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CHEMICAL ENGINEERING DIVISION
SUMMARY REPORT

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SUMMARY

CHEMICAL ENGINEERING DIVISION
SUMMARY REPORTI. Chemical-Metallurgical Processing (Pages 29 to 107)

Additional experiments have been conducted on the nitridation rates of irradiated uranium-fissium fuel pins. Data from 3 runs with pins of varying burnups and cooling times indicate that there is no large influence of irradiation of fissium alloys on the nitridation rate at 300 C. It is possible that the differences in rates may arise from secondary effects of the irradiation, such as an increase in area resulting from surface roughening. The nitridation rate of unirradiated uranium-fissium alloy at 300 C in nitrogen-argon mixtures at a total pressure of one atmosphere remained constant as the nitrogen content was varied from 2 to 100 percent.

The skull-reclamation process is being developed for the recovery of skull material which remains in a crucible after melt refining. The process presently involves removal of a melt refining skull from a crucible by oxidation of the skull to convert it to a powder, selective extraction of noble metals into zinc from the skull oxides suspended in a molten chloride salt, reduction of uranium oxides by magnesium in a zinc solution, two uranium precipitations (first as a uranium-zinc intermetallic compound and then as uranium) to separate uranium from various fission products, and a retorting step to isolate a uranium metal product. Small-scale demonstration runs of this process have been resumed in a recently completed inert atmosphere glove-box facility.

Considerable effort has been devoted to the development of methods for the various phase separations encountered in the skull-reclamation process. Because experience has shown that pressuring of liquid phases out through dip tubes (pressure siphoning) is a very expedient procedure and readily adaptable to remote operation, this method has received principal attention. Several relatively large-scale transfers of molten metal from solidified flux, as required after a noble-metal-extraction step, were made without difficulty and provided metal removals of about 90 percent. For separation of molten flux and liquid metal phases as required after the uranium oxide reduction step, a dual transfer-tube unit has been developed which provides a means of separation and transfer of the 2 phases without requiring the location of the flux-metal interface. Very satisfactory separations of the 2 molten phases have been repeatedly demonstrated at practical transfer rates. Methods for successive transfer of liquid metal and flux phases were also investigated. These have the disadvantages either of requiring continuous location of the flux-metal interface and the ability to stop the transfer at a desired point or of inherent imperfect separation of phases.

A phase separation common to both the blanket- and skull-reclamation processes is the removal of a 50 percent magnesium-zinc supernatant solution from precipitated uranium metal. On a 500-g-uranium scale, very good removals of 93.5 to 97.5 percent of the supernatant phase have been achieved without difficulty. In most of these runs entrainment of uranium metal was negligible.

The reduction rate of zirconium oxide by zinc-magnesium solution under the conditions of the skull-recovery process has been shown to be lower than that of uranium oxides. It may therefore be possible to effect some zirconium separation by limiting the time to that necessary for the reduction of uranium, thereby lessening the extent of zirconium removal required in the subsequent process steps.

Continuation of work on the reduction of thorium dioxide by zinc-magnesium solutions shows that effective reduction occurs within a limited composition region of the calcium chloride-magnesium chloride-calcium fluoride flux system. This region lies above 50 mole percent magnesium chloride and between 7 and 15 mole percent calcium fluoride.

Studies of uranium oxide reactions with chloride fluxes indicate that uranium trioxide on addition to a lithium chloride-magnesium chloride flux forms magnesium uranate and uranyl chloride.

In the processing of plutonium fuels typical of those expected for the plutonium loading of the EBR-II, one of the problems which needs solution is the separation of rare earths from plutonium. Two different methods of accomplishment, both utilizing liquid metal solvents, are being investigated. The first method consists of extracting the rare earths from a zinc-magnesium solution of uranium and plutonium by means of a magnesium chloride flux. The distribution of rare earths between the flux and zinc-10 weight percent magnesium solution at 800 C has been studied. The distribution coefficients (weight percent in flux/weight percent in metal) for yttrium, cerium, and praseodymium were found to be 1.9, 0.88, and 0.6, respectively. Plutonium data are now being collected. The second method makes use, at about 425 C, of a calcium-zinc solution in which the rare earths are soluble and the uranium and plutonium are relatively insoluble. The results of a recent exploratory experiment indicated that 97 percent plutonium and greater than 99 percent uranium can be precipitated from a zinc-63.5 percent calcium solution while 95 percent or more cerium remains in solution. On the basis of preliminary results, both methods appear promising for process use.

Development work has continued on the preparation of uranium carbide by addition of carbon to uranium dissolved in liquid metal media. The addition of small amounts of alkali metals to improve wetting of the carbon by zinc solutions increases the rate of the reaction and may permit closer

control of the carbon-to-uranium ratio of the product. For example, after 8 hr the reaction was 98 to 100 percent complete when sodium was added, compared with about 80 percent completion in the absence of sodium. The use of hydrocarbon gases as a means of adding carbon to the liquid metal solvent proved unsatisfactory.

Analytical results from 8 batches of uranium monocarbide prepared for fabricability tests showed high carbon-to-uranium ratios and considerable oxygen contamination. However, the material has excellent pressing and sintering characteristics, and with proper treatment yields densities exceeding 90 percent of theoretical. Modifications are being made in the equipment and procedures to improve the quality of the product.

Materials studies are in progress to evaluate the compatibility of various materials with the liquid metal-salt systems of the types contemplated for reprocessing reactor fuels. Based on metallographic examination and measurements of physical properties, it appears that tungsten has very high corrosion resistance to the zinc-magnesium and flux systems encountered in the skull-reclamation process, including flux systems containing zinc chloride. Transverse bend tests of various types of wrought tungsten before and after exposure for 100 hr at 800 C to the corrosion media mentioned above showed no significant loss of rupture strength. It was noted that heli-arc weldments were much weaker than the parent rolled sheet material.

Metallographic examination of molybdenum-30 percent tungsten alloy after exposure to zinc for 300 hr at 850 C indicated that very slight, if any, attack had occurred. No attack was detected on those samples exposed to zinc-magnesium solutions for 300 hr at 800 C. The addition of 2 mole percent zinc chloride to flux of composition (mole percent) 47.5 lithium chloride, 47.5 magnesium chloride, 5 magnesium fluoride greatly increased the extent of attack of this flux on tantalum and tantalum-10 percent tungsten during 100-hr tests at 800 C.

The excellent corrosion resistance of tungsten and molybdenum-30 percent tungsten to skull-reclamation processing systems has been confirmed in materials demonstration runs conducted in 5-in.-diameter pressed-and-sintered tungsten crucibles agitated with a molybdenum-30 percent tungsten stirrer. In addition, it was noted that the crucibles withstood freezing and remelting of contents and that no detectable amount of zinc vapor or liquid solution permeated the crucible walls.

The pressing-and-sintering technique appears to be the most feasible method of several being evaluated for making full-scale tungsten crucibles for the skull-reclamation process. By this method, crucibles can be made that have vertical mixing baffles formed during the pressing operation as integral parts of the crucible. Precipitation and retorting crucibles probably will be fabricated of beryllia by one of several methods now under

investigation. Agitators and transfer tubes can be made from arc-cast and swaged or forged molybdenum-30 percent tungsten alloy. Molybdenum-30 percent tungsten appears to be superior to tungsten for these applications because the molybdenum-tungsten alloy is easily machinable and has acceptable, though slight, room-temperature ductility in the wrought conditions.

