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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

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CHEMICAL ENGINEERING DIVISION SUMMARY REPORT

April, May, June, 1961

SUMMARY

I. Chemical- Metallurgical Processing (pages 28 to 133)

Pyrometallurgical processes for the recovery of fissionable material from spent reactor fuels offer promise of achieving a reduction in the cost of nuclear power. Their principal advantages over existing processes lie in their simplicity, compactness, low-volume dry wastes, and capability of handling short-cooled fuels, with an attendant reduction in fuel inventories. Melt refining will be the first pyrometallurgical process to be used for the recovery of uranium from the fuel alloy used in the second Experimental Breeder Reactor (EBR-II). This reactor, with an integrated fuel-processing facility, is now under construction at the National Reactor Testing Station in Idaho.

Several small-scale melt refining experiments, each utilizing about 400 grams of highly irradiated uranium-fission alloy, have been performed to observe the behavior of the material during various phases of the process. The manipulations have proved feasible and the anticipated removal of fission products has been realized. However, since the handling operations in the laboratory must be done in a shielded facility with an air atmosphere, some difficulty has been encountered in achieving satisfactory yields. The procedure has been modified to minimize exposure to air prior to melt refining, but the results obtained with the modified procedure are not yet available.

Experimental work was concluded on the release of fission product krypton and xenon during the heating of highly irradiated EBR-II-type fuel pins. The rate of gas release is relatively low below 750 C; the experimental activation energy was 3.6 kcal/mole. Above 750 C the rate rises sharply. At 850 C the quantity of radioxenon released in two hours was about 7000 times the amount released at 750 C.

In the melt refining process, significant quantities of volatile fission product activity are released into the furnace atmosphere. Radiochemical analysis of material from a filter in an off-gas line from a melt refining furnace showed iodine-131 to be the principal species, with much smaller amounts of barium-140, lanthanum-140, and cesium-137.

Outgassing studies on a sample of material taken from a plant-type zirconia melt refining crucible showed that only small amounts of gas are removed by heating to 1100 C under vacuum. The major gases removed are water vapor and carbon dioxide, with smaller amounts of oxygen, nitrogen, argon, and possibly hydrogen.

Since the possibility exists that small amounts of stainless steel cladding may accompany the decanned fuel pins into the melt refining process, the behavior of iron, nickel, and chromium was studied briefly. The stainless steel constituents appear in the uranium product in much the same manner as the noble metal fission products.

Work was continued on the development of a liquid metal process for recovery of fissionable material contained in melt refining crucible skulls produced in the EBR-II fuel cycle. Incorporation of a noble metal extraction step in the skull-reclamation process has resulted in considerable improvement in the separation of noble metal fission products (ruthenium, rhodium, palladium, and molybdenum) from uranium. In this step the relatively noble metal fission products are extracted into zinc from a slurry of skull oxides in a molten halide flux. The removals obtained are adequate for uranium reclaimed from skull material. Losses of uranium in the noble metal extraction step have been negligible. The extraction of noble metals was found to increase with temperature in the investigated interval from 650 to 750 C, and to increase with a decrease in particle size of the skull oxide, which normally ranges from 14 to -325 mesh. The extent of noble metal removal at 750 C from a normal mixture of skull oxides became constant after two hours at 63 percent for ruthenium, 80 percent for molybdenum, and 60 percent for palladium. Stainless steel constituents, which, by poor separation of cladding material, could become incorporated in the EBR-II fuel, were found to behave much the same as noble fission product metals.

Considerable work was devoted to the separation of the flux and metal phases after extraction of the noble metals. To date, the easiest and most reliable procedure has been pressure siphoning of the zinc phase after freezing the higher melting salt phase. The pressure siphon tube has been kept clear during freezing of the salt by a slow flow of argon. On a one-kilogram scale, zinc transfers have been consistently about 90 percent. A larger zinc charge would yield a higher percentage of transfer.

Some of the variables affecting the rate and extent of reduction of fissium oxides by zinc-magnesium alloys in the presence of a flux have been investigated. The results show that, with proper flux, flux-to-metal ratio, stirring, and crucible material, complete reduction of fissium oxide to produce a 4 weight percent uranium solution occurs between 2.4 and 13 weight percent magnesium. It is expected that complete reductions

could also be achieved at higher magnesium concentrations. A satisfactory range of magnesium ion concentration in the flux is 40 to 100 percent. Some insoluble uranium carbide is formed if graphite is used as a reaction vessel.

Preliminary observations have indicated that separation of plutonium and rare earth elements may be possible through selective reduction of the oxides from a halide flux by means of high magnesium-zinc systems. Although not pertinent to the present EBR-II fuel cycle, complete reduction of thorium oxide has also been achieved with a 5 percent magnesium-zinc alloy in the presence of a suitable halide flux.

A satisfactory material, which will permit ready removal of the uranium product after the retorting step of the skull-reclamation process, is still being sought. Beryllia crucibles that have been tested for this purpose have shown that good product removals (over 90 percent) are possible. The beryllia crucibles were made by incremental additions of the crucible material to a mold and tamping. This resulted in a layering effect up the crucible walls. Ultimately, the crucibles parted at stratification marks above the liquid level. Isostatically pressed crucibles which have densities that are 90 percent of the theoretical are now being obtained.

Work is in progress to determine the feasibility of decontaminating plutonium fuels, such as future core loadings of the EBR-II reactor, from rare earth fission products by virtue of the insolubility of plutonium in calcium. On the assumption that it is desirable to recover plutonium and uranium together, uranium solubilities in zinc-calcium systems were determined over a calcium concentration range from 0 to 30 percent (see Figure 15, page 68). Cerium solubilities were measured in zinc solutions containing 26 to 77 weight percent calcium. The cerium solubility is such that decontamination of plutonium from cerium and probably other rare earths is feasible if the plutonium can be completely precipitated and if coprecipitation effects are not serious.

A demonstration of the blanket process with a 1 percent plutonium-uranium alloy showed rapid and complete dissolution of both the uranium and plutonium in a 12 percent magnesium-zinc solution. All the plutonium (within analytical error) remained in solution whereas 99.7 percent of the uranium was precipitated by the addition of magnesium to a 50 percent concentration. The plutonium-bearing solution was removed and the uranium precipitate washed once with a 50-50, magnesium-zinc solution, also without incurring plutonium loss. The run is particularly encouraging because it shows the possibility of high plutonium recovery and good separation of uranium from plutonium.

The possibility of synthesizing refractory plutonium and uranium compounds in liquid metal media is being explored. A 400-gram quantity of uranium monocarbide was prepared by carbon precipitation of uranium dissolved in a 10 percent magnesium-zinc solution and will be used for the preparation of sintered bodies. A plutonium carbide was formed by reaction of plutonium dissolved in liquid magnesium with fine carbon powder. The material was isolated and was found by X-ray diffraction analysis to be Pu_2C_3 . Plutonium monocarbide was not detected. An initial attempt to prepare U_3Si by reaction of dissolved uranium with silicon resulted in the formation of USi_3 . A large excess of silicon was used. A second attempt using stoichiometric ratios of uranium to silicon (3 uranium to 2 silicon) resulted in formation of U_3Si_2 .

Solution-stability runs have shown that graphite (grades CS and ATJ) reacts too rapidly with uranium dissolved in magnesium-zinc solutions to be usable as a crucible material for containing these solutions.

Tests of the corrosion resistance of Type 405 stainless steel in cadmium-magnesium-zinc systems at 750 C have shown little or no corrosion at zinc levels below 15 atom percent zinc, irrespective of the cadmium-magnesium ratios. Above a zinc concentration of 15 atom percent, the rate of corrosion increases sharply as the zinc concentration increases. In this same system, at 850 C, tantalum showed good corrosion resistance up to zinc concentrations of about 60 atom percent, at which concentration slight attack was noted. At a 97 atom percent zinc concentration, the attack on tantalum was severe. In an 88 atom percent zinc system, sintered molybdenum was severely attacked while tungsten was unattacked.

Information is presented on the status of fabrication methods for fabrication of equipment components from tantalum, tungsten, and a tantalum-10 percent tungsten alloy.

Eight distillation runs have now been made in the large-scale cadmium distillation unit. Distillation temperatures were varied from 520 to 620 C and rates from 12 to 65 kg/hr. Overall power efficiencies ranged from 41 to 94 percent, with the higher values being obtained at the higher distillation rates. With the exception of some difficulties in line plugging (particularly in the cadmium feed system) and electrical liquid level measurement in the stillpot, the unit has functioned very well.

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.

Construction of the Fuel Cycle Facility Building was over 90 percent completed as of June 1, 1961, as compared to about 80 percent completed on March 7, 1961. Installation of in-cell crane and manipulator bridges has been completed. Work continues on equipment for building and process services.

Installation of the shielding windows has been delayed. It is necessary to rework some of the window components to achieve proper fit. The prime window contractor, Pittsburgh Plate Glass Company, has started this work and window installation should take place in August.

Fabrication of the eight operating manipulator carriages is completed. A prototype power inlet has been tested in the mockup area, and has been found satisfactory.

Two melt refining furnaces will be installed as part of the equipment in the Argon Cell. The furnaces are being constructed and should be completed during the next quarter.

Work continues on other equipment items for the Fuel Cycle Facility. Some small containers and handling tools for radioactive wastes have been ordered for testing. The degassing furnace has been received from the vendor and is being tested in the mockup area. The window shutters, drives, and brackets for the shielding windows have been ordered. The drive system has been tested. These shutters will cover some of the shielding windows when they are not in use so that the gamma dose received by the windows will be reduced.

Some bearing tests have been completed in which grease-lubricated roller bearings were alternately gamma irradiated in an air atmosphere and then run. These tests verified the assumption that roller bearings are a greater problem in the Air Cell than in the Argon Cell. A series of tests are planned to estimate the useful lifetime in the Air Cell.

Crucible performance in melt refining has been further improved. This has been accomplished by a change in operating procedure which reduces thermal gradients during crucible heatup.

Work has started on the development of designs for plant-scale equipment for the skull-reclamation process.

Fundamental studies are being made in support of process development activities. The solubilities of fission product, fissionable, and structural elements are of prime importance in the design of processes. The solubility of iron in liquid cadmium has been measured and may be represented by the empirical equation

$$\text{iron: } \log (\text{atom percent}) = 5.973 - 10960 T^{-1} + 3.023 \times 10^6 T^{-2} \quad .$$

The gamma intermetallic phase in the titanium-cadmium system has been shown to have the composition Ti_2Cd . This intermetallic phase has a body-centered tetragonal symmetry, with $a_0 = 2.865 \text{ \AA}$ and $c_0 = 13.42 \text{ \AA}$. The calculated and observed densities were 6.28 g/cc .

Studies of the vanadium-zinc system have shown the existence of at least one intermetallic compound. This compound has been tentatively assigned the stoichiometric formula VZn_3 , isostructural with $NbZn_3$.

Experiments, in which uranium-zinc alloys, containing the delta phase (U_2Zn_{17}) in the presence of excess uranium, were annealed for periods from one to three weeks at 300, 400, 450, and 500 C, indicated that the delta phase is stable in the presence of uranium down to 300 C.

The utility of distribution between two immiscible liquid metals for purification of spent reactor fuels is being investigated. The influence of bismuth on the distribution of uranium between the partially miscible liquids lead and zinc has been studied in an attempt to improve the distribution coefficient of uranium relative to the distribution coefficient of fission product elements. The distribution coefficient for uranium

$\left(\frac{w/o \text{ U in zinc rich layer}}{w/o \text{ U in lead rich layer}} \right)$, at 659 C, varied with the bismuth:busmuth-plus-lead ratio $\left(\frac{wt \text{ Bi}}{wt \text{ Bi} + wt \text{ Pb}} \right)$ as follows: $K = 208, 36.8, 54$, and 2.1 for values of the $\frac{Bi}{Bi + Pb}$ weight ratio of 0, 0.10, 0.26, and 0.36, respectively.

Similar experiments, in which the influence of lead on the distribution of uranium between liquid zinc and bismuth, at 550 C, was studied gave the following results: $K \left(\frac{w/o \text{ U in zinc rich layer}}{w/o \text{ U in bismuth rich layer}} \right) = 0.14, 0.16, 0.42$, and 1.1 for values of the $\frac{Pb}{Pb + Bi}$ weight ratio of 0, 0.10, 0.33, and 0.44, respectively.

Preliminary experiments on the influence of magnesium on the distribution of uranium between liquid zinc and lead showed that the distribution coefficient was decreased by magnesium additions.

The decomposition pressure of the uranium-cadmium intermetallic phase UCd_{11} has been measured over the temperature range from 305 to 368 C by means of the effusion method. The results may be represented by the equation

$$\log P_{mm} = 9.060 - 6105 T^{-1} \quad ,$$

where P_{mm} is the decomposition pressure of UCd_{11} . The results of the

effusion studies may be combined with results of an earlier galvanic cell study to give the following empirical equation for the standard free energy of formation of UCd_{11} :

$$\Delta F_f^0 (\text{cal/g atom}) = -5864 + 12.51 T - 6.250 \times 10^{-3} T^2 \quad ,$$

over the temperature range from 305 to 473 C.

The magnetic susceptibility χ of the uranium-cadmium intermetallic phase UCd_{11} from room temperature to 70 K has been found to follow a Curie-Weiss relation $\left(\chi = \frac{C}{T - \Delta} \right)$ in which $C = 1.276$ and $\Delta = -30$ K. The effective moment is $3.21 \mu_B$ (Bohr magnetons) per atom. The spin-only moment calculated for two electrons is $2.85 \mu_B$, whereas that for two 5f electrons, using the free gaseous ion model, is $3.58 \mu_B$. Below 70 K, the χ^{-1} vs T curve bends toward the susceptibility axis, indicating a non-degenerate ground state.

A series of combustions of zirconium dihydride in oxygen is in progress. It is necessary to enclose the sample in a Mylar bag prior to the combustion in order to prevent air oxidation of the sample.

A preliminary value of $\Delta E_c^0/M = 8549 \pm 6.2$ cal/g has been obtained for the heat of combustion of boron nitride in fluorine. The results of an earlier series have been discarded because of a side reaction involving adsorbed boron trifluoride and thermal equilibration difficulties.

A study is in progress to devise a method of burning uranium in fluorine which will not lead to the formation of any uranium fluorides except uranium hexafluoride. Total combustion has been obtained by using powdered uranium supported in an aluminum dish.

A series of combustions of hafnium in fluorine has given a preliminary value of $\Delta T/g = 0.73116 \pm 0.00013$ C/g.

Specific techniques have been developed for the combustions of cadmium, magnesium, aluminum, and zinc in fluorine. All of these metals melt in the initial stages of combustion. Preliminary calorimetric combustions are in progress. A literature survey of the fluorides of these metals has been completed.

Studies of the effect of magnetism of bomb parts on the behavior of a platinum resistance thermometer have shown that small deflections in the galvanometer are caused by the presence of magnetic materials in the bomb.

Construction of the high-temperature enthalpy calorimeter is in progress.

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (pages 134 to 188)

The volatilities of uranium and plutonium hexafluorides are the basis of a direct fluorination volatility process proposed for the recovery of uranium and plutonium from irradiated nuclear reactor fuels. In this process fluidization techniques are also used to advantage. 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 by making use of the variability of the rates of fluorination of the plutonium and uranium compounds and chemical reactivities of the hexafluorides.

The metal-decladding step for oxide fuels involves direct gas-metal reactions in the case of elements clad either with stainless steel or Zircaloy. The reactions, all highly exothermic, are carried out with the fuel elements submerged in an inert fluidized bed (alundum, calcium fluoride, or other inert material) which serves as the heat transfer medium. Dilute mixtures of hydrogen chloride in hydrogen fluoride in a single fluid-bed stage or the separate gases in a two-zone reactor have been successfully utilized where reaction with zirconium is involved. In recent work chlorine has replaced the hydrogen chloride for reaction with zirconium and also appears suitable for stainless steel decladding.

The two-zone fluid-bed reactor has been used in all cases outlined above. A chlorination reaction (referred to as primary) is carried out in the lower zone of the reactor. Volatile chloride reaction products pass into the upper zone where they are converted to solid fluorides by reaction with hydrogen fluoride. Solid chlorides also pass into the upper zone in the normal course of solids mixing which occurs between zones and are also readily converted to fluorides. The two zones are separated by an inverted conical baffle which minimizes back-mixing of the gases and prevents the formation of gas mixtures that have been shown to affect these reactions adversely.

In pilot-plant decladding studies, the reaction of 304 stainless steel tube sections with chlorine was scaled up from the $1\frac{1}{2}$ -inch-diameter two-zone reactor to a six-inch two-zone column. In 5.8 hours at temperatures near 600 C, about 95 percent of the charge, which consisted of 30 tubes, 31-mil wall by 9 inches long, was reacted using 50 mole percent chlorine in nitrogen. This was equivalent to an average penetration rate of 5.1 mils/hr.

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. In pilot-plant studies made to optimize process conditions for the direct fluorination of uranium dioxide pellet fuel, batches of one-half-inch pellets were completely fluorinated at 500 C in as little as 6 hours, with an overall rate of $41 \text{ lb UF}_6/(\text{hr})(\text{sq ft reactor cross-sectional area})$. Fluidization of inert material in the voids of the pellet bed resulted in good heat transfer during the course of the fluorination.

Temperature control by regulation of inlet fluorine was also successful in the fluorination of pellets without an inert fluid bed, but poor heat transfer in this case limited the allowable rate to about $\frac{2}{3}$ the value for the fluid-bed case.

The highest fluorination rates have been obtained with oxygen-fluorine mixtures. This procedure is involved in the use of off-gas recycle to maximize fluorine economy; about 70 percent overall fluorine efficiency has been achieved in runs made to date. Fluorinations made with nitrogen diluent proceed at an overall rate from three- to six-fold slower than with oxygen diluent. The oxygen reacts with the pellet surface to form higher oxides which spall off as fines. The high specific surface area of these fines results in a high, nearly constant fluorination rate until the fluorination is about 90 percent complete. The fines appear to be retained in the equipment and to be completely fluorinated without difficulty. Inert beds of calcium fluoride and aluminum oxide have both been used successfully. An investigation of the effect of temperature on reaction rate in the range from 350 to 500 C was made. With oxygen dilution, the fluorination rate was halved for every 50 C lowering of temperature. With nitrogen dilution, the temperature dependence was somewhat stronger.

Since the inert solids will be discarded as waste, it is important, for economic reasons, that very little of the uranium and plutonium be retained in the solids after fluorination. It was first demonstrated that plutonium and uranium could be removed by fluorination upon reacting fluorine with mixed oxides of uranium and plutonium, at 450 C, contained in nickel equipment. Satisfactory removal of uranium upon fluorination of the mixed oxides was achieved at various temperatures when zirconium tetrafluoride and calcium fluoride were used as bed materials. However, satisfactory removal of plutonium was not obtained using the same bed materials. Fluorination of the mixed oxides, with aluminum (crystalline alumina) as bed material, resulted in low plutonium concentrations (0.035 percent after a ten-hour fluorination at 450 C) in the residual solids. It appears that crystalline alumina is superior to calcium fluoride and zirconium tetrafluoride as an inert solid.

After decladding, an alternative to the Direct Fluorination Process (page 159) for reacting high-density uranium dioxide pellets appears feasible. The first step is chlorination-hydrofluorination in a two-zone fluid-bed reactor producing uranium tetrafluoride, followed by fluorination to the hexafluoride. Tube-furnace experiments conducted at 650 C indicated appreciable reaction of sintered uranium dioxide pellets occurs with chlorine (a decladding agent for stainless steel) alone, producing both volatile and nonvolatile reaction products. This reaction would be of some concern if it was found that there was interaction between cladding and fuel reaction products such that overall uranium and plutonium recovery is adversely affected. Sintered pellets were successfully chlorinated with mixtures of chlorine and carbon tetrachloride at reasonable rates. Exploratory trial fluorination of the final bed produced by chlorination of a 20-pellet (initially $\frac{5}{16}$ -inch diameter by $\frac{5}{8}$ -inch long, 121 g total) charge achieved 96.5 percent uranium removal in two hours at 350 C and little additional removal in a subsequent two-hour period in experiments conducted in a $1\frac{1}{2}$ -inch-diameter fluid-bed reactor.

Corrosion studies on nickel, Inconel and Hastelloy-C coupons aimed at preliminary evaluation of potential materials of construction for the chlorination-decladding of stainless steel-clad fuels were concluded. Tests conducted at 600 C in a one-inch horizontal tube furnace using once-through chlorine showed an initially high but diminishing corrosion rate during the first 25 hours, followed by a much reduced uniform corrosion rate during the subsequent period, which extended to 285 hours. The calculated corrosion rates were about 20 mils/month for the short term and lower by about a factor of 10 for the longer term for all metals. Photomicrographs showed severe intergranular attack in nickel, no changes in Inconel, and slight intergranular changes in Hastelloy-C attributed to age-hardening accelerated by high temperature.

Further study of the decomposition of plutonium hexafluoride has been made at 80 C and 100 cm pressure in a nickel vessel. An initial integral reaction rate of 2.4 percent per day was obtained in the first 25 hours, and an average of 1.4 percent per day decomposed in the following 164 hours.

Laboratory experiments have been performed at both Brookhaven and Argonne National Laboratories to determine the best procedure to be used in the recovery of uranium from enriched uranium-zirconium alloy fuels. It has been demonstrated that, for optimum recovery of uranium from enriched uranium-zirconium alloy fuels, it is best to remove the zirconium as volatile zirconium tetrachloride. The hydrochlorination of the zirconium can be carried out at or above 350 C. The uranium remains behind in the form of nonvolatile uranium chlorides. The hydrochlorination of the zirconium and the subsequent fluorination of the uranium chlorides can be carried out in a fluidized bed of granular solids. Of those

bed materials tested, alundum (refractory aluminum oxide) was most satisfactory. Poorer results were obtained when zirconium tetrafluoride was included in the bed material. Based on the amount of uranium remaining in the bed, uranium recoveries of 99.5 percent were achieved when alundum was used as the bed material. Experiments, using physical mixtures of uranium fluorides and zirconium tetrafluoride, indicated that the optimum fluorination temperature, using fluorine, is 350 C. When chlorine trifluoride was used as the fluorinating agent, best uranium removals were obtained at 200 C.

A two-step fluid-bed process for the preparation of high-density uranium dioxide suitable for use in nuclear fuel elements from uranium hexafluoride is being studied. Thirty-five hours of running time, including a 15-hour continuous period, have been accumulated in current studies on the hydrolysis step (first step) in which steam reacts with uranium hexafluoride to form uranyl fluoride. A feed rate of 100 g/min hexafluoride is being used. The problems of fines formation and of control of particle size encountered previously appear to have been solved by allowing the fines to be entrained from the reactor and collected separately, and by use of the proper rate of recycle of seed particles. Run interruptions were due only to plugging of the line used for entraining the solids, a problem readily soluble by improved design.

Additional batch studies of the second step, reduction of uranyl fluoride to the dioxide, were carried out in an auxiliary three-inch fluid-bed reactor with gas composition (steam in hydrogen) and temperature as independent variables. The optimum gas mixture, found to be near 50 percent steam in hydrogen, gave a residual fluoride content of 200 ppm in four hours at 650 C when a uniform bed of -20 +40 mesh particles was used. Temperatures of 550 to 650 C with beds of -40 +60 mesh particles gave residual fluoride contents of 2500 and 150 ppm, respectively, in four-hour periods. Appreciable particle breakup seems to occur (18 to 36 percent minus 200 mesh found in final beds), but this is not of process significance when pellets will be made, since all of the powder will be ground.

Feasibility studies on the use of small-diameter columns for continuous fluid-bed calcining continued. A $2\frac{1}{4}$ -inch-diameter column with 1 M aluminum nitrate feed is currently in use. The technique employed involves mounting the feed spray nozzle vertically in the apex of the cone bottom thereby permitting utilization of the atomizing and feed decomposition gases as the fluidizing gas medium. A reduction in the volume ratio of atomizing air to liquid feed from 1700 used in horizontal spray work in a six-inch-diameter column to 1080 in recent short-term experiments in the currently used $2\frac{1}{4}$ -inch column indicates some success toward meeting the objective of reducing the off-gas handling problem. Other experiments indicated that nozzle operation, heat supply, and feed pump operation are possible trouble areas, and modifications to the equipment are in progress.

Complete reliability of operation is required if the small-diameter aspect of this work is to be applied to systems such as plutonium nitrate or highly enriched uranium for which nuclear criticality must be considered.

III. Reactor Safety (pages 189 to 223)

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

Studies of the ignition of uranium monocarbide powders in oxygen by the burning-curve method are continuing. Studies have been extended to include powders consisting of spherical particles. Ignition temperatures varied from 405 to 385 C for sieved fractions of spherical powder varying in specific area from 4 to 40 sq cm/gram. Ignitions were not sharply defined, probably because of the hindered transport of oxygen through the gaseous combustion products.

Studies of the ignition of spherical zirconium powders by the shielded-ignition method have been initiated. A high-vacuum apparatus has been constructed which prevents the formation of an oxide film prior to the ignition test. Preliminary results have shown that the ignition temperature of 270/325 mesh powder was between 275 and 325 C. This ignition temperature is about 350 C lower than previous values for a single foil (1 mil thick) of similar specific area. The program will include a study of sample size, geometry, specific area, and effects of controlled preoxidation.

Studies of burning propagation along uranium and zirconium foil strips is continuing. Simultaneous measurements of propagation rates and burning temperatures were obtained with the photoelectric pyrometer described in the previous quarterly report. Studies were concentrated on the effects of additions of halogenated hydrocarbons to the air. Results have shown that increasing chlorination in the halocarbon molecule is generally beneficial in lowering propagation rates and burning temperatures of uranium foils. The presence of one hydrogen atom in the molecule is also beneficial.

Motion picture records of a series of experiments were taken demonstrating the effectiveness of a chlorobromomethane extinguishant on a fire involving about one cubic foot of fine zirconium turnings. The fire was "knocked down" quickly enough so that the fire could be approached and extinguished with a dry chemical agent. General use of halocarbons on metal fires cannot be recommended, however, until a large number of practical experiments fully demonstrate the effectiveness and safety of the procedure.

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. Measurement of mean particle diameters for runs with 60-mil zirconium wires in heated water were completed. Experimental results of particle size and total extent of reaction for the runs compared favorably with those computed by the analog computer method, reported previously.

A procedure for estimating the extent of zirconium-water reaction during a nuclear incident was developed. The method is based on the assumption that zirconium cladding on fuel elements will begin to form molten particles when the cladding temperature reaches the melting point (1840 C). Fully molten particles will then separate from the nuclear heat source (fuel element core) as the cladding melts. The individual particles will react with the water and eventually cool to water temperature. The time-temperature history of the particles and the extent of reaction should be identical to that experienced by particles formed from wires by condenser discharge and described by the computer studies. It is then possible to compute the overall extent of reaction occurring during a nuclear incident if the particle size distribution resulting from the nuclear incident can be estimated.

The method was applied to four Zircaloy-clad oxide core fuel pins which underwent severe transients while under water in autoclaves in the TREAT reactor. The following comparison was obtained of total extent of reaction computed from the measured particle size distribution and that measured experimentally from the quantity of hydrogen gas generated:

Computed	8.1, 8.3, 13.1, 14.4
Experimental	4.1, 8.0, 14.0, 24.0

A second method of studying metal-water reactions 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 uranium at 1200 to 1600 C are reported. The nature of the results suggested that the reaction rate was controlled by processes of gaseous diffusion and mixing within the reaction cell. A series of runs with sodium at 200 C was then initiated to compare with the uranium results. Only slightly more reaction occurred with sodium than with uranium. It is thus likely that both reactions occur as fast as water vapor can reach the metal surfaces. Rates with sodium and uranium were both markedly higher than rates reported in the previous quarterly with aluminum.

A third method of studying metal-water reactions has been initiated. This method involves the simultaneous levitation and heating of small metal pellets by a high-frequency field. The sample will be located in flowing

steam. The rate of reaction will be measured by determining the rate of generation of hydrogen. Initial studies have shown that levitated spheres of aluminum, one-quarter inch in diameter, will ignite and burn in air when heated to 1750 C. Ignited pellets when dropped into water will continue to burn to completion, both on the surface and under the water.

Studies of the behavior of ceramic core, metal-clad fuel pins during nuclear reactor excursions in TREAT were extended from the previous work on mixed oxide cores to include pure uranium dioxide cores. Four TREAT reactor transients were performed on fuel pins with a uranium core in a 304-stainless steel jacket; the test conditions were as follows:

UO₂ core: 0.33-inch diam x 0.50 inch long; uranium 20 percent enriched; 89 percent theoretical density.

SS cladding: type 304, 18-mil wall thickness; fuel pin submerged in water.

The following results were obtained:

CEN Transient Number				
	63	61	62	60
megawatt-second burst:	120	304	340	344
millisecond period:	121	116	50	48
neutron dose, nvt thermal:	2.1×10^{14}	3.8×10^{14}	5.4×10^{14}	4.7×10^{14}
% SS-H ₂ O reaction:	0.3	19.1	14.0	13.5
final appearance of fuel pin:				
clad:	intact, 7% increase in diameter	ruptured ~ $\frac{1}{2}$ melted	ruptured ~ $\frac{2}{3}$ melted	ruptured ~ $\frac{2}{3}$ melted
core:	cracked	fragmented into particles	fragmented into particles	fragmented into particles

Oscillograph records of the reactor bursts indicated that the stainless jacket was heated from room temperature to temperatures greater than 1200 C in about 0.3 sec. One experiment (CEN-62) gave a series of pressure pulses with a peak of 160 psi.

Particle size distributions were obtained on the meltdown products by sieve screen analyses; for CEN-62 and 60 the two major size fractions were in the range of particle diameter from 12 to 64 mils. The general appearance of the fuel pin after the transient meltdown in water was similar to those obtained in previous experiments on fuel pins with mixed oxide cores.

IV. Reactor Chemistry (pages 224 to 252)

The neutron capture cross sections of neptunium-237 and erbium-170 are being determined in the fast neutron energy range. The total neutron cross section of uranium-233 is also being determined.

Several types of experiments have been carried out in order to investigate operation of a regenerative lithium hydride fuel-cell system for converting nuclear energy to electricity. The thermally regenerative emf cell system is one in which heat is used to dissociate lithium hydride, which is then re-formed in an electrochemical cell with the production of electric power.

A program of research in thermoelectricity has been initiated to contribute to the technological development of direct conversion of nuclear reactor heat energy into electrical power by means of the thermocouple effect. Binary liquid systems comprised of elements in the area of the periodic system centering about the element tin are to be investigated. The Seebeck coefficients in the liquid indium-antimony system are under study as a function of composition and temperature. For high-temperature work refractory materials are required. Initial studies on these materials will be made in the thorium-sulfur and uranium-sulfur systems.

The Reactor Decontamination Program is directed toward determination of the seriousness of fuel element ruptures in boiling water reactors and the determination of methods of decontamination of contaminated surfaces. A 16-day run to determine whether zirconium-niobium content would reach an equilibrium value has 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 are being conducted with oxalic acid and citric acid-base solutions containing hydrogen peroxide.

V. Routine Operations (page 253)

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 four main sections of this report.

I. CHEMICAL-METALLURGICAL PROCESSING

Pyrometallurgical processes for the recovery of fissionable material from spent reactor fuels offer promise of achieving a reduction in the cost of nuclear power. Their principal advantages over existing processes lie in their simplicity, compactness, low-volume dry wastes, and capability of handling short-cooled fuels, with an attendant reduction in fuel inventories. Melt refining will be the first pyrometallurgical process to be used for the recovery of uranium from the fuel alloy used in the second Experimental Breeder Reactor (EBR-II). This reactor, with an integrated fuel-processing facility, is now under construction at the National Reactor Testing Station in Idaho.

Several small-scale melt refining experiments, each utilizing about 400 grams of highly irradiated uranium-fissium alloy, have been performed to observe the behavior of the material during various phases of the process. The manipulations have proved feasible and the anticipated removal of fission products has been realized. However, since the handling operations in the laboratory must be done in a shielded facility with an air atmosphere, some difficulty has been encountered in achieving satisfactory yields. The procedure has been modified to minimize exposure to air prior to melt refining, but the results obtained with the modified procedure are not yet available.

Experimental work was concluded on the release of fission product krypton and xenon during the heating of highly irradiated EBR-II-type fuel pins. The rate of gas release is relatively low below 750 C; the experimental activation energy was 3.6 kcal/mole. Above 750 C the rate rises sharply. At 850 C the quantity of radioxenon released in two hours was about 7000 times the amount released at 750 C.

In the melt refining process, significant quantities of volatile fission product activity are released into the furnace atmosphere. Radiochemical analysis of material from a filter in an off-gas line from a melt refining furnace showed iodine-131 to be the principal species, with much smaller amounts of barium-140, lanthanum-140, and cesium-137.

Outgassing studies on a sample of material taken from a plant-type zirconia melt refining crucible showed that only small amounts of gas are removed by heating to 1100 C under vacuum. The major gases removed are water vapor and carbon dioxide, with smaller amounts of oxygen, nitrogen, argon, and possibly hydrogen.

Since the possibility exists that small amounts of stainless steel cladding may accompany the decanned fuel pins into the melt refining process, the behavior of iron, nickel, and chromium was studied briefly. The stainless steel constituents appear in the uranium product in much the same manner as the noble metal fission products.

Work was continued on the development of a liquid metal process for recovery of fissionable material contained in melt refining crucible skulls produced in the EBR-II fuel cycle. Incorporation of a noble metal extraction step in the skull-reclamation process has resulted in considerable improvement in the separation of noble metal fission products (ruthenium, rhodium, palladium, and molybdenum) from uranium. In this step the relatively noble metal fission products are extracted into zinc from a slurry of skull oxides in a molten halide flux. The removals obtained are adequate for uranium reclaimed from skull material. Losses of uranium in the noble metal extraction step have been negligible. The extraction of noble metals was found to increase with temperature in the investigated interval from 650 to 750 C, and to increase with a decrease in particle size of the skull oxide, which normally ranges from 14 to -325 mesh. The extent of noble metal removal at 750 C from a normal mixture of skull oxides became constant after two hours at 63 percent for ruthenium, 80 percent for molybdenum, and 60 percent for palladium. Stainless steel constituents, which, by poor separation of cladding material, could become incorporated in the EBR-II fuel, were found to behave much the same as noble fission product metals.

Considerable work was devoted to the separation of the flux and metal phases after extraction of the noble metals. To date, the easiest and most reliable procedure has been pressure siphoning of the zinc phase after freezing the higher melting salt phase. The pressure siphon tube has been kept clear during freezing of the salt by a slow flow of argon. On a one-kilogram scale, zinc transfers have been consistently about 90 percent. A larger zinc charge would yield a higher percentage of transfer.

Some of the variables affecting the rate and extent of reduction of fission oxides by zinc-magnesium alloys in the presence of a flux have been investigated. The results show that, with proper flux, flux-to-metal ratio, stirring, and crucible material, complete reduction of fission oxide to produce a 4 weight percent uranium solution occurs between 2.4 and 13 weight percent magnesium. It is expected that complete reductions could also be achieved at higher magnesium concentrations. A satisfactory range of magnesium ion concentration in the flux is 40 to 100 percent. Some insoluble uranium carbide is formed if graphite is used as a reaction vessel.

Preliminary observations have indicated that separation of plutonium and rare earth elements may be possible through selective reduction of the oxides from a halide flux by means of high magnesium-zinc systems. Although not pertinent to the present EBR-II fuel cycle, complete reduction of thorium oxide has also been achieved with a 5 percent magnesium-zinc alloy in the presence of a suitable halide flux.

A satisfactory material, which will permit ready removal of the uranium product after the retorting step of the skull-reclamation process, is still being sought. Beryllia crucibles that have been tested for this purpose have shown that good product removals (over 90 percent) are possible. The beryllia crucibles were made by incremental additions of the crucible material to a mold and tamping. This resulted in a layering effect up the crucible walls. Ultimately, the crucibles parted at stratification marks above the liquid level. Isostatically pressed crucibles which have densities that are 90 percent of the theoretical are now being obtained.

Work is in progress to determine the feasibility of decontaminating plutonium fuels, such as future core loadings of the EBR-II reactor, from rare earth fission products by virtue of the insolubility of plutonium in calcium. On the assumption that it is desirable to recover plutonium and uranium together, uranium solubilities in zinc-calcium systems were determined over a calcium concentration range from 0 to 30 percent (see Figure 15, page 68). Cerium solubilities were measured in zinc solutions containing 26 to 77 weight percent calcium. The cerium solubility is such that decontamination of plutonium from cerium and probably other rare earths is feasible if the plutonium can be completely precipitated and if coprecipitation effects are not serious.

A demonstration of the blanket process with a 1 percent plutonium-uranium alloy showed rapid and complete dissolution of both the uranium and plutonium in a 12 percent magnesium-zinc solution. All the plutonium (within analytical error) remained in solution whereas 99.7 percent of the uranium was precipitated by the addition of magnesium to a 50 percent concentration. The plutonium-bearing solution was removed and the uranium precipitate washed once with a 50-50, magnesium-zinc solution, also without incurring plutonium loss. The run is particularly encouraging because it shows the possibility of high plutonium recovery and good separation of uranium from plutonium.

The possibility of synthesizing refractory plutonium and uranium compounds in liquid metal media is being explored. A 400-gram quantity of uranium monocarbide was prepared by carbon precipitation of uranium dissolved in a 10 percent magnesium-zinc solution and will be used for the preparation of sintered bodies. A plutonium carbide was formed by reaction of plutonium dissolved in liquid magnesium with fine carbon powder. The material was isolated and was found by X-ray diffraction analysis to be Pu_2C_3 . Plutonium monocarbide was not detected. An initial attempt to prepare U_3Si by reaction of dissolved uranium with silicon resulted in the formation of USi_3 . A large excess of silicon was used. A second attempt using stoichiometric ratios of uranium to silicon (3 uranium to 2 silicon) resulted in formation of U_3Si_2 .

Solution-stability runs have shown that graphite (grades CS and ATJ) reacts too rapidly with uranium dissolved in magnesium-zinc solutions to be usable as a crucible material for containing these solutions.

Tests of the corrosion resistance of Type 405 stainless steel in cadmium-magnesium-zinc systems at 750 C have shown little or no corrosion at zinc levels below 15 atom percent zinc, irrespective of the cadmium-magnesium ratios. Above a zinc concentration of 15 atom percent, the rate of corrosion increases sharply as the zinc concentration increases. In this same system, at 850 C, tantalum showed good corrosion resistance up to zinc concentrations of about 60 atom percent, at which concentration slight attack was noted. At a 97 atom percent zinc concentration, the attack on tantalum was severe. In an 88 atom percent zinc system, sintered molybdenum was severely attacked while tungsten was unattacked.

Information is presented on the status of fabrication methods for fabrication of equipment components from tantalum, tungsten, and a tantalum-10 percent tungsten alloy.

Eight distillation runs have now been made in the large-scale cadmium distillation unit. Distillation temperatures were varied from 520 to 620 C and rates from 12 to 65 kg/hr. Overall power efficiencies ranged from 41 to 94 percent, with the higher values being obtained at the higher distillation rates. With the exception of some difficulties in line plugging (particularly in the cadmium feed system) and electrical liquid level measurement in the stillpot, the unit has functioned very well.

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.

Construction of the Fuel Cycle Facility Building was over 90 percent completed as of June 1, 1961, as compared to about 80 percent completed on March 7, 1961. Installation of in-cell crane and manipulator bridges has been completed. Work continues on equipment for building and process services.

Installation of the shielding windows has been delayed. It is necessary to rework some of the window components to achieve proper fit.

The prime window contractor, Pittsburgh Plate Glass Company, has started this work and window installation should take place in August.

Fabrication of the eight operating manipulator carriages is completed. A prototype power inlet has been tested in the mockup area, and has been found satisfactory.

Two melt refining furnaces will be installed as part of the equipment in the Argon Cell. The furnaces are being constructed and should be completed during the next quarter.

Work continues on other equipment items for the Fuel Cycle Facility. Some small containers and handling tools for radioactive wastes have been ordered for testing. The degassing furnace has been received from the vendor and is being tested in the mockup area. The window shutters, drives, and brackets for the shielding windows have been ordered. The drive system has been tested. These shutters will cover some of the shielding windows when they are not in use so that the gamma dose received by the windows will be reduced.

Some bearing tests have been completed in which grease-lubricated roller bearings were alternately gamma irradiated in an air atmosphere and then run. These tests verified the assumption that roller bearings are a greater problem in the Air Cell than in the Argon Cell. A series of tests are planned to estimate the useful lifetime in the Air Cell.

Crucible performance in melt refining has been further improved. This has been accomplished by a change in operating procedure which reduces thermal gradients during crucible heatup.

Work has started on the development of designs for plant-scale equipment for the skull-reclamation process.

Fundamental studies are being made in support of process development activities. The solubilities of fission product, fissionable, and structural elements are of prime importance in the design of processes. The solubility of iron in liquid cadmium has been measured and may be represented by the empirical equation

$$\text{iron: } \log (\text{atom percent}) = 5.973 - 10960 T^{-1} + 3.023 \times 10^6 T^{-2}.$$

The gamma intermetallic phase in the titanium-cadmium system has been shown to have the composition Ti_2Cd . This intermetallic phase has a body-centered tetragonal symmetry, with $a_0 = 2.865 \text{ \AA}$ and $c_0 = 13.42 \text{ \AA}$. The calculated and observed densities were 6.28 g/cc .

Studies of the vanadium-zinc system have shown the existence of at least one intermetallic compound. This compound has been tentatively assigned the stoichiometric formula VZn_3 , isostructural with $NbZn_3$.

Experiments, in which uranium-zinc alloys, containing the delta phase (U_2Zn_{17}) in the presence of excess uranium, were annealed for periods from one to three weeks at 300, 400, 450, and 500 C, indicated that the delta phase is stable in the presence of uranium down to 300 C.

The utility of distribution between two immiscible liquid metals for purification of spent reactor fuels is being investigated. The influence of bismuth on the distribution of uranium between the partially miscible liquids lead and zinc has been studied in an attempt to improve the distribution coefficient of uranium relative to the distribution coefficient of fission product elements. The distribution coefficient for uranium $\left(\frac{\text{w/o U in zinc rich layer}}{\text{w/o U in lead rich layer}} \right)$, at 659 C, varied with the bismuth:bismuth-plus-lead ratio $\left(\frac{\text{wt Bi}}{\text{wt Bi} + \text{wt Pb}} \right)$ as follows: $K = 208, 36.8, 54, \text{ and } 2.1$ for values of the $\frac{\text{Bi}}{\text{Bi} + \text{Pb}}$ weight ratio of 0, 0.10, 0.26, and 0.36, respectively.

Similar experiments, in which the influence of lead on the distribution of uranium between liquid zinc and bismuth, at 550 C, was studied gave the following results: $K \left(\frac{\text{w/o U in zinc rich layer}}{\text{w/o U in bismuth rich layer}} \right) = 0.14, 0.16, 0.42, \text{ and } 1.1$ for values of the $\frac{\text{Pb}}{\text{Pb} + \text{Bi}}$ weight ratio of 0, 0.10, 0.33, and 0.44, respectively.

Preliminary experiments on the influence of magnesium on the distribution of uranium between liquid zinc and lead showed that the distribution coefficient was decreased by magnesium additions.

The decomposition pressure of the uranium-cadmium intermetallic phase UCd_{11} has been measured over the temperature range from 305 to 368 C by means of the effusion method. The results may be represented by the equation

$$\log P_{\text{mm}} = 9.060 - 6105 T^{-1} \quad ,$$

where P_{mm} is the decomposition pressure of UCd_{11} . The results of the effusion studies may be combined with results of an earlier galvanic cell study to give the following empirical equation for the standard free energy of formation of UCd_{11} :

$$\Delta F_f^0(\text{cal/g atom}) = -5864 + 12.51 T - 6.250 \times 10^{-3} T^2,$$

over the temperature range from 305 to 473 C.

The magnetic susceptibility χ of the uranium-cadmium intermetallic phase UCd_{11} from room temperature to 70K has been found to follow a Curie-Weiss relation $\left(\chi = \frac{C}{T - \Delta}\right)$ in which $C = 1.276$ and $\Delta = -30$ K. The effective moment is $3.21 \mu_B$ (Bohr magnetons) per atom. The spin-only moment calculated for two electrons is $2.85 \mu_B$, whereas that for two 5f electrons, using the free gaseous ion model, is $3.58 \mu_B$. Below 70 K, the χ^{-1} vs T curve bends toward the susceptibility axis, indicating a nondegenerate ground state.

A series of combustions of zirconium dihydride in oxygen is in progress. It is necessary to enclose the sample in a Mylar bag prior to the combustion in order to prevent air oxidation of the sample.

A preliminary value of $\Delta E_c^0/M = 8549 \pm 6.2$ cal/g has been obtained for the heat of combustion of boron nitride in fluorine. The results of an earlier series have been discarded because of a side reaction involving adsorbed boron trifluoride and thermal equilibration difficulties.

A study is in progress to devise a method of burning uranium in fluorine which will not lead to the formation of any uranium fluorides except uranium hexafluoride. Total combustion has been obtained by using powdered uranium supported in an aluminum dish.

A series of combustions of hafnium in fluorine has given a preliminary value of $\Delta T/g = 0.73116 \pm 0.00013$ C/g.

Specific techniques have been developed for the combustions of cadmium, magnesium, aluminum, and zinc in fluorine. All of these metals melt in the initial stages of combustion. Preliminary calorimetric combustions are in progress. A literature survey of the fluorides of these metals has been completed.

Studies of the effect of magnetism of bomb parts on the behavior of a platinum resistance thermometer have shown that small deflections in the galvanometer are caused by the presence of magnetic materials in the bomb.

Construction of the high-temperature enthalpy calorimeter is in progress.

A. Pyrometallurgical Development

1. Melt Refining

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

The irradiated fuel alloy discharged from the first core loading of EBR-II will be processed by melt refining. The fuel, in the form of rods

or pins clad with stainless steel jackets, consists of 50 percent enriched uranium alloyed with noble metal fission product elements. After the cladding has been removed by mechanical methods, the pins are chopped and charged to a zirconia crucible where they are melted and held at 1400 C for a period of three to four hours. This treatment removes about two-thirds of the fission products through the mechanisms of volatilization and selective oxidation. The purified fuel alloy is cast into an ingot by pouring the molten metal into a mold. (A separate process is used to recover the mixture of oxides and unpoured metal remaining in the crucible in the form of a skull.) Further results are reported on (1) demonstration experiments utilizing about 400 g of highly irradiated EBR-II type fuel alloy, (2) the release of fission product krypton and xenon as irradiated fuel pins are heated, (3) the transport of activity through components of the melt refining equipment, (4) the outgassing of melt refining crucible material, and (5) the behavior of stainless steel constituents in the melt refining process.

a. High-activity Level Melt Refining Experiments
(V. G. Trice, N. R. Chellew, W. H. Spicer, C. C. Honesty)

Several melt refining experiments, each utilizing about 400 g of highly irradiated uranium-fissium alloy, have been conducted to demonstrate the recovery and decontamination of EBR-II fuel and to observe the physical behavior of the fuel during various phases of the process. Three experiments with irradiated fuel have been completed. The complete results of the first experiment were reported in ANL-6287, page 32. Some preliminary data from the second and third experiments are now available.

The conditions employed and the pouring yields for the three experiments with irradiated fuel and for the corresponding reference experiments with unirradiated fuel are presented in Table 1. In all cases the pouring yields were lower for the irradiated fuel. Examination of the skulls (unpoured metal and oxides remaining in the crucible after pouring) showed that the low yields observed in the active runs were caused by excessive oxidation of the uranium. In Run 3, the skull was physically separated by breaking away the crucible. Close examination of the exposed skull revealed a spongelike mass of pinshell fragments which completely filled the melt volume of the crucible.

The available evidence indicates that the reduction in yield in the active experiments is not caused by a radiation effect during the melt refining process. It may occur, however, during the handling of the fuel prior to melt refining. In Experiment 2A, unirradiated fuel pins were melt refined in a highly radioactive crucible; a yield of 87.2 percent, normal for an inactive run, was obtained. Furthermore, the presence of pinshell fragments in the skull from Run 3 indicates the formation of an oxide coating on the pins before they were melted.

Table 1

HIGH-ACTIVITY LEVEL MELT REFINING EXPERIMENTS^a

	Experiment No.			
	1	2	2A ^b	3
Charge Weight (g)	387.6	392.3	398.1	362.5
Burnup (percent of total atoms)	0.56	0.22	-	0.86
Cooling Time (days)	42	28	-	14
Total Activity (curies/charge) ^c	2520	1100	-	6520
Melt Refining Conditions				
Time (hr)	3	3	3	1
Temperature (C)	1400	1400	1400	1400
Yield (percent)	72.4	69.3	87.2	52.2
Yield of Reference Experiment (percent) ^d	86.7	84.0	-	84.0

^aFurnace atmosphere:argon; crucible:Norton RZ5601 zirconia; wetted area of crucible:36 sq cm.

^bIn Experiment 2A unirradiated fuel was melt refined in the radioactive crucible from Experiment 2.

^cEstimated from fission yield data and conditions of irradiation.

^dThe reference experiments duplicated the conditions of the active experiments, but employed unirradiated alloy. The yields of the hot experiments are thought to be low because of oxidation of the irradiated fuel by the air atmosphere of the cave prior to the experiment. This situation will not arise in the EBR-II Fuel Cycle Facility, since the atmosphere is argon.

In a series of preliminary tests, the effect of oxide coatings on the melt refining of inactive fuel pins was examined briefly (see ANL-6145, page 33). Exposure of the pins to air for 65 hr, at temperatures of 150 and 200 C prior to melt refining reduced the yields to 72 and 47 percent, respectively.

Several operations must be performed in the air atmosphere of the cave facility before the pins can be placed under the controlled atmosphere of the melt refining furnace. These operations include polishing with a silicon carbide abrasive powder to remove any oxide coating, sampling, weighing, loading of the crucible, and insertion of the loaded crucible in the melt refining furnace. Because of the fission product decay heat, the irradiated fuel pins attain a temperature of about 80 C when handled individually and of about 300 C when loaded together in the insulated melt refining furnace assembly. It is believed that these temperatures, coupled

with the intense radiation flux at the surface of the pin, are sufficient to account for the observed oxidation effects in air. The laboratory procedure for melt refining has therefore been revised to minimize the time required for handling the fuel and to employ argon blanketing whenever possible.

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

The study of release of fission product krypton and xenon from highly irradiated EBR-II-type fuel pins has been completed. The primary objectives of the final experiment were (a) to obtain indications of the nature of fission product gas release at various equilibrium temperatures below the melting point of the alloy and (b) to observe the amount of swelling occurring in the unrestrained pin at these temperatures. The apparatus and techniques used in this work were described previously in ANL-6231 (pages 42 to 47) and ANL-6287 (pages 38 to 42). The results of two earlier experiments utilizing a similar alloy are reported in the latter reference.

The charge material was prepared by irradiating injection-cast pins of uranium-238 containing 10.7 weight percent uranium-235 and five weight percent fission elements in the CP-5 thermal reactor. A determination of the cesium-137 content and an isotopic analysis of the uranium in a sample of the material indicated the burnup to be 0.2 percent of the total atoms. Micrometer measurements of the irradiated fuel pins showed that no significant change had occurred in the original diameter of 0.144 in. During the irradiation, the pins, depending on their location within the capsule, were exposed to temperatures of 300 to 400 C. The 13.7-g pin used in the experiment was cooled 35 days and then cleaned with emery paper.

The experimental procedure was as follows. (1) the pin was charged to the furnace, which was evacuated for 30 min at 100 C and then cooled; (2) high-purity argon at a pressure of about 670 mm was introduced to the closed system, and circulation of the atmosphere through the counting loop at about 180 cc/min was started; (3) the pin was held for about two hours at each of the following equilibrium temperatures: 256, 379, 502, and 619 C, then allowed to cool overnight; (4) the pin was reheated to equilibrium temperatures of 749 and 850 C, held at each of these temperatures for about two hours, and then further heating was applied at a rate of about 5 C/min until no additional fission gas release was noted over a 35-min period. To determine the extent of fission gas release during this series of operations, the activity present in a sample of the atmosphere in the system at the end of the experiment was compared with the activity in a sample of the gas evolved when a portion of the alloy removed from the furnace was dissolved in acid. Gamma-spectrometric analyses of the two gas samples, with the introduction of appropriate

factors for the weight of alloy and the gas volumes involved, showed that 99.7 percent of the xenon and 99.8 percent of the krypton-85 initially present in the charge material had been removed during the experiment.

Data on the bulk release of xenon-133 and swelling of the fuel pin as functions of temperature and heating time are shown in Figure 1. The indicated isothermal periods each include a preliminary 10-min period required for temperature adjustment. The sharp break in the escape rate of xenon as the temperature was increased above 749 C and the completion of activity release at about 1070 C are in general agreement with previously reported observations (a sharp break at about 700 C and completion of activity release at about 1025 C). In the previous experiments, however, the burnup was higher by about a factor of three and the temperature was increased continuously at rates of 5.5 to 7.5 C/min to 1175 C. Similarly, the maximum diametrical increase of the pin (about 50 percent at 990 C) agrees with the increases of about 47 percent noted for the previous experiments. Within the estimated accuracy of pin diameter measurement by a filar eyepiece in the cave periscope (± 0.004 in.), the expansion of the pin heated to an upper temperature limit of 619 C was reversible. At equilibrium temperatures of 619, 749, and 850 C, the time of heating does not appear to be the dominant factor controlling the expansion.

FIGURE 1
DIAMETRICAL EXPANSION AND CUMULATIVE RELEASE OF XENON-133
DURING HEATING OF EBR-II-TYPE ALLOY PIN

The release of radioxenon at various equilibrium temperature periods of two hours is indicated in Figure 2. The data obtained at 502 C were not included because of their known inaccuracies caused by the malfunctioning of a sensitive detector probe in the gas-counting assembly during this heating period. (Relative activities were measured by gamma-spectrometric techniques.) Since the release of radioxenon appeared to be linear with time at constant temperature, the data were fitted to straight lines by the lease-squares method. The constants in the equations for these lines, $P = a + bt$, where P is the percentage of total xenon-133 evolved and t is the time in minutes, are as follows:

Temp (C)	$a \times 10^3$	$b \times 10^4$
256	0.2	0.65
379	6.1	1.74
619	3.7	2.72
749	0.2	3.86
850	18,350	991.6

FIGURE 2
FRACTIONS OF XENON-133 RELEASED FROM EBR-II TYPE
ALLOY AT EQUILIBRIUM TEMPERATURES TO 850C

In Figure 3 the temperature dependence of xenon release is shown in an Arrhenius plot. It is apparent that a pronounced break in the slope of the line occurs around 749 C. Below this temperature the slope corresponds to an experimental activation energy of 3.6 kcal/mole.

