the point of failure.

In another similar experiment, the top of the crucible was kept at the temperature of the melt, 800 C, thus preventing deposition of the uranium above the surface, but the loss of zinc by evaporation was increased because condensation did not take place on the inside of the cover.

Table 21

STABILITY OF URANIUM IN A ZINC-FUSED SALT SYSTEM
CONTAINED IN GRAPHITE AT 800 C

(Experiment SSDP-1)

Charge^a

Metal 4950 g

Magnesium: 5.10%

Uranium: 3.10%

Zinc: 91.80%

Flux^b 690 g

Calcium chloride: 47.5 m/o

Magnesium chloride: 47.5 m/o

Magnesium fluoride: 5.0 m/o

Equipment

Crucible: graphite, Grade CS, 5 $\frac{1}{2}$ -in. OD x 10-in. high
 x $\frac{1}{2}$ -in wall

Baffles: four, tantalum, $\frac{1}{2}$ -in. wide

Agitation: single, flat-blade tantalum paddle, 1-in.
 x 2 $\frac{1}{4}$ -in. blade 500 rpm.

Run Time (hr)	Uranium Concentration (%)	Run Time (hr)	Uranium Concentration (%)
1.3	2.96	53.7	3.07
2.0	3.07	65.8	3.16
4.0	2.96	73.4	2.91
8.1	3.09	77.8	3.05
8.1	3.08	89.8	3.08
19.2	3.04	96.7	3.09
19.2	3.02	103.8	3.31
30.1	3.02	103.8	3.31
43.8	2.86		

^aThe metal constituents were added separately without pre-melting. These constituents went into solution after one hr of mixing and before the first sample was taken.

^bThe flux constituents were liquated at 800 C for 15 min under air atmosphere, poured into a graphite mold, and stored under vacuum until used.

Tentative conclusions drawn from the runs are the following:

1. Uranium in zinc-5 percent magnesium solution at 800 C reacts only slightly or not at all with CS graphite.
2. Salt flux (specifically 47.5 mole percent CaCl_2 -47.5 mole percent MgCl_2 -5.0 mole percent MgF_2) permeates CS graphite only moderately at the conditions of the reduction step in the presently contemplated skull recovery process. Since grades of graphite of greater density are readily available, flux penetration does not appear to be a serious problem.
3. Tight closures and seals on the crucible and carefully adjusted temperature distributions will be required to prevent precipitation of uranium above the liquid level or loss of flux and metal from the crucible with resultant corrosion of the stainless steel outer vessel. This conclusion is as valid for the process equipment as it is for the experimental equipment for these studies

(3) Penetration of Graphite by Molten Salts
(T. R. Johnson, R. L. Christensen)

Before graphite can be used as a crucible material for the EBR-II skull-recovery process, it must be demonstrated that salt fluxes do not seriously penetrate the crucible walls and that the flux present in small pores does not have a deleterious effect on the graphite. Several methods of treating graphite specimens were surveyed to determine which would yield meaningful measurements of the extent of flux penetration. A crucible (1½-in ID with ¼-in. wall thickness) machined from unimpregnated CS graphite was filled to a depth of about 5 in. with a sodium chloride-magnesium chloride-magnesium fluoride flux (54.2, 41.1, 4.7 mole percent). The salt was held at 800 C without agitation for 75 hr. After cooling, the crucible was sectioned into rings one-inch thick, the salt was removed (it had separated from the graphite on cooling), and the graphite was polished dry with progressively finer emery paper down to 325 grit. Each ring was cut into four quarter rings and given a final polish on hard tracing paper. It was difficult to differentiate flux from graphite by microscopic examination of the "as polished" samples, although the pores of the graphite were easily seen. The following four techniques were used to determine the location of the flux and all proved to be useful.

1. Samples were leached by boiling in dilute hydrochloric acid for 24 hr. Analysis of the resulting solution showed one to three percent of the void volume in the graphite to be filled with the flux.

2. Autoradiographs were prepared using small sections of the quarter rings that had been irradiated and cooled for five days. One such autoradiograph is shown in Figure 14.

FIGURE 14
AUTORADIOGRAPH OF
CS GRAPHITE PENE-
TRATION BY MOLTEN
SALT FLUX

3. The polished samples were etched by heating them to 350 to 400 C in air for three hours. The contrast between the graphite and salt was greatly improved.

4. Samples were stained by pressing the polished face on filter paper that was wet with a silver nitrate solution. The procedure stained the salt phase so that it could be easily seen under a microscope. Some swelling of the salt was evident.

The last three methods indicated that the flux was present in a relatively few large pores throughout the crucible wall, even though there had been no salt visible on the outside surface of the crucible (see Figure 14). The greatest concentration of salt was near the inner surface. Very few of the total pores present in the graphite contained visible amounts of flux, possibly as a result of poor wetting of the graphite by the molten salts in this experiment. The results of the visual methods agree with results obtained from the leaching procedure, i.e., between 1 and 5 percent of the void volume had been filled.

(4) Evaluation of Advanced Materials (J. Wolkoff)

Tungsten is corrosion resistant to molten zinc systems, such as those being studied for skull-reclamation processes, but it is difficult to fabricate into complex shapes by usual metal-forming methods. However, the metal can be successfully coated onto surfaces by a vapor-deposition process to form pure impervious coatings. Coated equipment parts, such as transfer lines and agitators, would be useful if their reliability and corrosion resistance were known. Tests to evaluate the resistance of tungsten coatings to thermal cycling and to liquid zinc systems have been started to obtain this information.

A comparison of the linear expansion coefficients of tungsten with a number of common and possibly useful base materials is given in Table 22. Materials having reasonably close expansion coefficients are tantalum, molybdenum, Pyrocera, mullite, and silicon carbide. Because of its resistance to nitrogen at elevated temperatures, molybdenum tubing lined with tungsten may be useful as transfer lines in the nitrogen-containing argon atmosphere of the EBR-II fuel-processing cell.

Table 22

LINEAR EXPANSION COEFFICIENTS OF SELECTED MATERIALS

Metals	$10^{-6}/^{\circ}\text{C}$	Nonmetals	$10^{-6}/^{\circ}\text{C}$
Tungsten	4.5	Silica glass	0.5
Molybdenum	5.4	Vycor	0.7
Tantalum	6.6	Pyroceram 9608	0.7-2.0
Stainless Steel 446	9.9	Graphite	1.5-2.5
Stainless Steel 304	17.3	Silicon carbide	4.0-5.3
Inconel	11.5	Mullite	5.5
Low carbon steel	11.7	Pyroceram 9606	5.7

The adherence of a tungsten coating was first tested under relatively adverse conditions, i.e., on type 446 stainless steel which has a considerably higher expansion coefficient than tungsten. At the request of Argonne, tungsten was vapor deposited by the General Electric Company to a depth of about 6 mils on the inside of a $\frac{1}{2}$ -in. stainless steel pipe. After thermal cycling eight times between 800 and 100 C, weakening of the bond between the coating and the base metal occurred. Although the coating did not break away, it could be pulled away from the base metal when the pipe was cut apart for metallographic samples.

The surface texture of the tungsten coating was nodular and some cracks in the tungsten could be detected metallographically. Figures 15 and 16 show an "as polished" and an etched section of the coated stainless steel before thermal cycling at imperfections in the coating. Figure 17 shows the coating after the cycling test. Separation at the copper layer and the lack of enlargement of the micro-cracks in the tungsten coating are evident in the figure.

(5) Liquid Metal Distillation Unit
(J. DeKany, L. Dorsey, J. Hepperly)

A pilot plant-scale liquid metal distillation unit (100 kg of cadmium per hour distillation rate, 800-kg feed-tank capacity) to handle cadmium-uranium solutions has been constructed and is being tested prior to operation. This unit will be operated to provide design information pertinent to liquid metal fuel reprocessing. It will demonstrate the following operations on an engineering scale:

- (a) Distillation of cadmium-uranium alloy reprocessing solutions.
- (b) Transfer of liquid metal solutions from one vessel to another, involving the use of pressure differences and freeze valves.

- (c) The protection of instruments and service lines from liquid metal vapors through the use of vapor traps and filters.
- (d) The automatic control of liquid levels, pressures, and temperatures in the unit.

Operation of this unit is expected to begin in the next quarter.

FIGURE 15
VAPOR-DEPOSITED TUNGSTEN ON TYPE 446 STAINLESS
STEEL BEFORE THERMAL CYCLING
(200X, as polished)

FIGURE 16
VAPOR-DEPOSITED TUNGSTEN ON TYPE 446 STAIN-
LESS STEEL BEFORE THERMAL CYCLING
(200X, etched)

FIGURE 17
VAPOR-DEPOSITED TUNGSTEN ON TYPE 446 STAINLESS
STEEL AFTER THERMAL CYCLING
BETWEEN 800 AND 100 C
(300X, etched)

B. Fuel-processing Facilities for EBR-II

1. Design and Construction (J. H. Schraidt, M. Levenson)

a. Status of Fuel Cycle Facility Building Design and Construction (E. J. Petkus, H. L. Stethers)

The construction of the Fuel Cycle Facility has continued throughout the winter. The Facility was over 80 percent complete on March 7, 1961, as compared to 70 percent complete three months earlier. Metallizing of the Argon Cell liner plate with zinc was completed in January. Shot peening* of the zinc coating was completed during the second week in February. After shot peening, the cell was cleaned and the erection of major cell equipment, such as manipulators and cranes, was begun.

After installing the crane and manipulator bridges, the contractor has been grinding and cleaning the crane and manipulator rails. Installation of the two argon-cooling boxes in the subcell has begun. The argon-cooling boxes house refrigerant coils and are a portion of the recirculating system provided to remove the heat generated in the Argon Cell. Work has begun on the installation of the emergency pressure-relief system for the Argon Cell.

Architectural work is continuing throughout the building. Painting on both the service floor and operating floor is proceeding.

The contractor has begun installing heating and ventilating control instruments and piping. All types of electrical and piping work is continuing throughout the building. In addition, special equipment such as MI (mineral insulated) cable and manipulator panels are being installed.

b. Fuel Cycle Facility Equipment (G. J. Bernstein, A. A. Chilenskas, L. F. Coleman, J. Graae, D. C. Hampson, R. H. Jahnke, M. A. Slawewski, T. W. Eckels)

All the materials that are to be procured by ANL at Argonne, Ill., for the Fuel Cycle Facility melt-refining furnace off-gas system have been ordered. A work plan, job description, bill of materials, and drawings for the installation have been prepared.

*Shot peening is the impacting of steel balls, by means of air pressure, against a surface, in this case to increase the coating density and thus reduce porosity.

Two melt-refining furnaces will be installed in the Argon Cell. A purchase order has been placed with Trojan Manufacturing Company (a Division of Lindberg Engineering Company) for major components of the furnace. These furnaces will be controlled from panelboards in the operating area. A purchase order for two panelboards has been issued to Machinery Electrification Inc. of Northboro, Mass.

A system of space-radiation monitors will be installed in potentially hazardous areas of the Fuel Cycle Facility. Installation drawings are completed.

Drawings of the service feed-through plugs have been completed and sent out for bids. Services (gas, vacuum, and electrical lines) required for equipment inside the cell will penetrate the shielding floor in these feed-through plugs. The plugs have been described previously (see ANL-6231, page 35-37 and ANL-6287, page 132).

Solid radioactive wastes from radioactive areas will be shipped to burial grounds in sealed metal containers, 6 ft long and of $11\frac{1}{4}$ -in. ID. The container lids will be similar to 16-lug lids used on standard 5-gal pails. The containers will have no bails, but will be lifted magnetically by their lids. The lids will be modified by the attachment of a $\frac{3}{16}$ -in. steel plate to the underside to provide adequate metal thickness for carrying the magnetic flux. A standard capping machine was modified so as to be activated by the operating manipulator. The capper performed successfully. A test with a 5-gal pail showed that the lid lugs will support a load greater than 500 lb. Maximum scrap loads are expected to be about 200 lb. A design for a permanent magnet-type lifting device, which is mechanically actuated, is being prepared by a manufacturer of such magnetic lifters.

Bids for the interbuilding and scrap-handling coffins were received and evaluated, and purchase orders were placed. O. G. Kelley of Boston, Mass., was awarded a contract for the design and fabrication of one interbuilding coffin. The coffin will transport highly radioactive material between the Reactor Building and the Fuel Cycle Facility. Knapp Mills of Wilmington, Del., was awarded a contract for the design and fabrication of one scrap-handling coffin.

The design of window shutters and drives has been completed. Drawings and specifications are being printed. One drive-motor mount assembly and one wall bracket have been ordered for mockup and testing of the design.

An integrating gamma dosimeter capable of recording exposures from 10^7 to 10^{10} rad would be very useful for recording the gamma exposure to equipment within the Argon and Air Cells of the Fuel Cycle

Facility. Since the principal radiation sources and the equipment of interest will be moved about within the cells in a somewhat unpredictable manner, an integrating dosimeter will require certain characteristics to be useful. It should be small, self-contained, chemically inert, relatively unaffected by a considerable range in ambient temperature, and most importantly, it should be able to integrate a gamma exposure sustained over a period of from one to six months. A variation in exposure rate from 10^3 to 10^6 rad/hr should not cause serious variations in the integrated reading. For simplicity of handling, low cost, and straightforward interpretation, glass seemed very attractive. Bausch & Lomb Optical Company has a cobalt glass dosimetry system which is based on color formed by irradiation, but the range of the system is far below the requirements for the EBR-II Fuel Cycle Facility.⁴ Battelle Memorial Institute has reported two glass systems in which the darkening effect is utilized.⁵

During development work on glass formulations for the EBR-II Fuel Cycle Facility shielding windows, evidence was obtained at Argonne that gamma darkening of cerium-protected shielding glass is quite predictable for any given cerium oxide (CeO_2) content.

A number of experiments have been performed to investigate the possible use of Pittsburgh Plate Glass (PPG) Company's No. 6788 glass for dosimetry. This is the Company's regular 3.3-density lead shielding glass with the cerium oxide content reduced from about 1.85 to 0.85 ± 0.05 weight percent. The glass pieces used for the experiments were 0.060 ± 0.0005 in. thick $\times \frac{7}{32}$ in. wide $\times \frac{9}{16}$ in. high. The light transmittance of each piece was measured in a Bausch & Lomb Spectronic 20 colorimeter before and after irradiation. Readings were taken at 25-m μ intervals through the wavelength range from 350 to 625 m μ .

The irradiation exposures ranged from 10^6 to 10^9 rad and exposure rates ranged from 2.4×10^4 rad/hr to 1.6×10^6 rad/hr. Experiments were scheduled to investigate the following:

- 1) reproducibility of the dosimetry system;
- 2) effects of the rate of gamma exposure on the glass;
- 3) natural fading behavior of the glass at room temperature for each combination of rate and integrated exposure;
- 4) effect of 15-min heat treatment at 125 C upon the effects caused by different gamma-exposure rates on the glass and upon the subsequent fading of the glass at room temperature;

⁴Kreidl, N. J., and Blair, G. E., *Nucleonics*, 14, 56-60 (Jan 1956).

⁵Kircher, J. F., et al., A Survey of Glasses for High-level Gamma-radiation Dosimeters, Fall Meeting of Glass Div., Amer. Ceramic Society, Oct. 15-16, 1959.

- 5) the effect of conducting the heat treatment at times from 30 min to 5 hr after irradiation;
- 6) the effect of exposure temperature in the 25 to 75 C range;
- 7) the best practical time schedule for heat treatment and reading.

All irradiations were performed in the Argonne Gamma Irradiation Facility by means of spent reactor fuel.

Figure 18 shows the transmittances of irradiated and un-irradiated glass at different wavelengths. The readings were obtained 24 hr after the irradiations were completed. Each sample was heat treated at 125 C for 15 min. The heat treatment was administered one to five hours after removal of the glass from the gamma field.

Figure 19 shows the manner in which the internal absorption coefficient (in.^{-1}) changes with increasing gamma-ray exposure. These curves were calculated from the experimental data obtained with the 0.060-in.-thick samples.

Figure 20 shows the change of optical density with time at room temperature of glass samples irradiated to a total integrated dose of 1×10^9 rad. The dose rates were 6×10^5 and 1.6×10^6 rad/hr. (Similar results were obtained at dose rates as low as 2.5×10^4 rad/hr.)

FIGURE 19
EFFECT OF GAMMA RADIATION FROM MIXED FISSION PRODUCTS
ON ABSORPTION COEFFICIENT OF PPG* NO. 6788 GLASS

FIGURE 20
FADING OF PPG* NO. 6788 GLASS AFTER 1×10^9 RAD GAMMA EXPOSURE

The optical densities of the samples were measured at 400 m μ . The effect of heat treatment on the glass samples is also shown in the figure. Samples receiving identical exposures were found to have the same optical densities which decreased at the same rate with time. When some of the samples were heated at 125 C for 15 min, it was found that the optical densities decreased markedly and the subsequent rate of change with time became lower. Although the curves shown are for samples irradiated to 1×10^9 rad, it was found that the optical densities of samples after any given gamma exposure were very nearly equal following the heat treatment, regardless of the rate of exposure in the range from 2.5×10^4 rad/hr to 1.6×10^6 rad/hr. Thus the post-irradiation heat treatment removed effects caused by differences in exposure rate and reduced the rate of fading at room temperature.

The dosimetry system appears to have considerable promise. Calculations indicate, however, that, in the exposure range of particular interest in the Fuel Cycle Facility, samples 0.120 in. thick should give results which could be more accurately interpreted. Conceptual design of a container for protecting the samples from contamination while they are in storage within the cell and of a complete procedure for gathering, handling, and reading the samples is well advanced.

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

The cranes have been installed in the Air and Argon Cells at Idaho. All manipulator bridges have been installed. Installation of the carriages has been removed from the construction contract.

Manipulator bridge power inlets have been ordered from A. Dalkin Company. The prototype power inlet plug was wired. Some modifications were made and incorporated in the order to the A. Dalkin Company.

Brackets and receptacles for the general purpose manipulator arm have been ordered from Ideal Tool and Manufacturing Company. They will be mounted on the manipulator carriages to provide power and control for the articulated Model 300 Arm when this is used with the operating manipulators. This arm will be used when an operation requires greater dexterity than is possible with the operating manipulator.

Toggle switch control boxes for the control of the cranes, manipulators, and special removal hoist were received from the manufacturer. They were tested in the mockup. Because several errors were found, they were returned to the manufacturer for corrections. They are now back and will be retested before shipping to Idaho.

A collapsible manipulator carriage stand is being designed to occupy a minimum of storage space and to provide support for the crane trolley when it is lowered to the floor.

The combination lifting beam and lifting tools for bridge drives have been crated in preparation for shipment to Idaho.

d. Material Testing

(G. J. Bernstein, L. F. Coleman, J. Graae, M. Slawewski)

The irradiation of MI (mineral insulated) cable end seals and asbestos-insulated wire has been summarized in ANL-6287, page 87.

Asbestos-insulated wire samples have received an accumulated dose of 1.69×10^{10} rad to date. Insulation resistance of these samples was low, between 0.2 and 0.5 megohm. However, one sample of the wire, which had received a dose of 1.35×10^{10} rad, was heated to drive off absorbed moisture and then sealed in a vial containing a desiccant. It has since received an additional dose of 3.4×10^9 rad and its insulation resistance is still greater than 200 megohms. Therefore, the low insulation resistance of the unsealed samples can be attributed to moisture absorption and not to radiation effects.

From the time the Argon Cell is built to the time it is filled with argon, there may be a time interval of six months to one year. During this time the steel liner and other metal surfaces in the cell would be subject to corrosion if left unprotected. Therefore, the metal surfaces should be covered with an application of some protective coating or finish. Some of the properties of the coating that would be required are:

1. surface protection;
2. high reflectance without glare;
3. minimum of outgassing under radiation; and
4. radiation resistance.

A surface without glare and with a high reflectance is desirable in the cell in order to provide increased illumination efficiency. These surface features are of particular importance for objects with large areas, such as the cell walls. High levels of illumination are necessary because of the relatively poor transmittance of the 5-ft shielding windows.

Outgassing of the coating or finish would be of primary concern only where large surface areas are to be covered. Under radiation, paints tend to outgas the organic additives and their decomposition

products which, in large quantities, could be harmful to the cell argon purification system. The large surface area of the Argon Cell liner was of particular concern. The use of aluminum paint for this surface was rejected in favor of a flame-sprayed zinc metallized surface because under irradiation some gaseous products can be expected from the aluminum paints. However, for equipment in the cell the use of aluminum paint for protection should be acceptable, since the amount of paint used will be small.

A paint's reflectivity and outgassing is directly connected with its radiation-resistant qualities. In this respect it was believed that the metallic flake paints (e.g., aluminum paints specifically) would be the best for the job. A number of aluminum paints were irradiated and generally were found to be satisfactory for use in a high radiation environment (10^9 rad accumulated dose). In addition, they possessed the other required properties for in-cell use. The irradiated paints were visually compared with unirradiated control samples, and the results are tabulated in Table 23. All but paint "G" are aluminum paints. Paint "G" is a stainless steel pigment paint. Based on these tests and ease of application, aluminum paint "B" seemed to be the best for any protective finishes required in the cells. All but samples "A" and "G" are still being irradiated.

Table 23
EFFECT OF IRRADIATION ON VARIOUS PAINTS

Sample	Pigment	Vehicle		Dose (rad)				
		Type	Volatiles (Solvent)	0.1×10^9	0.5×10^9	1.0×10^9	2.5×10^9	5.0×10^9
A	Polished aluminum flakes	Spirit varnish	Aromatic hydrocarbons	No change	Slight brown discoloration	Slight pitting evident	Pitting more pronounced	
B	Polished aluminum flakes	Oleo-resinous varnish	Mineral spirits, aromatic solvents	No change	No change	No change	Slight brown discoloration	Very little change to 1.6×10^{10} rad
C	Polished aluminum flakes	Oleo-resinous varnish	Mineral spirits	No change	Slight loss of original gloss	Slight loss of original gloss	Slight surface roughness	Slight blistering and pitting
D	Polished aluminum flakes	Spirit varnish	Aromatic solvents, mineral spirits	No change	No change	Very slight pitting with some loss of gloss	Very little change to 9.0×10^9 rad	
E	Polished aluminum flakes	Oleo-resinous varnish	Aromatic solvents, mineral spirits	No change	No change	Lost some of original gloss	Very little change to 9.0×10^9 rad	
F	Polished aluminum flakes	Spirit varnish	Mineral spirits, tolvol	No change	No change	Lost some of original gloss	Slight surface roughness	Very little change to 1.3×10^{10} rad
G	Stainless steel flakes	Spirit varnish	Mineral spirits	No change	Light brown discoloration	Dark brown discoloration	Badly discolored and blistered	

In addition to the aluminum paints, several samples of zinc-base coatings were irradiated. These form a complex iron-zinc-lead silicate on a steel surface during curing of the coating. The coating is composed of a liquid portion containing a water solution of sodium silicate and a solid portion containing zinc dust with a small amount of lead. Curing is ordinarily done by chemical means using a curing solution containing a phosphate dissolved in a volatile organic solvent. However, the coating may also be cured by baking. Two coatings were tested. Samples were prepared from one formulation by chemical curing and from both formulations by baking. The irradiated coatings were compared with unirradiated controls. All samples were discolored after receiving a dose of 1×10^8 rad. After a dose of 4×10^8 rad, the discoloration had become more pronounced and samples had become sticky. Up to 2×10^9 rad, when irradiation of these samples was discontinued, they had become so discolored and sticky that the coatings were considered unfit for use.

One phase of the roller-bearing tests using irradiated radiation-resistant greases (see ANL-6287, page 85) has been completed. Of the three types of grease tested, NRRG-159 and NRRG-335 performed about equally well after irradiation to 5×10^9 rad. Data from these tests are summarized in Table 24.

Table 24

ROLLER-BEARING TESTS WITH IRRADIATED GREASES

Timken Bearing (No. 432 cup - No. 438 cone)
800 lb axial load at 40 rpm

Grease Type ^a	Irradiation (rad $\times 10^{-9}$)	Running Time (hr)	Remarks
NRRG-159	3 ^b	300 ^c	Ran well. Run terminated voluntarily.
NRRG-159	4	300	Slight squeak after 257 hr. Very slight darkening of bearing surface.
NRRG-159	5	300	Squeak after 180 hr. Cup and cone stuck together when load was removed after test. Some areas of heat darkening on rollers and cup.
NRRG-235	5 ^b	52	Failed due to breakdown of jelly and plating out of solid residual lubricants.
NRRG-335	5 ^b	300	Squeak after 176 hr. Cup and cone stuck together when load was removed after test. Some areas of heat staining on rollers and cup. Some solid deposit from grease on cup and rollers.

^aProducts of Standard Oil of California.

^bManufacturer's rated limit.

^cEstimated to be equivalent to four years of actual operating time in the Fuel Cycle Facility.

Tests were carried out to explore the likelihood of the greases becoming sufficiently fluid during irradiation to run away from the bearings. Samples of the three greases were placed in vials which were provided with drip holes, $\frac{1}{8}$ in. in diameter and about 20 mils in length. Loss of grease through the holes was checked after radiation to 5×10^8 , 1×10^9 , 1.5×10^9 , 2×10^9 and 3×10^9 rad. The samples were confined in bottles so that grease drippage during each period of irradiation could be collected and measured.

All three greases showed some loss through the drip hole, but there was no consistent relationship between irradiation and loss. None showed loss after 2×10^9 rad. On a cumulative basis, NRRG-335 lost the greatest amount and NRRG-159 lost the least. These results were in general agreement with the results from earlier tests in which bulk samples were examined at regular intervals. The earlier tests showed that NRRG-159 underwent the least loss of consistency during irradiation. On the basis of these and other results, NRRG-159 has been selected for lubricating the operating manipulators now being built by General Mills, Inc.

Additional tests with these greases and Timken roller bearings are being made. Three bearings which have been alternately irradiated and then run for 8-hr periods have been tested at 1×10^9 , 2×10^9 , and 3×10^9 rad. The bearing lubricated with NRRG-235 grease began to squeak after 7 hr following irradiation to 2×10^9 rad and after $\frac{1}{2}$ hr following irradiation to 3×10^9 rad. The bearings with NRRG-159 and NRRG-335 ran successfully in all tests. The results of these tests, which were carried out in air, should indicate performance of the bearings and greases in the Air Cell. Since greater damage occurs when these greases are irradiated in an air atmosphere than when they are irradiated in an inert atmosphere, the results of the tests may be used to estimate the performance of the bearings and greases in the Argon Cell.

2. EBR-II Fuel-processing Mockup (J. H. Schraidt)

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

The following redesigned components have been fabricated and installed on the manipulator: (1) bridge drive motor unit, (2) grip drive motor and clutch assembly, (3) pick-up brush assembly, (4) hoist clutch, and (5) additional mechanism for attaching the articulated Model 300 Arm.

As a result of experience with this new equipment, some changes have been made in the manipulators being built by General Mills.

The crane and manipulator-removal device are being installed in the roof of the Fuel Cycle Facility at Idaho.

Conceptual design of racks permitting storing of the Model 300 General Purpose Articulated Arm in the 24-in.-diameter storage pits in the Argon Cell has been developed.

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

(1) Equipment Performance

(a) Crucibles

Crucible behavior has been reported previously (see ANL-6183, pages 29 to 32, ANL-6231, pages 50 and 51 and ANL-6287, pages 89 and 90). The crucibles used were not degassed prior to use, as previous work had shown that when the crucible charge was bulk uranium, no measurable increase in yields resulted from the use of degassed crucibles. Therefore, there was no incentive to use degassed crucibles. Some recent work with charges in the form of fuel pins, however, gave evidence that yields could be increased by about 1.5 percent when degassed crucibles were substituted for nondegassed crucibles.

Stabilized zirconia crucibles have been used recently as a container for melting scrap fuel pins (as cast, not sodium coated). Thirty-eight pin-scrap melts were made in crucibles which were not degassed. The average yield for these pours was 92.2 ± 1.3 percent. Seven melts were made in crucibles which were degassed. The average yield was 93.9 ± 0.9 percent. The high yield for runs made with degassed crucibles was 95.4 percent and the low was 92.5 percent. Six of the crucibles were degassed at 1000 C. One was degassed at 800 C, the yield in this case being 94.2 percent. Of the seven crucibles, six showed fine diametrical cracks across the bottom after degassing. These cracks did not open up sufficiently in the melt-refining operation to allow escape of uranium.

One additional pin scrap melt was made in a crucible which had been degassed at 1000 C. In this case a crack in the crucible bottom allowed a small amount of uranium to seep out into the furnace susceptor. This decreased the pouring yield to 86.9 percent.

Degassing crucibles for melting fuel pins seems to be worthwhile from the standpoint of minimizing pin shells and increasing yield. However, there is a risk that slight cracks developed during degassing will propagate and allow uranium leakage during melting. The type of cracking encountered recently and described above is new. Some of the crucibles recently received from Norton have bottoms which are about $\frac{1}{4}$ in. thicker than usual. (The nominal thickness of the bottom of standard crucibles is one inch.) To study the effect of variations of bottom thickness on cracking crucibles which have walls and bottoms of the same thickness, $\frac{5}{8}$ in., are being obtained from Norton. Lower degassing temperature and shorter degassing periods are also being investigated as a means of eliminating cracking during crucible degassing.

(b) Skull Oxidation

Work has started on equipment to be used in the Argon Cell for oxidizing melt-refining crucible skulls. One approach is to build separate equipment with which to carry out the oxidation step; the other approach is to carry out the oxidation step in the melt-refining furnace.

To investigate the feasibility of oxidizing skulls in melt-refining equipment, a cerium-fissium skull from a melt-refining run was oxidized in the M-V furnace. The skull oxidation was carried out as if it were sequential to the melt-refining operation. The crucible containing the skull was heated to 1400 C under one atmosphere argon in the bell-jar furnace. The power to the furnace was shut off and the furnace was allowed to cool under one atmosphere argon until the skull temperature had dropped to 600 C. The furnace was then evacuated to 10 mm of mercury and vented to air. The furnace was evacuated and vented to air twice more within the next half hour to replenish the oxygen. After the last venting, the furnace stood overnight and was opened the next morning. The skull had powdered completely, except for a few scabs. The furnace susceptor had lost less than one gram. The coil did not appear to be adversely affected. In general, the oxidizing step did not injure the furnace components.

This approach to skull oxidation appeared to have several advantages. The number of crucible transfers would be cut down, and the melt refining and skull oxidation could be done in the same equipment. However, practical difficulties have been encountered. The crucible bottom cracks away from the side wall during oxidation and wedges in the furnace susceptor when the furnace is tilted to discharge the crucible. In addition, problems of possibly greater magnitude are introduced when oxygen is allowed to enter the melt-refining furnace. Since it would not be practical to degas the furnace between runs, a decrease would be expected in pouring yield of a subsequent melt-refining run. This approach, therefore, has been temporarily abandoned in favor of use of separate equipment.

Tests of furnace assemblies show that internal-resistance heating is a practical way to oxidize skulls. A schematic drawing of the skull-oxidation furnace is shown in Figure 21. A 1-kw alloy sheath Calrod placed inside a crucible containing a cerium-fissium slag oxidized the skull to a fine powder in $6\frac{1}{2}$ hr in air. Essentially 100 percent of the powder poured freely from the crucible. The maximum recorded skull temperature was 815 C. The maximum recorded heating element temperature was 760 C. During the oxidation, the zirconia crucible was held in a stainless steel secondary shell. An apparatus is being designed which will dump the slag from the zirconia crucible and which will subsequently dump the oxidized crucible from the stainless steel secondary shell.

FIGURE 21
OXIDATION FURNACE FOR MELT REFINING CRUCIBLE SKULLS

(c) Mechanical Development

The melt-refining ingot remover and sampler has been modified. The method of removing the sample protrusions from the ingot has been changed from a shearing operation to a drop hammer operation. When the blade shear was used, difficulties were encountered in getting the sheared samples to drop into the sample cans. The drop hammer uses impact to break off the samples and these are driven downward into the sample cans by the hammer motion.

Tests of an automatic Wahlstrom chuck mounted on a hand electric drill showed that this device was suitable for possible drilling operations in the cell, when the drill motor is held in the double hook of the operating manipulator. The chuck jaws open when pressure is

applied to the surface of the chuck collar in one direction and the jaws close when pressure is applied in the opposite direction to the barrel of the chuck. Figure 22 shows a device which facilitates remote drill changing when the drill is held in the automatic chuck.

(2) EBR-II Fuel Alloy Production

Nine more 10-kg batches of enriched uranium pin scrap, generated during the manufacture of fuel pins for EBR-II, were received from the Metallurgy Division. The scrap was melted down and poured into ingots, using melt-refining equipment. For the 47 runs made to date, the average yield was 92.5 ± 1.4 percent, with a high of 95.4 and a low of 87.9 percent.

C. Pyrometallurgical Research (H. M. Feder)

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

The chemistry of liquid metal systems is being investigated to provide basic concepts and data for the logical design of pyrometallurgical separations processes. In addition, the results of these studies provide ideas and data for the formulation and testing of theories concerning the influence of such characteristics as electronic structure, metallic radius, and electronegativity, on the properties of metallic solutions and inter-metallic phases.

a. Solubilities in Liquid Metals

The solubilities of the elements whose separations are being attempted are of prime importance in the design of fuel-reprocessing methods. The dependence of the solubility on temperature and solvent composition needs to be known. The solubility and temperature coefficient of solubility of a metallic phase in a liquid metal solvent are strongly dependent on interatomic forces and consequently may be used to determine how these forces vary with the basic properties of the solute and solvent atoms. For such basic studies, it is necessary to know the constitution of the solid phase in equilibrium with the saturated solution.

The determination of the solubilities of terbium, holmium, thulium, ytterbium, lutetium, cobalt, chromium, titanium, and uranium in liquid cadmium have been completed. The solubilities of iron and scandium in cadmium and vanadium in zinc are being determined.

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

The solubility of terbium in liquid cadmium has been measured by means of the standard method discussed in ANL-6068, page 66. Samples of 13.3 gm of terbium metal (99+ percent, Michigan Chemical Corporation) and 430 gm of cadmium metal (99.99 percent, American Smelting and Refining Corporation) were heated together at 630 C in a high-purity alumina crucible for 8 hr. A porcelain thermocouple well and tantalum stirrer were used. Samples were taken with magnesium oxide-coated quartz sampling tubes fitted with grade 60 porous graphite filters. No evidence of reaction between samples and sampling tubes was observed at the temperatures of these experiments. The first sample, taken at 630 C, contained 3.00 percent terbium, which is exactly the amount charged, and hence complete dissolution was accomplished. Samples were taken from 535 to 321 C.

The results are given in Table 25 and shown graphically in Figure 23. These data may be represented by the empirical equation

$$\text{terbium: } \log (\text{atom percent}) = 3.296 - 2425 T^{-1}$$

to within ± 3 percent.

The equilibrium solid phase was isolated from the ingot by electrolytically etching away the cadmium matrix. The X-ray pattern was found to be similar to that reported by F. H. Ellinger⁶ for the cerium-cadmium intermetallic phase CeCd_6 . The compound is presumably TbCd_6 .

⁶Ellinger, F. H., J. Phys. Chem. 64, 144 (1960).

Table 25

SOLUBILITY OF TERBIUM IN LIQUID CADMIUM

Temp (C)	Terbium (atom %)	Temp (C)	Terbium (atom %)
535	2.93	355	0.376
507	2.15	344	0.330
465	1.38	334	0.284 ^a
423	0.908	321	0.240
382	0.559		

^aSample taken on heating; all other samples taken on cooling.

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

The solubility of holmium in liquid cadmium was measured by means of the same procedure as previously described for terbium. Samples of 29.6 gm of holmium metal (99+ percent, Michigan Chemical Company) and 446 gm of cadmium (99.99 percent, American Smelting and Refining Company) were held together at 628 C for 25 hr in a high-purity alumina crucible. Samples were taken from 628 to 324 C.

The results are given in Table 26 and shown graphically in Figure 23. These data may be represented by the empirical equation

$$\text{holmium: } \log (\text{atom percent}) = 3.409 - 2494 T^{-1}$$

to within ± 4.8 percent.

Table 26

SOLUBILITY OF HOLMIUM IN LIQUID CADMIUM

Temp (C)	Holmium (atom %)	Temp (C)	Holmium (atom %)
628	4.39	424	0.646
580	3.36	387	0.415
545	2.23	351	0.259
501	1.52	334	0.205 ^a
461	0.979	324	0.179

^aSample taken on heating; all other samples taken on cooling.

The equilibrium solid phase was isolated from the ingot by electrolytically etching away the cadmium matrix. The X-ray pattern was similar to that found for the terbium-cadmium intermetallic phase and hence the compound is probably HoCd_6 .

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

The solubility of thulium in liquid cadmium has been measured by means of the same procedure as described previously for terbium. Samples of 13.2 gm of thulium metal (99.7 percent, Lindsey Chemical Division) and 370 gm of cadmium metal (99.99 percent, American Smelting and Refining Company) were held together at 634 C for 16 hr in a high-purity alumina crucible. Samples of the equilibrium liquid phase were taken from 524 to 324 C.

The results are given in Table 27 and shown graphically in Figure 23. These data may be represented by the empirical equation

$$\text{thulium: } \log (\text{atom percent}) = 3.488 - 2514 T^{-1}$$

to within ± 3 percent.

Table 27

SOLUBILITY OF THULIUM IN LIQUID CADMIUM

Temp (C)	Thulium (atom %)	Temp (C)	Thulium (atom %)
524	2.21	347	0.275 ^a
501	1.77	339	0.245
460	1.11	332	0.241 ^a
418	0.690	324	0.224
382	0.442		

^aSamples taken on heating; all other samples taken on cooling.