With the completion of the installation of a new induction-heating coil, operation of the large cadmium-distillation unit was resumed. Over 600 kg of cadmium has been distilled in 3 runs. Operation has been essentially troublefree, but an entrainment problem is suspected. The efficiency of the new induction coil assembly is lower by about 25 percent than that of the previous one, largely because the addition of extra insulation prevents the coil from radiating heat to the distillation crucible. This insulation is being removed.

The power input required to stir mercury at room temperature has been measured as a function of agitator speed and geometric variables. Work also is in progress (largely in the equipment building stages) on mass transfer in liquid metal systems.

Construction of the EBR-II Fuel Cycle Facility building was 98 percent completed by January 12, 1962. On this date, all uncompleted work was deleted from the construction contract. The remaining construction will be completed and process equipment will be installed on a cost-plus-fixed-fee contract under the direct supervision of Argonne National Laboratory personnel.

Installation of the shielding windows was resumed in February, but oil was discovered leaking through the welded steel structure of several oil-filled tank units. These are being repaired.

Design and fabrication of other equipment for the Fuel Cycle Facility continues. Fabrication of the service sleeve feed throughs is scheduled for completion by the end of March. The specifications for the off-gas monitoring have been prepared. This system will continuously monitor the activity of the gas discharged from the off-gas hold-up tanks. A purchase order has been issued for equipment to monitor the radioactivity in the discharge to the suspect stack at the EBR-II site.

The 5-ton cranes and manipulator bridges in the process cell are being disassembled to remove the abrasive dust from the bearings. This abrasive dust resulted mainly from the reworking of the crane and manipulator rails by the contractor. Damaged bearings are being replaced with new ones.

A skull-oxidation furnace for converting the skull from the melt refining furnace to an oxide is being tested, together with a control system

which maintains a constant burning rate during the oxidation run. Several skulls and one large uranium ingot have been oxidized in this furnace.

The sorption of magnesium-zinc vapors on Fiberfrax is being studied as a method of collecting these vapors when the magnesium-zinc alloy is distilled from the uranium product in the skull-reclamation process. A seal has been successfully tested which limits the amount of vapor that bypasses the Fiberfrax trap to a negligible quantity.

Fundamental studies are being made in support of pyrometallurgical process development activities. The solubilities of fission product, fissionable, and structural elements are of prime importance in the design of processes. The solubilities of praseodymium and beryllium in liquid zinc and the solubility of uranium in liquid indium have been measured. The solubility of praseodymium in liquid zinc may be represented by the empirical equation

$$(430 \text{ to } 725 \text{ C}) \text{ Praseodymium: } \log (\text{atom percent}) = 6.447 - 6764 T^{-1}.$$

The solubility of beryllium in liquid zinc may be represented by the equation

$$(430 \text{ to } 700 \text{ C}) \text{ Beryllium: } \log (\text{atom percent}) = 3.211 - 3233 T^{-1}.$$

The solubility of uranium in liquid indium may be represented by the equation

$$(455 \text{ to } 720 \text{ C}) \text{ Uranium: } \log (\text{atom percent}) = 3.78 - 5150 T^{-1}.$$

Separation by recrystallization from liquid metal solvents is often limited, not by a lack of sufficient differences in solubility, but by the extent that impurities coprecipitate. Studies are being made of the coprecipitation behavior of various fission product elements under process conditions. The coprecipitation of ruthenium by uranium when the latter is precipitated from magnesium-zinc solutions has been measured. At 810 C, at which gamma uranium is the precipitating phase, the coprecipitation coefficient was found to be 0.8, whereas at 752 C, at which beta uranium is the precipitating phase, the coprecipitation coefficient was 0.3.

The codistribution coefficients of uranium, plutonium, strontium, and cesium between lead and zinc have been measured. The distribution coefficient for uranium (weight percent in zinc-rich layer/weight percent in lead-rich layer) was found to be 68 at 701 C, 29 at 732 C, and 11 at 761 C. The distribution coefficient for plutonium in the same solutions was found to be 18 at 701 C, 10 at 732 C, and 5 at 761 C. These data are in substantial agreement with previous measurements in which only plutonium and uranium were present. The distribution coefficient for cesium is approximately unity over the range from 701 to 761 C, whereas the distribution coefficient for

strontium is about 0.2 over the same temperature range. The amounts in solution for cesium and strontium were too low to allow a more accurate determination of the distribution coefficients.

The mutual solubilities of lead and zinc were measured above 650 C.

The free energy of formation of the uranium-tin intermetallic phase USn_3 has been measured by means of the emf method. The free energy of formation over the temperature range from 373 to 677 C may be represented by the empirical equation

$$\Delta G_f^\circ (\text{cal/mole}) = -39,180 + 9.499 T + 3.062 \times 10^{-4} T^2$$

At 500 C, values of the free energy, enthalpy, and entropy of formation computed by means of this equation are: $\Delta G_f^\circ = 31.6_5$ kcal/mole, $\Delta H_f^\circ = -39.0_0$ kcal/mole, and $\Delta S_f^\circ = -9.97$ cal/deg-mole.

The excess partial molal free energy of uranium in liquid indium solutions has been estimated by combining the results of emf and solubility measurements. The solutions are found to exhibit small negative deviations from ideal behavior, which become less negative as the temperature increases.

The lanthanum-cadmium system has been studied by means of the continuous-weighing effusion balance. The following sequence of intermetallic phases are indicated: LaCd_{11} , La_2Cd_9 , $\text{LaCd}_{\sim 8}$, LaCd_2 , and LaCd .

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (pages 108 to 161)

Laboratory development work continued on the Direct Fluorination Process for the recovery of uranium and plutonium from oxide fuels. This fluid-bed process utilizes fluidized alumina as an inert medium for heat transfer. Studies have been concentrated on experiments designed to elucidate the factors involved in the removal of plutonium, by fluorination, from mixtures of alumina, uranium oxide, plutonium oxide, and fission product element oxides. Oxide mixtures have been prepared to simulate the feed material in the fluorination step of the process. The results of the experiments made to date lead to the following conclusions in regard to the problem of removing plutonium from inert solids: (1) Plutonium is retained on Alundum residues to about 0.03 weight percent. (This remaining plutonium corresponds to a plutonium loss of 2.25 percent, assuming we have Dresden-type fuel containing 100 kg uranium and 0.4 kg plutonium with 30 kg of Alundum and that we only use the Alundum once.) With the addition of fission product element oxides the retention is raised to between 0.05 and 0.06 weight percent. When fission product elements are present initially

as the fluorides, they do not increase the plutonium retention in Alundum residues. (2) Plutonium retained on Alundum residues can be effectively removed, leaving less than 0.020 weight percent plutonium on the residue, by either pyrohydrolysis followed by fluorination at 450 C or by a refluorination alone at 550 C. The presence of fission product element compounds does not hinder the effectiveness of these procedures. (3) On the basis of results obtained to date, a fluorination scheme which minimizes the initial heat generated by the reaction offers the greatest promise of resulting in low plutonium retention in fluorination residues. This is indicated by the results obtained with a 2-step procedure using 10 volume percent fluorine at 450 C initially followed by a second fluorination using 75 volume percent fluorine at 550 C.

The development of a laboratory-scale fluid-bed reactor is continuing. This unit will be incorporated into the presently available plutonium facility. Experimental work with this equipment will provide data which will more realistically approximate the conditions for the projected pilot-plant study.