FIGURE 3
ARRHENIUS PLOT OF XENON-133 RELEASE
FROM EBR-II-TYPE ALLOY
(FOR EXPERIMENTAL CONDITIONS, SEE FIGURE 1)

Above 749 C, the rate of radioxenon release increases very rapidly with temperature. The quantity of xenon released in a two-hour period at 850 C was about 250 times the quantity released at 749 C. The similarity between the temperature at which rapid xenon evolution begins and the temperature at which uranium-five percent fission alloy undergoes a final transformation to the single gamma phase (~ 725 C)¹ suggests the possibility that the two phenomena may be related.

c. Transport of Activity in Melt Refining Systems
(N. R. Chellew, C. C. Honesty)

During the melt refining of highly irradiated EBR-II alloy under an inert atmosphere, significant quantities of volatile fission product elements are released into the furnace. The fission gas release studies indicate that more than 99 percent of the noble gas fission products are evolved. Under plant conditions it is anticipated that the gas from the melt

¹Nevitt, M. V. and Zegler, S. T., Journal of Nuclear Materials 1, 6 (1959).

refining furnace will be pumped through suitable filters and traps and then detained in a hold tank. In order to gain some information on the type of radioactivity that may be carried along with the noble gases during this operation, analytical data were obtained for the fission products appearing in various components of the off-gas system used in a high-activity level melt refining experiment (uranium-fissium alloy irradiated to 0.2 total atom percent, Experiment 2, ANL-6333, page 36). A schematic diagram of the off-gas handling and storage system used in the experiment is shown in Figure 4.

During the course of the melt refining run, argon was added to the furnace and exhausted into the storage system at various times. The volumes (STP) of argon containing volatilized fission products pumped through the filter and into the storage cylinder at various stages of the experiment were (a) 122 liters during a 15-min. outgassing period as the charge was heated from 500 to 900 C, (b) seven liters during a furnace pressure reduction step with the charge at 1180 C, and (c) 91 liters after the charge had been heated at 1400 C for three hours and the furnace had cooled to room temperature. During operations (a), (b), and (c), the pressures in the furnace were reduced to 25, 750 and 30 mm, respectively. The linear gas velocities through the filter were adjusted to approximate those that will be used in the EBR-II Fuel Cycle Facility.

Gamma-spectrometric analyses were performed on samples of the gas taken from the storage tank, samples of the vacuum pump oil, and solutions obtained by successively leaching the filter media with 4N HNO₃ and 2N NaOH solutions. The initial analyses, which were performed about one month after the fuel material had been removed from

the reactor, showed a high specific activity of iodine-131. To relate this iodine activity to the total amount in the fuel charge, a 1.266-g control specimen from the original charge was analyzed. The distribution of iodine-131 in the various components of the off-gas system is shown in Table 2.

Table 2

DISTRIBUTION OF IODINE-131 IN NOBLE GAS STORAGE SYSTEM
DURING MELT REFINING EXPERIMENT WITH HIGHLY
IRRADIATED MATERIAL

Furnace Charge: Composition: uranium-5 w/o fissium
Burnup: 0.22 percent of total atoms
Cooling time: 28 days
Weight: 392 g
Total curies of iodine-131: 56

Conditions: See text

System Component	Iodine-131 Activity ^a
	(percent of total charged to furnace)
Primary Filter	0.3
Secondary Filter	0.02
Vacuum Pump Oil	0.01
Noble Gas Storage Tank	0.2
Copper Transfer Lines	(present) ^b
<hr/>	
Total Accountable	0.53

^aAnalyses by gamma-spectrometric techniques.

^bQualitatively identified but not amenable to quantitative analysis.

Re-analysis of the leachings from the first filter after more than 99 percent of the eight-day iodine-131 activity had decayed (total cooling time, 120 days), showed qualitatively that barium-140, lanthanum-140, and cesium-137 were present. The filter contained a glass medium designed for efficient collection of submicron particles. The ratio of total gamma to beta activity in the same sample obtained from the solutions used to leach the filter was approximately unity after complete removal of iodine by chemical techniques. This indicates an insignificant quantity of elements that decay only by beta emission (e.g., strontium). No specific fission product isotopes other than iodine-131 were identified positively in leachings from the second filter.

In the absence of complete quantitative information on all the volatilized fission products, the mechanism of iodine transport to the filter cannot be defined in detail. Gamma survey meter measurements made at the outer surface of the filter assembly during the experiment, however, provided some information on the bulk release of activities other than the noble gas fission products. No sharp increase in activity at this location was noted when the furnace atmosphere was removed at a fuel temperature below 900 C. However, when the pressure was reduced with the fuel at 1180 C (Step b above), a sharp increase in gamma activity from 0.02 to 3.25 r/hr was noted. Reduction in the pressure within the filter to 30 mm, which removed 95 percent of the noble gases in the container, did not cause an appreciable reduction in the activity level.

d. Outgassing of Melt Refining Crucible Material
(M. D. Adams)

It has been a general practice in the melt refining of uranium alloys to heat the zirconia crucibles under vacuum in order to remove adsorbed atmospheric gases and water before the crucibles are used. To gain insight concerning the effect of this treatment on the removal of the sorbed material, an experiment was performed to determine the amounts and compositions of the gases removed by this treatment from crushed zirconia.

A 100-g sample of 25 to 50 mesh material taken from a plant-type melt refining crucible was placed in a quartz tube which was sealed to a thoroughly outgassed vacuum line and evacuated at room temperature. The temperature was raised in a steplike manner to 1100 C. The gases evolved at 300, 500, 700, and 1100 C plateaus were collected and measured by a Toepler pump and saved for subsequent mass spectrometric analysis. The quantity and composition of gas collected at each temperature are indicated in Table 3.

Table 3

REMOVAL OF GASES FROM ZIRCONIA MELT REFINING
CRUCIBLE MATERIAL BY HEATING UNDER VACUUM

Sample: 100 g of 25 to 50 mesh zirconia from a plant-size
melt refining crucible exposed to air.

Temp (C)	Time (hr)	Volume Evolved (cc, STP)	Composition (percent) ^a						
			H ₂	H ₂ O	N ₂ + CO	O ₂	Ar	CO ₂	Other
25 to 150	6	0.047	25	28	14	0.1	0.1	28	4
300	20	0.502							
500	29	0.686							
700	47	0.595							
1100	7	0.643	0.2	55	1.5	24	10	9	1
Total		2.471							

^aMass spectrometric analysis.

Cooling of the zirconium oxide sample in a measured quantity of argon resulted in the adsorption of one cubic centimeter (STP) of the gas which could not be removed by evacuation at room temperature. A measured amount of air was then added and recovered quantitatively.

The surface area of the zirconium oxide sample as determined by a Perkin-Elmer-Shell Sorptometer was very low, probably as a result of sintering during the manufacture of the crucible.

The total quantity of gas released from the material during the outgassing experiment was about 2.5 cc. Extrapolation of this value to a plant-size crucible weighing 10 kg yielded a figure of 250 cc, or about 0.01 mole of gas. The amounts of gases sorbed by the intact crucible are probably somewhat smaller than the amounts sorbed by the powdered crucible material. However, in spite of the small amount of gas adsorbed, it is felt that outgassing and cooling of crucibles in an argon atmosphere is a desirable procedure.

e. Behavior of Stainless Steel Constituents in the Melt Refining Process
(T. R. Johnson, R. L. Christensen)

During the mechanical decanning of EBR-II fuel pins, there is a possibility that small amounts of the stainless steel cladding might accompany the pins to the melt refining process. It is therefore of interest to determine the fates of iron, chromium, and nickel in the melt refining and skull-recovery processes. In the experiment described below, it was determined that iron, chromium, and nickel behave much as the noble metal fission products in the melt refining process.

A small-scale experiment was performed in which 500 g of a uranium-six percent fission alloy containing one percent stainless steel (iron-9.3 percent nickel-17.2 percent chromium) and 0.6 percent cerium was melted in a zirconia crucible at 1350 C for 2 hr. The resulting skull, weighing 25 g, was powdered by oxidation and removed from the crucible.

The alloy before and after melting underwent no significant change in the stainless steel content. The skull oxide showed a slight, but significant, increase in stainless steel constituents over the quantity that would be expected if the iron, chromium, and nickel behaved strictly as noble metals. The actual stainless steel content of the skull oxide was 0.72 weight percent as compared to a concentration of 0.62 weight percent, which would have resulted if the stainless steel had shown typical noble metal behavior.

It can therefore be concluded that the major portion of any stainless steel cladding material accompanying the uranium-fission fuel pins to the melt refining process will appear in the product as a constituent of the uranium-fission alloy.

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

Liquid metal processes are being developed for the purposes of recovering the fissionable material remaining as a skull in the melt refining crucible and for the isolation of plutonium bred in EBR-II blanket material. Attention is also being given to the processing in liquid metal media of future EBR-II cores, which will contain plutonium as the fissionable material. Work was also continued on the utilization of liquid metal media for the preparation of various actinide element compounds, for example, uranium and plutonium carbides, and uranium silicides.

a. Oxidation of Radioactive Melt Refining Skulls (R. C. Cairns, I. O. Winsch, R. Nowak)

The initial step in the process for reclamation of melt refining skull material is oxidation of the skull in order to make possible its removal from the crucible. The skull material is oxidized at a temperature of 700 to 800 C by oxygen diluted to about 25 percent with argon. The presently preferred method of performing this oxidation is in closed equipment (see Figure 3, ANL-6333, page 44) with oxygen added as required to maintain the 25 percent concentration.

Since previous work with lightly irradiated material indicated iodine to be the only significant activity volatilized during the oxidation step, the behavior of iodine in this step has become of considerable interest because of possible problems which might arise in the handling of iodine in a plant operation. In order to check out equipment, two additional runs were made with skulls containing tracer levels of activity as precursors to work at high activity levels. Since at a tracer level the percentages of iodine occurring in various fractions may not be meaningful, it is appropriate to indicate iodine behavior in a qualitative fashion only. Most of the iodine present in the skull material and crucible after melt refining was still present in the skull oxide after oxidation. A significant fraction (10 to 20 percent) of the iodine was volatilized, the bulk of which was absorbed on the Fiberfrax absorbers. The Fiberfrax was employed as a stopper to close off the top of the stainless steel can in which the oxidation was performed. The Fiberfrax permits pressure fluctuations but prevents the spread of activity into external piping. Essentially no activity was detected beyond the Fiberfrax.

b. Demonstration of Skull Recovery Process (R. D. Pierce, T. R. Johnson, J. F. Lenc, K. R. Tobias, R. L. Christensen, M. A. Bowden, and J. D. Schilb)

The program to demonstrate the various steps of the process for recovery of uranium from melt refining skulls was continued during the past quarter. The objectives of the process demonstration experiments are:

- 1) to demonstrate the feasibility of the process,
- 2) to investigate the chemistry of the process,
- 3) to propose and investigate process modifications, and
- 4) to reveal and define problems of equipment design and operation.

The demonstration runs reported in the previous quarterly showed poor removal of ruthenium and molybdenum. Therefore, the process has been modified to include a noble metal extraction step in which the easily reducible noble oxides are removed from the skull oxide by selective reduction with zinc and extraction into the zinc. The process including this modification is shown in Figure 5.

FIGURE 5
SKULL-RECOVERY PROCESS FLOW SHEET
Basis: 1 kg U in Skull Oxide

It consists of the following steps:

- 1) controlled oxidation of the skull material to convert it to a freely flowing powder;
- 2) selective extraction of the noble metals into zinc from a dispersion of skull oxide in a halide flux;
- 3) reduction and dissolution of the uranium oxides with a 5 percent magnesium-zinc solution;
- 4) precipitation, by cooling from 800 C to about 500 C, of the uranium-zinc intermetallic compound from which the supernatant liquid is removed;
- 5) decomposition of the intermetallic compound and precipitation of uranium metal by increasing the magnesium concentration to 50 percent and removal of the supernatant liquid; and
- 6) retorting to vaporize the residual metal solvents and isolate the purified uranium.

The noble metal extraction, reduction, and precipitation steps were conducted in equipment which was shown in the previous report (see Figure 5, ANL-6333, page 47). As mentioned in the preceding report, the original furnace was modified to make possible the pressure siphon transfer operations which are required in a demonstration run. The modified furnace is serving until improved equipment now on order has been delivered and installed.

Results of two runs (Runs 7 and 8) made on an approximately 200-g uranium scale (250 to 300 g of skull oxide) are now available. These runs were carried out in accordance with the flowsheet shown in Figure 5.

General Observations on Physical Performance of Process Steps

In the first run (Run 7) an attempt was made, after the noble metal extraction operation, to transfer the oxide-flux slurry by pressure siphoning. Although 94 percent of the flux was transferred, it contained only 50 percent of the skull oxide because the heavy oxide particles settled out, some to the flux metal interface and some through the zinc phase to the bottom of the vessel. Some of the zinc phase was also transferred with the flux. This method of separation of phases is obviously impractical. A separate investigation of this phase-separation problem was therefore made (see page 53), which resulted in the development of a method involving siphoning away the zinc phase after freezing the flux phase.

Because of the poor skull oxide transfer in Run 7, this run was terminated after the reduction step. However, the zinc and oxide-flux heel was charged with additional zinc, flux, and oxide for the noble metal extraction step of Run 8. The product metal phase from the reduction step of Run 7 (a 6 percent magnesium-2 percent uranium-zinc solution) was also added to the reduction step of Run 8. In effect, nearly all of the uranium charge of Run 7 was employed in Run 8 together with additional quantities of zinc, skull oxide, and flux.

A tantalum crucible failed during the noble metal extraction operation in Run 8. This made it necessary to remove the flux phase physically after cooling to room temperature. The separated flux was premelted and cast into an ingot for charging to the reduction step.

Separation of the flux and metal phases after the reduction step and removal of the supernatant solutions after the two precipitation steps were accomplished by pressure siphoning. These transfers were made without difficulty.

The residual solvent metals were removed by retorting. The product was in the form of two large balls weighing 168 g and material weighing 38 g which adhered to the crucible. All the recovered product material was dissolved and analyzed.

Despite the difficulties encountered in these runs, a great deal of information was obtained about the behavior of uranium and various fission products in the process.

Uranium Behavior

Under the present philosophy of operation in the skull-reclamation process, material heels are left behind in some vessels to facilitate clean separation of phases. The product material in these heels is recovered in the course of repetitive operations. In a single run such as Run 8, however, it is not possible to show high product recoveries. Therefore, the behavior of uranium is considered from the standpoint of information pertinent to an equilibrium situation. This information may be summarized as follows:

- 1) In the noble metal reduction step, the uranium content of the zinc extract was less than 0.01 percent of that charged. Under the proposed method of phase separation, namely, removal of the zinc phase, which becomes a waste, uranium losses should be negligible.

- 2) As indicated by a flux analysis, the reductions of uranium oxides in Runs 7 and 8 were essentially complete (> 99 percent). However, the material balances in Runs 7 and 8 were not sufficiently accurate to confirm these high reductions by analyses of the magnesium-zinc product solution. Complete reductions should be expected in this step.
- 3) Losses of 1 and 2 percent occurred in the supernatant solutions from the intermetallic and uranium precipitation steps, respectively. These losses are not excessive for the skull-reclamation process, but they could be further reduced by lowering the temperature of the phase separations.
- 4) As indicated previously, about 20 percent of the final product material adhered strongly to the tantalum retorting crucible. This has been the usual experience. This problem is receiving separate study involving evaluation of alternative retorting materials (see page 62).

Fission Product Behavior

Skull oxide prepared from lightly irradiated fissionium was used as tracer material for following ruthenium, zirconium, and cerium. The activity concentrations of the individual elements were rather low, and so the accuracies of the results are not very high; they are estimated to be ± 25 percent for ruthenium and ± 15 percent for cerium and zirconium. Chemical analyses were obtained for molybdenum and palladium. The results are summarized in Table 4.

Table 4

FISSION PRODUCT REMOVALS IN SKULL RECLAMATION DEMONSTRATION RUNS 7 AND 8

Constituent	Concentration in Starting Material (oxygen-free basis) (w/o)	Product Concentration (w/o) ^a	Percent Removal
Uranium	91.0	97.8	
Cerium	3.2	0.05 ^b	98
Zirconium	1.23	0.19	84
Molybdenum	2.24	0.30	87
Ruthenium	1.69	0.50	70
Palladium	0.18	0.0096	99

^aBased on dissolution of 168 g of product removed from the metal crucible. Concentration of 0.6 percent magnesium and about one-half percent tantalum were present in the product.

^bAnalysis seems low; estimated as 0.25 weight percent. This would lower the removal to 92 percent.

Overall removals were between 70 percent for ruthenium and 99 percent for palladium. For purposes of the EBR-II fuel cycle, these removals are sufficient. The behavior of individual fission product elements may be summarized as follows:

Ruthenium - Nearly all of the ruthenium removal (about 70 percent) was achieved in the noble metal extraction step. Very little separation of ruthenium from uranium was provided by the uranium precipitations and removal of the supernatant liquids. The ruthenium apparently coprecipitated extensively with both the uranium-zinc inter-metallic compound and uranium metal.

Molybdenum - The bulk of the molybdenum removal was also provided by the noble metal extraction step. Its separation from uranium was probably further augmented by its insolubility in the reducing alloy (6 percent magnesium-zinc alloy).

Palladium - Palladium (and presumably rhodium) was also effectively extracted into zinc in the noble metal extraction step. It was also removed as a soluble component in the supernatant solutions of the precipitation steps. Consequently, very high removal of palladium was achieved.

Zirconium - The zirconium in the skull oxide comes from two sources: the zirconia crucible fragments, and the fission product zirconium in the fuel alloy. No zirconium removal was effected by the noble metal leach. Experiments have shown (ANL-6333, page 60) that the crucible fragments are reduced very slowly in the reduction step, and that the bulk of this material is removed in the waste flux phase. The fission product zirconium was largely reduced along with the uranium. About 60 percent of this zirconium was removed in the supernatant solution of the intermetallic precipitation step. About 50 percent of the remainder of the zirconium was removed in the supernatant solution following magnesium decomposition of the intermetallic compound.

Cerium - Cerium was not extracted by zinc from skull oxide. In the reduction step, essentially all of it was reduced along with the uranium. Also, as expected, it coprecipitated nearly quantitatively with the uranium in the intermetallic compound precipitation step. Therefore, all of the cerium removal was effected in the supernatant solution resulting from decomposition of the intermetallic compound and precipitation of uranium. In effect, the cerium removal is proportional to the percentage of supernatant liquid that is removed.

c. Noble Metal Extraction from Fissium Skull Oxides

(1) Effects of Particle Size and Temperature (J. B. Knighton, J. W. Walsh)

Further information was obtained on the extraction of noble metal fission products from fissium skull oxides by zinc in the presence of a flux. The effects of temperature and particle size on the efficiency of extraction are outlined in Table 5.

Table 5

NOBLE METAL REMOVAL BY ZINC EXTRACTION

Metal: 400 g Zn
 Flux: 200 g of 47.5 m/o CaCl_2 -47.5 m/o MgCl_2 -5 m/o MgF_2
 Mixing Rate: 400-500 rpm
 Atmosphere: Air
 Temperature: As indicated
 Oxide: Fission skull oxide "SO54;" particle size and quantity as indicated

Run Conditions

Quantity Skull Oxide, g	21.9	21.9	26.4	26.4	25.3
Particle Size, mesh	-325	-325	-14, +25	-14, +25	Reconstituted Oxide
Temp, C	650	750	650	750	750
<u>Time (min)</u>	<u>Percent Ru Extracted</u>				
30		91			
60	54	91	34	60	57
120	73		43	68	62
180					63
240					63
	<u>Percent Mo Extracted</u>				
30		80			
60	83	83	70	85	74
120	83		76	85	80
180					80
240					80
	<u>Percent Pd Extracted</u>				
30		80			
60	85	93	59	72	52
120	94		60	77	59
180					60
240					61

On the basis of these data, the following conclusions can be reached:

- (1) The degree of noble metal fission product extraction increases as the temperature is raised from 650 to 750 C. This effect was observed with both fine (-325 mesh) and coarse (-14, +25 mesh) particles.

- (2) The degree of extraction increases as the particle size is reduced, both at 650 and 750 C. (Fissium skull oxide particles normally range from 14 to -325 mesh and average about 100 mesh.)
- (3) With fissium skull oxide reconstituted from screen fractions in proportion to the size of the fractions originally present in the oxide, the extent of noble metal removal became constant after 2 hr at 750 C at the following levels:

ruthenium	63 percent
molybdenum	80 percent
palladium	60 percent

These removals are adequate for the skull-recovery process, especially since further noble metal removal occurs in the subsequent process steps as was indicated in the preceding section. It is believed that the extent of removal is controlled by access of the zinc to the interior of the particles. Any technique which breaks down the particles would be expected to increase the effectiveness of the extraction.

(2) Extraction of Stainless Steel Constituents
(T. R. Johnson, R. L. Christensen)

The behaviors of iron, nickel, and chromium from stainless steel in the melt refining process were discussed earlier in this report (page 44). The experiment was extended to determine the fates of these elements during the extraction of noble metals from skull oxides.

Twenty grams of the oxidized skull from the melt refining experiment was stirred with 400 g of zinc and 200 g of flux (47.5 mole percent calcium chloride-47.5 mole percent magnesium chloride-5 mole percent magnesium fluoride) for 6 hr at 800 C. This oxide contained 0.72 weight percent stainless steel components. Filtered metal samples taken in tantalum tubes gave the results shown in Figure 6.

The iron was extracted into the zinc phase rapidly and almost completely. Nickel was removed more slowly and to a lesser extent. A single sample showed that only 60 percent of the chromium was extracted after 6 hr. Since the standard free energies of formation (ANL-5750) indicate chromic oxide to be slightly more stable than zinc oxide, this chromium concentration in the zinc phase may represent an equilibrium condition.

It may be concluded that the stainless steel constituents will behave much the same as the noble metals in the skull-recovery process, thereby limiting the concentrations that would build up in the melt

refining fuel cycle. It is anticipated that these concentrations would be very low unless unexpectedly large amounts of cladding material are introduced into the melt refining process.

(3) Separation of Phases after Noble Metal Extraction (R. D. Pierce, K. Tobias)

Results reported in the last quarterly (ANL-6333, page 55) showed removal of the flux-oxide slurry by pressure siphoning to be an unattractive procedure. This conclusion was reached when it became apparent that the oxide could not be kept in suspension. The coarse oxide particles, although remaining wetted with flux, sank to the bottom, forming a small separate layer below the zinc phase. Consequently, attention was turned to removal of the zinc phase, either by pressure siphoning or pouring, after freezing of the salt phase. Preliminary work with pressure siphoning was encouraging, and, therefore, this procedure was further investigated along with pouring during the past quarter.

Transfers of over 90 percent have been made by both siphoning and pouring. For pressure siphoning a vent hole must be maintained through the flux and for pouring a suitable hole through the flux must be available. A vent opening can be consistently maintained through the flux by operating the agitator while the flux is freezing, but the narrow opening produced by this means has been too small to pour through. A heated tube through which argon was slowly passed has satisfactorily kept a pouring hole open, thereby making possible a nearly complete removal of the zinc by pouring.

To date, the easiest and most reliable procedure for the phase separation has been pressure siphoning. The siphon tube has been kept clear by slowly passing argon through the tube during the freezing

of the salt. A vent for the argon was provided by a crack between a slowly rotating stirrer and the bulk of frozen salt. Six successive runs were made without difficulty by this technique and excellent zinc removals were obtained (see Table 6). The zinc charge to these runs was sized at the minimum volume considered feasible. Since the zinc heel from a transfer would remain constant for a given arrangement, a larger charge would yield a more complete extraction.

Table 6

REMOVALS OF ZINC EXTRACT FROM NOBLE METAL
EXTRACTION STEP BY PRESSURE SIPHONING

Procedure: Transfers made at 525 C after salt phase frozen. Pressure siphon tube kept open by slow flow of argon during freezing of salt. Argon vent provided by crack between slowly rotating stirrer and bulk of frozen salt.

Zinc Charge (g)	Approx Distance of Transfer Tube Inlet above Crucible Bottom (in.)	Percent of Zinc Extractant Transferred
1268	1/4	90
1368	1/4	88
1151	3/16	93
1151	3/16	93
1151	3/16	94
1151	3/16	92

New pressure-siphon transfer experiments are planned in which equipment suitable for remote operation will be tested.

d. Pyrometallurgical Reduction Studies
(J. B. Knighton, J. W. Walsh, J. R. Pavlik)

(1) Reduction of Fissium Skull Oxides by a Magnesium-Zinc System

The oxidation of melt refining skulls for further treatment in the liquid metal skull-recovery process produces a product consisting mainly of U₃O₈ with smaller amounts of fission product oxides and zirconia crucible fragments. Since one of the steps in the process involves the reduction of this oxide mixture by a zinc-magnesium alloy in the presence of a flux, some of the variables affecting the rate and extent of reduction have been investigated. An argon atmosphere was employed to simulate the conditions in the EBR-II Fuel Cycle Facility.

Effect of Magnesium Concentration in the Metal Phase

A fissium skull oxide prepared by recombining the screen fractions in their original proportions was utilized in the experiments. The final magnesium concentration in the zinc phase was varied from 2.01 to 13.18 weight percent. The conditions employed and the results of the experiments are presented in Table 7 and Figure 7.

Table 7

EFFECT OF MAGNESIUM CONCENTRATION ON THE REDUCTION OF FISSIUM SKULL OXIDE BY MAGNESIUM-ZINC ALLOY

Oxide:	63.2 g fissium skull oxide "SO54" reconstituted from screen fractions
Metal:	1000 g Zn-Mg alloy (Mg concentration as indicated)
Flux:	1000 g of 47.5 m/o CaCl_2 -47.5 m/o MgCl_2 -5.0 MgF_2
Atmosphere:	argon
Temperature:	800 C
Mixing Rate:	600 rpm
Crucible:	ATJ graphite, except in last run in which tantalum crucible was employed.

Final U Concentration for Complete Reduction: 3.92 w/o

Mg Concentration in Zn Phase (w/o)		U Concentration in Zn Phase (w/o) ^a			
Initial	Final	30 min	60 min	90 min	120 min
3.35	2.01	2.3	2.9	2.9	2.9
4.00	2.12	2.3	2.9	3.0	3.2
4.00	- ^b	3.0	3.1	3.5	3.6
5.00	2.38	3.2	3.7	3.8	3.9
5.00	3.08	3.6	3.8	3.9	4.0
7.00	5.15	3.0	3.3	3.4	3.7
7.00	5.37	3.0	3.7	3.6	3.8
10.00	8.17	3.0	3.2	3.5	3.5
15.00	13.18	2.9	3.5	3.5	3.5
15.00 ^c	-	3.9	-	4.0	3.9

^aEstimated analytical accuracy: ± 5 percent of reported values.

^bSample lost; final magnesium concentration estimated to be 2.25 w/o.

^cTantalum apparatus.

The data show that a minimum of about 2.4 weight percent magnesium in the zinc phase in the final solution is required to reduce the fission oxide completely and to produce a four weight percent solution of uranium under the experimental conditions. When a graphite crucible was used, a decrease in the uranium concentration was observed at the higher magnesium concentrations. This effect is believed to result from an interaction of the uranium in solution with graphite to form insoluble uranium carbide. This difficulty was eliminated by substituting a tantalum vessel for the graphite crucible. In the last run, in which the initial magnesium concentration was 15 weight percent and a tantalum container was used, complete reduction of the uranium had occurred by the time the first sample was taken at 30 min.

The results show that with the proper flux, flux-to-metal ratio, stirring, temperature, and crucible material, complete reduction of fission oxide to produce a four weight percent uranium solution occurs at final magnesium concentrations between 2.4 and 13 weight percent. No upper limit of effective magnesium concentration was defined; it is expected, however, that complete reduction would take place at higher concentrations.

Effect of Magnesium Ion Concentration in the Flux Phase

In previous work on the reduction of uranium oxides by zinc-magnesium alloys, it was concluded that magnesium ion is an essential ingredient of the flux (ANL-6333, page 61). Additional experiments were performed with fission skull oxides to establish a range of magnesium ion concentrations in the flux within which satisfactory reductions can be achieved. The experimental conditions and results are presented in Table 8 and Figure 8.

Table 8

EFFECT OF MAGNESIUM ION CONCENTRATION IN THE FLUX ON THE
REDUCTION OF FISSIUM SKULL OXIDE BY MAGNESIUM-ZINC ALLOY

Oxide: 63.2 g fissium skull oxide "SO54" reconstituted from screen fractions
 Metal: 1000 g Zn-5 w/o Mg alloy
 Flux: 500 g (composition as specified)
 Atmosphere: argon
 Temperature: 800 C
 Mixing Rate: 600 rpm
 Crucible: ATJ graphite, except lastrun which employed tantalum crucible
 Final U Concentration for Complete Reduction: 3.92 w/o

Flux Composition (m/o)			U Concentration in Zn Phase (w/o) ^a			
CaCl ₂	MgCl ₂	MgF ₂	30 min	60 min	90 min	120 min
95	0	5 ^b	0.50	0.73	0.98	1.1
95	0	5	0.43	-	1.4	1.9
72.5	22.5	5	2.1	-	3.3	3.2
72.5	22.5	5	2.4	3.2	3.2	3.3
47.5	47.5	5	3.6	3.8	3.9	4.0
47.5	47.5	5	3.2	3.7	3.8	3.9
0	95	5	3.2	3.6	3.6	3.6
0	95	5	3.1	3.4	3.6	3.4
0	95	5 ^c	-	3.9	3.9	3.9

^a Estimated analytical accuracy: ± 5 percent of reported values.

^b CaF₂ (5 m/o) instead of MgF₂.

^c Tantalum apparatus.

FIGURE 8
EFFECT OF MAGNESIUM CATION CONCENTRATION
IN FLUX ON REDUCTION OF FISSIUM OXIDE

The data show that with a flux containing calcium and magnesium cations, about 40 mole percent magnesium cation concentration is required to produce complete reduction of the uranium oxide under the conditions employed in the experiments.

In experiments in which graphite crucibles were used and magnesium was the only cation in the flux, samples of the zinc phase showed a lower uranium concentration than would have been produced by complete reduction. Substitution of tantalum for the graphite equipment resulted in uranium concentrations corresponding to complete reduction.

The following conclusions can be drawn from these experiments: (1) Calcium is a less effective cation in the flux phase than magnesium in promoting the reduction of uranium from fissium skull oxide under the conditions of the experiments. (2) A satisfactory concentration range of magnesium in the flux for the reduction lies between 40 and 100 mole percent of the total cations present. (3) Graphite appears to cause instability in zinc-magnesium solutions, presumably through the formation of insoluble uranium carbide. This reaction has been observed in connection with other work (see ANL-6333, page 74). Presently, the use of graphite with zinc-magnesium solutions is avoided whenever possible.

(2) Reduction of U_3O_8 by a Magnesium-Zinc System:
Effect of Fluoride Ion Concentration in the Flux

The effects of several variables on the reduction of uranium oxides by a magnesium-zinc alloy have been reported previously (ANL-6287, page 51; ANL-6333, page 61). This work has been extended to include a study of the effect of fluoride ion concentration in fluxes composed primarily of calcium chloride and magnesium chloride in an air atmosphere. The experimental results from this study are shown in Figure 9.

Fluoride ion has been incorporated into the flux systems primarily as a means of producing a clean, well-defined, flux-metal interface that will permit good phase separations. It also has a beneficial influence on the rate of reduction, as indicated in Figure 9. Complete reduction (99+ percent) based on uranium determinations of flux and metal phases was achieved in 10 min (or less) with a flux containing 20 mole percent fluoride anion, compared to the 30-min period required when no fluoride ion was present.

FIGURE 9
EFFECT OF FLUORIDE ANION CONCENTRATION
ON RATE OF U_3O_8 REDUCTION IN CALCIUM CHLORIDE -
MAGNESIUM CHLORIDE-MAGNESIUM FLUORIDE-ZINC-MAGNESIUM SYSTEM

(3) Reduction of Thorium Oxide

Although the reduction of thorium oxide is not related directly to the EBR-II fuel cycle, the success achieved in the reduction of uranium oxides by magnesium-zinc alloys in the presence of fluxes suggested that a similar method could be applied to thorium oxide, and it was thought that this use of the technique might be of general interest. A few survey experiments were reported previously (ANL-6333, page 67). Some additional results have been obtained, and the present status of the study is shown in Figures 10, 11 and 12.

The following observations are made on the basis of these data:

- (1) Complete reduction of thorium oxide by magnesium-zinc alloy is possible if a properly chosen flux is employed.
- (2) The reduction of thorium oxide follows the same general pattern observed in the reduction of U_3O_8 (compare Figure 10 with data on page 53, ANL-6287).
- (3) The reduction rates are much slower for thorium oxide than for uranium oxide.

FIGURE 10
REDUCTION OF THORIUM DIOXIDE IN ZINC-5 WEIGHT PERCENT
MAGNESIUM-MOLTEN HALIDE SYSTEMS

FIGURE 11
REDUCTION OF THORIUM DIOXIDE IN ZINC-5 WEIGHT PERCENT
MAGNESIUM-GROUP II CATION FLUXES

FIGURE 12
REDUCTION OF THORIUM DIOXIDE IN ZINC-5 WEIGHT PERCENT
MAGNESIUM-LITHIUM CHLORIDE-MAGNESIUM
CHLORIDE-MAGNESIUM FLUORIDE SYSTEMS

- (4) Group II cations (Ca^{++} , Mg^{++}) promote the reduction reaction; magnesium ion in particular appears to be essential for complete reduction. All the fluxes which yielded 50 percent reduction, or better, contained at least 50 mole percent magnesium cation.
- (5) Poor reductions were obtained with fluxes containing only calcium or Group I cations (Li^+ , Na^+ , K^+).
- (6) Fluoride ion accelerates the reduction of thorium oxide in fluxes containing only magnesium as the cation (see Figure 11). In a lithium chloride-magnesium chloride-magnesium fluoride flux, however, the rate of reduction was decreased by the addition of fluoride ion (see Figure 12).
- (7) Complete reductions of thorium oxide were obtained with a lithium chloride-magnesium chloride-magnesium fluoride flux (47.5, 47.5, 5.0 mole percent). This particular flux also produced the highest rate in the reduction of U_3O_8 .

These experiments were conducted with an air atmosphere.

(4) Potential Separation of Rare Earths from Uranium and Plutonium by Selective Reduction of the Oxides

The chemical similarity of plutonium and the rare earth elements has led to problems in the effective removal of rare earth fission products from plutonium-containing reactor fuels. Preliminary observations have suggested that such a separation may be possible through selective reduction of the oxides. Therefore, an experimental program has been started in an attempt to define the more promising flux compositions which may permit a separation of this type.

The initial approach to the problem has been to investigate the effects of magnesium concentration in the zinc phase and the magnesium chloride concentration in the flux upon the distribution of cerium between the two phases. If plutonium and uranium distributions differ sufficiently from those of the rare earths, the technique would result in a separation. At the present time, the indications are that fluxes which favor the reduction of uranium and plutonium oxides are relatively ineffective in the reduction of cerium oxide. The converse also appears to hold

The results of preliminary experiments are shown in Figure 13. It is apparent from these data that the distribution of cerium between the flux and metal phases is dependent upon both the magnesium concentration in the zinc and the magnesium chloride content of the flux.

FIGURE 13
DISTRIBUTION OF CERIUM BETWEEN MOLTEN
HALIDE FLUXES AND MAGNESIUM-ZINC ALLOYS

In a magnesium chloride-magnesium fluoride flux, for example, effective reduction of uranium oxide is achieved at 800 C with a 50 percent magnesium concentration in the zinc phase. Cerium oxide, on the other hand, under these conditions, remains in the flux phase to the extent of 90 percent (see Figure 13). It is believed that plutonium oxide would also be completely reduced under these conditions, although the reaction has not been investigated at these specific compositions (see ANL-6287, page 57).

Further information will be obtained in an attempt to determine conditions under which higher separation factors can be achieved. Studies with rare earth oxides other than cerium are also planned.

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

In the proposed skull-reclamation process (see Figure 5), a final retorting step is required to recover the uranium precipitated in the decomposition step from the residual zinc and magnesium. Ideally, the retorted uranium should be recovered quantitatively in a form adaptable

to remote handling. Further, it should be sufficiently free of any impurities that would inhibit its incorporation with other fuel materials upon recycle to melt refining. As reported in ANL-6333, page 68, partial success in obtaining a product meeting these requirements was achieved in experiments in which the retorted uranium was in the form of compact, irregular-shaped agglomerates. These agglomerates were readily removed from a seamless tantalum crucible, but their yield (70 to 80 percent) was lower than that desired for practical process application.

Efforts to improve this yield by studying the effects of the agitation variables (type, speed, time, and temperature) during the decomposition step of the process were unsuccessful in quantitatively agglomerating the uranium (see Table 9, which includes five new runs in addition to four reported in the previous quarterly). The nonagglomerated portion of the retorted uranium (10 to 30 percent of the total) adhered tenaciously to the tantalum crucible in all nine runs. While it is recognized that this material could be recycled, it would be more desirable from a process viewpoint to maintain the quantity of recycle material at a lower level.

Table 9
YIELD OF URANIUM AGGLOMERATES FROM THREE-STEP^a RETORTING EXPERIMENTS
(Scale: ~180 g of uranium)

Run No.	Type of Agitator	Conditions of Agitation during Intermetallic Decomposition Step			Uranium Agglomerates (Percent of Total Retorted Product Easily Recovered)
		Speed Range (rpm)	Time (hr)	Temp (C)	
A-60	Flat Paddle	300 (1 hr) 700 (3.5 hr)	4.5	800 750	80.8
A-62	Flat Paddle	400-600	5	800	70.5
A-64	Propeller	200-600	4	800	82.3
A-66	Propeller	600	1	800	0
A-67	Flat Paddle	700	2	800	70.8
A-68	Propeller	600	2	800	68.0
A-69	Propeller	560-700 500 ^b	2	800 800-550	85.5
A-71	Propeller	550-650 200 ^b	2	825 825-550	81.7
A-72	Flat Paddle	500-725 200 ^b	2	825 825-550	90.5

^aThe three steps are the last three of the skull-reclamation process, all three of which are conducted in the same crucible. These steps are: (1) precipitation of uranium-zinc intermetallic compound and removal of supernatant, (2) decomposition of this compound with magnesium to precipitate uranium, and, following removal of supernatant liquid, (3) retorting to drive off residual zinc and magnesium.

^bReduced speeds on cooling to 550 C, the pour temperature.

Presently, other crucible materials, such as beryllia and boron nitride, are being tested in the hope that the nonagglomerated uranium can be easily recovered. One experiment was made in a beryllia crucible of about 66 percent theoretical density. The same procedure was used in this experiment as in the runs made in tantalum (see Table 9). About 90.5 percent of the retorted uranium dropped free from the beryllia crucible in the form of a relatively large, irregular-shaped agglomerate.

The remainder of the product adhered very slightly to the crucible side wall in the form of a thin ring. The location of this ring was in a horizontal plane coincident with the liquid-metal level present in the uranium-zinc intermetallic precipitation step prior to pouring.

Although the beryllia crucible remained intact through the three steps of the experiment, the side wall fractured circumferentially in attempting to reuse the crucible for a second experiment. This fracture occurred at one of several striations (see Figure 14) which were present in the crucible as a result of the manner in which the crucible was fabricated. The crucible had been formed by adding beryllia powder incrementally to a mold and cold tamping to the desired density. After firing, the stratification caused by this incremental addition and tamping of the beryllia powder was clearly discernible in the crucible. To eliminate this problem, isostatic pressing is to be used to fabricate crucibles for future experiments. It is anticipated that crucibles fabricated by this latter technique will have a density of about 90 percent of theoretical.

To simplify remote operation by eliminating the necessity for tight closures, an investigation is also underway to evaluate the possibility of conducting the retorting operation at atmospheric pressure. Three experiments have been made to recover uranium agglomerates enveloped in a zinc-high magnesium matrix from the decomposition step of the skull reclamation process. Atmospheric vaporization of this matrix alloy and subsequent melting of the uranium agglomerate will be attempted in a beryllia crucible.

FIGURE 14
BERYLLIA CRUCIBLE AFTER
FAILURE AT STRIATION MARK

f. Plutonium Recovery Processes

- (1) Development of Process for Recovery of Plutonium from EBR-II Core Materials
(M. Ader, J. T. Feeney, J. D. Schilb)

Current investigations are being made to determine the feasibility of decontaminating plutonium fuels, such as future core loadings of EBR-II as well as other fast breeder reactor fuels, from rare earth fission products by virtue of the insolubility of plutonium in calcium (mp, 851 C). The prospect for such separations is good as shown by previous related investigations. British workers^{2,3} at Harwell found that, at 1125 to 1225 C, calcium extraction of uranium and uranium-plutonium-cerium alloys containing up to 20 percent plutonium and 0.13 percent cerium gave the following distribution coefficients (weight basis): cerium, 9; plutonium, 0.08 to 0.008; and uranium, 0.005. However, practical application of these favorable ratios were precluded by a formidable container problem at molten uranium temperatures. At Los Alamos,⁴ a relatively low-temperature extraction of liquid plutonium-iron-fissium alloy was achieved by alloying calcium with 32 atom percent magnesium. At 600 C, the distribution coefficients (weight basis) found for plutonium and cerium were 0.015 and 1, respectively. In both cases, lanthanum extracted more favorably than cerium, and noble metals such as molybdenum and ruthenium were poorly extracted.

In applying this plutonium-rare earth separation concept to a uranium-plutonium fuel alloy, prior separation of plutonium from uranium may or may not be advantageous. Satisfactory liquid metal processes for removing plutonium from uranium, for example by extraction into magnesium or magnesium-zinc solution, are available and have been tested. The initial experiments undertaken in this research assumed that it was desirable to recover plutonium and uranium together, decontaminated from rare earths. It was assumed further that plutonium, uranium, and rare earths would be found together either dissolved in liquid zinc or coprecipitated as metal-zinc intermetallic compounds. Addition of enough calcium

² Martin, F. S., Jenkins I. L., and Keen, N. J., Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 17, 352-355 (1958)

³ Jenkins, I. L., et al., AERE-R-2949 (August 1960)

⁴ Leary, J. A., et al., Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 17, 376-382 (1958)

to the zinc solution or zinc-intermetallic compounds, it was expected, would precipitate plutonium and uranium metals.* The rare earth metals, it was hoped, would remain in solution, neither being precipitated nor coprecipitated.

Thus, scouting studies were undertaken which sought to establish over a range of calcium-zinc concentrations (a) the solubility of uranium; (b) the solubility of cerium; (c) the coprecipitation behavior of cerium with uranium; and (d) the mutual solubility behavior of plutonium, uranium, and cerium. Cerium was selected as representative of the rare earths because of its large fission yield and because it is believed that other rare earths would show even more favorable extraction into calcium solutions.

(a) Uranium Solubility in Zinc-Calcium Solutions

Uranium solubilities in zinc solutions containing 1.5 to 31 weight percent calcium were determined at 725 to 775 C in two experiments conducted under nearly identical conditions. The starting charges were (1) 1500 g zinc, 36.2 g (2.4 weight percent) uranium, and 0.135 g (0.0088 weight percent) neutron-irradiated cerium in Experiment MA-Ca-3; and (2) 1375 g zinc and 36.4 g (2.6 weight percent) uranium in Experiment MA-Ca-5. Cerium was included in MA-Ca-3 to study coprecipitation behavior, and these results will be discussed under cerium coprecipitation. It is believed that the cerium concentration used in the study was too small to influence uranium solubility. In both experiments, the charges were dissolved by stirring at about 750 C for about 5 hr in tantalum equipment under an argon atmosphere. Subsequently, calcium metal (nominally 99.5 percent with less than 0.5 percent magnesium) in the form of $\frac{1}{4}$ -in.-diameter sticks was added incrementally to the melt. Intervals of agitation (3 hr minimum), settling (0.5 hr minimum), and sampling at 775, 750, and 725 C followed each calcium addition. The temperature was measured by a calibrated (to ± 1 C) thermocouple set in a tantalum well immersed in the melt. Samples were taken by pressurizing the melt through Grade 60 graphite frits press-fitted into $\frac{1}{4}$ -in.-diameter tantalum tubes. Sample tubes were preheated to temperatures of the melt before pressurization. After acid dissolution, samples were analyzed for: (1) calcium by a method involving EDTA titration and complexing of zinc with potassium cyanide; (2) uranium by spectrophotometry by means of the color formed with dibenzoyl methane in a mixed organic solvent, or, at concentrations below 0.2 weight percent, by fluorimetry; and (3) cerium by counting cerium-141 gamma activity through an aluminum absorber in a well-type scintillation counter and comparing with the specific activity of a control taken from the same piece of irradiated cerium.

*The presence of zinc offers the possibility of operating at temperatures as low as 385 C, the melting point of the calcium-32 w/o zinc eutectic or, more practically, at 600 C for solutions containing 15 to 60 w/o zinc in calcium.

The uranium solubility data obtained are given in Table 10 and plotted in Figure 15 as a function of calcium concentration. Uranium solubility decreases as calcium is added to zinc, and reaches a minimum at about seven percent calcium. The solubility increases on further addition of calcium until a maximum is reached at about 13 percent calcium and thereafter decreases sharply. The solubility curves, as drawn in the region of about 13 percent calcium, are composed of arcs which intersect as cusps. The exact locations of the joins have not been determined. This behavior resembles that found for uranium in the zinc-magnesium-uranium system (see ANL-6101, page 66). In all likelihood, in the region of the zinc-calcium-uranium system investigated, the equilibrium solid phases are uranium-zinc intermetallic compounds from 0 to 13 percent calcium and uranium thereafter. The coprecipitation behavior found for cerium (see below) lends support to this belief.

Table 10

SOLUBILITY OF URANIUM IN ZINC-CALCIUM SOLUTIONS

Charge: 1500 g Zn, 36.2 g U, 0.135 g Ce in Expt MA-Ca-3; 1375 g Zn, 36.4 g U in Expt MA-Ca-5; Ca added incrementally

Equipment: Tantalum

Atmosphere: Argon

Sampling: Melt pressurized through graphite filters into tantalum tubes; data in chronological order

Experiment MA-Ca-3			Experiment MA-Ca-5		
Temp (C)	Calcium (w/o)	Uranium (w/o)	Temp (C)	Calcium (w/o)	Uranium (w/o)
749	0	2.07 ^{a,b}	750	0	2.35
724	0	1.59 ^a	776	4.53	1.14
699	0	0.96 ^a	774	5.44	0.83
750	1.48	1.74	775	10.2	1.60
723	1.53	1.11	750	10.6	1.08
750	2.88	1.16	725	11.3	0.52
725	2.89	0.68	776	12.2	2.14 ^b
750	4.50	0.69	750	12.5	2.07
726	4.42	0.43	725	12.6	1.37
749	6.28	0.48	775	14.5	1.04
724	6.58	0.22	751	14.5	1.00
750	9.40	0.73	726	14.7	0.88
723	9.51	0.36	776	20.7	0.0033
775	9.08	1.26	752	20.3	0.0050
775	11.6	2.20	727	21.0	0.0028
750	11.9	1.50	776	26.3	0.0011
725	12.3	0.83	751	26.1	0.00070
775	17.1	0.28	727	26.5	0.0015
749	17.3	0.30	776	31.6	0.00053
725	17.4	0.29	750	31.2	0.00051
			726	31.0	0.00078

^aSolubilities computed by means of the equation $\log w/o U = 6.946 - (6711/T)$ (see ANL-6333, page 110) are 3.50 w/o at 775 C, 2.45 w/o at 750 C, 1.64 w/o at 724 C, and 1.04 w/o at 699 C.

^b Probably unsaturated.

FIGURE 15
SOLUBILITY OF URANIUM IN ZINC-CALCIUM SOLUTIONS

The solubility curves in Figure 15 above about 17 weight percent calcium are not detailed because of uncertainty in the fluorimetric uranium data. In another experiment (MA-Ca-1) it was found that uranium solubility remained low, 0.005 weight percent or less, in zinc solutions containing 23 to 60 weight percent calcium. However, a word of caution should be mentioned in regard to accepting as final uranium solubility data obtained by sampling melts through graphite filters. Experience with the zinc-magnesium-uranium system has indicated that uranium in solution at about 700 C and higher reacts readily with many impurities, including graphite, whenever its activity and/or activity coefficient is close to unity. This is likely to be the case in the zinc-calcium-uranium system at calcium concentrations of about 13 percent and greater. However, the data are sufficiently informative to allow evaluation of possible separation processes.

(b) Cerium Solubility in Calcium-Zinc Solutions

Information on the solubility of cerium (mp, 804 C) in calcium is meager. Two eutectics are reported⁵ in the binary system: one containing 2 weight percent cerium and melting at 843 C,

⁵ Zverev, G. D., Doklady Akad. Nauk. SSSR, 104, 242 (1955).

and the other containing 0.086 weight percent calcium and melting at 802 C. A large miscibility gap covering almost the entire composition range between these eutectics is indicated. No calcium-cerium compounds have been reported.

Cerium solubilities in solutions containing 23 to 74 weight percent (16 to 64 atom percent) zinc in calcium were determined in Experiment MA-Ca-6 as follows. An outgassed Morganite alumina crucible was charged with 114 g zinc, 3.59 g cerium, 0.591 g neutron-irradiated cerium, and 0.1 g calcium. The mixture was heated at 800 C in an argon atmosphere without stirring for 5 hr to dissolve and homogenize the active and inactive cerium charges, and then cooled. Cerium solubility in zinc at 800 C is reported as five weight percent,⁶ whereas the nominal cerium concentration in the 115-g ingot which was obtained was 3.6 weight percent. After placing the ingot atop 366 g of calcium granules (99.9 percent) contained in a tantalum crucible, the mixture was stirred for 3 hr at 775 C in an argon atmosphere and then allowed to stand overnight at 750 C before sampling. There then followed periods of equilibration at various temperatures, settling, sampling, and additions of zinc metal in the same manner as described above for measurements of uranium solubility. Sampling temperatures were such as to stay above the liquidus of the calcium-zinc binary phase diagram,⁷ thereby attempting to avoid the presence of noncerium-containing solid phases. After nitric acid dissolution, melt samples were analyzed for (1) zinc by a method involving EDTA titration and complexing with potassium cyanide; and (2) cerium by counting cerium-141 gamma activity. In a number of cases, cerium was determined spectrophotometrically as the ceric tartrate complex in an ammoniacal tartrate buffer. The latter was done to ascertain whether the activated and inactive cerium charges had been homogenized in the original preparative procedure. Good agreement between results obtained by both analytical methods indicated that homogenization had occurred.

The cerium solubility data are given in Table 11 and plotted in Figure 16 as a function of temperature. Examination of the solubility curves shows that, in the concentration and temperature range studied, cerium solubility (1) decreases with decreasing temperature at constant zinc concentration; and (2) decreases, in general, as zinc concentration is increased. Figure 16 includes a portion of the solubility curve of cerium in pure zinc, from which it may be inferred that, if zinc additions had been continued, the cerium solubility would have increased

⁶Hansen, M., and Anderko, K., Constitution of Binary Alloys, 2nd Edition, McGraw-Hill Book Co., New York (1958), p. 465.

⁷Ibid., p. 412

Table 11

SOLUBILITY OF CERIUM IN ZINC-CALCIUM SOLUTIONS

Experiment No.: MA-Ca-6

Procedure: 3.59 g inactive Ce, 0.591 g irradiated Ce, and 0.1 g Ca dissolved at 800 C in 114 g Zn in alumina crucible. After cooling, ingot placed atop 366 g Ca in tantalum crucible and heated at various temperatures. Zn added incrementally.

Atmosphere: Argon

Sampling: Melt pressurized through graphite filters into tantalum tubes, data in chronological order

Temp (C)	Zinc (w/o)	Cerium (w/o)	Temp (C)	Zinc (w/o)	Cerium ^a (w/o)
751	23.4	0.74 _b	750	56.1	0.42 ₁
698	23.6	0.68 _b	700	56.4	0.41 ₆
650	23.7	0.45 ₆	651	55.6	0.39 ₈
598	23.3	0.39 ₁	600	56.3	0.38 ₉
			800	55.2	0.46 ₃
750	33.5	0.65 _b			
698	33.8	0.59 ₂	801	66.1	0.36 ₄
650	34.2	0.58 ₀	699	66.1	0.35 ₁
600	34.8	0.51 ₅	654	66.0	0.33 ₆
547	35.7	0.44 ₃			
498	34.5	0.41 ₂	798	74.6	0.26 ₅
449	34.8	0.36 ₃	750	73.2	0.26 ₀
			700	74.4	0.25 ₇
750	44.4	0.50 ₃			
702	45.6	0.48 ₂			
650	45.8	0.47 ₅			
601	47.1	0.46 ₈			
551	46.8	0.44 ₉			
499	46.3	0.43 ₀			

^aRadiochemical analysis

^bSpectrophotometric analysis

FIGURE 16
SOLUBILITY OF CERIUM IN ZINC - CALCIUM SOLUTIONS

A recently completed experiment to determine the solubility of cerium in calcium alone has indicated that cerium may react with the graphite filters used in the sampling procedure. Thus, as in the case with uranium (see above), the solubility data may be low. Further tests using fritted tantalum filters will be made to check this point. However, it would appear that cerium solubility in calcium-rich zinc solutions is such that decontamination of plutonium fuels from cerium and probably other rare earths is feasible if the two following conditions prevail: (1) the absence of coprecipitation of cerium and other rare earths with plutonium, and (2) the complete precipitation of plutonium.

(c) Coprecipitation Behavior of Cerium with Uranium

Coprecipitation of cerium with uranium was studied in Experiment MA-Ca-3 described above. The initial concentration of cerium, 0.0088 weight percent in zinc-2.4 weight percent uranium, was far below its solubility at the temperatures employed, and its solubility limit was not exceeded even after addition of calcium. Thus, disappearance of cerium from solution is attributable to coprecipitation phenomena.