The equilibrium solid phase was isolated from the ingot by electrolytically etching away the cadmium matrix. The X-ray pattern was similar to that found for the terbium-cadmium intermetallic phase. The intermetallic phase is probably TmCd₆.

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

The solubility of ytterbium in liquid cadmium was measured by means of the same procedure as previously described for terbium. Samples of 27.2 gm of ytterbium metal (99+ percent, Michigan Chemical Company) and 455 gm of cadmium metal (99.99 percent, American Smelting and Refining Company) were held together at 630 C for 21 hr in a high-purity alumina crucible. Samples of the equilibrium liquid phase were taken from 504 to 326 C.

The results are given in Table 28 and shown graphically in Figure 23.

Table 28

SOLUBILITY OF YTTERBIUM IN LIQUID CADMIUM

Temp (C)	Ytterbium (atom %)	Temp (C)	Ytterbium (atom %)
504	3.09	346	0.654
463	2.12	343	0.688 ^a
425	1.59	334	0.576 ^a
384	1.01	326	0.516

^aSamples taken on heating; all other samples taken on cooling.

These data may be represented by the empirical equation

$$\text{ytterbium: } \log (\text{atom percent}) = 2.992 - 1957 T^{-1}$$

to within ± 3.4 percent.

The equilibrium solid phase was isolated from the ingot by electrolytically etching away the cadmium matrix. The X-ray pattern was similar to that found for the terbium-cadmium compound and hence is probably YbCd_6 .

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

The solubility of lutetium in liquid cadmium has been measured by means of the same procedure described previously for terbium and the other rare earths. The experiment was done in two steps. In the first step, a charge consisting of 20.0 gm of lutetium metal (99+ percent, Michigan Chemical Company) and 292 gm of cadmium metal (99.9+ percent, electrolytic grade, original source unknown) was held at 632 C for seventeen hours in a high-purity alumina crucible. Samples of the liquid phase were taken from 528 to 340 C. Below 340 C it was impossible to sample the liquid phase because of the excessively large amount of intermetallic phase present. Accordingly, in the second step, a 200-gm portion of the ingot from the first part of the experiment was melted together with 100 gm of cadmium metal and held for 17 hr at 625 C. Samples of the saturated liquid phase were taken from 557 to 324 C.

The results of both parts of the experiment are given in Table 29 and shown graphically in Figure 23. These data may be represented by the empirical equation

$$\text{lutetium: } \log (\text{atom percent}) = 7.328 - 7630 T^{-1} + 1.745 \times 10^6 T^{-2}$$

to within ± 3.8 percent.

The equilibrium solid phase was isolated from a portion of the ingot from the first part of the experiment by electrolytically etching away the cadmium matrix. The X-ray pattern was found to be similar to that for the other heavy rare earth-cadmium intermetallic compounds. The intermetallic phase is probably LuCd_6 .

Solubility of Cobalt in Liquid Cadmium
(M. G. Chasanov and P. D. Hunt)

In ANL-6145, page 71, preliminary results for the solubility of cobalt in liquid cadmium were reported. The results of a more comprehensive solubility determination are shown in Figure 24 and Table 30.

Table 29

SOLUBILITY OF LUTETIUM IN LIQUID CADMIUM

Temp (C)	Lutetium (atom %)	Temp (C)	Lutetium (atom %)	Temp (C)	Lutetium (atom %)	Temp (C)	Lutetium (atom %)
557	4.90 ^c	486	1.99 ^c	416 ^a	0.897 ^b	352	0.373 ^c
528 ^a	3.28 ^b	472	1.71 ^b	394	0.638 ^c	340 ^a	0.347 ^b
526	3.18 ^c	459 ^a	1.47 ^b	377 ^a	0.560 ^b	340	0.308 ^c
515	2.84 ^b	440	1.12 ^c	359	0.422 ^b	324	0.288 ^b
499 ^a	2.32 ^b						

^aData obtained in the first step of the experiment; other data were obtained in the second step.

^bSamples taken on cooling.

^cSamples taken on heating.

FIGURE 24
SOLUBILITY OF COBALT IN LIQUID CADMIUM

Table 30

SOLUBILITY OF COBALT IN LIQUID CADMIUM

Temp (C)	Cobalt (atom %)	Temp (C)	Cobalt (atom %)	Temp (C)	Cobalt (atom %)	Temp (C)	Cobalt (atom %)
653.4	0.0338	523.4	0.0118	426.4	0.00617	353.5	0.00386
617.4	0.0259	501.5	0.0111	405.4	0.00414	334.6	0.00308
579.4	0.0208	483.4	0.00964	404.3	0.00413	333.5	0.00313
548.4	0.0161	454.5	0.00821				

These data were obtained by taking filtered samples of melts prepared from 99.95 percent cadmium rod and 99.95 percent cobalt powder. The data over the range from 334 to 653 C may be represented by the empirical equation

$$\text{cobalt: } \log (\text{atom percent}) = 3.594 - 6515 T^{-1} + 1.705 \times 10^6 T^{-2}$$

to within ± 11 percent.

Microscopic examination of the ingot from these solubility determinations gave no evidence of the presence of intermetallic phases. Although some early workers^{7,8} reported the existence of intermediate phases in this system, Lihl and Buhl⁹ were unable to prepare intermetallic phases either by immersion of cobalt in liquid cadmium at 700 C or from amalgams.

Solubility of Chromium in Liquid Cadmium
(M. G. Chasanov and P. D. Hunt)

The solubility of chromium in liquid cadmium was determined over the temperature range 450 to 650 C by counting chromium-51 in filtered samples of a melt prepared from 99.95 percent cadmium rod and 99.99 percent chromium which had been activated.

The rate of solution of chromium in liquid cadmium is extremely low; it required 180 hours at 650 C for the melt to become saturated. The solubility at 650 C is quite low,¹⁰ about 17 parts per million chromium. It was not possible to obtain consistent solubility results below 450 C because of the extremely low solubility in that temperature region. The results, reported in Table 31 and Figure 25, can be represented by the equation

$$\text{chromium: } \log (\text{atom percent}) = 0.3944 - 2605 T^{-1}$$

to within ± 5.6 percent.

Table 31

SOLUBILITY OF CHROMIUM IN LIQUID CADMIUM

Temp (C)	Chromium (atom %)	Temp (C)	Chromium (atom %)
650.6	0.00361	548.4	0.00180
599.9	0.00266	499.6	0.00107
599.4	0.00246	451.0	0.000601

⁷Lewkonja, K., Z. anorg. Chem. 59, 322 (1908).

⁸Westgren A. and Ekman, W., Arkiv. Kemi., Mineral Geol., B10 No. 11, 1 (1930).

⁹Lihl F. and Buhl, E., Z. Metallkunde 46, 787 (1955).

¹⁰Hendrichs, G., Z. anorg. Chem. 59, 427 (1908) reported that chromium does not dissolve in liquid cadmium at 650 C.

FIGURE 25
SOLUBILITY OF CHROMIUM IN LIQUID CADMIUM

Microscopic examination of ingots and X-ray examination of annealed powder compacts prepared from chromium and cadmium showed no evidence of any intermetallic phases.

Solubility of Titanium in Liquid Cadmium (M. G. Chasanov and P. D. Hunt)

The existence of two intermetallic phases "C" and "t" in the titanium-cadmium system were previously reported in ANL-6183 and ANL-6231; in future discussions, these materials will be referred to as the δ and γ phases, respectively.

The cadmium-rich phase, δ , has been found to correspond to the composition TiCd. The δ phase has tetragonal symmetry;¹¹ its structure type is B-11, γ -TiCu; the lattice parameters are $a_0 = 2.9 \text{ \AA}$ and $c_0 = 8.9 \text{ \AA}$. The calculated density for δ phase is 7.05 g/cc; experimental determinations yielded 7.0 and 7.1 g/cc for the density of two different preparations of δ phase.

In all likelihood, γ , the phase richer in titanium, is the intermetallic phase reported in Hansen¹² as Ti_2Cd . The composition of Ti_2Cd corresponds to 46 weight percent titanium; the titanium content of the γ phase has been experimentally bracketed between 44.3 and 49.5 percent. Additional preparations of the γ phase are being examined both by X-ray and chemical analysis to establish its composition and structure.

¹¹Schablaske, R. and Tani, B., private communication.

¹²Hansen, M. and Anderko, K., Constitution of Binary Alloys, 2nd Ed., McGraw-Hill, New York (1958). p. 445.

Thermal analysis and X-ray studies have shown that a peritectic reaction between the γ phase and cadmium to form the δ phase occurs at 620 C; the δ phase is stable below the peritectic temperature.

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

The solubility of uranium in liquid zinc in the temperature range from 822 to 901 C was measured by analyzing filtered samples removed from the saturated melt. The solubility data are shown in Figure 26 together with those previously reported (ANL-6029, page 53), which were obtained at lower temperatures. The new data are also tabulated in Table 32.

FIGURE 26
SOLUBILITY OF URANIUM IN LIQUID ZINC

Table 32

SOLUBILITY OF URANIUM IN LIQUID ZINC
ABOVE 820 C

Temp (C)	Uranium (wt %)	Temp (C)	Uranium (wt %)
821.6	6.4	881.0	11.6
841.9	7.9	900.4	14.1
855.3	8.5	901.4	13.7

The finding of a peritectic in this system at about 840 C (see ANL-6287, page 102) was considered to be justification for treating the solubility data below and above this temperature separately. The solubility equations which resulted are

$$\text{uranium: } \log (\text{weight percent}) = 6.946 - 6711 T^{-1} \text{ (420 to about 840 C)}$$

$$\text{uranium: } \log (\text{weight percent}) = 5.87 - 5550 T^{-1} \text{ (about 840 to 901 C) .}$$

The solid phase in equilibrium with the melt below the peritectic temperature apparently is the epsilon phase and that in equilibrium with the melt above the peritectic is the delta phase.

b. Coprecipitation Studies

The degree of separation which may be achieved by re-crystallization from metallic solvents is often limited, not by the lack of a sufficient difference in solubility, but rather by the extent of coprecipitation. Thus, even though the solubility of an impurity is not exceeded when the temperature is lowered, a large fraction of the impurity present may crystallize with the fissionable metal.

Coprecipitation by CeCd₁₁ from Cadmium Solutions (J. Moriarty)

A systematic study of the influence of atomic radius, metallic valence, and electronegativity on the coprecipitation phenomenon is continuing. The coprecipitation coefficients of a number of elements carried by the cerium-cadmium intermetallic compound CeCd₁₁ from liquid cadmium solutions have been measured. The data thus far obtained are presented in Table 33. Doerner-Hoskins distribution curves are shown in Figure 27 for all data obtained during this report period.

Table 33

COPRECIPITATION COEFFICIENT IN LIQUID CADMIUM

(Carrier: CeCd₁₁)

Tracer Element	Coprecipitation Coefficient, λ	Tracer Element	Coprecipitation Coefficient, λ
Sodium	0	Gadolinium ^a	0.23 $\pm$ 0.06
Lithium	0	Samarium ^a	0.17 $\pm$ 0.04
Potassium	0	Uranium	0.13 $\pm$ 0.04
Yttrium	0	Strontium	0.10 $\pm$ 0.02
Barium ^a	0	Europium	0.099 $\pm$ 0.009
Lanthanum	1.49 $\pm$ 0.11	Scandium ^a	0.05 $\pm$ 0.02
Thorium ^a	1.08 $\pm$ 0.09	Zirconium	0.04 $\pm$ 0.01
Praseodymium ^a	0.631 $\pm$ 0.007		

^aNew data.

FIGURE 27
COPRECIPITATION FROM LIQUID CADMIUM
BY INTERMETALLIC COMPOUNDS

It would be valuable to be able to predict the extent that a solute would be carried by a given precipitate. For many purposes it would be sufficient to be able to predict whether carrying would be large or nearly zero. Therefore, attempts have been made to relate coprecipitation coefficients to characteristics of the carrier and tracer species. To a first approximation it can be shown¹³ that the coprecipitation coefficient λ is related to the solubilities of the tracer, S_t , and carrier, S_c , in the liquid metal solution by the expression

$$\lambda = (S_c/S_t) \exp (-\bar{F}^{xs}/RT) \quad , \quad (1)$$

where $\bar{F}^{xs}$ is the partial molar excess free energy of solid solution of tracer in the carrier crystal lattice. Thus, it should be possible to estimate coprecipitation coefficients from values of the solubilities and excess free energy. Solubility data are readily available. Values of $\bar{F}^{xs}$ are not available and no exact method for computing $\bar{F}^{xs}$ values exists. However, a relatively inexact value of $\bar{F}^{xs}$ is sufficient to determine whether λ is large or very small. In order to test Equation (1), experiments have been carried out using complementary systems in which the values of $\bar{F}^{xs}$ are

¹³Vaslow, F., and Boyd, G. E., J. Amer. Chem. Soc. 74, 4691 (1952).

expected to be approximately equal. For example, the excess free energy of solid solution of lanthanum in the CeCd_{11} lattice might be expected to be approximately equal to the excess free energy of solid solution of cerium in the LaCd_{11} lattice. This assumption is reasonable since both solid phases are isostructural and the two rare earth elements, being adjacent in the periodic table, do not differ greatly in size or electronegativity.

The observed coprecipitation coefficient for the case of lanthanum carried by CeCd_{11} is 1.49. Using Equation (1) at 450 C,

$$1.49 = 2.112 \exp (-\bar{F}^{\text{xs}}/1436) \quad ,$$

where $S_c/S_t = 2.112$; a value for $\bar{F}^{\text{xs}}$ of +502 cal/mole is obtained. An estimated value of λ for cerium carried by LaCd_{11} would then be:

$$\begin{aligned} \lambda_{\text{est}} &= \frac{1}{2.112} \exp (-502/RT) \\ &= 0.33 \pm 0.03 \quad . \end{aligned}$$

The experimental value for the coprecipitation of cerium carried by LaCd_{11} is 0.56 ± 0.03 .

In an analogous manner, the coprecipitation coefficient of cerium when carried by UCd_{11} was estimated from the solubility ratio of the two metals in liquid cadmium and the experimental value of λ for uranium carried by CeCd_{11} . The calculated value is 2.30 whereas the experimental value was found to be 3.01. In this case both solid phases are isostructural.

The equilibrium solid phases for the gadolinium-cadmium and the cerium-cadmium systems are different. Consequently, one would not expect the excess free energy of solid solution of gadolinium in the CeCd_{11} lattice to be nearly equal to the value of the excess free energy of solid solution of cerium in the GdCd_6 lattice. The coprecipitation coefficient, calculated on the basis of equality of the excess free energies, for the carrying of cerium by GdCd_6 is 4.86 while the observed value is only 0.34.

These results tend to confirm the validity and utility of Equation (1). Generally, the excess free energy of solid solution will be large when the tracer element and the carrier element individually form entirely different structures with the solvent metal. This results in small coprecipitation coefficients, which may often be essentially zero. However, when compounds of similar structure exist for the two elements significant coprecipitation will occur, the actual magnitude being largely determined by the relative solubilities of the carrier and tracer.

c. Liquid-Liquid Distribution Studies
(F. Cafasso and J. Vincenzi)

Distribution of Cerium and Palladium between Lead and Zinc as a Function of Temperature

The potential utility of the partially immiscible liquid pair lead and zinc in the liquid metal separation processes is being evaluated in this study. Information concerning the temperature dependence of distribution for solutes of interest must be known. The temperature dependence of the distribution coefficient of uranium was reported in ANL-6231, page 75. Similar measurements have been made for both cerium and palladium over the temperature range from 650 to 740 C.

The procedure used was the same as used in the study of the uranium system. Lead, zinc, and the solute metal (either cerium or palladium) were placed in an alumina crucible and heated to the desired temperature. Upon reaching this temperature, the melt was stirred for one hour with a tantalum paddle and then allowed to settle for two hours before a sample of each layer was taken. Fused silica pipets, coated internally with magnesium oxide and fitted with graphite filters, were used to take three samples of each layer at each temperature.

Distribution coefficients, defined as the ratio of the weight percent of the solute in the zinc layer to the weight percent of the solute in the lead layer, at each temperature are recorded in Table 34.

Table 34

DISTRIBUTION DATA FOR CERIUM AND PALLADIUM IN THE
LEAD-ZINC SYSTEM

Average Temp (C)	Solute	Solubility of Solute in Zinc Layer (w/o)	Solubility of Solute in Lead Layer (w/o)	Distribution Coefficient, $K = \frac{\text{w/o Solute in Zinc Phase}}{\text{w/o Solute in Lead Phase}}$
650	Ce	0.24	1.0×10^{-2}	24.0
700	Ce	0.21	1.8×10^{-2}	11.7
730	Ce	0.21	3.7×10^{-2}	5.7
652	Pd	4.3	2.4×10^{-3}	1792
703	Pd	4.3	9.1×10^{-3}	473
740	Pd	4.1	2.3×10^{-2}	178

These data are shown in Figure 28 along with those previously reported for uranium (see ANL-6231, page 75). When these data are compared with the uranium system (see Figure 28), it is noted that the palladium shows the most pronounced effect of temperature. Over the same temperature interval (650 to 740 C), the palladium coefficient changed by a factor of about 10, the uranium coefficient by a factor of about 8.5, and the cerium coefficient by a factor of about 6. Studies are underway to determine the dependence of the uranium distribution coefficient on uranium in the zinc-lead system. The effect of magnesium on the uranium distribution coefficient in the zinc-lead system is also being determined.

d. Thermodynamic Studies

Thermodynamic functions for key elements in liquid metal solvents and for the more important solid intermetallic phases are being measured. Two methods are being used. Galvanic cells have proved to be especially useful for the measurement of activities in liquid metal solutions as well as for the determination of the free energy of formation of the equilibrium solid phase in solid-liquid two-phase regions. On the other hand, for systems containing several well-defined intermetallic phases, measurement of the decomposition pressure by the effusion method is proving to be most useful. The two methods supplement each other.

Uranium-Cadmium System (Effusion Studies) (E. Veleckis)

The existence of a single intermetallic compound in the uranium-cadmium system corresponding to the empirical formula UCd_{11} and its standard free energy of formation have been reported elsewhere (ANL-5924, page 129; ANL-5996, page 116).

The relative simplicity of this system led to its selection for the purpose of establishing unequivocally the potentialities of the continuous-recording effusion method in phase diagram and thermodynamic studies. Six effusion experiments were performed in the temperature range from 320 to 380 C. Figure 29 shows a typical observed record of an isothermal run at 350 C. Cadmium was evaporated from approximately 250 mg of alloy until no further change in weight was observed, i.e., until all the cadmium had vaporized, leaving a residue of uranium metal. The weight versus time curve exhibited a single break in the vicinity of 150 mg.

The variation of cadmium vapor pressure with composition of the alloy for this experiment is represented in Figure 30, which was obtained by a graphical differentiation of the curve in Figure 29. In the cadmium-rich side of the curve, the pressure remains nearly constant, corresponding to a two-phase region ($Cd + UCd_{11}$). Once all the free cadmium is evaporated, the pressure drops abruptly, indicating a first-order phase transformation at the composition corresponding to UCd_{11} . When the decomposition pressure of UCd_{11} is reached, the curve shows a second plateau that is indicative of another two-phase region ($UCd_{11} + U$) in which the intermetallic compound decomposes to yield metallic uranium and cadmium vapor. The decomposition continues until all remaining cadmium is effused from the crucible, whereupon the pressure drops to zero. The rounding of corners in the two-phase fields is due to the surface depletion of the sample as the concentration of the cadmium-producing phase is rapidly decreasing. A small depression observed to the right of the composition of UCd_{11} is caused by a delayed nucleation of metallic uranium.

FIGURE 29
VARIATION OF SAMPLE WEIGHT WITH TIME IN
URANIUM-CADMIUM SYSTEM AT 350 C

FIGURE 30
VAPOR PRESSURE COMPOSITION ISOTHERM AT 350 C IN
URANIUM-CADMIUM SYSTEM

The continuous-recording effusion balance thus provides a powerful tool for a quick survey of the phase diagram of a binary system. Only a single experiment is, in principle, necessary to provide information as to the number and composition of intermediate phases.

Cerium-Zinc System (Effusion Studies)
(E. Veleckis and N. Goetzinger)

The existence of stable intermediate phases corresponding to CeZn_{11} and CeZn_9 (both with an uncertain homogeneity range), and to CeZn , Ce_2Zn , and Ce_4Zn have been reported.¹⁴ In addition, for concentrations above 11 atom percent cerium, five three-phase equilibria exist, three of which have large thermal effects and are probably due to the peritectic formation of intermediate phases. A considerable uncertainty exists as to the exact phase relationships in this region of the phase diagram.

The cerium-zinc system was investigated by the continuous-recording effusion method. A number of isotherms were obtained in the temperature range from 480 to 570 C. Figure 31 illustrates a typical vapor pressure versus concentration plot for 512 C obtained in an experiment employing effusion crucible B (effective orifice size of 1.718×10^{-3} sq cm). The inset in Figure 31 shows a portion of an isotherm for a higher cerium content at 570 C, measured with crucible C (effective orifice size of 5.173×10^{-3} sq cm). It is evident from the graph that eight intermediate phases succeed one another: CeZn_{11} , $\text{Ce}_2\text{Zn}_{17}$, $\text{CeZn}_{\sim 7}$, $\text{CeZn}_{3.8-6.2}$, CeZn_2 , CeZn , Ce_2Zn , and Ce_4Zn .

The continuous-recording effusion method thus served to clarify the cerium-zinc phase diagram considerably. Existence of the intermetallic compounds CeZn_{11} , CeZn , Ce_2Zn , and Ce_4Zn is confirmed. Analogous to the uranium-zinc system, the phase previously identified as CeZn_9 is shown to be $\text{Ce}_2\text{Zn}_{17}$. The existence of CeZn_2 is quite probable; a similar phase has been structurally identified as Laves phase for the system lanthanum-zinc.¹⁴ The previously unknown region between the limits CeZn_2 and $\text{Ce}_2\text{Zn}_{17}$ exhibits two new phases: a rather unstable phase corresponding to $\text{CeZn}_{\sim 7}$, and a wide solid solution region extending from $\text{CeZn}_{\sim 3.7}$ to $\text{CeZn}_{\sim 6.4}$.

¹⁴Hansen, M. and Anderko, K., Constitution of Binary Alloys, McGraw-Hill Book Co., Inc., New York (1958).

FIGURE 31
VAPOR PRESSURE-COMPOSITION ISOTHERMS
IN CERIUM-ZINC SYSTEM

- A. Isotherm at 512 C.
B. Portion of an Isotherm for a Higher Cerium Content
at 570 C.

Magnetic Studies

(F. Cafasso and D. Gruen*)

Neodymium-Cadmium System (NdCd₁₁)

The magnetic susceptibilities of a series of AB₁₁ inter-metallic compounds, where A is either a rare earth or actinide element and B is cadmium, are being measured in a joint effort of the Chemical Engineering and the Chemistry Divisions.

An ingot of NdCd₁₁ was prepared by melting the pure metals together. The specimen was shown to be isomorphous with CeCd₁₁ by X-ray powder methods. A chemical analysis served to establish the atom ratio.

Magnetic susceptibility measurements with a powdered specimen were made by the Faraday method. The susceptibility apparatus has been described in ANL-6145, page 81. Measurements were made at ten fixed temperatures between the lambda point of helium and room temperature. Molar susceptibility values of the compound NdCd₁₁ [$M\chi_{\text{NdCd}_{11}}$] at each temperature are recorded in Table 35. This table also includes values of the molar susceptibilities of neodymium [$M\chi_{\text{Nd}}$] in the alloy, which were obtained by correcting for the diamagnetism of cadmium. Figure 32 shows the reciprocal of the molar susceptibility of neodymium plotted against absolute temperature. The susceptibility appears to obey a Curie-Weiss Law [$\chi = C/(T-\Delta)$], with a Δ value of -8 K. Least-squares treatment of the data yields a value of 1.66₇ for the Curie constant C. The effective moment of the alloy derived from the calculated Curie constant is 3.67 μ_B (Bohr magnetons) per atom.

Table 35

MOLAR MAGNETIC SUSCEPTIBILITY OF NdCd₁₁

Temp (K)	$M\chi_{\text{NdCd}_{11}} \times 10^3$	$M\chi_{\text{Nd}} \times 10^3$	$M\chi_{\text{Nd}}^{-1} \times 10^{-2}$
294.9	5.28	5.50	1.82
184.6	8.48	8.70	1.15
160.2	9.84	10.06	0.99
77.1	19.29	19.51	0.51
70.7	21.03	21.26	0.47
67.1	22.15	22.37	0.45
63.2	23.39	23.61	0.42
20.4	57.87	58.10	0.17
4.2	152.8 ₁	153.0 ₃	0.06 ₅
2.0	246.0 ₁	246.2 ₃	0.04 ₆

*Cooperating Chemist, Chemistry Division.

FIGURE 32
TEMPERATURE VARIATION OF MOLAR
SUSCEPTIBILITY OF NEODYMIUM IN NdCd_{11}

This value is in agreement with the theoretical value¹⁵ of 3.68 expected for a free gaseous trivalent neodymium ion in a $^4I_{9/2}$ ground state.

The neodymium-neodymium distance in the alloy is 6.57 Å. Exchange interactions between the paramagnetic atoms is very unlikely at this distance. The observed Δ value therefore may be assumed to arise solely from crystal field interactions. From the magnitude of the Δ value in both the cerium system (see ANL-6145, page 82) and the neodymium system, it appears that the crystal field produces only a very small splitting of the lowest energy levels of either paramagnetic ion.

For odd electron systems, the Kramers Theorem¹⁶ states that there will always be at least a twofold degenerate state regardless of the symmetry of the crystal field. At low temperatures this degeneracy would cause a $1/\chi$ vs T curve to bend towards the temperature axis. This effect begins to assert itself in the neodymium system at liquid helium temperatures, in agreement with the observed Δ values.

¹⁵Van Vleck, J. H., The Theory of Electric and Magnetic Susceptibilities, Oxford Clarendon Press (1932).

¹⁶Kramers, H. A., Proc. Amsterdam Acad. Sci. 33, 959, (1930).

2. Calorimetry (W. N. Hubbard)

Thermodynamic data are lacking for many compounds of interest in high-temperature chemistry because of the experimental difficulties involved in making the necessary measurements. A program has been undertaken to help fill this gap.

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

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

Some of the compounds of interest are borides, aluminides, carbides, silicides, nitrides, sulfides, and selenides of metals such as uranium, zirconium, molybdenum, and tungsten. One major problem in the determination of the thermodynamic properties of compounds such as these is the procurement of sufficiently pure samples. It is sometimes the case, even with "high-purity" samples, that the total uncertainty assigned to the final experimental result is due more to the uncertainty in defining the sample studied than to all the other uncertainties of the measurement combined. A program for the preparation of uranium compounds to be used in the calorimetric studies at Argonne is being carried out by Stanford Research Institute. Other compounds will be obtained from various laboratories. Boron nitride, obtained from Professor John Margrave of the University of Wisconsin, zirconium diboride, obtained from Elmer J. Huber, Jr., of Los Alamos Scientific Laboratory, and zirconium dihydride and dideuteride, to be obtained from Howard Flotow of the Chemistry Division of this Laboratory, are examples. Some of the compounds will be synthesized here. The disulfides of molybdenum and tungsten are examples of such compounds already studied.

a. Combustions of Uranium Mononitride in Oxygen
(D. R. Fredrickson, R. L. Nuttall, and E. Rudzitis)

The first of the samples prepared by Stanford Research Institute to be studied was Sample N-19 of uranium mononitride. The primary problem encountered in the development of techniques for the measurements was that of directing the course of the reaction to U_3O_8 . At first, an oxygen-deficient product $\text{U}_3\text{O}_{(8-x)}$ was usually obtained. The evidence for this was gathered from careful observation of the respective weight changes caused by the bomb reaction and by subsequent ignition of the reaction product in air at 900 C, as well as from X-ray diffraction studies of the oxygen-deficient product.

It was found that the formation of oxygen-deficient product was related to the reaction temperature. By spreading the sample over a relatively large area (~ 1 sq in.) on a platinum support plate and using only 5 atm oxygen pressure, a lowering of the temperature and a smooth quantitative reaction to the desired end product, U_3O_8 , was obtained.

To verify that the nitrogen product of the reaction was gaseous nitrogen rather than oxides of nitrogen, the product gases of the reaction were subjected to infrared analysis. No oxides of nitrogen were detected.

A series of six calorimetric combustions of Sample N-19 have been completed. A value of -843.71 ± 0.10 calories per gram of sample burned has been obtained as the standard energy of combustion for this series. The precision of the results obtained is excellent. However, insufficient proof of the exact composition of the sample leaves a large uncertainty in any value of the heat of formation calculated from the results. The analysis submitted for the sample showed 0.20 percent oxygen, 0.05 percent carbon, and 0.05 percent iron. It is assumed that the carbon is all present as uranium monocarbide, UC, and the iron as the iron nitride, Fe_4N . The state of the oxygen present is uncertain. The assumption that all the oxygen is present in solid solution rather than as uranium dioxide leads to values of the heat of formation of uranium mononitride, calculated from the results, that differ by 5.4 cal/g. This is many times the uncertainty in the value for the heat of combustion of the sample.

It appears that both oxygen in solid solution and uranium dioxide are present. The relative amounts of oxygen in the two phases is as yet unknown. After a discussion with Stanford Research Institute, it was decided (1) that an attempt would be made to determine the UO/UO_2 ratio in the sample by X-ray analysis after calibration with uranium dioxide, and (2) that an attempt would be made to prepare a new sample of uranium mononitride with a much lower oxygen content.

b. High-purity Fluorine for Fluorine Bomb Calorimetry
(J. Settle)

One of the first problems in the fluorine bomb calorimetry program was to determine the magnitude of the thermal effects that might be encountered from impurities in the fluorine used in calorimetric combustions. Early in the program a series of molybdenum combustions was conducted with commercial fluorine that contained 1.14 percent impurities. Major impurities were O_2 , N_2 , CF_4 , and C_2F_6 . Very small amounts of C_3F_8 , HF , NF_3 , SiF_4 , and possibly SF_6 and S_2F_{10} were also contained. Another series of molybdenum combustions was conducted with fluorine purified by L. Stein* by means of low-temperature fractional distillation. The purified fluorine contained 0.08 percent total oxygen and nitrogen as the only impurities. The observed heat of combustion of molybdenum in the commercial fluorine was about 1 kcal/mole more negative than the observed heat of combustion of molybdenum in the purified fluorine. This discrepancy was certainly significant and because no fluorine of high purity was available commercially it was necessary for this laboratory to purify commercial fluorine. An improved low-temperature still was designed and constructed.¹⁷ It has now been used to produce 6 batches of fluorine that contained from 0.02 to 0.08 percent impurities. A typical product of 99.94 percent pure fluorine contained about 0.04 percent oxygen and 0.02 percent nitrogen as the only impurities.

The General Chemical Division of Allied Chemical Company became interested enough in the problem to build a still similar to the one used here, and has recently sent to this laboratory for evaluation a 1-lb batch of distilled fluorine. This fluorine is 99.75 percent pure. The impurities are N_2 , 0.14 percent; O_2 , 0.08 percent; CO_2 , 0.02 percent; and CF_4 , NF_3 , and SiF_4 totaling 0.1 percent. It will be necessary to use this fluorine in comparative calorimetric combustions in order to determine whether there will be significant thermal effects from the oxygen, nitrogen, and carbon dioxide impurities.

c. Combustions of Boron Nitride in Fluorine
(S. Wise)

Boron nitride was the first compound to be burned in fluorine bomb calorimetry; previous combustion studies were made with elements. Boron nitride was also the first substance to be studied that reacted spontaneously with fluorine. For this study, the combustion bomb reaction vessel for spontaneously combustible materials described in ANL-6287,

*Cooperating chemist, Chemistry Division, Argonne National Laboratory.

¹⁷Stein, L., Rudzitis, E. and Settle, J. L., ANL-6264 (June 1961)

page 125, was calibrated and used. Seven calibrations, in which heat was supplied by the combustions of benzoic acid in oxygen, yielded a 3348.4 ± 0.4 cal/degree C for the energy equivalent of the system ANL-R₁-Ni₂-T₁. This value is approximately 230 cal/degree C less than for the same system without the surrounding fluorine tank. The precision of the results, approximately 0.01 percent, is about the same as for the system without the tank.

When fluorine is expanded from the tank to the evacuated bomb during the calorimetric experiment, a slight cooling effect is expected. Several blank expansions without samples were carried out in the calorimeter to see if this effect could be measured. Calculations from virial coefficients showed that 0.7 cal should be absorbed when 6.6 atmos pressure of fluorine in the tank is expanded to 2.6 atmos in the combined bomb and tank system. In practice, however, a slight heating effect was observed, caused by a slight fluorination of the nickel surfaces as the fluorine rushed into the evacuated bomb. This problem was eliminated by prefluorinating the bomb and tank system for 8 hr at 110 C with 3 atmos pressure of fluorine before expansion. Under these conditions the calculated energy change of $\Delta E = +0.7$ cal was observed. In order to preserve the prefluorinated nickel surfaces, the bomb is opened only in a dry box containing a helium atmosphere. All manipulation of the bomb contents including weighing are done in this enclosure.

A calorimetric series of combustions of boron nitride in fluorine is now in progress. For this study a high-purity hexagonal boron nitride sample, obtained from the National Carbon Company through the courtesy of Professor John Margrave, University of Wisconsin, was used. Chemical analysis for impurities in the sample showed, by weight, 0.40 percent oxygen, 0.12 percent carbon, 0.02 percent silicon, 0.01 percent hydrogen, and spectrographic analysis showed 0.008 percent titanium.

Preliminary experiments with boron nitride showed that the most satisfactory combustion characteristics were obtained with 0.4 gm of boron nitride compressed to form a $\frac{3}{5}$ -in.-diameter pellet which was supported on a disc of optically polished sapphire, 1 in. in diameter by $\frac{1}{16}$ in. thick. The sapphire disc is inert to reaction with fluorine under the combustion conditions employed and, in addition, has a relatively high resistance to thermal shock. The slight amount of unburned boron nitride in any one combustion can be determined by weighing, wiping, and reweighing the sapphire disc after combustion. The sapphire disc is supported in the bomb on a massive nickel disc held in a gimbel. The determination of unburned boron nitride is based on the assumption that only gaseous bromine trifluoride is formed in the combustion reaction.

d. Combustions of Zirconium and Molybdenum in Fluorine
(E. Greenberg and J. Settle)

Experimental work has been completed for the studies of the heats of formation of zirconium tetrafluoride and molybdenum hexafluoride. Revised values of -356.78 ± 0.25 and $-372.3_5 \pm 0.2_2$ kcal/mole have been obtained for the standard heats of formation [$\Delta H_f^\circ(25^\circ \text{C})$] of zirconium tetrafluoride crystal and molybdenum hexafluoride gas, respectively. Manuscripts, entitled "Fluorine Bomb Calorimetry: 1. The Heat of Formation of Zirconium Tetrafluoride," and "Fluorine Bomb Calorimetry: 2. The Heat of Formation of Molybdenum Hexafluoride," have been accepted for publication in the Journal of Physical Chemistry.

e. Combustions of Uranium in Fluorine
(J. Settle)

Determinations of the heats of formation of such compounds as the borides and silicides of uranium would be a very difficult task by oxygen bomb or solution calorimetry because of the difficulty of obtaining well-defined reaction products. To obtain the heats of formation of these compounds by fluorine combustion calorimetry, it is necessary to know the heats of formation of uranium hexafluoride (UF_6), boron trifluoride (BF_3), and silicon tetrafluoride (SiF_4). The heat of formation of boron trifluoride has recently been determined in this laboratory (see ANL-6287, page 125). The heat of formation of silicon fluoride has also recently been accurately measured.¹⁸ In contrast, the estimated uncertainty interval of the heat of formation of uranium hexafluoride^{19,20} is greater than 1 percent. It is evident that a more precise determination of the heat of formation of uranium hexafluoride is a desirable step in the proposed study of these uranium compounds.

In experiments carried out in the laboratory, the main sample was uranium rod about $\frac{1}{16}$ in. in diameter and $\frac{3}{4}$ in. long. The rods were ignited at the top by means of a uranium fuse wire and a small piece of uranium foil which acted as a kindler. With this sample arrangement, it was necessary to dilute the fluorine with an inert gas to reduce the temperature in the reaction zone and thereby to prevent the melting of the uranium. When the gaseous mixture consisted of one atmosphere fluorine and sufficient argon to make the total pressure 12 atmos, no melting

¹⁸Vorobiev, A. F., Kolesov, V. P., and Skuratov, S. M., the Bulletin of Chemical Thermodynamics, 3, 23 (1960).

¹⁹The Chemistry of Uranium, eds. Katz, J. J. and Rabinowitch, E., McGraw-Hill Co., New York, N. Y., (1951), p. 412.

²⁰Weinstock, B. and Christ, R. H., J. Chem. Phys. 16, 436 (1948).

occurred. However, the combustion reaction terminated before all of the uranium had reacted with fluorine. As a result, there remained a residue of unreacted uranium with a surface coating of lower fluorides. Preliminary experiments had demonstrated that about 98 percent of the uranium which reacted formed uranium hexafluoride. The other two percent of uranium which reacted formed mostly UF_3 and uranium tetrafluoride, together with very small amounts of U_4F_{17} , U_2F_9 , and UF_5 .