The engineering-scale studies of the direct fluorination of uranium dioxide pellet fuel are being made in a 3-inch-diameter air-cooled reactor. The technique of fluidization of alumina grain in the voids of the pellet bed is used as an aid in heat removal. The current series of batch fluorinations of larger charges of pellets has been continued. An 18-in.-deep pellet charge (13.2 kg uranium dioxide) was 96 percent fluorinated in 22 hr with an overall efficiency for fluorine utilization of 77 percent. Although this result was quite favorable with regard to fluorination time and efficiency, the run was unsatisfactory in that caking of the fluid bed occurred. This run was the first in which use was made of a modified gas-recycle scheme intended to maximize fluorine economy. A mathematical analysis of the process parameters of this partial recycle system indicates that high fluorine efficiency can be obtained through off-gas recycle while holding recycle oxygen to a minimum. In runs made thus far, high oxygen concentration has been shown to produce fines and to result in caking. Further recycle runs with lower oxygen concentrations are planned. An 18-in. pellet bed was also completely fluorinated at 500 C in a run without gas recycle, but with controlled oxygen introduction during a major part of the run. This run was quite satisfactory with respect to heat transfer, temperature control, and absence of caking; the fluorination time was 31 hr and the overall fluorination efficiency was 30 percent. Further runs with the modified recycle system will be made to optimize fluorine economy.

Selective thermal decomposition of plutonium hexafluoride is being considered as a means of separating the mixture of uranium and plutonium hexafluorides produced in the fluorination step of the Direct Fluorination Volatility Process. It has been demonstrated that the circulation of gaseous mixtures of uranium hexafluoride and plutonium hexafluoride through

nickel vessels containing nickel wool and plutonium tetrafluoride, at 200 to 300 C, reduces the ratio of plutonium to uranium by factors between 10^2 and 10^3 . The residence time of the gas in the heated vessel necessary to accomplish this is about one minute. The concentration of uranium in the plutonium, deposited as plutonium tetrafluoride, varied from 0.4 to 1.3 percent.

Experiments have been initiated to determine the efficiency of filter media used in AEC-type filters in removing plutonium particles from a gas stream. Controlled releases of plutonium hexafluoride (25 mg or less) have been made into air having various known moisture contents. Penetrations from 58 to 0.0002 percent for a single AEC filter and from 29 to 0.00002 percent for two AEC filters in series were observed. The variance in penetration appears to be dependent on the relationship of the quantity of plutonium hexafluoride released to the moisture content of the air.

A plutonium-handling facility is being constructed so that successful volatility-processing techniques developed in laboratory-scale fluorination experiments can be studied on a larger pilot-plant scale. The facility consists of 2 alpha-containment boxes in which, initially, equipment will be installed to study variables in the fluorination of uranium-plutonium dioxide pellets. Although the process is to be remotely monitored and controlled, the alpha boxes are to be equipped with glass windows and gloves to allow direct manipulations as required. A critical path analysis was applied to the construction and installation phases of the project in order to aid in planning and minimizing the time required.

Studies have been conducted on a fluidization volatility scheme for recovering enriched uranium from low-uranium-zirconium alloy fuels. Recent results of experiments conducted in a $1\frac{1}{2}$ -in.-diameter fluid-bed reactor coupled with a similarly sized down-flow filter bed, showed that holdup of uranium in the inert solids becomes constant upon re-use of the bed. Five separate hydrochlorination-fluorination cycles were made and the residual uranium values decreased from a value of 4.4 percent after one run to about one percent after the fifth trial. Individual charges contained about 17g of uranium as 5 weight percent alloy in the form of chips about $\frac{1}{8}$ to $\frac{1}{4}$ in. on a side. Hydrochlorination was conducted in the temperature range from 350 to 450 C and fluorination was conducted at 350 C. Hydrochlorination time ranged from 4 to 16 hr and fluorination time was 6 hr. Uranium hexafluoride collection in the cold traps has improved considerably with the new, 3 coil-type traps in series. Three successive runs showed collections of 96, 99, and 98 percent of the uranium charged. Overall uranium material balances (taking into account uranium remaining in the fluid and filter beds) were generally satisfactory. Uranium loss during hydrochlorination, as determined by analysis of streams collected downstream of the fixed-bed filter, continues to be low, being <0.2 percent of the uranium charge in each case. Higher temperatures for hydrochlorination

(up to 550 C) did not appear to improve overall uranium recovery nor did it improve zirconium removal (zirconium content of the fluid-bed ranged from 0.4 to 1.4 percent).

Studies intended to show whether or not there is an association of uranium retention in the inert solids with residual zirconium content have been initiated. Initial trials with higher hydrochlorination temperatures (to 550 C) effected no marked change in either the uranium recovery or the zirconium residual content (currently 0.4 to 1.5 weight percent of the inert solids). Further studies will be made at lower temperatures, since no advantage appears to be gained by the use of higher temperatures and, in addition, preliminary data indicated reactor corrosion may be excessive.

Additional studies on the conversion of zirconium tetrachloride vapor to a dense solid oxide by reaction with steam in a fluid-bed reactor were carried out. This reaction is under consideration as it offers a means of dealing with the off-gas from the hydrochlorination step of the zirconium alloy fuel-reprocessing scheme. Two new equipment modifications to the 6-in.-diameter reactor system were made. One was the installation of a continuous-feed system (a Vibra-Screw unit) upstream of the sublimation furnace for the solid zirconium tetrachloride feed. This has permitted operations at higher rates (to 2 kg/hr) and also will allow longer runs to be made. The other change was the installation of an electric boiler to supply steam directly to the unit replacing the water-atomizing nozzle system which is believed to be partly responsible for the fines buildup in the system.

Reaction conditions used in the current hydrolysis experiments, namely, a bed temperature of 500 C and feed rates of 2 kg/hr, resulted in only about 60 percent of the reaction products remaining on the bed particles. The remainder accumulated in the fines fraction found on the filters. A chloride analysis of the fines indicated an oxychloride intermediate may be forming.

A pilot-scale facility is being designed to demonstrate the proposed zirconium alloy fuel-reprocessing scheme. It is currently planned to carry out the principal process steps, first, with nonirradiated material and later with tracer or low levels of activity to determine the disposition of the important fission products. A preliminary chemical and equipment flowsheet is presented for the facility which will have a charge capacity of 20 kg of alloy feed.

Final experimental work on the 2-step fluid-bed process for converting uranium hexafluoride to uranium dioxide was carried out. The studies involved examination of the hydrolysis (steam-uranium hexafluoride reaction) step at higher temperatures (500 C instead of 200 C). A new investigation of

the one-step process (simultaneous reaction of uranium hexafluoride with steam and hydrogen) was initiated by using low feed rates and high temperatures to explore the possibility of preparing high-density dioxide particles. All of the work was done in a 3-in.-diameter Monel metal column.

Use of higher temperatures for hydrolysis essentially eliminated the problem of product deposition on internal reactor surfaces, which was noted previously in work at 200 C (deposition rate of $20 \mu/\text{hr}$ reported in ANL-6477, page 151). In the current work, steam only and 9:1 mixtures of steam and hydrogen were used; after an accumulated period of 14.5 hr of column operation, only a light dust film remained on the reactor. The product was dark-colored as compared to the light yellow color of uranyl fluoride (the 200 C product), and chemical analysis indicated the presence of some U_3O_8 and possibly traces of uranium tetrafluoride. Excessive fines were formed in some cases, but it is believed that these could be combined with the main product stream without difficulty for further processing to the dioxide.