The relative behavior of cerium and uranium may be shown by the coprecipitation coefficients, λ ,* computed on the assumption that cerium coprecipitation follows the Doerner-Hoskins Law. The

* $\lambda = \log \text{fraction of tracer left in solution} / \log \text{fraction of carrier left in solution}$

λ values calculated for discrete temperature intervals are given in Table 12 together with rearranged data from Table 10. The magnitude of the coprecipitation coefficients shows appreciable cerium coprecipitation from 0 to 12 percent calcium in zinc. In this concentration range, except for the two values in parentheses, the coprecipitation coefficients are similar to that found for coprecipitation of cerium with uranium-zinc intermetallic compound (see ANL-5924, page 136). The large values of λ found at about 4.5 and 6.5 percent calcium are believed to be caused by precipitation* of a calcium-zinc intermetallic compound, the precipitation being inferred from observed temperature halts. At 17 percent calcium (and beyond, as ascertained in another experiment) cerium no longer coprecipitates with uranium. In the present experiment, cerium that had been coprecipitated redissolved completely when the calcium concentration was increased from 12 to 17 percent. This behavior is what would be expected when the equilibrium solid phase changes from a uranium-zinc intermetallic compound to uranium. In fact, decomposition of a uranium-rare earth-zinc intermetallic compound to insoluble uranium and soluble rare earths by addition of excess magnesium has been used as the basis for separating rare earths from uranium in a proposed process for the recovery of uranium from melt refining skulls (see ANL-6333, page 57).

Table 12

COPRECIPITATION OF CERIUM WITH URANIUM FROM ZINC-CALCIUM SOLUTIONS

Experiment: MA-Ca-3 (see Table 10)
 Charge: 1500 g Zn, 36.2 g U, 0.135 g irradiated Ce; Ca added incrementally
 Equipment: Tantalum
 Atmosphere: Argon
 Sampling: Melt pressurized through graphite filters into tantalum tubes

Temp Change (C)	Corresponding Concentration Change In			Doerner-Hoskins Coefficient, λ^a
	Ca (w/o)	U (w/o)	Ce ($10^{-5} \times \text{cpm/g}$)	
749 to 724	0 to 0	2.07 to 1.59	4.66 to 3.88	0.69 ^b
724 to 699	0 to 0	1.59 to 0.96	3.88 to 2.82	0.63 ^b
750 to 723	1.48 to 1.53	1.74 to 1.11	4.08 to 3.05	0.65
750 to 725	2.88 to 2.89	1.16 to 0.68	3.01 to 2.21	0.59
750 to 726	4.50 to 4.42	0.69 to 0.43	1.97 to 0.20	(5) ^c
749 to 724	6.28 to 6.58	0.48 to 0.22	1.27 to 0.12	(3) ^c
750 to 723	9.40 to 9.51	0.73 to 0.36	2.00 to 1.20	0.73
775 to 750	11.6 to 11.9	2.20 to 1.50	5.01 to 3.65	0.83
750 to 725	11.9 to 12.3	1.50 to 0.83	3.65 to 2.41	0.70
775 to 749	17.1 to 17.3	0.28 to 0.30	4.96 to 4.96	0
749 to 725	17.3 to 17.4	0.30 to 0.29	4.96 to 4.96	0

^a $\lambda = \log \text{fraction of tracer left in solution} / \log \text{fraction of carrier left in solution}$.

^b Previously determined to be 0.66 (see ANL-5924, page 136).

^c Precipitation of calcium-zinc intermetallic inferred from temperature halt.

*It was intended to stay above the liquidus of the calcium-zinc binary system - the highest temperature being reported as $\sim 717^\circ\text{C}$, the melting point of CaZn_{13} .⁷ The liquidus temperature data may be in error.

(d) Behavior of Plutonium, Uranium, and Cerium in Calcium-Zinc Solutions

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

The behaviors of plutonium, uranium, and cerium were tested simultaneously in Experiment MA-Ca-4. A mixture of 1700 g zinc, 8.58 g plutonium (0.49 weight percent), 30.0 g uranium (1.73 weight percent), and 0.250 g neutron-irradiated cerium (0.014 weight percent) was dissolved by heating in a tantalum crucible under helium for a total of 23 hr at 750 C. The melt was stirred for about 12 hr with a tantalum paddle. After a 30-min settling time, the melt was sampled through graphite frits press-fitted into tantalum tubes. Calcium metal was next added incrementally, and periods of agitation, settling, and sampling followed each addition, as in the case of the uranium experiments. Samples were dissolved in 10 M nitric acid-1M hydrochloric acid and analyzed for (1) plutonium by alpha counting after separation of americium-241; (2) uranium by fluorophotometry; (3) cerium by first separating from plutonium-240 and americium-241 activities via extraction into and stripping from di-2-ethylhexylphosphoric acid in cyclohexane; and then counting cerium-141 gamma activity in a single-channel analyzer adjusted to discriminate against energies less than 125 kev; and (4) calcium by a method involving EDTA titration and complexing of zinc with potassium cyanide.

The analytical results are given in Table 13 together with material balance estimates based on assumptions regarding the weights of solution present at each temperature. Plutonium solubilities were calculated on the basis that all charge components were completely dissolved before addition of calcium, thereby enabling a computation of plutonium specific activity. Dividing the analyzed plutonium activity (cpm/g of sample) by the specific activity (cpm/g of plutonium) gave the weight fraction of plutonium in each sample.

Table 13

SOLUBILITY OF URANIUM, PLUTONIUM, AND CERIUM IN ZINC-CALCIUM SOLUTIONS

Experiment: MA-Ca-4
 Charge: 1700 g Zn, 30.0 g U, 8.58 g Pu, 0.250 g irradiated Ce; Ca added incrementally
 Equipment: Tantalum
 Atmosphere: Helium
 Sampling: Melt pressurized through graphite filters into tantalum tubes

Temp (C)	Calcium (w/o)	Uranium (w/o)	Plutonium		Cerium	
			(w/o)	Estimated % of Original Charge	(w/o)	Estimated % of Original Charge
748	0	1.73 ^a	0.49 ^a	100	0.0101	70
724	16.8	0.059, 0.17	0.40 ^b	96	0.0127	104
724	19.8	0.0037	0.34	85	0.0109	93
740	25.3	0.0025	0.32	86	0.0098	89
749	29.9	0.0006	0.30	85	0.0093	91

^a Unsaturated

^b May be unsaturated

The results shown in Table 13 indicate that plutonium solubility in zinc solutions containing up to about 30 percent calcium is high compared with uranium solubility. Uranium solubility, in fact, is approximately that which would be obtained in the absence of plutonium (see Figure 11). The cerium data are somewhat erratic and are known to have a low bias. Nevertheless, they tend to show that, as expected, cerium remained in solution as the calcium concentration increased. It is evident, however, that plutonium solubility (about 0.3 weight percent) is too high at the maximum calcium concentration employed (30 weight percent) to permit useful plutonium-cerium separations.

An experiment is now in progress to determine the distribution coefficient of cerium between a plutonium-2 weight percent cerium alloy and calcium at about 855 C. The effect on cerium and plutonium behavior of zinc additions (10 to 35 weight percent) to the calcium phase will also be studied so as to extend the range of calcium-zinc concentrations investigated in the above-described experiment.

Conclusions

1. Uranium metal can be completely precipitated from zinc solution or from uranium-zinc intermetallic compounds by addition of 20 percent or more calcium. The useful temperature range is broad and can be varied by adjusting calcium concentration.

2. Cerium and probably other rare earths can be separated from uranium by virtue of their solubility and the insolubility of uranium in zinc solutions containing greater than 20 percent calcium. The precipitated uranium does not coprecipitate cerium.

3. Plutonium exhibits relatively high solubility at 725 to 750 C in zinc solutions containing up to 30 percent calcium. Thus, practical separations of cerium from plutonium and/or plutonium plus uranium do not appear feasible with zinc-rich calcium solutions. Better separations may be found by using calcium-rich zinc solutions, since plutonium solubility is expected to decrease with increasing calcium concentration. Furthermore, the ability to operate at lower temperatures with calcium-rich zinc solutions may prove advantageous.

Processes whose main objective is to separate uranium from plutonium (for example, recovery of plutonium bred in the EBR-II blanket) could employ the solubility differences found for uranium and plutonium in zinc-rich calcium solutions.

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

Before discharge of the blanket material from the EBR-II reactor, plutonium will be allowed to build up in the depleted uranium blanket material to a concentration of about one percent. The blanket processes under investigation for the separation of plutonium from uranium by pyrometallurgical methods are based on the solubility of plutonium in magnesium-rich zinc alloys and the contrasting low solubilities of uranium in these alloys.

Work was continued during the past quarter on a procedure which consists of dissolution of uranium in a 12 to 15 weight percent magnesium-zinc alloy at 800 C to give a 14 weight percent uranium concentration followed by addition of magnesium to a 50 percent magnesium concentration to precipitate the uranium from solution. The plutonium remains in solution. In order to reduce the uranium solubility in the supernatant phase and thereby to improve the separation of plutonium from uranium, the solution is cooled to about 400 C prior to removal of the plutonium-bearing supernatant phase. Present plans are to isolate the plutonium by distilling away the magnesium and zinc.

Experiments reported in the previous quarterly (ANL-6333, page 72) showed dissolution of uranium blanket rods (0.433-in. diameter) within 8 hr, but solution instability was indicated by uranium concentrations which decreased or fluctuated with time. Work of the past quarter has shown that the apparent loss of uranium resulted merely from its precipitation on the relatively cool upper walls of the dissolution vessel after the liquid had been splashed upon the walls by the agitator. However, uranium in a 12 percent magnesium-zinc solution may be susceptible to precipitation by impurities, since the uranium activity in this solution will be high (nearly 1).

(a) Process Demonstration with a 1 Percent
Plutonium-Uranium Blanket Alloy

Since uranium loss from solution by precipitation on the vessel walls could be avoided by simply reducing agitator speed, it was decided to check process performance with a synthetic 1 percent plutonium-uranium alloy. About 418 g of this alloy were dissolved at 800 C under helium at a pressure of 5 psig in a 14 weight percent magnesium-zinc solution. The melt was contained in a $5\frac{1}{2}$ -in tantalum crucible and was agitated by means of a motor-driven, tantalum, flat-paddle agitator ($\frac{1}{2} \times 2$ in.) operating at about 100 rpm.

Analyses of solution samples showed that nearly all of the uranium and plutonium was in solution in 4 hr (see Table 14). Samples taken after 8hr showed no decrease in uranium and plutonium

concentrations. The uranium-plutonium alloy charged in this experiment had a carbon concentration of 600 ppm, and the zinc contained 160 ppm carbon. The carbon concentration apparently had no detrimental effect on the achievement of theoretical concentrations of the uranium and plutonium in the metal solution.

Table 14
SUMMARY OF BLANKET PROCESS DEMONSTRATION RUN NO. 1

After the dissolution step, additional magnesium was charged to the melt to produce a zinc-50 weight percent magnesium solution. Filtered samples were taken by means of tantalum tubes with tantalum frits at 800, 680, 530, and 440 C. The results shown in Table 14 indicate that the plutonium concentration remained essentially constant with a decrease in temperature. The uranium solubility decreased from 0.262 weight percent at 800 C to 0.025 weight percent at 440 C, thus giving a plutonium-to-uranium ratio of 3.6 to 1 in the liquid metal solution.

The magnesium-zinc-plutonium solution was removed from the precipitated uranium by pressure siphoning with the liquid metal transfer equipment described in ANL-6101, page 56. About 70 percent of the magnesium-zinc-plutonium solution was transferred.

On a larger scale, the percentage of the total liquid phase transferred should be much higher. The heel remaining in the crucible was washed with a zinc-50 weight percent magnesium solution at 600 C for 2 hr. Samples of the wash solution taken at 600 and 400 C showed plutonium concentrations of 0.032 and 0.034 percent, respectively. These are nearly the concentrations which should have resulted from dilution of the heel liquid with the wash solution. A phase separation of the wash solution from the precipitated uranium resulted in 73 percent of the magnesium-zinc wash being transferred.

Although confirmatory runs will be necessary, the results of this run are very encouraging, because they have shown the following:

- 1) The alloy dissolves rapidly, with 100 percent of the uranium and plutonium appearing in solution.
- 2) There was no apparent loss of plutonium from either the dissolving solution or the magnesium-rich solution despite the presence of sufficient carbon (probably in the form of uranium carbide in the uranium charge) to precipitate all of the plutonium.
- 3) There was no apparent loss of plutonium, within analytical error, on precipitation of the uranium and during cooling of the solution to around 400 C, thereby indicating no coprecipitation of the plutonium with the uranium.
- 4) Precipitation of 99.7 percent of the uranium results in a fairly good plutonium-uranium separation. If no further separation of the uranium were made, the final product would be about 70 percent plutonium, which is an appropriate composition to feed into the EBR-II core. However, further precipitation of the uranium would occur during evaporation of the magnesium-zinc-plutonium solution. By arranging a two-stage evaporation, it would be possible to increase the purity of the plutonium product substantially.
- 5) Washing would be effective, if it is needed, since the plutonium remained in solution; the decrease in the concentration of plutonium was essentially proportional to the dilution by the wash liquid. However, it is apparent that considerably better phase separations are required than those obtained. Operation on a larger scale should give better phase separations.

(b) Stability of Solutions of Plutonium in Magnesium

Knowledge of the stability of solutions of plutonium in magnesium is important in the processing of reactor fuels and blanket materials, since a magnesium-rich solution is used to effect a primary separation of uranium and plutonium, uranium being fairly insoluble in this

solution. Plutonium is subsequently recovered from solution by vaporizing the magnesium and zinc. Two previous stability runs (see ANL-6287, page 73) were somewhat inconclusive. In one experiment, the plutonium concentration stabilized after an initial drop in concentration, which appeared to be the result of a reaction with impurities.

Two additional long-term magnesium-plutonium stability experiments in tantalum have been concluded. The experiments were of two-week duration with periodic sampling of the melts which were held at 800 C under a static helium atmosphere. A graphite secondary crucible was used in Run 3; a tantalum secondary crucible was used in Run 4. Samples were taken in tantalum tubes and the melts were stirred by motor-driven tantalum agitators. The charge to the tantalum crucible in each run was a previously prepared magnesium-plutonium alloy containing about 1 percent plutonium.

The results of the experiments given in Table 15 show that the plutonium concentrations decreased to 91 percent of the original value in Run 3 and to 95 percent in Run 4 over periods of 322 and 364 hr, respectively. In a previous similar experiment (see ANL-6287, page 73) about 90 percent of the plutonium originally charged was in solution after 347 hr.

Table 15

STABILITY OF PLUTONIUM-MAGNESIUM SOLUTION
CONTAINED IN A TANTALUM CRUCIBLE AT 800 C

Charge: Run 3: 4.74 g plutonium-581 g magnesium

Run 4: 6.96 g plutonium-485 g magnesium

Type of Secondary Crucible: graphite in Run 3,
tantalum in Run 4.

Time (hr)	Percent Pu Charged in Solution	
	Run 3	Run 4
0	100	100
28	98	-
80	93	-
154	92	-
250	90	-
323	91	-
364	-	95

The slow loss could result from the slow introduction of impurities from the crucible or from the atmosphere. One possible source of atmospheric impurities is the graphite secondary

crucible. The secondary crucible, although degassed, might slowly contribute sufficient impurities to precipitate plutonium as the carbide. About 0.05 g of carbon would be required to account for the plutonium loss experienced.

A large quantity of magnesium was volatilized and refluxed during Run 4, so that erratic plutonium concentration values were obtained between the first and last sample. However, results based on the initial and final plutonium values, which are reliable, indicate that after 364 hr the plutonium in solution was 95 percent of the amount initially charged.

The results indicate that there probably would be little loss of plutonium from solution in plant runs since these will be of short duration. Plutonium in magnesium solutions is evidently susceptible to precipitation by impurities, and stringent precautions should be taken to eliminate introduction of impurities.

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

In a previous report (ANL-6333, pages 74 to 76) a method was described for the synthesis of refractory actinide compounds at relatively low temperatures in which volatile liquid metals are used as reaction media. This technique is believed to be useful for the preparation of nuclear feed materials as well as for the recovery of such fuels in a form suitable for recycling to a reactor after decontamination by pyrometallurgical methods. A possible scheme for the reprocessing of a uranium carbide fuel, which includes the pyrometallurgical decontamination procedure being developed (see ANL-6287, pages 48 and 49) for the recovery of crucible residues from melt refining of EBR-II fuel, is shown in Figure 17. Several of the steps shown in Figure 17 have not been thoroughly demonstrated. To date, the following compounds have been synthesized: uranium monocarbide, plutonium sesquicarbide, cerium sesquicarbide, uranium trisilicide, and U_3Si_2 .

Preparations of refractory metal carbides in liquid metals have been reviewed elsewhere.⁸ In these preparations, the carbides were isolated by dissolving away the solvent metal, as opposed to the evaporation of the metal solvent as carried out at this Laboratory. This latter procedure is generally applicable to systems satisfying the following requirements:

⁸ Schwarzkopf, P., and Kiefer, R., Refractory Hard Metals, Macmillan Company, New York (1953), pp. 60-63.

- a) The solvent metal must not form insoluble compounds with either of the reactants at the temperature at which the reaction is performed and in the concentration ranges used.
- b) At least one of the reactants must be fairly soluble in the solvent metal.
- c) The solvent metal must be sufficiently volatile to permit its complete removal by retorting under reduced pressure.
- d) The compound formed must be stable in the solvent metal at the temperature of the reaction.

FIGURE 17
PYROMETALLURGICAL REPROCESSING CONCEPT FOR URANIUM CARBIDE FUEL

In general, the compounds formed were found to be highly crystalline, as evidenced by the sharp lines of their X-ray diffraction patterns.

Uranium Monocarbide

Experimental conditions and results of uranium carbide syntheses are summarized in Table 16. From these experiments it is evident that uranium monocarbide can be synthesized with the use of a 9 to 10 weight percent magnesium-zinc solvent, a carbon excess of about 50 percent, and a temperature of 850 C. In this system, the uranium monocarbide that is formed settles rapidly, while any unreacted carbon rises to the surface. The segregation of these ingredients in the solidified ingot is sufficiently sharp to permit the removal of unreacted carbon by cropping the ingot prior to retorting. The progress of the reaction was indicated by the uranium content of filtered samples which were periodically withdrawn.

Table 16

SYNTHESIS OF URANIUM CARBIDE IN LIQUID METAL SOLUTIONS

Charge:
 Uranium: as metal
 Carbon: as -320 mesh Merck, vacuum-dried activated carbon
 Liquid Metal: as indicated
 Agitation: baffles and flat paddle stirrer at 300 rpm

Solvent Composition (w/o)			Uranium		Carbon		Temp (C)	Time (hr)	Yield ^a (% Theoretical)	Comments
Cd	Zn	Mg	(g)	(w/o)	(g)	(% Excess)				
99.94	-	0.06	15.6	1.9	2.0	150	550 700	8 0.5	64 80	Macroscopic examination showed segregation of UC and C in solidified ingot.
99.94	-	0.06	14.7	1.8	1.8	140	700 700	0.5 1.0	97 100	UC identified by X-ray diffraction. Carbon content by chemical analysis: 7.4%. This represents UC with 0.59 atom carbon excess.
99.94	-	0.06	16.9	2.0	0.85	0	700	4	73	UC identified by X-ray diffraction.
	95	5	18.8	2.9	1.5	57	800	4	87	
99.94	-	0.06	14.8	1.8	0.84	11	700	3	82	UC identified by X-ray diffraction and by microscopic examination of surface of arc-melted button. Carbon content by chemical analysis: 5.02% (carbon-to-uranium ratio: 1.05). Particle size (90%): 5 to 15 microns. Specific surface: 1.9 sq m/g.
	90.4	9.6	104.5	17.3	8.04	52	850	3	91	
							850	5.2	100	

^a Some of the yield figures would undoubtedly have reached higher values after a longer period of time (See Figure 18).

Typical reaction rate curves are shown in Figure 18. The results given in Table 16 indicate that temperature and amount of excess carbon charged had a marked effect on the rate of reaction. Uranium monocarbide was the only carbide formed, as evidenced by X-ray diffraction analyses. The product from a preliminary experiment in which a large carbon excess was used did not contain any uranium dicarbide, although the total carbon content of 7.4 percent was considerably higher than that calculated for the monocarbide (4.8 percent). This represents the formation of UC with a 0.59 atom carbon excess. The particle size of the product from a later experiment (the last run in Table 16) was from 3 to 30 microns, with about 90 percent in the 5- to 15-micron range (see Figure 19). The carbon-to-uranium atom ratio was 1.05. The specific surface, determined with a Perkin-Elmer "Shell" Sorptometer, was 1.95 sq m/g. This material was found to be quite pyrophoric and was handled in a helium glovebox. A larger batch of uranium monocarbide (380 g) has been successfully prepared. This material will be used in preparing sintered shapes by powder-metallurgical techniques.

The possibility of removing excess carbon by contacting a cadmium melt containing uranium carbide and unreacted carbon with a molten salt (calcium chloride, magnesium chloride, and magnesium fluoride in the respective mole percentages of 47.5, 47.5 and 5) was examined in one experiment. The experiment was carried out in air at 650 C. Both the uranium carbide and the unreacted carbon transferred rapidly to the flux phase, where rapid oxidation occurred with evolution of a gas (CO or CO₂). The solidified cadmium ingot did not contain any uranium or carbon.

FIGURE 19
URANIUM MONOCARBIDE PARTICLES (250X)
(See preparation conditions in Table 16.)

Plutonium Carbide

(A. Schneider, I. O. Winsch, G. Rogers, T. Cannon)

Considerable interest has recently been shown in plutonium carbide and plutonium-uranium carbides as potential fuels for high-temperature reactions. The existence of four carbide phases has been reported⁹: PuC , Pu_2C_3 , PuC_2 , and a phase, designated ζ (zeta), containing slightly less carbon than PuC .

The preparation of plutonium carbide was attempted by means of the general procedure previously described for uranium and cerium carbides. The equipment used in this experiment is sketched in Figure 20. In the first part of the experiment, 6.8 g of plutonium dissolved in 80 g of magnesium was precipitated by reaction with finely divided activated carbon (1.0 g) at 810 C. The rate of reaction, which was followed by determining the plutonium content of filtered magnesium samples, is shown in Figure 21. The reaction was complete in $3\frac{1}{2}$ hr, as evidenced by the insignificant plutonium content in samples withdrawn after that time. The excess carbon floated to the top of the melt and was easily removed by inverting the alumina crucible containing the solidified magnesium-plutonium carbide ingot. This ingot was then recharged to the furnace tube shown in Figure 20 and retorted under reduced pressure.

FIGURE 20
LIQUID METAL REACTION FURNACE AND RETORTING STILL

⁹ Mulford, R. N. R., et al., The Plutonium-Carbon System, Paper No. 32, International Conference on the Metallurgy of Plutonium, Grenoble, France (1960).

FIGURE 21
RATE OF REACTION OF PLUTONIUM WITH
CARBON IN LIQUID MAGNESIUM

The retorting residue consisted of a finely divided, black powder, identified by X-ray diffraction as Pu_2C_3 . The carbon content of this material was 7.73 percent (calculated carbon content of Pu_2C_3 is 7.01 percent). The formation of Pu_2C_3 rather than of the lower carbide, which was expected by analogy with the uranium and cerium carbides previously prepared, is somewhat surprising, since PuC has been claimed to be a stable compound up to 1654 C.¹⁰

Cerium Carbide

The preparation of Ce_2C_3 by precipitation from a magnesium solution was reported in ANL-6333, page 75. An attempt to synthesize the same compound in a cadmium solution was unsuccessful. The cerium content (1.6 percent) remained constant, after being contacted for 6 hr at 690 C with a 9 percent excess of carbon.

Uranium Silicides

Six compounds have been identified in the uranium-silicon system.¹¹ Of interest as potential nuclear fuel materials are U_3Si and

¹⁰ Mulford, R. N. R., op. cit.

¹¹ Rough, A. F., and Bauer, A. A., Constitution of Uranium and Thorium Alloys, BMI-1300 (June 2, 1958).

U_3Si_2 . Because of its high melting point (1665 C), the latter compound is attractive for high-temperature reactors, whereas U_3Si , which decomposes by a peritectoid reaction at 930 C, can be of limited use only.

In an exploratory experiment, 5.52 g of finely divided silicon metal were added to 691 g of a 1.48 percent uranium solution in cadmium. The melt, contained in an alumina crucible, was stirred for 5 hr at 700 C. The reaction proceeded very rapidly, since the first filtered metal sample withdrawn after 45 min did not contain any measurable amount of uranium.

The melt was liquated and the large excess of unreacted silicon was mechanically removed from the solidified ingot. The uranium-rich lower part of the ingot was retorted. X-ray diffraction analysis of the retorted residue showed it to be a single-phase, crystalline compound having a cubic lattice with $a_0 = 4.037 \text{ \AA}$. This structure is identical with that reported for USi_3 .¹² Chemical analysis indicated the composition to be $USi_{3.24}$. Since both uranium and silicon are soluble in cadmium, the formation of the compound richest in silicon is not surprising, in view of the large excess of silicon present. The synthesis of U_3Si_2 was then attempted by reacting stoichiometric quantities of the two elements in a zinc-8 percent magnesium solution. The product obtained after retorting of the magnesium and zinc was identified by X-ray diffraction as U_3Si_2 , in accordance with the crystallographic data of Zachariasen.¹³ Chemical analysis of the product resulted in the composition $U_3Si_{2.08}$.

h. Materials and Equipment Evaluation (P. A. Nelson)

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. Selection of materials for EBR-II processing equipment is the main objective, but data of more general interest are also being accumulated. Corrosion tests with metal coupons and runs in agitated crucibles under processing conditions are being used to evaluate materials.

(1) Solution Stability and Materials Demonstration Tests (P. Nelson, G. Bennett, J. Pavlik, L. Dorsey, W. Pehl)

Experiments were continued to determine the stability of uranium dissolved in zinc-magnesium solutions in contact with molten flux contained in a graphite crucible. Results of tests indicate that ATJ graphite reacts too rapidly with uranium dissolved in magnesium-zinc solutions to be usable. The ATJ graphite appears to react at a higher rate than are reported for CS graphite (ANL-6333, page 79).

¹²Kaufmann, A. R., et al., J. Metals, 9, 23-7 (1957).

¹³Zachariasen, W. H., Acta, Cryst., 2, 94-99 (1949).

The conditions of the tests and the results obtained with ATJ graphite are shown in Figures 22 and 23.

FIGURE 22
REACTION OF URANIUM IN ZINC-5 PERCENT MAGNESIUM
SOLUTION AT 850 C WITH GRADE ATJ GRAPHITE CRUCIBLE

CHARGE: Zn-5% Mg-3.5% U, 3970 g
47 1/4 m/o CaCl₂-47 1/2 m/o MgCl₂-
5 m/o MgF₂, 300g
CRUCIBLE: ATJ GRAPHITE, 4 3/4 in I.D. x 8 in. HIGH,
HEMISPHERICAL BOTTOM
AGITATOR: TANTALUM AGITATOR, 1 1/4-in. LONG x 1 in WIDE
BLADE, 550 rpm, FOUR 1/2-in. BAFFLES
TEMPERATURE: 850 C

FIGURE 23
EFFECT OF TEMPERATURE ON REACTION OF URANIUM IN
ZINC-5 PERCENT MAGNESIUM WITH GRADE ATJ GRAPHITE

CHARGE: Zn-5% Mg-O 5% U, 3990g; 47 1/2 m/o CaCl₂-
47 1/2 m/o MgCl₂-5 m/o MgF₂, 300g
CRUCIBLE: ATJ GRAPHITE, 4 3/4-in. ID X 8-in. HIGH,
HEMISPHERICAL BOTTOM
AGITATOR: TANTALUM AGITATOR, 1 1/4-in. LONG X 1-in. WIDE
BLADE, 550 rpm, FOUR 1/2-in. WIDE BAFFLES
TEMPERATURE: AS NOTED ON GRAPH

In Run A-2 (see Figure 22) conducted at 850 C with an initial uranium concentration of 3.5 percent, about 26 percent of the uranium in solution reacted in 78 hr. The rate of reaction decreased more rapidly than it would have if the rate were proportional to the concentration of uranium in solution. It is evident that a protective coating of uranium carbide is formed. The percent of the uranium charged remaining in solution was calculated from the uranium concentration and the mass of metal in the crucible assuming a constant rate of evaporation. Twenty-five percent of the metal evaporated in 135 hr, which finally caused failure of the outer stainless steel container due to zinc corrosion, thereby making it impossible to get samples at the end of the run.

In Run C-1 (upper portion of Figure 24) the temperature was controlled at 700 C for the first 24 hr, at 800 C for the next 24 hr, and at 850 C for the next 90 hr. In this run the initial uranium concentration was 0.5 percent. It is evident from the upper portion of Figure 24 that the rate of reaction of the dissolved uranium with the ATJ graphite crucible wall increased with temperature. No reaction was noted at 700C; the higher than theoretical concentration may have been caused by a slight bias in sampling or analysis. However, thermodynamic calculations¹⁴ indicate that a reaction would take place even at this low temperature. A rather high rate of reaction was noted at 800 C. The fact that the reaction rate did not increase further when the temperature was increased to 850 C may have been caused by plugging of the crucible pores by uranium carbide formation.

The percent of the uranium charged which remained in solution was calculated from the magnesium and uranium concentrations of filtered samples. The amount of metal which had evaporated up to the time of each sample was determined from the magnesium concentration and a calculated¹⁵ relative volatility of 25 atoms of zinc evaporated per atom of magnesium evaporated referred to the pure elements (see plotted values on lower part of Figure 24). The final samples indicated 19.2 percent evaporated as compared with a value of 21 percent calculated from the initial and final metal weights.

The extensive amount of vaporization of the metal charge experienced in these runs was believed to be due to diffusion through the permeable crucible wall and breathing through the top caused by slight temperature fluctuations. Later tests conducted in impermeable tantalum crucibles with the cover cooled to 650 C resulted in much less vaporization. The analytical results for these runs are not yet available.

¹⁴Johnson, I., Argonne National Laboratory, private communication.

¹⁵Feder, H. M., Argonne National Laboratory, private communication.

Tentative conclusions drawn from the runs are the following:

- 1) ATJ graphite reacts too rapidly at 800 and 850 C with uranium dissolved in zinc-magnesium solutions to be usable as a crucible material for containing these solutions. Although CS-graphite reacts less rapidly (see ANL-6333, page 79), this conclusion will be assumed to be true for all grades of graphite with the possible exception of pyrolytic graphite. Therefore, most of the future work in the materials testing program will deal with metals, especially tungsten and tantalum-10 percent tungsten.
- 2) Evaporation of the metal charge is a problem that must be dealt with in equipment designed for processes using zinc at 800 C. An impermeable crucible with a device to condense the vapor beneath the cover appears to be a necessary design feature.

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

The program was continued to determine the corrosion resistance of the refractory metals, graphite, and ceramics to molten metals, particularly zinc and zinc-magnesium solutions, and various halide flux-metal systems.

As reported in ANL-6333, page 76, several methods of determining attack by liquid metals are under investigation. To date the most useful method has been metallographic examination of corrosion specimens before and after exposure to the corroding media. Most of the results which follow are based on this means of determining the extent of corrosion. Other methods of determining corrosion, which are presently under study, include changes in weight, thickness, microhardness, ductility, yield strength, tensile strength, and elongation.

The metals used in these tests were commercial materials: zinc of 99.99+ percent purity, cadmium of 99.9+ percent purity, and magnesium of 99.95+ percent purity. The fluxes used were prepared from commercial anhydrous salts. Some of the fluxes were dried, after mixing the constituents, by melting and heating for one hour at 800 C in an alumina crucible under argon flow.

The corrosion capsules were prepared in the manner described in ANL-6287, page 74. Both static and dynamic tests were made. The latter were conducted in rocking furnaces which are also described in ANL-6287.

Corrosion of Refractory Metals in the Zinc-Magnesium-Molten Halide Systems

A set of tests conducted in a rocking furnace at 850 C for 100 hr has been completed to determine the corrosion resistance of tantalum, tantalum-10 percent tungsten, tungsten, and molybdenum coupons to the zinc-5 percent magnesium and salt flux system. Three fluxes were used: (1) 95 mole percent magnesium chloride-5 mole percent magnesium fluoride, (2) 47.5, 47.5, and 5 mole percent of magnesium chloride, lithium chloride, and magnesium fluoride, respectively, and (3) 47.5, 47.5, and 5 mole percent of magnesium chloride, calcium chloride, and magnesium fluoride, respectively. Results obtained are presented in Table 17. Weight changes of the coupons were measured, with the maximum change being a weight loss of only 0.007 g/sq cm. Microhardness and transverse bend tests were also performed as an alternative means of measuring corrosion, but the data have not yet been interpreted.

Table 17

CORROSION OF REFRACTORY METALS BY ZINC-MAGNESIUM-HALIDE FLUX SYSTEMS

Conditions 100 hr 850 C 1-in x 2-in x 0.030-in coupons contained in tantalum capsules with 40 to 60 g of solvent metal and/or 25 g of flux of indicated compositions Capsules were rotated 180 degrees at 2 cycles/min

Zn-5% Mg Present	Flux		Ta (annealed)			Ta-10% W (unannealed)			W (unannealed)			Mo (unannealed)		
			Thickness Change ^c (mils)	Corrosion Attack		Thickness Change ^c (mils)	Corrosion Attack		Thickness Change ^c (mils)	Corrosion Attack		Thickness Change ^c (mils)	Corrosion Attack	
	Type ^a	Dried ^b		Type ^d	Depth ^c (mils)		Type ^d	Depth ^c (mils)		Type ^d	Depth ^c (mils)		Type ^d	Depth ^c (mils)
No	1	No	+2	I	4 ^e	-	-	-	-	-	-	-	-	-
No	2	No	+3	I	2	-	-	-	-	-	-	-	-	-
No	3	No	+4	I	8	-	-	-	-	-	-	-	-	-
No	1	Yes	+1	I	1	-	-	-	-	-	-	-	-	-
No	2	Yes	+2	P	1	-	-	-	-	-	-	-	-	-
No	3	Yes	-3	I	2	-	-	-	-	-	-	-	-	-
Yes	1	Yes	0	SI	10	0	NE	0 ^e	0	NE	0 ^e	- ^f	PSP	>15 ^g
Yes	2	Yes	0	I	15	0	NE	0	0	NE	0	+2	PSP	4
Yes	3	Yes	+3	SI	5 ^e	0	NE	0	0	NE	0 ^e	+2	PSP	>15 ^g
Yes	None	-	-	I	<1	-	-	-	-	-	-	-	-	-

^aFlux composition 1) 95 m/o MgCl₂ 5 m/o MgF₂
2) 47.5 m/o MgCl₂, 47.5 m/o LiCl 5 m/o MgF₂
3) 47.5 m/o MgCl₂ 47.5 m/o CaCl₂ 5 m/o MgF₂

^bFlux dried by liquation at 800 C for 1 hr under argon flow

^cThe change in thickness and depth of corrosion attack measurements were accurate to within 1 mil

^dI - Intergranular attack, SI - Severe intergranular attack PSP - Penetration between sintered particles, NE - no evidence of attack P - Pitting

^eTantalum capsule failed during run Data obtained should be treated only as preliminary information

^fCoupon broke test could not be performed

^gAttack throughout the entire 30-mil thick coupon

Several of the tantalum capsules, which had 20-mil thick walls, failed during the run despite the fact that the tantalum coupons which some of them contained experienced an attack of only 5 mils or less. These failures may have been caused by an imperfect weld or by stress corrosion near the weld. Tantalum-10 percent tungsten capsules will be used in some future runs in an attempt to alleviate this problem.

Several observations can be made based on the results presented in Table 17.

- 1) Drying of the halide flux prior to use significantly reduces the depth of corrosion attack for tantalum.
- 2) The tantalum-10 percent tungsten alloy is not appreciably attacked by the salt flux-liquid metal system.
- 3) Tungsten is not appreciably attacked by the salt flux-liquid metal system.
- 4) Molybdenum produced by powder metallurgy is severely attacked by the salt flux-liquid metal system as indicated by the depth of corrosion attack determined metallographically.
- 5) The combined salt flux-liquid metal system is more corrosive to tantalum than either system alone (see Table 17 and see also ANL-6243, page 14, and ANL-6287, page 76).
- 6) The 47.5 mole percent lithium chloride-47.5 mole percent magnesium chloride-5 mole percent magnesium fluoride flux (designated Type 2 in Table 17) appears less corrosive to tantalum and molybdenum than the other types tested (Types 1 and 3) when all are dried by liquation at 800 C for 1 hr under argon flow. This conclusion is based on a comparison of the number of tantalum capsule failures, the type of corrosion, and the depth of corrosive attack.

Corrosion of Refractory Metals in the Zinc-Cadmium-Magnesium System

A run has been completed to test the corrosion resistance of tantalum, tungsten, and molybdenum in the zinc-cadmium-magnesium system. The run was conducted in the rocking furnace (see ANL-6287, page 75) for 500 hr at 850 C. Results are presented in Table 18.

It can be seen that tantalum is corrosion resistant to the zinc-cadmium-magnesium system except at very high zinc concentrations. The only case of severe attack noted was at a zinc concentration of 98 weight percent. Under similar conditions sintered molybdenum was severely attacked while tungsten appeared unaffected.

Table 18

CORROSION OF REFRACTORY METALS BY THE
ZINC-CADMIUM-MAGNESIUM SYSTEM

Conditions: 500 hr, 850 C, 1-in. x 2-in. x 0.030-in. coupons contained in tantalum capsules with 30 to 60 g of solvent metal of indicated composition. Capsules were rotated 180 degrees at 2 cycles/min.

Coupon	Zn (w/o)	Depth of Attack ^a (mils)				
		Mg (w/o)	0	1	5	15
Ta	0		-	0.5	-	0.5
Ta	2		-	0.5	-	0.5
Ta	10		-	0.5	-	1
Ta	40		-	-	-	1
Ta	50		-	1	-	-
Ta	75		-	-	-	1
Ta	98		-	8	-	-
Mo	95		-	-	15 ^b	-
W	95		-	-	0	-
W	100		0	-	-	-

^a The attack was intergranular. It was measured to an accuracy of 0.5 mil for observations of one mil or less and to an accuracy of 1 to 2 mils for observations greater than 1 mil.

^b Cracks followed the grain boundaries through the entire 30-mil coupon.

Corrosion of 405 Stainless Steel in the Cadmium-Magnesium-Zinc System

A run conducted at 750 C for 1000 hr under static conditions has been completed to test the corrosion resistance of Type 405 stainless steel in the cadmium-magnesium-zinc system. The results obtained are presented in Table 19 and Figure 24.

Initial variation of the zinc content was made on a weight percent basis, but the data correlate better when considered from an atom percent basis. The results show that corrosion of 405 stainless steel in the cadmium-magnesium-zinc system is accelerated by increasing the atom concentration of zinc in the corroding metal and, to a lesser extent, by increasing the atom concentration of cadmium.

Table 19

CORROSION OF 405 STAINLESS STEEL IN THE CADMIUM-MAGNESIUM-ZINC SYSTEM

Conditions: 1000 hr, 750 C, 1-in. x 2-in. x 0.250-in. coupons contained in tantalum capsules with 20 to 40 g of solvent metal of indicated composition. Static test conditions.

Composition (w/o)		Concentration (a/o)		Maximum Depth ^a of Attack (mils)
Mg	Zn	Mg	Zn	
1	0	4	0	0
1	5	4	8	2
1	10	4	16	3
1	15	4	22	9
1	20	4	29	12 (35 ^b , 12 ^c)
1	30	4	41	14
15	0	45	0	1
15	5	44	5	0
15	10	43	11	0.5
15	20	41	20	6
15	30	39	30	8
15	40	37	38	8
50	0	82	0	0
50	10	80	6	0
50	20	78	12	0
50	30	77	17	2
50	40	75	22	2
50	50	73	27	2

^aThe attack was primarily intergranular. The accuracy of measurement was 0.5 mil for observations of 2 mils or less and 1 to 2 mils for observations of greater than 2 mils.

^bType 304 stainless steel instead of 405 stainless steel.

^cType 1020 mild steel instead of 405 stainless steel.

(3) Fabrication of Equipment Components (P. A. Nelson, G. A. Bennett, M. Kyle)

Discussions have been held recently with refractory metal producers and fabricators in regard to fabrication of crucibles and other equipment for EBR-II fuel recovery processes. Each material has unique fabrication problems.

Tantalum-10 Percent Tungsten. In general, any fabrication technique which can be used with tantalum is applicable to the tantalum-10 percent tungsten alloy, although with greater difficulty. However, due to its greater corrosion resistance, more consideration will be given to the tantalum-tungsten alloy than to pure tantalum in future testing.

Tantalum-10 percent tungsten is not as easy to draw or spin as tantalum. Forming a crucible of process size (14- to 18-in. diameter by 18 to 24 in. tall) would require an expensive development program. However, a crucible of this size with a dished bottom could be fabricated according to standard methods by spinning the bottom and welding on a cylindrical section. A crucible with this design is expected to be less subject to failure on freezing and remelting of the crucible contents than one with a flat bottom. Tubing could be fabricated at about twice the cost of tantalum tubing. Experimental size crucibles with a dished bottom will be tested soon.

Molybdenum. In process sizes, molybdenum crucibles would be fabricated by processes similar to those used for making tungsten crucibles. Welding would not be practical because of lack of strength, and deep drawing or spinning would require expensive experimentation. Pressing and sintering to 95 percent density might be the most practical method. Experiments with molybdenum crucibles have not been planned because molybdenum does not appear to be as corrosion resistant as tungsten. However, corrosion testing is still continuing with arc-cast molybdenum and various molybdenum alloys.

Tungsten. Four methods have been found for fabricating crucibles from pure tungsten: welding from sheet, pressing and sintering, flame spraying on a removable mandrel and sintering, and spinning. Welded crucibles of process size have not been fabricated and there is some doubt concerning the integrity of the welds. Both cold pressing and sintering and flame spraying and sintering produce products of about 92 percent density, which may be dense enough for pyrometallurgical processing. The equipment presently available for cold pressing tungsten would limit the size of the crucible to 15-in. OD by 13-in. ID by 25 in. tall (30.5-liter capacity with 10-in. free board). It is the cheapest method for making a heavy-walled crucible.

Very large flame-sprayed and sintered crucibles with $\frac{1}{4}$ -in. walls could be fabricated with ease. Heavy-walled crucibles would be more expensive if made by this method than pressed and sintered crucibles.

Inquiries concerning the spinning of crucibles from tungsten indicate that this method may be feasible. The advantages of strength and high density which this method promises warrant a thorough study of the feasibility of this method of fabrication.

Straight tubes of tungsten in sizes of 30 in. long by $\frac{1}{2}$ - to 1-in. ID by $\frac{1}{2}$ -in. wall could be made by pressing and sintering. Elbows and unions mechanically sealed to the straight sections could be machined from sintered bar stock.

Evaluation of Vapor-deposited Tungsten Coatings (J. Wolkoff)

A thermal-cycling test of vapor-deposited tungsten on Type 446 stainless steel was previously described (ANL-6333, page 83), and separation of the tungsten layer was shown photomicrographically. A drop of molten zinc was later held on these samples for 6 hr at 750 C and metallographically examined. The photomicrograph is shown in Figure 25. Although wetting of the tungsten by the zinc did not occur, intergranular attack of the stainless steel in the immediate vicinity of a microcrack is evident. This also occurred in a test at 680 C. Since no attack on stainless steel by zinc vapor has been previously noted, a possible mechanism of attack is the absorption of zinc vapor by the copper flashing deposited on the steel prior to the deposition of the tungsten. Subsequent reaction of the alloy with the steel may then occur. Additional evidence of this attack mechanism is shown in Figure 25. Both the tungsten and the stainless steel show some attack and lamination.

Tests are planned with base materials having better linear expansion matches with tungsten and having better resistance to zinc.

i. Large-scale Cadmium Distillation Unit (P. Nelson, J. DeKany, J. Arntzen, J. Hepperly)

The pilot-plant-scale (100 kg/hr distillation rate, 750 kg feed capacity) distillation unit was placed into operation during the last quarter.. Operation of the equipment will provide design data pertinent to fuel reprocessing equipment.

FIGURE 25

THERMAL-CYCLED VAPOR-DEPOSITED TUNGSTEN ON TYPE 446
STAINLESS STEEL AFTER EXPOSURE TO ZINC AT 750 C
(250X, as polished)

Description of Equipment

As shown in Figure 26, the unit consists basically of four large vessels, a condenser, and the necessary transfer and service lines, all of which are fabricated of type 405 stainless steel. The major equipment components are mounted inside a furnace which maintains the vessels and transfer lines at about 500 C. The top, front, and end walls of the furnace are removable in two sections for access to the equipment.

The distillation vessel consists of an outer shell of type 405 stainless steel into which is fitted a crucible assembly and an induction coil as shown in Figure 27. The crucible assembly contains a hydraulic cylinder, the piston of which supports a distillation crucible with a tapered edge. When the crucible is hydraulically raised, it mates with a tapered ring installed inside of the top of the outer shell. Thus the crucible and the top of the outer shell form an inner vessel in which the distillation takes place. This mechanical seal between the crucible and the top of the shell prevents the escape of liquid metal vapor into the outer portion of the distillation vessel.

FIGURE 26

LARGE-SCALE CADMIUM DISTILLATION UNIT FOR THE STUDY OF ENGINEERING OPERATIONS

(The top, front, and end walls of the furnace enclosing the equipment have been removed. The finned-tube condenser which is forced-air cooled is located behind the rear panel.)

As a further safeguard, a pressure gradient is maintained across the seal. The distillation crucible is heated by an induction coil that fits inside the outer shell of the distillation unit. Power is transmitted to the induction coil by means of a coaxial bus assembly which enters through a nozzle in the outer shell

A finned tube condenser is mounted in the vapor-transfer line which connects the top of the distillation vessel to the cadmium receiver. The condenser is cooled by circulated air which is maintained at a temperature slightly above the freezing point of the vapor by controlled dilution with cold air.

The remaining vessels serve as holding tanks for feed, cadmium condensate, and discharge residue. These vessels are interconnected by transfer lines so that the following liquid metal transfers may be made:

- a) from feed tank to distillation crucible;
- b) from feed tank to discharge receiver;

- c) from distillation crucible to discharge receiver;
- d) from cadmium receiver to feed tank; and
- e) from cadmium receiver to discharge receiver.

FIGURE 2/
CROSS SECTION OF STILL OF LARGE SCALE CADMIUM DISTILLATION UNIT

All the transfer lines, with the exception of the line from the feed tank to the distillation vessel, are equipped with freeze valves. The feed-transfer line to the distillation vessel is equipped with a reservoir or surge tank and a ball-type check valve. By pressurizing the surge tank independently of the feed tank, the check valve is closed and the liquid metal in the surge tank is transferred into the distillation crucible. In this manner, batch-wise transfer of feed to the distillation crucible can be performed by manipulating the pressures, either manually or automatically, through the use of the feed-control instrument.

The feed tank has two access ports, one is a 4-in. diameter charging port and the other is an 8-in.-diameter nozzle through which a 2-hp mixer is introduced.

The discharge receiver is different from the feed tank and cadmium receiver in that the liquid metal transferred to this vessel is contained in a crucible which can be removed through a flanged opening in the bottom of the outer vessel which extends through the bottom of the furnace. This vessel thus provides a means of removing material from the unit.

Sampling ports have been provided on the feed tank and cadmium receiver so that samples may be taken.

Description of Runs

The feed tank was partially filled with 250 kg of cadmium. The liquid level bubble gauges were calibrated by adding the charge in 10-kg batches to obtain a plot of weight of cadmium charged versus differential pressure.

The first run was made, in order to test the capabilities of the equipment and its instrumentation, by evaporating under the conditions listed in Table 20.

Table 20

OPERATING CONDITIONS FOR INITIAL RUN IN CADMIUM DISTILLATION UNIT

	<u>Operating Conditions</u>
Distillation Temperature	600 C
Condenser Pressure	80 mm Hg
Feed Temperature	400 C
Cadmium Receiver Temperature	400 C
Feed Tank Pressure	80 mm Hg
Induction Power to Stillpot	12.5 kw
Calculated Power to Liquid Metal ^a	9.7 kw
Induction Coil Efficiency	77.6%
Induction Coil Temperature	500 C
Average Evaporation Rate	32 kg/hr
Weight of Cadmium Evaporated	80 kg
Condenser Air Temperature	375-400 C
Vapor Trap Temperatures	250 C
Freeze Valve Temperatures	200-300 C

^aNeglecting heat loss from stillpot.

The following observations and conclusions concerning the run may be noted:

1) The condenser pressure (80 mm Hg) corresponded well with the vapor pressure (82 mm Hg) at the distillation temperature, thereby indicating that the pressure drop across the condenser was negligible and that the instrumentation was accurate enough to provide excellent control of distillation temperatures. No plugging or slugging in the condenser occurred.

2) The observed distillation rate, induction heating, power level, induction coil temperature, and induction coil efficiency indicated that the design distillation rate of 100 kg/hr can be attained with more moderate changes in the coil-susceptor system than had been anticipated.

3) Condenser air temperatures showed that the condenser design was conservative and will probably be able to handle distillation rates greater than the designed rate of 100 kg/hr.

4) The use of differential pressure bubblers for liquid metal level measurement appears to be an accurate and reliable method for level measurement for this application. The electrical resistance probes in the distillation crucible did not function satisfactorily. It is believed that their erratic behavior can be attributed to lack of uniform wetting by the liquid cadmium.

5) The tapered distillation crucible failed to mate properly with the outer distillation vessel. Consequently, some of the refluxing metal spilled into the outer distillation vessel. This should not recur, since a method of detection of improper mating is available. However, the pan beneath the distillation crucible caught the spillage and prevented damage to the components.

6) During the run, the four freeze valves were filled with liquid metal and frozen. Despite the fact that cadmium does not wet 405 stainless steel well, the valves were found to be leak-tight.

7) All the instruments for automatic control of the equipment were operated and found to function well.

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 Fuel Cycle Facility was over 90 percent completed as of June 1, 1961, as compared with about 80 percent completed three months earlier. The contractor is working on the installation of equipment and other building items. During the past quarter, considerable effort has been concentrated on installation of laboratory-furnished equipment, such as cranes and manipulators.

Installation of the viewing windows for the Argon Cell was begun in April. Some difficulties which were initially encountered are now being rectified by the window manufacturer (see Section 1.e). Installation of the Argon and Air Cell cranes and manipulator bridges was completed in March.

Work was started or continued on the installation of such equipment as the Argon Cell emergency pressure-relief system, sodium-cleanup system, argon-purification equipment, and Air Cell transfer port.

Testing of the heating and ventilating equipment, controls, and piping has begun. Major electrical work such as installation of MI (mineral insulated) cable, wiring of shutter motors, installation of conduit, and wiring of the radiation-monitoring system continues through the building. Work such as caulking of window frames, casting of solid concrete blocks and splash pads, and painting of roof hatch plugs is continuing.

b. Fuel Cycle Facility Equipment

(G. J. Bernstein, A. A. Chilenskas, L. F. Coleman,
J. Graae, D. C. Hampson, R. H. Jahnke, M. A. Slaweki)

Eight bellows-sealed, air-operated valves and six metal-diaphragm isolation valves have been checked for leaks with helium and packed for shipment to Idaho. They will be used in the off-gas system of the melt refining furnace. Progress in the construction of the melt refining furnaces is satisfactory, and it is expected that the furnaces will be completed during the next quarter. Fabrication of the control panels for the melt refining furnace has been delayed because of problems encountered by Machinery Electrification, the vendor. The revised shipping date is about the end of June 1961.

A purchase order has been placed with Ex-Cell-O Corporation of Detroit, Michigan, for fabrication of service sleeve feed-throughs. Ex-Cell-O was chosen on the basis of low bid. The feed-throughs are used to provide services to the Argon Cell and have been described previously in ANL-6231, pages 35 to 37, and ANL-6287, page 132.

A purchase order has been placed for 100 scrap-handling pails, 6 ft long by $11\frac{1}{4}$ in. in ID. In addition, a small order for scrap-handling pails (3-gal capacity) which will fit inside the large scrap-handling pail has been placed. A magnetic lifting tool (manipulator operated) having a load capacity of 275 lb has been designed and a purchase request written. This tool is to be tested in the mockup facility, with both the large and small scrap containers, under various conditions to determine its suitability for use within the Fuel Cycle Facility.

Drawings for the scrap-handling coffin being designed and built by Knapp-Mills were received and approved. Materials of construction are now being procured by the manufacturer. Drawings for the inter-building coffin being designed by O. G. Kelley of Boston, Massachusetts, are expected before the end of this quarter.

The parts for the degassing furnace have been received and it has been assembled in the mockup area. A leak test of the assembly gave an acceptable leak rate of 4.5 microns/hr in the pressure range from 0.6 to 300 microns. The equipment will soon be made ready for shipment to Idaho.

Window shutters, drives, and brackets have been ordered. Brackets for the drive motors have been ordered for all windows, but shutters and drives have only been ordered for half the windows, namely, the ones that are expected to be in the heaviest fields of radiation. The shutters will be used primarily to minimize radiation darkening of the cell windows.

Each shutter installation consists of a 6-in.-thick steel slab with an attached drive rack, a drive motor with an attached drive gear, a permanently installed track from which the slab hangs, and a permanently installed motor bracket. The shutter is opened or closed by moving it horizontally across the window face. The motor with the attached gear may be remotely removed and replaced in the cell by an operating manipulator using a special tool, and the steel slab with the rack may be removed with an overhead crane.

Since installation is by remote means, an initial mesh between the drive gear and the rack may be difficult. Therefore, it is imperative that they engage when the drive motor is started and then remain engaged until either mechanism requires replacement. One drive motor with mounting frame, one bracket, and one drive gear and rack have been tested in the mockup. The tests show that the drive will engage when started, even if the gear and rack do not mesh initially on placing the drive unit in the wall bracket. Once engaged, the gear will not jump out of engagement when driving the rack against a dead stop. An out-of-mesh drive will engage when the motor is started and remain engaged even for the special case when the rack is initially against a dead stop in the direction that the drive is started.