Analysis of the combustion residue is necessary in order to make appropriate thermochemical corrections to the measured heat. However, because of the difficulty of analyzing the complex mixture of uranium metal and its lower fluorides, an uncertainty of about 0.2 percent is introduced into the calculation of the heat of formation of uranium hexafluoride gas. Improved analytical techniques are being sought.

The data obtained from three combustions were used to make approximate calculations of the heat of formation of uranium hexafluoride gas. Table 36 is a summary of the results of these experiments. Item 3 is the mass in vacuo of uranium that reacted. This value was determined by subtracting the total amount of uranium metal recovered (Item 2) from the mass of uranium introduced into the bomb (Item 1). Item 4 is the observed increase in the calorimeter temperature, corrected for heat exchanged between the calorimeter and its surroundings. Item 5 is the energy equivalent of the calorimetric system, 3575.50 ± 0.50 cal/deg, multiplied by the corrected temperature increase. Item 6 is the energy absorbed by the contents of the bomb during the hypothetical isothermal process at 25 degrees. Item 7 is the electrical energy input for ignition of the fuse. Items 8, 9, and 10 list the corrections applied for the lower fluorides formed during the combustions.

Table 36

RESULTS OF URANIUM COMBUSTIONS IN FLUORINE^a

1. Uranium charged to bomb, g	0.7689	0.7220	0.72327
2. Uranium recovered, g	0.26029 ± 0.00010	0.23292 ± 0.00010	0.23764 ± 0.00010
3. Uranium reacted, g	0.50760 ± 0.00010	0.48908 ± 0.00010	0.48563 ± 0.00010
4. Δt_c , deg	0.30260	0.29183	0.28855
5. ϵ (calor)($-\Delta t_c$), cal	-1081.95	-1043.44	-1031.71
6. $\Delta E_{\text{contents}}$, cal	-2.45	-2.29	-2.27
7. $\Delta E_{\text{ignition}}$, cal	1.19	1.19	1.15
8. $\Delta E_{\text{UF}_3 \text{ formation}}$, cal	-2.89 ± 0.5	-5.14 ± 0.7	-3.66 ± 0.4
9. $\Delta E_{\text{UF}_4 \text{ formation}}$, cal	-0.28 ± 0.2	-0.63 ± 0.2	-1.06 ± 0.3
10. $\Delta E_{\text{U}_2\text{F}_6 \text{ formation}}$, cal	-0.12	-0.14	-0.07
11. ΔE_{gas} , cal	0.82	0.77	0.81
12. $\Delta E_{\text{impurities}}$, cal	3.85	3.71	3.68
13. $\Delta E_c^\circ/M$, cal/g	-2131.3 ± 1.8	-2136.6 ± 4.3	-2127.4 ± 1.9

Average $\Delta E_c^\circ/M = 2131.8 \pm 2.7$ cal/g
Standard deviation of the mean = 14.7 cal/g

^aThe values given must be considered preliminary and subject to revision.

Item 11 is the net correction due to the hypothetical compression and decompression of the bomb gases. Item 12 is the net correction for impurities contained in the uranium sample. The impurities, in ppm, were hydrogen, 3; nitrogen, 80; oxygen, 220; silicon, 40; and carbon, 615. On the assumptions that these impurities were present as UH_3 , UN , UO_2 , U_3Si , and UC , respectively, and that the respective fluorination products were UF_6 , HF , N_2 , O_2 , SiF_4 , and CF_4 , the correction for the impurities was 7.58 ± 1.12 cal/g of sample reacted. Item 13 is the energy change per gram of uranium for the reaction $\text{U(c, } \alpha) + 3 \text{ F}_2(\text{g}) \longrightarrow \text{UF}_6(\text{g})$, with the reactants and product in their respective standard states at 25 C.

The data in Table 36 permit the calculation of an approximate value of -509 ± 3 kcal/mole as the standard heat of formation of uranium hexafluoride gas. Improvements in analytical procedure should reduce by about an order of magnitude the uncertainty in the value of the heat of formation of uranium hexafluoride derived from future calorimetric combustions.

f. Combustions of Cadmium in Fluorine
(E. Rudzitis and T. Kinsella)

Combustions in fluorine of four metals, cadmium, zinc, magnesium, and aluminum, have been studied over the past half year or so. These combustions differ from others that have been studied in that all four metals have relatively low melting points, which results in melting of the sample in the early stages of combustion. Containment of the molten metal during the rest of the combustion process presents a problem of sample support. The support material must be chemically resistant to the molten metal as well as to fluorine at elevated temperatures and, in addition, must be able to withstand the thermal shock that it receives during the combustion. The solution to the support problem was the use of cold-pressed, slightly concave discs of the fluoride of the metal to be burned.

The first of these metals to be studied calorimetrically was cadmium. In many respects the initial combustions were satisfactory. Slightly less than 2 gm of cadmium resting on the top one of two $\frac{1}{8}$ -in.-thick by 2-in. diameter cadmium fluoride discs was ignited electrically with a cadmium fuse wire and evolved approximately 3000 cal. Although temperatures higher than 1100 C were obtained, as indicated by the melting of portions of the discs, more than 99.99 percent of the metal reacted to form the fluoride.

In two respects, the initial combustions were somewhat unsatisfactory. First, it was found that a significant amount of sample reacted with fluorine before the sample was ignited. Further study, however, showed that corrections for this pre-ignition reaction could be made. Second, the

time required for thermal equilibrium to be attained in the calorimeter was impracticably long. To overcome this problem, the base of the bomb was redesigned and rebuilt in such a way that the nickel support for the ceramic discs was made a portion of the base, thus providing good thermal contact between the bomb and the calorimeter fluid. Experiments have shown that the problem of excessively long times to the attainment of equilibrium has been eliminated by the new bomb base. Recalibration of the bomb is now necessary before additional calorimetric measurements will be made.

g. Combustion of Titanium, Hafnium, and Thorium in Fluorine
(E. Greenberg)

Preliminary noncalorimetric combustion experiments for titanium and hafnium were completed and described in the last quarterly report (ANL-6287, page 129). Samples for calorimetric experiments are being fabricated by the Metallurgy Division. Some additional combustion experiments were carried out with thorium, but a satisfactory technique for calorimetric studies has not yet been developed.

h. Combustion of Vanadium, Niobium, and Tantalum in Fluorine
(E. Greenberg)

Exploratory experiments were initiated to develop techniques for calorimetric combustion studies of vanadium, tantalum, and niobium in fluorine. Using a glass bomb, in order to observe the combustion characteristics of these metals, satisfactory conditions have been worked out for tantalum and niobium. Additional experimentation is required for vanadium.

For tantalum and niobium, the sample, in the form of a rod approximately 0.125 in. in diameter by 1 to $1\frac{1}{2}$ in. long, was machined down to a thin pin at one end and inserted in a small hole in a relatively massive nickel stand. The vertically supported sample was ignited in the usual manner with an electrical fuse wire threaded through a small piece of 0.005-in. foil inserted in a slot at the top of the sample rod. In the early experiments with tantalum, the diameter of the pin which served to support the sample was about 0.035 in. and, because of preferential attack during the combustion, the rod burned away just above the pin. It was found that increase of the pin diameter to about 0.055 in. was sufficient to prevent burning through at the base despite the preferential attack, if the quantity of fluorine in the bomb was properly limited. Greater amounts of sample could be burned, without burning through the support pin, by

correspondingly increasing both the fluorine pressure and the length of tantalum sample rod. It is desirable to keep the support-pin diameter small in order to reduce the contact area between the sample and the nickel stand. In the case of niobium, preferential attack at the base of the sample was not as severe, and a support-pin diameter of 0.035 in. was adequate provided that the length of sample and quantity of fluorine were properly adjusted. Because of the high melting points of tantalum and niobium, the use of pure fluorine was not only feasible but desirable in order to shorten the combustion period. In a typical experiment with tantalum, a fluorine pressure of 2000 mm Hg and a $1\frac{1}{2}$ -in.-long tantalum rod weighing 5.3 gm were employed. Approximately 3.9 gm of sample were burned and evolved about 7.7 kcal of heat. In a typical niobium experiment, fluorine at 1500 mm Hg pressure and a $1\frac{1}{2}$ -in.-long sample rod weighing 2.8 gm were employed. About 1.6 gm of niobium were burned and evolved about 5.9 kcal of heat. In both the tantalum and niobium experiments the combustion product was a uniform white solid which had sublimed away from the hot combustion zone and condensed on the cooler walls of the bomb. The combustion period was about 4 min.

Preliminary vanadium combustions were conducted with 1-in.-long sample rods weighing about 1.7 gm and having a pin base of about 0.035 in. in diameter. Approximately one gram of sample was burned and evolved about 6.6 kcal of heat. There was no evidence of preferential attack at the base of the rod. However, the combustions lasted longer than 10 min, which is somewhat undesirable for a calorimetric experiment. It appears that problems may be encountered in handling and identifying the combustion product, which is considerably more volatile and reactive with the atmosphere than the fluorides of tantalum and niobium.

High-temperature Enthalpy Calorimeter
(R. L. Nuttall and D. A. Fredrickson)

The 1500 C furnace component of the drop calorimeter has been assembled. A high-vacuum system, with necessary electrical controls, to be used with the furnace has been built and installed. The furnace shell was found to contain leaks and, therefore, was disassembled to be rewelded. Leak testing of the calorimeter shell is now underway.

II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES

A direct fluorination volatility process has been proposed for the recovery of uranium and plutonium from irradiated nuclear reactor fuels. In this process advantage is taken of the volatilities of uranium and plutonium hexafluoride and of fluidization techniques. Attempts are being made to apply this process to uranium oxide and zirconium matrix fuels.

The proposed process for recovery of uranium and plutonium from spent uranium oxide involves decladding by an appropriate reaction in a fluidized bed. Plutonium and uranium hexafluorides, which result from the reaction of the declad oxide fuel with fluorine, may be separated using a combination of the variability of the rates of fluorination of the plutonium and uranium compounds and chemical reactivities of the hexafluorides.

The decladding step of the process for uranium dioxide fuels involves gas-metal reactions in the case of elements clad either with stainless steel or Zircaloy. The gas-metal reactions are carried out with the fuel elements submerged in an inert fluidized bed (calcium fluoride or alundum) which serves as a heat transfer medium. Dilute mixtures of hydrogen chloride in hydrogen fluoride or the separate gases have been successfully employed when zirconium decladding is necessary. In recent work, chlorine has replaced the hydrogen chloride. In the case of stainless steel cladding, chlorine appears to be a possible decladding reagent, based on results from pilot plant studies.

The decladding reactions (referred to as primary) are being carried out in a two-zone fluid-bed reactor. Volatilization of the clad or alloying material occurs in the lower zone during the chlorination reaction. The volatile materials pass upward into the upper zone, where hydrogen fluoride is admitted, thereby effecting conversion to solid fluorides. Where solid chlorides are formed, these will also be converted to solid fluorides, since there is solids mixing between zones. The two zones are separated by an inverted conical baffle (other types may also be suitable) which reduces back-mixing of the gases and prevents the formation of gas mixtures that have been shown to affect these reactions adversely.

In pilot-plant studies the reaction of 304 stainless steel tube sections with chlorine has been investigated in a $1\frac{1}{2}$ -inch diameter two-zone fluid-bed reactor. The rate of chlorination has been found to decrease rapidly with time because of the formation of an adherent film comprised primarily of nickel and chromium chloride on the surface of the cladding. An average penetration rate of 4.6 mils/hr was obtained in a 4.7-hour run at 575 C using 87 percent chlorine (in nitrogen). At a higher temperature of 625 C, using the same chlorine concentration, a 35-mil tube completely reacted in 3.8 hours. The effect of chlorine dilution at 625 C was noticeable at concentrations below 48 volume percent.

After decladding has been achieved, a subsequent fluorination step is expected to provide the necessary separation of the fissile elements. The direct fluorination of dense uranium dioxide pellets is being examined in fluid-bed pilot plant studies.

Substantial improvement in temperature control at higher reaction rates has been achieved by regulation of fluorine inlet flow in place of coolant regulation previously employed. Four runs have been made in which pellet batches of approximately 4.5 kg have been completely reacted at about 500 C; average uranium hexafluoride production rates of about 20 kg/(hr)(sq ft reactor cross section) were obtained with inert-fired pellets and approximately one-half this rate for hydrogen-fired pellets. The hydrogen-fired pellets ($\frac{1}{2}$ in. x $\frac{1}{2}$ in.) are considered more representative of reactor fuel material, and in these experiments 10 to 12 hr was required for processing a complete batch.

Fluorination runs have been made with inert fluid beds of calcium fluoride or magnesium fluoride to aid in removal of heat. Additional runs were made to demonstrate the feasibility of operating with a pure zirconium tetrafluoride fluid bed and without an inert bed.

Since heat transfer limits the maximum practical reaction rate in the direct fluorination process, a heat transfer study is being made in a mockup system. In these tests, measurements are made of heat transfer coefficients for the surfaces of the inner heater and of the outer cooling wall, and for effective bed thermal conductivities for systems consisting of pellet beds with a fluidized medium in the pellet voids. In several experimental tests, effective thermal conductivities along the radius of the bed of about 0.8 Btu/(hr)(sq ft)(F/ft) were found for the nonfluidized case and of 5 to 10 for fluidization. For the fluidized case, surface coefficients of about 80 Btu/(hr)(sq ft)(F) were found for the internal heating surface and 20 to 60 for the external cooling surface.

A new filter system with automatic blowback was demonstrated, in which the filters are located in chambers separated from the reactor by a length of one-inch pipe. This design promises to make filter replacement more convenient in radioactive systems.

The rate of thermal decomposition of plutonium hexafluoride has been studied at temperatures from 140 to 173 C by a static method and from 150 to 250 C by a flow method. A study of the kinetics of decomposition has established the mechanism of the reaction. The rate of the reaction has been formulated as concurrent first- and zero-order reactions with respect to plutonium hexafluoride pressure in the range between 50 and 1100 mm and, of temperature from 140 to 170 C. It has been inferred that, within the aforementioned temperature and pressure ranges, the decomposition proceeds by both a homogeneous and heterogeneous

unimolecular decomposition and that the heterogeneous decomposition occurs on the surface of the deposited plutonium tetrafluoride. Rates of decomposition of plutonium hexafluoride obtained in the flow system approximate conditions which may be found in the fluorination reactor of the Direct Fluoride Volatility process for uranium oxide power reactor fuels. This information will be useful for plant design and future experimental work.

The physical appearance of plutonium tetrafluoride resulting from both thermal decomposition and alpha-radiation decomposition has been observed and bulk densities have been determined. The bulk density of the product of thermal decomposition was 15 to 18 times greater than the bulk density of the product of radiation decomposition.

It has been demonstrated that a large quantity (32 gm) of plutonium tetrafluoride, which had been deposited in equipment by thermal decomposition of plutonium hexafluoride, could be refluorinated to plutonium hexafluoride at about 450 C with a recovery of 98 percent of the plutonium.

The reaction of elemental bromine with plutonium hexafluoride has been investigated. The stoichiometry of the reaction has been established. Primary products of the reaction are plutonium tetrafluoride and bromine pentafluoride. The utility of the reaction for the separation of uranium and plutonium hexafluorides has been demonstrated.

In studies of fission product behavior mixtures of uranium dioxide-ruthenium-106 were reacted with fluorine at 400 and 500 C. It was found that at both of these temperatures ruthenium was volatilized at a rate equal to or faster than that of uranium volatilization as uranium hexafluoride. However, it was found that ruthenium pentafluoride decomposed and was deposited on a colder portion of the walls of the fluorination vessel. No alteration of the results occurred when calcium fluoride and zirconium fluoride were added to the original mixture to be fluorinated. The fluorination of uranium dioxide-niobium-95 mixtures indicated that niobium is readily fluorinated out of uranium dioxide and that there is no reaction between niobium and calcium fluoride-zirconium fluoride bed materials. Niobium differed from the ruthenium in that very little (less than one percent) deposited on the reaction boat or furnace tube, indicating that niobium can be volatilized with little or no difficulty.

In studies of reactions which might be used to separate uranium and plutonium, the reactions of gaseous sulfur tetrafluoride with uranium trioxide and uranyl fluoride to produce uranium hexafluoride were studied. Sulfur tetrafluoride has the advantage that it will not react with plutonium dioxide or plutonium tetrafluoride to produce plutonium hexafluoride. It thus can serve as a selective fluorinating reagent in fluoride volatility processes. Kinetics of the reactions of sulfur tetrafluoride with uranium

dioxide and uranyl fluoride have been explored. This work serves as a classical example of the use of a thermobalance in the study of gas-solid kinetics in a reaction in which the final product is volatile.

A combined chlorination-fluorination (Direct Chlorination Process) process is being examined as an alternate to the fluorination step of the Direct Fluorination Volatility Process. The two-zone fluidized-bed concept has been employed successfully in the direct chlorination of sintered uranium dioxide pellets. The volatile uranium chlorides produced in the lower zone of the reactor are converted to solid fluorides by reaction with hydrogen fluoride in the upper zone. A charge of 20 pellets (121 g total) was 92 percent reacted at 550 C in only 2.5 hr by a gas stream containing 69 mole percent chlorine in carbon tetrachloride. An equimolar mixture of carbon tetrachloride and chlorine at 550 C has produced higher reaction rates than several other gas mixtures studied.

The reaction of sulfur tetrafluoride with uranium trioxide to form volatile uranium hexafluoride has been suggested as a basis for a possible fuel recovery scheme (ANL-6145, page 93). This reaction might also be considered an alternative for feed materials production. The overall reaction is considered to be: $\text{UO}_3 + 3\text{SF}_4 \rightarrow \text{UF}_6 + 3\text{SOF}_2$. One exploratory two-part run was made in a 2-in.-diameter fluid-bed reactor to supplement the results gained in the laboratory (ANL-6231, page 99).

The conversion of uranium hexafluoride to uranium dioxide by a two-step fluid-bed process is being studied in order to develop a simpler method for preparation of ceramic reactor fuel. The major problem in the first step, reaction of the hexafluoride with steam to form uranyl fluoride, continues to be fines formation. Proper sizing of starting beds assures particle growth (average particle diameter of $250\ \mu$ or coarser); however, continuous operation requires a seed particle feed stream to maintain bed fluidity. Regulation of the rate of seed particle addition to offset growth without entering the region of fines formation (average bed diameter less than $250\ \mu$) has not been successful due apparently to the continuous formation of small amounts of fines partially offsetting seed particle requirements. Runs made at hexafluoride feed rates of 100 g/min [174 lb uranium/(hr)(sq ft)] have been extended to seven hours before interruption by fines formation. The effect of starting bed particle size on fines formation was investigated in a number of short runs.

The reduction of uranyl fluoride to uranium dioxide is being studied in a series of batch fluidization runs in a 3-in.-diameter fluid-bed reactor. A mixed gas of steam and hydrogen gave much faster conversion than hydrogen alone. A typical product from a run was 3 kg of powder containing 210 ppm residual fluoride (specification grade). This was prepared in 5 hr at 650 C using a gas stream of three parts hydrogen to one part steam.

Fluid-bed calcination studies have been initiated in small-diameter columns in an attempt to reduce the overall gas requirements for these units and thus reduce the off-gas handling problems. This technique employs the atomizing and feed decomposition gases as the primary fluidizing medium by installing the spray nozzles in the apex of the cone-bottom reactors. The small-diameter aspect has application to the calcination of plutonium solutions, for which nuclear criticality considerations are necessary.

A mass transfer study using the silica gel-water system has been completed in the 6-in.-diameter multistage fluidization column designed to achieve controlled downward transport of solids without the use of internal downcomers. Murphree efficiencies of nearly 100 percent were obtained.

A. Laboratory Investigations of Fluoride Volatility Processes (J. Fischer)

1. The Kinetics and Mechanism of the Thermal Decomposition of Plutonium Hexafluoride* (L. Trevorrow, W. Shinn)

Plutonium hexafluoride undergoes thermal decomposition to plutonium tetrafluoride and fluorine. Knowledge of the equilibrium constants and rates for the thermal decomposition reaction of plutonium hexafluoride is important in the development of processes for recovery of plutonium from spent nuclear fuels by fluoride volatility techniques. Both the stoichiometry and the equilibria involved in the decomposition of plutonium hexafluoride have been investigated previously.²¹ In the present work, the rate of thermal decomposition of plutonium hexafluoride vapor has been studied by a static method at initial pressures of 14 to 110 cm Hg and at temperatures of 140, 161, and 173 C.

The plutonium hexafluoride used in the decomposition rate studies was prepared by reacting fluorine, at 400 to 550 C, with plutonium dioxide or plutonium tetrafluoride obtained from AEC sources. Figure 33 is a schematic diagram of the fluorination system. Fluorine at about one atmosphere pressure was preheated and circulated by means of a magnetic piston pump over the plutonium compound, in a nickel boat, within a tubular nickel reaction furnace. The volatile plutonium hexafluoride was collected in nickel traps, cooled with dry ice.

²¹Trevorrow, L., Shinn, W. A., and Steunenberg, R. K., J. Phys. Chem., in press.

*The experimental procedures and some preliminary data have been reported previously. For the sake of clarity and unity some of this information is included in this report. The data and conclusions of this report supersede any previously reported.

FIGURE 33
APPARATUS FOR PLUTONIUM HEXAFLUORIDE PREPARATION

All parts of the equipment exposed to fluorine and plutonium compounds were constructed of nickel or Monel. Component parts of the apparatus were connected by manifold systems to a high-vacuum system consisting of mechanical and oil diffusion pumps, to a helium supply, to a fluorine supply, and to pressure measuring devices, such as Bourdon gages and diaphragm pressure transmitters. Nickel valves, flare fittings, and silver-soldered and welded joints served to connect the various components of the apparatus. All of the equipment was pretreated with fluorine before use.

There is no change in the number of gas molecules during the thermal decomposition of plutonium hexafluoride vapor:

Therefore, it is not possible to follow the rate of decomposition of the vapor by pressure measurements in a static system. Since the deposition of plutonium tetrafluoride would interfere with measurement of the partial pressure of plutonium hexafluoride, many of the common physical methods which might be used to follow the reaction continuously are rendered inapplicable.

Rates of decomposition were obtained from initial and final compositions after heating a sample of plutonium hexafluoride for a given period. Prior to each experiment, the storage vessel containing the plutonium hexafluoride was evacuated to a pressure of about 2×10^{-4} mm at -196°C to remove fluorine accumulated from radiation decomposition. The plutonium hexafluoride was then transferred by vacuum distillation to a supply vessel where it was condensed, and any remaining fluorine was

removed by evacuation at -196°C . The 50-ml supply vessel was connected by a manifold to a 50-ml decomposition vessel which had been weighed previously. The supply vessel and associated lines were heated to about 70 to 80°C in order to aid the transfer of adequate quantities of plutonium. At these temperatures the rate of decomposition of the hexafluoride was extremely slow. The vessel was preheated to the experimental temperature in a thermostated aluminum block wound with Nichrome wire. The temperature of the decomposition vessel was held constant to $\pm 0.2^{\circ}\text{C}$. An experiment was initiated by opening the valve to the evacuated decomposition vessel, and allowing the warm plutonium hexafluoride to expand into it. The approximate amount of plutonium hexafluoride transferred to the reaction vessel was controlled by PVT measurements. At the end of the experiment, the furnace was lowered, and the decomposition vessel was quenched in liquid nitrogen. The vessel was cooled rapidly to approximately 100°C in one minute and to room temperature in two minutes. Thus, the error introduced by decomposition during the quenching period was small since the quenching period was short and the rate of decomposition decreases rapidly with decreasing temperature. After quenching, the decomposition vessel was warmed to room temperature, and weighed to determine the starting amount of plutonium hexafluoride. The vessel was then evacuated at 25°C to remove plutonium hexafluoride and the fluorine formed during the reaction. The vessel was weighed again to find the weight of plutonium tetrafluoride formed. The weights were used to calculate the amount of plutonium hexafluoride which had decomposed. Partial pressures of plutonium hexafluoride were calculated from the weights by means of the ideal gas law. A single reaction vessel was used for several consecutive experiments. Therefore, each experiment was carried out in the vessel containing plutonium tetrafluoride which had accumulated from previous experiments. A small correction was made to the volume of the vessel to account for the accumulation of plutonium tetrafluoride.

The rate of decomposition of plutonium hexafluoride was studied by the static method in two types of vessels at 161°C . The volumes of the vessels were almost equal, but the ratios of surface to volume were different. In one case the vessel was packed with nickel wool to increase the specific area. For the nonpacked vessel, the surface-to-volume ratio was 1.8 cm^{-1} and the volume was 52 ml. For the packed vessel, the surface-to-volume ratio was 14 cm^{-1} and the volume was 51 ml. The surface-to-volume ratios are values based on geometric measurements.

The first experiment in both vessels yielded very low decomposition rates. The rates increased rapidly as plutonium tetrafluoride was accumulated in the first few experiments for the nonpacked vessel, and then remained almost constant in subsequent experiments. In the packed vessel, the rates increased to a value much greater than those in the nonpacked

vessel containing about the same amount of plutonium tetrafluoride. In the packed vessel, the plutonium tetrafluoride probably was deposited over a greater area on the surface and in the interstices of the nickel wool. It was concluded that the rate of decomposition of plutonium hexafluoride is dependent upon the surface area of plutonium tetrafluoride.

One of the reaction vessels was cut open and the plutonium tetrafluoride was found as a coating on the walls of the vessel and as pieces on the bottom of the vessel. The distribution of the plutonium tetrafluoride was not uniform.

After the deposition of a small quantity of plutonium tetrafluoride in the nonpacked vessel, the rates appeared to be independent of the quantity of plutonium tetrafluoride in the vessel. This was true when the quantity of plutonium tetrafluoride in the vessel varied from about 3 to 6 gm. Because of the manner in which plutonium tetrafluoride accumulated in the vessel, the active surface area of plutonium tetrafluoride did not increase linearly with the weight of plutonium tetrafluoride. It is assumed that for this reason the active solid surface area did not increase significantly throughout the set of experiments in the nonpacked vessel reported here. Thus it was possible to obtain a set of results even though the weight of plutonium tetrafluoride in the reaction vessel was different for each experiment in the set. The results of the rate experiments at 140.1, 160.6, and 173.1 C in the nonpacked vessel are shown in Table 37. The rate was found to be dependent on the pressure of plutonium hexafluoride in the nonpacked vessel.

The experimental results can be expressed by a rate equation which is of concurrent first and zero orders with respect to plutonium hexafluoride pressure:

$$-dp/dt = k_0 + k_1p \quad (2)$$

The experimental procedure used, yielded integrated rates of decomposition; therefore the integrated form of the rate equation,

$$p = p_0 e^{-k_1t} + (k_0/k_1) e^{-k_1t} - (k_0/k_1) \quad (3)$$

where p_0 is the initial pressure and p the partial pressure after reaction time t , was used to correlate the data obtained. Each experiment yielded values of p and p_0 . If the reaction times are held constant for a set of experiments, then Equation 3 shows that p is a linear function of p_0 . Therefore most of the experiments at a given temperature were carried out for the same reaction time but at various initial pressures. The use of constant reaction times permitted the values of k_0 and k_1 to be calculated conveniently. The values of k_1 and k_0 for Equation 3 were calculated from the data of Table 37 by using the method of least squares. The rate constants obtained in this manner are listed in Table 38.

Table 37

RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE VAPOR^a

Static Technique

Initial Volume of Reaction Vessel: 52.0 ml

Nonpacked Reaction Vessel

Temp (C)	Reaction Time (min)	Initial Pressure PuF ₆ (cm)	Observed Final Pressure PuF ₆ (cm)	Observed Integral Rate (cm/hr)	Calculated ^b Final Pressure PuF ₆ (cm)	Deviation (cm)
140.1	120	101.8	86.8	7.5	86.9	+0.1
140.1	120	99.5	85.6	7.0	84.8	-0.8
140.1	120	86.7	73.6	6.6	73.1	-0.5
140.1	120	76.3	62.2	7.1	63.6	+1.4
140.1	120	70.0	56.1	7.0	55.9	-0.2
140.1	120	64.0	52.2	5.9	52.3	+0.1
140.1	120	56.4	45.7	5.4	45.3	-0.4
140.1	120	48.5	37.4	5.6	38.1	+0.7
140.1	120	41.1	30.9	5.1	31.3	+0.4
140.1	120	14.0	7.1	3.4	6.4	-0.7
Avg Dev						±0.4
160.6	90	98.1	70.4	18.5	69.2	-1.2
160.6	90	59.6	37.9	14.5	38.6	+0.7
160.6	90	51.2	31.5	13.1	31.9	+0.4
160.6	90	32.6	16.5	10.7	17.1	+0.6
160.6	90	16.8	5.9	7.3	4.5	-1.4
Avg Dev						±0.9
173.1	60	108.7	74.2	34.5	71.7	-2.5
173.1	60	92.8	59.9	32.9	59.3	-0.6
173.1	60	75.5	43.8	31.7	45.9	+2.1
173.1	60	75.4	46.3	29.1	45.8	-0.5
173.1	60	68.9	39.8	29.1	40.7	+0.9
173.1	60	63.7	35.4	28.3	36.7	+1.3
173.1	60	53.0	27.0	26.0	28.4	+1.4
173.1	60	44.9	20.0	24.9	22.1	+2.1
173.1	60	31.2	13.1	18.1	11.4	-1.7
173.1	60	25.7	8.3	17.4	7.2	-1.1
173.1	60	22.2	6.0	16.2	4.5	-1.5
Avg Dev						±1.4

^aThe quantity of plutonium tetrafluoride in the vessel during these experiments varied from 3 to 6 gm; however, the integral rates did not change as the weight of solid increased in this range.

^bCalculated from rate constants obtained by fitting the data to the equation $-dp/dt = k_0 + k_1p$, using the integrated form

$$p = p_0 e^{-k_1 t} + (k_0/k_1) e^{-k_1 t} - k_0/k_1.$$

Table 38

RATE CONSTANTS FOR THE THERMAL DECOMPOSITION
OF PLUTONIUM HEXAFLUORIDE

Temp (C)	k_0 (cm/min) ^a	k_1 (min ⁻¹)
140.1	$5.58 \pm 0.36^b \times 10^{-2}$	$7.25 \pm 0.53^b \times 10^{-4}$
160.6	$10.9 \pm 0.94^b \times 10^{-2}$	$25.0 \pm 1.8^b \times 10^{-4}$
173.1	$24.2 \pm 1.6^b \times 10^{-2}$	$41.9 \pm 2.8^b \times 10^{-4}$

^aThe reaction surface area of the experimental vessel is implicit in the constant k_0 .

^bThe uncertainty values are calculated probable errors.

The Arrhenius equation and the method of least squares were used to correlate the rate constants with temperature. The equations obtained were:

$$\log k_0 = 7.124 - \frac{3.469 \times 10^3}{T} \quad (4)$$

and

$$\log k_1 = 7.260 - \frac{4.292 \times 10^3}{T} \quad (5)$$

The experimental activation energies were 15.9 ± 1.5 kcal/mole for the zero-order reaction, and 19.6 ± 0.7 kcal/mole for the first-order reaction.

A few experiments were carried out at 150 C. The rate constants at 150 C, calculated from Equations 4 and 5, were used to calculate the final pressure at 150 C using the initial pressures. Both the observed and calculated final pressures were in agreement, as shown in Table 39. The rate constant for the zero-order reaction was dependent on the surface-to-volume ratio, i.e., $k_0 = k_0' (S/V)$. Thus a new rate constant is defined: $k_0' = k_0 (V/S)$, which is independent of the surface area and the gas volume. Laidler²² points out, however, that the constant k_0' is rarely used, since accurate values of surface areas are seldom available. Since measurements of absolute surface areas were not obtained in the present work, the values for k_0 derived from the experimental results must be considered to hold true only for the ratio of specific plutonium tetrafluoride surface to vessel volume used in these experiments.

²²Laidler, K. J., in "Catalysis, Volume I, Fundamental Principles (Part 1)," P. H. Emmett, editor, Reinhold Publishing Corporation, New York (1954) p. 124.

Table 39

THERMAL DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE:
COMPARISON OF OBSERVED WITH CALCULATED RESULTS^a

Temp 150.3 C					
Static Experimental Technique					
Vessel Volume: 52 ml					
Nonpacked Vessel					
No.	Reaction Time (min)	Initial Pressure PuF ₆ (cm)	Observed Final Pressure PuF ₆ (cm)	Calculated ^b Final Pressure PuF ₆ (cm)	Deviation (cm)
88	120	102.5	77.9	78.9	+1.0
89	120	49.8	31.9	33.0	+1.1
90	90	14.3	6.0	5.4	-0.6
92	90	14.0	6.1	5.1	-1.0
				Avg Dev	<u>±0.9</u>

^aThe weight of plutonium tetrafluoride in the reaction vessel varied from 2.8 gm at the start of Experiment 88 to 3.2 gm at the end of Experiment 92.

^bCalculated from the equation $p = p_0 e^{-k_1 t} + (k_0/k_1) e^{-k_1 t} - (k_0/k_1)$, using

$$\log k_0 = 7.1242 - \frac{3.469 \times 10^3}{T}$$

and

$$\log k_1 = 7.260 - \frac{4.292 \times 10^3}{T}$$

The rates obtained in the packed vessel at 161 C increased with the weight of plutonium tetrafluoride in the vessel. The rate constant k_1 for the homogeneous reaction, derived from experiments in the non-packed vessel at 161 C, was assumed to hold for the rates in both the packed and nonpacked vessels. The value of k_1 was then used together with the results obtained in the packed vessel and Equation 3 to calculate values of k_0 for the rates in the packed vessel (see Table 40). The values of k_0 thus calculated were not constant, but increased in order of the average weight of plutonium tetrafluoride present during an experiment. This is illustrated in Figure 34, which is a graph of k_0 versus the average weight of plutonium tetrafluoride present in the packed vessel.

Table 40

RATE OF DECOMPOSITION OF PLUTONIUM
HEXAFLUORIDE VAPOR AT 161 C

Static Technique

Initial Volume of Vessel: 51.1 ml

Vessel Packed with Nickel Wool

Reaction Time (min)	Initial Pressure PuF ₆ (cm)	Final Pressure PuF ₆ (cm)	Avg Wt PuF ₄ in Vessel (g)	Calculated ^a k ₀ (cm/min × 10 ²)
360	84.8	0.8	0.26	14
90	22.8	0.02	0.58	22
90	89.6	43.0	0.79	35
120	74.3	4.6	1.13	49
30	22.9	6.0	1.39	53
180	103.0	0.7	1.74	45
30	22.3	2.8	2.10	62
90	89.5	3.8	2.41	83
30	69.3	31.9	2.78	111
30	32.9	6.7	2.96	83

^aCalculated by substituting the value of k₁ at 161 C from Table 38 in Equation 3.

FIGURE 34
VARIATION OF ZERO ORDER RATE CONSTANT
WITH WEIGHT OF PLUTONIUM TETRAFLUORIDE
IN PACKED REACTION VESSEL

Since the surface area of plutonium tetrafluoride increases as more solid is deposited in the packed vessel, it serves to demonstrate that the rate of decomposition increases with increase in surface area. If the same amount of plutonium tetrafluoride were deposited in an unpacked vessel, the increase in k_0 would be much less.

The concurrent zero- and first-order dependence of the rate of reactant pressure is similar to that reported for the decomposition of germanium tetrahydride.²³ The first-order dependence can be attributed to the unimolecular, homogeneous decomposition of plutonium hexafluoride in the gas phase, and the zero-order dependence can be attributed to the simultaneous, heterogeneous decomposition of plutonium hexafluoride on the surface of plutonium tetrafluoride saturated by the chemically adsorbed gas.

2. Process Development: Plutonium Fluorination and Transport Studies

(L. Trevorrow, G. J. Vogel, L. Anastasia, R. Kessie, H. Griffin, J. Riha, G. Redding, T. Gerding, and T. D. Baker)

An initial fluorination of oxide fuel will remove a large fraction of the uranium as the volatile hexafluoride in the Direct Fluorination Volatility Process. In a second fluorination step, the remaining uranium and plutonium will be completely converted to the hexafluorides and transferred in the gas effluent from the fluorination reactor to a condenser. It has been shown that the fluorination of plutonium dioxide proceeds with an initial rapid conversion to plutonium tetrafluoride.²⁴ Therefore, the maximum ratio of plutonium hexafluoride to fluorine in the effluent from the fluorination reactor can be estimated from the equilibrium constant for the reaction

The plutonium hexafluoride-to-fluorine ratio in the effluent stream will be equal to or less than the equilibrium constant at the fluorination temperature. Since the equilibrium constant decreases with temperature, the plutonium hexafluoride-to-fluorine ratio in the effluent stream will be greater than the equilibrium constant somewhere in the process line between the fluorination reactor and condenser. This will favor decomposition somewhere along the line. A knowledge of the rate of thermal decomposition of plutonium hexafluoride is important in this step of the process. Since the rate of decomposition also decreases with temperature, the amount of decomposition can be reduced by cooling the effluent gas stream rapidly to a temperature at which the rate of decomposition is slow.

²³Tamaru, K., Boudart, M., Taylor, H., J. Phys. Chem. 59, 801 (1955).

²⁴Steindler, M. J., Steidl, D. V., Steunenberg, R. K., Nuclear Sci. and Eng 6, 333 (1959).