In the initial studies on the simultaneous reaction scheme in which uranium hexafluoride is reacted with a mixture of steam and hydrogen, uranium dioxide particles with a density of 8.9 g/ml (as determined by a mercury displacement technique) have been produced. This value is about 80 percent of theoretical. The starting material was a 6-kg bed of dioxide that had a density of 6.4 g/ml. Four separate runs have been made and the column has been operated continuously for about 55 hr. Hexafluoride feed rates ranged from 10 to 27 g/min, steam-to-hydrogen mole ratios were from 2.0 and 0.5, and steam excesses ranged from 1160 to 90 percent. The run procedure involved alternate periods of hexafluoride feed on-time followed by a (fluoride) cleanup period in which only steam and hydrogen are fed to the unit. For most of the work, these periods were 45 and 15 min each, respectively. Analysis of the products showed residual fluoride contents of 150 to 3000 ppm. Additional fluoride removal could probably be achieved by additional cleanup time.

Continued satisfactory operation of a small-diameter fluid-bed calciner has been achieved in recent studies. Intended application of this work is towards nuclear-critical situations in which size is of importance. Success of the technique of spraying feed vertically upwards from a nozzle mounted in the apex of the cone-bottom reactor (currently of $2\frac{1}{4}$ -in. diameter) makes the system operable and affords a method of utilizing the feed atomization and decomposition gases as the fluidizing medium. Aluminum oxide granules are now used as bed material and 1M aluminum nitrate solution as feed. A significant reduction in air-to-liquid volume ratios normally associated with calciners has been achieved in the most recent work. With the use of feed rates up to 23 ml/min as compared with 9 ml/min reported previously (see ANL-6477, page 153), the ratios have been reduced from 2000 to 600. Runs were made at 425 and 450 C for periods ranging from 5 to 14 hr.

A newly designed nozzle referred to as a submerged-tip model has been in use. Use of higher rates has introduced the problem of increased fines production and, as a consequence, additional work on optimizing the blowback cycle (cycle time and length of blowback pulse) appears to be needed.

III. Calorimetry (pages 162 to 167)

Two calorimetric series of combustions have been completed. One is a series of 9 combustions of cadmium in fluorine. The other is a series of 10 combustions of magnesium in fluorine. However, the calculation of values of heat of formation from the results of these 2 series awaits several additional calibration experiments.

The determination of the heats of formation of the tetrafluorides of titanium and hafnium has been completed with the definite characterization of titanium tetrafluoride as the product of combustion of the titanium combustions in fluorine.

Exploratory noncalorimetric experiments are being carried out to develop techniques for calorimetric studies with fluorine on several substances. Adequate techniques have been developed for the study of niobium and tantalum. The same techniques as used for silicon appear to be satisfactory for sulfur. Considerable additional exploratory work will be necessary for zirconium diboride and carbon.

The study of the heat of formation of uranium hexafluoride has developed into a complex problem of chemical analysis. If the problem is not solved soon, it may be necessary to settle for results considerably less precise than originally anticipated.

Work is continuing on the assembly of the 1500 C high-temperature enthalpy calorimeter. Vacuum systems for the calorimeter have been assembled and tested. Circuits for the dropping mechanisms are being tested.

IV. Reactor Safety (168 to 194)

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.

The program of theoretical studies designed to relate quantitatively ignition results to isothermal-oxidation data is continuing. Further studies of the isothermal oxidation of uranium at 300 C and higher are reported. The studies were made in a metal "heat sink" reaction cell which was

designed to prevent excessive self-heating. Temperature measurements at the center of uranium cube specimens indicated that the metal temperature increased only about 40 C during the course of an oxidation at 600 C even though the normal ignition temperature in oxygen is 595 C. The rate of oxygen uptake by the specimen was measured by means of a rapid-response strain-gage pressure transducer in some of the runs. Data with Argonne-base uranium, Battelle-base uranium, 1 atom percent copper-uranium alloy, and 1 atom percent aluminum-uranium alloy cubes showed substantially identical reaction rates up to 400 C. Reaction was self-accelerating in the range from 350 to 400 C. Oxidation with pure uranium and the copper alloy underwent a transition to a slower reaction in which the oxide was somewhat protective above 500 C. The self-accelerating reaction continued to higher temperatures for the aluminum alloy. The transition from an autocatalytic oxide to a protective oxide was gradual with Battelle-base metal but was very sharp in the case of Argonne-base metal. Oxide films on the copper alloy were considerably more protective above 500 C than those on the pure metal. The oxidation kinetics were consistent with the previously reported ignition data in which additions of aluminum to uranium decreased the ignition temperature 200 C and addition of copper increased the ignition temperature by 200 C.

Studies of X-ray diffraction patterns of oxidized uranium surfaces have been resumed. Recent literature studies have revealed the existence of higher oxides than uranium dioxide by noting the asymmetry of diffraction lines characteristic of uranium dioxide. It is now apparent that phases such as U_3O_7 and $UO_{2.3}$ can be determined only with a diffractometer. Previous conclusions based on studies with X-ray film are being re-examined. Preliminary results indicated that higher oxides are involved in the low-temperature oxidation of uranium.

Studies of the oxidation and ignition of plutonium and its alloys are being carried out in new glove-box facilities. Ignition experiments in air and oxygen have been completed on plutonium alloy samples containing silicon, nickel, copper, zinc, magnesium, and chromium. All alloys had slightly higher ignition temperatures than plutonium alone. Copper had the greatest effect, increasing the ignition temperature by 50 C. Isothermal-oxidation studies are being carried out at temperatures corresponding to each of the 5 solid metal phases. Two-stage oxidations, similar to uranium, were observed in the beta phase at 185 C. A linear reaction was found to occur in the gamma phase at 220 C.

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. A series of runs with stainless steel-316 wires was made in room temperature water. There was

no detectible reaction up to the melting point of the metal (1370 C). Only 10 percent of the metal was reacted at an initial metal temperature of 2500 C. Reaction reached 35 percent for the most energetic run, in which the initial metal temperature was 3800 C.

Studies of the reaction of solid uranium with steam have been undertaken by means of a simple volumetric apparatus. Steam at one atmosphere is passed over a ~1-cm uranium cube. Hydrogen generated by metal-water reaction is continuously swept from the reaction cell by flowing steam and is collected over water in a graduated vessel. The specimen is heated by an external induction coil, and the temperature is measured by means of a small thermocouple located in a hole at the center of the specimen cube. Preliminary results have shown that the reaction is nearly parabolic over the range from 600 to 900 C.

In-pile studies of metal-water reactions in TREAT are continuing. In these studies, small fuel pins are placed under water in a high-pressure autoclave located at the center of the TREAT reactor in Idaho. They are then subjected to a vigorous neutron burst. An in-pile metal-water test of an aluminum-uranium oxide cermet fuel pin showed 19 percent aluminum-water reaction from a 730-megawatt-second (760 cal/g of fuel) transient on a 39-msec period.

Three transients on urania core, stainless steel-304-clad fuel pins gave 3.7, 5.4, and 11.5 percent stainless steel-water reaction at energy inputs of 95, 320, and 520 cal/g uranium dioxide, respectively. The data from these urania-core fuel pins indicate that the energy is more important a parameter than the reactor period (over the range from 43 to 121 msec) in determining the physical changes and extent of metal-water reaction. Also, a sealed, water-logged urania-core fuel pin was found to have a lower threshold energy of destruction and more metal-water reaction than a pin with a dry core.

Two tests were made with fuel pins which had a core consisting of molybdenum wires interspersed in thoria-urania; the pins were clad in Zircaloy-2. The primary purpose of the molybdenum wires was to improve the thermal conductivity of the core fuel; a secondary purpose was to serve as a monitor for the core temperatures. A transient which gave rise to a 2600 C central core temperature caused incipient melting of the molybdenum wires as well as 6 percent reaction of the Zircaloy-2 with water, while the pin remained intact but swelled. A more energetic transient which resulted in an estimated core temperature of 3000 C produced melting of the wires, destruction of the fuel pin, and 29 percent Zircaloy-water reaction.