A special hook at the end of a 2-ft horizontal bar was built and used for installing and removing the drive unit. The horizontal bar was gripped by the manipulator dual hook, and the drive unit was hung on the hook of the 2-ft bar. Installing and removing the drive unit was not difficult, but care was required to assure proper engagement of hooks and guides.

c. Cranes and Manipulators
(J. Graae)

The eight manipulator carriages are completed and have been inspected. Minor adjustments are being made. A new design of a collapsible stand for the manipulator carriages has been completed and the stand has been ordered.

All parts for the manipulator bridge power inlet have been fabricated and inspected, and assembling and wiring has started.

Brackets and receptacles for the Model 300 articulated manipulator arm have been fabricated and inspected. Corrections are being made and the first assemblies will be inspected shortly. These will be mounted on each of the operating manipulator carriages to provide power and control for the Model 300 articulated arm when this is used with an operating manipulator.

The toggle switch control boxes for remote control of cranes, manipulators and blister have passed inspection and have been crated for shipment to Idaho.

A manipulator tool storage rack and changer with capacity for a dual hook, a parallel jaw hand and a shear has been designed and ordered. One shear which replaces the hook or hand on the operating manipulator has been designed and ordered.

d. Materials Testing

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

The asbestos-insulated wire samples whose insulating stability is being tested as a function of radiation exposure (see ANL-6287, pages 88 to 89) have received an accumulated dose of 1.99×10^{10} rad to date. One of these samples was placed in a sealed vial containing a desiccant after the sample had received a dose of 1.35×10^9 rad. Since the atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility will be dry, the atmospheric conditions within the vial more nearly approximate those which will be encountered in the Argon Cell. The insulation resistance of the sample in the sealed vial was greater than 200 megohms after the sample had received an accumulated dose of 1.99×10^{10} rad. The insulation resistance of samples which were not in sealed vials decreased to about 0.1 megohm from an initial resistance of greater than 200 megohms.

The samples of aluminum paint have received doses varying between 1.24 and 1.96×10^{10} rad to date. All samples were removed and compared visually with their respective control samples. It was decided to discontinue irradiation tests on these samples because of the increased difficulty of comparing them from one irradiation period to another. In preceding summary reports (ANL-6231, page 31, ANL-6287, page 89, and ANL-6333, page 94) it had been pointed out that the samples were discolored but still covering. It is now thought that this statement should be qualified. Up to about 1.0×10^{10} rad, the paint samples were for the most part in good condition. After this dose, however, changes were more difficult to observe and assess. The samples were discolored and the discoloration in most

cases was due to rust. Since the coating on portions of each surface had worn thin because of repeated handling, it was extremely difficult to differentiate between actual radiation damage and physical damage caused by the handling. The most promising type of the aluminum paints tested will be used on several components to be installed in the operating cells.

Previous reports have described the results of bearing tests in which Timken roller bearings (432 cup - 438 cone) lubricated with irradiated radiation-resistant greases were used. This type of bearing will be used on the manipulator bridge trucks in the Argon and Air Cells. No provision has been made for replacement of these bridges under normal operating conditions. Accordingly, the tests were conducted to indicate the useful lifetime of the bearings as limited by radiation hardening of the grease. The first set of tests involved new bearings lubricated with greases which had been separately irradiated in bulk. Two of these greases showed potential operating lifetimes beyond four years.

In these tests it was assumed that irradiating the grease in bulk approached conditions of the Argon Cell where the grease film would be protected against oxidation. It was anticipated that irradiation of the grease film in the Air Cell would result in more rapid deterioration.

Accordingly, a second set of bearing tests were made under conditions which approximated the most severe operating conditions anticipated in the Air Cell. Three roller bearings were lubricated with thin coatings of three kinds of radiation-resistant greases. These bearings were then alternately irradiated in an air atmosphere and run in a test stand. Irradiations to total doses of 1×10^9 rad, 2×10^9 rad, 3×10^9 rad, and 4×10^9 rad were made. Intervening running tests were for 8-hr periods at 40 rpm and 800-lb axial load. The running test which followed the 4×10^9 -rad irradiation was continuous to failure. No grease was added during the test nor was any attempt made to prevent loss of grease from the bearings. Under these severe conditions the bearing lubricated with the best-performing grease (NRRG-159*) accumulated a running time of 78 hr. This time compares with a running time of 300 hr with the same grease which had been irradiated in bulk. The tests therefore confirm the assumption that a thin film of grease will deteriorate more rapidly because of oxidation than will a bulk quantity.

The assumption has been held in these tests that 75 hr of running time in the test stand is equivalent to one year of operation in either cell of the Fuel Cycle Facility and that 1×10^9 rad is equivalent to one year's integrated dose at maximum anticipated radiation background. Accordingly, the last tests show an inconsistency in that radiation exposure was accumulated much more rapidly than running time. Thus, the 78 hr of running time show a projected life of one year, whereas the 4×10^9 -rad exposure is equivalent to four years. A reasonable assumption would be that bearings lubricated in the manner described above would operate beyond one year.

*Product of Standard Oil of California

In the bearings as installed on the manipulator bridges, a quantity of grease will be held in the bearings with retainer rings. Under these conditions the effect of surface oxidation should be largely mitigated, and a longer useful operating lifetime could be expected.

Similar bearing tests with the NRRG-159 grease are planned; the lubricated bearings will be run for 38 hr, after each irradiation of 5×10^8 rad. These tests should allow a more accurate estimate of the operating lifetime in the Air Cell.

A series of tests is being instituted to determine the performance of sintered bronze bearings impregnated with radiation-resistant oil. A test stand has been built for running thrust bearings under load. Bearings are currently undergoing irradiation.

e. Shielding Windows
(T. W. Eckels)

Installation work on the shielding windows started early in April. Because of various dimensional discrepancies determined as the installation proceeded, it was necessary to reduce progressively the scope of the installation contract with Diversified Builders, Inc. Aside from cleaning preparations on the steel liners which are cast into the concrete walls, all that now remains of the original installation contract is the placement of six C Slabs and the successful leak testing of four of the six. All the remaining window components have been removed from the site to a building in Idaho Falls, where the prime contractor for shielding windows, Pittsburgh Plate Glass Company, and their principal subcontractor, R. V. Harty Company are correcting the discrepancies. Full responsibility for repairs, installation, and leak testing is being assumed by Pittsburgh Plate Glass Company.

In connection with the installation by Diversified Builders, Inc., there were also certain dimensional deviations of the steel window liners themselves. These remain to be arbitrated.

Window installation will now take place after occupancy of the Fuel Cycle Facility by Argonne, probably in August.

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

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

A prototype power inlet has been mounted on the operating manipulator bridge extension and electrically connected. It worked well, except that the cable grip on the plug loosened when the cable was manually

pulled and shaken back and forth. A basket-weave grip has been installed, which greatly increases the holding power of the cable grip. Consequently, basket-weave grips have been added to the manipulator bridge power inlets now being manufactured.

The grip drive clutch has not operated in a satisfactory manner. There does not seem to be any reliable relationship between clutch excitation current and torque. The grip will operate, but the grip force varies erratically for any particular clutch voltage. Several modifications of the clutch have been tried, but without success. Different designs of clutches are being purchased to see if any of them will give better control than the one now installed. If they show promise, one or more might be adapted to the grip drive. The present clutch does perform satisfactorily as an on-off clutch.

b. Melt Refining Furnaces

(D. C. Hampson, W. E. Miller, R. Fryer)

(1) Equipment Performance

(a) Crucibles

The performance records of the crucibles used to prepare fuel alloy for EBR-II and of the crucibles used to remelt pin scrap were reviewed recently. The beneficial effects of measures taken (see ANL-6183, page 30) to reduce the incidence of crucible cracking were evident. The incidence of cracking and the severity of the cracks has been reduced, so that the problem of crucible cracking is no longer considered to be serious. However, since minor cracks still occur in some crucibles, some further work is being done.

Seven crucibles were degassed in the new degassing furnace which has been set up recently for testing prior to its shipment to the Fuel Cycle Facility in Idaho. None of the crucibles cracked when they were degassed at 1000 C and a pressure of 10 microns. Evidently the crucibles are subject to less thermal stress in this furnace than they are during degassing in the melt refining furnace. The problem of crucible cracking during degassing has thus been eliminated, since the crucibles will now be degassed in the new furnace.

Three approaches have been taken in attempts to improve crucible performance further. In the first approach, the crucibles themselves have been varied. Crucibles of different compositions and different dimensions have been tested. In the second approach, attempts have been made to find and eliminate "weak" crucibles prior to use. In the third approach, better operating procedures have been sought.

In previously reported work (see ANL-6231, page 34, and ANL-6183, page 30) crucibles of nonstandard composition and nonstandard dimensions were tested. During this quarter, tests were run with crucibles made by Norton from mix RZ-5601. No improvement was apparent, and Norton experienced difficulties in the production of crucibles of standard size from this mix.

The original Norton crucibles had a bottom thickness of $\frac{3}{4}$ in. and an overall height of $9\frac{1}{4}$ in. After Norton applied the improved method of manufacture discussed in ANL-6183, page 30, the thickness of the crucible bottom was increased to 1 in. to achieve an overall height of $9\frac{1}{2}$ in. It was felt that this increase in bottom thickness (from $\frac{3}{4}$ to 1 in.) was a contributing cause of the cracks that developed in the base of the crucibles. Therefore, two new crucibles were obtained which were manufactured by the new methods but which were of the old dimensions. Standard melt refining runs were made in these crucibles. No cracks developed in either crucible. More of the crucibles are being obtained for further testing.

The second approach to improving crucible performance is to eliminate "weak" crucibles before use. Visual inspection eliminates crucibles with initial cracks and extremely large grains. All crucibles received from the manufacturer are given this inspection.

Recently, the possibility of establishing nondestructive crucible tests has been explored. X-ray pictures were taken of a number of crucibles. A study of these pictures revealed many flaws in the crucibles, such as pinholes, local changes in density, and discontinuities in grain structure. However, in no case could an accurate prediction be made as to where a crack would develop in the crucible when it was used.

The crucibles are made from lime-stabilized zirconia. The stabilizing agent is added to alter the crystal structure and thereby render the zirconia more resistant to thermal shock. Inadequate stabilization of crucible material contributes to the failure of the crucible. One of the physical properties in which stabilized and unstabilized zirconia differ is in linear thermal expansion. For crucibles $9\frac{1}{2}$ in. in length and heated from room temperature to 200 C, the difference in expansion between a stabilized and an unstabilized condition is about 0.008 in.¹⁶ Overall lengthwise expansion measurements were made of seven crucibles and associated measuring apparatus. For the measurements the crucible was heated from room temperature to a 200 C wall temperature. Since the measuring apparatus was the same in each case, the differences in the overall measurements are equal to the differences in the expansion of the

¹⁶ Norton Trade Publication, Norton Refractory Grain, Norton Company, Refractories Division, Worcester 6, Mass. (1957), p. 16.

crucibles. After expansion measurements were taken, the crucibles were used to make standard melt refining runs. The measurements and crucible performance are recorded in Table 21. Differences in lengthwise thermal expansion between crucibles were noted, but no consistency could be found between the thermal expansion measurement and cracking severity when the crucibles were used.

Table 21
CORRELATION OF CRUCIBLE EXPANSION AND SUBSEQUENT CRACKING

Crucible Number	Expansion (in. ^a)	Melt Refining Run in Which Crucible Was Used	Remarks
254	0.027	Cr-Ex-4076 Cerium present	Crucible suffered coarse continuous No. 1 ^b crack and a No. 3 ^b crack. Coarse diametrical crack on bottom. Overall cracking very bad.
267	0.0235	Cr-Ex-4078 Cerium present	Crucible suffered a very coarse Y crack on bottom and one finger went up the side to form a No. 3 crack. Also a No. 1 crack, medium to fine, was observed. Overall cracking very bad.
222	0.0245	Cr-Ex-4077 Cerium present	Crucible suffered a No. 1 crack around 3/4 of its circumference. Also a 4-in.-long crack present on bottom with finger which traveled up the side to join the No. 1 crack. Overall cracking not as bad as No. 267 or No. 254.
250	0.023	Cr-Ex-4075 No cerium added	Crucible sustained coarse discontinuous No. 1 crack, and crack on outside bottom 1-1/2 in. long. Overall cracking not as bad as first three crucibles.
277	0.0255	FCP-47 No cerium added	Crucible suffered a diametrical crack on bottom during degassing which opened up a little more during the run. No other cracks observed. Overall cracking not serious.
280	0.030	Cr-Ex-4074 No cerium added	Crucible suffered slight Y crack on outside bottom. Not serious.
271	0.0245	FCP-45 No cerium added	No cracking observable. Crucible in excellent shape after run.

^aThe expansion values given are not absolute values of expansion for the crucibles, but are overall expansion of apparatus and the crucible height. The expansion of the apparatus is the same for each test. Differences between measurements are, therefore, equal to differences in crucible expansion. Expansion was measured at 200 C.

^bA No. 1 crack is a circumferential crack where the side wall joins the bottom. It may be continuous or partial in a particular case.

A No. 2 crack is one which starts at the top rim of the crucible and extends down the side wall from one to four inches. The occurrence of these cracks has been largely eliminated.

A No. 3 crack is a vertical crack starting at the bottom and extending upward from two to three inches.

The third approach to improving crucible performance has recently achieved greater success. The slight cracks encountered in crucibles used recently were largely radial cracks across the crucible bottom and/or circumferential cracks at a point where the barrel of the crucible joins the bottom. Such cracks could develop in a crucible which was heated rapidly in the barrel and slowly in the bottom, since this would subject the crucible to a shearing stress where the barrel joins the bottom. For this reason, temperature gradients were measured in crucibles as they were heated in the melt refining furnace.

Figure 28 shows the temperature gradient, which existed during part of a normal run cycle, between a point 2 in. from the bottom on the outside of the crucible wall and a point in the center of the outside bottom of the crucible.

FIGURE 28
CRUCIBLE TEMPERATURE GRADIENT OBTAINED
WITH METHOD A OF APPLYING POWER

In the induction-heated melt refining furnace, power for heating the furnace assembly and charge is applied outside the crucible to the graphite susceptor by the coupling action of the induction coil. Heat to raise the charge temperature flows by conduction through the side walls of the crucible. Heat to raise the temperature of the crucible bottom flows by conduction from the crucible and susceptor side walls and by radiation from the inner walls of the crucible. The method of applying power has been to increase the power level in three large increments as the temperature of the furnace rises. This has resulted in a temperature gradient greater than 260 $^{\circ}\text{C}$. The temperature gradient could not be measured because of thermocouple failure (the hottest thermocouple failed, evidently because of carburization by the graphite susceptor).

By increasing the power to the furnace in very small increments, the temperature gradients in the furnace have been reduced. The results are shown in Figure 29. To check any effect that the reduced temperature gradient might have on the incidence of crucible cracking, ten uranium-cerium-five percent fission alloy melts were made in initially sound crucibles which were free from visual defects. In five of the runs, the old method of applying power was used and, in the other five, the new method of applying power was used. The furnace equipment was the same in all runs and the melt size was approximately 10 kg in all cases. In each run, a $2\frac{1}{2}$ -hr heatup time was employed to reach the equilibration temperature, 1400 $^{\circ}\text{C}$, and each melt was held at this temperature for 2 hr prior to pouring. A reduction in the number and severity of cracks was noted when the five crucibles which were heated by Method B were compared with the five heated by Method A. The new method of applying power has been adopted as standard operating procedure.

FIGURE 29
CRUCIBLE TEMPERATURE GRADIENT OBTAINED
WITH METHOD B OF APPLYING POWER

(b) Reference Thermocouples

In the melt refining furnaces of the Fuel Cycle Facility it will not be practical to measure melt temperatures directly. For this reason, a bottom reference thermocouple was developed as part of the melt refining furnace (see ANL-6287, page 94). This thermocouple reflects the temperature of the bottom of the graphite susceptor. It has proved to be very reliable mechanically and gives melt temperatures indirectly by means of calibration curves. For runs utilizing unirradiated uranium all the heat is generated in the furnace susceptor and passes into the melt through the crucible wall (an insulator). In runs using irradiated fuel, as much as two-thirds of the heat required to reach the equilibration temperature (1400°C) will be generated in the melt itself by contained fission products, and tests have shown that the susceptor temperature will be lower than in the inactive runs. Consequently, calibration curves for the bottom reference thermocouple made during inactive runs will not be applicable to runs with irradiated fuels. Therefore, a method is required to determine calibration curves for the bottom reference thermocouple as a function of fission product heating by the charge.

A top reference thermocouple has been tested. Such a thermocouple reflects the melt temperature directly, rather than the susceptor temperature, as does the bottom reference thermocouple. In practice, the top reference thermocouple would be sent into the Argon Cell attached to the Fiberfrax fume trap and would be discarded with the trap after the run. This procedure will be complicated and time consuming and, therefore, it is planned to carry out the procedure on only enough runs to collect sufficient data to calibrate the bottom reference thermocouple. The bottom reference thermocouple will be used for routine furnace operations. The relative positions of the thermocouples are shown on Figure 30.

FIGURE 30
POSITION OF THERMOCOUPLES FOR CALIBRATION OF
TOP REFERENCE THERMOCOUPLE IN MELT REFINING FURNACE

Since a different thermocouple unit and a different fume trap will be utilized for each run, there was some question as to the reproducibility of temperature measurements. Three thermocouples of the same design were made in the shop, and three different Fiberfrax fume traps were picked from the fume trap supply. Combinations of these were used in five runs. The ratio of the melt temperature to the top reference temperature was calculated from data obtained from each of these runs at the 1400 C melt temperature. The variation of the ratio (melt temperature to reference temperature) between the five runs was less than one percent. This variation of one percent would allow the calculation of the actual melt temperature, based on the top reference temperature, to within ± 14 C at a 1400 C melt temperature. It is felt that this variation is sufficiently small to be acceptable for operation of the melt refining process.

In addition, temperature data were obtained at a 1000 C melt temperature. The ratios of the melt temperature to top reference temperature at 1000 C and at 1400 C differed by less than one percent.

3. Skull-reclamation Process (J. H. Schraidt)

a. Design Considerations (G. J. Bernstein, A. A. Chilenskas, T. W. Eckels, W. E. Miller, H. Stethers)

The Design Group is cooperating with the Semi-Works Group in the development of designs for plant-scale equipment for the skull-reclamation process. The present design basis for equipment is 5 kg of skull material, which is approximately the quantity of skull produced from the melt refining of five batches of fuel pins. The effects of radiation self-heating upon insulation design is being studied. In addition, equipment is being built for testing methods for transferring molten salts and metals between furnaces. Layouts of furnaces are being made to determine limitations on equipment size as dictated by dimensions within the Argon Cell.

The feed material for the skull-reclamation process consists of the skull from the melt refining process in which considerable fission product concentration has occurred. The skull material is removed from the crucible by oxidation which converts the skull into a powder. This oxide powder is then subjected to a number of process steps which lead to the recovery of the fissionable material. Five kg of skull oxide will generate about 5 kw of heat for skulls produced from 2 percent burnup, 15-day-cooled fuel. It is of interest to determine whether or not solidification of salt flux containing 5 kg of skull oxide can be achieved in a practical system. (Solidification is desirable in order to permit clean phase separation upon completion of the noble metal leaching operation.) Calculations were made on the basis of a 5-kg skull oxide; the problem was examined for a tungsten crucible insulated with a range of Fiberfrax* thicknesses.

In addition, calculations were made to examine the effect of varying the insulation thickness upon the system power requirements, heat-up time, and cooling time. The objective was to indicate a range of operating conditions which would strike a practical balance between the variables.

The results of these calculations showed that for short-cooled, high-burnup fuel in a practical system the center of the salt phase containing the dispersed skull oxide will remain molten while the salt surface is frozen. Storage of the skull oxide for 30 days prior to processing will so reduce fission product heat output that complete solidification of the salt flux would be achieved even in a well-insulated crucible. In order to heat a 5-kg skull oxide-salt-zinc batch (leach step) contained in a well-insulated crucible from room temperature to a process temperature of 800 C in about

*An alumina silicate type of insulation manufactured by the Carborundum Company.

2 hr, a power input to the crucible of 20 kw is required. To reduce the temperature of the same system from 800 C to 550 C (to permit a phase separation) will require about $2\frac{1}{2}$ hr in the case of skull oxide given no cooling time, and about $1\frac{1}{4}$ hr for skull oxide cooled for 30 days prior to processing.

C. Pyrometallurgical Research (H. M. Feder)

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

Investigations of the chemistry of liquid metal systems are being conducted to provide basic concepts and data for the rational design of methods for the reprocessing of reactor fuels. In addition, the results of these studies provide the basis for the formulation and testing of theories of liquid metal solutions.

a. Solubilities in Liquid Metals

The solubilities of the metals 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 coefficients of solubility of a metallic phase in a liquid metal solvent are strongly dependent on the interatomic forces operative in the solution and consequently may be used to gain greater insight into the way these forces vary with the basic properties of the solute and solvent atoms. For such fundamental studies, it is necessary to know the constitution of the solid phase in equilibrium with the saturated liquid phase.

Iron-Cadmium

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

Preliminary values for the solubility of iron in liquid cadmium were reported in ANL-6101, page 64. Those results are now superseded by the new data reported in Table 22. These new values were obtained by taking filtered samples of melts prepared from 99.95 percent cadmium rod and 99.90 percent iron wire. Iron analyses were done by counting iron-59 produced in the wire by neutron activation. The data obtained at temperatures below 420 C were not included in the calculation of the solubility equation because of the poor precision obtained at these extremely low concentrations. An empirical equation representing the solubility of iron in liquid cadmium over the range from 421 to 647 C is

$$\text{iron: } \log (\text{atom percent}) = 5.973 - 10960 T^{-1} + 3.023 \times 10^6 T^{-2} \quad .$$

The standard deviation for this fit is 8.3 percent. Figure 31 is a plot of iron solubility versus the reciprocal of absolute temperature.

Table 22

SOLUBILITY OF IRON IN LIQUID CADMIUM

Temp (C)	Iron (atom %)
647	0.0044 ₇
630	0.0034 ₈
609	0.0027 ₀
575	0.0017 ₇
555	0.0013 ₁
524	0.00090 ₀
501	0.00076 ₃
475	0.00052 ₅
450	0.00045 ₇
421	0.00026 ₀
375	0.00007 ₄
373	0.00008 ₈
351	0.00007 ₁
323	0.00006 ₀

FIGURE 31
SOLUBILITY OF IRON IN LIQUID CADMIUM

No evidence was found to indicate the existence of any iron-cadmium intermetallic compounds over the temperature range studied.

Titanium-Cadmium

(M. G. Chasanov, R. Schablaske,* B. Tani,* M. Homa,* and P. D. Hunt)

Two intermediate phases have been found in the titanium-cadmium system: a gamma phase and a delta phase. The gamma phase is richer in titanium than the delta phase. The gamma phase has been produced both by the peritectic decomposition of the delta phase (see ANL-6333, page 108) and by direct synthesis from titanium and cadmium. Chemical analyses indicate that the gamma phase has the formula Ti_2Cd while the delta phase corresponds to TiCd . The structures of these two phases have been elucidated by means of X-ray powder and single-crystal studies. An intermediate with the stoichiometry Ti_2Cd was reported previously;¹⁷ however, no information other than the composition was given.

The gamma-phase Ti_2Cd (46.0 weight percent titanium) is body-centered tetragonal, with $a_0 = 2.865 \text{ \AA}$, $c_0 = 13.42 \text{ \AA}$, and $c/a = 4.684$. It has six atoms per unit cell, and both calculated and observed densities are 6.28 g/cc. Systematic reflection absences indicate that the space group is $D_{4h}^{17}-I4/mmm$. The structure is C11 type.

The delta-phase TiCd (29.9 weight percent titanium) is primitive tetragonal, with $a_0 = 2.904 \text{ \AA}$, $c_0 = 8.954 \text{ \AA}$, and $c/a = 3.083$. With four atoms in the unit cell, the calculated density is 7.05 g/cc; the observed value was 7.07 g/cc. The absence of all $hk0$ reflections for which $h + k = 2n + 1$ is characteristic of space groups C_{4h}^3-P4/n and D_{4h}^7-P4/mmm . The structure is similar to that reported by Karlsson¹⁸ for TiCu , B11 type.

Vanadium-Zinc

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

Corrosion data¹⁹ indicate that the solubility of vanadium in molten zinc may be considerable; in a preliminary solubility determination it was found that the vanadium concentration varied from 0.14 weight percent at 448 C to 0.71 weight percent at 656 C. Metallographic examination of the ingot from this solubility determination showed the presence of at least one intermetallic compound. Chemical analysis of crystals leached from this ingot yielded a vanadium content of 20.7 percent. The pycnometric density of this material was 7.22 g/cc. Powder compacts prepared from zinc and

*Members of the X-ray Diffraction and Spectroscopy Group.

¹⁷ California Institute of Technology, Letter Report No. 10, on Contract No. DA-04-495-ORD18, to Watertown Arsenal, December, 1952.

¹⁸ Karlsson, J. *Inst. Metals*, 79, 391 (1951).

¹⁹ Hodge, W., Evans, R. M., and Hoskins, A. F., *J. Metals* 7, 824 (1955).

vanadium and annealed for two weeks at 435 C gave a homogeneous phase for the atomic ratio of one vanadium to three zinc. The X-ray patterns of this compact and the material leached from the solubility ingot were the same.²⁰ These patterns are similar to those previously reported (see ANL-6145, page 75) for NbZn_3 . The calculated vanadium content of VZn_3 is 20.6 percent; therefore, the stoichiometric formula VZn_3 has been assigned to the intermetallic compound which was found. Additional work is continuing on the solubility of vanadium in liquid zinc and on the characterization of VZn_3 .

Figure 32 shows the cross section of an ingot from a holding experiment in which vanadium was immersed in molten zinc at 580 C for five days. The photomicrograph has three main regions: the vanadium metal, VZn_3 , and the zinc matrix containing a eutectic. There is a light-colored band between the VZn_3 and vanadium regions which may correspond to another intermetallic compound. Compacts are being prepared to determine if other intermetallic compounds are present in the system.

FIGURE 32

PHOTOMICROGRAPH (75X) OF VANADIUM-ZINC INGOT
(Vanadium Held in Molten Zinc at 580 C for 5 Days)

²⁰Schablaske, R., and Tani, B. S., private communication.

The Zinc-Uranium System (A. E. Martin and C. Wach)

A zinc-uranium charge containing 35 percent uranium was melted and heated to 970 C under a pressure of 3 atmos of helium in a tantalum crucible. The composition of the ingot which was formed on cooling was 39.5 percent uranium, as determined by weight loss. The structure of the ingot was such as would be expected on the basis of the published zinc-uranium phase diagram,²¹ namely, delta zinc-uranium particles plus a eutectic structure made up of uranium particles and the delta zinc-uranium phase.

Portions of this ingot were annealed for periods from one to three weeks at 300, 400, 450, and 500 C. X-ray diffraction examination of the products of all these tests disclosed that no change had occurred in the identity of the phases present. Thus the delta intermetallic phase appears to be the stable intermetallic phase in the presence of uranium at the temperatures of these anneals. This information is also consistent with the published phase diagram, but verification was needed because there had been some indication from effusion tests made in the temperature range from 420 to 504 C that at these temperatures no intermetallic phase existed between the epsilon phase and uranium itself.

Differentiation between the epsilon and delta intermetallic phases in zinc-uranium alloys has been assisted in the past by the use of chromic acid, which has been employed at different concentrations as a chemical and as an electrolytic etching agent. Recently, a potassium hydroxide-potassium ferricyanide etching agent, which had been reported²² as useful for alloys of zinc-iron-nickel, was applied to some zinc-uranium alloys. It was found to be particularly useful in distinguishing between contiguous layers of the two intermetallic phases such as form between uranium and molten zinc. An example of this is shown in Figure 33.

b. Liquid-Liquid Distribution

Studies of the distribution of representative fission product elements between immiscible pairs of liquid metals are being made to accumulate sufficient data to evaluate liquid metal solvent extraction for process use. Since distribution coefficients are equal to the ratio of the activity coefficients of the solute in the two immiscible liquid metals, the results may be used to obtain activity coefficients in binary solvents.

²¹ Chiotti, P., Klepfer, H. H., and Gill, K. J., Trans. AIME 209, 51-57 (1957).

²² Raynor, G. V., and Noden, J. D., J. Inst. Metals 86, 269-271 (1958).

FIGURE 33

REACTION LAYER FORMED BETWEEN A URANIUM ROD
AND MOLTEN ZINC AFTER 20 HOURS AT 618 C

(Etched with a 8.6 percent KOH-8.6 percent $K_3Fe(CN)_6$ aqueous solution. 300X. The layers visible are, left to right: zinc, epsilon zinc-uranium intermetallic phase, delta zinc-uranium intermetallic phase, and uranium.)

Effect of Bismuth and Magnesium on the Distribution
of Uranium between Liquid Zinc and Lead
(F. Cafasso and J. Vincenzi)

To achieve effective separations of two solutes by difference in their distribution between two immiscible liquids, the ratio of the distribution coefficient of the two solutes must be large. In neither the zinc-bismuth nor the zinc-lead system has the ratio of the distribution coefficient of uranium to the distribution coefficients of various fission products been found to be as large as would be desirable for effective

separation with a small number of stages. It is possible that the addition of a third component to the solvent system may affect the distribution coefficient of one solute more than another. To explore this possibility, the influence of additions of either bismuth or magnesium on the distribution coefficient of uranium between zinc and lead is being investigated.

Lead, zinc, and uranium were placed in an alumina crucible and heated to the desired temperature. Upon reaching this temperature the melt was stirred for one hour and allowed to settle for 2 hr before a sample of each layer was taken. After the distribution coefficient in the additive-free system was established, either bismuth or magnesium was added incrementally. The stirring, settling, and sampling operations were repeated after each addition and between sampling. Fused silica pipets, coated internally with magnesium oxide and fitted with graphite filters, were used to sample.

The bismuth additions to the lead-zinc-uranium melt were made at 659 ± 3 C. The added bismuth, which concentrated preferentially in the lead layer, caused the distribution coefficient to vary progressively toward unity. The coefficient $\left[\frac{\text{w/o uranium in the zinc-rich layer}}{\text{w/o uranium in the lead-bismuth layer}} \right]$ changed from 216 to 36.6 to 5.6 to 2.0 as the $\frac{\text{Bi}}{\text{Bi} + \text{Pb}}$ weight ratio was increased from 0 to 0.10 to 0.26 to 0.36, respectively. These data are shown on a triangular plot in Figure 34 and reported in Table 23. Nine percent bismuth in the lead layer had a pronounced effect, causing about a sixfold change in the coefficient, while only increasing the mutual solubility of zinc in lead by 14.5 percent (from 8.3 percent to 9.7 percent). Thirty percent bismuth in the lead layer caused about a 100-fold change in distribution, but produced about a 50 percent increase in the solubility of zinc. The bismuth-free distribution coefficient of 216 agrees well with the values reported earlier (ANL-6231, page 75).

An experiment was also performed in which lead was added incrementally to a two-phase bismuth-zinc melt containing uranium at 550 ± 4 C. With changes in the $\frac{\text{Pb}}{\text{Pb} + \text{Bi}}$ weight ratio from 0 to 0.10 to 0.33 to 0.44, the value of the distribution coefficient, defined as above, changed from 0.14 to 0.16 to 0.42 to 1.1, respectively. These results are also shown in Figure 34 and reported in Table 24. The coefficient measured before lead was added agrees with earlier measurements (see ANL-6287, page 109) within experimental error. The addition of about 10 percent lead to the bismuth layer appeared to have a negligible effect on the distribution.

Table 23

EFFECT OF BISMUTH ON THE DISTRIBUTION OF URANIUM BETWEEN
ZINC AND LEADTemperature: 659 ± 3 C

Initial Charge: 990 g Zn; 475 g Pb

Zinc-rich Layer			Lead-rich Layer			Average Distribution Coefficient (w/o U in Zn / w/o U in Pb-Bi)
w/o U	w/o Pb	w/o Bi	w/o U	w/o Zn	w/o Bi	
0.27	7.2	0	1.4×10^{-3}	8.4	0	216
0.27	9.2	0	1.1×10^{-3}	8.2	0	
0.29	4.0	5.0	8.2×10^{-3}	9.5	9.2	36.6
0.27	8.6	1.0	7.1×10^{-3}	9.7	8.7	
0.25	7.5	3.6	5.5×10^{-2}	13.3	22.4	5.6
0.28	7.7	3.4	4.6×10^{-2}	13.1	23.2	
0.25	6.9	3.0	4.4×10^{-2}	12.9	22.6	
0.22	5.7	5.8	1.0×10^{-1}	17.2	31.0	2.0
0.24	5.2	5.3	1.2×10^{-1}	17.4	28.0	
0.22	7.8	5.5	1.2×10^{-1}	17.5	30.0	

Table 24

EFFECT OF LEAD ON THE DISTRIBUTION OF URANIUM BETWEEN
ZINC AND BISMUTH

Temperature: 550 ± 4 C
 Initial charge: 499 g Bi; 996 g Zn

Zinc-rich Layer			Bismuth-rich Layer			K_{avg}
w/o U	w/o Bi	w/o Pb	w/o U	w/o Zn	w/o Pb	
8.5×10^{-3}	11.3	0	6.0×10^{-2}	33.9	0	0.14
7.9×10^{-3}	11.6	0	5.7×10^{-2}	34.8	0	
9×10^{-3}	8.3	0.6	5.5×10^{-2}	27.4	7.8	0.16
9×10^{-3}	7.0	0.5	5.5×10^{-2}	27.2	8.2	
1.3×10^{-2}	5.6	1.4	3.1×10^{-2}	16.4	28.2	0.42
1.1×10^{-2}	4.8	1.3	2.9×10^{-2}	15.4	28.2	
1.3×10^{-2}	5.0	1.3	2.8×10^{-2}	15.6	27.2	
1.6×10^{-2}	3.6	1.8	1.5×10^{-2}	11.3	39.0	1.1
1.6×10^{-2}	3.7	1.7	1.5×10^{-2}	11.5	37.0	

In order to examine the influence of magnesium additions on the lead-zinc-uranium system, two changes were made. Firstly, tantalum tubes equipped with graphite filters instead of fused silica tubes were used to sample the phases. Secondly, the experiment was performed at 601 ± 2 C, a temperature 50 degrees lower than that of the bismuth experiment. The lower temperature was necessary to prevent closure of the miscibility gap with only small additions of magnesium. The data obtained by Obinata and Muira²³ on the ternary lead-zinc-magnesium diagram indicated that the miscibility gap may close with the addition of as little as 4 percent magnesium at temperatures close to 600 C.

Attempts to obtain samples of the melt were unsuccessful at first because the entire sample ran out of the tantalum sampling tube upon its withdrawal from the melt. This problem was minimized, but not eliminated, by inserting a tantalum plug with a 0.20-in. drilled hole into each sampling tube. In almost every sample some dripping from the tube was observed. Despite this difficulty, several observations were still possible. The added magnesium was found to distribute approximately two to one in favor of the zinc layer. The distribution coefficient, again defined as above, changed from 1077 in the magnesium-free system to 286 with the addition of 0.14 percent magnesium to the lead phase. Subsequent magnesium additions, which amounted to 0.76 percent in this phase, changed the

²³ Obinata, I. and Muira, I., Nippon Kiazoku Gakkai-Shi B-14, No. 8, 19-22 (1950).

coefficient only slightly from 286 to 217. Although these values are provisional and a great deal of confidence cannot be placed in the absolute magnitude of the coefficients, it is believed that the observed trend is real.

Apparatus is being assembled for the measurement of the distribution of plutonium between liquid lead and zinc. The measurement of the distribution coefficient of a large variety of fission product elements, when present together in the relative proportions typical of irradiated fuels, is planned.

c. Thermodynamic Studies

Thermodynamic functions for key elements in liquid metal solvents and for the more important solid intermetallic phases are being measured by two methods. 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 phase diagram of the uranium-cadmium system has been recently established (see ANL-5924, page 129). Only one intermetallic phase, UCd_{11} , which at 473 C decomposes peritectically into 2.5 weight percent uranium melt and α -uranium, was found. The existence of UCd_{11} was also demonstrated in a study (see ANL-6333, page 115) of composition dependence of vapor pressure of cadmium over uranium-cadmium alloys with a continuous-recording effusion balance. Decomposition pressures of UCd_{11} , measured in the course of that study and later, are of special interest in obtaining the thermodynamic properties of formation of the intermetallic compound. Analogous thermodynamic data are available from galvanic cell measurements (see ANL-5996, page 116) in which the activities of uranium in cadmium-rich fields of the phase diagram have been determined in the temperature range from 424 C up to the peritectic temperature (about 475 C). The two methods complement one another, since the data of one method can be extrapolated into the fields studied by the other, thereby providing a means of comparison of the two techniques.

Thirteen experiments in the temperature range from 305 to 378 C were carried out employing effusion crucibles B and C with the respective effective orifice areas of 1.718×10^{-3} and 5.173×10^{-3} sq cm. The observed decomposition pressures of UCd_{11} are tabulated as a function of temperature in Column 3 of Table 25 and are plotted on the usual $\log P_{\text{mm}}$ vs $1/T$ graph in Figure 35.

Table 25

DECOMPOSITION PRESSURE AND FREE ENERGY OF FORMATION OF UCd_{11}
(Recording Effusion Balance Method^a)

Effective Orifice Area k_a , (sq cm)	Temp (C)	P_{mm} (obs)	P_{mm} (corr)	$-\Delta F_f^\circ$ (cal/g - atom)
Cell B: $1.71_8 \times 10^{-3}$	378.1	0.448 ^b	-	-
	367.8	0.334	0.351	430
	360.0	0.247	0.260	494
	349.2	0.172	0.181	533
	340.6	0.122	0.128	574
	330.2	0.0842	0.0885	585
	320.4	0.0570	0.0599	630
Cell C: $5.17_3 \times 10^{-3}$	355.2	0.172 ^b	-	-
	345.1	0.127 ^b	-	-
	335.3	0.0912	0.105	592
	324.9	0.0626	0.0722	604
	315.3	0.0424	0.0489	644
	304.9	0.0273	0.0315	693

^aSee ANL-5959, page 125.

^bMeasurements that show deviations from linearity.

FIGURE 35
DECOMPOSITION PRESSURE OF UCd_{11}
EFFUSION MEASUREMENTS

One point with crucible B and two points with crucible C in the high-temperature portions of the curves exhibit deviations from linear behavior. These deviations are probably due to unfavorable mean free path-orifice radius ratios, consistent with rather large vapor pressures at these temperatures. The vapor pressures measured with crucible C are 9 percent lower than those measured with crucible B. This behavior, found frequently in effusion studies, implies that the evaporation coefficient α of cadmium vapor over UCd_{11} is less than unity. A correction of pressures for the low evaporation coefficient was accomplished by means of the relation $P_{\text{corr}}/P_{\text{obs}} = 1 + (ka/\alpha A)$, where ka is the effective orifice area and A the evaporating surface area of the condensed phase. From the two sets of data, αA was estimated to be 0.0335 sq cm. If the evaporating area is assumed to be the geometrical surface area of the sample (about 0.3 sq cm), an evaporation coefficient of about 0.1 may be inferred. The corrected decomposition pressures are listed in Column 4 of Table 25, and are shown in Figure 35 as a line obeying the equation

$$\log P_{\text{mm}} = 9.060 - 6105 T^{-1} \quad .$$

The standard free energy of formation per gram atom of UCd_{11} from solid α -uranium and liquid cadmium can be obtained from the relation $\Delta F_f^0 = x_{\text{Cd}} RT \ln (P/P^0)$, where x_{Cd} is the atom fraction of cadmium in the intermetallic compound (11/12), P the decomposition pressure of the alloy at temperature T , and P^0 the vapor pressure of pure liquid cadmium at the same temperature. For the latter, the equation given by Kelley was used, $\log P_{\text{mm}}^0 = 11.655 - 1.086 \log T - 5706 T^{-1}$. The free energies calculated from the corrected experimental data are listed in Column 5 of Table 25. These data may be represented by the formula

$$\Delta F_f^0 \text{ (cal/g atom)} = -2861 + 3.753 T \quad ,$$

with a standard deviation of 14 cal.

The extrapolated decomposition pressure line intersects the vapor pressure curve for cadmium at 480 C; this temperature corresponds to a hypothetical peritectic decomposition of the compound into pure uranium and cadmium. After making a small correction for the solubility (2.5 weight percent uranium) of uranium in liquid cadmium (ANL-5924, page 129), the predicted peritectic temperature becomes 476 C. In view of the 100 C linear extrapolation of the effusion data, this value must be considered to be in satisfactory agreement with the observed peritectic temperature of 473 C.

The decomposition pressures calculated from the galvanic cell measurements (see ANL-5996, page 116) are also shown in Figure 35. In the most unfavorable instance, the pressure calculated from the emf measurements is only seven percent higher than our extrapolated value.

This difference is certainly within the combined experimental errors. Both sets of data may be represented by the empirical equation ΔF_f^0 (cal/g atom) = $-5864 + 12.51 T - 6.250 \times 10^{-3} T^2$, with a standard deviation of 12 cal over the range from 305 to 473 C.

d. Magnetic Studies
(F. Cafasso and D. Gruen*)

Uranium-Cadmium System (UCd₁₁)

The magnetic susceptibilities of the magnetically dilute isomorphous series CeCd₁₁, PrCd₁₁, NdCd₁₁, and UCd₁₁ are being measured in a joint effort of the Chemical Engineering Division and the Chemistry Division. Results on the cerium system and the neodymium system appear in ANL-6287, page 118, and ANL-6333, page 118, respectively. In this section, a preliminary report on the magnetic susceptibility of polycrystalline UCd₁₁ is presented.

A specimen of UCd₁₁ was prepared by melting the pure metals together. This specimen was shown to be isomorphous with both CeCd₁₁ and NdCd₁₁ by X-ray methods. The atom ratio was confirmed by chemical analysis.

Measurements were made on a powdered sample from about 2 K to room temperature. The Faraday method was used. The apparatus and experimental procedures have been described elsewhere (see ANL-6145, page 81).

Molar susceptibilities of the compound [_MχUCd₁₁] and of the uranium atoms in the compound [_MχU] are recorded in Table 26. In Figure 36 the reciprocal of the molar susceptibility of uranium is shown plotted against absolute temperature. The susceptibility from room temperature to 70 K can be represented by a Curie-Weiss expression

$\left[\chi = \frac{C}{T - \Delta} \right]$ where $C = 1.276$ and $\Delta = -30$ K. The effective moment calculated from the Curie constant C is $3.21 \mu_B$ (Bohr magnetons) per atom. The spin-only moment calculated for two electrons is $2.85 \mu_B$, whereas that calculated for two 5f electrons using the free gaseous ion model is $3.58 \mu_B$.

*Cooperating chemist, Chemistry Division.

Table 26

MOLAR MAGNETIC SUSCEPTIBILITY OF UCd_{11}

Temperature (K)	$M\chi_{\text{UCd}_{11}} \times 10^3$	$M\chi_{\text{U}} \times 10^3$	$M\chi^{-1}_{\text{U}} \times 10^{-2}$
298.4	3.67	3.89	2.57
184.5	5.75	5.97	1.68
176.7	5.97	6.20	1.61
166.8	6.27	6.49	1.54
159.5	6.48	6.70	1.49
77.2	11.7 ₁	11.9 ₄	0.84
72.7	12.2 ₇	12.4 ₉	0.80
70.0	12.4 ₃	12.6 ₅	0.79
67.5	12.8 ₁	13.0 ₃	0.77
63.2	13.2 ₈	13.5 ₀	0.74
20.3	23.1 ₅	23.3 ₇	0.43
4.2	32.3 ₈	32.6 ₁	0.31
2.3	34.4 ₉	34.7 ₁	0.29

FIGURE 36
TEMPERATURE VARIATION OF THE RECIPROCAL OF
MOLAR SUSCEPTIBILITY OF URANIUM IN UCd_{11}

Below 70 K, the bend in the $M^{\chi^{-1}}_{\text{U}}$ vs T curve toward the susceptibility axis indicates that the ground state is nondegenerate. For magnetically dilute systems, Kramers²⁴ has shown that only even electron systems can have nondegenerate ground states. The shape of the low-temperature portion of the susceptibility curve coupled with the observed moment suggests strongly that there are only two unpaired 5f electrons per atom of uranium. In the cogenetic neodymium system, three unpaired electrons per atom were found (see ANL-6333, page 118). Apparently, one of the three 5f electrons in uranium is promoted to a valence band or a conduction band.

The large Δ value (-30 K) found, coupled with the relatively high temperature (70 K) at which splitting first appears, suggests that the crystalline field interactions are strong in the uranium system. It is well known from measurements on ionic crystals that 5f electrons are not as well shielded from their environment as are 4f electrons. Any treatment of the susceptibility data, therefore, should consider perturbations caused by the crystalline field. Models which treat interactions of the magnetic electrons with crystalline fields of specific symmetries will be investigated in the hope that an adequate interpretation of the magnetic data can be found.

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.

²⁴Kramers, H. A., Proc. Amsterdam Acad. Sci., 33, 959 (1930).

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 Zirconium Dihydride in Oxygen
(D. R. Fredrickson and R. L. Nuttall)

Experiments are underway to determine the heat of combustion of zirconium dihydride in oxygen according to the equation

Since experiments have shown that powdered zirconium dihydride is oxidized slowly by air prior to ignition, a technique has been developed to enclose a combustion sample of the powder in a sealed plastic bag. One gram of powdered zirconium dihydride gains approximately 0.06 percent in weight by oxidation if it is either exposed to air for 24 hr or exposed to 15 atmos of oxygen for $1\frac{1}{2}$ hr. The sample of zirconium dihydride, prepared in lump form by Howard Flotow of the Chemistry Division, was handled only in inert atmosphere. Lumps were ground to a fine powder, the powder was placed in a Mylar bag, and the bag was sealed and weighed, all operations being carried out in an inert atmosphere box.

Calorimetric combustions are being carried out in a platinum-lined bomb by burning 1 g of zirconium dihydride powder (enclosed in a 1-in. sq Mylar bag) in 15 atmos of oxygen with the bag lying on a pressed layer of zirconium oxide in an alumina dish. A cotton fuse attached to a platinum wire ignites the bag and powder. One ml of water is also placed in the bomb before closing, as is customary for combustions in which water is formed in the process.

Results of preliminary calorimetric combustions of zirconium dihydride in oxygen are incomplete at this time.

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

Boron nitride is the first of a series of elements and compounds which react spontaneously with fluorine to be studied. For this study the combustion bomb reaction vessel for spontaneously combustible materials described in ANL-6287, page 125, has been used. Two series of calorimetric combustions have been made. The results of the first series of runs were discarded because of a spurious side reaction and difficulties with thermal equilibration. The preliminary values of $\Delta E_c^0/M$ for five successive acceptable runs of the second series are as follows: 8551, 8567, 8555, 8534 and 8538 cal/g. The average value for the five determinations was 8549 cal/g. The standard deviation of the mean was 6.2 cal/g or 0.07 percent.

After the first series of boron nitride combustions, it was discovered that a secondary reaction was occurring on the walls of the bomb. For the duration of that series the bomb had not been exposed to air atmosphere, but was opened only in a dry box with a helium atmosphere. After eight runs had been completed, the bomb was examined outside the box. A layer of greenish material was observed on the bomb walls and identified by X-ray analysis as $\text{Ni}(\text{BF}_4)_2 \cdot 6 \text{H}_2\text{O}$. The dry box atmosphere was also found to contain about 0.1 percent water vapor. It is believed that small amounts of boron trifluoride remained on the bomb walls after evacuation of the product gases and reacted with the walls when exposed to the water vapor in the dry box to form the hydrate. During the next boron nitride combustion, the hydrate reacted further with fluorine and boron trifluoride to give a secondary source of heat.

Another problem which was encountered in the first series was the length of time required for the main reaction period. More than an hour was needed, after the ignition of the sample, for the rate of change of temperature with time to approach a normal "after rate." This was found to be caused by poor thermal contact between the heavy-sample support arrangement in the center of the bomb and the bomb itself.

In the second series of combustions of boron nitride, steps were taken to minimize both problems. To eliminate the problem of the spurious side reaction in which $\text{Ni}(\text{BF}_4)_2 \cdot 6 \text{H}_2\text{O}$ was formed, the bomb walls were washed with water after each combustion to remove any adsorbed boron trifluoride. To shorten the time of the main reaction period, the thermal contact was improved by altering the sample support arrangement within the bomb so that the boron nitride sample was supported directly by a massive nickel dish clamped to the bottom of the bomb. It was found from benzoic acid combustions in oxygen in which this arrangement was used, that the main reaction period of the experiments was of normal duration, about one-fourth the time required for benzoic acid experiments in which the arrangement for the first series of boron nitride experiments was used.

The results cited are preliminary. Corrections for impurities in the sample have not been applied. Additional work is necessary before final results can be reported.

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

The calorimetric combustions of uranium in fluorine previously reported (see ANL-6333, page 124) were somewhat unsatisfactory because of the formation of considerable amounts of uranium fluorides other than uranium hexafluoride. About one-third of the uranium placed in the reaction vessel was recovered after the combustion as unreacted metal. On the surface of the recovered metal was a mixture of UF_3 , UF_4 , U_4F_{17} , U_2F_9 , and UF_5 . Analysis of the combustion residue was 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, and because the heats of formation of the lower fluorides are not well known, an uncertainty of at least 0.2 percent was introduced into the calculation of the heat of formation of uranium hexafluoride.

It is apparent that the determination of the heat of formation of uranium hexafluoride can be made much more precisely if the amounts of lower uranium fluorides remaining after a combustion can be reduced. One method of achieving this reduction is to obtain complete reaction of the uranium metal with fluorine. Many exploratory combustions were performed in an attempt to obtain complete combustion. These included the burning of a uranium pin supported by a consumable zirconium pin, the burning of pelleted mixtures of uranium powder and Teflon powder supported by nickel, alumina, or synthetic sapphire discs, and the burning of uranium powder spread in a thin layer on nickel, molybdenum, aluminum trifluoride, or aluminum discs. None of the exploratory combustions yielded complete combustion of the uranium to uranium hexafluoride. They did indicate, however, that the desired result might be obtained if higher fluorine pressures were used to burn a thin layer of uranium powder supported by a dish made of a substance having high thermal conductivity and resistance to thermal shock and alloying with liquid uranium. A combustion was performed in which powdered uranium, supported by an aluminum dish, was burned in fluorine at about 18 atmos. This arrangement resulted in nearly complete conversion of uranium to uranium hexafluoride. Unfortunately, there was also considerable surface fluorination of the aluminum dish. An attempt will be made to vary this technique so that the attack upon the supporting dish will be reduced.

d. Combustions of Titanium, Hafnium, and Thorium in Fluorine
(E. Greenberg)

During this quarter, calorimetric combustions of hafnium in fluorine were initiated and completed. Prior to the hafnium combustions the

calibration of the nickel-titanium bomb was checked by carrying out a series of benzoic acid combustions.

The results of the calibration experiments are summarized in Table 27. The average value of the energy equivalent of the system, ϵ (calorimeter), obtained in this series is approximately a calorie per degree less than the average of a previous series, but the current combustion values still fall within the range of the previous measurements. An unusually high precision was achieved in the present series.

Table 27

CALIBRATION OF NICKEL-TITANIUM BOMB BY
COMBUSTION OF BENZOIC ACID

Combustion No.	Heat Transfer Coefficient $\alpha \times 10^4$ (sec ⁻¹)	Mass of Benzoic Acid (g)	Temperature Rise ΔT (C)	ϵ (calorimeter) (cal/deg)
17	0.3399	0.99870	0.76924	3565.30
18	0.3409	1.00035	1.77218	3565.59
19	0.3099	1.00129	1.77401	3565.65
20	0.3386	1.00042	1.77202	3565.81
21	0.3262	0.99934	1.77087	3565.60

Average = 3565.59

Standard deviation of mean = ± 0.08 or 0.002%

Table 28 summarizes the preliminary results obtained from nine successful calorimetric combustions of hafnium in fluorine.

Table 28

COMBUSTION OF HAFNIUM IN FLUORINE

Run No.	Temperature Rise ΔT (C)	Mass (in vacuo) Zr Burned (g)	ΔT due to Zr Fuse (C)	ΔT due to Hf (C)	Mass (in vacuo) Zr Burned (g)	$\Delta T/g$ Hf (C/g)	Source of Fluorine
1	1.37236	0.01118	0.01563	1.35673	1.85279	0.73049	ANL
2	1.51552	0.00912	0.01275	1.50277	2.05693	0.73059	ANL
3	1.34466	0.00947	0.01324	1.33142	1.82157	0.73092	Gen. Chem. Co.
4	1.51349	0.00750	0.01048	1.50301	2.05486	0.73144	Gen. Chem. Co.
5	1.38410	0.00966	0.01350	1.37060	1.87370	0.73149	Gen. Chem. Co.
6	1.46073	0.00866	0.01211	1.44862	1.98066	0.73138	ANL
8	2.20270	0.00929	0.01299	2.18971	2.99433	0.73129	ANL
10	1.79775	0.01085	0.01517	1.78258	2.43776	0.73124	ANL
12	2.29126	0.00779	0.01089	2.28037	3.11682	0.73163	ANL

Average = 0.73116

Standard deviation of mean = ± 0.00013 or 0.01%

Zirconium fuse wire was used for these experiments. With the aid of the previously obtained combustion data on zirconium, the temperature rise due to combustion of the fuse was subtracted from the overall temperature increase in order to obtain the net temperature rise attributable to the hafnium burned. The respective weights of hafnium and zirconium burned in the bomb were determined by subtracting the weight of unburned metal recovered after combustion from the weight of metal originally charged to the bomb. The standard deviation of the mean of 0.02 percent is the same as that obtained for combustion of zirconium by the same technique and compares favorably with modern thermochemical data.

As indicated in Table 28, Runs 3, 4, and 5 were carried out with high-purity fluorine (~99.75 percent) obtained from the General Chemical Company. The remaining runs were carried out with high-purity fluorine (~99.95 percent) prepared in this Laboratory by low-temperature distillation of commercial fluorine. No significant difference in results was obtained with the two grades of fluorine. However, because of the limited number of experiments with the General Chemical Company fluorine, it is quite likely that this fluorine will be used again when carrying out the calorimetric combustions of titanium in fluorine.