Laboratory preparation of plutonium hexafluoride with high yields (ANL-6287, page 134) is proof in itself that the compound can be recovered efficiently from a fluorination reactor. Plant conditions, however, must be chosen which will permit the maximum recovery of plutonium hexafluoride from the fluorination reactor effluent. Most of the decomposition in the process fluorinator will probably occur in a disengaging section above the fluidized bed. The temperature of this section is expected to range from 550 C at one end to about 150 C at the other end. A considerable portion of the process development program on the laboratory scale has been devoted to a study of the factors affecting the recovery of plutonium from a fluorination reactor.

Several experiments designed to investigate this problem have been reported previously (ANL-6287, page 142 to 144). These experiments consisted of passing plutonium hexafluoride-fluorine mixtures through a heated (550 C) pipe and a length of tubing to a condenser in simulation of process conditions. The quantity of plutonium hexafluoride decomposed in this system was determined by the difference in the weight of plutonium hexafluoride entering the system and that recovered from the system. The results of these experiments showed that 98 to 100 percent of the plutonium hexafluoride which passed through the system could be recovered in the condenser. In the following paragraphs further experiments are described which are pertinent to the problem of decomposition of plutonium hexafluoride under various process conditions.

Decomposition of Plutonium Hexafluoride in the Effluent from Fluorination of Plutonium Tetrafluoride

In further experiments, the quantity of plutonium hexafluoride decomposed was determined by direct weight rather than by differences in the weight of plutonium hexafluoride entering and leaving the system. The plutonium hexafluoride-fluorine mixtures used in these experiments were components of the effluent gas stream from a laboratory-scale fluorination of plutonium tetrafluoride.

The experimental procedure was as follows: Fluorine gas was passed over a sample of plutonium tetrafluoride at 550 C. The resulting gas mixture of plutonium hexafluoride and fluorine was passed through a nickel decomposition vessel, simulating the line which will exist between the fluorination reactor and the condenser in process equipment. The vessel was detached from the system and weighed before and after an experiment to determine the quantity of plutonium tetrafluoride deposited in it. The vessel had been preconditioned with fluorine gas at 350 C for several hours until the weight change for an eight-hour fluorination period was comparable to the weighing error. The plutonium hexafluoride-fluorine mixture was passed from the decomposition vessel through two traps, cooled to -78 C, where the plutonium hexafluoride was condensed. The fluorine was recirculated over the plutonium tetrafluoride in the fluorination boat at 550 C. Figure 35 is a schematic diagram of the system used in these experiments.

FIGURE 35
APPARATUS USED IN FLUORINATION AND RECOVERY OF
PLUTONIUM HEXAFLUORIDE FROM EFFLUENT STREAM

Results of experiments on decomposition of plutonium hexafluoride in the effluent stream are listed in Table 41. The total number of moles of plutonium hexafluoride in the effluent stream leaving the fluorinator was calculated by taking the sum of the moles of plutonium hexafluoride in the cold trap and the moles of plutonium tetrafluoride in the decomposition vessel. The number of moles of fluorine in the effluent stream was calculated from the ideal gas law, with the aid of the average volume flow rate, the total flow time, the average pressure, and the temperature at the flow meter. These calculated values of total moles of plutonium hexafluoride and fluorine were used to calculate the average ratios of moles plutonium hexafluoride to moles fluorine in the effluent stream. Data in Table 41 show that in all experiments, the plutonium hexafluoride-fluorine ratios of the gas mixtures entering the decomposition vessel were much higher than the equilibrium ratio at the temperature of the decomposition vessel. This insured that some decomposition would occur in the decomposition vessel.

It is rather difficult to control the variables in these experiments. However, the work has yielded several useful results. Data from Experiments 17, 19, and 20 are plotted as a function of temperature in Figure 36.

In a comparison of the results of Experiments 28 and 19, the difference in decomposition rates were assumed to be mainly the result of the difference in surface-to-volume ratio. In a comparison of the results of Experiment 17 with the results of Experiments 32A and 32B, the difference in decomposition rates were mainly the result of the difference in surface-to-volume ratio and are partly the result of the differences in plutonium hexafluoride-to-fluorine ratio.

Table 41
DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE IN THE EFFLUENT STREAM
FROM FLUORINATION OF PLUTONIUM TETRAFLUORIDE

Decomposition vessel dimensions: Experiments No. 17, 19, 20, 28, inside diameter 4.76 cm, length 25.1 cm. Vessel packed with nickel wool in Experiment No. 28.

Experiments No. 32A and 32B, inside diameter 4.76 cm, length 6.7. Vessel packed with nickel wool in both Experiments 32A and 32B.

Exp No.	Decomp Vessel Temp (C)	Decomp ^a Vessel Surface-to-volume Ratio (cm ⁻¹)	Avg Mole Ratio PuF ₆ /F ₂ Entering Decomp Vessel	Equilibrium Constant ^a PuF ₆ /F ₂ at Temp of Decomp Vessel	Total Reaction Time (hr)	PuF ₆ Recovered Cold Trap (g)	PuF ₆ Decomp (g)	PuF ₆ Decomp (percent)	PuF ₆ Decomp Rate (g/hr)
19	144 ± 25	1	0.008	0.00033	25.2	23.83	0.093	0.4	0.004
28	152 ± 1	16	0.010	0.00039	23.0	30.66	4.70	13	0.20
20	206 ± 2	1	0.008	0.00087	22.3	19.91	2.32	10	0.10
17	244 ± 30	1	0.008	0.0014	24.2	16.19	5.98	27	0.25
32A	251 ± 3	15	0.012	0.0015	2.0	1.89	1.26	40	0.63
32B	252 ± 2	15	0.015	0.0015	2.0	0.97	3.20	77	1.6

^aANL-6101, page 82.

Experiments 32A and 32B were carried out under similar conditions except that the average mass of plutonium tetrafluoride present in the vessel was 0.56 gm in Experiment 32A and 2.55 gm in Experiment 32B. This further demonstrates that the decomposition rate is dependent on the surface area of plutonium tetrafluoride and supports the fundamental work reported in Section 1, page 133.

In summary, results listed in Table 41 have yielded some information on the change of decomposition rate with temperature. It has been concluded that the rate increases with the surface-to-volume ratio of the vessel, and that the rate is dependent on the surface area of the solid product, plutonium tetrafluoride.

Decomposition of Flowing Plutonium Hexafluoride Vapor at a Partial Pressure of 18 mm

The rate of decomposition of flowing plutonium hexafluoride vapor was studied by another technique in which the variables were more easily controlled. In these experiments a vessel containing several grams

of plutonium hexafluoride was cooled in an ice bath. The vapor pressure of plutonium hexafluoride at the ice point is 18 mm. Plutonium hexafluoride vapor was circulated through a decomposition vessel positioned vertically in a furnace, and then back through the vessel containing the solid plutonium hexafluoride at 0 C. The system was thus filled with plutonium hexafluoride vapor at a constant partial pressure of 18 mm throughout the experiments, even though the total pressure of the system increased as a result of the series of reactions: $\text{PuF}_6(\text{s}) \longrightarrow \text{PuF}_6(\text{g}) \longrightarrow \text{PuF}_4(\text{s}) + \text{F}_2(\text{g})$. Both the rate of pressure rise and the weight of plutonium tetrafluoride deposited in the decomposition vessel could be used to calculate a rate of decomposition. The dimensions of the decomposition vessel were 4.76 cm for the inside diameter and 25.1 cm for the length. The volume of the vessel was about 446 ml. A set of experiments was also carried out in which the vessel was packed with nickel wool to increase the surface-to-volume ratio. In the nonpacked vessel the surface-to-volume ratio was 1.2 cm^{-1} . In the packed vessel the surface-to-volume ratio was 16 cm^{-1} .

Decomposition in Packed and Nonpacked Vessels

Data on the rate of decomposition of plutonium hexafluoride measured by the flow technique in the nonpacked vessel at a partial pressure of 18 mm are listed in Table 42. The changes of total pressure with time are compared in Figure 37 for three different decomposition temperatures. The total pressures are almost a linear function of time; thus the rate of decomposition (tangent to the curve) does not change much during each experiment.* Considering this observation together with the fact that the mole fraction of fluorine in the gas increased from almost 0 to about 0.96 in the experiment at 256 C, it was concluded that the fluorine represses the rate of decomposition to a very small degree. The rates of decomposition at a partial pressure of 18 mm are plotted as a function of temperature in Figure 36.

Data on the rate of decomposition in the packed vessel of plutonium hexafluoride vapor at 18 mm pressure obtained by the gas flow technique are listed in Table 43. The packed vessel had been prefluorinated with fluorine gas at temperatures ranging from 25 to 400 C, but at the start of Experiment 25 the vessel contained no plutonium tetrafluoride. The rise of total pressures with time for decompositions at 150 C are shown for the packed vessel in Figure 38. In Experiment 25 the rate of pressure rise (and therefore the rate of decomposition) was slow at first and gradually increased. This increase of pressure rise in Experiment 25 is interpreted to mean that the rate of decomposition of plutonium hexafluoride vapor is accelerated by the increasing surface area of solid plutonium tetrafluoride on the inner surface of the vessel.

*This is similar to the results obtained with the nonpacked vessel of the static experiments reported in Section 1.

Table 42

RATE OF THERMAL DECOMPOSITION OF PLUTONIUM
HEXAFLUORIDE IN A NONPACKED VESSEL

Gas Flow Technique, Nonpacked 446-ml Decomposition Vessel
PuF₆ partial pressure: 18 mm

Decomposition Temp (C)	Avg Wt PuF ₄ in Decomp Vessel (g)	PuF ₆ Decomposed (g)	Reaction Time (hr)	Integral Decomposition Rate (g PuF ₆ /hour)	
150	15.4	0.60	24	0.025 ^a	0.001 ^b
200	17.2	3.41	23.5	0.145	0.142
256	23.3	10.3	24	0.429	0.430

^aCalculated from the weight of PuF₄ collected in the decomposition vessel.

^bCalculated from the total pressure increase, with correction for radiation decomposition.

Table 43

RATE OF THERMAL DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE
IN A NICKEL WOOL-PACKED VESSEL

Gas Flow Technique

Decomposition Vessel (446 ml) Packed with Nickel Wool

PuF_6 Partial Pressure: 18 mm

Exp No.	Decomp Temp (C)	Average Mass PuF_4 in Decomp Vessel (g)	PuF_6 Decomposed (g)	Reaction Time (hr)	Decomp Rate (g PuF_6 /hr)	
25	150	0.9	1.96	24	0.08 ^a	0.06 ^b
25-II	150	2.7	2.12	7.5	0.28	0.26
27	150	15.1	3.65	5.0	0.73	0.74
26	200	8.5	10.95	10.0	1.09	1.09
30	200	28.2	8.50	8.0	1.06	1.06

^aCalculated from weight of PuF_4 collected in the decomposition vessel.

^bCalculated from the total pressure increase with correction for radiation decomposition.

The increase of total pressure with time in the nonpacked vessel is also shown in Figure 38 for comparison. There was about 16 g of plutonium tetrafluoride in the nonpacked vessel at the start of the experiment. The experiment with the packed vessel started with no plutonium tetrafluoride and ended with about 1.7 g plutonium tetrafluoride in the vessel. The rate in the packed vessel was much higher probably because the plutonium tetrafluoride was distributed over a much larger surface.

In Experiment 25-II the increase of pressure with time appeared to be linear (Figure 38). Also, the rate was about the same as that of the last part of Experiment 25. Other experiments which started with an appreciable quantity of plutonium tetrafluoride in the decomposition vessel do not show an increase of rate during the course of an experiment. This was interpreted to mean that after the deposition of a quantity of plutonium tetrafluoride the increase in surface area of the plutonium tetrafluoride was small even though more plutonium tetrafluoride was formed. Thus the rate of decomposition of plutonium hexafluoride per gram of plutonium tetrafluoride was even smaller.

The rate of decomposition was measured again at 150 C (Experiment No. 27, Table 43) after larger quantities of plutonium tetrafluoride had been added to the vessel. The rate increased with each succeeding experiment.

The rates of decomposition of plutonium hexafluoride at 200 C in two experiments (26 and 30, Table 43) with widely different initial quantities of plutonium tetrafluoride in the vessel were about the same. Both experiments were carried out after a large quantity of plutonium tetrafluoride had been deposited in the vessel. Presumably the point had been reached where further increases of plutonium tetrafluoride surface area were small even though more plutonium tetrafluoride was accumulating in the vessel. Therefore, a large change in the quantity of plutonium tetrafluoride in the vessel would increase the rate of decomposition of plutonium hexafluoride only slightly.

Comparison of Physical Appearance and Bulk Density of Plutonium Tetrafluoride Samples

Two large vessels containing plutonium tetrafluoride were cut open. In one vessel, 25 g of plutonium tetrafluoride had deposited on the walls from the thermal decomposition of plutonium hexafluoride at temperatures of 150 to 250 C. In the other vessel, 34 g of plutonium tetrafluoride had accumulated as a loose powder from the low-temperature alpha-radiation decomposition of plutonium hexafluoride. The object of the experiment was to examine any differences between the physical properties of plutonium tetrafluoride produced by radiation decomposition and that made by thermal decomposition. The physical form, colors, and bulk

densities for the two samples are compared in Table 44. The bulk density of the product of thermal decomposition was 15 to 18 times greater than the bulk density of the product of radiation decomposition. It is clear that there is a great difference in the physical properties of the plutonium tetrafluoride produced by the two methods.

Table 44

COMPARISON OF PHYSICAL PROPERTIES OF PLUTONIUM
TETRAFLUORIDE PRODUCED BY THERMAL AND
RADIATION DECOMPOSITION OF
PLUTONIUM HEXAFLUORIDE

PuF ₄ Source	Physical Form	Color	Bulk Density (g/cc)	Tap Bulk Density (g/cc)
Thermal decomposition of PuF ₆ at 150 to 250 C	mostly small, pointed, crystalline particles; some powder; some chunks - one chunk was about $1 \times \frac{3}{4} \times \frac{1}{8}$ in.	dark reddish-brown	4.2 ^a	4.3 ^a
Radiation decomposition of PuF ₆ mostly at low temperatures (~25 C)	mostly small, feathery particles; a few pea-sized chunks	gray or light green	0.23	0.28

^aThe crystal density of plutonium tetrafluoride is 7.0 g/cc; Zachariassen, W. H., Paper 20.5 of The Transuranium Elements, National Nuclear Series, Division IV, Volume 14B, McGraw-Hill Book Company, Inc., New York (1949).

Also of interest was the observation that the plutonium tetrafluoride produced by thermal decomposition of plutonium hexafluoride could be removed to a large extent from the walls of the vessel by mechanical vibration. This suggests that plutonium tetrafluoride deposited on the walls of the disengaging section above a fluidized bed could be periodically dislodged by mechanical means and returned to the bed for re-fluorination.

Recovery of Plutonium Tetrafluoride Previously Deposited
on Nickel Wool by Thermal Decomposition of Plutonium
Hexafluoride

Experiments on the thermal decomposition of plutonium hexafluoride left a total of 32.1 g of plutonium tetrafluoride in a vessel packed with nickel wool. It was necessary to recover this plutonium for future use. The plutonium tetrafluoride could not be mechanically recovered without cutting the vessel open. If the vessel were opened, the recovery of small particles of the solid from the nickel wool would be extremely difficult. It is possible that an analogous situation may be encountered in the operation of a fluoride volatility separations plant, i.e., a quantity

of plutonium tetrafluoride may deposit at a site in process equipment from which simple mechanical recovery of the solid is impossible. Therefore, it was of interest to demonstrate that the plutonium could be recovered by fluorination.

Fluorine gas was circulated through the vessel, which was heated to various temperatures. The gas was passed through a series of two cold traps cooled to -78°C for condensation of the plutonium hexafluoride produced. The traps were weighed before and after the fluorinations to determine the degree of recovery of plutonium as the hexafluoride. The fluorination was carried out in three steps: Part A at 430°C , Part B at 220°C , and Part C at 450°C . These are average temperatures. The temperature of the vessel was nonuniform in each experiment. The initial volume of the vessel was about 446 ml (~ 1.9 in. in diameter and ~ 9.9 in. in length), and it was packed with 123 g of nickel wool. The calculated total nickel surface area in the vessel was 6100 sq cm.

The conditions and results of the fluorinations are listed in Table 45. Since the plutonium tetrafluoride was probably not distributed uniformly on the surface, the geometric area should not be used to express the fluorination rate as a value per unit of surface area.

Table 45

FLUORINATION AND RECOVERY OF PLUTONIUM PREVIOUSLY
DEPOSITED ON NICKEL WOOL BY THERMAL DECOMPOSITION
OF PLUTONIUM HEXAFLUORIDE

Percentage Recovery

Weight of PuF_4 initially present on nickel wool = 32.1 g

Complete conversion of 32.1 g PuF_4 would yield 36.0 g PuF_6

Percent recovery = $35.2/36.0 \times 100 = 98\%$

No.	Fluorination Time (hr)	Avg Temp ($^{\circ}\text{C}$)	F_2 Flow Rate (cc/min)	PuF_6 Recovered (g)	Fluorination Rate (g PuF_4 /hr) ^c
31A	5	~ 430	~ 283	14.2(0.1) ^a	2.5
31B	10	~ 220	~ 456	3.4(0.1)	0.3
31C	16 ^b	~ 450	~ 500	17.6(0.3)	2.2 ^b
				35.2 total	

^aCorrection, grams, to account for radiation decomposition of PuF_6 .

^bA sharp break in the graph of fluorine consumption versus time indicated that most of the material was completely fluorinated after 7.1 hr. This time was used for calculation of the fluorination rate.

^cRate calculated from weight of PuF_6 recovered.

After completion of the fluorination, the vessel was cut open for an examination of the interior. The nickel wool was intact. The surface of the walls and the nickel wool were covered with a dull, thin, gray-green film.

The fluorination rate at 450 C appears to be lower than that at 430 C. This was probably caused by the nonuniformity of the temperature of the vessel and the nonuniformity of distribution of plutonium tetrafluoride in the vessel. Thus it is possible that a major fraction of the plutonium tetrafluoride in Part C of the fluorination was at a much lower temperature than the nominal average vessel temperature of 450 C. The more important result of these experiments is the demonstration that a large quantity of plutonium tetrafluoride which has deposited in equipment can be fluorinated to plutonium hexafluoride at a practical rate with high percentage recoveries. In this case 98 percent of the plutonium was recovered.

Summary of Results on Recovery of Plutonium from the Fluorination Reactor

The following results have been obtained from experiments on the laboratory scale relating to the problem of recovery of plutonium from the fluorination reactor:

(a) The rate of decomposition of plutonium hexafluoride in flowing gas streams has been determined at temperatures ranging from 150 to 250 C. The rate of decomposition depends on the surface area of plutonium tetrafluoride in the equipment. Since the surface area of the plutonium tetrafluoride was not measured, it is not possible to make an exact extrapolation to the conditions of large-scale process conditions. It should be possible, however, to extrapolate the rates obtained in the laboratory by scaling up both the quantities of plutonium tetrafluoride present in equipment and the wall areas to give an estimate of the rate of decomposition in process equipment. The surface area of plutonium tetrafluoride will not be a linear function of the quantity of plutonium tetrafluoride in a piece of equipment but will vary with the particular distribution of the solid on the walls of equipment. The distribution of the solid can be expected to be nonuniform.

(b) The thermal decomposition of plutonium hexafluoride at temperatures from 150 to 250 C produced crystalline deposits of plutonium tetrafluoride which could be removed by mechanical vibration. It is probable that deposits of plutonium tetrafluoride in the disengaging section of a fluidized bed could be dislodged by mechanical vibration to fall back into the bed for re-fluorination.

(c) Deposits of plutonium tetrafluoride which cannot be removed by mechanical means can be removed by re-fluorination and this can be done efficiently at temperatures between 430 and 450 C.

3. The Reaction of Plutonium Hexafluoride and Bromine
(M. J. Steindler, D. V. Steidl, T. Gerding)

A thorough knowledge of the chemical properties of plutonium hexafluoride is required for the development of fluoride volatility processes. Differences in the chemical behavior of plutonium and uranium hexafluorides may be utilized in the separations processes.

The oxidizing power of plutonium hexafluoride is one of the properties of this substance which illustrates a usable difference between the hexafluorides of uranium and plutonium. A study of the reaction between sulfur tetrafluoride and plutonium hexafluoride, reported previously (ANL-6231, page 96), indicated that, although the reaction proceeds quantitatively at slightly elevated temperatures, the corresponding reaction with uranium hexafluoride does not proceed. It is, therefore, possible to utilize this reaction for separating plutonium hexafluoride from uranium hexafluoride.

The reaction of elemental bromine and plutonium hexafluoride has been investigated with the same general aims. It has been possible to establish the stoichiometry of the reaction, make some observations on the rate of the reaction, and to demonstrate the utility of the reaction for the separation of uranium and plutonium hexafluorides from each other.

The experimental procedure was as follows. Plutonium hexafluoride, prepared by the fluorination of the tetrafluoride was checked for purity by measuring the vapor pressure at the ice point ($P_{\text{calc}} = 18 \text{ mm}$, $P_{\text{obs}} = 19 \text{ mm}$).²¹ Reagent grade bromine was purified by trap-to-trap distillation and the purity checked by measurement of its vapor pressure at the ice point ($P_{\text{calc}} = 63.3 \text{ mm}$, $P_{\text{obs}} = 65 \text{ mm}$).²² The reagents were distilled at low pressures into a tared nickel reaction vessel which had been previously pretreated with elemental fluorine and also with plutonium hexafluoride. At the end of the reaction time, the unreacted reagents were hydrolyzed in water and plutonium determined.

In those experiments in which the gaseous products were identified by infrared spectroscopy, a 10-cm nickel cell equipped with silver chloride windows was used to contain the gases. The infrared spectrophotometer (Beckman IR-4) was calibrated prior to use by the air spectrum (H_2O , CO_2).

²¹Weinstock, B., Weaver, E. E., and Malm J. B., J. Inorg. and Nucl. Chem. **11**, 104 (1959).

²²Fischer, J., and Bingle, J., J. Am. Chem. Soc., **77**, 6511 (1955).

The reaction between bromine and plutonium hexafluoride carried out at ambient temperatures, as summarized in Table 46, does not proceed to completion. No explanation can yet be given for the large differences in the extents of reaction observed in the data of Table 46. When the reaction was carried out at approximately 80 C, however, essentially complete reaction was observed in one hour or less.* Table 47 summarizes the data obtained at elevated temperatures. In the absence of direct data on the kinetic effect of varying bromine concentrations no more definitive comments on the rate of reaction may be made.

Table 46

EXTENT OF REACTION OF PLUTONIUM HEXAFLUORIDE
AND BROMINE

Temperature: Ambient (approximately 30 C)

Initial PuF ₆ (millimoles)	Initial Br ₂ (millimoles)	Time (hr)	PuF ₄ (millimoles)	% Reacted
0.24	0.088	18	0.01	4
0.24	0.59	21	0.03	12
0.23 ^a	0.075	17	0.11	48
0.21 ^a	0.066	17	0.15	71
0.25	0.26	17	0.03	13

^aPreviously reported in ANL-6287, page 143.

Table 47

EXTENT OF REACTION OF PLUTONIUM HEXAFLUORIDE
AND BROMINE AT 78 C

Time: 1 hr

Initial PuF ₆ (millimoles)	Initial Br ₂ (millimoles)	PuF ₄ (millimoles)	PuF ₆ unreacted (millimoles)
0.21 ^a	0.29	0.21	0.009
0.088 ^a	0.65	0.084	-
0.28 ^a	0.079	0.25	0.004

^aPreviously reported in ANL-6287, page 143.

*No reactions were carried out for less than one hour and thus only an upper limit to the time necessary for complete reaction is available.

Although the data on the weight change of the reaction vessel strongly indicated that the plutonium product of the reaction was plutonium tetrafluoride, more positive identification was desirable. Attempts to obtain X-ray diffraction patterns of the solid product failed. This work, as well as previous experience, indicated that solids produced by the reduction of plutonium hexafluoride at low (less than 150 C) temperatures are microcrystalline or amorphous and do not yield identifiable diffraction patterns.

As previously reported in ANL-6287, page 143, an experiment in which approximately equal molar quantities of bromine and plutonium hexafluoride were reacted at 78 C for two hours produced a light buff-colored solid. Chemical analysis of this solid gave a fluorine to plutonium ratio of 4.11, indicating that the solid product of the reaction is indeed plutonium tetrafluoride.

In order to establish the identity of the gaseous products of the reaction, samples of the gas phase were analyzed by infrared spectroscopy. Data from the literature^{23,24,25} as well as standards prepared in the apparatus used for the experiments were compared with the gaseous products of the reaction. Samples of bromine used in the experiments were scanned to determine the absence of infrared-absorbing impurities. None was found. The results of the experiments, summarized in Table 48, indicate that the reaction of plutonium hexafluoride and bromine produces bromine pentafluoride. The presence of bromine trifluoride in the gaseous products from reactions carried out at slightly elevated temperatures may be explained as being formed by the secondary reaction of bromine and bromine pentafluoride.²³ It appears unlikely, however, that the mechanism of the reaction between bromine and plutonium hexafluoride involves the direct formation of bromine pentafluoride. Thus it may be suggested that the reaction proceeds as follows:

Although all but Reaction 1 have been demonstrated, the possibility of as yet unidentified intermediates cannot be completely eliminated. More light may be shed on the mechanism by a careful study of the kinetics of the reaction. The use of a heated infrared cell represents a possible approach to the detection and measurement of the rates of formation of the several bromine fluorides.

²³Stein, L., J. Am. Chem. Soc. 81, 1273 (1959).

²⁴Claassen, H. H., Weinstock, B., and Malm, J. G., J. Chem. Phys. 28, 285 (1958).

²⁵Malm, J. G., Weinstock, B., and Claassen, H. H., J. Chem. Phys. 23, 2192 (1955).

Table 48

ANALYSIS OF THE GAS PHASE AFTER REACTION OF
PLUTONIUM HEXAFLUORIDE AND BROMINE

Initial PuF ₆ (millimoles)	Initial Br ₂ (millimoles)	T (C)	Time (hr)	PuF ₄ (millimoles)	Gas Phase IR Analysis
0.64	0.29	84	2	0.64	BrF ₅ , BrF ₃
0.41	0.42	30	19	0.38	BrF ₅ only
		50	1		
0.73	0.70	27	1	0.76	BrF ₅
		53	1		BrF ₅ , trace BrF ₃
0.60	0.29	27	22		BrF ₅ , PuF ₆
		83	1	-	BrF ₅ , BrF ₃
		27	17		BrF ₅ , BrF ₃ ^a
0.78	0.66 BrF ₃	180	20	0.65	BrF ₅ , trace BrF ₃

^aThe quantity of BrF₃ increased after exposure at 27 C and 17 hours.

The application of the reaction of bromine and plutonium hexafluoride to the separation of uranium from plutonium was briefly investigated. Mixtures of uranium hexafluoride and plutonium hexafluoride were treated with bromine and the gaseous products analyzed to determine their uranium and plutonium content. Although the data summarized in Table 49 (previously reported in ANL-6287, page 144) reflect experimental difficulties attending the manipulation of mixtures of uranium hexafluoride, plutonium hexafluoride and bromine, it may be concluded that the separation of uranium hexafluoride from plutonium hexafluoride by the reduction of the latter is applicable to process conditions.

Table 49

REACTION OF MIXTURES OF PLUTONIUM HEXAFLUORIDE AND
URANIUM HEXAFLUORIDE WITH ELEMENTAL BROMINE

Time: 2 hr

Initial PuF ₆ (millimoles)	Initial UF ₆ (millimoles)	Initial Br ₂ (millimoles)	Temp (C)	PuF ₄ (millimoles)	Volatile Products	
					U (millimoles)	Pu (millimoles)
0.61 ^a	7.7	0.67	80	0.72	8.0	0.006
0.32 ^a	2.8	0.40	94	0.35	2.8	0.008

^aPreviously reported in ANL-6287, page 144.

In summary, the reaction of plutonium hexafluoride and bromine has been studied from several viewpoints. It has been shown that the primary products of the reaction are plutonium tetrafluoride and bromine pentafluoride. At ambient temperatures excess bromine remains mostly unreacted, whereas at higher temperatures a secondary reaction between bromine and bromine pentafluoride produces bromine trifluoride. Finally, the reduction of plutonium hexafluoride has been shown to be applicable to process conditions for the separation of uranium hexafluoride from plutonium hexafluoride. There is at present a very low specification for bromine in cascade-grade uranium hexafluoride (1 ppm). This factor would tend to discourage the use of bromine in separation of uranium hexafluoride and plutonium hexafluoride if the material is to be processed in the diffusion plant.

4. Fluorination of Uranium Dioxide-Ruthenium-106 and Uranium Dioxide-Niobium-95 Mixtures
(H. A. Porte and M. J. Steindler)

The first step in the Direct Fluorination Volatility Process is the removal of the fuel cladding. Next, the oxides are fluorinated to their respective fluorides. Since uranium dioxide is converted to uranium hexafluoride at a faster rate (ANL-5924, page 28) than plutonium dioxide is converted to plutonium hexafluoride,²⁶ the majority of uranium will be volatilized before significant amounts of plutonium are removed from the fuel, thus affording a partial separation of uranium and plutonium. The relative rates of fluorination of ruthenium and niobium were not known with respect to uranium. Ruthenium and niobium are fission products of particular interest because they contribute a significant amount of the total fission product activity and they have volatile fluorides.*

It was the purpose of this investigation to determine whether these fission products would be volatilized and carried over with the bulk of the uranium or remain with the plutonium. To study this problem, a series of uranium dioxide-ruthenium and uranium dioxide-niobium mixtures were prepared, and the relative rates of removal of fission product and uranium from the mixture were determined.

The mixtures were prepared by an adaptation of the method of Wilson.²⁷ Approximately 20 g of uranyl nitrate hexahydrate was dissolved in 100 ml of water producing a solution 0.6 M in uranyl ion. One to two millicuries of carrier-free niobium-95 or ruthenium-106 were then

* RuF_5 , b. p. 313 C; NbF_5 , b. p. 233 C.

²⁶Steindler, M. J., Steidl, D. V., and Steunenbergh, R. K., Nuclear Sci. and Eng. 6, 333 (Oct 1959).

²⁷Wilson, A. S., HW-55319 (March 1958).

added, and ammonium diuranate was precipitated by the addition of 40 ml of concentrated ammonium hydroxide, which coprecipitated niobium-95 or ruthenium-106. Carrier-free niobium-95 and ruthenium-106 were obtained from Oak Ridge National Laboratory. In one batch, 40 mg of inactive ruthenium carrier were also added. An experiment in which the supernate was counted showed that 95 percent of the ruthenium activity coprecipitated with the uranium. The solids were filtered by means of suction through a medium-grade sintered glass filtering funnel. The yellow precipitate was dried in air at room temperature and then further dried overnight at 110 C to yield an orange solid. The precipitate was reduced at 900 C for 4 hr in a 40 volume percent hydrogen in nitrogen gas stream with a flow rate of 400 cc/min. A dark-brown uranium dioxide was produced, which very often converted rapidly to black U_3O_8 on exposure to air. In such cases, the reduction procedure was repeated. A typical analysis of the uranium dioxide product gave: U^{+4} , 82.2%; U^{+6} , 5.7% (theoretical value for $UO_{2.00}$ is U^{+4} , 88.17%).

The apparatus used in this work is shown in Figure 39. It consisted of a reaction tube connected in series with two cold traps, a bubbler, and two traps filled with activated alumina used for disposal of fluorine. The entire apparatus was made of nickel except for the bubbler, which was made from Fluorothene, and the activated alumina traps, which were of copper. Mixtures of high-purity fluorine and dry helium were prepared in a 4-liter supply vessel by adding suitable volumes of the two gases. The mixture was allowed to stand at least 16 hr before it was used.

FIGURE 39
APPARATUS FOR FLUORINATION OF URANIUM DIOXIDE-FISSION PRODUCT MIXTURES

The gas flow rate was adjusted to approximately 50 cc/min 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 activated alumina traps.

Approximately one gram of the uranium dioxide-ruthenium-106 or uranium dioxide-niobium-95 mixture was weighed in a nickel reaction boat for each experiment. The sample was heated to the desired temperature in a flowing helium atmosphere. The reaction boat and contents were weighed again after the experiment. The amount of uranium remaining in the residue was computed on the basis that the residue was uranyl fluoride, as had been shown by X-ray diffraction analysis.

The amount of ruthenium or niobium volatilized was determined by counting the gamma rays from the mixture in the reaction boat before and after each experiment. A Harshaw Chemical Company Type 8S8/2 Integral Line scintillation detector consisting of a thallium-activated sodium iodide crystal (2-in. diameter and 2 in. thick) directly attached to a photomultiplier tube was employed. The rest of the instrumentation consisted of a preamplifier, a linear amplifier, a single-channel pulse-height analyzer, and a count-rate meter. The detector was shielded from background in the laboratory by a $2\frac{1}{2}$ -in.-thick lead shield (Figure 39). The beam from the reaction boat was collimated by two lead plugs with $1\frac{1}{2}$ -in. and 1-in. openings.

The usual procedure was to count the furnace tube, the empty boat, and finally the boat plus sample before each experiment. After the experiment, the procedure was to count the boat plus residue, the empty boat, and finally the furnace tube. It was necessary to follow this procedure to determine the quantity of activity left in the residue, since ruthenium had the tendency to deposit on the reaction boat and on the furnace tube in the vicinity of the boat.

The experimental results are summarized in Table 50. Fluorinations of uranium dioxide-ruthenium-106 mixtures were carried out at 400 and 500 C. It was originally intended to follow the removal of ruthenium activity from the mixture as a function of time. However, after the first experiment it became apparent that an appreciable amount of ruthenium activity which was fluorinated out of the mixture remained on the boat or on the furnace tube in the vicinity of the boat. This may be due to thermal decomposition of ruthenium pentafluoride to nonvolatile products or to reaction of ruthenium pentafluoride with the nickel boat or furnace tube. After each ruthenium experiment, the residual activity was removed by passing fluorine over the boat at 575 C for two hours.

Table 50

FLUORINATION OF URANIUM DIOXIDE-RUTHENIUM-106 AND
URANIUM DIOXIDE-NIOBIUM-95 MIXTURES

Total Pressure: 1 atm

Gas Mixture: Fluorine and helium as indicated

Experiment	Sample ^a	Sample Weight (mg)	Temp (C)	Time (min)	Gas ^{b,d} Flow Rate (cc/min)	U Left in Residue ^c (%)	Activity Remaining		
							in Residue (%)	on Boat (%)	on Furnace Tube (%)
1	U-Ru1	1076	400	30	42	32	e	e	e
2	U-Ru2	852	400	30	61	f	f	27	44
3	U-Ru2	1000	400	30	37	46	15	16	26
4	U-Ru2	1255	500	20	72	f	f	1	0
5	U-Ru2	1020	500	30	26	32	19	23	35
6 ^g	U-Ru2	959	500	30	85	0	0	6	1
7 ^h	U-Ru2	1001	500	30	54	5	1	30	15
12	U-Ru3	961	500	20	34	51	58	7	4
13	U-Ru3	1050	500	22	53	f	f	17	11
8	U-Nb1	1012	300	75	34	86	56	1	1
9	U-Nb1	1075	400	20	43	59	8	1	1
10 ^h	U-Nb1	1038	500	30	32	8	4	1	1
11 ^h	U-Nb1	980	500	30	52	0	1	1	1

^aU-Ru1 contains 1 mg inactive Ru carrier/g UO₂,
 U-Ru2 contains 65 μ c Ru¹⁰⁶/g UO₂,
 U-Ru3 contains 119 μ c Ru¹⁰⁶ and 2.5 mg inactive Ru carrier/g UO₂,
 U-Nb1 contains 95 μ c Nb⁹⁵/g UO₂

^bFor conversion to linear flow: 1.96 cc/min = 1 cm/min

^cCalculated on the basis that residue is UO₂F₂. Residue from Experiment 1 analyzed by X-ray diffraction and found to contain only UO₂F₂ (no UO₂ detected). Residue from Experiment 6 analyzed by X-ray fluorescence and found to contain 0.2% U.

^dGas composition was 25 v/o F₂ in all runs except 2 and 4 where it was 75 v/o F₂.

^eNot applicable.

^fNo residue left.

^g360 mg CaF₂ and 230 mg ZrF₄ added to sample.

^h600 mg CaF₂ and 460 mg ZrF₄ added to sample.

With pure fluorine or 75 v/o fluorine-25 v/o helium, uranium dioxide fluorinated rapidly at 400 C, and therefore it was necessary to dilute the gas to a 25 v/o fluorine-75 v/o helium mixture in order to carry out experiments of at least 20-min duration.

At both 400 and 500 C, the percent ruthenium fluorinated out of the uranium dioxide-ruthenium mixture was equal to or greater than the percent uranium volatilized. The addition of inactive ruthenium carrier (Experiments 12 and 13) did not increase the rate of ruthenium removal from the sample.

A mixture of calcium fluoride and zirconium fluoride has been considered as a heat transfer medium in the fluidized-bed fluorination reactor to be used for the Direct Fluorination Volatility Process. In several experiments, some calcium fluoride and zirconium fluoride was added to the uranium dioxide-ruthenium mixture to see whether ruthenium activity would remain in the inert bed material. No activity appeared to remain in the bed and it was concluded that there was no reaction between ruthenium and the calcium fluoride-zirconium fluoride mixture.

The fluorination of uranium dioxide-niobium-95 mixtures was studied in the temperature range from 300 to 500 C. The same conclusions were reached as in the ruthenium study: First, niobium is readily fluorinated out of uranium dioxide and, second, there is no reaction between niobium and the calcium fluoride-zirconium fluoride bed material. Niobium differed from ruthenium in that very little ($<1\%$) of the niobium activity remained on the reaction boat or on the furnace tube in the vicinity of the boat.