V. Energy Conversion (pages 195 to 206)

A regenerative lithium hydride fuel cell system to convert nuclear energy into electricity is being developed. This thermally regenerative system is one in which heat is used to disassociate lithium hydride which is then re-formed in an electrochemical cell with the production of electric power. Hydrogen-diffusion measurements have been made with pure iron diaphragms welded to their holders by electron-beam welding instead of by the previously used shear-seal technique of mounting. The results agree with the previous rates of hydrogen diffusion (see ANL-6477, pages 204 to 207). At present, the diffusion of hydrogen through the iron diaphragm limits power production from the lithium hydride cells. Ionization of the hydrogen behind the iron diaphragm by means of a radioactive source has been suggested as a possible method of increasing the rate of hydrogen diffusion. At low temperatures (400 C), diffusion rates with alpha sources were twice those in the absence of a source; at 750 C the diffusion rates were 20 percent higher with alpha ionization than without.

Studies are continuing to select possible bimetallic concentration cells for investigation in a regenerative system. During the present quarter, current-voltage characteristics have been determined for lithium-bismuth, lithium-cadmium, lithium-lead, lithium-tellurium, and lithium-zinc bimetallic cells.

Thermoelectric methods for direct conversion of nuclear reactor heat energy into electrical power are being investigated. Measurements are being made in the areas of liquid thermocouple systems and refractory solid thermocouple systems. Studies have begun on the indium-bismuth liquid system. Data taken to date indicate indium has only a minor influence on the contributing band structure of bismuth in the composition range from 20 to 52 percent indium. Room-temperature Hall coefficient measurements made on the refractory solid uranium monosulfide gave a value of Hall coefficient, $R \approx -9 \times 10^{-3}$ cc/coulomb; resistivity, $\rho \approx 200 \times 10^{-6}$ ohm-cm; Hall mobility, $U \approx 45$ sq cm/(volt)(sec); carrier density, $n \approx 0.7 \times 10^{21}$ /cc.

VI. Determination of Nuclear Constants (pages 207 to 211)

The cross sections of ytterbium-176, antimony-121, and molybdenum-98 for neutron capture are being determined in the neutron energy range from 0.2 to 2.2 Mev. For molybdenum-98, the capture cross section shows a rise from 45 mb at 0.35 Mev to a peak of 70 mb in the energy range around 0.6 Mev. This is attributed to a contribution of neutrons of high angular momentum with respect to the target nucleus. Twelve monoenergetic irradiations have been carried out on natural ytterbium oxide in the energy range from 0.25 to 2.2 Mev. Three monoenergetic irradiations

have been made on antimony oxide at neutron energies of 0.57, 0.68, and 0.79 Mev. Studies are also being made of the factors contributing to the neutron energy spread (neutrons not actually monoenergetic) in the flux produced by a Van de Graaff accelerator.

VII. Reactor Decontamination (pages 212 to 218)

Two runs were made in the Reactor Decontamination pilot-plant loop at 200 psi pressure and a steam velocity of 1.2 ft/sec. For equal assumed concentrations of fission products in the steam, depositions of zirconium and ruthenium were higher by a factor of 100 and 2, respectively, than for cesium (cesium deposition, $\sim 3 \times 10^{-4} \mu\text{c/sq cm}$). For most fission products monitored, deposition was found to be higher by a factor of 2 to 10 on sample strips that were horizontally, rather than vertically, oriented. The factor for cesium was 27.

Ruthenium disengaging factors were 40 to 50, thus suggesting a mechanism of reaching the vapor phase by other than entrainment - probably volatilization.

In a run made at 600 psi pressure, in which both mild steel and stainless steel sample strips were used, fission product deposition on the latter was found to be slightly greater than on the former. The loop was decontaminated by a 4-step treatment of which the first 2 used solutions of carbonates, bicarbonates, and potassium permanganate. The second 2 employed solutions of a proprietary material designated as CS-100. The effectiveness of each solution on each fission product is reported.

VIII. Routine Operations (page 219)

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

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CHEMICAL ENGINEERING DIVISION SUMMARY REPORT

January, February, March, 1962

I. CHEMICAL-METALLURGICAL PROCESSING*

Pyrometallurgical processes for the recovery of fissionable material from discharged reactor fuels offer promise of achieving a reduction in the reprocessing costs associated with nuclear power. The principal characteristics of pyrometallurgical processes which are likely to result in reduced costs are their simplicity, compactness, low-volume dry wastes, and capability for handling short-cooled fuels, with an attendant reduction in fuel inventories. Among the pyrometallurgical processes under development are melt refining (a simple melting procedure for metallic fuels) and other processes for core and blanket materials which utilize liquid metal solvents as processing media. Pyrometallurgical techniques also show promise for the preparation of various reactor fuel materials, including metals and carbides. The melt refining process is presently in the most advanced state of development and will be used for recovery of enriched uranium from the first core loading of the second Experimental Breeder Reactor (EBR-II).

A. Pyrometallurgical Development

1. Melt Refining (R. K. Steunenbergh, L. Burris, Jr.)

The melt refining process will be used to recover enriched uranium from the first core loading of EBR-II. The metallic fuel pins, consisting of approximately 50 percent enriched uranium alloyed with noble metal fission elements, are clad with stainless steel thermally bonded with sodium. The irradiated pins are declad mechanically, chopped to a convenient length, and charged to a lime-stabilized zirconia crucible in which they are melted and held in a liquid state at 1400 C for a period of 3 to 4 hr. This procedure removes about two-thirds of the fission products through volatilization and selective oxidation. The purified metal is cast into an ingot from which new pins are prepared by injection casting. A mixture of oxides and unpoured metal which remains in the crucible in the form of a skull is recovered by a separate process utilizing liquid metal solvents. Two small-scale experiments with highly irradiated uranium-fissium alloy have been performed to determine the behavior of condensable fission products volatilized during melt refining. Analytical results from these experiments are not yet available. Experimental results reported for the quarter are confined to nitridation rate studies with irradiated fissium alloy.

*A summary of this section is given on pages 1 to 6.

Nitridation Rates of Irradiated Fuel Pins
(J. P. LaPlante, C. C. Honesty)

The argon atmosphere in the EBR-II Fuel Cycle Facility is expected to contain up to 5 percent nitrogen. Declad fuel pins will be handled in this atmosphere prior to melt refining. It is expected that, because of fission product decay heat, the temperature of the pins will be raised. Since excessive nitride formation is known to affect melt refining yields adversely, the nitridation rates of irradiated fuel pins under these conditions are of interest.

The fuel pins, consisting of 10 percent enriched uranium alloyed with 5 weight percent fissionium, were irradiated in MTR. Individual pins with varying burnups and cooling times were used in the nitridation experiments:

	Weight (g)	Burnup (total atom percent)	Specific Activity (c/g)
Pin A	8.71	0.74	1.2
Pin B	7.67	~1.0	4.3
Pin C	6.15	~1.0	4.8
Pin D	4.64	~1.0	4.8

With Pins A and B, the NaK coolant used in the irradiation capsule was removed from the pins by washing with butyl alcohol. To avoid the possibility of contamination by degradation products of the organic solvents with Pins C and D, the NaK was removed by a carefully controlled reaction with oxygen. The surface coatings on the pins resulting from these treatments were removed by a mixture of 30- and 60-mesh silicon carbide in a jar mill. Although slight swelling and distortion of the pins had occurred during irradiation, the surfaces appeared sound on visual inspection.