The solid combustion product from one of the calorimetric experiments was submitted for X-ray diffraction analysis and found to be monoclinic hafnium tetrafluoride. The diffraction pattern resembled closely that of monoclinic zirconium tetrafluoride. In two of the calorimetric experiments the gaseous products remaining in the bomb after combustion were sampled for infrared and mass spectrometric analyses. The gaseous impurities found could be qualitatively accounted for as arising from contaminants in the hafnium sample and in the fluorine charge.

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

No additional work has been carried out with these metals during the past quarter. Preliminary noncalorimetric combustion experiments have been completed for tantalum and niobium, but additional experimentation is still necessary for vanadium.

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

The "soft" metals, cadmium, magnesium, aluminum, and zinc, supported by their respective fluorides, can be ignited and burned in fluorine at a pressure of 100 psi. General combustion characteristics of these metals have been determined, and specific techniques for carrying out combustions have been developed. All of these metals melt in the initial stages of combustion.

These metals differ somewhat in their combustibility; therefore, different techniques must be used for different metals. Smooth and virtually complete combustion of cadmium is obtained with a 5-mil foil, using a 10-mil cadmium wire fuse. Because of the low boiling point of magnesium, its combustion is accompanied by the sputtering of the liquid metal. The sputtering can be avoided by the use of finely divided magnesium mixed with magnesium fluoride in a ratio of approximately one to one. Because of the difficulty of igniting aluminum and zinc, it was advantageous to use materials such as cadmium and molybdenum to initiate the combustion. The combustion of zinc presented additional difficulty because of the excessive melting of the zinc fluoride support. This caused the metal to sink into the support and resulted in incomplete combustion. This was remedied by the use of an aluminum fluoride support. Aluminum fluoride does not appear to react with zinc fluoride.

Other problems were encountered in this effort to establish specific techniques for calorimetric combustions of these metals. These problems involved the geometry of support, heat transfer, fluorination during the pre-ignition period, and determination of unburned metal.

Preliminary calorimetric experiments are currently in progress. The main objective of the experiments is to determine to what extent the impurities in the fluoride supports produce any side reactions. The analysis of the product gases and the consistency of the calorimetric measurements are expected to indicate the magnitude of the side reactions.

A preliminary calorimetric combustion series of cadmium in fluorine has been completed. The results are not yet complete pending the determination of the unburned metal.

A literature survey on the thermochemistry of the fluorides of cadmium, magnesium, aluminum, zinc, and lead has been completed.

- g. Magnetic Effect on Temperature Measurement with a Platinum Resistance Thermometer
(D. R. Fredrickson and R. L. Nuttall)

With a slightly magnetic sealing nut and pressure ring (No. 400 stainless steel) placed on the platinum-lined bomb, a deflection in the galvanometer was observed when the bomb was rotated in the calorimeter. This deflection was caused by movement of the magnetic material near the coil of the platinum resistance thermometer. The magnitude of these deflections was equivalent to that which would be caused by temperature fluctuations of about 0.0002 C.

This magnetic effect should be eliminated by using a nonmagnetic material for construction of bomb parts, particularly for those cases in which rotation is desired through the final period in a

calorimetric combustion. The overall error due to this magnetic effect is probably negligible. However, the effect is quite disturbing to an operator trying to obtain a constant rate in the after period of a combustion.

h. High-temperature Enthalpy Calorimeter
(D. R. Frederickson, R. L. Nuttall, E. D. West*)

The calorimetric system to measure changes in enthalpy up to 1500 C is being assembled. The drop calorimeter has five main parts which are as follows: (a) supports, (b) furnace, (c) vacuum valve, (d) calorimeter, and (e) drop mechanism.

Supports and completed furnace are assembled. A high-vacuum system for the furnace is assembled and at the present time provides a vacuum of 2.0×10^{-6} mm Hg in the furnace component. Further testing and outgassing will be necessary.

The vacuum valve is complete but not installed in the equipment. The calorimeter components are complete but not assembled in the calorimeter shell. The calorimeter shell has been installed and leak tested. The leaks found will be repaired.

A dual vacuum system has been designed to be used for both the calorimeter and vacuum valve. Certain components will be fabricated by the shop and the system will be assembled here. The drop mechanism is nearing completion at the shop.

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

II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES

The volatilities of uranium and plutonium hexafluorides are the basis of a direct fluorination volatility process proposed for the recovery of uranium and plutonium from irradiated nuclear reactor fuels. In this process fluidization techniques are also used to advantage. 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 by making use of the variability of the rates of fluorination of the plutonium and uranium compounds and chemical reactivities of the hexafluorides.

The metal-decladding step for oxide fuels involves direct gas-metal reactions in the case of elements clad either with stainless steel or Zircaloy. The reactions, all highly exothermic, are carried out with the fuel elements submerged in an inert fluidized bed (alundum, calcium fluoride, or other inert material) which serves as the heat transfer medium. Dilute mixtures of hydrogen chloride in hydrogen fluoride in a single fluid-bed stage or the separate gases in a two-zone reactor have been successfully utilized where reaction with zirconium is involved. In recent work chlorine has replaced the hydrogen chloride for reaction with zirconium and also appears suitable for stainless steel decladding.

The two-zone fluid-bed reactor has been used in all cases outlined above. A chlorination reaction (referred to as primary) is carried out in the lower zone of the reactor. Volatile chloride reaction products pass into the upper zone where they are converted to solid fluorides by reaction with hydrogen fluoride. Solid chlorides also pass into the upper zone in the normal course of solids mixing which occurs between zones and are also readily converted to fluorides. The two zones are separated by an inverted conical baffle which minimizes back-mixing of the gases and prevents the formation of gas mixtures that have been shown to affect these reactions adversely.

In pilot-plant decladding studies, the reaction of 304 stainless steel tube sections with chlorine was scaled up from the 1 $\frac{1}{2}$ -inch-diameter two-zone reactor to a six-inch two-zone column. In 5.8 hours at temperatures near 600 C, about 95 percent of the charge, which consisted of 30 tubes, 31-mil wall by 9 inches long, was reacted using 50 mole percent chlorine in nitrogen. This was equivalent to an average penetration rate of 5.1 mils/hr.

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. In pilot-plant studies made to optimize process conditions for the direct fluorination of uranium dioxide pellet fuel, batches of one-half-inch pellets were completely fluorinated at 500 C in as little as 6 hours, with an overall rate of 41 lb UF_6 /(hr)(sq ft reactor cross-sectional area). Fluidization of inert material in the voids of the pellet bed resulted in good heat transfer during the course of the fluorination.

Temperature control by regulation of inlet fluorine was also successful in the fluorination of pellets without an inert fluid bed, but poor heat transfer in this case limited the allowable rate to about $\frac{2}{3}$ the value for the fluid-bed case.

The highest fluorination rates have been obtained with oxygen fluorine mixtures. This procedure is involved in the use of off-gas recycle to maximize fluorine economy; about 70 percent overall fluorine efficiency has been achieved in runs made to date. Fluorinations made with nitrogen diluent proceed at an overall rate from three- to six-fold slower than with oxygen diluent. The oxygen reacts with the pellet surface to form higher oxides which spall off as fines. The high specific surface area of these fines results in a high, nearly constant fluorination rate until the fluorination is about 90 percent complete. The fines appear to be retained in the equipment and to be completely fluorinated without difficulty. Inert beds of calcium fluoride and aluminum oxide have both been used successfully. An investigation of the effect of temperature on reaction rate in the range from 350 to 500 C was made. With oxygen dilution, the fluorination rate was halved for every 50 C lowering of temperature. With nitrogen dilution, the temperature dependence was somewhat stronger.

Since the inert solids will be discarded as waste, it is important, for economic reasons, that very little of the uranium and plutonium be retained in the solids after fluorination. It was first demonstrated that plutonium and uranium could be removed by fluorination upon reacting fluorine with mixed oxides of uranium and plutonium, at 450 C, contained in nickel equipment. Satisfactory removal of uranium upon fluorination of the mixed oxides was achieved at various temperatures when zirconium tetrafluoride and calcium fluoride were used as bed materials. However, satisfactory removal of plutonium was not obtained using the same bed materials. Fluorination of the mixed oxides, with alundum (crystalline alumina), as bed material resulted in low plutonium concentrations (0.035 percent after a ten-hour fluorination at 450 C) in the residual solids. It appears that crystalline alumina is superior to calcium fluoride and zirconium tetrafluoride as an inert solid.

After decladding, an alternative to the Direct Fluorination Process (page 159) for reacting high-density uranium dioxide pellets appears feasible. The first step is chlorination-hydrofluorination in a two-zone fluid-bed reactor producing uranium tetrafluoride, followed by fluorination to the hexafluoride. Tube-furnace experiments conducted at 650 C indicated appreciable reaction of sintered uranium dioxide pellets occurs with chlorine (a decladding

agent for stainless steel) alone, producing both volatile and nonvolatile reaction products. This reaction would be of some concern if it was found that there was interaction between cladding and fuel reaction products such that overall uranium and plutonium recovery is adversely affected. Sintered pellets were successfully chlorinated with mixtures of chlorine and carbon tetrachloride at reasonable rates. Exploratory trial fluorination of the final bed produced by chlorination of a 20-pellet (initially $\frac{5}{16}$ -inch diameter by $\frac{5}{8}$ -inch long, 121 g total) charge achieved 96.5 percent uranium removal in two hours at 350 C and little additional removal in a subsequent two-hour period in experiments conducted in a $\frac{1}{2}$ -inch-diameter fluid-bed reactor.

Corrosion studies on nickel, Inconel and Hastelloy-C coupons aimed at preliminary evaluation of potential materials of construction for the chlorination-decladding of stainless steel-clad fuels were concluded. Tests conducted at 600 C in a one-inch horizontal tube furnace using once-through chlorine showed an initially high but diminishing corrosion rate during the first 25 hours, followed by a much reduced uniform corrosion rate during the subsequent period, which extended to 285 hours. The calculated corrosion rates were about 20 mils/month for the short term and lower by about a factor of 10 for the longer term for all metals. Photomicrographs showed severe intergranular attack in nickel, no changes in Inconel, and slight intergranular changes in Hastelloy-C attributed to age-hardening accelerated by high temperature.

Further study of the decomposition of plutonium hexafluoride has been made at 80 C and 100 cm pressure in a nickel vessel. An initial integral reaction rate of 2.4 percent per day was obtained in the first 25 hours, and an average of 1.4 percent per day decomposed in the following 164 hours.

Laboratory experiments have been performed at both Brookhaven and Argonne National Laboratories to determine the best procedure to be used in the recovery of uranium from enriched uranium-zirconium alloy fuels. It has been demonstrated that, for optimum recovery of uranium from enriched uranium-zirconium alloy fuels, it is best to remove the zirconium as volatile zirconium tetrachloride. The hydrochlorination of the zirconium can be carried out at or above 350 C. The uranium remains behind in the form of nonvolatile uranium chlorides. The hydrochlorination of the zirconium and the subsequent fluorination of the uranium chlorides can be carried out in a fluidized bed of granular solids. Of those bed materials tested, alundum (refractory aluminum oxide) was most satisfactory. Poorer results were obtained when zirconium tetrafluoride was included in the bed material. Based on the amount of uranium remaining in the bed, uranium recoveries of 99.5 percent were achieved when alundum was used as the bed material. Experiments, using physical mixtures of uranium fluorides and zirconium tetrafluoride, indicated that the optimum fluorination temperature, using fluorine, is 350 C. When chlorine trifluoride was used as the fluorinating agent, best uranium removals were obtained at 200 C.

A two-step fluid-bed process for the preparation of high-density uranium dioxide suitable for use in nuclear fuel elements from uranium hexafluoride is being studied. Thirty-five hours of running time, including a 15-hour continuous period, have been accumulated in current studies on the hydrolysis step (first step) in which steam reacts with uranium hexafluoride to form uranyl fluoride. A feed rate of 100 g/min hexafluoride is being used. The problems of fines formation and of control of particle size encountered previously appear to have been solved by allowing the fines to be entrained from the reactor and collected separately, and by use of the proper rate of recycle of seed particles. Run interruptions were due only to plugging of the line used for entraining the solids, a problem readily soluble by improved design.

Additional batch studies of the second step, reduction of uranyl fluoride to the dioxide, were carried out in an auxiliary three-inch fluid-bed reactor with gas composition (steam in hydrogen) and temperature as independent variables. The optimum gas mixture, found to be near 50 percent steam in hydrogen, gave a residual fluoride content of 200 ppm in four hours at 650 C when a uniform bed of -20 +40 mesh particles was used. Temperatures of 550 to 650 C with beds of -40 +60 mesh particles gave residual fluoride contents of 2500 and 150 ppm, respectively, in four-hour periods. Appreciable particle breakup seems to occur (18 to 36 percent minus 200 mesh found in final beds), but this is not of process significance when pellets will be made, since all of the powder will be ground.

Feasibility studies on the use of small-diameter columns for continuous fluid-bed calcining continued. A $\frac{1}{4}$ -inch-diameter column with 1 M aluminum nitrate feed is currently in use. The technique employed involves mounting the feed spray nozzle vertically in the apex of the cone bottom thereby permitting utilization of the atomizing and feed decomposition gases as the fluidizing gas medium. A reduction in the volume ratio of atomizing air to liquid feed from 1700 used in horizontal spray work in a six-inch-diameter column to 1080 in recent short-term experiments in the currently used $2\frac{1}{4}$ -inch column indicates some success toward meeting the objective of reducing the off-gas handling problem. Other experiments indicated that nozzle operation, heat supply, and feed pump operation are possible trouble areas, and modifications to the equipment are in progress. Complete reliability of operation is required if the small-diameter aspect of this work is to be applied to systems such as plutonium nitrate or highly enriched uranium for which nuclear criticality must be considered.

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

1. Fluorination of Plutonium-Uranium Oxides (L. Anastasia, L. Trevorow, R. Kessie, T. Baker, J. Riha)

In the conceptual flowsheet of the Direct Fluorination Volatility Process, uranium and plutonium are removed from oxide fuels by fluorination

at about 500 C. This step will probably be carried out in a fluidized bed of inert solids. Since the inert solids will be discarded as waste, it is important, for economic reasons, that very little of the uranium and plutonium be retained in the solids after fluorination. The effect of plutonium retention on the economy of the fuel cycle can be illustrated by the following example: In the process-scale fluorinator, the charge from a power reactor, such as the Dresden reactor, will probably consist of about 100 kg of uranium, 400 g of plutonium, and about 30 kg of inert solids. If one percent of the plutonium remains in the inert solids after fluorination, the composition of the solids would be 0.013 percent plutonium. The current processing scheme calls for processing a charge every two days. Therefore, on the basis of a 300-day working year, the loss of one percent of the plutonium would mean a total loss of 600 g of plutonium per year. If the value of the plutonium is assumed to be about \$15 per gram, the total loss would amount to \$9000 per year. The economic significance of the experimental results reported below can be evaluated by assuming that a concentration of 0.01 percent plutonium in the bed solids after fluorination corresponds to a monetary loss of about \$6900 per year. This estimate is based on the practice of discarding each batch of solids after each fluorination. It has been suggested that the plutonium losses could be decreased by processing several batches of fuel with the same batch of solids. The number of times a given batch of solids could be used would be limited, however, by the generation of heat from the fission products which are expected to accumulate in the bed.

An experimental program on the laboratory scale has been started to determine the efficiency of removal of uranium and plutonium from mixtures containing solid solutions of plutonium dioxide in uranium dioxide and various inert solids. The percent uranium and plutonium remaining in the solids after fluorination is employed as a measure of efficiency.

Apparatus used in this work was assembled in a glove box of the type described in a recent report.²⁵ The fluorination experiments were carried out in nickel and Monel apparatus which has been described previously in ANL-6145, page 102. A magnetic piston pump, previously used, was replaced with a Lapp Pulsafeeder* pump for the circulation of fluorine and other gases. The Lapp pump is equipped with a remote Monel diaphragm pumping head which has been located inside the glove box.

²⁵ Malecha, R. F., Smith, H. O., Schraidt, J. H., Natale, J. V., Ross, N. E., and Brown, H. O., Jr., Low Cost Glove Boxes, Proceedings of the Eighth Conference on Hot Laboratories and Equipment, San Francisco, California, TID-7599, p. 485, December, 1960.

* Lapp Pulsafeeder Model No. CPS-1, Lapp Insulator Co., Inc., LeRoy, New York.

The materials used in this work were fluorine gas, the mixed oxides (solid solutions) of plutonium and uranium, and the inert solids: zirconium tetrafluoride, calcium fluoride, and alundum. The fluorine was obtained from the Allied Chemical Corporation; it was passed through a heated bed, at about 100 C, of sodium fluoride pellets to remove hydrogen fluoride prior to use. Solid solutions of uranium and plutonium dioxides were prepared following the procedure recommended by Wilson.²⁶ The starting materials were uranyl nitrate hexahydrate and a plutonium nitrate solution, both obtained from AEC sources. Ammonium diuranate and plutonium hydroxide coprecipitated following the addition of aqueous ammonia to a solution of the plutonium and uranium nitrates. The precipitates were collected by centrifugation, dried overnight at 140 C, and then reduced to the oxides by heating at a temperature of 1000 C in an atmosphere of nitrogen containing two volume percent hydrogen. The oxides were ground to a fine* powder before use. The composition of most of the mixed oxide preparations was about 3.78 percent plutonium. This composition was chosen because it is expected that the initial fluorination of oxide fuel of the Dresden type will remove about 85 to 90 percent of the uranium (ANL-6101, page 84), leaving a residue which is about 4 percent plutonium. It is the efficiency of removal of uranium and plutonium from this residue of the first fluorination step which is the subject of interest here. These oxides were mixed thoroughly with one of the granulated, inert solids for use in the fluorination experiments. Zirconium tetrafluoride was obtained from the Allied Chemical Corporation; the concentration of the major impurities, iron and hafnium, was about 10 ppm. Two types of calcium fluoride were used: fluorspar, and a reagent grade which was fused either in air or in an inert atmosphere. The calcium fluoride was ground and classified for particle size. Only the material that fell between 140 and 170 mesh was used. These narrow limits were set on particle size so that interparticulate spaces would not be filled with fine particles of the inert solids, which would inhibit the diffusion of gases. The alundum was fused, 60 mesh, crystalline alumina obtained from the Norton Company.

The procedure in a typical fluorination experiment was as follows: A weighed quantity of solids was spread in a layer, $\frac{1}{32}$ to $\frac{1}{8}$ in. deep, on the flat bottom of a shallow, nickel reaction boat, the bottom area of which was about 26 sq cm. The reaction boat was placed inside a horizontal, tubular furnace reactor, and the system was evacuated. The solids were dried in vacuo for about 2 hr while the temperature of the system increased from 25 C to the temperature used for a particular fluorination experiment. The system was then filled slowly with fluorine to a pressure of about one atmosphere, and the fluorine was circulated over the sample for the remainder of the experiment at a rate of about 800 cc/min. The gas flowed in series across the surface of the solids in the furnace reactor, through a trap cooled

²⁶ Wilson, A. S., Uranium Dioxide-Plutonium Dioxide Ceramics, HW-55319 (March 1, 1958).

*No size classification was made.

in dry ice, through a thermal flow meter, through the remote head of the Lapp pump, and finally back to the furnace reactor. Uranium and plutonium hexafluorides, which formed in the reactor, condensed and accumulated in the cold trap. At the end of a given fluorination time, the system was evacuated and filled with helium. After cooling, the boat containing residual solids was removed from the furnace reactor and weighed. The residual solids were mixed thoroughly. Samples were taken from this mixture and dissolved completely prior to analysis. Both the zirconium tetrafluoride and the calcium fluoride were dissolved by digestion in aluminum nitrate-nitric acid mixtures. The aluminum was dissolved in 20 hr in a sodium borate-sodium carbonate flux at 1000 C. The resulting melt was dissolved in nitric acid, and the solutions were analyzed for plutonium by alpha counting,* and for uranium by a fluorophotometric analysis.

In order to determine if there were anything inherent in the mixed uranium and plutonium oxides and in the procedure which would cause the retention of plutonium after fluorination, a sample of the mixed oxides was fluorinated in the absence of any inert solid. A nickel foil liner was placed in the reaction boat, and the mixed oxides were spread on the liner and fluorinated at 450 C. After fluorination, the nickel liner and the contents were removed from the boat and dissolved prior to analysis for uranium and plutonium. The original mixture spread on the liner contained 1618 mg of uranium and 73.3 mg of plutonium. Analysis of the dissolved liner and contents, after fluorination, indicated that 0.21 mg of uranium and 0.12 mg of plutonium had remained on the liner. The details of this experiment are summarized in Table 29. From the quantity of inert solids used in subsequent fluorination experiments and the quantity of plutonium remaining on the foil after fluorination, it is calculated that the residual concentration of plutonium in a truly inert solid would be 0.002 percent after fluorination at 450 C. This then sets a lower limit of plutonium removal which can be expected in the fluorination experiments.

Table 29
REACTION OF MIXED OXIDES OF PLUTONIUM AND URANIUM WITH FLUORINE AT 450 C

Oxides spread on nickel foil								
No inert solids present								
Fluorination Time 10 hr								
Fluorine Recycle Rate 800 cc/min								
Fluorine Pressure ~1 atm								
Initial Sample					Residue ^b			
Total Wt (g)	Total U (mg)	Total Pu (mg)	U (wt %)	Pu (wt %)	Fluorine Excess Ratio ^a	Wt Solids (g)	Total U (mg)	Total Pu (mg)
1.95	1618	73.3	93.0	3.76	450	0.1 ^c	0.21	0.12

^aFluorine Excess Ratio = $\frac{\text{Total F}_2 \text{ Circulated}}{\text{Min F}_2 \text{ Required}}$ The minimum F₂ required was calculated from the initial quantity of plutonium and the equilibrium constants for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$ given in ANL-6101, page 80

^bAfter fluorination the nickel foil was completely dissolved and the resulting solution was analyzed for uranium and plutonium

^cMost probably nickel fluoride

* Plutonium was extracted from the nitrate solution, using hexone, prior to alpha counting to eliminate interference from americium.

Contamination from small amounts of plutonium left in the box or reaction furnace from previous experiments was considered a possible source of error in the determination of the concentration of residual plutonium. In order to determine the extent of contamination by environment, a number of samples of inert solids were placed in the furnace reactor and treated with fluorine by the same experimental procedure as that used in fluorination of oxide-inert solid mixtures. As shown by the data listed in Table 30, uranium and plutonium concentrations in these blank samples were much lower than the concentrations in residual solids after fluorination of oxide-inert solid mixtures. It was concluded that contamination had not caused a significant error in the concentration of uranium or plutonium remaining after fluorination of oxide-inert solid mixtures.

Table 30

CONTAMINATION OF ZIRCONIUM TETRAFLUORIDE
USED IN BLANK EXPERIMENTS

The blank samples initially contained
no uranium or plutonium.^a

New sample boats used for all experiments
except 15 and 16.^b

Exp No.	Temp (C)	Time (hr)	Original Sample ZrF ₄ (g)	Concentration in ZrF ₄ after Fluorination	
				U (w/o)	Pu (w/o)
15	350	5	~3	0.088	0.042
16	500	5	~3	0.02	0.004
21	350	5	2.99	0.008	0.002
22	350	10	2.34	0.007	0.001
29	350	5	3.28	0.009	0.0008
18 ^c	500	5	3.82	0.003	0.0005
25	500	15	2.48	0.006	0.0007

^a Blank samples were placed in the furnace along with samples being fluorinated. The numbers correspond to the same experiments shown in Table 31.

^b Experiments 15 and 16 performed in the same boat used in Experiments 5 through 14.

^c Blank sample was placed in the furnace alone and fluorine was circulated over the sample.

Table 31

REACTION OF URANIUM-PLUTONIUM DIOXIDES ZIRCONIUM TETRAFLUORIDE MIXTURES WITH FLUORINE

Fluorine Recycle Rate 800 cc/min
Fluorine Pressure ~1 atmos

Exp No	Temp (C)	Accumulative Time ^a (hr)	Initial Sample						Fluorine ^b Excess Ratio	Residue				
			Residue from Exp	Wt ZrF ₄ (g)	Wt U (mg)	Wt Pu (mg)	U (w/o)	Pu (w/o)		Wt ^e (g)	Wt U (mg)	Wt Pu (mg)	U (w/o)	Pu (w/o)
15	350	5	-	2.72	1224	56.0	30.6	1.40	183	2.60	3.1	1.0	0.12	0.40
21	350	10	15	1.98	2.4	8.0	0.12	0.40	1.290	1.97	1.9	3.6	0.097	0.18
22	350	15	21	1.43	1.4	2.6	0.097	0.18	2.450	1.46	1.5	3.2	0.10	0.22
29	350	5	-	2.67	876	42.7	24.4	1.19	239	2.26	1.4	4.1	0.060	0.18
30	350	10	29	1.86	1.1	3.4	0.060	0.18	3.420	1.88	1.2	2.4	0.061	0.13
31	450	5	-	2.71	888	43.3	24.4	1.19	395	2.04	1.3	4.1	0.062	0.20
32	450	10	31	1.57	0.97	3.1	0.062	0.20	5.690	1.30	0.78	2.2	0.060	0.17
16	500	5	-	2.72	1224	56.0	30.6	1.40	438	1.60	0.27	4.8	0.017	0.30
23	500	10	16	0.72	0.12	2.2	0.017	0.30	12.800	0.22	0.02	0.19	0.010	0.088
5	400	1	-	4.27	1730	78.4	28.5	1.29	2 ^c	4.09	9.4	6.1	0.23	0.15
6	500	5	-	-	-	-	-	-	15 ^c	-	-	-	-	-
	400	2	-	2.11	855	38.7	28.5	1.29	29 ^d	1.63	1.1	2.2	0.07	0.14
	500	10	-	-	-	-	-	-	232 ^d	-	-	-	-	-

^a Accumulative time-e.g. - Exp. 22 - Total fluorination time (Exp. Nos. 15 + 21 + 22) was 15 hr at 350 C. Sample used was the same sample used in Exp. No. 21 less that used for analysis.

^b Fluorine Excess Ratio $\frac{\text{Total F}_2 \text{ Circulated}}{\text{Min F}_2 \text{ Required}}$ The minimum F₂ required was calculated from the initial quantity of plutonium and the equilibrium constants for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$ given in ANL-6101, page 80.

^c F₂ recycle rate was 46 cc/min.

^d F₂ recycle rate was 175 cc/min.

^e The discrepancies between Wt ZrF₄ in the initial sample and the Wt of recovered solids at the higher temperatures were probably caused by sublimation of ZrF₄.

The fluorination of mixed oxide-inert solid mixtures resulted in a residue in which the concentration of uranium was reduced to a satisfactory level.* The concentration of plutonium in the residual solids, however, was not always considered satisfactory. Discussion of the results, therefore, will deal mainly with plutonium. The details of the experiments are given in Tables 31, 32, and 33, and the pertinent results are summarized and compared in Table 34.

The experimental conditions and results of the fluorination of mixtures of plutonium-uranium dioxides and zirconium tetrafluoride are listed in Table 31. In a series of fluorinations at 350 C (Nos. 15, 21, 22), samples of the solids were fluorinated for a total of 15 hr, and the solids were sampled at the end of 5, 10, and 15 hr. The concentration of plutonium in the solids was reduced to about 0.2 percent after 10 hr of fluorination, and it was not reduced by an additional 5 hr of fluorination. A series of experiments were then carried out in which the solids were sampled after 5 hr and 10 hr of fluorination. The plutonium concentrations were reduced to about 0.13 percent by fluorination for 10 hr at 350 C (Exp. No. 30); the plutonium was reduced to 0.17 percent by fluorination for 10 hr at 450 C (Exp. No. 32); and it was reduced to 0.088 percent by fluorination for 10 hr at 500 C (Exp. No. 23).

* In the case of the Dresden Fuel, the uranium will be less than one percent enriched.

Table 32

REACTION OF URANIUM-PLUTONIUM DIOXIDES-CALCIUM FLUORIDE^a MIXTURES WITH FLUORINE

Fluorine Recycle Rate 800 cc/min
Fluorine Pressure ~1 atmos

Exp No	Temp (C)	Time (hr)	Initial Sample						Fluorine Excess ^b Ratio	Residue				
			Residue from Exp	Wt CaF ₂ (g)	Wt U (mg)	Wt Pu (mg)	U (w/o)	Pu (w/o)		Wt (g)	Wt U (mg)	Wt Pu (mg)	U (w/o)	Pu (w/o)
7	400	2		2.68 ^c	855	38.8	15.4	0.70	37 ^e					
	500 ^d	8							292 ^e	4.55	0.91	0.82	0.020	0.018
8	400	2		3.02	935	43.6	23.4	1.09	120					
	500 ^d	22							2660	2.97	0.06	1.3	0.002	0.043
9	400	1	8 ^f	2.74	725	35	20.7	0.99	74					
	500 ^d	4							590	2.52	0.2	2.3	0.009	0.090
10	400	1	9 ^f	2.36	634	32.0	21.0	1.06	80					
	500 ^d	4							639	2.12	0.2	2.5	0.008	0.12
11	400	1	10 ^f	1.87	713	37.5	27.6	1.38	68					
	500 ^d	4							545	1.79	0.30	3.9	0.017	0.22
12	400	1	11 ^f	1.53	716	35.3	31.7	1.54	72					
	500 ^d	4							578	1.39	0.15	1.9	0.011	0.14
13	400	1	12 ^f	1.10	752	38.0	39.8	2.01	67					
	500 ^d	4							538	1.04	0.34	2.8	0.033	0.27
17	500	24	13	0.42	0.13	1.13	0.033	0.27	1 x 10 ⁵	0.6	0.05	0.5	0.008	0.08
36	450	10		2.30	683	30.4	22.7	1.01	1085	2.16	0.73	6.5	0.034	0.30
37	550	10		2.30	686	30.5	22.7	1.01	2100	2.55	7.9	7.4	0.31	0.29
45 ^g	450	10		2.12	919	42.2	29.8	1.37	785	2.18	0.2	1.9	0.008	0.088
46 ^g	550	10		2.34	1015	46.7	29.8	1.37	1380	2.65	1.8	3.2	0.066	0.12

^aThe calcium fluoride used was as follows: Experiment No. 7 - fluorspar; Experiment Nos. 8 through 17 - reagent grade CaF₂ fused in air; Experiment Nos. 36 through 46 - reagent grade CaF₂ fused in inert atmosphere.

^bFluorine Excess Ratio = $\frac{\text{Total F}_2 \text{ Circulated}}{\text{Min F}_2 \text{ Required}}$. The minimum F₂ required was calculated from the initial quantity of plutonium and the equilibrium constants for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$ given in ANL-6101, page 80.

^cInitial sample No. 7 also contained 1.97 g ZrF₄.

^dAdditional fluorination at the higher temperature made with the same sample used at the lower temperature.

^eF₂ recycle rate was 220 cc/min.

^fOne gram of mixed plutonium and uranium oxides added.

^gCalcium fluoride pretreated with UF₆.

Table 33

REACTION OF URANIUM-PLUTONIUM DIOXIDES-ALUMINUM MIXTURES WITH FLUORINE

Fluorine Recycle Rate 800 cc/min
Fluorine Pressure ~1 atmos
Aluminum Particle Size 60 mesh
Fluorination Time 10 hr

No	Temp (C)	Initial Sample					Fluorine Excess ^a Ratio	Residue				
		Wt Al ₂ O ₃ (g)	Wt U (mg)	Wt Pu (mg)	U (w/o)	Pu (w/o)		Wt Solids Recovered (g)	Wt U (mg)	Wt Pu (mg)	U (w/o)	Pu (w/o)
40	350	2.38	847	41.2	25.9	1.26	488	2.23	0.1	0.62	0.006	0.028
48 ^b	450	2.17	815	39.0	27.0	1.29	915	1.92	0.2	0.67	0.008	0.035
38	550	2.17	772	37.5	25.9	1.26	1710	2.28	0.55	1.55	0.024	0.068

^aFluorine Excess Ratio = $\frac{\text{Total F}_2 \text{ Circulated}}{\text{Min F}_2 \text{ Required}}$. The minimum F₂ required was calculated from the initial quantity of plutonium and the equilibrium constants for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$ given in ANL-6101, page 80.

^bPrefluorinated aluminum used.

Table 34

COMPARISON OF PLUTONIUM AND URANIUM CONCENTRATIONS IN
INERT SOLIDS AFTER FLUORINATION OF MIXED OXIDES^a

		Uranium%				Plutonium%			
Temp (C)	Inert Solid	Initial Sample	Fluorination Time (hr)			Initial Sample	Fluorination Time (hr)		
			5	10	15		5	10	15
350	ZrF ₄	30.6	0.12	0.097	0.10	1.40	0.40	0.18	0.22
350	ZrF ₄	24.4	0.060	0.061	-	1.19	0.18	0.13	-
450	ZrF ₄	24.4	0.062	0.060	-	1.19	0.20	0.17	-
500	ZrF ₄	30.6	0.017	0.010	-	1.40	0.30	0.088	-
450	CaF ₂	22.7	-	0.034	-	1.01	-	0.30	-
450	CaF ₂	29.8	-	0.008	-	1.37	-	0.088	-
550	CaF ₂	22.7	-	0.31	-	1.01	-	0.29	-
550	CaF ₂	29.8	-	0.066	-	1.37	-	0.12	-
350	Al ₂ O ₃	25.9	-	0.006	-	1.26	-	0.028	-
450	Al ₂ O ₃	27.0	-	0.008	-	1.29	-	0.035	-
550	Al ₂ O ₃	25.9	-	0.024	-	1.26	-	0.068	-

^a See Tables 30, 31, and 32 for additional data.

The experimental conditions and results of fluorination of the mixed oxides in the presence of calcium fluoride are summarized in Table 32. Several experiments consisted of a short initial fluorination at 400 C, followed by a longer fluorination at 500 C. Since uranium oxides react with fluorine at a faster rate than plutonium oxides, it was anticipated that this treatment would result in an initial removal of most of the uranium, creating a more favorable situation for fluorination of the remaining plutonium. The data of Table 32 indicate, however, that this treatment does not result in significantly lower concentrations of plutonium in the residual solids.

If a quantity of calcium fluoride were used to process several batches of fuel, and if plutonium did not accumulate in the solids with repeated use, the plutonium loss could be decreased. A set of fluorinations, the results of which are shown in Table 32 (Nos. 8, 9, 10, 11, 12, 13, 17), were executed to determine whether or not plutonium accumulates in the inert solids with repeated use. In each of these experiments, the residue from the previous experiment was used as the inert solid. For example, the solids fluorinated in Experiment No. 9 were prepared by mixing about 1 g of oxides with the residue of Experiment No. 8. The solids were sampled before and after each experiment and analyzed for plutonium and uranium.

The concentration of plutonium in the re-used solids increased from 0.043 percent after the first use to 0.22 percent after the fourth use. The plutonium concentration did not increase very much beyond this level after two subsequent experiments. On the basis of these results, the plutonium concentrations in a batch of calcium fluoride in a fluidized bed reactor might be expected to increase during the course of three or four usages, and to remain at that level during subsequent use. On the process scale, however, a given quantity of inert solid probably can be used only a few times because of the accumulation of fission products and the associated heat.

If the retention of plutonium were caused by a mechanism involving chemisorption, it might be possible to decrease the retention by satisfying the solid surface forces with something other than a plutonium compound. To test this possibility, a set of experiments were carried out in which calcium fluoride was exposed to uranium hexafluoride prior to use. The exposure was accomplished by mixing uranium tetrafluoride with a batch of calcium fluoride and fluorinating the material at 500 C. After this treatment, analysis of the calcium fluoride showed that the solid contained about 0.04 percent uranium. Samples of this pretreated calcium fluoride were mixed with the oxides, and fluorinated at 450 and 550 C. The plutonium concentrations after fluorination in the pretreated calcium fluoride (Nos. 45, 46) are compared in Table 32 with the results of similar experiments (Nos. 36, 37) using nontreated calcium fluoride. Fluorinations at 450 and 550 C in the presence of pretreated calcium fluoride reduced the plutonium concentrations to about 0.1 percent, which is one-third the concentrations found in the nontreated calcium fluoride. It was concluded that, although the pretreatment appears to affect the plutonium removal favorably, it does not result in a plutonium concentration in the residual solids which is low enough to be satisfactory.

The results of fluorinations of oxides using alundum as the inert solid are listed in Table 33. These fluorinations have resulted in low plutonium concentrations in the residual solids. On the basis of these results, it appears that alundum is superior to calcium fluoride and zirconium tetrafluoride as an inert solid. The results of these experiments warrant additional work to verify that plutonium concentrations in alundum can be reduced to satisfactory levels by fluorination.

The effects of time and temperature of fluorination on the concentration of plutonium and uranium remaining in inert solids after fluorination are presented in Table 34, where they can be more easily compared than in the preceding tables of data.

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

(C. Johnson, J. Stockbar, W. Gunther)

The procedures utilized in the development of fluoride volatility processes for enriched uranium-zirconium alloy fuels have recently undergone significant changes. A previous concept of this work involved aqueous dissolution of the fuel, drying of the solution and subsequent fluorination of the solids to recover the uranium, after which the solids could be discarded as waste (ANL-6145, page 114).

Currently, a processing scheme is being investigated which utilizes gas-metal reactions to convert the constituents of the alloy to compounds from which the uranium can be recovered by reaction of the uranium compound with fluorine to produce volatile uranium hexafluoride. The process may involve one of the following procedures, each of which may be accomplished in a single vessel:

- 1) direct fluorination using elemental fluorine,
- 2) reaction of the fuel with a mixture of hydrogen chloride and hydrogen fluoride followed by fluorination of the residue,
- 3) reaction of the fuel with hydrogen chloride in the lower zone of a reactor. The uranium remains behind in the lower zone as uranium tetrachloride while zirconium tetrachloride is volatilized into the upper zone of the reactor, where it is reacted with hydrogen fluoride to form zirconium tetrafluoride which condenses in the upper zone. The uranium compound in the lower zone is then reacted with fluorine to produce volatile uranium hexafluoride which is distilled from the reaction vessel.

The latter approach will be referred to as a "two-stage operation." The reactions are carried out with the alloy submerged in a fluidized bed of inert granular material which serves as a heat transfer medium for the exothermic gas-metal reactions.

A program was drawn up which considered both the fundamental and applied aspects of the work. The results were used to deduce the optimum conditions necessary for the recovery of uranium from enriched uranium-zirconium alloy fuels. A "fundamental" study was proposed to elucidate the species which resulted when the uranium-zirconium alloy fuel was reacted with various gases and gas mixtures. Knowledge of the products of these reactions would facilitate the approach to be taken for subsequent uranium recovery.

The first reaction studied in the investigation was the direct reaction of the alloy with a mixture containing 10 volume percent hydrogen chloride in hydrogen fluoride. In the second series of reactions the alloy was reacted with either hydrogen chloride or chlorine. Interest in the hydrogen chloride-hydrogen fluoride gas mixture originated from a recently reported (see ANL-6183, page 101) discovery that a 10 volume percent addition of hydrogen chloride to hydrogen fluoride greatly accelerated the reaction between hydrogen fluoride and the uranium-zirconium alloy to produce zirconium tetrafluoride.

Gas-solid reactions may be carried out in fluidized beds to control highly exothermic reactions. In this approach, the metal to be reacted is submerged in a bed of granular solids which are in constant motion about the metal. The "applied" studies were designed to answer some of the problems associated with the recovery of uranium from material, which could be utilized in inert fluidized media. Variables which were of interest include (1) temperature of fluorination, (2) time of fluorination, and (3) effect of bed material on uranium recovery.

"Fundamental" Studies

Two uranium-zirconium alloys were used in the "fundamental" investigations. One contained 5 weight percent uranium, the other 30 weight percent uranium. The alloy with a higher uranium concentration was used to facilitate identification of the uranium species involved by providing a larger concentration of the resultant uranium compound. The purities of the gases (hydrogen fluoride, hydrogen chloride, and chlorine) used in these experiments were checked by infrared analyses (where applicable) and by measurements of vapor pressure and vapor density.

The apparatus used in these experiments was a horizontal tube reactor in which the reacting gases were passed over samples contained in nickel boats within the reactor. The reactor was made from a 14-in. length of 1-in.-OD, schedule 40 nickel pipe and was heated by a resistance-wound furnace. The front end was fitted with a Teflon-gasketed, water-cooled, flanged cover and gas-entry tube. The rear of the furnace was fitted with a $\frac{1}{4}$ -in. nickel tube for gas exit and a $\frac{1}{4}$ -in.-OD nickel thermowell which extended into the reactor about $3\frac{1}{2}$ in., thus positioning the sample boat in the center of the reactor. The tube reactor was fitted with a hemicylindrical slide to allow flat-bottomed sample boats to be used. The sample boats, which were 0.8 by 4.0 by 0.2 in., were made from 16-mil nickel sheet and were welded at the corners. The various components of the apparatus were joined to a manifold which provided sources of vacuum, helium, and reacting gases, such as hydrogen chloride-hydrogen fluoride gas mixtures, hydrogen chloride, chlorine, or fluorine.

The following experimental procedure was used. A 6-g sample of alloy was degreased, weighed, and placed in a tared nickel boat, which was positioned against the thermocouple well in the tube reactor. Helium was passed over the sample while the furnace was brought to the reaction temperature. When the experimental temperature had been reached, the reacting gas (hydrogen chloride-hydrogen fluoride mixtures, hydrogen chloride, or chlorine) was substituted for helium and the flow was measured by means of a calibrated thermal flow meter. When reaction was complete, helium was again substituted for the reacting gas and the sample was cooled in a helium atmosphere. Samples of all residues were taken for X-ray diffraction analysis. In some experiments, reactions with fluorine were carried out in the same reactor after conversion of the alloy to chloride or fluoride compounds. In order to control the working atmosphere, sample loadings and transfers were made in a dry box.

The initial experiments involved conversion of a 5 weight percent uranium-zirconium alloy to fluoride solids in 4 hr at 400 C, using both a 10 and 20 volume percent hydrogen chloride in hydrogen fluoride gas mixture. The compounds formed were β -zirconium tetrafluoride and uranium tetrafluoride, irrespective of the hydrogen chloride concentration used. The resulting fluoride solids were fluorinated for 3 hr at 350 C. A removal of only 67 percent of the uranium was achieved. These results appear to be indicative of the uranium recoveries to be expected when zirconium tetrafluoride is produced simultaneously with conversion of the alloy to fluoride solids. The results differ markedly from those obtained from fluorinations of physical mixtures of uranium compounds and zirconium tetrafluoride, which will be discussed later.

In the next set of experiments, the uranium-zirconium alloy was reacted with hydrogen chloride to remove the zirconium from the uranium as volatile zirconium tetrachloride. In this reaction nonvolatile uranium chlorides were formed. Table 35 contains the results of these experiments.

Table 35

REACTION OF HYDROGEN CHLORIDE
WITH URANIUM-ZIRCONIUM ALLOY

Reaction Time: 4 hr

Reaction Temperature: 400 C

Apparatus: Horizontal Tube Reactor

Alloy Composition (w/o Uranium)	Species Found ^a
5	UOCl ₂ (UCl ₃) ^b
30	UCl ₄ (UOCl ₂ , UCl ₃) ^b

^a X-ray diffraction.

^b Species present in minor amounts are included in the parentheses.

Reaction of the 5 weight percent alloy with hydrogen chloride yielded uranous chloride as the major species, with uranium trichloride as a minor constituent. A similar reaction with the 30 weight percent alloy resulted in the formation of uranium tetrachloride as the major species, with uranous chloride and uranium trichloride present in minor amounts. Differences in alloy preparation may have led to uranium tetrachloride being present as the predominant species in one case and absent in the other. The presence of oxygen as a constituent in the resultant compounds may have resulted from oxygen, as the oxide or free oxygen, in the alloy. The volatilized zirconium tetrachloride was analyzed and found to contain 0.014 and 0.017 weight percent uranium for the 5 weight percent and 30 weight percent alloys, respectively.

Additional experiments were run to determine to what extent the uranium compounds produced in the previous experiments could be reacted with fluorine to form volatile uranium hexafluoride. Duplicate experiments of those just described were performed. The alloy samples were placed in small nickel foil boats within the reactor. After hydrochlorination of the uranium-zirconium alloy, the nickel boat and its contents were dissolved in dilute nitric acid and analyzed for uranium. These results are given in Table 36. For both experiments about 0.5 percent of the uranium initially present remained after fluorination.

Table 36

FLUORINATION OF URANIUM RESIDUE
FROM HYDROCHLORINATION OF
URANIUM-ZIRCONIUM ALLOY

Fluorination Time: 4 hr
Fluorination Temperature: 350 C
Apparatus: Horizontal Tube Reactor

Alloy Composition (w/o Uranium)	Uranium, (mg)	
	Initial	Final
5	410 ^a	2.6
30	1800 ^a	9.5

^a Calculated values based on concentration in the alloy.

"Applied" Studies

The applied studies can be subdivided further into those experiments which elucidated the variables affecting uranium recovery from mixtures of uranium compounds and bed materials, and those studies which tested the direct fluorination process approach using laboratory-scale reactors.

Materials, used in experiments assessing the variables affecting uranium recovery from bed materials, were physical mixtures of uranium tetrafluoride, uranyl fluoride, or uranium dioxide mixed with either zirconium tetrafluoride or calcium fluoride. These mixtures were prepared by mixing reagent grade materials in quantities such that the final uranium concentration was about one percent. This concentration was chosen as typical of what might be found in process applications. The solids were mixed a minimum of 6 hr in a mechanical blender to insure homogeneity of the final material.

Experiments were carried out in a horizontal tube reactor similar to that used in the "fundamental" studies. In these experiments fluorine and chlorine trifluoride were the fluorinating gases used.

The experimental procedure was as follows. About 7 g of material to be fluorinated was weighed into a tared nickel boat, which was positioned against the thermocouple well in the tube reactor. Helium was passed over the sample while the furnace was brought to the reaction temperature. Fluorine was then substituted for helium and the gas flow was measured by means of a calibrated thermal flowmeter. At the completion of the experiment, helium was substituted for fluorine and the sample was allowed to cool in a helium atmosphere. In those experiments in which chlorine trifluoride was used, the procedure was the same except for the substitution of chlorine trifluoride for fluorine. Safe handling practices for chlorine trifluoride as outlined in ORNL report K-1416 were rigorously followed. Uranium concentration in the solids was obtained by X-ray fluorescence analysis (see ANL-6117, page 19) of the initial material and of the final residue taken from the boat after fluorination.

Early experimental work indicated that, at reaction temperatures above 400 C and in beds greater than $\frac{3}{16}$ in. in depth, caking of the sample occurred. To reduce the gas diffusion barrier, caused by caking, the sample size was reduced so that the bed depth approximated $\frac{1}{32}$ in.

Results from experiments on the effect of temperature on uranium removal from physical mixtures of uranium tetrafluoride and zirconium tetrafluoride are given in Table 37. Best removal of uranium, using fluorine, was obtained at 350 C. As the temperature of fluorination was increased above 350 C, greater retention of the uranium by zirconium tetrafluoride was noted.

For comparative purposes, fluorinations have been run to test the relative fluorinating ability of chlorine trifluoride as compared with that of fluorine. These data, shown in Table 37, indicate that the optimum fluorination temperature for uranium removal is 200 C when chlorine trifluoride is used. The rate of reaction between chlorine trifluoride and uranium tetrafluoride is fast compared with the rate with fluorine at the lower temperature

Table 37

FLUORINATION OF URANIUM TETRAFLUORIDE-ZIRCONIUM
TETRAFLUORIDE MIXTURES: EFFECT OF TEMPERATURE
AND FLUORINATING GAS ON URANIUM REMOVAL

Initial Uranium Concentration: 0.98 w/o
 Fluorination Time: Chlorine Trifluoride, 1 hr
 Fluorine, 3 hr
 Fluorinating Gas Flow Rate: 160 cc/min
 Apparatus: Horizontal Tube Reactor

Final Uranium Concentration Using Indicated
Gas As the Fluorinating Agent

Temp (C)	Chlorine Trifluoride (% U)	Fluorine (% U)
100	0.018	-
200	0.010	-
250	0.024	0.074
350	0.035	0.012
450	0.046	0.044
525	0.071	0.083
600	0.081	0.12

Labaton²⁷ has estimated that at 265 C fluorination by chlorine trifluoride is 160 times faster than that using fluorine. This difference in reaction rate does not subsist with increasing temperature, as the activation energy for the respective fluorinating agents differ considerably. For fluorine $E_a \approx 19$ kcal/mole, and for chlorine trifluoride $E_a \approx 3$ kcal/mole.

Table 38 contains data which are the results of the fluorination of mixtures of calcium fluoride-uranyl fluoride and calcium fluoride-uranium tetrafluoride. It is seen that similar results are obtained, namely, that at higher temperatures greater retention of uranium by the calcium fluoride was noted.

Additional experiments have been run on mixtures of uranium dioxide and zirconium tetrafluoride. The data appear in Table 39. It has been shown (see ANL-5924, pages 28 to 33) that uranyl fluoride is an intermediate product in the reaction between uranium dioxide and fluorine. In carrying out a fluorination in which an intermediate uranium species is known to occur, promotion of an interaction between the uranium and zirconium might result. As can be seen from the data, no difficulty was encountered with respect to uranium removal at 350 and 450 C.

²⁷ Labaton, V. Y., J. Inorg. Nucl. Chem. 10, 86 (1959).

Table 38

FLUORINATIONS OF CALCIUM FLUORIDE-URANIUM TETRAFLUORIDE,
AND CALCIUM FLUORIDE-URANYL FLUORIDE MIXTURES:
EFFECT OF TEMPERATURE ON URANIUM REMOVAL

Initial Uranium Concentration: 0.94 w/o
Fluorine Flow Rate: 170 cc/min
Time of Fluorination: 2 hr
Apparatus: Horizontal Tube Reactor

Exp	Material	Temp	% U
74	CaF ₂ -UF ₄	350	0.012
78	CaF ₂ -UF ₄	450	0.012
79	CaF ₂ -UF ₄	525	0.038
80	CaF ₂ -UF ₄	600	0.073
75	CaF ₂ -UO ₂ F ₂	450	0.012
76	CaF ₂ -UO ₂ F ₂	525	0.016
77	CaF ₂ -UO ₂ F ₂	600	0.054

Table 39

FLUORINATION OF URANIUM DIOXIDE-ZIRCONIUM TETRAFLUORIDE
MIXTURES: EFFECT OF TEMPERATURE ON URANIUM REMOVAL

Initial Uranium Concentration: 0.49 w/o
Time of Fluorination: 3 hr
Apparatus: Horizontal Tube Reactor

Exp No.	Temperature (C)	Final Uranium Conc (% U)
43	250	0.12
42	350	0.011
41	450	0.016

Results from experiments on the effect of time of fluorination on uranium removal from mixtures of uranium tetrafluoride-zirconium tetrafluoride are given in Table 40. The experiments were run at two temperatures with essentially the same results. The results of these experiments, in which thin beds of physical mixtures of the solids were reacted with fluorine, indicate that a minimum of 3 hr at 350 C appears necessary to achieve good uranium removal from the solids.

Table 40

FLUORINATION OF ZIRCONIUM TETRAFLUORIDE-URANIUM
TETRAFLUORIDE MIXTURES: EFFECT OF TIME OF
FLUORINATION ON URANIUM REMOVAL

Initial Uranium Concentration: 0.98%
Fluorine Flow Rate: 160 cc/min
Apparatus: Horizontal Tube Reactor

Temp (C)	Time (hr)	Final Uranium Conc (% U)
350	1	0.021
350	3	0.012
450	1	0.083
450	3	0.044

The second area of applied experimental study centered around the testing of the various direct fluorination process schemes previously mentioned. The objective of this approach was to convert the alloy fuel to granular solids by a simple process, and then to react the uranium in the residue with fluorine, producing volatile uranium hexafluoride. The experiments were carried out in a laboratory-scale fluid-bed reactor using "single-stage" or "two-stage" operation. For single-stage experiments, all reactions were carried out in the heat transfer bed of the lower zone. For two-stage experiments, volatile zirconium tetrachloride was formed in the lower zone and converted to solid zirconium tetrafluoride in the upper zone by reaction with hydrogen fluoride.

Two materials were used as inert solids in these experiments. They were commercial-grade calcium fluoride (fluorspar) of -60 +120 mesh size and refractory grain alundum of -60 +80 mesh size.* Five weight percent uranium-zirconium alloy was used.

A vertical tube reactor, in which the reaction gases passed upward through the solid, was used for these experiments. The reactor, shown in Figure 37, was fabricated from a 15-in. length of 1-in.-OD, schedule 40 nickel pipe. A porous Monel disc was fitted to the bottom of the reactor to serve both as a gas distributor plate and as a support for the sample. A thermocouple well was positioned $1 \frac{1}{2}$ in. above the Monel disc, parallel to the disc, and extended into the reactor $\frac{3}{8}$ in. A gas-entry line was positioned 10 in. up from the bottom of the reactor. This allowed entrance of anhydrous hydrogen fluoride used for conversion of chlorides to fluoride, when "two-stage" type experiments were run. A resistance-wound tube furnace was

* Alundum has been successfully used at BNL in similar experiments.

FIGURE 37
TWO-STAGE REACTOR FOR CONVERSION OF
URANIUM-ZIRCONIUM ALLOY TO FLUORIDE SOLIDS

used to heat the reactor. The exit line from the reactor led to a gas-disposal system. This consisted of an aqueous caustic solution when hydrogen chloride-hydrogen fluoride gas mixtures were used and an activated alumina trap when fluorine was used.

The experimental procedure was essentially the same for either the single-stage or the two-stage operation. For single-stage experiments, all reactions were carried out in the solid bed. The reactor was loaded with 20 g of uranium-zirconium alloy and 100-g charges of the inert solid to be tested. The reacting gas entered the bottom of the reactor and passed upward through the bed. Fluorine was used initially as a reactant; subsequently various hydrogen chloride-hydrogen fluoride gas mixtures were used. The latter experiments were done to demonstrate the

conversion of the alloy to fluoride solids, from which the uranium could be removed by fluorination to the volatile uranium hexafluoride.