5. Kinetics of the Reaction of Uranium Trioxide and Uranyl Fluoride with Sulfur Tetrafluoride
(C. Johnson, J. Stockbar)

The investigation of the stoichiometry of the reactions of sulfur tetrafluoride with uranium trioxide and uranyl fluoride was summarized in ANL-6231, page 99. In the current work, studies were made of the kinetics and mechanism of the reaction between sulfur tetrafluoride and uranium trioxide or uranyl fluoride.

A Sartorius Selecta thermobalance was used for the kinetic studies. A continuous record of weight change versus time was obtained on a Bristol Dynamaster recording potentiometer. A sample pan was suspended, by a nickel chain in the reaction chamber, from the stirrup of the balance. The reaction chamber was fabricated from a 2-in. nickel pipe and was heated by a resistance-wound furnace. Hot convection currents from the furnace were kept out of the balance by a baffle and gas-blanket arrangement. The Sartorius balance was protected from attack by corrosive gases by keeping a small positive pressure of argon in the balance at all times.

A gas-distribution manifold attached to the reaction chamber allowed choice of reaction gas, whose flow rate was measured with a calibrated thermal flow meter. The gases passed through a preheat furnace prior to entering the reaction furnace. The sample temperature was

measured by a calibrated thermocouple positioned directly beneath the sample pan. A record of the sample temperature versus time was obtained on a multipoint-recording potentiometer. In addition, the temperatures of the preheat furnace and reaction furnace, and the output of the thermal flow meter were monitored continuously.

In a typical experiment, 400.0 mg of a -200 + 230 mesh fraction of either uranium trioxide or uranyl fluoride was placed on a tared platinum pan and then lowered into the preheated reaction chamber. The weight of sample plus pan was checked on the Sartorius balance while temperature equilibrium between gas and solid was being attained. During this period, argon was purged through the reaction chamber. When temperature equilibrium had been achieved, the purge gas was shut off and sulfur tetrafluoride was allowed to flow through the reaction chamber at a flow rate of 150-200 cc/min.

Each experiment was performed under conditions of constant temperature and constant total flow of reacting gas. The gas manifold, connected to the reaction chamber, was equipped with a 14-liter ballast tank which was charged with various mixtures of nitrogen and sulfur tetrafluoride. The gas mixture was then passed over the sample at atmospheric pressure at a constant flow rate.

If the reaction between a solid and a gas is one in which the active sites of the surface of a solid is saturated with gas molecules, the rate of reaction should be zero order with respect to the pressure of the reactant gas. If this is not the case, the rate will be fractional or higher order. At constant pressure, the rate of such a process will be proportional to the area of the interface at any time during the reaction. A system of solid and gas may be idealized by assuming the solid to consist of spherical particles of uniform size with reaction starting at $t = 0$ on all particles. In such a reaction the following relationship can be deduced.²⁸

If the initial mass of a solid particle, $M_0 = (\frac{4}{3})\pi r_0^3 \rho$, where r_0 is the initial radius and ρ the bulk density, the rate of reduction in mass at a given temperature maybe assumed to be proportional to the surface area of the particle:

$$\frac{dM}{dt} = k4\pi r^2 \quad , \quad (5)$$

where r is the radius of the particle at time t and k is the constant for a given temperature and partial pressure of reactant gas.

²⁸Anderson, J. S., Bull. Soc. Chem., 20, 781 (1953).

The fraction of reaction F that has taken place in time t is given by

$$F = \frac{M_0 - M}{M_0} = 1 - \left(\frac{r}{r_0}\right)^3 .$$

When this is substituted in Equation (5) the latter becomes

$$\frac{dM}{dt} = -k \, 4\pi r_0^2 (1-F)^{2/3} . \quad (6)$$

Integration of expression (6) yields

$$(1-F)^{1/3} = 1 - k't , \quad (7)$$

where $k' = k/r_0$.

When the quantity $(1-F)^{1/3}$ is plotted against time for a typical experiment, as shown in Figure 40, the points lie on a straight line, in agreement with the equation, except that there is some deviation at the beginning and the end of the reaction. Experimental conditions govern the deviations at the beginning of each experiment. The reaction chamber is full of argon at the start of each experiment; therefore, it is believed that at least five minutes are needed for displacement of argon by sulfur tetrafluoride to take place. Consequently, the rates will be abnormally low at the beginning of each run.

Deviation from the expected kinetics at the end of the reaction may be caused by a number of variables, not the least of which is the small amount of sample remaining. Chemisorption of sulfur tetrafluoride on the surface of the remaining solid may contribute significantly to the final weight of the sample, thereby biasing the results.

The results of a typical reaction of sulfur tetrafluoride with uranium trioxide is shown in Figure 41. The initial increase in weight at the start of the reaction is attributed to the formation of uranyl fluoride. In several experiments in which the reaction was stopped before completion, it was noted that the material remaining in the pan was of two distinct phases: the top 60 percent was pale yellow in color, the lower material orange. Chemical analysis confirmed an uptake of fluorine. X-ray diffraction analysis indicated the yellow material to be anhydrous uranyl fluoride and the orange material to be unreacted uranium trioxide.

Thermobalance data on the reaction of sulfur tetrafluoride with uranyl fluoride, also shown in Figure 41, gave no indication of increase in weight prior to formation of volatile uranium hexafluoride. If an intermediate such as UOF_4 does form, it evidently reacts too fast for the anticipated weight increase to be observed.

FIGURE 41
RATE OF FLUORINATION OF URANIUM TRIOXIDE AND
URANYL FLUORIDE WITH SULFUR TETRAFLUORIDE

Early experiments had shown that uranyl fluoride was a product of the first step in the reaction of uranium trioxide and sulfur tetrafluoride; therefore, subsequent work was done using anhydrous uranyl fluoride as the starting material.

The variations of the reaction rate constants k' of Equation 7 with temperature for the reaction of sulfur tetrafluoride at one atmosphere pressure with uranium trioxide and uranyl fluoride are given in Figure 42. The logarithm of the reaction rate constant k' was plotted against the reciprocal of the absolute temperature, from which the activation energy for the reaction of uranyl fluoride with sulfur tetrafluoride was calculated to be 32.4 kcal/mole.²⁹ Surface reactions, in general, have activation energies of the order of 5 kcal.

²⁹Glasstone, S., Laidler, K. J., and Eyring, H., Theory of Rate Processes, McGraw-Hill Book Co., Inc., New York, N. Y. (1941).

FIGURE 42
ARRHENIUS PLOT FOR REACTION OF SULFUR TETRAFLUORIDE
WITH URANIUM TRIOXIDE AND URANYL FLUORIDE

The greatest portion of the experimental work was carried out at one atmosphere pressure of sulfur tetrafluoride. In several experiments, however, the partial pressure of sulfur tetrafluoride was varied while keeping temperature and gas flow rate constant. This was done by charging the 14-liter ballast tank with various mixtures of sulfur tetrafluoride and nitrogen. Each gas mixture was then passed over the sample at atmospheric pressure at a constant rate. These data are given in Table 51. A slope of 1.55 obtained from a plot of the logarithm of the rate constant versus the partial pressure of sulfur tetrafluoride in atmospheres illustrates the pressure dependence of the reaction rate constant.

Table 51

REACTION OF SULFUR TETRAFLUORIDE WITH URANYL FLUORIDE:
EFFECT OF PARTIAL PRESSURE OF SULFUR TETRAFLUORIDE
ON THE RATE CONSTANT AT 333 C

Total Pressure: 750 ± 10 mm

Partial Pressure of Sulfur Tetrafluoride (atm)	Flow Rate of SF ₄ (cc/min)	Rate Constant k' (min ⁻¹) ^a
1.0	200	0.0920
0.8	160	0.0435
0.6	120	0.0225
0.3	60	0.00867 ^b
0.2	40	0.00505

^aFrom Equation 7, page 162: $(1-F)^{1/3} = 1 - k't$

^bInterpolated value.

To ascertain whether the pressure dependence of the rate constant was not a dilution effect, additional experiments were run keeping temperature and partial pressure of sulfur tetrafluoride constant and varying the flow rate of gas. These data are given in Table 52. It is evident that if the sulfur tetrafluoride flow rate is greater than 30 cc/min, the rate constant at a fixed temperature and fixed partial pressure of sulfur tetrafluoride becomes independent of flow rate. In all of the experimental work the flow rate of sulfur tetrafluoride varied between 40 and 200 cc/min.

Table 52

REACTION OF SULFUR TETRAFLUORIDE WITH URANYL FLUORIDE:
EFFECT OF GAS FLOW RATE ON RATE CONSTANT

Diluent Gas: nitrogen

Total Flow Rate (cc/min)	SF ₄ Flow Rate (cc/min)	Temp (C)	Partial Pressure of SF ₄ (atm)	Rate Constant k' (min ⁻¹)
36	21.6	362	0.60	0.0202
76	45.6	362	0.60	0.0747
162	97.3	362	0.60	0.0765
240	144	362	0.60	0.0757
57	18.8	360	0.33	0.0151
82	27.1	360	0.33	0.0244
180	59.4	360	0.33	0.0295
278	91.8	360	0.33	0.0268
110	22.0	365	0.20	0.0088
165	33.0	365	0.20	0.0168
266	53.2	365	0.20	0.0172

The rate of fluorination of uranyl fluoride of high surface area from a bed of material about 5 mm deep is shown in Figure 43. The rate constant calculated as a diminishing sphere rate function of $(1-F)^{1/3}$ is plotted vs time. The conversion of uranium trioxide to uranyl fluoride takes place in a relatively thin layer ($\sim 150 \mu$ in depth) of material. It appears that this effect holds also for deep beds of uranyl fluoride. As this reaction zone proceeds downward through the bed, the rate of reaction appears to be linear with time. When the amount of reactant in the pan becomes 350 mg or less (about one particle layer in thickness), the rate of reaction reverts to a diminishing sphere model.

FIGURE 43
EFFECT OF BED DEPTH ON RATE OF FLUORINATION
OF URANYL FLUORIDE WITH SULFUR TETRAFLUORIDE

In considering the total reaction of uranium trioxide with sulfur tetrafluoride, the following mechanism is suggested:

The first step in this mechanism has been demonstrated by chemical analysis and by X-ray diffraction analysis of the reaction product. The reaction is apparently one of solid-phase conversion of uranium trioxide to uranyl fluoride. Unsuccessful attempts were made to observe the reaction boundary between uranium trioxide and uranyl fluoride.

At this time the second and third steps in the mechanism can only be deduced from considerations of steric effects. Stoichiometry studies indicated two moles of sulfur tetrafluoride are needed for each mole of UO_2F_2 converted to UF_6 . In all the experiments for which infrared data were compiled, the only gaseous sulfur product found was thionyl fluoride. Molecular structure evidence indicates the sulfur tetrafluoride molecules to have a configuration approximating a trigonal bipyramid

with one of the three equatorial positions unoccupied (point group C_{2v}). The molecular configuration of thionyl fluoride is thought to be either pyramidal (C_s) or trigonal by pyramid (C_{2v}) in nature. Assuming that the C_{2v} structure predominates in both reactant and product, it is easily seen that each sulfur tetrafluoride molecule contributes only two of its fluorines to the solid. This further suggests that in order for Steps (2) and (3) of the reaction mechanism to take place in a single step, two molecules of sulfur tetrafluoride must simultaneously reside on an active site on the surface of the uranyl fluoride for fluorine oxygen exchange to take place. Because bimolecular gas-solid reactions of this type are extremely rare, some credence is given to the existence of UOF_4 as a reaction intermediate. Attempts at the preparation and isolation of UOF_4 have up to now been unsuccessful. However, the formation of UOF_4 as a reaction intermediate can not be completely ruled out.

B. Engineering-scale Investigations of Fluoride Volatility Processes (A. A. Jonke)

1. Direct Fluorination of Uranium Dioxide Fuels

a. Fluorination of Uranium Dioxide Pellets

(J. Gabor, J. Gates, R. Kinzler, A. Rashinskas, J. Wehrle, and W. J. Mecham)

Pilot plant-scale work has been directed toward the control of the highly exothermic reaction between fluorine and uranium dioxide. Previous work, summarized in ANL-6287 (pages 147 to 152), showed the effects of process variables (temperature, fluorine concentration, bed height) on fluorination rates and fluorine efficiency. It was evident from the data obtained that the fluorination proceeded as a two-step mechanism, with uranyl fluoride fines as an intermediate product, and that pellets with different histories showed different chemical reactivity. Subsequent work has been limited to pellets of the hydrogen-fired type (sintered for 4 hr at ~ 1700 C in a hydrogen atmosphere), which have shown lower reactivity than pellets fired in an inert atmosphere and are believed to be representative of reactor fuel material.

Complete Fluorination of Inert-fired Pellets

A run was made (UOF-25) to investigate the production capacity of the air-cooled reactor while fluorinating uranium dioxide pellets at 500 C and while using as high a fluorine concentration as possible. This was the last run made with pellets of the inert-fired type. In order to use available pellet material, broken pieces of about $\frac{1}{4}$ -in. size were utilized. The pellet bed was 6 in. deep. Magnesium fluoride was used as an inert fluid bed.

In this run, the cooling air was set at the maximum rate and the inlet fluorine concentration was adjusted manually to maintain a temperature of approximately 500 C.

Results of the run are shown in Figure 44. The uranium hexafluoride production rate was determined from cold-trap collections weighed every half hour. The average fluorine inlet concentration (48 percent), the average production rate (1000 g/hr, based on 5.5 hr), and the average fluorine efficiency (52 percent) were calculated from the overall material balance. All but one percent of the uranium was accounted for in the weighed fractions.

FIGURE 44
FLUORINATION OF URANIUM DIOXIDE PELLETS
URANIUM HEXAFLUORIDE PRODUCT COLLECTION
(RUN UOF-25)

Because of the highly exothermic nature of the uranium dioxide-fluorine reaction, temperature control in general imposes a limitation on the allowable reaction rate according to the heat transfer achieved in the reaction zone. In Run UOF-25, the radial temperature difference between the wall and the center of the reaction zone was large, indicating relatively poor heat transfer typical of a static bed rather than the better heat transfer typical of fluid beds. Under the heat transfer conditions in this run, the values obtained for inlet fluorine concentration (48 percent) and uranium hexafluoride production rate (1000 g/hr) are believed to be at or near the maximum allowable for operation at a controlled temperature.

Modification of the Control System to Maximize the Production Rate

Earlier means of automatic temperature control utilized variation of the flow rate of coolant air passing over the external fins on the reactor. Although this system operated usefully under most conditions, it was evident in these tests that the temperature response of the reaction system under coolant regulation was much slower than under fluorine regulation. Also, to achieve maximum reaction rate, the coolant flow would have to be kept at or near its maximum value. Therefore, the control system was modified so that fluorine regulation could be used to provide temperature control while operating at maximum practical fluorination rates.

Two test runs (UOF-26 and 28) were made in the course of setting up this new control system. The final control system is shown in Figure 45. Fluorine from an 18-cu ft storage tank is throttled to provide a constant pressure in a 1.5-cu ft surge tank. Another control valve regulates the fluorine flow from the surge tank to the reactor according to the reactor temperature controller setting.

In one of these test runs (UOF-28), the pellet charge consisted of partially reacted pellets (of the inert-fired type) together with a substantial amount of intermediate uranium fluoride fines in the magnesium fluoride bed. This bed caked at 500 C shortly after fluorine was first introduced, and the run was terminated because of high pressure drop. It is believed that some of the uranium fines in the fluid bed below the pellet-support plate reacted to produce uranium hexafluoride, which in turn reacted with the uranium dioxide pellets higher in the bed. Examination of the caked bed showed pellets cemented together with black, green, and yellow-green material. The black and dark green materials were identified as UF_4 or U_4F_{17} , and the yellow and green

materials as two types of UO_2F_2 .^{*} This type of plugging has occurred only when starting the fluorination with a high concentration of fines, and was not encountered previously. However, it shows a problem that exists under conditions favoring intermediate fluoride formation.

Subsequently, a run (UOF-29) was made in which very satisfactory operation was obtained with the new fluorine control system.

Complete Fluorination of Hydrogen-fired Pellets

The objective of Run UOF-29 was to make a high-rate fluorination at 500 C with nearly maximum air cooling and with temperature control maintained by regulation of the fluorine inlet flow. Nitrogen gas was charged continuously at 0.25 cu ft/min (25 C, 1 atm) so that, even for zero fluorine flow, fluidization would be maintained.

In this run, a 6-in. deep bed of hydrogen-fired pellets was used. The pellets were $\frac{3}{8}$ -in. diameter cylinders, 1 in. in length. The nonequal axis lengths gave a bed of higher void space, and consequently lower pressure drop, compared with previous charges of pellets with equal height and diameter. A 24.5-in.** inert bed of magnesium fluoride (60 to 200 mesh) was also used.

An initial period of fluorination was carried out at the predetermined 500 C control point. However, since the heat generation was not as high as allowable with full cooling, it was decided to operate at 530 C. This latter temperature was maintained as the fluorination was carried to completion.

Temperature profiles obtained during the major part of the run (at 530 C) are shown in Figure 46. The control temperature was measured at the center of the bed (at about the midpoint) by a thermowell entering from the side; the control temperature was maintained within ± 10 C. Through a vertical thermowell (entering from the bottom), the temperature in the bed was measured at about the same elevation, but at a point 1 in. from the wall. The wall temperature was measured through a side-entering thermowell flush with the inside wall of the column. Outside skin temperatures were measured by thermocouple junctions welded on the reactor wall and on one of the cooling fins. The lower half on the column was heated by calrods (3 kw), and the air coolant flow control (butterfly valve) was $\frac{2}{3}$ open. About 20 min after the fluorine adjustment a change in the temperature controller band width was made which reduced the amplitude and frequency of the cycling.

^{*}That is, type "h" and type "A". Brooks, L. H., Garner, E. V., and Whitehead, E., Chemical and X-ray Crystallographic Studies on Uranyl Fluoride, IGR-TN/CA-277 (Feb 9, 1956).

^{**}Measured without pellets.

The substantial temperature difference between the two thermowells in the bed is thought to be due to partial caking. A calculation was made of the effective thermal conductivity of the bed based on the temperature difference between the center of the bed and the inside wall; the calculated thermal conductivity was $0.5 \text{ Btu}/(\text{hr})(\text{sq ft})(\text{F}/\text{ft})$. This value is lower by a factor of about 10 than that obtained under conditions of good fluidization in the mockup heat transfer tests of a packed fluid system (ANL-6287, page 158). In order to make the thermal conductivity calculation, the temperature drop for the film coefficient was subtracted. A value of $30 \text{ Btu}/(\text{hr})(\text{sq ft})(\text{F})$ was assumed for the film coefficient, since this value was found to be typical in mockup tests.

The rates of collection of uranium hexafluoride and of fluorine efficiency obtained during the run are shown in Figure 47. In six hours the pellets were completely fluorinated. The integrated average values of product collection rate, fluorine utilization, and fluorine inlet concentration derived from the data are also given in Figure 47. The average product-collection rate obtained in this run was the highest obtained thus far from a six-inch pellet bed of hydrogen-fired pellets. The six-hour run time shown in Figure 47 applies to the fluorination of only the final fifty percent of the original pellet batch. Therefore, the total time required for complete fluorination of $\frac{1}{2}$ -in. hydrogen-fired pellets is $\sim 12 \text{ hr}$.

A material balance for this run showed 97 percent of the uranium charged accounted for in weighed product fractions. This included one percent of the uranium left in the column at shutdown. The three percent of uranium not accounted for in the fractions weighed is believed to be

about equally divided between condenser losses and fines retention on the upper parts of the column. This magnitude of condenser loss is based on a value of uranium determined in a condenser off-gas sample.

FIGURE 47
URANIUM HEXAFLUORIDE COLLECTION AND FLUORINE ADDITION RATES
DURING FLUORINATION OF URANIUM DIOXIDE PELLETS

The chief result of this run was the demonstration of automatic fluorine regulation to maintain a nearly constant center-of-bed temperature. The lower reactivity of the hydrogen-fired pellets in this run compared with that of the inert-fired pellets in UOF-25 was shown by the difference in uranium hexafluoride production rates under similar conditions. The reaction rate in this run could have been somewhat higher if more cooling air had been used, which would have allowed a higher inlet fluorine concentration. However, the temperature difference from wall to the center of the bed was quite large, indicating rather poor heat transfer conditions, viz, effective bed thermal conductivities of about 10 percent obtained with good fluidization. Thus this run showed satisfactory operation under the conditions which obtained, but should not be taken as indicating the maximum production rates that could be achieved with this system.

Pellet Fluorination Tests under Different Bed Conditions (E. Carls, L. Marek)

Uranium dioxide pellet fluorinations have been carried out in the presence of an inert fluid bed consisting of calcium fluoride or magnesium fluoride particles of 60 to 200 mesh. Because of the possibility that the final fluorination process can generate its own fluid bed of zirconium fluoride produced in the decladding step, it was considered important to demonstrate the fluorination with a bed of this chemical type (Run UOF-27). Also, a fluorination run was made without an inert fluid bed (Run UOF-30).

The objective of Run UOF-27 was to determine whether any special difficulties appeared in the case in which pure zirconium tetrafluoride was used as the inert fluid bed. A two-inch-diameter column was charged with 834 gm of uranium dioxide pellets of the inert-fired type (in a three-inch bed depth) and 1467 gm of zirconium tetrafluoride. The screen analysis and other pertinent data for this material are given in Table 53.

Table 53

SCREEN ANALYSIS OF ZIRCONIUM FLUORIDE
FLUID BED MATERIAL IN RUN UOF-27

Source: ADF Process Run UZr-104 (See ANL-6183, page 113)
drier product ZCP-74HF (See ANL-6145, page 115)
(3 hr at 600 C)

Screen Analysis before Fluorination		Screen Analysis after Fluorination	
Screen Size	Wt %	Screen Size	Wt %
+ 20	0.2	+ 20	-
+ 40 - 20	3.0	+ 40 - 20	3.2
+ 60 - 40	13.1	+ 60 - 40	15.1
+100 - 60	41.1	+100 - 60	41.9
+200 -100	42.6	+200 -100	37.1
+325 -200	0	+325 -200	2.7
-325	0	-325	0.1
	<u>100.0</u>		<u>100.1</u>

Fluorine was added cautiously at 315 C to prevent any temperature excursions which might harm the bed and which might confuse the results concerning the feasibility of zirconium tetrafluoride as an inert bed material. For the first 40 min the fluorine concentration was gradually increased to 20 percent and the bed temperature to 500 C. The column was then operated for about one hour at 500 C with 20 percent fluorine. After satisfactory operation under these conditions, the fluorine concentration was increased to 40 percent. The column was then operated with the increased fluorine for about an hour. Table 54 describes the conditions of the run and gives uranium hexafluoride collection rates.

Table 54

URANIUM HEXAFLUORIDE COLLECTION RATES DURING
URANIUM DIOXIDE FLUORINATION RUN UOF-27

Two-inch-diameter Reactor

Total Gas Rate 0.5 ft/sec

Three-inch Bed of 1/2-in. hydrogen-fired pellets (834 g)

Thirteen-inch Bed of ZrF_4 (1467 g)

Run Time (hr)	Temp (C)	Inlet F_2 Conc (%)	Total F_2 Utilization ^a (%)	F_2 Efficiency to Form UF_6 ^b (%)	Cumulative UF_6 Collected (g)	Average UF_6 Collection Rate in Period (g/hr)
0-0.7	315-500	0-20	-	-	35	-
0.7-1.8	500	22.4	21	23	125	82 ^c
1.8-2.8	500	40.0	12	16	260	135 ^d

^a F_2 utilization = $\frac{F_2 \text{ in} - F_2 \text{ out}}{F_2 \text{ in}}$ as determined by gas analysis.

^b F_2 efficiency to form UF_6 = $\frac{F_2 \text{ in } UF_6 \text{ product}}{F_2 \text{ in}}$ as determined by weight of product collected.

^cIf done in a 3-in. column the rate in this period would be about 180 g/hr.

^dIf done in a 3-in. column the rate in this period would be about 300 g/hr.

The zirconium tetrafluoride was screened after the run. Table 53 shows the screen analysis. Evidently no significant degradation or sintering occurred. Only 13 gm of fines was collected in the filters. From the standpoint of chemical and mechanical stability it appears that the zirconium tetrafluoride would be a satisfactory inert bed material. The fluorination rates in Run UOF-27 are close to those obtained previously under similar conditions (UOF-24A, B, see ANL-6287, page 148).

The objective of Run UOF-30 was to determine the extent and magnitude of control problems that might develop for the case in which no inert fluid bed is used in the pellet fluorinations. This information is of interest (1) for comparison with the fluid bed case and (2) as preliminary feasibility evaluation for processing conditions in which the inert fluid bed approach has certain disadvantages; namely, caking problems or excessive retention of fissionable material.

In this run, the three-inch-diameter air-cooled reactor was used together with the fluorine regulator system described above for Run UOF-29. A constant nitrogen flow was also used as before.

The uranium dioxide pellet charge consisted of a six-inch deep bed of hydrogen-fired pellets ($\frac{1}{2}$ in. by $\frac{1}{2}$ in.). No inert fluid bed was used, but a small bed of fused calcium fluoride lumps ($\frac{1}{4}$ - to $\frac{1}{2}$ -in. size, total 224 gm) was used as an additional pellet bed support and gas distributor on top of the perforated nickel support plate in the reactor. The reaction was actually carried out in two parts; it was shut down one day and started up again the next day and carried to completion.

The pellet bed was quickly brought to reaction temperature (500 C) with the column heaters, and the fluorine was introduced on the initial temperature decline following the starting of the coolant air flow. A certain amount of experimentation was used with controller settings, but at no time was there a control problem. Full coolant air flow was used. The center-of-bed temperature at the control point held at 505 ± 10 C over the whole run; during most of the run the temperature variation was more nearly ± 5 C. Because of the high coolant rate, the wall, skin, and fin temperatures all were about 50 C throughout the run. The product collection rate and fluorine efficiency and inlet concentration during the run are shown in Figure 48. The reactor was shut down before the fluorination was quite complete; 215 gm of unreacted pellets were found (out of the original 4,400 gm). No fines were evident with the pellet residue. The weight material balance was 95 percent, thus being comparable with previous runs (see Run UOF-29, above).

As can be seen from Figure 48, the product collection rate and the fluorine efficiency were generally satisfactory in comparison to previous runs. The fluorine efficiency shown in Figure 48 was obtained from off-gas analyses; the overall average fluorine efficiency calculated from a material balance was 57 percent. The overall average uranium hexafluoride production rate calculated from a material balance was 430 g/hr. The time for complete fluorination of this batch of pellets was 9.5 hr.

For comparison of effective heat transfer with fluid bed Run UOF-29, an effective thermal conductivity of the pellet bed in Run UOF-30 was calculated for a period of maximum fluorination rate (85 percent fluorine efficiency). Assuming a six-inch effective bed height and a film coefficient of 25 Btu/(hr)(sq ft)(F) at the wall, the effective k of the bed was 0.52 Btu/(hr)(sq ft)(F/ft). This value is comparable to that (0.50) obtained in Run UOF-29, although in that run the low value (compared to about 5 expected for good fluidization) was attributed to poor fluidization.

Summary of Batch Fluorinations Carried to Completion

The fluorination runs to date have been made under a variety of process conditions and control procedures. This fact has given a great deal of practical information as to process feasibility, but largely

Table 55

OVERALL PROCESS CONDITIONS IN BATCH FLUORINATION
OF URANIUM DIOXIDE PELLETS

Pellets Completely Fluorinated
 Three-inch-diameter Air-Cooled Reactor
 0.25-cu ft/min N₂ Flow (Approx)
 Constant F₂ Inlet Concentration Run 20; Variable in Others
 Initial Pellet Bed Approx 6 in. Deep

Run	Temp Control	UO ₂ Pellet Charge	Inert Bed	Bed Temp (C)	F ₂ Inlet Conc (%)	Fraction of Charge Reacted to UF ₆ (%)	Batch Reaction Time (hr)	Overall UF ₆ Rate (g/hr)	Overall F ₂ Utilization (%)	Overall Batch Reaction Time (hr)
20	auto coolant control	1/2-in. inert-fired 4.19 kg	MgF ₂ ~34 in.	500	20 (const)	78	6.2	650	72	8.2 ^a
25	manual F ₂ control	1/4-in. inert-fired 4.25 kg	MgF ₂ ~24 in.	500	48 (avg)	99	5.6	1000	53	5.6
29	auto F ₂ control	3/8-in. H ₂ -fired, type M, 4.89 kg	MgF ₂ ~24 in.	530	42 (avg)	50.5 ^b	6.0 ^b	505 ^c	55 ^c	12 ^a
30	auto F ₂ control	1/2-in. H ₂ -fired, type N-2, 4.40 kg	no inert bed	505	30 (avg)	95	9.5	430	57	10

^aCalculated from total charge, and experimental overall UF₆ production rate.

^bFraction of total UF₆ collected in this final six-hour period of the batch fluorination.
 The overall UF₆ collected was 96 percent of the charge.

^cData obtained in final six hours of fluorination.

prevents strictly quantitative comparisons among the various runs. Part of this difficulty is inherent in the study of unsteady-state behavior (in batch processing) of a rather complicated heterogeneous reaction. Nevertheless, the data obtained in four batch runs in which pellets were completely fluorinated can be considered as indicative of practical process conditions under which the fluorination process can be successfully carried out. These data are summarized in Table 55.

FIGURE 48
RUN UOF-30
URANIUM HEXAFLUORIDE PRODUCTION RATE, FLUORINE EFFICIENCY,
AND FLUORINE INLET CONCENTRATION

Different pellet materials and/or different initial sizes were used in these runs. The hydrogen-fired types are regarded as more typical of reactor fuels. In each run, the uranium hexafluoride production rate varied, and in all but one run the fluorine inlet rate varied in response to the temperature of the system. Overall rates and efficiencies therefore should not be expected to be quantitatively consistent with total fluorination time. Higher fluorine efficiencies could be achieved by using deeper beds, but it is doubtful that inlet fluorine concentrations over 50 percent can be used. Deeper beds will give initially higher fluorine efficiency, but this efficiency will of course decrease during the run, and the additional amount of material to be fluorinated will tend to add somewhat to the batch processing time.

b. Heat Transfer Study in Packed Fluid Beds
(C. Bayens,* W. Murphy)

Reactions of halogen gases with solid materials are exothermic processes in which practically achievable rates are often limited by heat transfer. Heat transfer tests in a mockup system are being made to assist in the analysis of temperature-control problems in the fluorination step of the Direct Fluorination Process applied to uranium dioxide pellet fuel. In this process inert material fluidized in the voids of the pellet bed is used to aid in heat removal and temperature control.

Previous reports (ANL-6231, page 114 and ANL-6287, page 158) described film coefficients for internal heating surfaces in packed fluid beds and preliminary values for the effective thermal conductivity of the bed in the radial direction. In the present period additional work was performed to check the accuracy and reproducibility of the values of bed thermal conductivity, and to extend the data over a range of gas velocities.

The reproducibility study was carried out in the 2.88-in. column described previously in ANL-6287, pages 154 and 155. A 10-in.-high pellet pack, in which the bed thermocouples were centered, was contained in a 12-in.-high wire basket. The basket, which fit closely inside the column, was so suspended that there were 9 in. of unhindered fluid bed below the pellet pack and 10 in. of fluid bed above. The pellets were of brass, $\frac{3}{8}$ in. $\times$ $\frac{3}{8}$ in. The bed material was 80 percent 60 mesh and 20 percent 80 mesh glass beads (minimum fluidization velocity, 1.0 ft/sec). The superficial gas velocity for all runs was 1.5 ft/sec. An outline of the calculations used in these tests is given in Table 56.

Table 56

CALCULATION OF EFFECTIVE THERMAL CONDUCTIVITY

k = Effective thermal conductivity along radius of
packed fluid bed, Btu/(hr)(sq ft)(F/ft)

q = Heat transfer rate, Btu/(hr)

r, r' = Radial distance of thermocouple junctions, ft

L = Length of heat transfer zone, ft

$$k_1 = \frac{q \log (r/r')}{2 L \Delta T_1}$$

$$\text{Average } k = (k_1 + k_2)/2 = k_{av}$$

$$\text{Deviation of } k_1 = k_1 - k_{av} = \text{dev } k$$

$$\text{Average Deviation of } k = (\text{dev } k_1 + \text{dev } k_2)/2$$

*Co-operative student from the University of Detroit.

In order to measure the radial temperature gradient, thermocouple junctions were positioned by axial holes in the pellets (six in a line on one diameter). This arrangement is shown as Type I, Figure 49. Three arrangements of thermocouples mounted on pellets were used: (1) all six pellets with axes vertical; (2) alternate pellets with axes horizontal; (3) four pellets only, each only half size. The variations in effective thermal conductivity for different configurations are shown in Table 57. In general, these variations are believed to have allowed successively less interference with the "normal" void patterns in the pellet bed. The objective of these various arrangements was to obtain closer checks between values of k obtained for the two different radii measured in each run. The half-sized pellets appeared to give the best results in this respect, as shown by smaller average deviations from the mean.

In Table 58 are shown the results for a 10-in. pellet pack suspended in the middle of the fluid bed and for a 29-in. pellet pack. In this latter case the pellet pack and the fluid bed were the same height and heat transfer proceeded radially only, without longitudinal heat transfer due to "open" fluidization on the top and bottom. A lower value of thermal conductivity in this second case, $\sim 5 \text{ Btu}/(\text{hr})(\text{sq ft})(\text{F}/\text{ft})$, indicates that fluidization above and below the pellets is beneficial.

Table 57

VARIATIONS OF EFFECTIVE THERMAL CONDUCTIVITY OF
A PACKED FLUID BED FOR DIFFERENT
THERMOCOUPLE ARRANGEMENTS

Conditions: 2.9-in.-ID column
 3/8-in. x 3/8-in. brass pellets; 10-in. pellet pack
 29-in. fluid bed; glass beads, avg diameter 0.011 in.
 Minimum fluidization velocity: 1.0 ft/sec
 Corrected gas rate: 3.0 x min. fluidization rate
 (Corrected for pellet void volume)

Pellet Arrangement	Orientation of Pellet Axes	Run	Gas Temp (C)	Avg k ^a [Btu/(hr)(sq ft)(F/ft)]	Avg Dev k (%)
Six whole pellets	All vertical	K-1-A	50	10.8	35
		K-1-B	50	17.2	13
		K-2	48	4.2	20
		K-5	51	6.8	26
		K-3	97	8.6	26
		K-4	97	8.0	15
	Alternate, Vertical-Horizontal	K-6	106	10.3	20
Four whole pellets	All vertical	K-7	94	5.8	16
Four halved pellets	All vertical	K-8-A	97	10.0	6
		K-9-A	102	9.7	0
		K-8-B	50	5.6	11
		K-9-B	51	6.5	3

^aAverage of two thermal conductivities obtained on opposite radii at the same elevation.

Table 58

END EFFECT IN HEAT TRANSFER TESTS

Four halved pellets; Axes vertical
 29-in. fluid bed; Glass bead, Avg diameter 0.001 in.
 Minimum fluidization velocity, 1.0 ft/sec
 Corrected Gas Rate: 3.0 x min. fluidization rate
 (Corrected for pellet void volume)

Height of Pellet Pack (in.)	Run	Gas Temp (C)	Avg k ^a [Btu/(hr)(sq ft)(F/ft)]	Avg Dev k (%)
10 ^c	K-8-A	97	10.0	6
	K-9-A	102	9.7	0
20 ^d	K-10-A	104	4.9	19
	K-11 ^b	102	5.4 ^b	3
	K-10-B	54	3.6	19

^aAverage of two thermal conductivities obtained on opposite radii at the same elevation.

^bWithout wire screen basket.

^cFluid bed above and below pellet pack.

^dNo fluid bed above or below pellet pack.

In all runs up to and including K-10, a 12-in.-high wire mesh basket (closely fitting the column wall) was used to position the pellet pack. In Run K-11 the basket was not used. No significant difference was noticed in the results for this case.

The other runs carried out in this series of tests used a fluid bed of smaller particle size: glass beads with an average diameter of 0.0045 in. A base-line run (L-3) without pellets was made similar to that done with the larger glass beads to obtain the vertical temperature profile for the bed (ANL-6287, page 155). In order to eliminate the possible influence of the wire mesh thermocouple guide, an open welded-wire thermocouple junction was used to make the longitudinal temperature traverse. The wire was positioned by being tightly drawn over an insulated pulley mounted at the bottom of the fluid bed.

The temperature profile is shown in Figure 50; it is generally of the same form as that obtained previously, but the bed temperature is much closer to the exit gas temperature. The superficial gas velocity was 0.57 ft/sec (100 C); the minimum fluidization velocity was 0.16 ft/sec (25 C). It is concluded that the temperature of the exit gas is the same as the top of the bed, and that the wire mesh thermowell gave slightly inaccurate results.

FIGURE 50
TEMPERATURE DISTRIBUTION IN THE FLUID BED
RUN L 3

The effect of gas rate on the effective thermal conductivity and the film coefficients is shown in Figures 51 and 52. The general run conditions are shown in Table 59.

FIGURE 51
THERMAL CONDUCTIVITY AS A FUNCTION OF SUPERFICIAL GAS VELOCITY

FIGURE 52
FILM COEFFICIENT, h , AS A FUNCTION OF
SUPERFICIAL GAS VELOCITY

Table 59

PERTINENT CONDITIONS IN HEAT TRANSFER TESTS

RUNS K-12 THROUGH K-23

Pellet Bed Height: 28 in.