The nitridation rates were determined in 100 percent nitrogen and in nitrogen diluted with argon. The rates were measured by manometric determinations of the nitrogen consumed in a constant-volume system. The nitrogen-uranium reaction followed a parabolic rate law at temperatures ranging from 300 to 650 C.

In Figure 1 the quantity of nitrogen consumed per unit area is plotted against time. The nitridation rates obtained at 300 C for Pins A, B, and C fall in the same order as the specific activities. The results of duplicate experiments were identical with those reported in Figure 1. It is possible, however, that the different pretreatments of the pins or the differences between the actual and calculated surface areas, because of surface damage on irradiation, may account for the differences in rates.

Figure 1
NITRIDATION RATES OF IRRADIATED
URANIUM-FISSIUM ALLOY

Since identical rates were obtained at nitrogen concentrations of 2, 5, and 100 percent in nitrogen-argon mixtures at one atmosphere and 300 C, it appears that the partial pressure of nitrogen is not a significant variable within this range.

Further experiments on nitridation are being carried out at higher temperatures.

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

Engineering development was continued of liquid metal processes for recovering the fissionable material remaining as a skull in the melt refining crucible and for the isolation of plutonium bred in the EBR-II blanket material. Laboratory work is in progress on the development of processes for other fuel materials, especially future EBR-II cores, which will contain plutonium as a fissionable material. Various actinide element compounds, such as uranium and plutonium carbides, are being prepared in liquid metal solvents, and the characteristics of the materials are being determined. In progress also are studies of various unit operations in liquid metal systems (distillation, mass transfer, and mixing).

a. Demonstration of Skull Recovery Process
(R. D. Pierce, K. R. Tobias)

A schematic diagram of the skull-reclamation process, presented in the preceding quarterly report (ANL-6477, page 36) is presented again in this report for reference purposes (see Figure 2). Briefly, this process consists of: (1) oxidation of the skull material to convert it to a free-flowing powder which is readily dumped from the crucible, (2) suspension of the oxide in a halide flux and extraction of the relatively noble fission product elements into zinc, which is discarded, (3) reduction of the uranium oxides by a magnesium-zinc alloy in which the uranium is dissolved, (4) precipitation of the uranium from solution (after transfer to a new crucible) as a uranium-zinc intermetallic compound, (5) after removal of the supernatant liquid, decomposition of the intermetallic compound with magnesium, which precipitates uranium metal, and (6) retorting of the uranium concentrate remaining after removal of the supernatant metal solution to give a uranium metal product. Fission products are largely separated in the noble metal-extraction step and in the supernatant solutions of the precipitation steps.

Figure 2

EBR-II LIQUID METAL PROCESS FOR RECLAMATION OF
MELT REFINING SKULLS

Demonstration of this process in small-scale runs was interrupted in the middle of 1961 for construction of an inert-atmosphere glove box (see Figure 3) in which additional demonstration runs will soon

be made. A recirculation system (located under the box) is provided for maintaining the purity of the argon atmosphere in the box. Filters, Molecular Sieves* dryers, copper at 600 C, and titanium sponge at 850 C are utilized to purify the gas. Water vapor is removed by the Molecular Sieves, oxygen is removed by the copper bed, which also supplies oxygen for the oxidation of any hydrogen which may be present, and nitrogen and oxygen are removed by the titanium sponge. The flowsheet for the purification train is shown in Figure 4. The system is now in operation without the recuperative heat exchanger, which is on order. Experience with a similar purification system is reported on page 73.

Figure 3

INERT-ATMOSPHERE GLOVE BOX FOR DEMONSTRATION OF
SKULL-RECLAMATION PROCESS

The skull-process demonstration runs have been resumed in the furnace shown assembled in the glove box in Figure 3. The furnace is shown with part of the bell jar removed in Figure 5 and is sketched in cross section in Figure 6. Phase transfers are made by pressure siphoning from the crucible to the outside of the bell jar. The crucible elevation in the furnace is variable and can be adjusted during a run if desirable.

*Product of the Linde Co.

Although crucibles of 7-in. outside diameter can be used, a 5-in. tungsten crucible is currently being employed. Tantalum transfer tubes and a tungsten stirrer are now employed. Some data from the initial skull-reclamation process demonstration runs should be available by the end of the next quarter.

Figure 4

ARGON PURIFICATION SYSTEM FOR INERT ATMOSPHERE GLOVE BOX

Figure 5

BELL JAR FURNACE WITH TOP REMOVED SHOWING INDUCTION COIL, INSULATION, AND CRUCIBLE

Figure 6
BELL JAR FURNACE FOR SKULL
RECLAMATION PROCESS
OPERATIONS

b. Phase-separation Studies
(J. C. Hesson, G. Rogers)

Considerable work was done in the past quarter on the first 2 phase separations which are encountered in the skull-reclamation process. For convenient reference to the phase separations encountered in the skull reclamation process, the process flowsheet is presented in Figure 2, page 32 of this report. The phase separations are:

- 1) Removal of the zinc extract from the flux-skull oxide slurry after the noble metal-extraction step. Preliminary work on this separation has previously been reported (ANL-6379, page 53).
- 2) Separation and removal of the molten metal and flux phases at 800 C after the skull-oxide reduction.
- 3) Separation at about 500 C of the zinc-rich supernatant phase from the uranium-zinc intermetallic compound precipitate. This phase separation has previously been studied extensively (see ANL-6029, page 40). Phase separations of zinc containing 2 to 6 weight percent magnesium from a uranium-zinc intermetallic precipitate cake were made at 500 C by pressuring the supernatant phase out through transfer tubes inserted into the precipitate cake. This liquid phase-removal procedure

is usually called pressure siphoning. In these separations, coarse filters or screens with $\frac{1}{32}$ -in. openings were used on the end of the transfer tubes. The loss of uranium with the zinc was essentially only that represented by the solubility of uranium in zinc at 500 C; a loss of considerably less than one percent of the uranium in this step was indicated.

4) Removal of the magnesium-rich zinc supernatant phase at about 400 C from precipitated uranium after decomposition of the uranium-zinc intermetallic compound. Experimental work on separating magnesium-52 weight percent zinc at about 400 C from precipitated uranium by pressure siphoning with a transfer tube has shown over 95 percent removal of the supernatant phase to be easily achievable with low loss of uranium with the transferred supernatant (see page 57 of this report).

5) Removal of adhering magnesium and zinc from the uranium precipitate by vaporization. This operation is known as retorting and is discussed in the following section.

Because experience has shown that pressure transfers are very suitable for removing liquid phases encountered in the skull-reclamation process, it has been necessary to develop appropriate designs for transfer tubes. Metal-phase transfer tubes are simple heated pipes which are appropriately bent to direct the discharging metal into a receiver. Molten flux-transfer tubes are of similar design but have been equipped with an enlarged section to disengage any entrained metal phase. The designs are shown later in Figure 7, where they are discussed in connection with molten flux-metal phase separations.

The pipes are heated externally by $\frac{1}{8}$ -in.-OD, stainless steel-sheathed, magnesia-insulated heating elements, which were wound around the tubes with an approximately 1-in. spacing. In combination with the exterior Fiberfrax insulation, temperatures of about 800 C along the length of the tubes were achieved with a power input of 500 w, which is about one-quarter of a heater element rating.

Tubing fabricated of tungsten, molybdenum, tantalum, or alloys of these elements will be required for handling molten zinc under process conditions. Since the necessary fabrication techniques for pipes made of these materials are still being developed, the transfer studies were performed with stainless steel tubes; cadmium, which may be satisfactorily contained in stainless steel, was used as a stand-in for zinc.