In the two-stage operation, the reactor was charged in a similar fashion, and a uranium-zirconium alloy was reacted with hydrogen chloride in the lower zone of the reactor. The volatile zirconium tetrachloride formed was converted to zirconium tetrafluoride by reaction with hydrogen fluoride in the upper zone of the reactor. The zirconium tetrafluoride was collected on nickel wool which separated the two stages. The hydrochlorinations were run at gas velocities (about 0.02 ft/sec) such that the solid bed in the lower zone remained static at all times. The hydrogen fluoride gas velocity was 0.6 of the hydrogen chloride gas velocity. When hydrochlorination was complete, the reactor was placed in a dry box, disassembled, and the solid bed was removed and thoroughly mixed. The bed was then replaced in the reactor for fluorination. The zirconium tetrafluoride was removed from the upper zone of the reactor in those experiments in which fluidization of the bed was attempted during reaction with fluorine.

Direct fluorination of the uranium-zirconium alloy using fluorine gas resulted in poor uranium removal. Laboratory experiments with the metal fluorine reaction have shown the zirconium tetrafluoride film to be porous and nonprotective in nature. However, experiments, carried out in the vertical reactor in the presence of calcium fluoride as the bed material, have shown interaction between the zirconium tetrafluoride and the bed

material. The result of this interaction is the formation of a solid barrier which significantly lowers the fluorine-penetration rate, and contributes to poor uranium removal.

Typical of what might be expected are the following results. A reaction with fluorine was carried out for 7 hr at 400 C with calcium fluoride as the bed material. About 40 percent of an initial 36-g charge of 5 weight percent uranium-zirconium alloy had reacted. Analysis of the bed material indicated 0.024 weight percent uranium. The zirconium tetrafluoride crust adhering to the alloy was found to contain 0.57 weight percent uranium.

It was recently reported (see ANL-6145, page 119) that a 10 volume percent addition of hydrogen chloride in hydrogen fluoride greatly accelerated the reaction of hydrogen fluoride with Zircaloy. The reaction proceeds readily above 350 C. Data from laboratory experiments utilizing this approach are shown in Table 41. For the most part, very little success was achieved with this approach. Again, problems were encountered with solid buildup around the alloy, which significantly reduced the penetration rate.

Table 41

REACTION OF HYDROGEN CHLORIDE-HYDROGEN FLUORIDE
GAS MIXTURES WITH URANIUM-ZIRCONIUM ALLOY

Exp No.	HCl Conc (v/o)	Time (hr)	Temp (C)	Initial Weight		Alloy Conversion (%)
				CaF ₂ Bed Material (g)	U-Zr Alloy (g)	
45 ^a	20	3.0	400	100	20.8	4.1
47 ^b	12	5.6	400	100	20.1	3.2
48	9.8	3.3	525	Expt 47 ^c	18.5	10.2
49	10	5.0	550	100	15.9	5.0
50 ^d	8.2	3.0	500	None	5.07	19.4
51 ^d	9.1	2.6	500	None	5.10	21.6
52 ^d	11	2.0	500	None	5.10	21.5

^a Total gas flow diluted 50 v/o with helium; residual alloy coated with CaF₂-ZrF₄ mixture.

^b Residual alloy coated; bed material loose.

^c Bed material was residual solids from Expt 47.

^d Adherent fluoride coat on alloy.

Because the experiment in the "single-stage" reactor resulted in poor uranium removal, attention was directed to the use of the two-stage approach. Hydrogen chloride was reacted with the uranium-zirconium alloy, submerged in an inert bed, in the lower zone of the reactor, and the volatile zirconium tetrachloride formed was converted to zirconium tetrafluoride in the upper zone. When hydrochlorination was complete, the hydrogen fluoride was shut off and fluorine was substituted for hydrogen chloride. Data from these experiments are given in Table 42. Removal of the uranium from the bed material was very good. The results of Experiments 56 and 78 indicated there was some entrainment of uranium solid compounds in the hydrogen chloride gas stream when high gas velocities were used. Previous experiments indicate that there was no formation of a volatile uranium compound during the hydrochlorination reaction. The lower value for uranium removal in Experiment 56 may be due to short fluorination time. Because the initial uranium concentration in this experiment was much higher than normally encountered, a longer fluorination time may have been required.

Table 42

FLUORINATION OF URANIUM FROM BED MATERIAL IN
A TWO-STAGE REACTOR AT 350 C

Material fluorinated was solids remaining in lower
zone of reactor after hydrochlorination

Exp No.	Fluorination Time (hr)	Bed Material	Uranium Concentration (%)		Uranium Conc in ZrF ₄ in Upper Stage (w/o)
			Initial	Final	
56	3	CaF ₂	4.0 ^a 0.2 ^b	62 x 10 ⁻³ ^c	2 x 10 ⁻³
69	5	Alundum	(~1.0) ^e	5.2 x 10 ⁻³ ^c 4.0 x 10 ⁻³ ^c	-
75	7	Alundum	2.0	12 x 10 ⁻³ ^d	-
78	5	Alundum	2.0	6.8 x 10 ⁻³ ^d	60 x 10 ⁻³
81	5	Alundum	2.0	43 x 10 ⁻³ ^d	6 x 10 ⁻³
84	5	CaF ₂	(~1.5) ^e	0.11 ^d	-

^a Concentration of lower fraction of bed; bed divided into three fractions for analysis; lower fraction fluorinated.

^b Concentrations of middle fraction of bed.

^c Fluorinations of thin beds in flat boats.

^d Fluorination in a vertical reactor. Materials were mixed in a dry box after hydrochlorination and returned to the lower zone of the reactor for reaction with fluorine. Previous experiments have shown that there was no formation of volatile uranium during the hydrochlorination reaction.

^e Calculated value.

It has been demonstrated that, for optimum recovery of uranium from enriched uranium-zirconium alloy fuels, it is best to dechlorinate and remove the zirconium by hydrochlorination at or above 350 C. This results in removal of zirconium as volatile zirconium tetrachloride. The uranium remains behind in the form of nonvolatile uranium chlorides. The hydrochlorination of the zirconium and the subsequent fluorination of the uranium chlorides can be carried out in a fluidized bed of granular solids. Of those bed materials tested, alundum (refractory aluminum oxide), was most satisfactory. This is in essential agreement with the results obtained at Brookhaven National Laboratory.²⁸ Poorer results were obtained when zirconium tetrafluoride was included in the bed material. Based on the amount of uranium remaining in the bed, uranium recoveries of 99.5 percent were achieved when alundum was used as the bed material. Experiments, with physical mixtures of uranium fluorides and zirconium tetrafluoride, indicated that the optimum fluorination temperature using fluorine is 350 C. When chlorine trifluoride was used as the fluorinating agent, best uranium removals were obtained at 200 C.

3. Decomposition of Plutonium Hexafluoride at 80 C (L. Trevorrow, W. Shinn)

Plutonium hexafluoride decomposes to plutonium tetrafluoride and fluorine. The rate of the decomposition reaction was studied at temperatures between 140 and 170 C, and the results were reported in ANL-6333, page 137. A processing application is being considered which involves the use of plutonium hexafluoride vapor at a temperature lower than any used in the rate experiments previously reported. This application has prompted the determination of the rate of decomposition of plutonium hexafluoride at a pressure of about 100 cm and a temperature of 80 C.

The experimental procedure used in this work was similar to that described previously in ANL-6333, page 134: The decomposition was carried out in a 53-ml nickel vessel. An experiment was initiated by allowing plutonium hexafluoride to expand into the evacuated vessel at the reaction temperature. When the expansion was complete, a valve on the vessel was closed, and the decomposition was allowed to proceed for a measured time interval. The reaction was stopped by quenching the vessel in liquid nitrogen. The vessel was weighed before filling with plutonium hexafluoride; it was weighed again after the quenching to determine the initial charge of plutonium hexafluoride. The vessel was then evacuated again to remove the remainder of the plutonium hexafluoride and the fluorine formed during the reaction. The vessel was weighed again to

²⁸Reilly, J. J., Regan, W. H., Wirsing, E., and Hatch, L. P., Status Report: Reprocessing of Reactor Fuels by Volatilization through the Use of Inert Fluidized Beds, BNL-663 (T-217) (May 1961).

determine the quantity of plutonium tetrafluoride formed in the reaction. The volume of the vessel, the reaction temperature, and the weights of plutonium hexafluoride were used together with the ideal gas law to calculate the initial and final pressures of plutonium hexafluoride. In contrast to the previous work, the nickel vessel was not treated with fluorine prior to use with plutonium hexafluoride. The only conditioning of the vessel consisted of exposure to plutonium hexafluoride vapor at 25 C for 3 hr, during which time about 7 mg of plutonium tetrafluoride deposited in it.

The results of four experiments are listed in Table 43. Pressures were not measured directly, but were calculated from other observed measurements as outlined above. The first experiment gave a higher reaction rate than any of the others. This may have been caused partly by reaction between plutonium hexafluoride and the nickel wall of the vessel, since the vessel had not been conditioned with fluorine prior to use. The reaction rate was lower in the second experiment, but the last three experiments showed successive increases in rate.

Table 43

RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE VAPOR

Vessel Volume: 53 ml
 Temperature: 80 C
 Static System
 Initial Pressure: ~100 cm^b
 Final Pressure: ~98 cm^b

Reaction Time (hr)	PuF ₄ Initially in Reaction Vessel (g)	PuF ₆ Decomposed (g)	Integral Rate	
			Observed ^c (%/day)	Predicted ^d (%/day)
25	0.0071 ^a	0.0225	2.4	4.6
46	0.0272	0.0202	1.2	4.5
71	0.0452	0.0319	1.3	4.6
47	0.4050	0.0301	1.8	4.6

^aPuF₄ formed during initial treatment of vessel with PuF₆ at 25 C for 3 hr.

^bPressures were not observed directly, but were calculated from weights of plutonium hexafluoride, the vessel volume, and the reaction temperature, using the ideal gas law.

^cThis is a total rate of decomposition, a large fraction of which is probably due to radiation decomposition by alpha particles.

^dPredicted by extrapolation of experimental data reported in ANL-6333, page 137.

The increase in reaction rate was probably caused by an increase of the surface area of solid plutonium tetrafluoride in the reaction vessel. Previous work (see ANL-6333, page 136) indicated that part of the decomposition was attributable to heterogeneous decomposition of plutonium hexafluoride on the surface of plutonium tetrafluoride, and that the rate increased as the surface of plutonium tetrafluoride increased in a vessel. Reaction rates for plutonium hexafluoride at 80 C predicted by extrapolation of data from the previous work are also included in Table 43. The observed rates for the last three experiments vary from 1.2 to 1.8 percent per day. The predicted results are about 4.6 percent per day. The disagreement between the predicted and observed rates is most likely caused by the difference in the surface area of plutonium tetrafluoride in the present reaction vessel compared with that used in the previous work.

Inherent in the observed decomposition rate is the radiation decomposition rate due to alpha particles emitted by plutonium-239, the predominant plutonium isotope in the material used in this work. The rate of radiation decomposition by alphas is possibly of the same order of magnitude as the total decomposition rate observed at 80 C. The literature value²⁹ for the rate of such decomposition of plutonium hexafluoride vapor in nickel equipment is 0.35 percent per day. This value was determined at a partial pressure of 21 to 28 mm, whereas all of the experiments reported here were carried out at a much higher pressure, about 100 cm. Since the rate of decomposition by alpha particles probably increases with pressure, the rate which occurred in the present experiments is assumed to be higher than 0.35 percent per day. Because of the uncertainty in the rate of decomposition at a pressure of 100 cm, it is impossible to correct the observed rates to obtain a rate attributable to thermal decomposition alone at 80 C.

B. Engineering-scale Investigations of Fluoride Volatility Processes (A. A. Jonke)

1. Direct Fluorination of Uranium Oxide Fuels: Fluorination of Uranium Dioxide Pellets (W. J. Mecham, J. Gabor, R. Kinzler, A. Rashinskas, J. Wehrle)

The direct fluorination process applied to uranium dioxide reactor fuel is being studied in pilot-plant experiments. Emphasis has been placed on demonstrating temperature control and optimum processing conditions. Inert material fluidized in the voids of the oxide pellet bed has been used to improve heat transfer during fluorination.

²⁹Weinstock, B., and Malm, J. G., J. Inorg. and Nuclear Chem. 2, 380 (1956).

In the previous quarterly report (ANL-6333, pages 167 to 177), results were summarized for several experiments in which the fluorination of approximately 4-kg batches of uranium dioxide pellets was carried to completion in a 3-in.-diameter air-cooled reactor. In these runs the temperature was controlled at 500 C with inlet fluorine concentrations of 20 to 48 mol percent. Nitrogen gas at a constant 0.25 ft/sec was used to dilute the fluorine, and total gas rates ranged from 0.37 to 0.5 ft/sec. With the use of reactor-grade pellets of different types and sizes, the overall batch fluorination times observed were from 5.6 to 12 hr. These times were regarded as reasonably short for practical application. A major objective was the demonstration of control techniques for this exothermic reaction. Two techniques of automatic temperature control, regulation of coolant air flow, and of inlet fluorine flow were shown to be feasible. The latter method was faster and more positive in its action, and was required for close control at maximum reaction rates. Of the types of pellets used, the least reactive variety ($\frac{1}{2}$ -in. diameter and height, hydrogen-fired) was considered the most typical reactor fuel grade, and was selected for subsequent experimental study.

In the present period, additional experiments have been carried out to determine the most favorable fluorination conditions. In these more recent runs, several modifications of fluorination conditions were made. The total gas rate was increased to maintain better fluidization and better heat transfer. Oxygen rather than nitrogen was employed as fluorine diluent, and condenser off-gas was recycled to achieve maximum overall fluorine economy. In addition to complete-fluorination batch runs, several shorter-time runs were carried out to obtain comparative fluorination rates for temperatures from 350 to 500 C. In the latter series of runs, an inert fluidized bed of alundum grain was utilized instead of the calcium fluoride employed in earlier runs.

Batch Runs with an Inert Fluid Bed at 500 C

Four batch runs were carried out in which charges of $\frac{1}{2}$ -in. hydrogen-fired pellets (Type N-2)* were completely fluorinated at 500 C in a fluid bed of inert calcium fluoride. These conditions are presently considered to be most favorable for the rapid, controlled fluorination of pellets of reactor-grade fuel.

The fluid-bed material in these runs was fused, reagent-grade calcium fluoride, ground to -40 +140 mesh. The same batch of calcium fluoride was re-used for each run, since there was no noticeable deterioration of this material during the fluorination.

*Batch 2 of Numec pellets.

Automatic temperature control during the runs was achieved by regulation of the fluorine inlet flow. The control system consisted of a standard single-point potentiometer recorder-controller, with proportional and reset functions. A pneumatic valve positioner operated a control valve regulating the flow of fluorine from a constant-pressure surge tank. Heat was carried away from the outer (finned) surface of the reactor by coolant air. A blower with a flow control valve was provided with a maximum capacity available of about 400 cu ft/min. For startup and for conditions of low reaction rate, electric resistance heaters bonded to the outer reactor surface were used to maintain the desired temperature. Heater and blower controls were set manually, since rapid and positive temperature control during the runs was achieved by the automatic fluorine regulation. The required adjustments of the heaters and blowers were infrequent because of the fairly uniform reaction rate obtained during most of the batch-processing time.

The operating conditions and results obtained for these batch fluorinations are summarized in Table 44. Operating conditions were similar except for the gas rates and the type of gas used to dilute the fluorine. The lower gas rate used in Run 31 (and some earlier runs) is associated with poor heat transfer presumably due to poor fluidization. In later runs, a total gas velocity of greater than 0.6 ft/sec (based on the reactor cross-sectional area and gas at 500 C) appeared capable of maintaining adequate fluidization.

The use of oxygen rather than nitrogen as a diluent gas resulted in higher overall fluorination rates by a factor of 2 to 3, as shown in Table 44. This effect is presumably due to the reaction of oxygen with the pellets to form fines, which fluorinate rapidly due to their high specific surface area. No operational difficulties were encountered with these fines. Fines elutriated from the fluid bed were trapped on the sintered nickel filters and fell back into the reaction zone when the filters were blown back. Blow-back was accomplished by a one-second reverse gas flow at the filter every 15 min.

Two sets of temperature measurements are of interest in these runs. One concerns the amount of fluctuation of the control temperature during the runs, and is an indication of the precision of temperature control. Another concerns the temperature differences that exist at various locations; these differences indicate the quality of fluidization and of heat transfer.

In the case of constancy of the control temperature, the temperature record of these runs showed maximum cycles of temperature fluctuations of ± 30 C in Run 33, where fluidization was poor. Minimum cycles of about ± 5 C (or less) were observed during most of Runs 32 and 34, in which fluidization was good.

Table 44

RESULTS OF BATCH FLUORINATION OF URANIUM DIOXIDE PELLETS
IN A FLUID-BED REACTOR

Operating Conditions:

Three-inch-diameter air-cooled reactor.

Six-inch-deep bed of $\frac{1}{2}$ -in. diameter and height UO₂ pellets
(4.5 kg H₂-fired, Type N-2).

Thirty-six-inch-deep inert fluid bed of CaF₂.

Control temperature: 500 C; fluorination carried to completion.

Run No.	Diluent Gas Introduction ^a	Average Inlet F ₂ Conc (%)	Average Total Gas Rate (ft/sec) ^b	Extent of Reaction and Time of Batch Fluorination	Overall F ₂ Efficiency (%)	Overall UF ₆ Collection Rate [lb UF ₆ /(hr). (sq ft reactor cross section)]	Fluidization Heat Transfer ^c
UOF-31	O ₂ at 0.20 cu ft/min	45	0.32	96% reacted in 11.5 hr	45	27	poor
UOF-32	N ₂ at 0.40 cu ft/min	42	0.62	80% reacted in 12 hr	16	18	good
UOF-33	O ₂ in recycle at 0.60 cu ft/min	~40	0.57 - 0.75	80% reacted in 4.8 hr 95% reacted in 7.0 hr	71	35	poor
UOF-34	O ₂ in recycle at 0.60 cu ft/min	42	0.6 - 0.7	80% reacted in 4.6 hr 95% reacted in 6.0 hr	62	41	good

^aVolumetric rate at 1 atmos and 25 C.

^bSuperficial gas velocity (1 atmos 500 C), based on reactor cross-sectional area.

^cGood heat transfer = low temperature differentials between center-of-bed and wall temperatures (25 to 50 C);
Poor heat transfer = high temperature differentials between center-of-bed and wall temperatures (~400 C).

These cycles had a period of about 1 min, and are considered characteristic of the reactor configuration and of the mode of automatic fluorine control. In all cases the control temperature was measured by a thermocouple in a $\frac{3}{8}$ -in.-OD nickel tube ($\frac{1}{16}$ -in. wall) entering the reactor from the bottom. The thermocouple was located as nearly as possible to the center of the pellet bed.

In the case of temperature differences, observations were made of interior temperatures at the center of the pellet bed with a bare-wire thermocouple and at the reactor wall with a $\frac{1}{4}$ -in.-OD nickel thermowell entering horizontally. The differences between these temperatures and the control thermowell temperatures showed the magnitude of the temperature gradients in the reaction zone. Outer skin temperatures of the reactor at the same elevation were also measured, giving an overall gradient. Poor heat transfer was shown in Runs 31 and 32 by a temperature differential of over 400 C between the center of the bed and the reactor wall. In Runs 32 and 34 good heat transfer was shown by low values of the differential, the most significant ones being in the range of 25 to 50 C. Also in Runs 32 and 34, the bare-wire (20-ga.) thermocouple in the center of the bed gave a measurement nearly identical with the control thermowell. This served as a confirmation of the high heat transfer coefficients and the relative uniformity of temperature expected with good fluidization.

The poor fluidization in Runs 31 and 33 is attributed to initial temperature surges due to sudden introduction of oxygen during the fluorination. Severe caking encountered in Run 31 is also believed due at least in part to poorer fluidization accompanying the lower gas rate. Run 32 showed that good fluidization could be maintained at a higher gas rate during batch fluorination under the selected conditions of temperature and fluorine concentration, and Run 34 showed also that fluidization could be maintained with oxygen diluent at high fluorination rates. To avoid initial temperature surges, in Run 34 the oxygen was introduced gradually by displacement of nitrogen in a recycle system. A schematic diagram of the recycle flow system is shown in Figure 38.

FIGURE 38
SCHEMATIC DIAGRAM OF EQUIPMENT
FOR DIRECT FLUORINATION OF URANIUM DIOXIDE

The uranium hexafluoride production during Run 32 is shown in Figure 39. The production rate is indicated both by the rate data obtained from incremental changes of weight of uranium hexafluoride collected in the condenser in half-hour periods and by the slope of the cumulative collection plot. The decrease in rate shown in Figure 39 is attributed to the decrease in pellet surface area. Because of the use of nitrogen diluent, very little fines formation was involved in this run.

FIGURE 39
RATE OF URANIUM HEXAFLUORIDE
PRODUCT COLLECTION FOR RUN UOF-32

FIGURE 40
FLUORINE INLET CONCENTRATION AND FLUORINE
EFFICIENCY FOR RUN UOF-32

Samples of inlet and off-gas were analyzed for fluorine during the runs by a mercury reaction technique. The efficiency of fluorine utilization was calculated by the formula

$$\frac{\text{fluorine in} - \text{fluorine out}}{\text{fluorine in}}$$

Inlet fluorine concentrations and fluorine efficiencies in Run 32 are plotted in Figure 40.

The uranium hexafluoride production during Run 34 is shown in Figure 41. The inlet and outlet fluorine concentration together with the calculated fluorine efficiency are plotted in Figure 42. The higher rates obtained here indicate that the oxygen reacted with the

uranium dioxide pellets to form higher oxides which spalled off the pellet surface. The fines produced by the oxidation apparently presented a fairly constant surface area for the fluorine reaction. The resulting nearly uniform rate of uranium hexafluoride production is evident from the slope of the cumulative gain of product shown in Figure 41.

The percent fluorine utilization during Run 34 (see Figure 42) showed a decrease as the run progressed and as the pellet bed was depleted. High efficiencies, of the order of 90 percent, were indicated for about the first half of the reaction, and the efficiency fell to zero at the end of the fluorination.

FIGURE 41
URANIUM HEXAFLUORIDE COLLECTION
AND FLUORINE ADDITION FOR RUN UOF-34

FIGURE 42
ANALYSIS OF FLUORINE STREAMS AND FLUORINE
UTILIZATION DURING URANIUM DIOXIDE PELLET
FLUORINATION IN RUN UOF-34

Samples of the fluid bed were taken during Runs 31, 32, and 34. These were analyzed for uranium content, and the results are shown in Figure 43. In the two runs (31 and 34) made with oxygen diluent, the uranium concentration in the fluid bed went above 5 weight percent during the high rate period, whereas in the nitrogen diluent run the concentration remained below 0.07 weight percent. The low uranium concentration in Run 34 for the first half hour was probably due to the slow buildup of oxygen during this initial period. This would be expected from the startup technique. The high initial uranium concentration in Run 31 is attributed to the different method of startup, in which oxygen was introduced (at 500 C) before the fluorine. The uranium concentration in Run 34 fell off sooner than in Run 31; this was probably due to the somewhat higher fluorine/oxygen ratios in Run 34.

The overall fluorine efficiencies for these batch runs were calculated from the total uranium hexafluoride product collection and the total fluorine input; values are reported in Table 44. The highest efficiency was 71 percent, achieved in a gas-recycle run. Some improvement may be possible by more careful programming of fluorine introduction, particularly near the end of the batch fluorination, where little uranium remains to react with the fluorine.

Batch Run without an Inert Fluid Bed at 500 C

The inert fluidized bed has the advantages that it improves heat transfer and hinders the elutriation of uranium fines. However, because any inert material (a) adsorbs some uranium and plutonium and reduces product recovery, (b) restricts the gas velocities to the range suitable for fluidization, and (c) adds to the system material susceptible

to bed caking, fluorination without an inert fluidizable medium has been given some consideration as an alternative technique. Previously (see ANL-6333, page 174), the results of a batch fluorination of uranium dioxide without an inert fluid bed at 500 C with a fluorine-nitrogen gas mixture were described. In the present period a similar run was made with a fluorine-oxygen gas mixture, using the gas-recycle technique described above.

In this run (UOF-35), the pellet charge was the same as for the runs reported in Table 44. The reactor was brought up to 500 C under nitrogen recycle at 0.3 cu ft/min. Fluorine was then introduced and the rate of fluorine introduction was used to control the temperature, by the same method as described above. The low gas rate was selected to minimize elutriation of fines from the reaction zone. Even with the buildup of oxygen, after an hour the rate of uranium hexafluoride product ion was rather low (about one lb/hr) and the gas-recycle rate was increased to 0.6 cu ft/min to improve heat transfer and allow a more rapid reaction. At this higher gas rate, the uranium hexafluoride product collection rate increased to about 1.5 lb/hr. This gas rate was held to the end of the run. Production rates during the run are plotted in Figure 44. The slope of the curve of cumulative product collection indicates a fairly constant rate of uranium hexafluoride formation. This effect is apparently typical of runs in which oxygen is the fluorine diluent. Evidently the oxygen causes the pellets to disintegrate to fines which present a fairly uniform surface area for fluorine reaction. The fluorination was complete in 10 hr with an overall fluorine utilization of 74 percent and an overall average rate of uranium hexafluoride production of 25 lb UF_6 /(hr)(sq ft reactor cross section).

FIGURE 44
URANIUM HEXAFLUORIDE COLLECTION
AND FLUORINE ADDITION FOR RUN UOF-35

Inlet and outlet gas samples were taken during the run and analyzed for fluorine concentration; these results, together with calculated values of fluorine efficiency during the run, are shown in Figure 45. Although a final gas sample failed to show the expected low fluorine efficiency, this may have been an analytical error. Both uranium hexafluoride collection and subsequent examination of the reactor showed complete fluorination and very little unreacted residue. No operational problems with fines were encountered.

FIGURE 45
ANALYSIS OF FLUORINE STREAMS FOR RUN UOF-35

In this run the fluorination time was about 50 percent longer than in a fluid-bed run (UOF-34), and the temperature distributions were quite different. As in other runs, the control thermocouple was located in a vertical thermowell and a bare-wire thermocouple was also used to measure the bed temperature at the bed center. The temperature of the bare-wire thermocouple cycled between 500 and 850 C as the control thermocouple cycled 30 C. The relatively poor heat transfer to the thermowell presumably resulted in the thermowell reading an average bed temperature. In the presence of an inert fluid bed, the above two thermocouple readings would have been the same. The relatively poor heat transfer conditions were also shown by the low reactor wall temperature (65 C) maintained during the run, indicating an overall temperature gradient of about 800 C. Although attack of the bare-wire thermocouple in the center of the bed was severe, no attack was observed on the reactor walls. With such a low wall temperature, the corrosion at the wall would be expected to be negligible.

Effect of Temperature on Fluorination Rate

In all the pilot-plant fluorination studies reported above, the control temperature has been 500 C. This temperature has appeared to be optimum from the standpoint of maximizing the reaction rate while still allowing a long equipment life. Also, in previous runs either magnesium fluoride or calcium fluoride was used as an inert bed material. However, in laboratory experiments uranium and plutonium have been shown to be retained in the calcium fluoride and to be not readily removed by fluorination. On the positive side, these experiments also have shown the most favorable removals from fused aluminum oxide (alundum grain) at fluorination temperatures below 400 C. In order to demonstrate pellet fluorinations under such conditions on the pilot-plant scale, a series of runs has been made to determine the reaction rate dependence on temperature, using an inert fluid bed of alundum. These runs have been made in the temperature range from 350 to 500 C with both oxygen and nitrogen diluents. Shallow pellet beds and short reaction times were used to minimize variations of fluorine concentration and of pellet surface during the tests.

The alundum grain used as inert fluid bed had the screen size distribution shown in Table 45. It is expected that the fluidizing and heat transfer characteristics of this material would not be different from the fluorides used previously. The higher melting point of the alundum may be of advantage in avoiding caking.

In each of these runs (UOF-36 through 39), for the first 1.5 hr fluorine was diluted with nitrogen and for the second 1.5 hr oxygen was the diluent. The fluorine concentration was held constant during each run, and the levels of fluorine concentration for the series varied from 16 to 25 percent. The total gas rate was 0.5 cu ft/min at 25 C and 1 atmos. At the highest reaction rates in this series, namely 450 and 500 C, temperature control could no longer be maintained by coolant air regulations. It has been demonstrated previously that fluorine regulation can provide temperature control under these conditions, but in the present case a constant fluorine concentration was desired. Therefore, to complete the series of temperatures, the reaction rate was obtained for a fluorine-oxygen mixture at 450 and 500 C by dilution of this mixture with 38 percent nitrogen. The results are summarized in Table 45. The different rates shown in the table depend on, besides temperature, the particular pellet charge, gas rates and composition, and possibly other special circumstances. However, the process conditions are believed to be sufficiently similar during the series so that the effect of temperature is indicated for typical operation. The rate values in Table 45 were put on a common fluorine concentration basis and plotted in the Arrhenius form in Figure 46, assuming that a first-order rate constant can be expressed as $k = Ae^{-E'/RT}$, the calculated values of E' were 14 kcal/g mol for both the nitrogen- and oxygen-diluent runs. These temperature coefficients are consistent with earlier laboratory experiments.

Table 45

URANIUM HEXAFLUORIDE COLLECTION RATES AS A FUNCTION OF
TEMPERATURE AND OXYGEN CONCENTRATION

Inert Fluid Bed: Alundum^a (bed height: ~36 in.)

Gas Rate: 0.5 cu ft/min (at 25 C and 1 atmos)

Pellet Bed Height: ~3 in.

Reactor: 3-in. diameter

Run No.	Temp (C)	Gas Mixture	Run Time (hr)	UF ₆ Collection (g)	UF ₆ Average Collection Rate (g/hr)	
					N ₂ Diluent	O ₂ Diluent
UOF-36	350	23% F ₂ 77% N ₂	0.5	0		
			1.0	0		
			1.5	10	7	-
	400	21% F ₂ 79% O ₂	2.0	40		
			2.5	51		
			3.0	69	-	107
UOF-37	400	25% F ₂ 75% N ₂	0.5	11		
			1.0	7		
			1.5	55	49	-
		22% F ₂ 78% O ₂	2.0	109		
			2.5	147		
			3.0	160	-	278
UOF-38	450	20% F ₂ 80% N ₂	0.5	78		
			1.0	46		
			1.5	50	116	-
		16% F ₂ 46% O ₂ 38% N ₂	0.5	412		
			1.0	178		
			1.5	52	-	428
UOF-39	500	25% F ₂ 75% N ₂	0.5	126		
			1.0	115		
			1.5	107	232	-
		16% F ₂ 46% O ₂ 38% N ₂	0.5	149		
			1.0	456		
			1.5	460	-	710

^aAlundum screen analysis (mesh size, w/o): +40, 0.1; -40 +60, 18.0; -60 +80, 24.3; -80 +120, 25.3; -120 +140, 11.0; -140 +200, 20.1; and -200, 1.2.

FIGURE 46
FLUID BED FLUORINATION OF URANIUM DIOXIDE PELLETS.
TEMPERATURE DEPENDENCE
(RUNS UOF-36, 37, 38, 39)

2. Chlorination-Fluorination of Reactor Fuels (N. Levitz)

Reactions of halogen gases with metal and oxide nuclear fuel components are being studied for application to uranium- and plutonium-recovery schemes. These reactions may be used to de-clad stainless steel or zirconium-clad power reactor fuels, and to convert uranium dioxide fuel and uranium-zirconium alloy fuel to solid fluorides. The uranium and plutonium fluorides are in a form suitable for further processing with fluorine and are then treated as in the Direct Fluorination Volatility Process (see page 159).

These reaction studies are being carried out in two-zone fluid-bed reactors with inert solids as heat transfer media. The fuel specimen is submerged in the bed in the lower zone of the reactor. Here a chlorination reaction (referred to as primary) is carried out. The volatile chlorides pass into the upper zone where they are reacted with anhydrous hydrogen fluoride and are converted to solid fluorides. The solid chlorides which form also pass into the upper zone in the normal course of solids mixing and are also readily converted to fluorides. The reaction in the upper zone occurs preferentially on the surface of the inert bed particles, and results in relatively thin deposits of material.

Previous work carried out in a $1\frac{1}{2}$ -in.-diameter two-zone fluid bed has achieved the following results for the process steps indicated:

Decladding: Four-hour experiments gave average penetration rates of 5 and 10 mils/hr for the reaction of 304 stainless steel tube sections with chlorine at temperatures of 575 C and 625 C, respectively. No distinct advantage was evident at chlorine concentrations above 48 mole percent, whereas lower concentrations gave correspondingly lower penetration rates.

Chlorination of Uranium Dioxide: Sintered pellets ($\frac{5}{16}$ -in. in diameter x $\frac{5}{8}$ in. long) were more than 90 percent reacted in 2.5 hr using 69 mole percent chlorine in carbon tetrachloride. The chlorides were successfully converted to the tetrafluoride by hydrofluorination.

Results are presented this quarter on a scaled-up decladding study, on additional chlorine-uranium dioxide pellet reaction studies, on the extent of uranium removed by fluorinating material produced by the chlorination-hydrofluorination of uranium dioxide pellets, and on both weight loss and intergranular effects noted during corrosion studies on nickel, Inconel, and Hastelloy C, which are potential materials of construction.

a. Decladding Studies
(J. Barghusen, J. Kincinas)

The decladding step of a process for the recovery of fissile materials from stainless steel-clad uranium dioxide fuels involves the reaction of chlorine with stainless steel to form volatile ferric chloride. This process step has been demonstrated in a 6-in.-diameter, two-zone fluid-bed Inconel reactor. The volatile ferric chloride formed in the lower zone is converted to the solid fluoride by reaction with hydrogen fluoride in the upper zone of the reactor. The two zones are separated by an inverted nickel cone baffle, with a one-inch opening, positioned $11\frac{1}{2}$ in. above the gas-distribution plate. The cone baffle minimizes back-mixing of hydrogen fluoride admitted in the upper zone at a point $18\frac{1}{2}$ in. above the distribution plate.

A 2.1-kg charge consisting of 30 tubes of Type 304 stainless steel ($\frac{5}{8}$ -in. OD, 31-mil wall thickness, 9 in. long) was placed within the reactor and supported vertically such that the tubes rested on the bubble-cap-type gas-dispersion plate. The tubes, which simulated clad reactor fuel elements, were filled with alundum particles similar to the bed material and were crimped shut at both ends. The tube charge occupied 33 percent of the reactor cross-sectional area. Approximately 22 kg of alundum particles (Norton Co. Type 38), -40 +200 mesh, were added as inert-bed material, providing a static bed height of 24 in.

The stainless steel tubes were reacted at bed temperatures between 580 and 640 C with chlorine diluted to 50 volume percent with nitrogen. Fluidizing gas velocity was 0.5 ft/sec at process conditions. Table 46 presents specific process conditions and results. During the first quarter-hour, sufficient heat was evolved by the reaction that the bed temperature rose from 600 to 640 C. Thereafter the bed temperature was maintained near 600 C. After 5.8 hr, the stainless steel tubes were almost completely consumed. A photograph of the uncleaned metal residue is shown in Figure 47. The final metal weight, including all +20 mesh fragments, was 0.103 kg, which corresponds to 95 percent reaction, or an average penetration rate of 5.1 mils/hr.³⁰ Actually, the thickness of the tubing employed represented the maximum stainless steel-cladding thickness presently considered in nuclear reactor design. Cladding thicknesses as low as five mils are being considered in specific cases. Therefore a 6-hr chlorination decladding operation should be adequate for all stainless steel claddings.

Also during the initial reaction period, the temperature in the vicinity of the filters rose from 325 to 419 C. In view of the corrosive nature of the off-gas, this condition is considered unsuitable for long-term operation of sintered metal filters. By removing the insulation from the disengaging section of the reactor and installing cold water-cooling coils, it was possible to maintain the temperature at the top of the reactor below 240 C throughout the remainder of the run.

Table 46

RESULTS OF FLUID-BED CHLORINATION OF 304 STAINLESS STEEL AT 600 C

Reacting Gas Composition: 50 v/o chlorine in nitrogen
 Simulated Fuel Element: $\frac{5}{8}$ -in. OD, 31-mil wall, 9 in.
 long; 30 tubes; 2.134 kg.
 Final Element Weight: 0.103 kg - 95% metal reacted
 Run Time: 5.8 hr
 Weight of Alundum Bed: 22.0 kg

Mesh Size Fraction	Mesh Size Fraction in Bed (w/o)	Chemical Composition (w/o)		
		Cl	F	Fe
+60	15.6	1.9	5.6	3.1
-60 +200	78.2	1.2	8.5	4.9
-200	6.2	2.2	15.1	8.6
Filter Fines	-	9.5	-	7.5

³⁰Reference Data Manual, Nucleonics, 18, 148 (Nov 1960).

FIGURE 47
CHLORINATION OF STAINLESS STEEL TUBE SECTIONS

Calculations based on results of chemical analyses (Table 46) of separate size fractions of final bed samples showed that the major fraction of the iron was deposited as iron fluoride on the alundum bed particles. Similar results had been obtained with zirconium in chlorination-hydrofluorination studies (see ANL-6287, page 165). Chloride concentration, nearly two percent in the final bed, however, is approximately twice that which was found in the zirconium studies. There was no noticeable increase in the quantity of -200 mesh particles throughout the chlorination run indicating the hydrofluorination (upper zone) reaction efficiently "traps" the volatiles on the surface of the bed particles and little gas-phase reaction occurs.

The off-gas from the fluid-bed reactor was processed to remove both the hydrogen fluoride and chlorine content before being fed into the laboratory exhaust system. The hydrogen fluoride was removed as an aqueous condensate by injecting steam into the off-gas stream and

condensing the dilute acid in a water-cooled Karbate condenser. The chlorine was removed in an ammonia scrubber* which consisted of a liquid reservoir surmounted by a packed column. Ammonia gas was introduced into the scrubber above the liquid reservoir in an annular tube surrounding the chlorine inlet. The ammonium chloride formed in the reaction was scrubbed from the gas in the packed column by the liquid (ammoniacal liquor) recycle stream. The scrubber was successful in that no chlorine was detected in the exhaust stream, but scrubber operation indicated some slight modifications are in order, since ammonium chloride solids occasionally plugged the gas-inlet line.

b. Chlorination-Fluorination of Uranium Dioxide
(J. T. Holmes, D. Raue)

The chlorination of uranium dioxide was investigated because this reaction might be involved during the decladding of uranium dioxide fuels clad with stainless steel. It is also possible that chlorination might be an important reaction in the direct processing of this type of fuel. A possible procedure for direct chlorination of uranium dioxide fuels involves a dual reaction scheme for initial conversion to the tetrafluoride: a chlorine-carbon tetrachloride mixture is used to convert the dioxide pellets to volatile uranium chlorides in the lower zone of a two-zone fluid-bed reactor; the volatile chlorides are then converted to solid fluorides in the upper zone of the two-zone reactor by reaction with hydrogen fluoride. Further treatment with fluorine would recover the uranium as the volatile hexafluoride, which could be purified by standard volatility techniques. Inert-bed material (such as alundum) is used as a heat transfer material for these exothermic reactions. A major advantage of this scheme is that the reagent cost for converting to the hexafluoride is reduced by a factor of at least two 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 produced by the Direct Fluorination Process.

In further experiments, a separate series of experiments was carried out in an all quartz and Vycor apparatus (see Figure 48) in an attempt to identify the products of the chlorine-uranium dioxide reaction. It would be necessary to suppress such a reaction in the event exposure of the dioxide during decladding results in appreciable reaction of the fuel such as to have a deleterious effect on overall uranium and plutonium recovery.

Single pellets (manufactured by Numec Corporation) were reacted at 650 C using chlorine at a rate of one gram mole per hour and no diluent. No quantitative weight-loss data were obtained, but in one case,

*The reaction between chlorine and ammonia can be represented by

$$8 \text{ NH}_3 + 3 \text{ Cl}_2 \longrightarrow \text{N}_2 + 6 \text{ NH}_4 \text{ Cl}.$$

approximately half of the 16-g, $\frac{1}{2}$ -in.-diameter by $\frac{1}{2}$ -in. long pellet was reacted in 3.0 hr. The entire reactor was transferred to a dry box for material transfer for sample containers.

The reaction products were deposited in three locations in the reactor and were identified by X-ray diffraction methods and wet chemical analysis (Table 47).

Table 47

REACTION OF CHLORINE WITH SINTERED URANIUM DIOXIDE PELLETS

Equipment: Quartz boat, Vycor furnace tube
Temperature: 650 C
Flow rate: One gram-mol/hr chlorine
Pellets: UO_2 , $\frac{1}{2} \times \frac{1}{2}$ in., 16 g each, made by Numec
Reaction periods: 2 and 3 hr

Material	X-ray Diffraction Analysis		Wet Chemical Analyses (moles per mole uranium)		
	Major Phase	Minor Phase	U	Cl	O ^a
"Liquid phase"	UO_2Cl_2	"J" ^b	1	2.0	2.2
Coating on unreacted portion of pellet	UO_2Cl_2 , "J"	-	-	-	-
Yellow deposit at cold end of reactor	"J"	UO_2Cl_2 ^c	1	1.9	-

^aOxygen determined by difference.

^bPhase "J" is not UCl_3 , UCl_4 , UCl_5 , UOCl_2 , or UO_2Cl_2 , for which X-ray data are available. Other known solid chlorine-oxygen-uranium compounds are UOCl_3 , UOCl_4 , or $\text{UO}_2 \cdot \text{UOCl}_3$, but there are no X-ray data for these compounds.

^cIn a second experiment no minor phase was reported.

The unreacted portion of the pellet was coated with an adherent brown powder which had UO_2Cl_2 and phase "J"* as the major components. The lower end of the quartz sample boat was filled with a brown liquid which solidified upon cooling and was identified as UO_2Cl_2 with phase "J" as a very minor component. Anhydrous uranyl chloride has been reported to melt at a relatively low temperature (red heat).³¹ The cold, off-gas end of the reactor was coated with a very small amount of yellow powder which had phase "J" as the major component and UO_2Cl_2 as a very minor component. A duplicate experiment showed only phase "J" present in the yellow deposit. Chemical analysis of this material showed a chlorine-to-uranium ratio of 1.9, near two, as for UO_2Cl_2 , but the uranium and chlorine content did not correspond to that of UO_2Cl_2 .

Since the reaction of chlorine and uranium dioxide yields both liquid and volatile or entrainable reaction products at temperatures above 600 C, consideration must be given to this problem in a chlorine process scheme.

In further experiments, sintered dioxide pellet charges (up to 20 pellets, $\frac{5}{16}$ -inch diameter by $\frac{5}{8}$ inch long, 121 g) have been successfully converted to the tetrafluoride in 4 hr at 550 C using a $1\frac{1}{2}$ -in.-diameter, two-zone fluid-bed reactor.

The extent of uranium removal by fluorination at 350 C was investigated with the bed produced in the 20-pellet uranium dioxide chlorination experiment reported in ANL-6333, page 189. The unreacted pellets (eight percent of the original charge) remaining after chlorination were removed from the bed before fluorination. The analyses before and after fluorination are shown in Table 48.

Uranium removal was about 96.5 percent after 2 hr. Little improvement was effected by a second 2-hr fluorination. The fines which collected on the filters (mounted directly above the bed) retained about 1.5 percent of the initial uranium charge and constituted about five percent of the total bed charge. This uranium fraction is not to be considered a loss, since the material can be returned to the bed by filter blowback. No attempt was made in these exploratory studies to recover the uranium hexafluoride quantitatively for a material balance.

*Phase "J" is not UCl_3 , UCl_4 , UCl_5 , UOCl_2 , or UO_2Cl_2 , for which X-ray data are available. Other known solid chlorine-oxygen-uranium compounds are UOCl_3 , UOCl_4 , or $\text{UO}_2\cdot\text{UOCl}_3$, but there are no X-ray data for these compounds.

³¹Katz, J. J., and Rabinowitch, E., The Chemistry of Uranium, McGraw-Hill Book Co., Inc., New York (1951), p. 580.

Table 48

RESULTS OF FLUID-BED FLUORINATION OF
MATERIAL PRODUCED BY CHLORINATION-
HYDROFLUORINATION REACTIONS ON
SINTERED URANIUM DIOXIDE PELLETS

Temperature: 350 C
 Gas Composition: 54 mole percent fluorine in nitrogen
 Fluidizing Velocity: 0.5 ft/sec
 Bed Material: -40, +200 mesh alundum

Material	Wt (g)	Fluorination Time (min)	Uranium Content	
			Weight (g)	Weight Percent
Initial Bed	889	-	77.0	8.7
Fluorinated Bed ^a	780	120	1.9	0.24
Refluorinated Bed	750	240	1.4	0.19
Fines ^b	30	120	0.7	2.5
Fines	15	240	0.5	3.6

^aDifference in weight from initial bed due to uranium pellet and sample removal.

^bFines not returned for second 2.0-hour fluorination.

Three major objectives should be considered in future work:

1. Find conditions for improved removal of uranium from the alundum bed.
2. Study the effect of the presence of the chlorides and fluorides from the decladding step on uranium removal.
3. Find the behavior of plutonium oxides in this chlorination process scheme. No further experimental work is planned on this proposed process scheme. Interest in continuing the stainless steel-decladding studies has been shown by BNL personnel in recent informal discussions.

c. Corrosion Studies of Process Vessel Materials
(J. T. Holmes, D. Raue)

During the current period, a preliminary study of the corrosion of nickel, Inconel, and Hastelloy-C by chlorine gas at 600 ± 5 C was completed. These metals are being considered for construction of

vessels for the chlorination-decladding of stainless steel-clad fuels. Both the metal weight loss due to the formation of chlorides and intergranular attack were investigated. Coupons of these materials were reacted in an alumina boat in a 1-in.-diameter horizontal tube reactor using once-through chlorine gas at a rate of 0.3 g mole/hr. After the reaction period, the coupons were washed in warm distilled water, which removed the chloride film for the weight-loss determination.

The data for weight loss per unit area are shown as a function of time on Figure 49. The results are similar for all three metals; there is an initial relatively high but diminishing rate of weight loss, followed by a significantly lower, uniform rate of weight loss. The uniform weight-loss period starts after about 25 hr. The weight-loss rate and corresponding calculated penetration rates for the constant rate period are shown in Table 49. These rates are much lower than the 20-mil/mo rates reported previously for short-term experiments of 2- to 20-hr duration with nickel and Inconel (ANL-6287, page 162). The buildup of chloride films on the metal apparently restricts diffusion of the chlorine, giving reduced overall corrosion rates. This initially high reaction rate, before the diffusion barrier is set up, will contribute less than one mil to the total corrosion.

FIGURE 49
CORROSION BY CHLORINE AT 600°C

Table 49

CORROSION BY CHLORINE GAS AT 600 ± 5 C

	Weight-loss Rate, mg/(sq in.)(hr)	Penetration Rate, mils/mo
Nickel	0.38	1.9
Inconel	0.35	1.9
Hastelloy-C	0.54	2.7

A comparison of photomicrographs of nickel, Inconel, and Hastelloy-C (see Figure 50) shows that nickel undergoes severe intergranular attack whereas Inconel and Hastelloy-C do not. The intergranular attack in nickel was present at depths greater than $\frac{1}{64}$ in. after 212 hr at 600 C. The photomicrographs of Inconel and Hastelloy-C show a comparison of a coupon reacted with chlorine at 600 C for 146 hr and a coupon held at 600 C for 26 hr. Hastelloy-C shows some grain-boundary modifications believed to be age hardening which is accelerated by the high temperature.

Because of the severe intergranular attack, nickel is no longer being considered as a material of construction for the high-temperature chlorination reactions. Although the results for Inconel and Hastelloy C are encouraging, a more detailed corrosion study should be undertaken including an investigation of the effect of temperature, the effect of the abrasive action of the fluidized bed, the effect of impurities in the reactants, the effect of radiation, and the possibility of using the reactor for both chlorination and fluorination.

C. Conversion of Uranium Hexafluoride to Uranium Dioxide
(I. Knudsen, H. Hootman,* N. Levitz, M. Jones, J. Kincinas)

A fluid-bed process for the preparation of ceramic-grade uranium dioxide from uranium hexafluoride is being studied for 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. Uranium losses from the system have been consistently below 0.01 percent. High sintered densities (from 93 to 97 percent of theoretical; see ANL-6183, page 123, and ANL-6231, page 134) have been obtained in pellet fabrication tests. Work is being concentrated on the two-step procedure because of greater flexibility in choice of reactor conditions and process control.

*Resident Student Associate from Michigan College of Mining & Technology.

FIGURE 50
CORROSION BY CHLORINE AT 600 ± 5 C

NICKEL

212-hr exposure,
50 X magnification,
30-sec etch with
one part conc HNO₃ and
one part glacial acetic acid.

INCONEL

146-hr chlorine (bottom),
26-hr no chlorine (top)
200 X magnification;
10-sec etch with
5 parts conc HCl and
1 part conc HNO₃.

HASTELLOY-C

146-hr chlorine (bottom),
26-hr no chlorine (top),
200 X magnification,
15-sec electrolytic etch with
5 parts conc H₂SO₄ and
95 parts water at
3-volt potential.

1. Steam Hydrolysis of Uranium Hexafluoride

Significantly longer-term operation has been demonstrated in the latest series of fluid-bed uranium hexafluoride runs. Thirty-five hours of hexafluoride feed have been accumulated in four runs including a continuous 15-hr period. A total of 410 lb of uranyl fluoride was produced.

Earlier tests (ANL-6333, page 193) have shown that the extent to which uranyl fluoride produced in the uranium hexafluoride-hydrolysis reaction will deposit as a solid on the particles of a fluid bed or form fines in the bed voids (gas phase), depends, in part, on the average particle size of the bed. Attempts at long-duration runs have been interrupted repeatedly by fines formation due to inadequate control of the bed particle size.

Continuous operation in the region of particle growth (average bed particle size, 200μ or greater) requires seed particle addition to offset growth and maintain bed fluidity; previous tests have been made with both constant recycle rates and with adjustment of recycle, the latter based on particle size analysis of samples taken during the run. In both cases seed particle requirements may vary due to a small variable rate of fines formation during normal operation. Another problem is that particle size analyses are time-consuming and, hence, lag the process too much.

In view of these operating difficulties, several successive modifications in the 3-in.-diameter Monel column were made to permit the entrainment of the fines fraction from the fluid bed and allow fines collection separately in the filter chamber. The current equipment layout is shown in Figure 51. A 1-in. pipe now connects the reactor with the filter section. During filter blowback, the fines collect in the lower portion of the chamber and are periodically withdrawn.

The particle size behavior during steam hydrolysis using entrainment separation of fines for Runs 62, 62A, 62B, and 62C is shown in Figure 52. Since the modification of the unit, good control of the bed particle size has been maintained in the 35 hr of run time accumulated to date including a continuous 15-hr period. Seed particle addition at about 14 percent of the hexafluoride feed rate maintained the average particle size near 315 ± 50 microns. Only negligible adjustments of the recycle rate were made. The maximum value for the minus 200 mesh fraction in the bed was held to 0.2 percent. Operating conditions were those used in previous work and are summarized in Table 50. The amount of carryover into the filter chamber is fairly high in some runs (e.g., 5.9 percent of the hexafluoride rate in Run 62), but the minus 200 mesh fraction in this stream averaged only one percent of the hexafluoride rate. The presence of the coarser material (up to plus 60 mesh), although of little process significance since it can be blended with the product stream, is attributed

to the absence of either adequate freeboard or an enlarged disengaging section directly above the bed. Ideally the carryover, including fines, would be used for recycle stock. The results of these runs indicate that the fines formation problem can be avoided by control of the bed particle size using the entrainment-separation technique for preventing accumulation of fines in the bed.

FIGURE 51
MODIFIED FLUID-BED REACTOR FOR
URANIUM HEXAFLUORIDE HYDROLYSIS

FIGURE 52
PARTICLE SIZE BEHAVIOR DURING STEAM HYDROLYSIS OF URANIUM HEXAFLUORIDE
USING ENTRAINMENT SEPARATION OF FINES

Table 50

CONDITIONS FOR STEAM HYDROLYSIS OF URANIUM HEXAFLUORIDE

Equipment: 3-in.-diameter Monel reactor
 Temperature: 200 to 225 C
 UF₆ Feed Rate: 100 g/min
 Steam Superficial Velocity: 0.75 ft/sec
 Steam Excess: 225 percent
 Bed Height (static): 15-18 in.

Run No.	Run Duration (hr)	Recycle Rate (-60 +200 mesh) % of UF ₆ Fed	Carryover	
			Total Overhead, % of UF ₆ Fed	Average Fines Content, %-200 Mesh
62	4.5	14.6	5.9	15
62A	7.5	13.7	2.4	25
62B	4.2 ^a	17.0	2.8	35
62C	19.3 ^b	14.0	5.0	35

^aInterrupted by plugging of $\frac{1}{2}$ -in. connecting line.

^bInterrupted by plugging of 1-in. connecting line after 4 hr hexafluoride feed; resumed operation after 2 hr.

A problem encountered in these runs was accumulation of entrained solids and eventual plugging in the line connecting the reactor and filter sections. This caused involuntary termination of Run 62B after 4 hr. In this case, the connecting line was a $\frac{1}{2}$ -in.-OD tube. Even after enlarging the line to one-inch IPS, the same difficulty arose (Run 62C) and a 2-hr shutdown (noted on Figure 52) was necessary; thereafter, periodic rapping permitted clearing of the line and continuation of the run. Relief from line-plugging may be achieved by providing additional heating of the transfer line in case condensation was a contributing factor (this has not yet been determined) or by improved design or further enlarging to avoid impingement of particles on the wall.

Two additional short runs were made in the study of operating variables that might contribute to excessive fines formation. Changing the location of the product take-off to the top of the reactor instead of the bottom (which is in the vicinity of the hexafluoride inlet point) did not counteract fines formation nor did lowering the superficial gas velocity from 0.75 to 0.375 ft/sec.

Future work will include establishing a range of operability with respect to gas velocity, particle size, and recycle rate. Higher feed rates will also be tried. Consideration is being given to additional testing of the simultaneous steam and hydrogen system.

2. Reduction of Uranyl Fluoride to Uranium Dioxide

The second step in the conversion of uranium hexafluoride to uranium dioxide by the two-step method involves the reduction of uranyl fluoride to uranium dioxide. This reaction has been found to be the rate-controlling reaction of the process. Previous work (see ANL-6333, page 195) has shown that a hydrogen-steam gas mixture will remove the fluoride more rapidly than hydrogen alone.