Fluid Bed Height (Expanded): 29 in.

Fluid Bed: Glass Beads, 20% 120 mesh, 70% 140 mesh,
10% 170 mesh; avg diameter, 0.0045 in.

Base Gas Temperature: 100 C

Fluidizing Gas: Air

Superficial Velocity (100 C): 0.088 to 0.995 ft/sec

Corrected Superficial Velocity^a (100 C): 0.215 to 2.41 ft/sec

Incipient Fluidization (100 C): 0.2 ft/sec

Thermocouple Arrangement: Four halved pellets (Type IV, Figure 49)

^aCorrected to true void space.

In this series of runs (K-12 through K-23), the height of the pellet pack was the same as that of the fluid bed and therefore the heat transfer in other than a radial direction was a minimum. The incipient fluidization velocity of the glass beads was 0.2 ft/sec, which is a value very close to that for inert fluid beds used in fluorination studies. The effective thermal conductivities of the packed fluid bed are shown in Figure 51 as a function of gas velocity. The conductivities measured along each of the two radii at the same elevation are plotted separately. Variations in thermal conductivity were found at gas rates just above the incipient fluidization point, but these conductivity values converge at a gas rate of about $3\frac{1}{2}$ times the minimum fluidization velocity, where the fluidization is probably more uniform. It appears that this packed fluid bed system has an effective radial thermal conductivity of about 10 Btu/(hr)(sq ft)(F/ft) when the gas velocity is more than three times the minimum fluidization value. This conductivity is about 10 times the value for the same bed in a nonfluidized state.

It is planned to continue this study in a rectangular-section column better suited to making measurements of heat flux and temperature gradients.

c. Filter Chamber Tests
(E. Carls, L. Marek)

Preliminary design of a pilot plant for processing of uranium oxide-plutonium oxide fuels by the Direct Fluorination Process is underway. The proposed filter system consists of sintered nickel filters (bayonet type) mounted in chambers external to the reactor and provided with automatic blowback for powder return to the reactor. Such an arrangement has the advantage of allowing ready replacement of the filter as a unit.

A glass and plexiglass mockup of a filter unit of this type was made as shown in Figure 53. A three-inch-diameter fluid bed column was used and operated with the usual gas velocities.

The column was charged with zirconium tetrafluoride with a high percentage of fines (13.5 percent 200 mesh) to insure adequate loading of the filters. The blowback air pressure supply was 100 psig. Pressure gages were mounted on the inlet to the filter, the filter chamber, and the column itself. A small pneumatic vibrator was used to aid in solids transport from the angled filter chamber lines to the column.

The maximum increase in pressure in the filter chambers was 3 to 4 psi with a blowback duration of 2 sec. As far as could be determined, at the instant of blowback this same pressure increase occurred both inside the filter itself and also in the opposite filter chamber not undergoing blowback. The reverse pressure drop across the filter during blowback was only about 2 psi. The pressures were measured with Bourdon gages, as shown in Figure 53. The increase in column pressure caused a momentary 10 percent decrease in fluidizing gas flow but no visual effect on fluidization quality.

The system operated satisfactorily with a blowback duration of 0.5 sec and with a 2-min duration between blasts for each filter. This operation was conducted for approximately eight hours with no noticeable increase in pressure drop across the filters and no apparent holdup of large amounts of material in either the filter chambers or return lines. The solids return line on a 60° angle held up less powder than the 45° return line. An angle greater than 60° would be desirable for minimum solids holdup.

The system was operated with and without a 10-in.-diameter disengaging section between the column and the filters. The elimination of such a section had no noticeable effects on pressures reported here. More powder seemed to be carried up into the filter chambers when the disengaging section was not used. However, no quantitative information as to the merit of the disengaging section in keeping fines in the bed was obtained.

2. Direct Halogenation Process for Stainless Steel-clad or Matrix Fuels (N. Levitz)

Work has continued in a 1½-in.-diameter, two-zone fluid-bed reactor on the decladding step of a process for the recovery of fissile materials from stainless steel-clad fuels of sintered uranium dioxide. The decladding step involves the reaction of chlorine and stainless steel to produce a volatile iron chloride which is converted to the solid fluoride by reaction with hydrogen fluoride in the upper zone of the fluid-bed reactor. The complete reaction of chlorine with the cladding was found to be inhibited by the formation of adherent films on the surface. Higher chlorination temperatures than reported previously (ANL-6287, page 160) may be necessary to provide sufficiently high penetration rates.

The two-zone fluidized bed has been employed in the direct chlorination of sintered uranium dioxide pellets. The volatile uranium chlorides are converted to solid fluorides by reaction with anhydrous hydrogen fluoride in the upper zone of the reactor. An equivolume mixture of carbon tetrachloride and chlorine at 550 C has produced higher reaction rates than several other gas mixtures studied.

a. Decladding Stainless Steel-clad Fuels
(J. T. Holmes, J. J. Barghusen, D. J. Raue, and
J. E. Kincinas)

The chlorination of simulated stainless steel-clad reactor fuel elements is being studied in the lower zone of a $1\frac{1}{2}$ -in.-diameter, two-zone, fluidized-bed reactor. The zones are separated by an inverted conical baffle which prevents gas backmixing from the upper zone, where anhydrous hydrogen fluoride is used to convert the volatile and solid chlorides, formed in the lower zone, to solid fluoride. Abrasive grain alundum, -40 +200 mesh, is used as the inert fluidized bed.

Reaction rate data were obtained at 575 and 625 C (see Table 60). At the higher temperature, the effect of chlorine concentration (13 to 87 mole percent in nitrogen) on the reaction rate was studied. Reaction time varied from 1.0 to 4.7 hr. The test elements were Type 304 stainless steel welded tube sections, $\frac{3}{8}$ in. in diameter, $4\frac{3}{8}$ in. long, of 35-mil wall thickness, with one end welded shut and the other end crimped closed.

Experiments 01 and 12 show that the overall penetration rate (4.6 to 4.9 mils/hr) was low for closed-end coupons in chlorine at 575 C for run times over four hours. The higher rates (9.0 to 10.2 mils/hr) reported in ANL-6287, page 160, were for short, open-end coupons and reaction times of less than one hour. The overall penetration rate, calculated from weight-loss data, is unrealistically large for the open-end coupons because of the abrasive action of the fluid bed, which removes the nonvolatile nickel and chromium chlorides from the ends of the samples. When these effects are small (long, closed-end coupons), the dependence of the fluid-bed reaction rate on time can be predicted from the tube reactor experiments summarized in ANL-6231, page 124. Complete reaction of 35-mil cladding would take about ten hours at 575 C.

Experiments 14, 17, 18, 19, 20, 21, and 23 were conducted to obtain reaction rate data at 625 C. Runs 14 and 17 showed that essentially complete decladding can be achieved in less than four hours with either 87 or 48 mole percent chlorine in nitrogen at 625 C. Runs 18 and 19 show that the penetration rate is time dependent, as were the experiments below 600 C, but is initially higher and has an apparently lower coefficient of time dependence. Runs 19, 20, and 21 show that decreasing the chlorine concentration below 48 mole percent decreases the reaction rate. No excess heat effects (temperature excursions) were observed in any of the runs.

Separate experiments were made to determine the ignition temperature of stainless steel with 87 and 27 mole percent chlorine in nitrogen. The procedure followed was to introduce the chlorine with the bed temperature at about 565 C and gradually increase the temperature.

Table 60

FLUID-BED REACTION OF SIMULATED STAINLESS STEEL
CLADDING WITH CHLORINE

Reactor: 1 1/2-in.-diameter, nickel, two-zone
 Fuel sections charged: Type 304 SS tubes, 3/8-in. diameter,
 4 3/8-in. long, 35-mil wall, closed ends.
 Bed: Abrasive grain alundum (-40 + 200 mesh).
 Superficial gas velocity: 0.4 to 0.5 ft/sec, lower zone.
 0.8 to 1.0 ft/sec, upper zone.

Run No.	Lower Bed Temperature ^a (C)	Flow Rates		Mole Percent Chlorine ^b in lower zone	Reaction Time (hr)	Penetration Rate ^c (mils/hr)	Percent of Specimen Reacted
		Chlorine (g mole/hr)	Hydrogen Fluoride (g mole/hr)				
01	575	8.8	9.2	88	4.7	4.6	62
12	575	7.9	8.1	87	4.3	4.9	61
14	625	8.1	6.6	87	3.8	-	98
17	625	5.0	6.0	48	3.8	-	100
18	625	5.0	5.7	48	2.5	10.4	74
19	625	5.0	7.5	48	1.0	11.3	32
23	625	4.3	6.9	39	1.0	5.5	15
21	625	2.7	6.3	27	1.0	4.2	12
20	625	1.3	5.7	13	1.0	3.3	9.5

^aThe upper bed temperature was 500 C for all experiments.

^bRemainder nitrogen diluent.

^cBased on initial surface area, weight loss, and total reaction time.

Ignition was achieved only with the higher concentration of chlorine gas in the stream. This occurred at 645 C; the temperature rose rapidly to 680 C and was sustained by the heat of reaction between 670 and 680 C for an additional 40 min. At this time, sintering of nonvolatile chlorides and bed material around the two tubular specimens caused a pressure buildup, and the run was terminated. Sintering of bed material also occurred in the run with 27 mole percent chlorine at about 670 C. With the higher chlorine concentration, the tubes were about 95 percent reacted, but the "meat" was not exposed because of the sintering of solids on the specimen. Temperatures above 650 C should therefore be avoided to preclude sintering and ignition problems.

The high-temperature (~625 C) chemical decladding of stainless steel fuel elements presents two major process considerations: first, the reaction of the uranium dioxide "meat" is expected to be rapid in chlorine at the high decladding temperatures. It was shown (ANL-6287, page 162) that volatile reaction products are formed when uranium dioxide is reacted with chlorine at 600 C. A higher reaction rate would be expected above 600 C, which may complement a process involving complete chlorination of the fuel elements. Second, the corrosion of nickel and Inconel becomes appreciable above 550 C, about 10 mils/mo at 575 C and 35 mils/mo at 625 C (ANL-6287, page 162). Since the temperature coefficient for corrosion is about the same as that for the stainless steel chlorination, the total reactor corrosion would be independent of decladding temperature and new materials of construction must be considered.

Calculations indicated that an alumina sleeve, $\frac{5}{8}$ -in. thick, would be sufficient to provide a 100-degree temperature gradient from the reactor wall to the fluidized bed for a typical loading of fuel elements and a 10-mil/hr penetration rate. If the metal wall temperature were maintained below 550 C, the extent of corrosion would be acceptable for process applications. Use of an insulating liner would require the reaction to be self sustaining.

b. Chlorination of Uranium Dioxide

The chlorination of uranium dioxide is being investigated as an alternate to the Direct Fluorination Process (page 51). Since chlorine reacts appreciably with uranium dioxide at the decladding temperatures, a dual reaction scheme was proposed for conversion of the dioxide to the tetrafluoride. A chlorine-carbon tetrachloride mixture would be used to convert the dioxide pellets remaining in the reactor after decladding to volatile uranium chlorides. The volatile chlorides are converted to solid fluorides in the upper zone of the two-zone reactor by the reaction with hydrogen fluoride. An additional treatment with fluorine would recover the uranium and plutonium as the volatile hexafluorides, which could be purified by standard volatility techniques. A major advantage of the

chlorination process over the Direct Fluorination Process is that the reagent cost for conversion to the hexafluoride is considerably reduced, since hydrogen fluoride, rather than fluorine, is used for converting to the tetrafluoride. Also, the heat produced by the chlorination reaction is less than half that obtained in the Direct Fluorination Process.

It was previously shown (ANL-6287, page 162) that a mixture of chlorine and carbon tetrachloride gave higher production rates of volatile uranium chlorides than chlorine or carbon tetrachloride alone. An investigation of the effect of relative amounts of chlorine and carbon tetrachloride gave a maximum reaction rate [about 800 mg/(sq cm)(hr)] for a 50 mole percent mixture at 550 C.

The reaction of phosgene and a phosgene-chlorine mixture with uranium dioxide pellets was also studied by means of the tube furnace reactor. The reaction of the pellets with 30 mole percent phosgene in chlorine proceeded at a rate of 350 to 500 mg/(sq cm)(hr) at 500 to 600 C, compared with 380 to 800 mg/(sq cm)(hr) for a chlorine-carbon tetrachloride mixture (ANL-6287, page 162). A chlorination rate for phosgene alone was lower by about a factor of two than with the phosgene-chlorine mixture. Since the phosgene reactions are slower, and the cost is about 1.4 times the cost of carbon tetrachloride per mole of chlorine, phosgene does not appear to offer any advantage for the chlorination reaction.

In larger-scale studies, twenty uranium dioxide pellets (121 g), submerged in an alundum bed (800 g, -40 +200 mesh) in the lower zone of a 1.5-in., two-zone, fluid-bed reactor, were reacted with 69 mole percent chlorine in carbon tetrachloride. The pellets occupied a space about 1 in. in diameter by 1.5 in. high, and were supported in a wire basket about 2 in. above the cone bottom of the reactor. A thermocouple located in the pellet basket gave temperatures which varied between 550 and 555 C and indicated no temperature excursions. Hydrogen fluoride was introduced to the upper stage (maintained at 440 to 450 C) to convert the uranium chlorides to fluorides. This reaction occurs primarily on the surface of the bed material. The superficial velocity in the lower and upper zones was 0.4 and 0.8 ft/sec, respectively. Reaction for 2.5 hr achieved 92 percent volatilization of the pellets and introduced about 8.7 weight percent uranium into the total bed. Analysis of the final bed material indicated that the alundum reacted with the chlorinating agents to a slight extent. The extent of this reaction is being determined. Analysis of the ammonia off-gas scrub solution showed a negligible uranium carry-over (0.007 percent total loss).

Two conclusions were reached from the work performed to date. The chlorination rate is high enough for dissolution of uranium dioxide pellets in a reasonable time and the heat of reaction is easily dissipated by the fluidized bed. Proposed future work includes the following:

(a) The stainless steel decladding reactions will be studied in a 6-in.-diameter, two-zone fluidized-bed reactor.

(b) Recovery of uranium by fluorination from the final bed of the uranium dioxide chlorination experiments will be studied using the 1.5-in. fluid-bed reactor.

3. Production of Uranium Hexafluoride by Reaction of Uranium Trioxide with Sulfur Tetrafluoride in Fluidized Beds
(E. Carls, N. Levitz, and L. Marek)

The production of uranium hexafluoride directly from uranium trioxide by reaction with sulfur tetrafluoride was studied in an exploratory experiment carried out in a two-inch-diameter fluid bed reactor. The overall reaction was considered to be $\text{UO}_3 + 3\text{SF}_4 \longrightarrow \text{UF}_6 + 3\text{SOF}_2$. Hexafluoride production rates of 22 and 66 lb/(hr)(sq ft reactor area) were achieved at temperatures near 400 C using concentrations of sulfur tetrafluoride of 25 and 44 percent, respectively. Improved production with higher concentration (possibly coupled with a temperature effect) indicates significantly higher rates might be attained with optimized conditions.

The uranium trioxide used was produced by the fluid-bed calcination of uranyl nitrate solutions. Analysis and size distribution of this material is shown in Table 61. These data showed the material was quite pure, about 99 percent trioxide, and of a size distribution suitable for fluid-bed work.

Table 61

CHEMICAL ANALYSIS AND SIZE DISTRIBUTION OF
URANIUM TRIOXIDE USED IN
SULFUR TETRAFLUORIDE REACTION STUDIES

Chemical Analysis		Size Distribution	
		Mesh Size	(w/o)
Total U, w/o	82.6	+ 20	0
U ⁴⁺ , w/o	0.28	- 20 + 40	7.9
NO ₃ , w/o	0.86	- 40 + 60	51.2
Wt loss at 350 C for 1 hour, w/o	0.60	- 60 +100	36.9
		-100 +200	3.7
Bulk Density, g/cc	4.0	-200 +325	0.1
		-325	0.2
			100.0

The sulfur tetrafluoride (in 10-lb cylinders) was purchased from E. I. du Pont. Specifications* describe the material as 90 to 95 percent purity with thionyl fluoride as the major impurity. The tetrafluoride was metered through a Matheson pressure regulator (No. 15C-330) and a glass rotameter. Since the cylinder was mounted on a beam balance, the flow rate was also checked by observing the weight change of the cylinder.

Approximately 1700 g of uranium trioxide were charged to the reactor, giving about an 8-in. static bed height. The bed was fluidized with nitrogen and preheated to the desired temperature, at which time part of the nitrogen was replaced by the sulfur tetrafluoride. A given concentration of reactant was maintained long enough to determine the rate of uranium hexafluoride production (as determined by weighing the cold-trap collectors at $\frac{1}{2}$ -hr intervals). The concentration was then increased to a second level to determine the effect of concentration on hexafluoride production rate. The cold traps (copper coils) were maintained at -25 C by immersion in a mixture of dry ice, ethylene glycol, and water. Samples of the off-gas exiting from the cold traps were also taken and analyzed for fluoride and sulfur content.

The run was divided into two parts, the first with a concentration of 25 percent sulfur tetrafluoride in nitrogen and the second with a concentration of 44 percent (see Table 62 and Figure 54). The temperature in the first part ranged from 370 to 400 then rose somewhat in the second part to 385 to 425 C because of the increased heat of reaction. Durations of the two periods were 66 and 15 min, respectively.

Table 62

PRODUCTION OF URANIUM HEXAFLUORIDE BY REACTION OF
URANIUM TRIOXIDE WITH SULFUR TETRAFLUORIDE IN A
FLUIDIZED-BED REACTOR

Equipment.	2-in.-diameter nickel fluorinator	
Fluidizing		
Velocity.	0.5 to 0.8 ft/sec at column conditions	
Bed Charge.	1700 g UO ₃	
Bed Height	8-in., static	
Temp of SF ₄		
Introduction	370 C	
	<u>Time (min)</u>	
	<u>0-66</u>	<u>66-81</u>
SF ₄ concentration (%)	25	44
Temperature (C)	370 to 400	385 to 425
Grams SF ₄	775	370
Avg SF ₄ rate (g/min)	11.7	24.5
UF ₆ collected (g)	254	175
UF ₆ collection rate (g/min)	3.85	11.6
UF ₆ rate [lb (hr) ^{1/2} sq ft reactor area]	22	66
UF ₆ rate [lb (hr) ^{1/2} (cu ft UO ₃)]	54	192
g UF ₆ g SF ₄	0.55	0.47
% Efficiency based on stoichiometry	51	44
% Efficiency based on gas samples	36	62

*Sulfur Tetrafluoride Technical Bulletin, E. I. du Pont Dyes and Chemicals Information Bulletin

FIGURE 54
PRODUCTION OF URANIUM HEXAFLUORIDE BY REACTION OF SULFUR TETRAFLUORIDE
WITH URANIUM TRIOXIDE IN A FLUID-BED REACTOR

The uranium hexafluoride collection rates were 3.85 and 11.6 g/min, equivalent to 22 and 66 lb/(hr)(sq ft reactor area) or 34 and 102 lb/(hr)(cu ft of bed). These rates correspond to efficiencies of 30.6 and 43.5 percent for the lower and higher sulfur tetrafluoride concentrations. The increased efficiency is attributed to both the increased sulfur tetrafluoride concentration and the increased temperature. Approximately 35 percent of the bed was consumed in this batch run.

The analyses of the off-gas samples were used primarily to check on the efficiency of sulfur tetrafluoride utilization. Efficiencies based on these results were somewhat higher than those based on uranium hexafluoride collection, 36 and 62 percent, instead of 31 and 44 percent, possibly indicating some intermediate compound (uranyl fluoride) formation. Final analysis of the bed showed a fluoride content equivalent to about 10 weight percent uranyl fluoride.

Preliminary conclusions may be drawn from this work. Uranium hexafluoride may be produced directly from the reaction of uranium trioxide and sulfur tetrafluoride in continuous fluid-bed reactors. Improved rates would probably be achieved with higher concentrations of reactant. Operating temperatures must be maintained below the point at which uranium trioxide loses oxygen to form U₃O₈ (~450 C) since this fluorinating agent is selective for hexavalent uranium compounds.

C. Conversion of Uranium Hexafluoride to Uranium Dioxide
(I. Knudsen, H. Hootman,* N. Levitz, M. Jones, and J. Kincinas)

A fluid-bed process for the preparation of ceramic-grade uranium dioxide from uranium hexafluoride is being studied by application to the production of nuclear fuel. Uranium hexafluoride is reacted with steam to form uranyl fluoride, which is then reduced to uranium dioxide with hydrogen. The reactions have been carried out simultaneously in a single reactor and in separate steps; conversion to solids is about 99.99 percent complete. Work is being concentrated on the two-step procedure because of greater flexibility in choice of reactor conditions and process control. High sintered densities have been obtained in pellet fabrication tests.

1. Steam Hydrolysis of Uranium Hexafluoride

Continuous operation of the uranium hexafluoride-conversion reactor has been hampered by occurrences of fines formation. However, runs have been carried out for as long as 7 hr with satisfactory performance. Reasonably consistent behavior in terms of particle size effects has been observed as related to bed particle size, both in the simultaneous reaction system and in the steam-hydrolysis step. It has been possible to avoid fines formation on startup by proper sizing of the bed, an average particle diameter of 250μ or greater giving particle growth. Particle growth must be offset by seed particle addition to maintain desired bed fluidity. However, proper adjustment of the rate of addition to avoid entering the area of fines formation (avg bed particle diameter $< 250\mu$) has proved difficult.

A number of short-duration runs was made in an attempt to isolate factors contributing to unexplained occurrences of fines in coarse beds (316 to 350μ average diameter). Operating conditions for the 3-in.-diameter reactor were held constant at 100 g/min hexafluoride feed [$174\text{ lb uranium}/(\text{hr})(\text{sq ft})$], 225 percent excess steam, 0.75 ft/sec superficial velocity (steam only - gaseous reaction products increase velocity about 30 percent), 18-in. bed height, and 200 C reactor temperature. Screen analyses of grab samples were found to be so widely at variance with final bed analyses that it was apparent that inadequate mixing was occurring. Subsequent runs were started with finer beds (average diameter nearly 250μ) and improved agreement was noted between grab samples and final bed as well as between samples taken from the two sample points located about 10 in. apart. Also, during these runs the hexafluoride inlet was removed from a side-entering position in the bottom flange and brought through a fitting at the apex of the cone bottom. The steam then entered through an annulus around the hexafluoride inlet,

*Resident Student Associate from Michigan College of Mining and Technology.

an open-end $\frac{1}{4}$ -in. tube, which projected about $1\frac{1}{2}$ in. up into the cone. This position of the inlet was expected to eliminate any unusual wall effects in the proximity of the reaction zone. Seed particle feed rates of 7 to 16 percent of the hexafluoride rate were tested with the higher rates apparently counteracting the growth rate.

Two approaches were taken in controlling the rate of seed particle addition in attempts to maintain runs of longer duration: one, maintaining a constant rate based on previous run data; or, two, adjusting the rate based on particle size analyses and column indications (column temperatures, bed weight indication, etc.). In spite of good control of all feed streams, the longer runs up to 7-hr duration were also interrupted by fines formation. It appears from the changes in bed particle size after periods of steady state that there is a variable rate of fines formation which affects the seed particle requirements. These fines also affect seed particle requirements which are lower by about a factor of two than that calculated from the equation developed by Griffin³⁰ *et al.*, for fluid coking, a similar solids-deposition process.

In view of these results, a brief study is being made of the occurrence of fines. Four runs, 61 through 61C (see Table 63), made with no seed particle feed stream and no product take-off showed normal particle behavior (growth) with starting bed particle sizes ranging from 194 to 225 μ . Runs 61B and 61C showed no effect of particle size distribution (differences in calculated final bed particle size are partially due to initial bed weight differences).

Runs 61D through 61H with finer starting beds showed either reduced particle growth or fines formation. Run 61E was an additional 45-min run with the final bed of Run 61D. The change from a reduced growth rate to fines formation appears to be a time effect, apparent also in Run 61G, in which the bed particle diameter increased from 128 to 133 μ in 45 min and then decreased to 92 μ after an additional 45 min. Apparently particle growth initially overcomes fines formation but is then overcome by it. This may also explain the accumulation of fines in coarser beds when seed particle addition is being used.

Run 61F was made with the final bed from a previous run (Run 59) which was interrupted by fines formation after 6 hr; fines continued to be formed.

Future plans call for study of the effect of variables such as fluidizing velocity and top bed take-off *vs.* bottom bed take-off. Consideration is being given to operation with a separate filter section in which case fine particles would not be returned to the bed but rather collected separately.

³⁰Griffin, L. I., Jr., Moser, J. F., Jr., Dunlap, D. D. Chem. Eng. Prog. 54, 39 (1958).

Table 63

PARTICLE SIZE EFFECTS NOTED AS A FUNCTION OF
STARTING BED PARTICLE SIZE

Equipment: 3-in.-diameter Monel column
 UF₆ rate: 100 g/min
 Steam Superficial Velocity: 0.75 ft/sec
 Steam Excess: 225%
 Starting Bed: 7 to 8 kg
 (No Seed Particle Recycle)

Run No.	Duration (hr)	Average Particle Size (μ)		
		Starting Bed	Final Bed	Calculated
61 ^a	0.33	219	230	234
61A ^a	1.5	225	291	282
61B ^a	0.75	200 (63% 60-100 mesh)	237	232
61C ^a	0.75	194 (84% 60-100 mesh)	235	222
61D ^a	0.75	140	153	160
61E	0.75	153	144	-
61F	0.75	106 ^c	90	-
61G ^b	1.50	128	92	-

^aNo product take-off.

^bAverage bed particle diameter after 0.75 hr was 133 μ ; however, the minus 325 mesh fraction had increased from 0.1 to 2.3 percent.

^cFinal bed of Run PY-59 which was interrupted by fines formation after 6 hr.

2. Reduction of Uranyl Fluoride

The second step of the conversion of uranium hexafluoride to uranium dioxide by the two-step method involves the reduction of uranyl fluoride, the pyrohydrolysis product of the first step. A series of batch fluidization runs has been carried out in a 3-in.-diameter fluid-bed reactor

to study the reduction reaction. In general, a mixed gas of steam and hydrogen gave much faster conversion than hydrogen alone, although a thermobalance study using hydrogen at 600 C achieved about 97 percent conversion on a 2-gm sample in 85 min. At present, there is no satisfactory explanation for this difference in behavior.

The uranyl fluoride feed material was produced at 200 C by steam hydrolysis of uranium hexafluoride. Analysis showed that the feed material contained the nearly theoretical content of the fluoride (12.3 percent).

With a 20-in.-deep bed and 100 percent hydrogen as the reacting gas, the conversion of the feed material was only eight percent after 6 hr at 650 C. Shallow (8-in. and 4-in.) beds gave a slightly higher conversion, 21 percent at 650 C after 4 hr.

The use of steam in the hydrogen stream gave almost complete reduction in 2 hr. The gas stream contained three volumes of hydrogen to one volume of steam. The effect of temperature with the mixed gas is pronounced; only 32 percent reduction was achieved at 550 C in one hour as compared to 83 percent at 650 C in an equivalent period. Specification grade material (210 ppm fluoride) was obtained in 5 hr at 650 C with a 3-kg bed and a gas composition of three parts hydrogen to one part steam.

The reduction of uranyl fluoride has been found to be the rate-controlling reaction of the two-step process. Future work will include the optimization of the batch fluidizing process option, and a survey of a moving-bed process option.

D. Fluid-bed Calcination Studies in Small-diameter Columns (J. Loeding, C. Schoffstoll)

Studies have recently been initiated to investigate a scheme which would reduce the quantity of off-gas which would be handled by normal fluid-bed calcination techniques. The practice from which this scheme will deviate employs a fluidizing medium entering through the bottom of the calciner and a two-fluid (i.e., liquid feed and air or steam-atomizing medium) nozzle entering through the side or top of the unit. The present studies entail positioning the atomizing nozzle in the bottom of the unit, directed upward, thus utilizing the atomizing medium as the fluidizing medium. The tests are being conducted in small-diameter columns (of $2\frac{1}{4}$ -in. diameter) and some success has been realized in the preliminary work. If this scheme is found feasible, the work is applicable to calcination of plutonium solutions where nuclear criticality considerations are necessary.

E. Multistage Fluidization Studies (K. Williamson, Jr.)

A mass-transfer study using the silica gel-water system has been completed in the 6-in.-diameter multistage fluidization column designed to achieve controlled downward transport of solids without the use of internal downcomers. This is the final phase of the experimental work carried out as a doctoral research thesis study. Previous studies on column design variables were reported in ANL-6183, page 124. The work has been completely summarized as a topical report, ANL-6267.

For the mass-transfer study the adsorption of water vapor in air by silica gel was studied. This system was chosen because it lent itself readily to the fluidization technique and presented no difficult analytical problems. The equilibrium relationship between silica gel and water vapor was determined for temperatures from 20 to 40 C and pressures from atmospheric to 20 psia. These data were then used to evaluate the Murphree vapor efficiency (a measure of the degree of approach to theoretically perfect contacting) for the adsorption of water vapor from air by silica gel in the 6-in.-diameter multistage fluidization column. From the efficiency, a modified mass-transfer coefficient was calculated. Runs were made at bed depths from $\frac{3}{4}$ in. to 8 in. and at superficial air velocities from 0.20 to 0.98 ft/sec.

The silica gel used for this work was a mixture consisting of particles from 28 to 200 mesh with an average weight-mean diameter of 277μ . Three-mm-diameter inert glass beads were incorporated into each of the three stage supports.

The Murphree efficiency* was found to be approximately 100 percent for all bed depths investigated and for all but the highest superficial air velocity. At an air velocity of 0.98 ft/sec the efficiency dropped to 96.5 percent, corresponding to a modified mass-transfer coefficient of 35.4 lb/(sec)(cu ft)(lb/cu ft). As a point of reference, Cox³¹ reported mass-transfer coefficients for the silica gel-water system, which, when translated to Murphree efficiencies, gave values of 40 percent for 4-in. beds to 80 percent for 2-in. beds. In the reference work relatively large (1.8-in. diameter) gel particles with air velocities from 6.25 to 7.90 ft/sec in a multistage column equipped with downcomers were used as compared to our small particles (~0.01-in.-diameter) and low velocities (less than 1 ft/sec) which offered more contact area and greater contact time.

*The Murphree vapor efficiency is defined as follows:

$$E_{mv} = (Y_{n+1} - Y_n) / (Y_{n+1} - Y_n^*)$$

in which Y_{n+1} is the moisture content of the air entering stage n, Y_n the moisture content of the air leaving stage n, and Y_n^* the moisture content of the air in equilibrium with the solids on plate n. The efficiency is related to the mass-transfer coefficient, $K_g a$, as follows:

$$E_{mv} = 1 - e^{-K_g a (H'/G_s)}$$

in which H' is the bed depth and G_s the mass flow rate of air.

³¹Cox, M., Trans. Instn. Chem. Engrs., 36, 29, (1958).

III. REACTOR SAFETY

The oxidation, ignition, and combustion processes of uranium, zirconium, and plutonium are being studied to provide information to aid in minimizing the hazards associated with handling these metals.

Studies of the effect of pre-oxidation on the burning curve ignition temperatures of uranium powders were continued. Ignition temperature, at first, decreased with extent of pre-oxidation for both a fine and a coarse powder fraction. Ignition temperatures began to rise after more than 50 percent pre-oxidation. Weight gain versus time measurements at 150 C with both powder fractions showed a two-stage reaction identical with that found in previous studies of the isothermal oxidation of uranium cubes. The decreased ignition temperature of pre-oxidized powder may have been due to the faster reaction rates that occur in the second-stage reaction.

Ignition studies of uranium monocarbide powders are reported for powders from two sources. The powders were composed of irregular particles. An estimate of the roughness factor was obtained by the Armour Research Foundation using a Fischer Sub-Sieve Sizer. From this information, it was possible to compute the specific area of a series of powder fractions. Ignition temperatures in oxygen varied from 255 to 320 C for specific areas from 314 to 20 sq cm/g. Ignition temperatures of uranium monocarbide were 40 to 60 degrees higher than values previously reported with spherical uranium powders of corresponding specific area.

A series of measurements of burning-curve ignition temperatures in air were made with uranium foil squares of two thicknesses (one-half and five mils). Studies were made with stacks of one, two, four, and eight foil squares. Ignition temperatures decreased 45 degrees in going from one to two 5-mil foils. Only a small additional decrease occurred with four or eight foils. Studies are aimed at developing means to calculate ignition temperature decreases which are due to decreased heat loss by aggregation.

A brief study was made of uranium plates of the type used in ZPR-III blanket assemblies. Eighteen plates out of a total of 20,000 were found to be crumbling. Unaffected plates had a burning curve ignition temperature of 480 C while deteriorated plates ignited at 115 C in either air or oxygen. The affected plates were made by powder metallurgical techniques. It appears that these plates are reverting to powder.

Studies of the rate of burning propagation along uranium and zirconium foil strips is continuing. A new instrument has been devised to measure simultaneously the propagation rate and the burning temperature. A new program was undertaken to determine the effects of halogenated hydrocarbons on propagation rates and burning temperatures. It is proposed

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to study several homologous series of hydrocarbons in which both R and X of a hydrocarbon RX are systematically varied. It is anticipated that this new program will shed further light on the mechanism by which the hydrocarbons inhibit burning.

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. One method involves the rapid melting and dispersion of metal wires in a water environment by a surge current from a bank of condensers. The series of runs with 60-mil zirconium wires at pressures up to 1500 psi is continuing. Runs made with water at 315 C (1500 psi) were identical in character to runs made in water from 90 to 200 C (10 to 225 psi). Explosive rates of pressure rise occurred at initial metal temperatures of 1900 C in heated water.

Results of previous studies at Battelle and Westinghouse were re-examined and shown to be consistent with rate data deduced from condenser discharge studies of the zirconium-water reaction. The following rate law was obtained:

$$V_2 = 4.82 \times 10^8 \left(\exp - \frac{45,500}{RT} \right) t \quad ,$$

where V is cc of hydrogen at STP per sq cm of surface and t is time in min.

The lowered reactivity of zirconium in room-temperature water could be explained by a lowered rate of diffusion of water vapor through the hydrogen-steam mantle surrounding reacting particles. A diffusion rate of one-half of the value in heated water produced semiquantitative agreement with the experimental data.

The explosive reactions reported previously for zirconium at initial temperatures of 2600 C in room temperature water and those at 1900 C in heated water could be explained by a critical particle diameter (500 μ in room-temperature water) below which rapid hydrogen evolution drives the particles through the water at high velocity. The high-speed motion results in rapid reactions. The reactions, however, are not complete because the increased velocity also increases the convective heat loss rate.

A second method involves the rapid contact of steam with heated metal. In this method, the metal receives a "pressure pulse" of water vapor. The apparatus is entirely enclosed in a box heated to 105 C. Runs with one atmosphere of water vapor reacting with molten aluminum at 1000 and 1200 C are reported. Contact times varied from 0.1 to 1000 seconds. The data can be represented approximately by the cubic rate law.

A brief study was made of the reactions occurring between aluminum or stainless steel and uranium dioxide or U_3O_8 in cermet fuel pins. The method of differential thermal analysis (DTA) was used. A very mild exothermic reaction was found to occur between aluminum and uranium dioxide or U_3O_8 at about 900 C. Reaction products included UAl_2 , UAl_3 , and UAl_4 , which were identified by X-ray diffraction. It was concluded that the reactions were not violent or dangerous.

Two series of in-pile, metal-water experiments were completed. Meltdowns were conducted on stainless steel-urania cermets, uranium wires, and on ceramic core, metal-clad fuel specimens. Cermets made of 90 weight percent stainless steel with urania showed similar behavior when submerged in water irrespective of whether the sample was in the form of pins or plates; metal temperatures greater than 1500 C were attained. The original geometry was changed into one or two large globules together with many fine particles; the more energetic transients also produced some fine (1-mil diameter) powder. Chemical analyses indicated that a separation of the urania from the stainless steel took place during the melting-quenching cycle of the reactor burst. The larger globules were depleted in uranium (0.017 to 0.055 weight percent uranium) whereas the fine particles were more concentrated in uranium (30 to 64 weight percent uranium). The plate type cermet elements gave only slightly more metal-water reaction than the cylindrical elements; both reacted more as the energy of the burst was increased. The stainless steel-urania cermet fuel pins gave 6.6 and 10.2 percent metal-water reaction at reactor bursts of 435 and 512 Mw-sec on a 50-ms period. The corresponding specific-energy inputs to the fuel specimen, as determined by the average from molybdenum-99 determinations, are 379 and 445 cal/gm, respectively.

A Zircaloy-2 clad, ceramic core fuel pin subjected to a 648 Mw-sec pulse (606 cal/gm) on a 50-ms period gave nearly complete destruction of the specimen with 24.0 percent of the metal jacket reacting with the water. The data obtained to date from the various ceramic and cermet core fuel pins were correlated as a function of the energy of the reactor burst. The following table summarizes the results at two different energies:

Type of Fuel Pin	Percent Metal-Water Reaction		
	at 400 Mw-sec	at 500 Mw-sec	Reaction
Zr-2 clad, oxide core	8.0	13.0	Zr-H ₂ O
SS-UO ₂ cermet	5.0	9.3	SS-H ₂ O
Al-U ₃ O ₈ cermet	3.2	4.7	Al-H ₂ O
SS clad, oxide core	0.0	0.8	SS-H ₂ O
Al clad, oxide core	0.4	0.8	Al-H ₂ O

The conversion from reactor to absorbed energy for the oxide core pins is 0.935 (cal/gm)/Mw-sec and 0.87 (cal/gm)/Mw-sec for the stainless steel-urania cermets.