(1) Separation of Molten Metal from Frozen Flux (after Noble Metal Extraction)

To facilitate the removal of the zinc waste after noble metal extraction, the molten salt is first frozen by cooling to below 600 C. The zinc phase, which freezes at about 420 C, may then be removed at any

temperature between 420 C and about 575 C. The molten zinc is transferred out by pressure through a pipe inserted to near the bottom of the zinc phase. Since a part of the flux phase which is heavily laden with uranium oxide often sinks through the molten zinc to the bottom of the vessel, it is necessary to maintain a small flow of argon through the transfer tube to prevent closure of the transfer tube opening with the lower frozen flux phase and also to produce and maintain a vent opening in the flux.

A relatively low melting flux, Dow 230,* which freezes at about 440 C, was used in conjunction with cadmium (which freezes at 321 C as compared with 419 C for zinc). Cadmium transfers were made at 375 C. Except for this general lowering of temperature, the phase-separation problem is the same as that encountered in the actual process.

In each of 3 transfer experiments made after simulated noble metal extractions, about 4.5 kg of a 5-kg cadmium charge was transferred without difficulty at 375 C under 10 psig pressure from a frozen flux-skull oxide slurry (1.5 kg of flux and 0.375 kg of skull oxide). These charge weights are equivalent to about 600 to 700 cc of each phase. The 90 percent separation of metal achieved in these experiments is more than adequate for process needs and should be still higher at the full process scale of operation. It appears that this transfer will be a straightforward operation and that high transfer efficiencies should be readily achievable.

In one of the above runs, the receiver crucible was placed in the open (rather than in a closed vessel) to simulate plant operation. A gasketed fitting was clamped to the discharge end of the tube to allow backflow of argon at a rate of about 140 cc/min. No difficulty was encountered in the subsequent phase separation.

(2) Separation of Molten Metal and Molten Flux Phases

After the uranium oxide-reduction step of the skull-reclamation process, it is necessary to effect at 800 C a clean separation of the flux and metal phases. The flux is disposed of as a waste; the metal phase is transferred to another crucible in which the final process steps are effected. Because both phases are molten, this is probably the most difficult phase separation encountered in the process. In order to avoid contamination of one phase by the other, it is permissible to leave a heel of each phase in the reduction crucible.

*The composition of Dow 230 flux in weight percent is as follows:
KCl-43 minimum, $MgCl_2$ - 31 to 37, $BaCl_2$ - 8 to 11, CaF_2 - 2 to 5,
MgO - 4 maximum, and NaCl - 6 maximum.

Three methods of phase separation were investigated during the past quarter and are described below.

(a) Controlled Removal of Both Phases in Conjunction with Continuous Interface Determinations

This method consists of successive removal of the flux and metal phases in the order which is most convenient. Regardless of whether the flux phase is transferred first (leaving a flux heel) or last, the method requires continuous determination of the interface location during transfer of the metal phase, since the transfer of the metal phase must be stopped (by pressure reversal) as the flux-metal interface nears the tip of the transfer tube; otherwise, any flux phase present quickly transfers into the metal receiver. Although very clean and efficient separation of the phases can be effected by this procedure (see Table 1), the necessity of accurate and continuous interface measurements would make adaptation to remote operation difficult. In the experimental work, interface determinations were made manometrically by means of two argon-bubbler tubes, one on each side of the interface and separated by a distance of 3 in. In order to keep the interface between the tips of the bubbler pipes, it was necessary to raise the crucible during transfer of the metal phase. The metal transfer pipe was at the same level as the lower bubbler tubes.

Table 1

FLUX-METAL PHASE SEPARATIONS BY CONTROLLED PHASE REMOVAL
IN CONJUNCTION WITH INTERFACE DETERMINATION

Run	Temp of Separation (C)	Charge (kg)		Cadmium Transfer from beneath Flux		Flux Transfer	
		Cadmium	Flux	Weight (kg)	%	Weight (kg)	%
58	500	5.48	1.09	4.95	90	0	0
62	540	4.95	1.41	4.49	91	0	0
60	570	4.95	1.43	0	0	1.27	89
61	540	4.95	1.41	0	0	1.24	88

(b) Use of Pressure Control to Effect Initial Transfer of Flux Only

In this procedure, the pressure is controlled at a value insufficient to transfer metal but in excess of that required to transfer flux. Through movement of the flux transfer tube, the interface may be approached from either the flux or metal phase. In either case, material transfer stops or does not take place when the transfer tube tip is in the metal phase. Consequently, determination of the interface location is unnecessary, although in practice it would be necessary to control the interface location to within several inches of a fixed value. A flux transfer

tube with a movable bellows seal several inches long would permit sufficient movement of the tube at its stationary seal to allow for some variation in the interface location.

After as complete a flux transfer as possible, the metal phase is also essentially completely transferred at a higher pressure and through a separate pipe. An advantage of this procedure, besides that of eliminating the necessity of accurate interface location, is that minimum heels of both flux and metal remain. The disadvantage of this procedure is that a thin flux layer remains on the metal after the flux transfer, and a portion of this flux layer transfers with the metal phase. As shown in Table 2, the quantity of flux transferred with the metal is generally small (50 g or less) and probably would not have serious consequences in plant operation.

Table 2
USE OF PRESSURE CONTROL TO EFFECT INITIAL REMOVAL OF
FLUX PHASE ONLY

		Charge: 5 kg of cadmium 1 $\frac{1}{2}$ kg of flux		
		Temperature: 600 C		
Run No.	Restriction ^a in Flux Line	Metal Transferred with Flux (g)	Flux Remaining with Metal Heel (g)	Flux Transferred with Metal (g)
T7	None ^b	0	62	33
T8	None	114	100	10
T9	5/16-in. rod	0	112	19
T10	1/4-in. rod	10	109	13
T12	1/4-in. rod	0	57	46
T23 ^c	None ^d	0	~100	51

^aUsed to reduce rate of flux transfer and therefore metal entrainment.

^bMost of the flux transferred before the flux transfer tube was inserted below the interface.

^cMagnesium oxide was present in the flux at a concentration of 9 weight percent; transfers were made to receiver crucibles in the open.

^dA one-in.-ID enlargement was added to the end of the flux transfer tube to reduce the flux velocity and thereby metal entrainment in the flux.

(c) Automatic Separation and Transfer Phases

A third method has been developed in which flux and metal transfer tubes are utilized simultaneously as shown in Figure 7, and the phase separation is automatic. Separation is dependent

upon the difference in density of flux and metal (the density of the flux is about 2 g/cc, whereas the density of zinc or cadmium phases is between 6 and 8 g/cc). The flux transfer tube extends somewhat higher (about a foot or so) above the charge crucible and the receiver crucibles than the metal transfer tube. The metal transfer tube extends to within $\frac{1}{4}$ in. of the bottom of the charge crucible; the flux transfer tube extends to within about $\frac{1}{2}$ in. of the end of the metal transfer tube. Thus, before a transfer, both transfer tubes extend through the flux phase into the metal phase.

Figure 7

TRANSFER TUBES FOR MOLTEN METAL-SALT SEPARATIONS

In order to make transfers, the pressure is slowly increased to a value sufficient to force the metal through the metal transfer tube, but not sufficient to force the metal through the flux transfer tube. The metal, of course, also rises in the flux transfer tube, but not high enough to transfer through it. The transfer rate of metal is controlled by the rate of introduction of pressurizing gas to the pressure vessel. When the liquid metal-flux interface falls below the open end of the flux transfer tube, liquid metal can run out of this tube while flux runs into it. Since the flux is lighter than the metal, the liquid level rises in the flux transfer tube until the flux starts to transfer. Because of its low density, the flux transfers very rapidly and the metal stops transferring because of the pressure reduction occurring when flux transfer begins. As soon as the flux level falls below the end of the flux dip tube, the gas pressure is vented through the flux transfer tube and transferring stops. A heel of flux and metal equal to the distance from the bottom of the charge crucible to the end of the flux transfer tube remains.