Additional studies on the effect of gas composition and temperature on the rate of fluoride removal were carried out in batch fluidization experiments conducted in a 3-in.-diameter Monel reactor. Uranyl fluoride produced in the uranium hexafluoride-hydrolysis step was used as feed material. The runs were evaluated on the basis of the fluoride removal for different time periods of reaction.

Gas Composition

Runs were made at 650 C with 3-kg beds of uranyl fluoride at steam concentrations of 7, 12, 27, 45, and 77 percent in hydrogen. The results are tabulated in Table 51 and shown graphically in Figure 53, where the fraction residual fluoride, F/F_0 , in the sample is plotted against gas composition with run time as the parameter. The reaction times are indicated on the isochrons. The optimum mixture of hydrogen and steam appears to be in the vicinity of a fifty percent mixture. A 4-hr run period gave a residual fluoride content of 200 ppm. The relatively high hexavalent uranium content, about two to four percent of the powder product, is attributed to oxidation of the material upon being exposed to air.

Particle breakup was noted in these runs, the degree of breakup shown in Table 51 as the "Breakup Index." This index is defined as weight fraction of final bed below the minimum size in the starting bed, in this case minus 40 mesh. More particle breakup was noted in the runs where more than ten percent steam was used, the indices ranging from 0.15 with no steam to 0.27 with 12 percent steam. Surface area measurements (see Table 51) show no appreciable variation with gas composition, all of them being below 1 sq m/g.

Temperature

The effect of temperature on the rate of fluoride removal was studied over the temperature range from 550 to 650 C. Material used was -40 +60 mesh size.

Table 51

SUMMARY OF THE HYDROGEN-STEAM MIXED GAS CONVERSIONS
OF URANYL FLUORIDE TO URANIUM DIOXIDE

Conditions: 650 C
3-kg bed of uranyl fluoride (12.3% F⁻)
-20 +40 mesh particles

Gas Composition (vol %)			Superficial Velocity (ft/sec)	Weight Percent Fluoride in Sample after Time (min)					Surface Area (sq in./g)	Tap Density (g/cc)	Breakup Index ^a (-40 mesh basis)
H ₂	Steam	N ₂		30	60	120	240	Final Bed (240 min)			
50	0	50	3.0	-	12.20	11.70	7.48	54.5	-	4.1	0.15
93	7	0	1.8	6.82	2.46	0.10	0.09	2.08	0.88	3.8	0.16
88	12	0	1.8	7.63	3.46	0.16	0.07	2.34	0.82	4.0	0.27
73	27	0	1.9	6.20	2.00	0.09	0.03	1.70	0.75	4.5	-
55	45	0	1.9	4.08	0.50	0.06	0.02	3.92	0.82	4.0	0.22
23	77	0	1.8	6.20	2.86	0.15	0.03	2.61	0.94	4.6	-
0	33	67	1.6	-	4.60	0.50	-	-	-	4.3	0.23

^aWeight fraction of final bed below the minimum size in the starting bed.

FIGURE 53
FLUORIDE REMOVAL WITH
RESPECT TO GAS COMPOSITION

In 4-hr periods, residual fluoride contents were reduced from 12.3 percent (theoretical for uranyl fluoride) to 2500 and 150 ppm, for the lowest and highest temperatures, respectively (see Table 52). Particle breakup seems to increase with decreasing temperature, the Breakup Index (on a -60 mesh basis) ranging from 0.55 at 650 C to 0.65 at 550 C. Sieve analyses also show that appreciably more fines (up to 26 percent -200 mesh) are produced at the lower temperature, although this amount of particle degradation did not affect the operability of the unit. Based on the Breakup Index, the coarser material (+40 mesh) used in the gas composition study suffered less breakdown than the somewhat smaller particles (+60 mesh) used in the temperature study.

Clayton³² reasons that greater particle breakdown occurs at lower temperatures because strains resulting from phase transformation are less easily annealed out at lower temperatures.

Future studies will include determination of effect of bed depth and gas velocity on rate of fluoride removal.

D. Calcination Studies in Small-diameter Columns (J. Loeding, C. Schoffstoll)

During the previous report period, a program investigating the feasibility of using small-diameter columns for the continuous fluid-bed calcination processing technique³³ was initiated. The major objectives of this program are: (1) to extend this technique to systems where nuclear criticality must be considered, such as in the processing of highly enriched uranium solutions or plutonium solutions, and (2) to demonstrate that a substantial reduction in the quantity of off-gas produced by this technique may be achieved. During the course of this work it is expected that new skills for dealing with critical systems will be developed.

³²Clayton, J. C., and Seymore, D., Some Preparative Methods and Physical Characteristics of Uranium Dioxide Powders, Jour. Chem. Eng. Data 6, 43 (Jan 1961).

³³Jonke, A. A., et al., The Use of Fluidized Beds for the Continuous Drying and Calcination of Dissolved Nitrate Salts, Nuclear Science and Engineering 2, 303-319 (1957).

Table 52

THE EFFECT OF TEMPERATURE ON THE CONVERSION OF
URANYL FLUORIDE TO URANIUM DIOXIDE IN A
3-INCH MONEL FLUID-BED REACTOR

Conditions: 3 kilogram beds (-40 +60 mesh particles)
1.20 ft/sec superficial velocity

Run No.	Temp (C)	Weight Percent Residual Fluoride after Time (min)				Breakup Index (-60 basis)	Screen Analysis					
		60	120	180	240		+40	+60	+100	+200	+325	-325
20	650	-	0.26	-	0.015	0.55	-	0.45	0.31	0.06	0.10	0.08
21	600	6.90	2.64	0.69	0.045	0.61	0.01	0.38	0.26	0.08	0.20	0.07
22	550	-	3.30	-	0.250	0.65	-	0.35	0.17	0.12	0.22	0.14

The method of approach to this work is to position the liquid feed atomizing nozzle in the bottom of the unit, directed upwards. This permits the use of the atomizing gas plus the feed decomposition gases as the fluidizing medium, thereby eliminating a separate fluidizing air stream such as was used in previous work, i.e., those systems where the feed was sprayed horizontally into the bed. The nozzles being tested are of the narrow-angle spray type, which facilitates work in small-diameter columns. The unit being tested currently has a $2\frac{1}{4}$ -in. diameter. The lower 4 in. consists of a 25-degree-tapered section to correspond to the shape of the spray and, at the same time, being of reduced cross section, requires less gas for fluidization.

Initial studies in which 1 M aluminum nitrate solution was used as feed, feed rates were of the order of 11 ml/min, and with bed temperatures of 320 to 420 C have been carried out in glass units and, more recently, in a stainless steel column. The initial bed charge of 290 g aluminum oxide gave a static bed height of 6 in. Successful runs of up to 5-hr duration have been made, although problems associated with nozzles, heat supply, and the feed pump have caused numerous involuntary shutdowns. Equipment modifications are being directed toward correcting these problems.

The extended tip nozzle (ANL-6068, page 94), covered with a cap such that the tip of the liquid orifice is recessed about $\frac{3}{32}$ in. below the cap orifice, has been the most reliable type to date. The cap creates, in effect, a form of pressure nozzle. With this nozzle, some reduction in the ratio of atomizing air rate to liquid feed rate has been attained. This ratio is a criterion of the degree of success achieved in minimizing the off-gas volume. Work in a 6-in.-diameter calciner (ANL-6322) utilized a ratio of 1700. Early work in the $2\frac{1}{4}$ -in. column used in these studies utilized a ratio of 2040, whereas in more recent work the ratio has been reduced to 1080.

Future studies will be directed toward a further reduction in the air-to-feed-rate ratio, calcine size distribution, and the establishment of reproducible run conditions.

III. REACTOR SAFETY

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

Studies of the ignition of uranium monocarbide powders in oxygen by the burning-curve method are continuing. Studies have been extended to include powders consisting of spherical particles. Ignition temperatures varied from 405 to 385 C for sieved fractions of spherical powder varying in specific area from 4 to 40 sq cm/gram. Ignitions were not sharply defined, probably because of the hindered transport of oxygen through the gaseous combustion products.

Studies of the ignition of spherical zirconium powders by the shielded-ignition method have been initiated. A high-vacuum apparatus has been constructed which prevents the formation of an oxide film prior to the ignition test. Preliminary results have shown that the ignition temperature of 270/325 mesh powder was between 275 and 325 C. This ignition temperature is about 350 C lower than previous values for a single foil (1 mil thick) of similar specific area. The program will include a study of sample size, geometry, specific area, and effects of controlled preoxidation.

Studies of burning propagation along uranium and zirconium foil strips are continuing. Simultaneous measurements of propagation rates and burning temperatures were obtained with the photoelectric pyrometer described in the previous quarterly report. Studies were concentrated on the effects of additions of halogenated hydrocarbons to the air. Results have shown that increasing chlorination in the halocarbon molecule is generally beneficial in lowering propagation rates and burning temperatures of uranium foils. The presence of one hydrogen atom in the molecule is also beneficial.

Motion picture records of a series of experiments were taken demonstrating the effectiveness of a chlorobromomethane extinguishant on a fire involving about one cubic foot of fine zirconium turnings. The fire was "knocked down" quickly enough so that the fire could be approached and extinguished with a dry chemical agent. General use of halocarbons on metal fires cannot be recommended, however, until a large number of practical experiments fully demonstrate the effectiveness and safety of the procedure.

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. Measurement of mean particle diameters for runs with 60-mil zirconium wires in heated water were completed. Experimental results of particle size and total extent of reaction for the runs compared favorably with those computed by the analog computer method, reported previously.

A procedure for estimating the extent of zirconium-water reaction during a nuclear incident was developed. The method is based on the assumption that zirconium cladding on fuel elements will begin to form molten particles when the cladding temperature reaches the melting point (1840 C). Fully molten particles will then separate from the nuclear heat source (fuel element core) as the cladding melts. The individual particles will react with the water and eventually cool to water temperature. The time-temperature history of the particles and the extent of reaction should be identical to that experienced by particles formed from wires by condenser discharge and described by the computer studies. It is then possible to compute the overall extent of reaction occurring during a nuclear incident if the particle size distribution resulting from the nuclear incident can be estimated.

The method was applied to four Zircaloy-clad oxide core fuel pins which underwent severe transients while under water in autoclaves in the TREAT reactor. The following comparison was obtained of total extent of reaction computed from the measured particle size distribution and that measured experimentally from the quantity of hydrogen gas generated:

Computed	8.1, 8.3, 13.1, 14.4
Experimental	4.1, 8.0, 14.0, 24.0

A second method of studying metal-water reactions 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 uranium at 1200 to 1600 C are reported. The nature of the results suggested that the reaction rate was controlled by processes of gaseous diffusion and mixing within the reaction cell. A series of runs with sodium at 200 C was then initiated to compare with the uranium results. Only slightly more reaction occurred with sodium than with uranium. It is thus likely that both reactions occur as fast as water vapor can reach the metal surfaces. Rates with sodium and uranium were both markedly higher than rates reported in the previous quarterly with aluminum.

A third method of studying metal-water reactions has been initiated. This method involves the simultaneous levitation and heating of small metal pellets by a high-frequency field. The sample will be located in flowing steam. The rate of reaction will be measured by determining the rate of

generation of hydrogen. Initial studies have shown that levitated spheres of aluminum, one-quarter inch in diameter, will ignite and burn in air when heated to 1750 C. Ignited pellets when dropped into water will continue to burn to completion, both on the surface and under the water.

Studies of the behavior of ceramic core, metal-clad fuel pins during nuclear reactor excursions in TREAT were extended from the previous work on mixed oxide cores to include pure uranium dioxide cores. Four TREAT reactor transients were performed on fuel pins with a uranium core in a 304-stainless steel jacket; the test conditions were as follows:

UO₂ core: 0.33-in. diameter x 0.50 in. long; uranium 20 percent enriched; 89 percent theoretical density.
 SS cladding: type 304, 18-mil wall thickness; fuel pin submerged in water.

The following results were obtained:

	CEN Transient Number			
	63	61	62	60
megawatt-second burst:	120	304	340	344
millisecond period:	121	116	50	48
neutron dose, nvt thermal:	2.1×10^{14}	3.8×10^{14}	5.4×10^{14}	4.7×10^{14}
% SS-H ₂ O reaction:	0.3	19.1	14.0	13.5
final appearance of fuel pin:				
clad:	intact, 7% increase in diameter	ruptured ~1/2 melted	ruptured ~2/3 melted	ruptured ~2/3 melted
core:	cracked	fragmented into particles	fragmented into particles	fragmented into particles

Oscillograph records of the reactor bursts indicated that the stainless jacket was heated from room temperature to temperatures greater than 1200 C in about 0.3 sec. One experiment (CEN-62) gave a series of pressure pulses with a peak of 160 psi.

Particle size distributions were obtained on the meltdown products by sieve screen analyses; for CEN-62 and 60 the two major size fractions were in the range of particle diameter from 12 to 64 mils. The general appearance of the fuel pin after the transient meltdown in water was similar to those obtained in previous experiments on fuel pins with mixed oxide cores.

A. Metal Oxidation and Ignition Kinetics
(L. Baker)

1. Ignition Studies of Uranium Monocarbide Powders by the
Burning Curve Method
(M. Tetenbaum, R. Wagner, J. D. Bingle)

The burning curve procedure has been used extensively to provide reproducible data on the ignition characteristics of uranium and uranium carbide powders. The powder samples are contained in crucibles which are mounted on a thermocouple. They are heated at a uniform rate (usually 15 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 temperature 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 and sample geometry on ignition temperatures of uranium powder (see ANL-6183, page 130, and ANL-6231, page 138).

Measurements of the ignition behavior of uranium monocarbide powder have been extended to include spherical particles. Previous measurements on sieved fractions of irregular uranium monocarbide powders from various sources gave ignition temperature values approximately 40-50 C higher than the values obtained with spherical uranium powders when compared on the basis of specific area (see ANL-6333, page 202).

With uranium carbide fractions, ignitions in oxygen were not sharply defined on the burning curve as in the case of uranium powder ignitions. The absence of a sharp temperature rise at ignition can be attributed to hindered transport of oxygen through the gaseous products resulting from the reaction of uranium monocarbide and oxygen. To emphasize this effect further, no ignition was observed when -50 +60 mesh spherical uranium monocarbide powder (representing the smallest particle size fraction in the lot) was heated in an air atmosphere.

The results are summarized in Figure 54. It is apparent from Figure 54 that ignition temperatures obtained with spherical uranium monocarbide powders vary only slightly (385-405 C) with specific area. The spherical carbide powders show ignition temperature values approximately 100 C higher than spherical uranium powders, and approximately 75 C higher than irregular uranium monocarbide powders (Source A) when compared on the basis of specific area. Photographs of sieved fractions of irregular and spherical powders are shown in Figure 55.

FIGURE 54
IGNITION BEHAVIOR OF URANIUM AND URANIUM
MONOCARBIDE POWDERS IN OXYGEN

Figure 55

PHOTOGRAPHS OF URANIUM MONOCARBIDE POWDERS AS RECEIVED

Source A: -35 +40 Mesh Irregular
Uranium Monocarbide (1 mm grid)

Source C: -20 +25 Mesh Spherical
Uranium Monocarbide (1 mm grid)

2. Ignition Studies of Zirconium Powders by the Shielded Ignition Method
(J. G. Schnizlein, R. Wagner, J. D. Bingle)

Previous studies of the ignition of zirconium foils have been reported in ANL-5974, page 152. The study is being extended to zirconium powders.

The specific area was found to be the most important variable in studies of ignition. Careful control of the specific area of powders can be achieved when the individual particles are spherical. Irregular particles are likely to have a much higher specific area than one would calculate from average particle diameters. Spherical zirconium and Zircaloy-2 powders, smaller than 100 mesh, prepared and packaged in inert atmosphere, have been obtained from the Linde Company.

Apparatus has been constructed and vacuum tested to perform shielded ignition experiments. The sample is heated to the test temperature in high vacuum before admission of the oxidizing gas (air or oxygen). Provisions are included for gettering the apparatus with an electrically heated zirconium wire. This will allow experiments in which any oxide film on the particles can be diffused into the zirconium to provide an oxide-free surface.

Preliminary experiments with 0.3-g samples of the subsieve and 270/325 mesh fractions were performed in 1-cm-ID copper crucibles. The ignition temperature in oxygen of the subsieve fraction is between 250 and 275 C, and of the 270/325 mesh fraction between 275 and 325 C. These ignition temperatures are approximately 350 degrees lower than those for a single foil (1 mil thick) of similar specific area.

The continuing program will include studies of sample size, geometry, specific area, and effects of controlled prior oxidation.

3. Burning Propagation Studies - The Effect of Halogenated Hydrocarbons on the Combustion of Uranium
(L. Leibowitz, L. W. Mishler)

The rate of advance of a combustion zone along a wire or strip of foil, i.e., the burning propagation rate, is a useful and reproducible quantity for studying the effects of various factors on metal combustions. A pyrometer has been constructed which permits simultaneous measurements of burning velocity and temperature (see ANL-6333, page 210). This instrument is being used to examine the effect of halogenated hydrocarbons on uranium combustion.

It has been found that the presence in air of a few percent of various halogenated hydrocarbons causes a marked reduction in burning propagation velocity (see ANL-6231, page 152). In order to help clarify the mechanism by which these substances are effective, several series of compounds were selected to provide systematic variation of constitution (see ANL-6333, page 209). Although not all the compounds selected have been examined, some interesting results are now available. Figures 56 and 57 show the effect of varying CF_3Cl concentration on the maximum burning temperature and burning propagation velocity of strips of 0.13×3 -mm uranium foil. The temperatures reported are brightness temperatures, since no emissivity corrections have been made. It is evident that the first additions of CF_3Cl produce the most marked inhibition of burning propagation.

FIGURE 56
EFFECT OF CHLOROTRIFLUOROMETHANE ON BURNING
TEMPERATURE OF URANIUM FOIL (0.13×3 mm) IN AIR

It is also evident that increasing chlorination yields increasing effectiveness of the agent. This is shown by the data summarized in Table 53. The general trend of increasing chlorination leading to increasing effectiveness is clear despite a few reversals.

The effectiveness of a hydrogen atom in the molecule is illustrated in the comparison given in Table 54. The inhibiting effect is then not specifically due to halogen atoms and is in accord with the suggestion made earlier (see ANL-6333, page 209) that the inhibition results from the decreased net diffusion of oxygen to the burning metal.

FIGURE 57
EFFECT OF CHLOROTRIFLUOROMETHANE ON BURNING PROPAGATION VELOCITY
OF URANIUM FOIL (0.13 x 3 mm) IN AIR

Table 53

EFFECT OF VARIOUS HALOGENATED HYDROCARBONS ON BURNING
PROPAGATION VELOCITY AND MAXIMUM BURNING TEMPERATURE
OF URANIUM FOIL (0.13 x 3 mm) IN AIR

Compound ^a	Concentration in Air (by volume)			
	2%		4%	
	Burning Velocity (cm/sec)	Burning Temp (C)	Burning Velocity (cm/sec)	Burning Temp (C)
He	-	-	0.51	1285
Ar	-	-	0.47	1275
N ₂	-	-	0.47	1290
CHF ₃	0.43	1195	0.42	1165
CHF ₂ Cl	0.40	1065	0.31	1020
CHFC1 ₂	0.38	1160	0.31	975
CHCl ₃	0.30	1120	0.32	1110
CF ₄	0.51	1220	0.49	1170
CF ₃ Cl	0.49	1180	0.41	1130
CF ₂ Cl ₂	0.37	1095	0.32	1040
CH ₃ Cl	0.41	1190	0.39	1165
CH ₂ Cl ₂	0.36	1160	0.33	1130
CHCl ₃	0.30	1120	0.32	1100
CCl ₄	0.35	1110 ^b	0.33	1025 ^b

^aValues in uncontaminated air: Burning Velocity = 0.52 cm/sec;
Burning Temperature = 1335 C.

^bTemperature questionable because of smoking during combustion.

Table 54

EFFECT OF HYDROGEN ATOMS IN HALOCARBON MOLECULES ON
BURNING PROPAGATION VELOCITY AND MAXIMUM BURNING
TEMPERATURE OF URANIUM FOIL (0.13 x 3 mm) IN AIR

Compound	Concentration of Halocarbon in Air (by volume)			
	2%		4%	
	Burning Velocity (cm/sec)	Burning Temp (C)	Burning Velocity (cm/sec)	Burning Temp (C)
CF ₄	0.51	1220	0.49	1170
CHF ₃	0.43	1195	0.42	1165
CCl ₄	0.35	1110 ^a	0.33	1025 ^a
CHCl ₃	0.30	1120	0.32	1100
CF ₃ Cl	0.49	1180	0.41	1130
CHF ₂ Cl	0.40	1065	0.31	1020

^aTemperature questionable because of smoking during combustion.

Work in this area is continuing with studies of the effects of halocarbon additive on ignition temperature. It will also be determined whether halocarbon additives affect zirconium burning in the same manner as uranium.

4. Zirconium Scrap Burning Studies
(J. G. Schnizlein, D. F. Fischer, J. D. Bingle)

Because the various halogenated hydrocarbons have proven to have an important effect in reducing the intensity of burning of both uranium and zirconium (for example, see Section 3), the use of these substances as extinguishing agents has been proposed. A preliminary series of experiments indicated the possibility of effectiveness of a halocarbon extinguisher. Recently, several experiments to observe the extinguishing ability of chlorobromomethane on fine zirconium turnings were performed. One-gallon, nitrogen-pressurized extinguishers obtained from the American LaFrance Company were used.

Although a fire involving approximately one cubic foot of turnings was not extinguished, it was "knocked down" quickly enough that the fire could be approached and some other agent, such as Ansul Dry Chemical, could be used to complete the extinguishment. A smaller fire was extinguished when attacked early enough. The use of a carbon dioxide extinguisher on a similar fire only succeeded in aggravating it.

B. Metal-Water Reactions (L. Baker)

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. Measurement of mean particle diameters for runs with 60-mil zirconium wires in heated water were completed. Experimental results of particle size and total extent of reaction for the runs compared favorably with those computed by the analog computer method, reported previously.

A procedure for estimating the extent of zirconium-water reaction during a nuclear incident was developed. The method is based on the assumption that zirconium cladding on fuel elements will begin to form molten particles when the cladding temperature reaches the melting point (1840 C). Fully molten particles will then separate from the nuclear heat source (fuel element core) as the cladding melts. The individual particles will react with the water and eventually cool to water temperature. The time-temperature history of the particles and the extent of reaction should be identical with that experienced by particles formed from wires by condenser discharge and described by the computer studies. It is then possible to compute the overall extent of reaction occurring during a nuclear incident if the particle size distribution resulting from the nuclear incident can be estimated.

The method was applied to four Zircaloy-clad oxide-core fuel pins which underwent severe transients while under water in autoclaves in the TREAT reactor. The following comparison was obtained of total extent of reaction computed from the measured particle size distribution and that measured experimentally from the quantity of hydrogen gas generated:

Computed	8.1, 8.3, 13.1, 14.4
Experimental	4.1, 8.0, 14.0, 24.0.

A second method of studying metal-water reactions 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 uranium at 1200 to 1600 C are reported. The nature of the results suggested that the reaction rate was controlled by processes of gaseous diffusion and mixing within the reaction cell.

A series of runs with sodium at 200 C was then initiated to compare with the uranium results. Only slightly more reaction occurred with sodium than with uranium. It is thus likely that both reactions occur as

fast as water vapor can reach the metal surfaces. Rates with sodium and uranium were both markedly higher than rates reported in the previous quarterly with aluminum.

A third method of studying metal-water reactions has been initiated. This method involves the simultaneous levitation and heating of small metal pellets by a high-frequency field. The sample will be located in flowing steam. The rate of reaction will be measured by determining the rate of generation of hydrogen. Initial studies have shown that levitated spheres of aluminum, $\frac{1}{4}$ in. in diameter, will ignite and burn in air when heated to 1750 C. Ignited pellets when dropped into water will continue to burn to completion, both on the surface and under the water.

Studies on the behavior of ceramic-core, metal-clad fuel pins during nuclear reactor excursions in TREAT were extended from the previous work with mixed oxide cores to include pure uranium dioxide cores. Four TREAT reactor transients were performed with fuel pins with a urania core in a 304-stainless steel jacket; the test conditions were as follows:

UO₂ core: 0.33-in. diameter x 0.50 in. long, uranium 20% enriched, 89 percent theoretical density.
 SS cladding: type 304, 18-mil wall thickness; fuel pin submerged in water.

The following results were obtained:

	CEN Transient Number			
	63	61	62	60
megawatt-second burst:	120	304	340	344
period, msec:	121	116	50	48
neutron dose, nvt thermal:	2.1×10^{14}	3.8×10^{14}	5.4×10^{14}	4.7×10^{14}
% SS-H ₂ O reaction:	0.3	19.1	14.0	13.5
final appearance of fuel pin:				
clad:	intact; 7% increase in diameter	ruptured; ~1/2 melted	ruptured; ~2/3 melted	ruptured; ~2/3 melted
core:	cracked	fragmented into particles	fragmented into particles	fragmented into particles

Oscillograph records of the reactor bursts indicated that the stainless jacket was heated from room temperature to temperatures greater than 1200 C in about 0.3 sec. One experiment (CEN-62) gave a series of pressure pulses with a peak of 160 psi.

Particle size distributions were obtained on the meltdown products by sieve screen analyses; for runs CEN-62 and 60 the two major size fractions were in the range of particle diameters from 12 to 64 mils. The general appearance of the fuel pin after the transient meltdown in water was similar to those obtained in previous experiments on fuel pins with mixed oxide cores.

1. Condenser Discharge Method
(L. Baker, R. Warchal, R. Koonz*)

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 residue indicates the surface area exposed to reaction.

Analysis of 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. In this way an attempt is made to interpret experimental work as it proceeds.

a. Zirconium Runs at High Pressure

The series of runs with 60-mil zirconium wires in the high-pressure reaction cell has been completed. Measurements of the mean particle diameters of residue from the runs has also been completed. The method used to determine particle size was described in a previous quarterly report (ANL-5996, page 241). Results for the zirconium runs in heated water are given in Table 55. Similar results for zirconium in room temperature water were presented in a previous quarterly report and in more detail in a recent topical report (ANL-6257).

Results for the extent of reaction as determined by analysis of the hydrogen generated by reaction are plotted in Figure 58. Computed results are included on the figure.**

*Summer employee from Wabash College.

**Computations performed on the Pace Analog Computer by Mr. L. Just of the Applied Mathematics Division.

Table 55

RESULTS OF 60-MIL ZIRCONIUM RUNS IN HEATED WATER

Run	Energy Input (cal/g)	Calc Metal Temp (C) and Physical State	Saturated Vapor Pressure of Water (psia)	Mean Particle Dia (μ)	% Reaction
<u>Runs with Water at 90-125 C</u>					
194	150	1800, solid	10	2300 ^a	8.6
191	150	1800, solid	32	2300 ^a	7.8
196	204	1840, 80% liq	16	1260	31.5
206	205	1840, 80% liq	26 ^b	830	37.6
200	216	1840, 100% liq	19	1320	51.7
223	219	1900, liquid	22	690	55.5
225	221	1900, liquid	28	650	51.3
217	244	2200, liquid	19	495	90.3
219	271	2600, liquid	16	480	82.9
222	309	3000, liquid	19	670	81.0
<u>Runs with Water at 140-200 C</u>					
195	157	1840, solid	215	2300 ^a	9.0
190	161	1840, 10% liq	225	2300 ^a	8.5
189	169	1840, 20% liq	205	1500	14.5
203	203	1840, 80% liq	50	670	55.2
188	206	1840, 80% liq	155	800	30.7
227	230	2100, liquid	88	650	55.1
218	252	2300, liquid	79	1150	52.0
220	277	2600, liquid	150	420	73.8
<u>Runs with Water at 280-315 C</u>					
216	151	1800, solid	1500	2300 ^a	11.4
234	186	1840, 50% liq	1500	630	25.9
213	194	1840, 60% liq	900	700	25.9
233	205	1840, 80% liq	1500	1370	30.0
230	215	1840, 100% liq	1500	730	49.1
229	232	2100, liquid	1500	520	54.6

^aWires remained intact; particle sizes are those having the same surface-to-volume ratio as original wires.

^bArgon gas added (20 psia).

It is assumed in the computation that spherical zirconium particles are heated instantaneously to the initial metal temperature in a water environment. Reaction is controlled initially by the counter-diffusion of gaseous steam toward the metal surface and hydrogen away from the surface.

At a later time, the reaction becomes controlled by ionic diffusion of either metal or oxide ions through the oxide film. It is also assumed that the ionic diffusion rate is described by the parabolic rate law. The spherical particle is simultaneously influenced by heat generated by reaction and by heat losses both by radiation and convection (film conduction). Equations used to describe the processes are detailed in previous quarterlies. The markedly lesser reaction of hot zirconium spheres in room temperature water compared to that in heated water was attributed to a decrease in the rate of counter-diffusion of water vapor and hydrogen because of the low vapor pressure of water at room temperature.

The comparison between computed extent of reaction and experimental values, shown in Figure 58, is seen to be reasonably satisfactory. The largest source of error in the procedure is the assumption that runs can be characterized by a single particle diameter. Particles, once formed, act independently. Smaller ones react more rapidly and to a greater extent than larger ones. The Sauter mean diameter was chosen to represent the runs because it has the property that the total surface-to-volume ratio of the sample is the same as the surface-to-volume ratio of a particle having the mean diameter.

b. Procedure for Estimating Extent of Zirconium-Water Reaction during a Nuclear Incident

Zirconium base alloys are frequently used as the cladding material in water-cooled reactors. A nuclear transient or a loss of coolant could cause extreme overheating of the cladding metal. Two types of

accidents might be envisioned. A mild overheating might leave the clad essentially intact. An estimate of the extent of metal-water reaction could be made by incorporating the parabolic rate law into equations for the transient heating. Integration would yield the thickness of oxide film formed and the extent of metal-water reaction. The extent of reaction would be small in this case because of the protective nature of the oxide film formed on zirconium.

A more serious accident would result in melting and dispersion of the cladding into fine particles. It is likely that dispersion would not occur until the cladding was almost fully melted. Molten particles would then separate from the heat source (fuel element core) and would not be heated significantly above the melting point by the fission heat source. The extent of reaction for fully melted zirconium spheres at the melting point can be obtained from Figure 58. These results obtained by computed calculation are replotted as a function of particle diameter in Figure 59 for zirconium in heated water (100-315 C). Previous results in room-temperature water are included on the figure. The following two-step method is recommended to obtain an estimate of the extent of the zirconium water reaction:

1. The particle size distribution formed during the nuclear incident must be estimated. Studies of the particle sizes produced by a nuclear transient are being conducted in TREAT and are described in a later section.
2. The extent of reaction of each particle size range can be determined from Figure 59. A weighted average extent of reaction can then be computed.

FIGURE 59
EXTENT OF REACTION AS A FUNCTION OF PARTICLE DIAMETER FOR
MOLTEN ZIRCONIUM SPHERES FORMED AT 1840 C IN WATER

The nature of the results is such that particles formed above the melting point or not fully melted will cause only slight errors in the estimation of total metal-water reaction. Particle size ranges expected

to react very rapidly (within a few milliseconds) are indicated on the figure. Larger particles require up to 0.1 sec to reach their final extent of reaction. In an actual incident, particles might be formed over a considerable period of time as more and more cladding melts. The overall rate of reaction (rapid or slow) would then be determined by the rate at which cladding is melted and not by the reaction rate of individual particles.

Only limited studies have been carried out with Zircaloy-2; however, there are good indications that Zircaloy-2 and pure zirconium will react to a similar degree. Condenser discharge runs with Zircaloy series alloys are planned.

Experimental studies with uranium metal are nearly complete; however, computer studies have not yet begun. Estimations of total uranium-water reaction will, in general, be more complex because the particles themselves are sources of nuclear heat. Reaction time of individual particles will depend upon the flux-time distribution of the nuclear incident.

Zirconium-uranium alloy fuel elements also represent a complex case different from the pure zirconium case. Particles formed from such elements would continue to undergo nuclear heating after melting. Chemical reactivity could not be assumed to be identical with that of either pure uranium or pure zirconium.

c. Theoretical Calculation of Extent of Zirconium-Water Reaction for TREAT Runs

A method for estimating the total extent of zirconium-water reaction was developed in the previous section for the case of a nuclear incident in which the particle size distribution of the debris is known. This method was applied to four runs performed in the TREAT reactor. The method of application of these data is demonstrated to give the reader a better feeling for the approach being taken. However, it is expected that the method and the data used may be refined later. The four TREAT runs were made with ceramic-core, Zircaloy-2-clad fuel pins and are reported in previous quarterlies (see Runs 28, 29, 30, ANL-6231, page 159, and Run 49, ANL-6333, page 227). Pertinent data for the runs, including the particle size distribution, are given in Table 56. The estimated extent of reaction for each size group was obtained from analog computer results for runs in room-temperature water (given by the lower curve in Figure 59) and is given in the table. The anticipated reaction of each particle size group was then summed to give the calculated overall extent of reaction. The calculated values and the experimental values agree accurately for two of the runs but deviate considerably for the highest and the lowest energy runs. One reason for a deviation is the fact that the particle size distribution includes oxide particles from the core of the fuel pin.

Table 56

RESULTS OF IN-PILE METAL-WATER EXPERIMENTS IN TREAT
(Room-temperature Water)

Core material: mixed oxide (composition, w/o: 81.5 ZrO₂,
9.1 CaO, 8.7 U₃O₈, 0.7 Al₂O₃)
Clad material: Zr-2 (20 mils thick)
Overall diameter: 0.38 in.
Overall length: 1.05 in.

	CEN Transient Number			
	28	29	30	49
<u>Reactor Characteristics</u>				
Mw-sec burst	320	385	550	648
period, msec	60	63	62	50
Energy, cal/g of oxide core	301	362	517	610

Particle Diameter - Reaction Data

Size Group (mils)	Theoretical Percent Reaction for Each Size Group ^a	Particle Size Distribution ^b (weight percent)			
1-4	70	0.0005	0.0002	0.1	0.03
4-8	60	0.01	0.024	1.3	0.2
8-16	46	0.2	0.10	6.5	2.8
16-32	28	2.1	3.0	2.0	15.2
32-64	14	11.2	9.7	12.8	25.2
64-128	9	22.3	27.8	77.3	57.6
128-256	6	64.3	59.4	0	0
256-512	-	0	0	0	0

Percent of Metal Reacted with Water

Calculated	8.1	8.3	13.1	14.4
Experimental	4.1	8.0	14.0	24.0

^aData taken from Figure 59.

^bParticle size distribution for total sample (metal and oxide).

Efforts will be made to separate core particles from cladding particles before determining particle sizes in future runs in TREAT. It is also pertinent to note that, because there is a range of particle sizes produced, rather than a single size, some of the fine particles are in the range that

would be predicted to be explosive on the basis of the laboratory data. The particles, however, were formed over a period of time, so that the overall reaction rate would not be explosive. No explosive pressure rises were observed in the TREAT runs referred to in Table 56.

Cladding metals other than zirconium are also under study. The development of the theory of the zirconium-water reaction utilized low-temperature isothermal data reported by previous investigators as well as data obtained by the condenser discharge method. No satisfactory low-temperature data exist for aluminum or stainless steel. The pressure-pulse method and a method based on levitation melting are being used to obtain this kind of data. Current results of these studies are reported in succeeding paragraphs. Condenser discharge studies with stainless steel are currently in progress.

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

The pressure-pulse technique was developed to study the kinetics of reactions of molten metals with water vapor under isothermal conditions. The results are to be used to help interpret the data obtained from other metal-water studies. This method should best determine the form of the rate law.

The metal is initially under a pressure of about 3-16 mm of argon. The argon is introduced to reduce vaporization of the hot metal. The sample is heated by an induction heater. When the sample is at the desired temperature, electronically controlled valves are operated in proper sequence to contact the molten metal with water vapor of known pressure 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).

The results of the reaction of uranium at 1200 to 1600 C with water vapor (500 mm pressure) are given in Table 57. Average values of reaction at 1200, 1400, and 1600 C are plotted in Figure 60. It is apparent from the figure that little change in reaction rate occurs over the temperature range. This is probably due to a rate-limiting step involving gaseous diffusion and mixing within the reaction cell. A series of runs with sodium were undertaken to test this hypothesis. Sodium reacts rapidly with water vapor. At least one other investigator concluded that the sodium-water vapor reaction was controlled by gaseous diffusion processes.³⁴

³⁴Furman, S. C., Metal-Water Reactions: V. The Kinetics of Metal-Water Reactions - Low Pressure Studies, GEAP-3208, July 1959.

Table 57

RESULTS OF THE REACTION OF URANIUM AT 1200 TO 1600 C
WITH STEAM AT 500 mm PRESSURE BY THE
PRESSURE-PULSE METHOD

Time (sec)	Volume H ₂ Evolved Per Unit Area (cc STP/sq cm) at				
	1200 C	1400 C	1470 C	1550 C	1600 C
0.11	0.006	-	-	-	0.030
0.11	0.025	-	-	-	0.173
1.04	0.80	0.61	0.74	0.89	0.97
1.04	0.81	0.63	-	-	1.26
9.2	2.59	2.27	2.89	-	2.70
9.2	4.60	2.44	-	-	2.90
9.2	-	2.60	-	-	-

FIGURE 60
REACTION OF SODIUM AND URANIUM WITH STEAM
AT 500 mm PRESSURE BY THE PRESSURE-PULSE METHOD

Results of runs with sodium at 200 C are given in Table 58. Average results are included on Figure 60 for comparison with the uranium results. Reaction with sodium at 200 C is only slightly greater on the average than reaction with uranium in the 1200-1600 C range. It, therefore, seems likely that reaction rates with uranium are controlled by the rate

at which water vapor can reach the metal surface. Some means of achieving more rapid transport would be required in order to determine the ultimate rates of reaction.

Table 58

RESULTS OF THE REACTION OF SODIUM AT
200 C WITH STEAM AT 500 mm PRESSURE
BY THE PRESSURE-PULSE METHOD

Reaction Time (sec)	Volume H ₂ Per Unit Area (cc STP/sq cm)
0.11	0.027
0.11	0.23
1.04	1.10
1.04	1.26
1.04	1.29
1.04	1.29
1.04	2.67
9.2	3.33
9.2	3.41
9.2	5.47

Results of runs with aluminum were reported in the previous quarterly. The aluminum rates were well below the rates given in Figure 60 for uranium and sodium.

3. Levitation Method
(R. E. Wilson, P. Martin)

A new series of experiments has been undertaken to extend the data on the aluminum-steam reaction to temperatures above 1200 C. The pressure-pulse method is limited to lower temperatures because of excessive vaporization of the aluminum (see ANL-6287, page 189). It has been shown at temperatures below 1200 C that the rate of reaction of aluminum in water is relatively slow. However, Higgins and Schultz³⁵ have shown that the aluminum-water reaction becomes explosive under some conditions above 1400 C, indicating a need for more precise data in this temperature range.

Preliminary efforts have been aimed at the development of an induction coil suitable for simultaneously levitating and heating the sample.

³⁵Higgins, H. M. and Schultz, R. D., The Reaction of Metals in Oxidizing Gases at High Temperatures, IDO-28000 (April 1957).

The induction coil is shown in Figure 61 with an aluminum sample suspended in the coil. The coil is similar in design to one described by Comenetz and Salatka.³⁶ The induction coil consists of three turns of copper tubing, with the top turn reversed to provide an opposing field to prevent the sample from being ejected from the coil. The coil thus provides the means of support as well as the means of heating. Using this type of coil, $\frac{1}{4}$ -in. balls of aluminum were levitated at temperatures from about 1000 to 1800 C in air.

FIGURE 61
LEVITATION COIL, SHOWN WITH A ONE-QUARTER-INCH
MOLTEN ALUMINUM SPHERE SUSPENDED IN THE
HIGH-FREQUENCY FIELD

The surface temperature of the sample is measured by means of the two-color optical pyrometer previously developed for studies with the pressure-pulse method (see ANL-6101, page 144). During the development of the induction coil, it was noted that when the surface temperature of the aluminum exceeded 1750 C in air the sample ignited. Once ignited, the aluminum burned to completion in air or in water unless the sample was quenched by some means. Figure 62 shows the aluminum sample of Figure 61 after ignition. In Figures 63 and 64 one can see the aluminum burning under water and on the surface of the water, where the sample floats due to the bubbles of hydrogen and steam produced by the reaction.

³⁶Comenetz, G., and Salatka, J. W., J. Electrochem. Soc. 105, 673 (1958).

FIGURE 62

ALUMINUM SAMPLE OF FIGURE 61 AFTER
IGNITION IN AIR AT 1750 C

(Sample is obscured by aluminum oxide smoke)

FIGURE 63

ALUMINUM BURNING UNDER
WATER WITH THE EVOLU-
TION OF LARGE BUBBLES OF
HYDROGEN AND STEAM

(Enlarged from one frame of
16 mm motion pictures taken
at 850 frames/sec)

FIGURE 64
ALUMINUM BURNING ON A WATER SURFACE
AFTER LARGE HYDROGEN BUBBLES
BROUGHT SAMPLE TO THE SURFACE

(Enlarged from one frame of 16 mm motion
pictures taken at 850 frames/sec)

A typical oscilloscope trace of the output of the two-color pyrometer is shown in Figure 65. The amplitude of the lower trace is proportional to the light emitted by the aluminum pellet after passing through a $600\text{-m}\mu$ interference filter. The upper curve is the light passing through an $800\text{-m}\mu$ filter. The temperature (light emission) can be seen to rise regularly with time up to the point of ignition. The traces then become irregular because of the interference of the light beams by dense aluminum oxide smoke. The ignition temperature of 1750°C was determined from the ratio of the intensities of the two light beams at the ignition point.

A detailed study of the rate of reaction between 1200 and 1750°C will be made by passing steam over levitated spheres in a closed system. Reaction rate will be followed by collecting the hydrogen generated by reaction. In this way it is anticipated that the rate law for the aluminum-steam reaction can be determined.

FIGURE 65

OSCILLOGRAM OF OUTPUT OF TWO-COLOR
PYROMETER DURING HEATING AND IGNITION
OF ALUMINUM PELLET IN AIR

- a. Lower Curve: Light emission at $600\text{ m}\mu$
b. Upper Curve: Light emission at $800\text{ m}\mu$

4. In-pile Testing in TREAT Reactor* - Uranium Oxide Core, Stainless Steel-304-clad Fuel Pins
(R. C. Liimatainen, R. O. Ivins, M. Deerwester, F. Testa)

One of the important fuel materials for water-cooled power reactors is uranium dioxide clad in stainless steel. Commonly, the uranium dioxide is in the form of sintered pellets. To obtain information on the behavior of this type of fuel element when subjected to a power excursion, fuel pins containing a single uranium oxide pellet clad in stainless steel-304 were exposed to fast transients in TREAT. These experiments on pure uranium oxide-core fuel pins represent an extension of the previously reported work on meltdowns on stainless steel-clad, mixed-oxide-core fuel pins in water (see ANL-6183, page 145, and ANL-6333, page 226). Table 59 gives a summary of the data; the runs are given in order of the energy of the reactor burst.

*The cooperation of the ANL Metallurgy Division (for furnishing the fuel pins) and of the ANL Idaho Division (for operation of TREAT) is gratefully acknowledged.

Table 59

SUMMARY OF DATA ON STAINLESS STEEL-WATER REACTIONS
URANIA-CORE FUEL PINS

Test Conditions: Water initially at 25 C under 20 psia of helium pressure; fuel pins submerged in water.
 Composition of Core: UO_2 (89.0% of theoretical density), 20% enriched.
 Core Size: 0.33-in. diameter $\times$ 0.50 in. long;
 Reaction: $\text{Fe} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2$
 Cladding: 18-mil wall thickness of SS-304

CEN Transient Experiment Number

Reactor Characteristics	63	61	62	60
megawatt-second burst:	120	304	340	344
peak power, Mw:	425	459	2320	2620
period, msec:	121	116	50	48
Gap Between Core and Clad, mils:	3	3	2	4
Thermal Neutron Dose				
nvt by gold foil activation:	2.1×10^{14}	3.8×10^{14}	5.4×10^{14}	4.7×10^{14}
Fission Energy Input				
cal/g of core:	-	387	467	479
Peak Surface Temp of Pin, C:	-	-	1265	1235
Peak Pressure Rise, psi:	-	142	160	-
Percent of Metal Reacted with Water:	0.3	19.1	14.0	13.5
Appearance of Fuel After Transient:				
Clad:	Intact; 7% increase in diameter; evidence of hot central zone	Ruptured; ~1, 2 melted	Ruptured; ~2, 3 melted	Ruptured; ~2, 3 melted
Core:	Cracked	Fragmented into particles	Fragmented into particles	Fragmented into particles

Figure 66 shows a view of the core pellet, the stainless steel-304 jacket, and the stainless steel-304 end caps before assembly. The urania core was sintered in hydrogen, and the final sealing of the fuel pin by welding was done in a flowing helium atmosphere. The average mass of the uranium oxide core was 6.4 g, and the average mass of the stainless steel cladding was 4.2 g.

In Experiment CEN-63 (Figure 67), a 120-Mw-sec burst on a 121-msec period caused some cracking of the uranium oxide core, but no rupture or melting of the stainless steel cladding. However, there was a 7 percent increase in the overall diameter of the fuel pin. Also, the central portion of the outer surface of the jacket was darkened, giving visual evidence of intense heating with some oxidation of the metal by the water.

FIGURE 66
COMPONENTS OF URANIUM OXIDE CORE,
STAINLESS STEEL-304 CLAD FUEL PIN

FIGURE 67
URANIA CORE, STAINLESS STEEL-304 CLAD
FUEL PIN AFTER TRANSIENT CEN-63

The amount of metal-water reaction corresponded to 0.3 percent as based on the hydrogen evolution. Figure 68 shows the appearance of a polished section of the fuel pin after CEN-63; there is evidence of rather extensive cracking and also of a dark circumferential area approximately one-third of the way in from the surface of the oxide core.

FIGURE 68
MACROGRAPH OF FUEL PIN AFTER TRANSIENT CEN-63

The temperature attained by the uranium oxide core during the transient CEN-63 was calculated. The thermal neutron dose of 2.1×10^{14} nvt in CEN-63 corresponds to a specific energy input of 204 cal/g of UO_2 core (corrected for self-shielding). This increase in heat content gives a peak adiabatic core temperature of 2600 C. Since the melting range of type 304-stainless steel (which did not melt in this burst) begins at approximately 1500 C, it is likely that there are some fairly steep thermal gradients near the edge of the pin.

It is of interest to look into the reason for the expansion of the cladding observed in CEN-63. Two analyses of the original uranium dioxide core (before irradiation in TREAT) showed hydrogen contents of 40 and 45 ppm (the analyses were reported as 40 and 45 ppm hydrogen; however, actually atomic hydrogen was determined, which could also have come from water vapor trapped in the uranium dioxide). An average hydrogen concentration of 42.5 ppm corresponds to 3.0 cc STP of hydrogen in the ceramic fuel pellet (this is to be compared to 0.077 cc of void volume in the pellet). The free volume (for a 3-mil annulus between the core and the clad) within the fuel is 0.034 cc. Thus, if the 3 cc of hydrogen trapped

in the core were released into the gap and heated to a temperature of 1000 C, the resulting gas pressure inside of the cladding would be 6050 psia. From the equation, $\sigma_t = P_1 r_1 / t$ for the cylindrical jacket, where σ_t is the stress in a thin wall cylinder, P_1 the internal pressure (6050 psia), r_1 the internal radius of cylinder (0.168 in.), and t the thickness of clad (0.018 in.), the stress produced is 56,500 psia. At 900 C (the highest temperature at which data on the strength of SS-304 are available), stainless steel-304 has a yield strength of 14,000 psi and an ultimate (tensile) strength of 22,000 psi. Hence, the stress calculated from the estimated pressure would be sufficient to cause elongation of cladding, since the stress is well above the yield point for the stainless steel-304. Evidently, rupture did not occur because the internal pressure was applied as an impulse of short duration rather than as a steady load. Also, it is probable that this estimate of the internal pressure is high; cracks created in the core as a result of the transient cause an increase in the free volume and thus would tend to make the internal gas pressure lower than that calculated on the basis of only the volume corresponding to the clearance between the fuel and the clad.

Another factor of possible interest is the differential thermal expansion of the core and clad. Type 304 stainless steel has a coefficient of linear expansion of $18.2 \times 10^{-6}/(C)$, whereas that of uranium dioxide is $13.0 \times 10^{-6}/(C)$. Thus, for a given temperature rise, the stainless steel clad undergoes a greater amount of expansion. However, since the uranium dioxide core attained a higher temperature than the stainless steel, the total relative expansion of the core could be comparable to that of the clad.

Increasing the integrated power of the burst to 304 Mw-sec in CEN-61, while keeping the period relatively the same as in CEN-63, gives destructive fragmentation of both the core and clad, as shown in Figure 69, with 19.1 percent of the stainless steel reacting with the water.

Figure 70 shows the particle size distribution obtained for the meltdown products from CEN-61. These distributions for the meltdown products were obtained by sieving the fragments and particles, and weighing the fraction retained on each screen size. It is important to bear in mind that the population of particles consists both of the pulverized uranium dioxide core and of the fragmented stainless steel jacket. It is realized that, purely from the standpoint of metal-water reactions, it would be desirable to obtain the size-frequency data on the fragmented stainless steel jacket alone. However, from the general viewpoint of reactor safety, it is of interest to have information on the breakup of the entire fuel pin, since such possibilities as entrainment of fine particles into high-velocity steam, or atmospheric carryover and subsequent fallout in the event of a penetration of reactor containment structures are dependent also on the particle size distribution of the fission product bearing core.

FIGURE 69

URANIA CORE, STAINLESS STEEL-304 CLAD FUEL PIN
AFTER TRANSIENT CEN-61

304 mw-sec burst
459 mw peak power
116 ms period
19.1% SS-H₂O reaction

0.5"

FIGURE 70
PARTICLE SIZE DISTRIBUTION FOR TRANSIENT CEN 61
Determined by sieve screen analysis

Run CEN-62 gave 14.0 percent stainless steel-water reaction with extensive fragmentation of the fuel pin (see Figures 71 and 72). One somewhat unusual point concerning Run CEN-62 was the pressure trace from the transducer; this is shown in Figure 73. The signal, during part of the transient, was in the form of a damped oscillation. This could be caused by a ringing of the hydraulic system (water plus gas) inside the autoclave at its natural frequency or by periodic spurts of metal-water reaction releasing pulses of steam and hydrogen. This sinusoidal type of signal for the output from the strain gage pickup has not been observed previously. The frequency of about 200 cps does not correspond to either the natural frequency of the strain gage pressure pickup or to the light-beam galvanometers on the oscillograph. Figure 74 shows that some significant structural changes also took place during Run CEN-62. The original uranium dioxide core, as indicated in the bottom photomicrograph, has a characteristic porosity (black areas) whereas after the transient heating the pores have become consolidated (middle photomicrograph). However, the densified urania does have cracks. The stainless steel has a structure which implies having been heated to a high temperature and then rapidly quenched.

FIGURE 71

URANIA CORE, STAINLESS STEEL-304 CLAD FUEL PIN
AFTER TRANSIENT CEN-62

340 mw-sec burst
2320 mw peak power
50 ms period
14.0% SS-H₂O reaction

0.5"
└────────┘

FIGURE 72
PARTICLE SIZE DISTRIBUTION FOR TRANSIENT CEN -62
Determined by sieve screen analysis

FIGURE 73
OSCILLOGRAPH RECORD OF TRANSIENT CEN - 62

Transient CEN-60, a 344-Mw-sec burst on a 48-msec reactor period, produced extensive melting and fragmentation (see Figure 75) with 13.5 percent of the stainless steel reacting with the water. Figure 76 shows a portion of the oscillograph record from CEN-60; in this run, the fission heating from the reactor pulse caused the temperature of the stainless steel jacket to increase from room temperature to 1235 C in 0.3 sec.

FIGURE 74
PHOTOMICROGRAPHS OF PORTIONS OF FUEL PIN FROM CEN-62

FIGURE 75

URANIA CORE, STAINLESS STEEL-304 CLAD FUEL PIN
AFTER TRANSIENT CEN-60

344 mw-sec burst
2620 mw peak power
48 ms period
13.5% SS-H₂O reaction

0.5"
└────────┘

FIGURE 76
OSCILLOGRAPH RECORD OF TRANSIENT CEN-60

As shown in the photographs (Figures 69, 71 and 75) of the fuel pins after the energetic transients, there were extensive changes in geometry. In Runs 61, 62, and 63, respectively, 40.2, 34.1, and 35.3 percent of the original weight (core plus clad) were converted into particles. The remainder of the weight was in the form of the one or two large fragments which were excluded from the sieving operation. Figure 77 indicates for CEN-60 that 40.3 percent by weight of the particles were in the size range from 28 to 64 mils diameter. It is interesting to make a comparison of the particle sizes between these three meltdown runs. In Run CEN-61 (see Figure 70), a 304-Mw-sec burst on a 116-msec period, there was a progressive increase in the weight of each fraction as the particle size increased up to the particle range from 64 to 132 mils. However, Runs CEN-62 and 60 (see Figures 72 and 77), which had shorter reactor periods (50 msec as compared with 116), gave a peak in the particle size distribution at diameters from 12 to 64 mils. Thus, the shorter periods appear to produce a greater proportion of fine particles. Therefore, it might have been expected that more metal-water reaction would have resulted for CEN-60 and 62 relative to CEN-61 (since CEN-61 had approximately twice as long a reactor period); however, this increase in reaction was not observed. Further work will be done to check on the influence of reactor period on the behavior of oxide core, metal-clad fuel pins.

FIGURE 77
PARTICLE SIZE DISTRIBUTION FOR TRANSIENT CEN-60
Determined by sieve screen analysis

A comparison of CEN-62 and 60 is also of interest. The only difference between Runs 62 and 60 (since they received reactor bursts of comparable energy and period) is the clearance between the pore pellet and the metal jacket. With a 2-mil gap, CEN-62 gave 14.0 percent reaction, whereas CEN-60 gave 13.5 percent reaction with a 4-mil gap. Also, both fuel pins gave similar changes in geometry as a result of the meltdown in water. It appears, therefore, that the width of the space between the core and clad, at least over the range from 2 to 4 mils, is not of major importance in determining the transient meltdown behavior of oxide-core fuel pins. It should also be noted that the general appearance of the core and cladding after the transient meltdowns in water were quite similar to the previous mixed-oxide fuel pin meltdowns (see ANL-6183, page 147 and ANL-6333, page 266).