Transients conducted on 64-mil diameter uranium (93 percent enriched) wires gave 33.2 and 50.2 percent molten uranium-water reaction at reactor periods of 440 and 152 ms, respectively. The average energy input to the wire was 554 cal/gm from molybdenum-99 analyses. The wires were converted into fine particles and powder. It is planned to correlate these experiments with condenser discharge experiments, which were also carried out with wires.

A. Metal Oxidation and Ignition Kinetics
(L. Baker)

1. Ignition Studies of Uranium Powder by the Burning-curve Method

The burning-curve procedure has been used extensively to provide reproducible data on the ignition characteristics of uranium. The sample, mounted on a thermocouple, is heated at a uniform rate of temperature increase (usually 10 deg/min) in a flowing oxidizing atmosphere. As the rate of reaction increases, the sample self-heats and finally ignites. A graphical intersection method is used to determine ignition temperature. The difference between furnace and sample temperatures gives an indication of the rate of reaction over a wide temperature range. The burning-curve method has been used to define the effects of varied specific area, alloy additives, and gas compositions on ignition and maximum burning temperature (see ANL-5974, pages 10 to 39).

a. Effect of Pre-oxidation on the Ignition of Uranium Powder
(M. Tetenbaum and R. Wagner)

It was reported in the previous quarterly (ANL-6287, page 172) that ignition temperature decreases, levels off, and finally increases with extent of pre-oxidation of a fine fraction of spherical uranium powder (-140 +170 mesh, $d = 88 \mu$). Studies were extended to a coarse fraction (-20 +25 mesh, $d = 710 \mu$) to see if a lower specific area powder would show a similar effect. The results are summarized in Figure 55. It is apparent that the trends are about the same for the coarse and fine uranium fractions. With coarse powder, however, the changes of ignition temperature are less than the changes obtained with the higher specific area fraction.

Pre-oxidation was accomplished by heating a thin layer of the powders in air at approximately 150 C for varying lengths of time. After cooling and weighing, microscopic examination of both powders after pre-oxidation revealed that the surfaces had become coated with black oxide nodules, the thickness increasing with heating time. Figure 56 shows photomicrographs of -140 +170 mesh powder as received and after 20 hr at 150 C. The oxygen uptake (weight gain) of the powders is plotted in Figure 57 as a function of time. Results reported previously (ANL-5974, page 51) for the oxygen uptake of polished 1-cm uranium cubes is plotted for comparison. It is apparent that both powder fractions show a first-stage reaction, followed by acceleration to a more rapid, linear second-stage process previously reported for uranium cubes. The accuracy and stability of the temperature during the powder studies, however, were of a lower order than those obtained in the isothermal studies with cubes. Quantitative comparisons of the rates are, therefore, not made.

The minimum ignition temperatures in Figure 55 are reached after 5 to 10 percent of the powder has been reacted at 150 C. Ignitions initiated in the burning-curve apparatus probably begin in the more rapid second stage. This may account for the decreased ignition temperature.

b. Ignition of Uranium Monocarbide Powders
(M. Tetenbaum, R. Wagner)

Measurements of the ignition behavior of uranium monocarbide powder (hereby designated as Source A) were reported in the previous quarterly (ANL-6287, page 173). Since then, burning-curve studies have been made with powder from a different source (designated as Source B).

FIGURE 56

EFFECT OF PRE-OXIDATION AT 150 C IN AIR ON NODULE FORMATION OF -140 -170 MESH SPHERICAL URANIUM POWDER

a. As received

b After 20 hours at 150 C

FIGURE 57

COMPARISON OF URANIUM POWDER OXIDATION DATA
WITH ISOTHERMAL OXIDATION OF URANIUM CUBES

Microscopic examination of these powders revealed that Source A powder was much more irregular in shape than Source B. Source A powder, as originally received, was relatively coarse and gave sieved fractions in the range -20 +100 mesh, whereas Source B powder gave fractions in the range -170 +325 mesh. In order to intercompare the ignition behavior of the two products, the coarse Source A powder was ground with a mortar and pestle, and sieved to yield powder fractions corresponding to Source B mesh size. The results of ignition temperature measurements in pure oxygen on various sieved fractions are summarized in Table 64.

An estimate of the specific areas of these powders was obtained on -270 +325 mesh samples by means of a Fischer-Sieve Sizer.^{*,**} Roughness factors of approximately 3.1

and 1.6 were derived from these measurements for Source A and B powders, respectively. It was then possible, therefore, to assign specific area values to various Source A and B powder mesh fractions using these roughness factors, and hence to compare ignition temperatures on the basis of specific area.

Table 64

IGNITION BEHAVIOR OF URANIUM MONOCARBIDE
POWDERS IN OXYGEN

Mesh	Source A Powder (roughness factor, 3.1)		Source B Powder (roughness factor, 1.6)	
	Specific Area ^a (sq cm/g)	Ignition Temperature (C)	Specific Area (sq cm/g)	Ignition Temperature (C)
-270 +325	314	255	157	280
-230 -270	-	-	131	290
-200 +230	223	275	112	305
-170 +200	187	275	93.5	315
-140 +170	157	290		
-80 +100	93.0	280		
-70 +80	78.0	295		
-50 +60	55.5	300		
-35 +40	33.0	310		
-25 +30	23.5	315		
-20 +25	19.5	320		

^aSource A samples with specific areas above 100 were obtained by grinding with mortar and pestle.

*We are indebted to M. Fischer and R. Werle of Armour Research Foundation for these measurements.

**This instrument operates on the principle that particles in the path of a regulated air flow will affect the air flow in relation to their size.

The specific area values are given in Columns 2 and 4 of Table 64, and Figure 58 shows the plot of specific area *vs.* ignition temperature for these uranium monocarbide powders. Included in this figure are ignition temperature values obtained on spherical uranium powder fractions.

Examination of the data in Table 64 and Figure 58 shows that (1) Source B powder is less pyrophoric (ignition temperatures ~25 C higher) than Source A powder on the basis of equivalent mesh size fractions; (2) ignition temperature values obtained with both powders compare reasonably well on the basis of specific area, but differ somewhat (when extrapolated) from the values obtained with the lower specific area fractions of Source A powder before grinding; (3) uranium monocarbide powders are not as pyrophoric as uranium powders of similar specific area.

c. Ignition of Uranium Foil Aggregates
(L. Baker, J. G. Schnizlein, and J. D. Bingle)

The most important variable leading to lower ignition temperatures of single samples has been the specific area (surface area per gram) of the sample. It was shown previously that there is also a decided lowering of ignition temperature when aggregate samples are

studied. The ignition temperatures of spherical uranium powders decreases up to a certain critical point as the amount of sample is increased (see, for example, ANL-6183, page 130). A brief series of burning curves with bundles of wires in oxygen (ANL-6231, page 139) also showed a greatly decreased ignition temperature when compared with individual wire specimens of the same specific area. A similar series of runs with bundles of wires in air has since shown virtually the same results.

In addition, two series of burning curves were made with one, two, four, and eight thicknesses of uranium foils in air. Specimens were 1.6 x 1.6-cm squares and were either pressed together in a tight stock or arranged vertically with a spacing of 2.6 mm between each foil square. Runs were made with 0.13-mm (nominal 5-mil) and 0.01-mm (nominal one-half-mil) thick foils. The sensing thermocouples were located at the center of the foil stacks or pressed against the center of the single foil squares.

The results are given in Table 65. It is apparent that the ignition temperatures of foil stacks are considerably lower than those in individual foils. This series of runs has important practical consequences because of the common practice of storing metal sheets or plates in stacks. The results are also significant from a theoretical point of view because of the systematic lowering of heat loss rates in going from a single foil to a stack of foils. A single foil will lose heat by radiation and convection, from both faces. Two foils will lose heat principally from the exposed faces. Adjacent faces will be mutually insulated. Surface available for heat loss would, therefore, be halved relative to the surface available for reaction. Relative heat loss rates would again be halved when four foils are used. Effective heat transfer area will eventually reach some constant fraction of the total reactive surface when losses from the edges become significant. Results in Table 65 indicate that the principal lowering of ignition temperature occurs in going from one to two foils.

Table 65

BURNING-CURVE IGNITION TEMPERATURES OF
STACKS OF URANIUM FOILS^a IN AIR

<u>Sample</u>	<u>Ignition Temperature (C)</u>	
	<u>0.13-mm foil</u>	<u>0.01-mm foil</u>
one foil	400	320
two foils	355	305
four foils	350 (360 ^b)	300
eight foils	340 (350 ^b)	290

^aFoils were 16 mm square and spaced 2.6 mm apart in a ceramic holder.

^bFoils pressed together in a tight stack.

Attempts to compute burning curves from isothermal rate data and heat transfer coefficients are underway. It may be possible to show quantitatively how increased specific area and increased aggregation (lowered heat losses) will lower measured ignition temperatures.

d. Ignition of Certain ZPR-III Blanket Plates
(J. G. Schnizlein, J. D. Bingle)

Because approximately 18 out of a total of 20,000 of the $\frac{1}{8}$ -in.-thick uranium plates in use in ZPR-III to make up blankets in critical assemblies were observed to be deteriorating and crumbling, the possibility of an increased pyrophoricity hazard was investigated.

Both deteriorated and apparently solid material from the same batch were obtained, and samples were prepared in the form of approximately 3-mm cubes. Spectrographic, oxygen, and hydrogen analyses were obtained and burning-curve ignition experiments were performed. The only impurities out of the ordinary, except oxygen, may have been present as surface contamination acquired during handling in the assembly. An extremely high oxygen content (24,000 ppm) of the deteriorated sample and a high content (530 ppm) in the unaffected sample suggested porosity of the samples.

The ignition temperature in oxygen of the unaffected material (480 C) was approximately 60 degrees lower than that obtained for reactor-grade uranium in previous experiments with samples of similar size. The deteriorated samples ignited at 115 C in either oxygen or air. This temperature is slightly lower than the lowest ignition temperature previously obtained, i.e., 120 C, for a compacted sample of irregular uranium powder which had a measured specific area of 6,500 sq cm/gm.

It would appear that the deterioration process is resulting in a reversion to powder. It is understood that these plates were prepared by powder metallurgical methods using hydrided-dehydrided metal powder and that a larger fraction of such plates are showing signs of deterioration than are the plates formed by rolling or casting and stamping. Metallographic examination also indicated porosity.

The deterioration of uranium formed by a powder metallurgical process due to slow oxidation within the pores can cause a pyrophoricity hazard. If porosity is an inherent property of powder metallurgically formed uranium, then it must be protected from the air to avoid such hazard.

Personnel at ZPR have minimized the hazard by recoating the metal with a fluorocarbon plastic periodically. Careful frequent inspections are also made to remove affected pieces. The deteriorated plates have been stored in an inert atmosphere in sealed paint cans which were placed approximately 6 in. apart in a sand bath.

2. Burning-propagation Studies (L. Leibowitz, L. W. Mishler)

The burning-propagation rate, i.e., the rate of advance of a combustion zone along a foil or wire, has proven to be a useful, reproducible quantity for studying the nature of metal combustion, as well as for judging the influence of various factors on the burning process.

The metal is ignited at one end by an electrically heated platinum wire and, heretofore, a motion picture record made of the process. Linear propagation rates were obtained from these motion pictures. A new instrument has been developed, however, which permits the simultaneous and rapid determination of burning velocity and temperature. This device will be used to study systematically the effect of various halogenated hydrocarbons on the burning metal.

a. Proposed Studies of the Effect of Halogenated Hydrocarbons on Burning Propagation

The effectiveness of halogenated hydrocarbons in combatting fires has been recognized for some time. The early literature has been summarized by Fryburg.³² As part of a search for practical methods of controlling and preventing metal fires, a large number of substances have been examined for their effect on burning-propagation rate and burning temperature. The presence of a few percent in air of various halogenated hydrocarbons caused a marked reduction in burning propagation rate (ANL-6231, pages 142, 152). Although some study has been made of the mechanism by which halogenated hydrocarbons inhibit hydrocarbon combustion,³³ it is not at all clear how these compounds influence metal combustion. Because of the low vapor pressure of uranium³⁴ at the burning temperature, a gas-phase combustion in air is unlikely. The halogenated hydrocarbon thus could not operate in the same manner with metals as with hydrocarbon fuels.

Examination of the effect of the halogenated agents on the thermal conductivity and heat capacity of air eliminate these properties as the source of the effect. Two principal mechanisms may be suggested: (a) the halogenated agents decompose on the burning metal surface and

³²Fryburg, G., Review of Literature Pertinent to Fire-extinguishing Agents and to Basic Mechanisms Involved in Their Action, NACA-TN-2102 (May 1950).

³³Belles, F. E., Chemical Action of Halogenated Agents in Fire Extinguishing, NACA-TN-3565 (Sept. 1955).

³⁴Rauh, E. G., and Thorn, R. J., J. Chem. Phys., 22, 1414 (1954).

remove heat by the reaction

where X is a halogen atom and $R\cdot$ an organic radical; or (b) Reaction (1) is followed by

and the rate of the diffusion-controlled combustion is lowered because of a net reduction in oxygen availability. Bond-dissociation energies for a series of halomethanes are listed below.³⁵

	<u>D(R-X), kcal</u>
CH ₃ -F	107
CH ₃ -Cl	80.7
CH ₃ -Br	67.5
CH ₃ -I	54

Considerable heat could be removed from the burning region by such a dissociation. Reactions such as (2) have been proposed by several workers. Blaedel, Ogg, and Leighton,³⁶ for example, in studying the photo-oxidation of methyl iodide proposed

as part of the reaction scheme.

A number of experiments were performed to determine the effectiveness of the halogenated compounds in cooling an electrically heated platinum foil. These results have been reported (ANL-6287, page 179) and indicate that reaction (1) is not the source of the combustion inhibition if results with the platinum can be applied to burning uranium or zirconium.

Several series of compounds have been selected to explore systematically the relative importance of reactions (1) and (2) in the case of metal combustion in air contaminated with halogenated hydrocarbons. These compounds are listed below.

³⁵Szwarc, M., Chem. Rev., 47, 75 (1950).

³⁶Blaedel, W. J., Ogg, R. A., and Leighton, P. A., J. Am. Chem. Soc., 64, 2500 (1942).

CHF_3	CF_4	CH_3Cl	$\text{C}_2\text{H}_5\text{Cl}$	CH_3Cl
CHF_2Cl	CF_3Cl	CH_3Br	$\text{C}_2\text{H}_5\text{Br}$	CH_2Cl_2
CHFCl_2	CF_3Br	CH_3I	$\text{C}_2\text{H}_5\text{I}$	CHCl_3
CHCl_3				CCl_4

These will provide groups of compounds with R or X fixed and the other fragment variable, so that the importance of the R-X bond energy and the R· oxygen affinity can be evaluated independently. In addition, the heat contributed by oxidation of the organic component will be considered as well as possible specific halogen effects.

b. Simultaneous Measurement of Burning-propagation Rate and Maximum Burning Temperature

A device has been developed which allows simultaneous measurements of burning velocity and temperature. A schematic diagram of this instrument is shown in Figure 59.

Light from the burning foil is focused on a plate bearing two slits a known distance apart. This light, after passing through the filters, is received by the phototubes, the output of which is displayed on an oscilloscope and photographed.

The burning velocity is easily calculated from the time required for the burning front to travel the distance between the slits. The burning temperature may be found in two ways. The radiation intensity in the normal direction, $i_{bn\lambda}$, at wave length λ for a black body at absolute temperature T is given by the Planck equation

$$i_{bn\lambda} = \frac{2hc^2}{\lambda^5 (\exp [hc/\lambda kT] - 1)} = \frac{2C_1}{\lambda^5 (\exp [C_2/\lambda T] - 1)}, \quad (6)$$

where h is Planck's constant, k Boltzmann's constant, c the velocity of light, and C_1 and C_2 are constants defined by these equations. Neglecting unity in the denominator,

$$i_{bn\lambda} = \frac{2C_1}{\lambda^5 \exp(C_2/\lambda T)}, \quad (7)$$

and for a non-black body

$$i_{n\lambda} = \frac{\epsilon C_1}{\lambda^5 \exp(C_2/\lambda T)} = \frac{2C_1}{\lambda^5 \exp(C_2/\lambda T_B)} \quad (8)$$

where ϵ is the emissivity and T_B the brightness temperature.

Interference filters and the Jena glass filter, RG-10, transmit sharply defined wave lengths to the phototubes. Wave lengths of 805 and 976 $m\mu$ are received by the left- and right-hand phototubes, respectively. With the availability of emissivity values for tungsten,³⁷ it was possible to calibrate the instrument using a tungsten ribbon lamp, the temperature of which was measured using a Leeds and Northrup optical pyrometer. Good agreement was found with the theoretical equation.

It is also possible to use the instrument as a two-color pyrometer. The ratio of intensities (r) at the two wave lengths λ_1 and λ_2 is given by

$$r = \frac{i_{\lambda_1}}{i_{\lambda_2}} = \frac{\lambda_2^5 \epsilon_{\lambda_1}}{\lambda_1^5 \epsilon_{\lambda_2}} \exp \left[\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \frac{C_2}{T} \right], \quad (9)$$

and a similar calibration may be carried out. In measuring the temperature of objects of unknown emissivity, the ratio method offers the advantage that it is generally a better approximation to assume the ratio of emissivities to be unity than to assume that the emissivity itself is unity. It was

³⁷De Vos, J. C., *Physica*, 20, 698 (1954)

FIGURE 60
OSCILLOSCOPE RECORD OF TYPICAL BURNING
PROPAGATION OF URANIUM FOIL BURNING IN AIR

found, however, that the maximum temperature of the burning front is not precisely constant along the entire length of the foil. Since the ratio method is far more sensitive to variations in intensity, the brightness temperature will be measured using the instrument as two single-color pyrometers.

A typical oscilloscope record of the burning is shown in Figure 60. A 3-mm wide, 0.13-mm (5-mil) thick uranium foil was burned in air. Since 6.3 sec were required for the burning front to cover the 3.225 cm between the slits, a burning velocity of 0.51 cm/sec results. From the peak heights, brightness temperatures of 1325 and 1320 C are found at 0.8 μ (at 4 sec) and 1.0 μ (at 10 sec), respectively. This burning

velocity agrees well with the value 0.56 cm/sec found by the previous method (ANL-6068, page 130).

Measurements of burning velocity and temperature will be carried out in air contaminated with small quantities of the organic compounds listed in the preceding section. Both uranium and zirconium will be studied in this way.

B. Metal-Water Reactions (L. Baker)

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

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

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

reaction temperature. The transient pressure measures reaction rate, the amount of hydrogen generated gives the extent of reaction, and the particle size of the residue indicates the surface area exposed to reaction. Analysis of the results is based on one of the usual laws of metal oxidation (parabolic rate law) and on the laws of gaseous diffusion and heat transfer.

a. Zirconium Runs at High Pressure

The series of runs with 60-mil zirconium wires in the high-pressure reaction cell is continuing. Five runs were completed in

water at 315°C under a corresponding vapor pressure of 1500 psi. The total extent of reaction is plotted as a function of initial metal temperature in Figure 61. The average line (25 runs) for runs in water from 90 to 200°C (10 to 225 psi) is included on the figure. The average line (30 runs) for runs in room temperature water is also included for reference. It is now evident that an increase in pressure from 225 psi to 1500 psi does not change the character of the reaction.

Pressure traces from the runs indicated that very rapid rates of rise of pressure occurred just above the melting point, at about 1900°C. The residue from runs both above and somewhat below this temperature showed many more very fine particles than runs at corresponding initial temperatures in room-temperature water. Most of the particles were heavily coated with white oxide, whereas residue from room-temperature runs

had the thinner, black oxide coating. It seemed unlikely that the initial breakup of the specimen wire into particles would be influenced by changes in the ambient pressure. It is more likely that the smaller particles of the normal size distribution produced by the discharge were capable of rapid self-heating to temperatures above the melting point of zirconium dioxide (2700°C). Particles coated with molten oxide could very likely undergo repeated subdivision resulting in many fine particles and rapid reaction. The larger particles of the initial distribution could not self heat sufficiently. The coating of solid oxide on the larger particles thus was able to prevent the liquid metal from subdividing into smaller particles.

Two pressure traces from runs in water at 110 C (20 psi vapor pressure) are plotted in Figure 62. The metal in Run 200 was fully melted at the melting point. The metal in Run 223 was also fully melted but at a slightly higher temperature. The initial spike in both traces is at least partly electrical in origin, for it occurs in test discharges when no water is present. The circuit recovers from the interference pulse in about 3 ms. In Run 223, the reaction was nearly completed after 3 ms, whereas in Run 200, about 50 ms were required to reach a pressure corresponding to the final pressure. Both traces, however, can be interpreted as a composite of two reactions, one very fast and one much slower. In Run 200 very few of the metal particles produced initially were small enough to undergo the rapid reaction, whereas in Run 223 most of the particles were small enough to undergo the rapid reaction.

Average particle sizes for runs in room-temperature water were reported in a previous quarterly (ANL-5996, page 238). It was shown that mean particle diameters first begin to decrease below values equivalent to the original wire when the metal became fully melted. Metallographic and size studies of particles from more recent runs in heated water are planned.

b. Interpretation of Previous Studies of the Zirconium-Water Reactions

A mathematical analysis of the zirconium-water reaction was presented in the previous quarterly (ANL-6287, pages 182 to 187). It was shown that the reaction rate was limited by the rate of diffusion of water vapor through the hydrogen barrier surrounding hot metal particles during the initial stages of the reaction. At a later time, the reaction

becomes limited by the parabolic rate law. The parabolic rate law is generally considered to apply when reaction is limited by the rate of diffusion of either metal ions or oxygen ions through the oxide lattice. The rate of the first process, gaseous diffusion, was considered to depend only on the mean temperature between the metal and the water and on the vapor pressure of water at the water-water vapor interface. The rate of the second process, solid-state diffusion, was considered to depend only on the temperature of the oxide and the thickness of the oxide film. The rate of the solid-state process decreases very rapidly as the oxide film thickens. The rate of the solid-state process is theoretically infinite at zero time; however, it rapidly decreases and eventually becomes less than the gaseous diffusion rate. At this point, the reaction becomes controlled by solid-state processes.

Some of the results of previous investigators were examined in the light of the above concepts. One isothermal study of the Zircaloy-2-water reaction and one of the Zircaloy-2-steam reaction were examined in particular. The studies with water were carried out by Bostrom at Westinghouse³⁸ by induction heating under water. Reaction was followed by collecting successive fractions of hydrogen generated by reaction. Studies with steam were carried out by Lemmon *et al.* at Battelle.³⁹ In this study, steam at 20 or 50 psi was passed over inductively heated metal and the extent of reaction determined by measurements of the hydrogen collected. The results of both studies were summarized in the Battelle Report.³⁹

Neither investigator considered the possibility that the reaction might have been limited by gaseous diffusion during the early part of a run. Results reported by Bostrom at 1750 C deviated seriously from the parabolic slope on a plot of the log of hydrogen gas evolved *vs.* the log of time.³⁹ The reaction appeared to be somewhere between parabolic and linear. Bostrom's data at 1750 C is replotted in Figure 63. The square of the quantity of hydrogen evolved is plotted as a function of time. A straight line on this type of plot indicates a parabolic rate. It is apparent that the first three points indicated a lower slope than the remainder, which followed a satisfactory straight line. This change in slope could be accounted for by transition from a reaction limited by gaseous diffusion to one limited by the parabolic rate law. The lowered initial rate could also be due to failure to heat the specimen to reaction temperature rapidly enough. In either case the log-log plot does not show the transition. The true parabolic rate constant can be obtained from the slope of the line in Figure 63.

³⁸Bostrom, W. A., The High Temperature Oxidation of Zircaloy in Water, WAPD-104 (March 1954).

³⁹Lemmon, A. W., Jr. Studies Relating to the Reaction between Zirconium and Water at High Temperatures, BMI-1154 (Jan. 1957).

FIGURE 63
REACTION BETWEEN ZIRCALOY-2 AND
WATER AT 1750 C
(DATA FROM BOSTROM, WAPD-104)

Bostrom's data at other temperatures indicate an increasing rate when oxide films become about 25 mils thick. Oxidation to this degree is normally not encountered in the condenser-discharge studies. Battelle data also showed some tendency toward a decreased initial rate.

The results of replotting both sets of data are indicated in Figure 64, where the log of the parabolic rate constants are plotted as a function of reciprocal absolute temperature. The falling off of the Battelle data above 1300 C is not understood. The reaction rate at 1840 C (melting point of zirconium) used in the computer studies of the condenser-discharge experiment is also included on Figure 64.

energy of 45.5 kcal/mole and fits condenser data, Bostrom's data, and the low-temperature Battelle data. The activation energy obtained in this way is believed to be more satisfactory than one obtained solely from condenser-discharge studies.

The following rate law was then calculated:

$$V^2 = 4.82 \times 10^8 \left(\exp - \frac{45,500}{RT} \right) t \quad , \quad (10)$$

where V is cc hydrogen at STP per sq cm of surface and t is time in min.

c. Comparison of Computed Results with Experimental Results

Computed results presented in the previous quarterly referred to runs with heated water. It was shown that extensive reaction occurred with a particle, 1.05 mm in diameter, which was only partially melted. This result was consistent with the experimental results which indicated that reaction rapidly increased with initial metal temperature for metal in the melting point region (see Figure 61).

It was suggested that the much less extensive reaction occurring in room-temperature water was the result of a decreased rate of gaseous diffusion. The very low vapor pressure of water at room temperature (0.5 psi) caused a lowering of the rate of diffusion of water vapor through the hydrogen barrier surrounding the metal particles. Several methods of describing the decrease were investigated theoretically. A very simple assumption provided reasonable agreement with the data.

Runs with water at room temperature were done both with and without inert gas. Runs without added inert gas generated enough hydrogen and steam almost immediately so that the bulk water temperature (room temperature) was below the boiling point of the water determined by the total pressure. This condition is generally referred to as subcooling. In order to realize the full diffusion rate, water at the surface facing heated metal must be uniformly at the boiling point. If turbulence or heat transfer into the water causes a decrease in the average temperature of the water surface, then a decreased diffusion rate would result. It was assumed that the average vapor pressure driving diffusion was one-half of the total pressure. Diffusion rates would then be one-half of those calculated for runs in heated water.

Results of computed reactions using one-half of the theoretical diffusion rate are compared to experimental results in Figure 65. Average particle sizes for runs in which the metal was not fully melted were approximately 1050 μ for 30-mil wires, and 2100 μ for 60-mil wires. The experimental mean particle diameters for runs with molten metal are included on the figure. It is apparent that the calculated results agree qualitatively with the experimental results for the total extent of reaction.

FIGURE 65
COMPUTED AND EXPERIMENTAL RESULTS OF ZIRCONIUM
RUNS IN ROOM-TEMPERATURE WATER

d. Discussion of Explosive Reactions

A combination of the parabolic rate law and the law of gaseous diffusion have provided a reasonable description of both the rate and extent of the "nonexplosive" reaction occurring at lower initial metal temperatures. Runs showing only the slow pressure rise inevitably resulted in larger particles. Particle diameters greater than $500\ \mu$ in room-temperature water were generally associated with "slow" runs. Particle diameters less than $500\ \mu$ were associated with "explosive" runs. Calculations for a $525\text{-}\mu$ particle, shown in Figure 65, indicate about 30 percent total reaction but do not predict the rapid rates that are observed. This discrepancy indicates that a higher Nusselt number should be used in the calculations. The Nusselt number controls both the rate of gaseous diffusion and the rate of convective cooling. An increased Nusselt number would increase the rate of the overall process almost proportionately, but would not greatly change the total extent of reaction. Only the radiation heat loss term is unaffected by changes in the Nusselt number. Heat loss, however, occurs principally by convection (or film conduction) for the smaller particles.

The explosive runs are also associated with total reactions of the order of 30 percent or more. The high degree of reaction along with the apparently high Nusselt number suggest that perhaps the particles are driven through the water at high velocity by the rapid hydrogen evolution. The motion picture films of explosive runs, which incidentally corroborated

the pressure traces in indicating a very rapid reaction, were examined. Motion pictures of explosive runs do show evidence of high speed "streaks" indicative of rapid particle motion.

Computed data shown in Figure 65 suggest that the term ignition temperature is not of fundamental significance. Rather, "ignition particle size" would be more correct. The critical particle diameter in room-temperature water is, accordingly, about 500μ . Calculations indicate that 1050- and 2100- μ particles will not give more than 20 percent reaction at any temperature. Runs with 30- or 60-mil wires, however, show an apparent ignition at 2600 C. This seems to result from spontaneous subdivision of the larger particles when the oxide can no longer encase large particles.

The critical particle size is somewhat larger in heated water, probably closer to 1000μ , because of the increased diffusion rate. This results in a lowering of the apparent ignition temperature to 1900 C.

e. Discussion of Results with Zirconium

A combination of experimental and theoretical studies has provided an accurate picture of the reaction of zirconium particles formed almost instantaneously under a water surface. The following rate law was obtained from an analysis of the condenser-discharge studies and previous studies at lower temperatures:

$$V^2 = 4.82 \times 10^8 \left(\exp - \frac{45,500}{RT} \right) t \quad ,$$

where V is cc hydrogen at STP per sq cm of surface and t is time in min. Battelle results indicate that the equation applies at 1000 C. Condenser studies are satisfactorily explained by the rate law up to initial metal temperatures of the order of 3000 C when proper account is taken of role of gaseous diffusion in the overall process.

The rate law at the melting point of zirconium (1840 C) is accurately determined from condenser-discharge experiments as follows:

$$V^2 = 10,060t \text{ at } 1840 \text{ C} \quad .$$

The rate constant at the melting point is determined by the data to within 10 percent. Rate constants at higher temperatures were considerably less accurate because of the dominance of the melting temperature in the time-temperature history of the particles. Results obtained by other investigators at lower temperatures were, therefore, used to evaluate the activation energy of the reaction.

Computed results of the type shown in Figure 65 for runs in room-temperature water can be used to estimate the extent of reaction to be expected during an accident in a water-cooled reactor. The particle sizes produced in the incident and the temperature at which they are formed must be estimated from considerations of reactor kinetics. Particle size distributions and breakup patterns are determined directly in the TREAT studies to be discussed in a later section.

Results of the type shown in Figure 65 for runs in heated water will be compared to experimental data in a succeeding publication. Particle size measurements for runs in heated water have not been completed

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

The pressure-pulse technique has been developed to study the kinetics of reactions of molten metals with water vapor under isothermal conditions. Results obtained from this method are to be used as an aid in analyzing the data obtained from other metal-water studies. The pressure-pulse method should give the best determination of the form of the rate law.

The pressure in the reaction cell which contains the molten metal is about 3 mm, due to the presence of argon to reduce the vaporization of the molten metal. An induction heater is used for heating the sample. When the sample is at the desired temperature, electronically controlled valves are operated in proper sequence to contact water vapor at known pressure with the molten metal for a specified period of time. A more complete description of the apparatus and operating procedure appears in a previous report (ANL-6287, page 190).

Aluminum Runs

Figure 66 shows the results of the reaction of water vapor (500 mm pressure) with aluminum. Reasonably complete data are shown for 1000 and 1200 C, although it is planned to check a few additional points.

In five decades of reaction time, the reaction between aluminum and steam appears to follow the cubic law. There is some doubt about the rate at 0.1 sec, but large deviations are to be expected at the short reaction times. A thin layer of alumina already present on the aluminum would give a low result at 0.1 sec. A small amount of vaporized aluminum deposited on the cell walls would cause a high result. As reaction time is increased, both effects become less important compared to total reaction.

FIGURE 66
REACTION BETWEEN ALUMINUM AND STEAM AT 500 mm PRESSURE

Attempts have been made to run the aluminum-water reaction at higher and lower temperatures. However, evaporation becomes quite severe above 1300 C, leading to expected high results. The quantity of gas expected at 800 C is rather small. This causes difficulties in analysis. It is anticipated that some useful data may be obtained outside the present temperature range.

3. Thermal Analysis of Uranium Oxide-Metal Cermets (D. F. Mason, J. D. Bingle)

Recent differential thermal analyses (DTA) of aluminum- UO_2 cermets have indicated some tendency for them to react.⁴⁰ If the reaction is similar to the thermite reaction, i.e.,

there is the possibility that a large amount of heat might be released. Calculations⁴¹ indicate that the free energy of formation is about +2 kcal at 800 C, and more positive at higher temperatures. However, this calculation assumes the products are only the two phases uranium and aluminum oxide. If other products such as uranium-aluminum compounds are formed, the

⁴⁰Private communication, J. D. Fleming to J. M. Simmons, AEC Washington.

⁴¹Alvin Glassner, The Thermochemical Properties of Oxides, Fluorides, and Chlorides to 2500 K, ANL-5750 (1957).

The uranium oxide-metal cermets were also studied by X-ray diffraction. This enabled a determination of the major reaction products.

a. DTA Apparatus and Procedure

The cermet pin and the reference substance are contained in small alumina crucibles. The crucibles are located symmetrically in a nickel boat which is inserted into a high-temperature porcelain furnace tube. The differential thermocouples (Pt; Pt, 10% Rh) are connected inside the furnace, and are protected by alumina tubes before insertion into pre-drilled holes in the sample and the reference substance.

The boat temperature is measured by a chromel-alumel thermocouple located in a hole drilled close to the center of the block. A grounded platinum shield is located around the center of the furnace to reduce electrical pickup which disturbs the differential thermocouple recorder. The nickel boat is itself grounded also. The furnace controller-programmer thermocouple is located inside the platinum-resistance furnace but outside of the porcelain furnace tube. The programmer-controller is a Minneapolis-Honeywell Brown Electronic. The recorder is a 2-pen Bristol with scales of 0 to 1200 C and -0.5 to +0.5 mv.

All samples were run in a slowly flowing purified argon atmosphere at one atmosphere pressure. It was felt that an air or oxygen atmosphere might complicate analysis of the results.

All samples were run from room temperature to 1200 C and then back again to about 500 or 550 C. The temperature was again increased to determine which of the reactions observed on the DTA chart were reversible.

b. Differential Thermal Analysis Runs

In Figure 67 are shown the results of a number of DTA runs. The heats of reaction of most major peaks are indicated on the figure. Figure 67a is the result of a sample of copper run against silver. This was used to check the temperature scale and also to determine the magnitude of the heats of reaction involved in the cermet runs. Figures 67b and 67c give results for stainless steel, 10 weight percent uranium dioxide and stainless steel, 10 weight percent U_3O_8 , respectively, run against stainless steel. If a reaction has occurred here, it is too small to be distinguished for certain. It is possible that a higher percentage of uranium oxide would give a measurable reaction. Figure 67d gives the results for a run of aluminum, 10 weight percent U_3O_8 vs. aluminum. The deflections observed are due to the heat of fusion of the aluminum in the two samples.

Figures 67e and 67f are data for aluminum plus 50 weight percent U_3O_8 and uranium dioxide, respectively, vs. alumina. Although there are some minor differences in the two runs, they are essentially similar. A definite exothermic reaction occurs between 900 and 950 C in both uranium dioxide- and U_3O_8 -aluminum cermet. This reaction was not reversible. It is probably the same reaction observed by J. D. Fleming,⁴⁰ since it occurs in the same temperature range (840 to 950 C).

The heat of reaction was estimated from the calibration run of copper vs. silver, and also from the heat of fusion of aluminum in the run itself. Using the copper vs. silver calibration, the energies of the aluminum-50 weight percent uranium dioxide and aluminum-50 weight percent U_3O_8 samples comes out to 90 ± 20 cal/gm sample. Subtracting the heat of fusion of aluminum, the energy becomes 60 ± 15 cal/gm sample.

Samples of the uranium dioxide + aluminum, U_3O_8 + aluminum, uranium dioxide + stainless steel, and U_3O_8 + stainless steel cermets were analyzed by X-ray diffraction. The DTA samples with 10 weight percent uranium oxide in them were, for the most part, indistinguishable from samples of the original cermet that had not been run. In some cases, the material was found to be slightly changed, but the concentration of uranium dioxide or U_3O_8 was too low to assure identification of product species. This tended to confirm the negative results of those DTA runs.

The 50 weight percent uranium dioxide and U_3O_8 aluminum cermets gave more positive results with X-ray diffraction analysis. The results are summarized in Table 66 along with the 10 weight percent uranium dioxide aluminum cermet data for comparison.

Table 66

RESULTS OF X-RAY DIFFRACTION ANALYSIS OF
URANIUM OXIDE-ALUMINUM CERMETS

Original Composition	X-Ray Analysis - Before DTA		X-Ray Analysis - After DTA	
	Major Components	Minor Components	Major Constituents	Minor Constituents
10 w/o U_3O_8 + Al (fired to 1200 C)	Al	UO_2 perhaps U_3O_8	Al	UO_2
50 w/o UO_2 + Al (pressed, unfired)	Al, UO_2	-	UAl_4	UAl_3 , UAl_2 , and Al(?)
50 w/o U_3O_8 + Al (pressed, unfired)	Al, α - U_3O_8	β - U_3O_8	UAl_4 , UAl_3^a	UAl_3^a , UAl_2

^aIn one sample a major constituent, in another a minor constituent.

Some samples were mixed by hand while some were machine mixed and cold pressed. There was no effect of the method of preparation. Segregation occurred in all cases.