During this quarter, work was completed for the preparation of some preirradiated fuel specimens for later use in meltdowns in TREAT. Currently, eight uranium-rich (zirconium-niobium alloy) fuel pins are being irradiated in the MTR. These are scheduled to arrive at Argonne on September 4, 1961. The main purpose in this portion of the metal-water program is to study the influence of fission products on the extent of dispersion and on the extent of reaction (for comparison with previous in-pile data on "cold" fuel pins).

Also, preliminary tests were performed on a new, high-pressure autoclave which will run at 1500 psia; pressure checks and temperature control tests were made. Meltdowns in high-pressure water will be compared with the work performed to date in which the initial pressure was 20 psia.

IV. REACTOR CHEMISTRY

The neutron capture cross sections of neptunium-237 and erbium-170 are being determined in the fast neutron energy range. The total neutron cross section of uranium-233 is also being determined.

Several types of experiments have been carried out in order to investigate operation of a regenerative lithium hydride fuel-cell system for converting nuclear energy to electricity. The thermally regenerative emf cell system is one in which heat is used to dissociate lithium hydride, which is then re-formed in an electrochemical cell with the production of electric power.

A program of research in thermoelectricity has been initiated to contribute to the technological development of direct conversion of nuclear reactor heat energy into electrical power by means of the thermocouple effect. Binary liquid systems comprised of elements in the area of the periodic system centering about the element tin are to be investigated. The Seebeck coefficients in the liquid indium-antimony system are under study as a function of composition and temperature. For high-temperature work refractory materials are required. Initial studies on these materials will be made in the thorium-sulfur and uranium-sulfur systems.

The Reactor Decontamination Program is directed toward determination of the seriousness of fuel element ruptures in boiling water reactors and the determination of methods of decontamination of contaminated surfaces. A 16-day run to determine whether zirconium-niobium content would reach an equilibrium value has 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 are being conducted with oxalic acid and citric acid-base solutions containing hydrogen peroxide.

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

The number of fissions and captures which a given nuclide will undergo in a reactor can be calculated if one knows (1) the neutron energy spectrum of the reactor as a function of core age and position in the core; (2) the capture and fission cross sections as a function of neutron energy; and (3) the production rate of the nuclide from other nuclides. Increasing attention has been given in recent years to the cross sections which are useful in calculations involving the use of uranium and plutonium isotopes as fast reactor fuels.

Further, it can be stated that a large body of fast neutron reaction data has accumulated in the literature, including neutron total cross sections and capture cross sections for species over most of the range of the nuclide

chart. There are, however, still many gaps in the data, which, when filled, will provide exact data for refined calculations on several problems associated with the operation of fast reactors. One class of such data includes the capture cross sections of species which build up in reactors through the capture process in the original fuels. One of these byproducts is uranium-236, whose fast neutron capture cross section has been determined recently in this group.³⁷ Similar measurements are now in progress for neptunium-237. Fast neutron data are also lacking for a group of elements which have sometimes been discussed as structural and control materials. Among these are the rare earth elements, several of whose cross sections are now being measured. A more detailed discussion of these measurements follows:

1. Fast Capture Cross Sections
(D. C. Stupegia, E. H. Dewell)

Fast capture cross sections are being determined as a function of neutron energy by measuring the disintegration rate of the capture product in a known amount of target material when the target is irradiated in a known flux of monoenergetic neutrons. The neutron source is the reaction $\text{Li}^7(p,n)\text{Be}^7$, produced when a lithium target is bombarded with protons from the Van de Graaff accelerator. With the present arrangement it is possible to obtain neutrons ranging in energy from about 0.3 to 2.0 Mev. The neutron flux is measured with a fission chamber which counts fissions in a thin sample (~200 mg/sq cm) of enriched uranium. The target sample and the uranium monitor foil are placed in the fission chamber so that they subtend the same polar angle with respect to the proton beam; hence, target and monitor receive the same neutron flux. After irradiation, the target is analyzed for the gamma-ray spectrum of the activation product with the sodium iodide crystal and 256-channel pulse-height analyzer. The absolute disintegration rate corresponding to the gamma spectrum is determined by comparing the spectrum to one of a known activity of the same species counted in the same geometry, the activity of this species having been determined by absolute beta counting. Further discussion of the specific nuclides being studied follows:

Rare Earth Elements

The capture cross sections of several of the elements from atomic numbers 57 to 71 are presently unknown in the neutron energy region above 0.17 Mev. This cross section has been measured for several of the rare earth elements for neutron energies between 0.01 and 0.17 Mev.³⁸

³⁷Stupegia, D. C., Heinrich, R. N., McCloud, G. H., Journal of Nuclear Energy, in press.

³⁸Gibbons, J. H., Macklin, R. L., Miller, P. D., and Neiler, J. H., Bull Am. Phys. Soc., Ser. II, 4, 385 (1959).

Among those studied were erbium and gadolinium, which, in the presently reported work are being studied in the range from 0.35 to 2.0 Mev, and ytterbium and lutetium, for which the same measurements are planned in this range of higher energy.

Several of the rare earths have received attention in recent years as possible reactor control materials. A brief review of this work follows.

1. The Bureau of Mines³⁹ has investigated the metallurgy of alloys of titanium with dysprosium and erbium for use as burnable poisons in control rod materials.
2. Workers at Argonne (see ANL-6269, page 50) have constructed absorber materials consisting of dysprosium oxide dispersed in aluminum, and the oxides of gadolinium, samarium, europium, and erbium dispersed in cobalt.
3. Sintered oxides of gadolinium, samarium, and dysprosium have been proposed⁴⁰ for use as control rods in the Dresden reactor.

These studies have been directed generally toward the use of these materials as thermal reactor control materials, making use of the high thermal absorption cross sections. It is useful, however, to know the capture cross sections of these elements for higher neutron energies in order to be able to make calculations involving reactors with a considerable fast neutron energy component.

Erbium-170: Ten neutron irradiations have been carried out on erbium oxide targets with neutrons ranging in energy from 0.35 to 1.30 Mev. Of the six naturally occurring isotopes, four of these, erbium-162, 164, 168, and 170, yield radioactive capture products. The first two are of such low isotopic abundance that their capture products are not visible in the gamma spectra. Nor can the erbium-168 cross section be measured by the present method, since erbium-169 has no gamma rays. It is possible, therefore, only to measure the cross section of erbium-170, which yields the 7.8-hr beta and gamma emitter, erbium-171. Preliminary analysis of the gamma spectral data indicates that the cross section of erbium-170 shows a slight rise with neutron energy in this region. Such a rise, although contrary to the usually expected trends, has been found in uranium-236, uranium-238, and, apparently for only one other nuclide in the rare earth region, samarium-154.

³⁹USBM-U-623 (1959) Quarterly Metallurgical Progress Report No. 3, Period April 1, 1959-June 30, 1959.

⁴⁰WAPD-MRP-84, Technical Progress Report, Pressurized Water Reactor (PWR) Project, Period December 24, 1959 to February 23, 1960.

Gadolinium-158: Seven irradiations have been carried out on natural gadolinium oxide targets in the neutron energy range from 0.46 to 1.10 Mev. The capture reactions produce 18-hr gadolinium-159 and 3.7-min gadolinium-161, which decays to 6.9-day terbium-161. Gamma analyses of the irradiated targets show the 18-hr activity. Although the 3.7-min activity is too short-lived to be observed by the present method, it was hoped that one would be able to see its 6.9-day daughter, terbium-161. This however, has not been accomplished, the 1- to 2-hr irradiation times having been too short. These irradiations, therefore, will yield only the gadolinium-158 cross sections, unless much larger irradiation times are used later.

Neptunium-237: Work on the fast capture cross sections of neptunium-237 has continued. This nuclide builds up in reactor cores of high burnup through the reactions

The neutron activation of this isotope forms the 2.1-day beta and gamma-emitter neptunium-238, which, in turn, decays to the long-lived alpha-emitter plutonium-238.

Neutron cross sections of neptunium-237 have been measured in some energy regions. The total cross section has been determined between 0.02 ev and 40 ev,⁴¹ and the fission cross sections between 0.12 and 4 ev,⁴² and between 0.4 and 8 Mev.⁴³ No other cross sections have been reported.

Neptunium-237 is a 2.2×10^6 -year alpha emitter which decays to 27.4-day protactinium-233. When the neptunium-237 target is activated, therefore, the resulting gamma spectrum contains the gamma rays of neptunium-238 together with those of the target material and its daughter. Although the activity of the target material is several orders of magnitude greater than that of the capture product, gamma rays of the latter near 1 Mev are still observable in the spectrum.

⁴¹Block, R. C., Slaughter, G. G., and Harvey, J. A., Bull Am. Phys. Soc. Ser. II, 4, 34 (1959).

⁴²Leonard, B. R., and Seppi, E. J., Bull. Am. Phys. Soc., Ser. II, 4, 31 (1959).

⁴³Schmitt, H. W., and Murray, R. B., Phys. Rev. 116, 1575 (1959).

Seven irradiations have been completed, and the gamma spectra recorded and analyzed. Conversion of these data to cross-section values awaits the calibrations based upon absolute beta counting, as discussed earlier.

2. Neutron Total Cross Section of Uranium-233 (D. C. Stupugia)

The total cross section of uranium-233 has previously been measured up to 10-keV neutron energy.⁴⁴ In the present work, the total cross section has been determined in the range from 3 keV to 1611 keV.

Metallic samples of uranium containing 98 percent uranium-233 were exposed to monoenergetic neutrons derived from the $\text{Li}^7(p,n)\text{Be}^7$ reaction. The total cross section was obtained from neutron transmission measurements according to the relation:

$$I/I_0 = e^{-N\sigma} \quad ,$$

where I and I_0 are, respectively, the neutron beam intensities with and without the sample in place in the beam, and N is the sample thickness in atoms/sq cm. The results are given in Figure 78.

⁴⁴Hughes, D. J., and Harvey, J. A. Neutron Cross Sections, BNL-325 (July 1, 1955).

The standard deviations of the cross sections are near 1.5 percent. Neutron energy spreads about each point vary from ± 1.3 kev at the lowest energies to ± 8 kev at the highest. Part of the lower-energy data are shown on the curve. The two sets of data join consistently, the fine structure in the region of lower energy continuing into the higher range. The dashed portion of the curve represents a small hiatus in the data, in which has been interpolated the probable structure of the curve. This gap will be filled when more beam time becomes available.

The neutron beam used in this work was obtained from the ANL Physics Division Van de Graaff accelerator. Time on the machine as well as the use of the neutron collimation and detection equipment is gratefully acknowledged.

A detailed report on this work has been prepared for publication.

B. Thermally Regenerative Emf Cell

(C. E. Crouthamel, M. Foster, D. Anthes)

In studies directed at the development of methods of converting nuclear energy to electricity, a thermally regenerative emf cell has been investigated. The thermally regenerative emf cell system is one in which heat is used to dissociate a compound which then is recombined in an electrochemical cell with the formation of the same compound and the generation of electric power. The thermally regenerative emf cell differs from the conventional fuel cell in that in the latter oxygen and hydrogen, or perhaps a hydrocarbon gas, are combined in the cell to produce electricity. The product of the cell reaction is not regenerated.

The overall efficiency of a regenerative emf cell system is not expected to exceed that of a high-efficiency steam plant. Other potential advantages, however, make an investigation of a thermally regenerative emf cell appear worthwhile. Some of these advantages are the virtual elimination of moving mechanical parts, the ability to adapt to a wide range of plant sizes, a greater potentiality for compactness with lower weight per unit output wattage, and the ability to isolate the operating system rigorously for the duration of its useful life.

In a regenerative cell, any aqueous system would appear to be unsuitable because of the relatively large quantities of water which must be circulated between high- and low-temperature sources. The water would pass through a phase change, liquid to gas and back, involving an extremely large quantity of heat per cycle to be transferred. In general, there are relatively few inorganic compounds which are amenable to thermal dissociation at temperatures of 1000 C or below and whose dissociation products can be separated conveniently. Finally, of course, the combination of the dissociation products must be accomplished in an emf cell in an approximately reversible manner with the production of an

acceptable voltage and current density. Cell kinetics, thermodynamics of the system, and physical and chemical properties of the phases (e.g., densities and solubilities) may in any particular application create very difficult problems. The alkali and alkaline earth hydrides appeared to be compounds to have a demonstrated potential application. The inert, dry atmosphere required for the lithium hydride cell is the most rigorous isolation anticipated for a system. The effort in selecting emf-conversion systems has been limited enough so that the probability of other useful systems existing is still relatively high within the limits of existing technology. Also, as the possibility of increasing the regenerative temperature develops with the discovery of new high-temperature containers, the number of useful compounds possible for thermal regeneration will increase sharply.

For the reasons mentioned above, the lithium hydride system was selected for the first experiments. The literature indicates that there are two other current efforts directed toward regenerative emf cells. The Mine Safety Appliance Research Corporation (MSA) has investigated a number of alkali and alkaline earth hydride cells. The results of these experiments have been reported in a series of reports⁴⁵ to the U.S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey. One cell was operated with lithium metal and lithium chloride-potassium chloride molten salt electrolyte. A porous stainless steel hydrogen gas electrode was employed. Maximum open circuit voltage was 0.385 volt at 357 C. In a similar cell containing lithium fluoride-lithium chloride electrolyte at 570 C, a maximum open circuit voltage of 0.72 volt was obtained. In the latter cell, current densities of 245 amp/sq ft at 0.30 volt are reported.

Snoko and Fuscoe (Thompson Ramo Wooldridge Co. Inc.) reported at the Society of Automotive Engineers in January 1961 that they were also working on a regenerative lithium hydride emf cell system. These programs will be closely followed to avoid duplication. The Argonne program will attempt the collection of basic data needed for the satisfactory evaluation of regenerative emf cells in addition to running laboratory-scale devices.

There are certain general thermodynamic considerations which should introduce any discussion of regenerative emf cells. The maximum efficiency of the cell reaction and the regeneration step may be calculated

⁴⁵Shearer, R. E., Study of Energy Conversion Devices, Report 1, Progress Report to U.S. Army Signal R and D Lab., Fort Monmouth, N. J., October 31 (1959), (MSAR-59-119); Ibid. MSAR-60-12 Report 2, January 31, 1960; MSAR-60-56, Report 3, April (1960); MSAR-60-110, Report 4, August (1960).

as the Carnot Cycle maximum efficiency, as discussed by Liebhafsky⁴⁶ and Wood.⁴⁷ In this cycle a quantity of heat is absorbed isothermally and reversibly by a system at a higher temperature, T_2 , and a smaller quantity of heat is rejected isothermally and reversibly at a lower temperature, T_1 . Ideally, the entire cycle must be reversible, and this requires two adiabatic reversible steps for changing the temperature. The Carnot efficiency e_c for a system operating between temperatures T_1 and T_2 would be

$$e_c = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \quad , \quad (1),$$

where w is the work done by the system, and q_1 and q_2 are heats absorbed by the system at temperatures T_1 and T_2 . If the cell operating temperature is taken as 395 C and the regenerative temperature as 1000 C, the Carnot maximum efficiency would then be 49 percent for the cycle.

The quantity of work done by a system in a Carnot cycle includes all possible forms of work. In the case of emf cells, it includes the work associated with volume changes of the system as well as the electrical work; however, in most applications only the electrical work will be of interest. In this case the maximum useful efficiency e_m may be defined as

$$e_m = \frac{EnF}{q_2} = \frac{EnF}{T_2 \Delta S_2} \quad , \quad (2),$$

where E is the reversible emf of the cell at the temperature T_1 , F is the value of the Faraday, and n is the number of equivalents of the chemical reaction. The thermodynamic data are not available for the calculation of this efficiency with any degree of certainty in the case of the lithium-hydrogen cell. If this cell proves of lasting practical interest, it will be one of the Argonne program objectives to collect these thermodynamic data.

1. General Description of Regenerative Emf Cell

The assembled cell is shown in Figure 79. The cathode is formed by a 10-mil Armco iron diaphragm welded across the bottom of an Armco iron cup. The hydrogen diffuses through this diaphragm. This is unlike the MSA electrode, which is a porous metal frit. The anode is an inverted funnel trapping floating lithium on the melt surface. The Armco iron crucible containing the fused salt electrolyte and the integral 10-mil Armco iron diaphragm is approximately $4\frac{3}{4}$ in. in diameter by 4 in. high.

⁴⁶ Liebhafsky, H. A., J. Electrochem. Soc. 106, 1068 (1959).

⁴⁷ Wood, Scott, Illinois Institute of Technology, September, 1960 (Private Communication).

FIGURE 79
LITHIUM HYDRIDE CELL AS OPERATED IN ARGON ATMOSPHERE

The crucible is insulated from the outer container by means of quartz rings and lengths of quartz rod. The depth of the electrolyte is about 2 in. The hydrogen gas inlet tubes leading to the bottom of the Armco crucible are $\frac{1}{8}$ -in. stainless steel tubing, welded into the bottom of the crucible. All welding on this assembly is heliarc welding. The lithium-Armco iron inverted cup anode was first welded to a stainless steel tube. This arrangement was replaced with a stainless steel rod and vent hole, as shown in Figure 80, to obviate the possibility of forcing molten lithium and eutectic through the tube by an imbalance of pressures. The thermocouple sheath consists of a length of $\frac{1}{8}$ -in. stainless steel tubing, welded shut at the bottom. The hydrogen reference electrode is of Armco iron welded to a length of $\frac{1}{8}$ -in. stainless steel tubing. The entire cell is contained in an outer stainless steel jacket, with a gasketed (Buna N), water-cooled lid. The total length of the outer container is $10\frac{1}{2}$ in. Insulation for the electrodes is

provided in the cooled lid by means of high-temperature halocarbon plastic bushings, nylon washers, and neoprene gaskets. Argon gas, previously purified by passing over uranium metal turnings held at 350 C, is bled through the cell during operation.

FIGURE 80
LITHIUM HYDRIDE CELL COMPARTMENT

The emf was measured with a Leeds and Northrup K-3 potentiometer calibrated with a standard Weston Cell. The current was measured by obtaining the potential drop across a calibrated resistor.

The eutectic used in this cell (41 mole percent potassium chloride and 59 mole percent lithium chloride⁴⁸) was purified by the method reported by Maricle and Hume.⁴⁹ Reagent-grade lithium chloride

⁴⁸Elchardus, E., and Laffitte, P., Bull Soc. Chim., France, 51, 1572 (1932).

⁴⁹Maricle, D. L., and Hume, D. N., J. Electrochem. Soc., 107, 354 (1960).

and potassium chloride were weighed in air and mixed to form the approximate eutectic composition. The mixed powder was then placed in a quartz cell and heated and fused under chlorine. After bubbling the gaseous chlorine through the melt for approximately one-half hour, the melt was flushed with argon which had been purified by passing through uranium metal turnings which were held at a temperature of 350 C. The purified eutectic was then forced through the medium-porosity quartz frit into a Pyrex tube, and sealed off under vacuum until used.

Polarography was used to determine the extent of hydroxide impurity remaining in a purified melt. This was accomplished through the use of a Pt-Pt (II) reference electrode and a tungsten microelectrode. Polarograms indicated a residual hydroxide impurity of the order of 10 ppm. This value, while not so low as that reported possible for either the chlorine⁴⁸ or hydrochloric acid⁵⁰ purification processes, was considered sufficiently low for preliminary cell studies.

2. The Equation for the Cell Reaction

The chemical reaction at the anode is the oxidation of lithium metal to lithium ions:

The hydrogen gas is introduced at the cathode, the reaction being the reduction of hydrogen gas to hydride ions:

The overall cell reaction is then

For Equation (5) we may write the change in free energy (ΔF) as

$$\Delta F = \Delta F_0 + RT \ln \frac{(a_{\text{Li}^+}) (a_{\text{H}^-})}{(p_{\text{H}_2})^{1/2}} \quad , \quad (6)$$

⁴⁸See previous page.

⁵⁰Laitinen, H. A., Ferguson, W. S., and Osteryoung, R. A., J. Electrochem. Soc., 104, 516 (1957).

and, since

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

we have

$$E = E_0 - \frac{RT}{nF} \ln \frac{(a_{Li^+})(a_{H^-})}{(p_{H_2})^{1/2}} \quad (8)$$

and

$$(a_{Li^+})(a_{H^-}) = (\gamma_{\pm}^2) (M_{Li^+})(M_{H^-}) \quad . \quad (9)$$

Standard states could be defined as follows:

H_2 (g) - pure gas at one atmosphere pressure, assuming hydrogen obeys the ideal gas law;

Li (liq) - pure molten lithium metal;

LiH - hypothetical one-molal solution obeying limiting law corresponding to Henry's law:

$$f_2 = kM^2; \frac{a_{LiH}}{M^2_{LiH}} \rightarrow 1 \text{ as } M \rightarrow 0 \quad .$$

Equation (8) will not accurately represent the working cell potential in actual operation, since the solubility of lithium hydride is known to be appreciable in lithium metal. In this case, Equation (8) should be written as follows:

$$E = E_0 - \frac{RT}{nF} \ln \frac{(a_{Li^+})(a_{H^-})}{(a_{Li})(p_{H_2})^{1/2}} \quad . \quad (10)$$

In order to apply the above equation, additional and independent measurements of some of the basic quantities: E_0 , $\gamma_{\pm}$, and the k in Henry's law for lithium hydride in the molten salt solution, would have to be obtained. At present, in Equations (8) and (9), E , M_{LiH} , and p_{H_2} are the only quantities whose numerical values are known in cell measurements. It is possible to run an experiment so that E_0 , a_{LiH} , and T are constants, so that

$$E = (E_0 - \frac{RT}{nF} \ln (a_{Li^+})(a_{H^-}) + \frac{1}{2} \frac{RT}{nF} \ln p_{H_2} \quad (11)$$

and

$$E = K + \frac{1}{2} \frac{RT}{nF} \ln p_{H_2} \quad . \quad (12)$$

The above relationship will be used as described later in an examination of the pressure dependence of the voltage.

3. The Diffusion-type Hydrogen Electrode

The diffusion-type gas electrode appears to be well suited to easy control and continuous trouble-free operation. Porous metal discs are subject to flooding with either gas or molten salt electrolyte. Porous disc electrodes must be made with very uniform pore size to prevent channeling. Also, porous metal discs used by other investigators appear to yield erratic voltages, possibly because of many variables which can change the effective operating surface at the gas-melt interface.

Diffusion of hydrogen through a solid metal diaphragm takes place through the body of the solid and not along grain boundaries. Edwards⁵¹ and Smithells and Ransley⁵² have shown that the rate of diffusion of hydrogen through a large single crystal of iron remained the same after the sample was recrystallized into smaller crystals. Diffusion of diatomic gases takes place in the atomic state, as evidenced by the rate dependence following the square root of the pressure. Gases with no chemical affinity for the metal, such as helium, show no measurable diffusion. Hydrogen produced against a metal surface by chemical or electrochemical means will diffuse through the metal against several hundred atmospheres of hydrogen pressure on the outlet side. This is further evidence that the total process of permeability of hydrogen includes dissociation into atoms at the surface, diffusion of the atoms through the volume of metal, and recombination to escape as gas.

In order to understand all the variables affecting hydrogen diffusion through a metal diaphragm, consider the case with exit gas pressure equal to zero. We may write the following equation:

$$Q = \frac{SDAt}{\ell} \sqrt{p} \exp\left(-\frac{E_0}{RT}\right) \quad , \quad (13)$$

⁵¹Edwards, C. A., J. Iron Steel Inst., 110, 9 (1924).

⁵²Smithells, C. J., and Ransley, C. E., Proc. Roy. Soc. (Lond), A150, 172 (1935).

where

Q = amount of gas diffusing, cc at STP
 S = solubility constant
 D = diffusion constant
 A = area of diaphragm
 ℓ = thickness of diaphragm
 p = hydrogen pressure
 E_0 = activation energy for the process
 R = gas constant
 T = absolute temperature, K
 t = time.

The variation of the amount of hydrogen diffusing with the square root of pressure indicates that diffusion occurs in the atomic rather than in the molecular state. Diffusion of molecular hydrogen through a porous disc varies directly with pressure.

At a given temperature and pressure, Equation (13) may be simplified to

$$Q_{(T,p)} = \bar{S}At/\ell$$

where

$$\bar{S} = SD\sqrt{p} \exp \left(-\frac{E_0}{RT} \right) .$$

From the above equations it can readily be seen how the rate of supply of hydrogen by diffusion through a metal diaphragm may be controlled by the more obvious variables of temperature, pressure, diaphragm area, and diaphragm thickness. The variables which affect E_0 , the activation energy or the population density of atomic hydrogen at the surface of the metal diffuser, are not so obvious. Values for $\bar{S}$ have been tabulated by Flint⁵³ for mild steel decarburized for 4 hr at 870 C in wet hydrogen and etched with acid. Experimentally, $\bar{S}$ for the above steel was found to be^{51,52} 0.12 cc (STP)/(sq cm)(hr)(mm) at 400 C.

If the hydride electrode operated with 100 percent efficiency, the following calculation would give the maximum possible current density for a 10-mil low-carbon steel diaphragm. Applying Equation (14) and the experimental value of $\bar{S}$ given above,

⁵¹See previous page.

⁵²See previous page.

⁵³Flint, P. S., The Diffusion of Hydrogen through Materials of Construction, KAPL-659 (1951).

$$Q(400 \text{ C}, 760 \text{ mm}) = \frac{(0.12)(930)(2.78 \times 10^{-4})}{0.254}$$

$$= 0.122 \text{ cc hydrogen}/(\text{sec})(\text{sq ft}),$$

where

$$1 \text{ sq ft} = 930 \text{ sq cm};$$

$$\ell = 10 \text{ mils} = 0.254 \text{ mm}$$

$$1 \text{ sec} = 2.78 \times 10^{-4} \text{ hr}$$

$$\bar{S} = 0.12 \frac{\text{cc (STP)}}{(\text{sq cm})(\text{hr})(\text{mm})} \text{ at } 400 \text{ C and } 760 \text{ mm hydrogen}$$

$$i = \frac{0.122 \left(\frac{\text{cc}}{(\text{sec})(\text{sq ft})} \right) \times 2 \left(\frac{\text{g-equiv}}{\text{mole}} \right) \times 96,500 \left(\frac{\text{coulombs}}{\text{g-equiv}} \right)}{22,415 \left(\frac{\text{cm}^3}{\text{mole}} \right)}$$

$$= 1.05 \text{ amp/sq ft}$$

4. Cell Operation

Several types of experiments have been carried out in order to investigate the operation of the cell. The hydrogen pressure has been varied as well as the load on the cell. Runs of 73 hr have been carried out, although this should not be considered a time test of the cell, since many operational variables were changed during the run.

In order to test the dependence of cell emf on hydrogen pressure, two separate cell loadings were made, the results of which are shown in Figures 81 and 82. The voltages apparently are not stable enough, and the variations of cell potential with hydrogen pressure are not large enough, in these measurements to demonstrate strict obedience to the slope expected from Equation (12). The widest deviations from Equation (12) as shown in the data of Figure 82 are about 2.0 mv, and in Figure 81 about 1.0 mv.

Platinum and palladium-silver diaphragms have been tried, but they did not resist attack by the melts for an appreciable time. Diaphragms of Armco iron have been used extensively. The observed emf values for a typical run of the cell shown in Figures 81 and 82 are summarized in Table 60. The initial high voltages quickly reached a steady voltage of a little over 0.72 volt. Platinum and palladium-silver gas diaphragms also have given cell voltages of 0.75 volt.

FIGURE 81
VARIATION OF CELL EMF WITH HYDROGEN PRESSURE,
ARMCO IRON DIAPHRAGM, NO LOAD (EXPERIMENT 1)

FIGURE 82
VARIATION OF CELL EMF WITH HYDROGEN PRESSURE,
ARMCO IRON DIAPHRAGM, NO LOAD (EXPERIMENT 2)

Table 60

SUMMARY OF EMF VALUES OF A LITHIUM HYDRIDE CELL WITH AN
ARMCO IRON DIAPHRAGM GAS ELECTRODE

(LiCl/KCl Solution at 385 C as Electrolyte)

Time hr:min	Emf, volts Li (2) vs large Armco iron diaphragm, ^a 10 mils thick	Emf, volts Li (2) vs small Armco iron diaphragm, ^a 10 mils thick	Results
0:0	1.20		Zero time measured from lowering lithium metal in the retaining cup into molten salts
0:2	0.98		Voltage falling
0:04	0.860		Voltage falling
0:10	0.7280		
3:10	0.7255		
3:20	0.7250		Steady voltage before loading cell
3:30	0.7255		
3:35	0.7165		36-ohm load for 30 sec plus 4-min recovery time 0.7255 - 0.6900 - 0.7165.
3:40	0.710	1.28	Lowered small reference Armco iron diaphragm into melt
3:42	0.710	0.920	
3:44	0.708	0.810	
4:00	0.694	0.704	
4:05	0.696	0.703	
4:10	0.696	0.706	
4:10			Placed 36 ohms across large iron diaphragm and lithium electrode
5:15	0.653	0.690	760 mm hydrogen pressure
49:00	0.583	0.598	Cell still under 36-ohm load
50:00	0.596	0.603	Load removed at 49:01
50:10			Placed 3,328-ohm resistance across large hydrogen lithium electrodes
51:00	0.467	0.560	Steady voltages: under load
52:00	0.575	0.577	Steady voltages: no load
69:00	0.573	0.575	Cell had been left overnight with no load
69:01			Placed 2.42-ohm load on cell
70:00	0.416	0.533	Steady voltages: under load
70:15	0.448	0.540	Increased H ₂ pressure from 760 to 820 mm
70:16			Load removed
71:00	0.554	0.560	Steady voltage at no load
72:00			1,204-ohm load placed across cell
73:00	0.265	0.48 fluctuating	Steady voltage under load at 760 mm H ₂ pressure
73:15	0.318	0.48 fluctuating	Increased H ₂ pressure to 800 mm
73:30	0.264	0.48 fluctuating	Reduced H ₂ pressure to 760 mm

^aAreas of the large and small iron diaphragms were 0.11 and 0.0055 sq. ft.

The voltage then continues to drop (Table 60) as the cell is operated, building up soluble lithium hydride in the melt. Note that the small Armco iron diaphragm started at about the same high voltage as the large diaphragm, and then quickly dropped to a stable value. Both iron diaphragms were saturated with hydrogen several hours before being immersed in the melt. The same initial high voltages occurred with both new and old iron diaphragms when first placed in operation. This initial voltage is believed to be due to the reduction of iron oxides on the surface of the gas diaphragms by lithium metal.

Both the large and small Armco iron diaphragm potentials were referred to the same lithium metal electrode, as shown in Table 60. When a resistive load was placed across the cell, the small reference iron diaphragm potential showed an appreciable drop. This was taken as an indication of concentration polarization of the molten lithium electrode. Most of the additional voltage drop under resistive load shown by the large iron hydrogen gas diffuser was interpreted as due to the slow diffusion rate of hydrogen through the 10-mil-thick iron diaphragm. Increasing the hydrogen pressure from 760 mm to 800 mm effected a rapid change in potential under load, as would be expected for diffusion polarization. The original potential quickly reappeared with the return to 760 mm hydrogen pressure. The current drawn through the external calibrated resistor of 1.204 ohms was 220 and 264 ma at 760 mm and 800 mm hydrogen pressure, respectively. The area of the large hydrogen diffuser was 0.11 sq ft and that of the lithium molten metal pool 0.0090 sq ft. The current densities at the iron metal diaphragm and lithium pool were 2 amp/sq ft and 25 amp/sq ft, respectively. A reduction in iron diaphragm thickness from 10 mils to about 0.2 mil would allow current densities to approach 100 amp/sq ft. The lithium molten metal pool also could be increased in area by a factor of fifty in the cell used.

The 10-mil-thick Armco iron diaphragms have yielded current densities in excess of 2 amp/sq ft. The hydrogen diffusion rates in Armco iron must be at least double that reported for decarbonized steel, as shown by previous calculation using Equation 14 and a value of 0.12 for $\bar{S}$. Two possible methods are apparent to increase the rate of hydrogen diffusion, $Q(400\text{ C}, 760\text{ mm})$: first, by modifying the iron surface to increase the population of atomic hydrogen at the gas-iron interface, and second, to reduce the thickness of the iron diaphragm. Both effects are capable of giving large factors (10 to 100); however, it must be recalled that either one may become limiting. It is, for example, possible to evaporate uniform 0.1-mil pure iron surfaces on a supporting diaphragm of platinum, palladium, or palladium-silver. The diffusion through the latter is very rapid at 400 C, and if the 0.1-mil iron would still be the limiting factor, a hundredfold increase in diffusion could be obtained by varying the thickness alone. The iron surface would provide the necessary protection of platinum and palladium from the cell environment. Thin layers of platinum or palladium also may be evaporated on iron to modify its diffusion rate. In either case, the iron interface population of atomic hydrogen would be affected. No information appears to be available on hydrogen diffusion in such diaphragms. Experiments to obtain quantitative values on the diffusion of hydrogen through iron-platinum diaphragms are being designed.

Figure 83 shows the behavior of the cell potential vs time when current is drawn and under conditions such that the rate of diffusion of hydrogen accounts almost entirely for the cell polarization. This is the case when the area of a 10-mil-thick iron diaphragm is equal to or less than the area of the molten lithium pool.

FIGURE 83
2.5-cm-DIA AND 10-mil-THICK ARMCO IRON DIAPHRAGM RESPONSE
AND RECOVERY FROM RESISTANCE LOADING

In the data of Table 60 the area of the iron diaphragm was about ten times that of the molten lithium, and concentration polarization at the lithium electrode was beginning to contribute to the overall polarization of the cell. The varying degree to which a porous electrode can form and support a population density of atomic hydrogen at the melt-gas interface may account for its erratic behavior. The above discussion also suggests possible ways of obtaining abnormally high diffusion rates to support the high current densities desired in a hydride cell. Thus, pure iron which appears to be stable to the molten salt-lithium environment may be given special treatment on the gas side of the diaphragm which would increase the population of atomic hydrogen at the diaphragm surface. Plating the iron surface with platinum, palladium, or uranium is being tried presently in this laboratory.

C. Thermoelectricity Research (R. K. Edwards)

A program of fundamental research in thermoelectricity has been initiated to contribute to the technological development of direct conversion of nuclear reactor heat energy into electrical power by means of the thermocouple effect. Because, as with the other areas of direct conversion, there are large-scale and intensive research efforts in many locations within the United States and abroad, the group program here was not envisioned to be a major effort in this field, but the purpose is rather to establish a competence and to contribute toward the time when nuclear reactor direct conversion might become reasonably justified. The judgment was made that a

small group devoted to certain limited and more unique aspects of thermocouple development would best serve the purpose in mind.

Two areas have been selected as of special interest. The area of liquid thermocouple research is under investigation because of several favorable experimental factors and because very little work has been and is being carried out for such materials. In direct association with this, certain solid state work is likely to be carried out, presumably on systems where interest arises as an outgrowth of liquid state work. Refractory solid thermocouple systems form the other major area, since they are considered to be of particular interest to reactor energy conversion.

In addition to Seebeck coefficient measurements, electrical conductivities and thermal conductivities are of interest because of their significance in elucidating the mechanism of charge-carrier transport which gives rise to an important contribution to the Seebeck coefficient. Also, practical thermocouple devices are subject to materials efficiencies expressed as a "figure of merit" Z :

$$Z = \hat{S}^2 \sigma / k \quad ,$$

in which $\hat{S}$ is the Seebeck coefficient, σ is the electrical conductivity, and k is the thermal conductivity of the material. The higher the value of Z (usually taken in units of reciprocal degrees Kelvin) the more efficient is the material. Plans have been made to set up suitable equipment for these correlating measurements. The thermal conductivity measurements involve rather exceptional investments in time and will be carried out only in selected cases.

Initial efforts have been concerned with literature work, equipment design and acquisition, and with some exploratory measurements.

1. Liquid Thermocouple Systems (R. K. Edwards and P. Danielson)

Principal unique points of theoretical interest lie in the evaluation of the degree of correlation which might be found between the change in the Seebeck coefficient on mixing of a binary pair to form a solution, and the excess entropy of mixing measured thermodynamically for the same solution. Thus, mixing involves changes in electronic distributions and these, of course, imply entropy changes. The Seebeck coefficient relates to electronic entropy changes on transfer, but it is also dependent upon the mechanism of transfer and so may only sometimes relate simply to the true equilibrium electronic distributions. There is a considerable interest concerning the extent to which excess entropies may be used as an additional guide to the prediction of promising thermoelectric materials.

Several experimental factors appear to be especially favorable to liquid state work, and should enhance productivity in a limited group effort consistent with the present plans. These factors are as follows: (a) homogeneous preparations are more readily obtained without special attention to mechanical factors; (b) anisotropy factors are eliminated; (c) contact problems are simplified; (d) wide composition ranges may be investigated continuously without limitations as to phase separation; and (e) measurements as a function of temperature are not interrupted by abrupt changes because of structural changes at phase transformations.

Binary liquid systems comprised of elements in the area of the periodic system centering about the element tin are to be investigated. The particular area chosen is that for which solid state investigations have shown many semiconducting compounds of promising thermoelectric efficiencies. Equipment for measurement of Seebeck coefficients in the liquid indium-antimony system is being assembled.

2. Refractory Solid Thermocouple Systems (M. Tetenbaum)

For high-temperature use, a refractory material is required and a broad band semiconductor is desirable so that the thermoelectric properties will be favorable over a large temperature interval. The lanthanide and actinide sulfide systems provide such structures. The materials are highly refractory and have phases with electron concentrations in the semiconducting range. Promising high-temperature thermoelectric properties (to 1400 K) have been reported⁵⁴ for CeS_x (with and without SrS doping) and SmS_x . Preliminary studies^{55,56} in the literature indicate that ThS_x and US_x nonstoichiometric phases are similarly of interest.

The program plan is to study the actinide and lanthanide sulfide phases and certain of their ternary solid solution phases. The ternary systems will have particular significance to eventual power generation when solid solutions between lanthanide and actinide sulfides are involved. This is so because significant differences in masses of the metallic components and the consequent disruption of lattice harmonicity will lead to a reduction of the lattice contribution to the thermal conductivity.

Initial studies will be in the thorium-sulfur and uranium-sulfur systems.

⁵⁴Status Report on Thermoelectricity, December 1960 - January 1961, Naval Research Lab., Washington, D. C., NRL-Memo-1127, pp. 8 to 13 and 34.

⁵⁵Ibid., p. 32.

⁵⁶Thermoelectric Nuclear Fuel Element Quarterly Progress Report, January - March 1960, Westinghouse Electric Corp., Commercial Atomic Power Activity, Pittsburgh, WCAP-1545, pp. 11 to 13.

D. Reactor Decontamination (W. B. Seefeldt)

The Reactor Decontamination Program has two principal objectives: (1) to determine experimentally in pilot-plant equipment the degree of contamination to be expected in the steam phases of a boiling water reactor system in the event of fuel cladding failure, and (2) to find suitable methods of removing deposited activity from internal surfaces, should it be necessary because of excessive radiation levels. The pilot-plant equipment used for the first objective consists of a stainless steel type 304 loop that simulates the action of a boiling water reactor. Fuel ruptures are simulated by inserting tracer activities or irradiated metallic uranium. In a parallel effort, studies are being made in the laboratory to find suitable means of removing deposited activities.

In a 16-day loop run in which samples of liquid were taken every 8 hr, the content of cesium remained reasonably constant with time. Barium-lanthanum, cerium, and zirconium contents decreased steadily for 80 to 120 hr, following which they reached a minimum value, rose a relatively small amount, and reached what appeared to be an equilibrium value. Ruthenium decreased steadily to nondetectable levels. Iodine showed some erratic behavior. The data indicate that reasonable deposition information on metal samples in the vapor phase can be obtained for all isotopes except ruthenium provided such information is obtained after operating the loop for 100 hr or more, and provided that variation of isotopic content by a factor of five about a central value is acceptable.

Current laboratory efforts are being directed at a reagent system consisting of oxalic acid and hydrogen peroxide. Decontamination of zirconium-niobium-95 from stainless steel type 304 appears to be excellent (>1000), whereas ruthenium-103 decontaminations have varied widely even under duplicate conditions (4 to >200). Cerium-141 decontamination was 100 or better in all tests except one conducted at room temperature (decontamination factor = 55). The stability of these solutions is under study. Reduced temperature, controlled pH (4 to 4.8), and excess buffered acid reduce the rate at which hydrogen peroxide concentration decreases.

In scouting tests for evaluating material compatibility with oxalate-peroxide buffered with acetic acid and sodium acetate, the weight loss rate of low alloy steels (one sq in.) at 90 C was 7 mg/hr during the first 3 hr of exposure. During an additional 7 hr, the weight loss rates of chromium-molybdenum and type 4140 steels were 11 and 2 mg/hr, respectively. The presence of metal in contact with peroxide solutions increases the rate of peroxide decomposition.

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 Laboratory⁵⁷ for potential application in the Gas Cooled Reactor, uses a solution of hydrogen peroxide and sodium oxalate. Such a solution gives very good decontamination (see ANL-6287, page 203).

a. Decontamination of Stainless Steel with Oxalate-Peroxide Solutions

A group of experiments have been performed to examine the effectiveness of oxalate-peroxide solutions in decontaminating stainless steel type 304. Conditions of solution composition, temperature, time, and pH are being examined. The specimens were prepared by corroding a piece of irradiated uranium metal in deionized water in an autoclave containing a stainless steel liner. The autoclave was kept at 600 psi for $6\frac{1}{2}$ days. At the end of this time, the autoclave was cooled and emptied. Prior to heating with uranium, the liner was first heated with water alone under the same conditions to produce an oxide film. The vapor space portion of the liner was then cut into one-inch squares which were used as the decontamination samples. These were counted for gamma activity with a 256-channel scintillation spectrometer, both before and after the decontamination tests.

The results of the experiments to date are given in Table 61. An examination of the results indicates that the zirconium was essentially completely removed under all conditions so far tested. The cerium decontamination fell off somewhat at the lowest temperature tried. Ruthenium was the most difficult to remove and the most erratic in behavior. Several tests indicated excellent removal at 90 C. However, a duplicate experiment gave more modest results and further investigation appears necessary.

Occasionally, in examining the data it was observed that cesium, which was usually masked by the other isotopes in gamma scans made before the tests, was more evident at the completion of the test. Rough attempts at calculating the cesium decontamination indicated a value of 2 to 4.

⁵⁷Chemical Technology Division Annual Report for Period Ending August 31, 1960, ORNL-3009, pp. 110-111.

Table 61

DECONTAMINATION OF STAINLESS STEEL TYPE 304 WITH
OXALATE-PEROXIDE SOLUTIONS

Metal: Prepared as indicated in text

Time: 1/2 hr

Solution Composition			Temp (C)	Decontamination Factor ^c		
K ₂ C ₂ O ₄ (M)	H ₂ O ₂ (M)	pH		Cerium	Ruthenium	Zirconium
0.05	3	3	90	100	>200	>1000
0.5	3	3	90	>200	10	>1000
0.5	3	4.5	90	100	100	>1000
0.5	3	4.5	60	>200	12	>1000
0.5	3	4.5	25	55	4	>1000
0.05	0.3	4.5	60	>200	5	>1000
a	3	4.8	90	140	29	>1000
b	0	7	90	5	2	4

^a10 percent ammonium citrate

^bDistilled water

^cDecontamination factor is defined as the ratio of the counts before and after the decontamination cycle.

b. Stability of Oxalate-Peroxide Solutions

Data reported in the last quarterly (ANL-6333, pages 242 and 243) indicated that, when oxalate-peroxide solutions were heated, the pH of the solution rose spontaneously. When a certain pH value was reached, there was a rapid evolution of gas with the almost complete disappearance of the hydrogen peroxide. Therefore, such a solution would not be suitable as a decontamination reagent. It was shown that the stability of such solutions could be increased by maintaining the pH of the solution at approximately 4 by the periodic addition of oxalic acid.

Another method of stabilizing hydrogen peroxide-oxalate solutions is buffering. Oxalic acid, because of its relatively high ionization constant, is difficult to buffer at pH 4 with oxalate ion. However acetic acid-acetate ion solutions should provide suitable buffering action. A solution was prepared which contained oxalic acid, hydrogen peroxide, and a buffering system of the composition shown in the heading of Table 62.

Table 62

STABILITY OF OXALATE-PEROXIDE SOLUTIONS
BUFFERED AT pH 4

Solution Composition: 0.5 M $\text{H}_2\text{C}_2\text{O}_4$
(added as oxalic acid)

3.0 M H_2O_2

1.0 M CH_3COOH

0.175 M CH_3COONa

Temperature: 90 C

Elapsed Time (hr)	pH	H_2O_2 (M)	Elapsed Time (hr)	pH	H_2O_2 (M)
0	3.6	3.0	6	4.2	2.31
1	3.6	-	7	4.2	2.27
2	3.6	-	23 ¹	5.35	1.25
2 ³	-	2.52	25 ²	5.40	1.21
3 ⁴	3.65	-	26	5.45	1.17
4	3.90	2.45	27	5.45	1.14
5	4.0	2.36	28	5.5	1.08 ^a

^aAt this point the oxalate concentration was determined to be 0.07 M.

This solution was kept at 90 C; the pH and hydrogen peroxide content were determined periodically. These results are summarized in Table 62. The data show a slow increase in the pH of the solution, which results from the reaction of the hydrogen peroxide with the oxalate ion. The hydrogen peroxide concentration also decreased slowly. These results demonstrate at least a tenfold increase in the stability of hydrogen peroxide-oxalate solutions.

c. Corrosion

Previous corrosion tests indicated that the addition of hydrogen peroxide to oxalate solutions reduced the metallic corrosion. In the current period, some preliminary corrosion tests were made with buffered solutions.

The following solution was used for these first corrosion tests:

0.5 M sodium oxalate	1.0 M acetic acid
3.0 M hydrogen peroxide	0.175 M sodium acetate

At 90 C, over a 3-hr interval with periodic measurements, the weight loss for chromium-molybdenum steel and AISI 4140 averaged approximately 7 mg/hr. With an additional 7-hr exposure, the chromium-molybdenum steel weight loss rose to approximately 11 mg/hr, while the AISI 4140 weight loss was approximately 1 to 2 mg/hr. Under the test conditions, a weight loss of 1 mg is equivalent to a penetration of 5×10^{-3} mil. Stainless steel type 304 showed negligible weight losses under the same conditions.

When the temperature of the test was reduced to 60 C, a 7-hr test indicated a weight loss of less than 1 mg/hr for both of the low-chromium steels.

These corrosion tests at 90 C indicated a more rapid decrease in the hydrogen peroxide concentration than reported previously in the section on solution stability. For example, after three one-hour exposures, the hydrogen peroxide concentration had fallen to 0.01 molar, whereas in the absence of metal, the hydrogen peroxide was barely affected over a like period of time. In the 60 C corrosion tests, the hydrogen peroxide concentration had changed by less than ten percent during the test. These data, together with the decontamination data, indicate that adequate decontamination might be achieved at lower temperatures, with less metallic attack.

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 fuel ruptures. It is of interest to know the amount and the kinds of fission products that will be distributed 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 by the uranium as it corrodes in the circulating water. Deposition of activity in the steam disengaging space is monitored by inserting a metallic sample strip into the loop; 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.

In the preceding report period, data were presented from a series of three-day reproducibility runs in which the objective was to determine how constant or variable the fission product content of the circulating loop liquid and vapor was during the run. This is considered important in interpreting the deposition of fission products on the metal sample strips in the steam disengaging section. Optimum conditions for

data interpretation would include constant compositions of liquid and vapor. A significant result from these runs was that the zirconium-niobium content was high beginning with a cold loop and decreased during the three-day runs. No semblance of equilibrium was achieved in this period.

A long run of 16-day length was made (Run U4) in order to determine whether an equilibrium could be achieved or whether the zirconium-niobium content would continue to decrease with time. The behavior of the other fission products was also monitored. Liquid samples were taken at 8-hr intervals, with some exceptions over weekends. The total number of samples was forty. The loop was operated at 200 psi pressure and a steam velocity of 0.8 ft/sec.

Fission product content of loop samples was monitored with the use of a 256-channel gamma scintillation spectrometer. Data obtained from this instrument together with reference data from known quantities of individual fission products were run through an IBM 650 computer to analyze the gamma spectra. Such computations for Run U4 have been completed for the circulating loop liquid and are shown graphically in Figure 84. Most of the data points (~90 percent) fall within 30 percent of the curves shown. A statistical analysis of the data is being made.

The quantity of cesium present did not vary greatly during the course of the run. The downward slope of the cesium curve corresponds approximately to the cesium dilution caused by withdrawal of samples and addition of water. During the first 80 hr, the rate of disappearance of ruthenium, zirconium-niobium, cerium, and barium-lanthanum are similar and considerably greater than cesium. After 80 hr, cerium, barium-lanthanum, zirconium-niobium, and iodine reach a minimum and increase in a nonsimilar manner. Ruthenium continues to decrease with time until the data scatters because of an insufficient quantity present. It is significant that all fission products except ruthenium do not continue to decrease, but reach what might be termed equilibrium if a variation of a factor of five is considered acceptable. Iodine concentration in the liquid decreased with time in a nearly exponential manner.

The patterns obtained in this run suggest that if fission product content variation of a factor of five around some central value is acceptable, that correlatable deposition data can be obtained provided the loop has been

operated for about 100 hr prior to increasing the steam velocity to the desired value. This is necessary in order to be assured that the deposition occurring in the vapor phase results from entrainment from liquid having a known and reasonably steady fission product content. The first 100 hr need to be excluded, since several of the fission product concentrations in the liquid are high and are rapidly decreasing during this period. It appears that good data cannot be obtained for ruthenium at all because of its continued disappearance from the liquid and a nonattainment of an equilibrium condition.

Data from vapor samples and metal sample coupons are being analyzed.

The liquid portion of the loop was decontaminated by a series of four treatments, two of them with sodium bicarbonate-sodium carbonate-peroxide, and one each with oxalate-peroxide and nitric acid. Results are shown in Figure 85 and Table 63. Decontamination factors varied from 11 in the heating section to 250 in the bottom horizontal run of the loop. It is evident from the data that the first solution decreased radiation levels more than the others. This is to be expected as the solution was intended to dissolve uranium dioxide particles remaining in the loop following draining. Fission products associated with the uranium are also dissolved, and hence radiation levels are reduced considerably although only a small amount of decontamination of metallic surfaces may have occurred. The possible conclusion that solution one is a superior decontaminating agent is not warranted. When available, the activity to uranium ratios of the four decontaminants will be computed to determine how much of the decontamination is attributable to uranium oxide dissolution as compared to direct fission product removal.

FIGURE 85
LOCATION OF RADIATION LEVEL CHECK POINTS
FOR LOOP RUN U4 DECONTAMINATION

Table 63
DECONTAMINATION OF STAINLESS STEEL TYPE 304 LOOP FOLLOWING RUN U-4

Decontaminant Used	Loop Condition at time of Radiation Reading	Decontamination Cycle		Radiation Level at Check Points Indicated ^a mr/hr ^b									
		Time (hr)	Temp (C)										
				1	2	3	4	5	6	7	8	9	10
-	loop full of operating liquid	-	-	2 4R	6 5R	6 5R	10R	-	10R	4R	3 5R	3R	10R
-	loop drained	-	-	5R	20R	15R	30R	-	19R	17R	6R	4R	20R
Soln 1	loop full	7	50	450	450	350	350	175	2R	150	250	250	175
Soln 1	loop empty	-	-	130	460	250	150	200	360	140	160	200	150
Soln 1, Fresh Batch	loop empty	5	50	500	1 5R	300	150	250	250	175	350	400	300
Soln 2	loop empty	7	RT ^c	250	460	350	300	250	190	340	550	500	500
Soln 3	loop empty	72	RT and 50 ^d	60	140	120	120	100	125	195	160	350	440
Decontamination Factor ^e				83	143	125	250	-	152	87	37	11	45

^aCheck points location shown in Figure 85
^bValues shown followed by 'R' are roentgen per hour
^cLiquid heated from pumping to 35 to 40 C
^dTemperature was varied between ambient (RT) and 50 C
^eRatio of 2nd to last values in each column (for example, in column one "loop drained" value is 5R/hr - 5000 mr/hr and soln 3 "loop empty" value is 60 mr/hr giving a decontamination factor of 5000/60 = 83)

V. ROUTINE OPERATIONS (H. G. Swope)

A. Waste Processing

(H. G. Swope, J. Harast, K. Bremer, B. Kullen and R. Juvinall)

There were 35,043 gal of liquid radioactive wastes processed during the quarter. The methods used and volumes were as follows:

<u>Process</u>	<u>Gal</u>
Evaporation and Concentration	24,760
Filtration	4,150
Ion Exchange (Cation only)	2,800
Flocculation	54
Neutralization of HF Wastes	105
Absorption on Vermiculite	474
Decay	2,700
Total	35,043

B. High-level Gamma-irradiation Facility

(H. G. Swope, J. Harast, N. Ondracek, R. Jarrett, G. Teats and V. Lemke)

A summary of irradiations performed in Racks M-1 and M-2 for April through June 1961 is given in Table 64.

Table 64

SUMMARY OF IRRADIATIONS PERFORMED IN RACKS M-1 AND M-2 DURING APRIL THROUGH JUNE, 1961

Month	Rack M-1				Rack M-2				
	No of Samples ^a	No of Special Dosimetry Samples	Total Urn Units Based on Rads ^b		No of Urns	No of Special Dosimetry Samples	Total Urn Units Based on Rads		Dosimetry Urn Units
			Day	Night			Day	Night	
April	641	26	1515	2224	0	0	-	-	-
May	296	28	866	1699	1	16	2	25	2
June	476	55	1291	2530	1	16	2	34	2
Totals	1413	109	3672	6453	2	32	4	59	4

^aEquivalent to a No 2 sized can (3 7/16 in. diam x 4 9/16 in. high)

^b1 urn unit = 2×10^6 rad