Although it seems apparent that the formation of uranium-aluminum intermetallic compounds is responsible for the observed DTA patterns, it is not clear what happens to the oxygen. No uranium dioxide, U_3O_8 , or alumina were detected, even as a minor constituent, in any of the X-ray patterns of samples after DTA runs. It is probable that alumina is formed. Even if all the oxygen in uranium dioxide were converted to alumina, the alumina would only constitute a little over 10 percent of the sample weight. This might be difficult to detect by X-ray diffraction. A large excess of aluminum would still be left to form intermetallic compounds with uranium.

The thermite reaction

postulated earlier, is apparently not the reaction taking place. The uranium undergoes further reaction with the excess aluminum forming intermetallics with it. The net result is a rather different overall thermite reaction of the following form:

and similarly for U_3O_8 .

It is likely that the course of the reaction is as follows: Assuming a considerable molar excess of aluminum over oxygen, the uranium oxide reacts to form Al_2O_3 and UAl. Depending on the excess of aluminum available, the degree of mixing, and the relative stability of the various intermetallic compounds, UAl_2 , UAl_3 , and UAl_4 will also be formed. The heat of reaction involved is about 70 cal/gm of 50 w/o aluminum + uranium oxide.

It is concluded, therefore, that no violent "thermite" reaction is likely to occur which would seriously disrupt cermet fuel elements in a reactor. This is especially true since these reactions are largely brought about during the preparation of the cermets prior to incorporation into a reactor fuel.

4. In-pile Testing in the TREAT Reactor* (R. C. Liimatainen, R. O. Ivins, M. Deerwester, F. Testa)

The purpose of the program of testing in TREAT is to investigate metal-water reactions initiated by nuclear reactor bursts. The method consists basically of exposing a fuel specimen immersed in water to a neutron pulse from the TREAT reactor. Two series of transients were performed during this quarter.

The recent work has emphasized meltdowns of stainless steel-urania cermet fuel. High-energy transients were also conducted on oxide core pins and on uranium wires. The data obtained are summarized in Tables 67 and 68. The cermet fuel had the following characteristics:

composition: 90 w/o SS-304, 10 w/o UO_2 (93% enriched)

density: 6.1 g/cc

technique of fabrication: -200 to 325 mesh powder prepressed, then isostatically pressed at 55,000 psi and fired for 100 min at 1205 C in a vacuum.

dimensions:	<u>Plates</u>	<u>Pins</u>
	0.10 in. thick	0.34-in. diameter
	0.46 in. wide	0.55 in. long
	0.93 in. long	

Table 67

SUMMARY OF IN-PILE DATA ON STAINLESS STEEL-WATER REACTIONS FOR STAINLESS STEEL-URANIUM DIOXIDE CERMET CORE FUEL PINS AND PLATES IN A WATER ENVIRONMENT

Composition of Core: 90 w/o SS-304, 10 w/o UO_2 (93% enriched).

Test Conditions: Water initially at 25 C under 20 psia of helium pressure.

	CEN Transient Experiment Number					
	51	50	52	54	53	55
<u>Fuel Material</u>						
Clad:	None	None	SS-304	None	None	None
Geometry:	Pin	Pin	Pin	Plate	Plate	Plate
<u>Reactor Characteristics</u>						
Burst, Mw-sec:	435	510	512	368	490	495
Peak power, Mw:	2770	2850	2880	2550	2800	2810
Period, r's:	50	50	49	51	52	51
<u>Thermal Neutron Dose:</u>						
by gold foil activation, nvt:	6.0×10^{14}	6.8×10^{14}	6.9×10^{14}	3.7×10^{14}	8.8×10^{14}	6.6×10^{14}
<u>Fission Energy Input</u>						
by Mo99 Analysis (or Zr95), cal/cm of core:	-	618 (796)	-	298	446 (822)	279 (320)
<u>Peak Surface Temp of Pin, C:</u>	>1550	>1550	~500	>1030	-	-
<u>Peak Pressure Rise, psi:</u>	960	100	0	190	-	-
<u>Percent of Metal Reacted with Water:</u>	6.6	9.6	10.2	5.2	9.1	11.0
<u>Appearance of Fuel after Transient</u>						
Clad:	-	-	melted	-	-	-
Core:	fine particles	fine particles and powder	melted, particles	melted, particles	melted, fine particles and powder	melted, fine particles and powder

*The cooperation of the TREAT operations group of the Idaho Division is appreciated; also, the effort of the Metallurgy Division in furnishing fuel specimens is gratefully acknowledged.

Table 68

SUMMARY OF IN-PILE DATA ON METAL-WATER REACTIONS, OXIDE CORE FUEL PINS
AND URANIUM WIRE FUEL SPECIMENS IN A WATER ENVIRONMENT

Composition of Oxide Core: 81.5 w/o ZrO_2 , 9.1 w/o CaO , 0.7 w/o Al_2O_3 , 8.7 w/o U_3O_8 (93% enriched).

Uranium Wire: 64-mil diameter; 93% enriched.

Test Conditions: Water initially at 25 C under 20 psia of helium pressure.

	CEN Transient Experiment Number					
	47	48	56	49	57	55
<u>Fuel Material</u>						
Clad:	Al	SS-304	Zr-2	Zr-2	None	None
Core:	oxide	oxide	oxide	oxide	U	U
Geometry:	pin	pin	pin	pin	wire	wire
<u>Reactor Characteristics</u>						
Burst, Mw-sec:	290	490	270	648	90	100
Peak power, Mw:	1220	1405	630	2700	293	47
Period, ms:	72	72	105	50	152	440
<u>Thermal Neutron Dose</u> by gold foil activation, nvt:	4.9×10^{14}	5.7×10^{14}	2.8×10^{14}	9.1×10^{14}	0.8×10^{14}	1.1×10^{14}
<u>Fission Energy Input</u> by Mo99 Analysis (or Zr95), cal/gm of core:	(342)	(530)	-	(671)	648 (508)	460 (285)
<u>Peak Surface Temp of Pin, C:</u>	-	-	>100	>220	1500	-
<u>Peak Pressure Rise, psi:</u>	-	-	-	-	0	-
<u>Percent of Metal Reacted with Water:</u>	0.3	4.2	0.3	24.0	50.2	33.2
<u>Appearance of Fuel after Transient</u>						
Clad:	end plug pushed out	ruptured, hole melted	not melted	ruptured, melted	melted	melted
Core:	broken into large fragments	fine particles	cracked	fine particles	fine particles and powder	fine particles

The data from the stainless steel-urania cermet (Table 67) showed an increase in the extent of metal-water reaction (from 6.6 percent in Run CEN-51 to 10.2 percent in CEN-52 for pins) as the reactor burst becomes more energetic (from 435 to 512 Mw-sec, respectively). Also, the data indicated that the increase in surface area which results in changing from pin to plate-type elements causes only a slight increase in the amount of stainless-steel water reaction for a given energy input. For example, comparing transients CEN-53 and 55 (plates) with CEN-50 and 52 (pins), it is evident that bursts of comparable energy (~500 Mw-sec) and period (~50 Mw-sec) give substantially the same amount of metal-water reaction (9.6 and 10.2 percent for pins, and 9.1 and 11.0 percent for plates). The plate specimens had an initial total surface area of 7.3 sq cm and the cylindrical specimens had an initial surface area of 4.6 sq cm; the volumes were comparable (0.72 and 0.75 cc, respectively).

Figure 68 is a reproduction of an oscillograph record from one of the transients, CEN-54, which indicates the time scale of the experiment and shows the shape of the neutron pulse. From the parameters recorded during the reactor transient and from the measured thermal neutron dose to the fuel plate, the peak flux may be obtained simply from the ratio

$$\frac{\text{Mw-sec}}{\text{Mw peak}} = \frac{\text{nvt}}{\text{nv peak}} \text{ or } \frac{368}{2550} = \frac{3.7 \times 10^{14}}{\phi_{\text{max}}}$$

Thus the thermal flux to the

cermet specimen in CEN-54, at the peak of the burst, was 2.56×10^{15} neutrons/(sq cm)(sec). The chemical changes caused by the meltdown of the stainless steel in water were calculated according to the reaction $\text{Fe} + \text{H}_2\text{O} \longrightarrow \text{FeO} + \text{H}_2$. The physical changes were indicated by photographing the specimens after the irradiation.

FIGURE 68
CEN-54 OSCILLOGRAPH RECORD
SS- UO_2 Cermet Fuel Plate in Water

The changes in geometry for typical cermet runs are shown in Figures 69 and 70. In general, one or two large globules were formed together with many smaller fragments and particles. As the transients became more energetic, more fine powder was formed. Quantitative results on particle size distributions were obtained by weighing the material retained on screens of progressively smaller sizes. The distributions of weight per cent vs. diameter for CEN-53 and 54 are shown in Figure 71. These distributions do not include the large globule whose size is apparent from the photograph. In Runs CEN-53 and -54, 8.7 and 5.6 percent, respectively, of the total mass were converted into particles.

In addition to the data on the amount of molten stainless steel-water reaction and the accompanying changes in geometry of the cermet fuel, some results of interest were obtained on the behavior of the urania in the cermet.

FIGURE 69

IN-PILE RUN CEN-51, 90 WEIGHT PERCENT SS-304,
10 WEIGHT PERCENT URANIUM DIOXIDE, (93 PER-
CENT ENRICHED), CERMET FUEL PIN, UNCLAD

By comparing photomicrographs (Figure 72) of the cermet before and after the transient, it was observed that considerable densification (of the large globule) had occurred and that the cermet had the appearance of a metal with a dendritic structure. Chemical and X-ray analyses indicated that segregation of the uranium dioxide had taken place. The large globules were depleted in uranium, whereas the fine particles consisted of more concentrated urania. For comparison, the original cermet was homogeneous with 10 w/o urania. Samples from some of the runs on cermet pins and plates have shown the following:

	<u>Uranium concentration (weight %)</u>	
	<u>Large globule</u>	<u>Fine particles</u>
CEN-51	0 017	-
CEN-52	0 032	~UO ₂ by X ray
CEN-53	-	30
CEN-54	-	64
CEN-55	0.055	-

Evidently, during the transient when the metal is molten and then rapidly quenched in the water, a partial phase separation of the urania from the stainless steel occurs. Possible mechanisms for this segregation are (1) insolubility of the urania in the molten stainless steel and (2) vaporization of the urania away from the metal.

FIGURE 70

IN-PILE RUN CEN-53, 90 WEIGHT PERCENT SS-304,
10 WEIGHT PERCENT URANIUM DIOXIDE, 93 PER-
CENT ENRICHED, CERMET FUEL PLATE, UNCLAD

CEN-53

Original Fuel
Plate

490 megawatt-seconds
2800 megawatt-peak power
52 millisecond period
9.1% SS-H₂O reaction

To generalize the data on stainless steel-water reactions from TREAT to other reactors, it is necessary to convert from the total energy of the reactor burst (Mw-sec) to the fission energy actually absorbed by

the cermet specimen (cal/gm). To accomplish this, direct fission product analyses were made on samples of the meltdown products from the transients. For the stainless steel-urania cermets, four determinations of molybdenum-99 gave values of 1.20, 0.81, 0.91, and 0.57 (cal/gm)/Mw-sec, for an average of 0.87. The reason for the variations is probably connected more with the sampling problem rather than with the actual analysis. One method of eliminating this would be to dissolve all of the meltdown products (fragments, particles) completely and to leach the walls of the autoclave (this total dissolution technique has been used in some previous runs with uranium core pins). However, this method, while improving the burnup determination, has the disadvantage that

none of the specimen is left for such useful observations as particle size analysis, X-ray analysis, and metallographic examination. Three determinations of zirconium-95 gave values of 1.56, 1.68, and 0.64 (cal/gm)/Mw-sec, for an average of 1.29. It is recommended that the value 0.87 cal/gm = 1 Mw-sec be used, since the validity of the molybdenum-99 analyses has been previously established with uranium pins. The zirconium-95 analysis is being tried because its longer half-life (relative to molybdenum-99) makes it potentially an attractive isotope to lessen the decay problem, thus permitting more time for analysis. To obtain a better evaluation, a "standard" transient was run where the fuel pin did not melt. This should give a more accurate comparison between the zirconium and molybdenum analyses. However, these data are not yet available.

The work on meltdowns of oxide-core, metal-clad fuel pins was continued. The appearance of the oxide-core fuel specimens after the transients is shown in Figures 73, 74, and 75. Run CEN-49 resulted in extensive damage to the fuel pin with 24.0 percent of the Zircaloy-2 jacket reacting with the water for the energetic burst of 648 Mw-sec on a 50-ms reactor period. The specific energy input was 609 cal/gm for Run CEN-49, as calculated from the previously obtained correlation of 0.94 (cal/gm)/Mw-sec for the same oxide-core pellets jacketed in aluminum; that is, $0.94 \times 648 = 609$. This value of 609 is to be compared to the value of 671 cal/gm determined for CEN-49 by a zirconium-95 fission product analysis.

FIGURE 72

PHOTOMICROGRAPHS OF SS-UO₂ FUEL PINS BEFORE AND
AFTER TRANSIENT CEN-51

Before
Transient

SS-UO₂ Cermet Standard

0.01"

After
Transient

CEN-51

FIGURE 73
 RUN CEN-47, CERAMIC CORE, ALUMINUM-CLAD FUEL PIN

FIGURE 74
 RUN CEN-48, CERAMIC CORE, STAINLESS STEEL-304-
 CLAD FUEL PIN

FIGURE 75

RUN CEN-49, CERAMIC CORE,
ZIRCALOY-2-CLAD FUEL PIN

Figure 76 shows the details of changes in the metal jacket as a result of the oxidation by water; it is evident there are local differences in the amount of reaction depending on the size of the fragment. The extent of reaction was computed simply by direct measurement of the size of the fragment and of the thickness of the oxide film. From these measurements, and from the density of the metal and oxide, the fraction of metal reacted can readily be calculated. The oxide film is assumed to be pure zirconia and the unreacted metal is assumed to contain no oxide. Thus, this estimate of the amount of metal-water reaction neglects any mutual solubility of zirconium metal and zirconium dioxide.

In the TREAT metal-water program, fuel specimens have been tested which contain metals of interest in water reactor technology. Aluminum, stainless steel, and Zircaloy-2 are commonly used either as jackets of oxide-core fuel elements or in the core itself as a cermet fuel. It is, therefore, of interest to compare these three metals on the basis of their chemical reactivity towards water in reactor bursts of sufficient intensity to cause the metal to become molten.

FIGURE 76
 PHOTOMICROGRAPHS OF PORTIONS OF THE ZIRCALOY-2 JACKET
 AFTER METAL-WATER MELTDOWN RUN CEN-49 WITH
 OXIDE CORE FUEL PIN

EXTENT OF Zr-2 METAL REACTED AS MEASURED FROM OXIDE FILM THICKNESS

<u>SECTION</u>	<u>% REACTION</u>
A	16
B	25
C	44

(240 percent metal-water reaction as determined by hydrogen evolution)

Figure 77 shows a correlation of extent of metal-water reaction as a function of the integrated power of the TREAT transient. On the basis of the

results obtained to date from the in-pile, metal-water, meltdown experiments, the following observations can be made:

in the cermet fuel elements, whereas for jacketed pins with a ceramic core there is more opportunity for heat loss from the metal.

4. For each of the three metals, the extent of metal-water reaction is dependent on the energy input with an increase in energy causing more reaction.

It is important to point out that these conclusions on the dependence of the extent of metal-water with energy input also contain implicitly another variable, namely, the surface area. For example, the stainless steel-uranium oxide cermets undergo more dispersion than the aluminum-uranium oxide cermets for a given amount of fission heat input during a transient on the same period. Thus the larger amounts of reaction with stainless steel may be caused by more surface rather than because the stainless steel may be inherently more reactive toward water than aluminum. Other factors could be the protectiveness of the oxide film or the vapor pressure of the metal. Hence, the data do not indicate, at least directly, the mechanism for one metal giving a larger amount of reaction than another. However, for purposes of reactor hazards analysis, it is important to know how much of the metal will react with water for a given burst energy, and these data supply that information for the various fuel elements studied thus far in this work.

In-pile meltdowns of uranium wires are being conducted to give comparisons with the laboratory data on wires which are heated electrically by a condenser discharge (data of L. Baker and R. Warchal). Two runs (CEN-57 and 58) were made with 64-mil-diameter wires of uranium, 93 percent enriched. In CEN-57, a transient on a 152-ms period with a 648-cal/gm analytically determined energy input, 50.2 percent of the uranium reacted with the water (see Figure 78). This is the largest extent of reaction that has been found to date for any metal in the in-pile tests.

FIGURE 78
URANIUM WIRE FUEL SPECIMEN AFTER
MELTDOWN CEN-27

Figure 79 shows these results, together with previously reported runs. The importance of the reactor period is illustrated. The energy inputs are the ones from molybdenum-99 analyses. The energy of 554 cal/gm is simply an arithmetic average of the two molybdenum-99 determinations (648 and 460 cal/gm). Finally, Figure 80 shows the data for all the uranium-water transients plotted as the extent of reaction vs. the energy input. Since only four data points are available with uranium wires at high-energy transients (and periods of about 100 ms), the location of the curve beyond about 300 cal/gm is to be considered tentative. Additional runs will be made to indicate the slope more precisely.

FIGURE 79
IN-PILE METAL REACTIONS WITH 64-MIL DIAMETER
URANIUM (93% ENRICHED) WIRES

FIGURE 80
METAL-WATER EXPERIMENTS IN TREAT

Finally, it is appropriate to review briefly the status and plans of this in-pile work. Thus far, 58 transient metal-water experiments have been conducted in TREAT. Data have been obtained on the meltdown behavior in water of aluminum, stainless steel, uranium, and Zircaloy-2. Three kinds of cores have been studied: metal, oxide, and cermet. The geometries tested have been wires, pins, and plates. The next major phase of this program will be the extension to high pressure and also to preirradiated fuel specimens. The results that have been obtained thus far will serve as a comparison to indicate the importance and magnitude of pressure and fission product gases on the particle size of the meltdown products and on the extent of metal-water reaction for a given reactor excursion. Then an attempt will be made to apply all of the data to the analysis of full scale reactor incidents.

IV. REACTOR CHEMISTRY

The neutron-capture cross sections of neptunium-237 are being determined in the fast neutron energy range. Work has also begun on the determination of the total neutron cross section of uranium-233. The capture-to-fission ratios in the EBR-I, Mark III are being determined for uranium isotopes 233, 235, 238 and for plutonium isotopes 239 and 240.

The Reactor Decontamination Program is directed at determining the seriousness of fuel element ruptures in boiling water reactors and the determination of methods of decontamination of contaminated surfaces. Several runs have been made in a stainless steel loop which simulates the action of a boiling water reactor. Current laboratory experiments on the decontamination of stainless steel 304 have been conducted with oxalic acid and citric acid base solutions containing hydrogen peroxide.

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

1. Fast Neutron Cross Sections (D. C. Stupegia, E. Dewell)

Neptunium-237

The neutron cross sections of neptunium-237 for mono-energetic neutrons are being determined in the neutron energy range between about 0.4 and 1.7 Mev. Neptunium-237 is a buildup product produced in reactors by neutron capture of uranium-236 and the (n, 2n) reaction of uranium-238. Four samples of neptunium-237 dioxide* with weights varying between 10 and 24 mg have been exposed to mono-energetic neutrons from the ANL Physics Division Van de Graaff accelerator.

Neptunium-238, formed by neutron capture in neptunium-237, is a 2.1-day beta emitter; a little over half of its disintegrations give rise to gamma of about 1-Mev energy. A literature review indicated that this peak could be counted with little interference from either the activity associated with the neptunium-237 target or other isotopes likely to be excited under the expected conditions. A test exposure to thermal neutrons in the CP-5 rabbit channel supported this conclusion. As few as 60 disintegrations per second were easily observed against a background of 10 mg neptunium dioxide on a 4 x 4-in. NaI(Tl) gamma spectrometer using a 256-channel pulse analyzer. A mercury absorber was used to reduce the intensity of the low-energy components.

*The dioxide was recovered from a stock solution of neptunium (VI) in perchloric acid by reduction to neptunium (V) with sodium nitride and precipitation of neptunium (V) hydrated oxide with aqueous ammonia. The hydrated oxide was calcined at 600 C to give neptunium dioxide.

Proton beam energies of 2.275, 2.43, 2.52, and 2.60 Mev were arbitrarily chosen for the first four samples. These gave neutron energies from a lithium target [$\text{Li}^7(\text{p},\text{n})\text{Be}^7$] of 0.544, 0.716, 0.806, and 0.890 Mev in the direct beam path (0° scattering angle). The exposure times varied between 6 and 9 hr each at proton beam intensities near $28 \mu\text{a}$. The neutron flux was monitored constantly with a conventional gas-flow fission chamber directly behind the sample. Collection of counting data is in progress.

Uranium-233

Work has recently started on the determination of the total neutron cross sections of uranium-233 in the neutron energy range extending from several kev to about 1.2 Mev. These measurements are being made in the Physics Division, using the Van de Graaff accelerator and associated equipment. The basic measurement in this work is the determination of the attenuation of a collimated neutron beam by a known thickness of sample, which in this case is metallic uranium. Several measurements have been made and the data are being analyzed.

2. Determination of Capture-to-fission Ratios in EBR-I, Mark III (C. E. Crouthamel, R. R. Heinrich, G. McCloud)

Capture-to-fission ratios in EBR-I, Mark III are being determined for uranium isotopes 233, 235 and 238 and for plutonium isotopes 239 and 240. Samples have been removed from the blanket brick and the core and blanket rods of EBR-I, Mark III, and are to be analyzed.

The samples have been cleaned by means of an ultrasonic generator to remove the fission product contamination from the surface of the aluminum capsules containing the samples. Analyses of the wash solutions have indicated the decontamination to be complete and the samples are ready for dissolution.

A control sample of uranium-233 has been dissolved. A dissolver solution sample has been submitted for mass spectrometric analysis. The result of this analysis will determine whether the aluminum jacket and reagents used in sample preparation have caused any change in the predetermined uranium-234/uranium-233 ratio.

B. Reactor Decontamination (W. B. Seefeldt)

The reactor decontamination program has two main objectives: (1) to determine the seriousness of fuel ruptures in boiling water reactors as measured by the quantities of radioactive material which deposit in the steam system, and (2) to determine what methods of decontamination can be used to remove these deposited activities. The first study is being made with a

stainless steel Type 304 loop that simulates the action of a boiling water reactor; mixed fission products are introduced into the loop to simulate a fuel rupture. Quantities and types of fission products deposited on internally mounted metal sample strips are determined principally with the aid of a 256-channel gamma-scintillation spectrometer. In a parallel effort, studies are being made in the laboratory to find a suitable means of removing the deposited activities.

Reproducibility runs were made with the stainless steel Type 304 pilot-plant loop. Marked variations with time were observed in the fission product content of liquid and vapor samples, and differences were similarly observed in the deposition characteristics of several fission products as a function of elevation on both stainless steel and mild steel sample strips.

Current laboratory experiments are being conducted on oxalic acid and citric acid based solutions containing hydrogen peroxide. A gross decontamination factor of 30 was obtained on stainless steel Type 304 surfaces when a solution of 0.16 M sodium oxalate and 1 M hydrogen peroxide, pH adjusted to 4 (with oxalic acid), was used. The effects of several parameters, such as solution composition, pH, temperature, and time, on decontamination were studied with a solution of three molar hydrogen peroxide adjusted to a pH of 3 and containing 0.5 to 0.05 molar potassium oxalate.

The compatibility of hydrogen peroxide with both citrate and oxalic acid based solutions was determined on two low alloy steels. The addition of hydrogen peroxide was found to result in a marked decrease in the corrosion while decreasing pH increased the attack.

1. Laboratory Investigations
(S. Vogler, H. Tyler)

The principal objective of the laboratory investigations is to study and modify existing decontamination or film removal procedures that have been developed by either industry or other AEC contractors. In general, developed procedures are applicable to the primary circuits of pressurized water reactors. Modifications are directed toward use in the vapor spaces of boiling water reactors.

One such procedure, which is under study at Oak Ridge National Laboratory for potential application in the Gas Cooled Reactor, requires the use of a solution of hydrogen peroxide and sodium oxalate. Preliminary results reported last quarter (ANL-6287, page 203) indicated that a solution of hydrogen peroxide and oxalic acid gave very good decontamination. Current experiments indicate that a solution of 0.16 M sodium oxalate and 1 M hydrogen peroxide with pH adjusted to 4 with oxalic acid, yields a gross decontamination of 30 on stainless steel when used at 95 C for one-half hour.

In order to ascertain the effects of parameters such as solution composition, pH, temperature, and time on the decontamination, a series of experiments was planned. With three molar hydrogen peroxide adjusted to a pH of three, tests with potassium oxalate* at 0.5 and 0.05 molar gave good decontamination. In these first two tests, the zirconium decontamination was greater than 10^3 , the cerium decontamination was greater than 100, and the ruthenium decontamination was greater than 10. In both experiments only the ruthenium activity was of any consequence after the decontamination. In some cases, the indicated decontamination was limited by the amount of activity originally present on the plate.

a. Corrosion

Because of the susceptibility of structural materials to corrosion, a series of screening tests was run to evaluate the resistance of several steels to reagents of interest. Only the low chromium steels were tested since they are most sensitive to corrosion. These data, which are given in Table 69, indicate that for both oxalate- and citrate-based solutions, the addition of hydrogen peroxide results in a marked decrease of the rate of attack. The peroxide evidently enhances the ability of the surfaces to retain a passive condition. As might be expected, decreased pH of these solutions resulted in increased attack.

Table 69

COMPATABILITY OF LOW ALLOY STEELS IN CITRATE AND OXALATE BASE SOLUTIONS

Temperature 95 C		Time 30 min		Sample Area ~2 sq in	
Reagent	Conc	pH	1 M H ₂ O ₂ Added	Wt Loss (mg) ^a	
				AISI 4140	Cr-Mo Steel (1% Cr-0.5% Mo)
Oxalic Acid	0.16 M	1	yes	-	230
Sodium Oxalate	0.16 M	4 ^b	no	200	170
		4 ^b	yes	-	0.2
		2.5 ^b	yes	2.0	2.3
Citric Acid	10%	1.7	no	-	Very Reactive 270 ^c
	10%	1.7	yes	-	
Ammonium Citrate	10%	4.8	no	37	75
	10%	4.8	yes	0.7	1.3
	10%	4 ^d	no	196	125
	10%	4 ^d	yes	0.5	1

^aA weight loss of one mg corresponds to a penetration of 4×10^{-3} mil

^bThe pH of a sodium oxalate solution is approximately 6. These solutions were adjusted to the indicated pH with oxalic acid

^cThe reaction was so vigorous that this value was obtained during a 2-min exposure

^dThe pH was adjusted with citric acid

*Potassium oxalate was used in these experiments instead of sodium oxalate because its greater solubility allowed solution preparation to be done more conveniently.

b. Stability of Oxalate-Peroxide Solutions

Information from Oak Ridge National Laboratory⁴² has indicated that pH control of oxalate-peroxide solutions was important in order to maintain solution stability. At low pH's (~1), reaction between oxalate and peroxide was found to increase, whereas at high pH's (~4), hydrogen peroxide decomposed.

Several tests to explore these factors revealed the following results:

1. When a solution of 0.5 molar oxalic acid and 3.0 molar hydrogen peroxide (pH 0.4) was prepared, gassing was immediately evident. Under these conditions the following reaction⁴³ takes place:

2. A solution of 0.5 molar potassium oxalate and 3.0 molar hydrogen peroxide adjusted to a pH of 4, by the addition of oxalic acid, showed a slow decrease in the peroxide concentration when kept at 90 C. However, after a period of from $\frac{1}{2}$ to 2 hr, there was a rapid evolution of gas with the almost complete disappearance of the hydrogen peroxide. Subsequent examination of the solution revealed that the pH of the solution had risen to approximately 9 to 10. Tests also indicate that the bulk of the oxalate (about 80 percent) remained in solution, thus indicating decomposition of the peroxide.
3. Such a solution can be stabilized by the continuous addition of oxalic acid to maintain the pH at approximately 4. The results of such an experiment in the presence of a small piece of stainless steel are given in Table 70. These results indicate that with pH control the solution was quite stable to peroxide loss.

⁴²Meservey, A. B., 2nd Meeting, Committee on Reactor Decontamination, Argonne National Laboratory, December 1, 1960; Meservey, A. B., Chilton, A. M., Ferguson, D. E., Decontamination of EGCR Charge and Service Machine, ORNL-60-10-46 (Oct. 13, 1960)

⁴³Hatcher, W. H., Transactions of the Royal Society of Canada, 17, Section III, 119, (1923).

4. A solution of 3 M hydrogen peroxide showed a gradual decrease in the peroxide concentration when heated at 90 C. In the presence of a piece of stainless steel, the half-time was about 280 min.
5. Similar tests with citric acid and hydrogen peroxide indicated that the solution was reasonably stable. In both the presence and absence of stainless steel, there was a rapid 20 percent decrease in the hydrogen peroxide concentration followed by a period of from three to four hours with essentially constant peroxide concentration.

Table 70

STABILITY OF POTASSIUM OXALATE-HYDROGEN
PEROXIDE SOLUTION IN THE PRESENCE OF
STAINLESS STEEL TYPE 304

Solution: 0.5 M $K_2C_2O_4$
 3 M H_2O_2
 pH 4.6 (by addition of $H_2C_2O_4$)

Temp: 90 C

Time (hr)	pH ^a	H_2O_2 (m/l)
0	4.6	2.78
0.75	5.2	2.70
1.5	5.1	2.63
2.25	4.9	2.56
3	5.0	2.45
3.75	4.8	2.41
4.5	4.8	2.32
5.25	5.0	2.27
6	4.9	2.20

^a After each pH determination, the pH was brought back to 4.5 by the addition of oxalic acid.

2. Loop Studies
(D. Grosvenor, C. Bally)

A stainless steel Type 304 loop which simulates the action of a boiling water reactor has been installed in a shielded cell in order to study the effects of simulated fuel ruptures. It is of interest to know how much

and what kind of fission products will distribute through the system in order to ascertain the degree to which maintenance might be impaired in a practical system should fuel cladding failure occur.

Fuel ruptures are simulated in the loop by introducing irradiated metallic uranium. Fission products are released as the uranium corrodes in the circulating water. Deposition of activity in the steam disengaging space is monitored by inserting a metallic sample strip. This is removed following a run, cut into convenient lengths, and counted in a 256-channel gamma-scintillation spectrometer. This is correlated with similar information obtained from liquid and condensed steam samples.

Two series of runs were made in the loop to determine the degree of reproducibility of the data obtained. All runs were made at a pressure of 200 psi, a steam velocity of 0.8 ft/sec, and time period of 68 hr. Fission products were introduced as long-cooled irradiated metallic uranium. In the first three of these runs, a stainless steel Type 304 sample strip was inserted into the steam disengaging section while in the latter two runs a mild steel (SAE Type 1018) sample strip was used. Liquid and condensed steam samples were obtained daily. The principal interests in the experiment were twofold: (1) was the composition of the circulating liquid phase constant with time, and (2) if so, was the deposition of fission products on the metallic sample strips reproducible from run to run?

To determine the fission product content of the liquid and condensed steam samples, gamma-energy spectra were obtained with the use of the 256-channel gamma-scintillation spectrometer. The gamma-energy peaks associated with individual fission product isotopes were identified and the areas under these peaks determined and converted to counts per minute per ml. Due to the differences in activity levels between the two types of samples, sample preparation did differ in detail. As a result, numbers obtained for liquid and condensed steam samples are not directly comparable. The results obtained for the cesium-137 and zirconium-niobium-95 activities are shown in Table 71. Data for cerium-141 and ruthenium-103 were fragmentary in nature because peaks as determined visually were obscured. Within any one given run, the cesium-137 content of the liquid appeared to be reasonably consistent, with the exception of the one-day sample of liquid from Run U3D, in which a value nearly twice those of the second- and third-day samples was observed. The average value for each run showed a consistent increase up to Run U3D followed by a decrease to Run U3F. The effect is probably real. The cesium-137 content of the condensed steam samples was reasonably consistent except for the second- and third-day samples of Run U3F, in which values increased by a factor of 3 to 8. A possible cause for this effect is cross-contamination occurring during the sampling procedure. However, such an effect should also have been observable in condensed steam samples from the preceding four runs.

Table 71

CESIUM-137 CONTENT OF LIQUID AND VAPOR DURING
LOOP REPRODUCIBILITY RUNS

Pressure: 200 psi
 Steam Velocity: 0.8 ft/sec
 Source of Activity: Irradiated natural uranium,^a
 105-day cooled

Run No.	Time after Run Start (days)	Cesium Content (cpm/ml) ^b		Zirconium-Niobium Content (cpm/ml)	
		Liquid	Vapor	Liquid	Vapor
U3B	1	1317	2.7	d	2.8
	2	1548	5.9	d	0.63
	3	1940	3.3	d	0.43
U3C	1	1702	3.1	798	1.1
	2	1694	2.1	d	0.18
	3	2217	c	c	c
U3D	1	5120	2.4	15,600	0.92
	2	2664	1.1	190	0.18
	3	2872	2.2	116	0.51
U3E	1	c	5.3	c	0.55
	2	2703	2.5	101	d
	3	2090	2.0	61	d
U3F	1	2162	2.7	468	d
	2	1873	9.5	213	0.52
	3	2210	23	28.3	1.0

^aIrradiated 64 days in CP-5 (41 MWD/ton).

^bThe exact relationship between these values and disintegration rate has not been determined, nor has the relationship between liquid and vapor counts been established as the sample preparation methods were not identical.

^cSample was not representative (gamma-scan results inconsistent with other data).

^dNot detected.

The zirconium-niobium-95 content of the liquid samples showed a consistent decreasing pattern for each individual run. The effect was likewise observable in the condensed steam samples. In Run U3B, the first one of the group made, no zirconium peaks were observable on any of the gamma scans obtained of liquids. One operating difference occurred in this run as compared to the four others, which may explain the discrepancy. Run U3B was begun after a 48-hr period of operation of the loop in which the intent was to corrode the uranium. During this period, the steam velocity in the steam disengaging section was kept as close to zero feet per second as possible in order to prevent premature fission product deposition. There was no cool-down of the loop following this corrosion period and immediately preceding Run U3B. All of the other runs were begun following a shut-down period (which included a cool-down) in which new metallic sample strips were inserted. It appears that when one begins with a cold loop initial zirconium contents are high. This gradually decreases with exposure time until some equilibrium value is achieved. The time required to achieve this equilibrium is something in excess of three days. Additional runs are indicated to clarify the time required to reach equilibrium.

Several observations have been made regarding the ruthenium-103 and cerium-141 contents during the reproducibility runs. A small ruthenium peak was consistently observed in gamma-ray spectra of condensed steam samples, but this peak was not detectable visually in spectra of liquid samples. The opposite was true for cerium. The reasons are not clear, but the data thus indicate that, while some small enrichment of ruthenium is occurring in the vapor, a depletion is occurring for cerium. There likewise appeared to be a downward trend in the ruthenium content in condensed steam samples as a run progressed through the third day.

Activity deposition data on the metallic sample strips in the disengaging section of the loop were obtained. The relationship of the fission product deposition data to the fission product content of liquid and steam cannot be defined because of the large variation of the latter. The deposition patterns of the five runs likewise did not show similarities. The results for Run U3C, shown in Figure 81, illustrate the wide variations of deposition obtained as a function of elevation. The series of gamma spectra on which Figure 81 is based is shown in Figure 82.

FIGURE 82
GAMMA SPECTRA OF STAINLESS STEEL TYPE 304
FOLLOWING LOOP RUN
RUN USC

V. ROUTINE OPERATIONS (H. G. Swope)

A. Waste Processing

(H. G. Swope, J. Harast, K. Bremer, B. Kullen and N. Ondracek)

There were 32,205 gal of liquid radioactive wastes processed from January through March, 1961. Methods of processing and volumes were as follows:

Process	Gal
Evaporation and Concentration	23,258
Filtration	3,670
Ion-Exchange (Cation, only)	3,670
Neutralization of HF Wastes	126
Absorption on Vermiculite	381
Decay	1,100
Total	32,205

B. High-level Gamma-irradiation Facility

(H. G. Swope, J. Harast, R. Juvinal, R. Jarrett, G. Teats, and V. Lemke)

A summary of irradiations performed in Racks M-1 and M-2 for January through March, 1961 is given in Table 72.

Table 72

ARGONNE HIGH-LEVEL GAMMA IRRADIATION FACILITY

SUMMARY OF IRRADIATIONS PERFORMED IN RACKS M-1 AND M-2 DURING JANUARY THROUGH MARCH 1961

Rack M-1					Rack M-2					
Month	No. of Samples ^d	No. of Direct Samples	Total (Dn Units Based on Rack ^a)		Month	No. of Urns	No. of Sp. Dosimetry Samples	Total (Dn Units Based on Rack ^a)		Dose Rate Urn Unit
			Day	Night				Day	Night	
January	575	18	754	848	January	3	3	2	1	1
February	510	107	515	2459	February	1	16	2	5	1
March	400	11	94	547	March	1	16	1	4	1
Totals	1485	216	1363	3454	Totals	5	35	5	10	3

^aEquivalent to 1000 rads per hour (calculated as 1000 rads/hr)

^bOne urn unit = 2×10^6 rad

A mockup rack (M-3) was fabricated so that experiments could be performed on the vertical placement of fuel rods for uniform dosimetry throughout an irradiation cylinder. The new rack will accommodate No. 10 sized cans ($6 \frac{3}{16}$ -in. diameter x 7 in. high).