If a disengaging chamber, as shown in Figure 7, is not used, most of the metal in the flux transfer tube at the start of flux transfer is pushed through the tube ahead of the transferring flux and is lost. While the amount of metal lost with the flux could be reduced by providing increased opportunity for the metal to interchange with flux in the tube (e.g., by a restriction to reduce flow), the simplest and a very effective remedy is the disengaging chamber.

At high rates of flux transfer, some metal can be entrained in the flux at the transfer tube tip. This can be eliminated by enlarging the inlet end of the flux tube, as shown in Figure 7, to reduce the flux velocity.

The runs made by this method have been summarized in Table 3. In the first 4 runs (T1 through T4), a disengaging chamber was not used, and various restrictions in the flux transfer line in combination with an enlargement at the entry end were used in an attempt to prevent metal present in the flux transfer tube from transferring at the start of flux transfer.

Table 3

AUTOMATIC SEPARATION OF FLUX AND METAL PHASES

Charges: 5 kg of cadmium; 1.5 kg of flux
 Separation Temperature: 600 C
 Transfer Tubes: 3/8-in. ID in Runs T1 through T5;
 1/4-in. ID thereafter

Run No.	Difference in Height between Tube Ends (in.)	Argon Flow Rate (cc/min)	Design Variable (flux transfer tube only)	Flux Transferred with Metal (g)	Metal Transferred with Flux (g)
T1	1/2	Not measured	Open tubes only	0	922
T2	1/2	Not measured	1/8-in. orifice at outer end of flux tube and 1-in. enlargement at entry end	0	936
T3	1/2	Not measured	1-in. enlargement at entry end and 0.345-in. disc at first bend	0	259
T4	1/2	Not measured	1/4-in. rod restriction at entry end and enlargement	0	78
T5	1/2	Not measured	5/16-in. rod restriction at entry end and enlargement	0	0.25
T13	11/16	140	Disengaging chamber ^a	0	0
T14	5/16	140	Disengaging chamber	563	37
T15A	1/2	35	Disengaging chamber	0	0
T15B	1/2	400	Disengaging chamber	0	0
T16	7/16	950	Disengaging chamber	837	0
T17	7/16	~ 15	Disengaging chamber and 1-in. enlargement	0	0
T18	1/2	650	Disengaging chamber and 1-in. enlargement	184	0
T19	1/2	400	Disengaging chamber and 1-in. enlargement	0	0
T24 ^b	7/16	280	Disengaging chamber and 1-in. enlargement	0	0
T25 ^c	7/16	280	Disengaging chamber and 1-in. enlargement	0	0
T28 ^{c,d}	11/16	140	Disengaging chamber and 1-in. enlargement	0	0
T29 ^{c,e}	5/8	270	Disengaging chamber and 1-in. enlargement	0	0
T30 ^{c,e}	3/8	270	Disengaging chamber and 1-in. enlargement	0	0

^aDimensions of disengaging chamber: 1-5/8-in. ID by 6-1/2 in. long.

^bReceiver crucibles in open; 9 weight percent magnesia in flux.

^cReceiver crucibles in open; 13 weight percent magnesia in flux.

^dQuantity of flux increased to 2.3 kg.

^eQuantity of flux increased to 3.7 kg.

None of these worked well, although an appreciable reduction in metal loss was effected by them. The combination of a disengaging chamber and an entry enlargement essentially eliminated metal transfer with the flux (Runs T5 through T30). Runs T14, T16, and T18 show the importance of controlling the rate of metal transfer or, alternatively, the distance between the ends of the tubes. The smaller the height difference between the ends of the tubes, the lower must be the rate of metal transfer to avoid flux transfer through the metal tube. At high rates of metal transfer, the inertial effects are so great that the interface drops to the metal-transfer tube level before flux transfer can be initiated through the flux tube, and hence some flux is transferred through the metal tube.

Because of the simplicity of design and control, the clean separation of both phases, and the fact that knowledge of interface location is unnecessary, the automatic separation procedure appears to be the most suitable of the 3 methods for remote operation. It is planned to adopt this procedure in future scale-up work.

(3) Fume Filters for Waste Metal Containers and Flux Containers

Since it is contemplated that in plant operation the waste metal and flux will be discharged directly from the transfer lines into open waste containers, filter covers will be needed to trap the (particulate) fumes. Experimental work was done during the transfers with bonded fiberglass filters (American Air Filter Air Mat #12) held by perforated metal screens. This bonded fiberglass weighs about $6\frac{1}{3}$ gm/sq ft, and its uncompressed thickness is about $\frac{1}{8}$ in. Six layers of the fiberglass were held between 2 discs of perforated metal and compressed to about $\frac{3}{16}$ -in. thickness. The filters and seals are shown in Figure 8.

Figure 8
FUME FILTER ARRANGEMENT
FOR A RECEIVER CRUCIBLE

The filters were first tried when transfers were being made with the receiver crucibles in closed vessels. When there was no evidence of fumes passing the filters, transfers were made with the crucibles in the open. During these transfers, there was no evidence of fumes leaking from either the flux-receiver crucibles or the metal-receiver crucibles. After cooling and removal of the filters, considerable dust and particulate material was found on and in the filter material and crucibles, indicating that these filter assemblies were highly efficient.

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

Isolation of the uranium metal precipitated in the inter-metallic compound-decomposition step of the skull-reclamation process is accomplished by distilling away the residual magnesium-zinc solution in a final retorting operation. Experimental studies of the retorting operation have been directed toward achieving easy removal of the uranium product from the retorting crucible in high yield and in a form suitable for remote handling.

Consideration is also being given to the removal of the uranium concentrate (uranium and associated magnesium-zinc alloy) produced by the magnesium decomposition. The concentrate would then be regarded as the end product of the skull-reclamation process. In this event, the vaporization of the magnesium and zinc would take place during melt refining, with suitable provisions made to handle the magnesium and zinc vapors.

(1) Performance of Beryllia Crucibles

Numerous experiments have been carried out to date in a variety of crucible materials. Easy recovery of the uranium in high yield has been achieved only in experiments conducted in beryllia crucibles (isostatically pressed and sintered). Ready removal of the product probably would also be realized with other ceramic crucibles which are not wetted by the metal systems, but beryllia has the advantage of high thermal conductivity and, therefore, high resistance to thermal shock, together with high chemical stability.

The seventh and eighth successive retorting experiments were successfully conducted in the same isostatically pressed beryllia crucible. The yields of easily recovered uranium were 99.2 and 100 percent. The crucible failed during the ninth use, when it was inadvertently subjected to excessive thermal stress.

(2) Fabrication of Beryllia Crucibles

The problem of hairline cracks developing in isostatically pressed beryllia crucibles during initial use has been reported in ANL-6477, page 45. The occurrence of these cracks has been attributed to the high internal stresses that are inherent in isostatically pressed beryllia bodies. In an effort to remedy this problem, crucibles of beryllia fabricated by the following 3 procedures are being procured for testing:

1) An anodized (beryllium oxide-coated) beryllium metal crucible. This type of crucible is being investigated to determine whether the excellent properties of beryllium oxide can be combined with the better mechanical strength of beryllium as compared with beryllia.

2) A thixotropically cast beryllia crucible. Thixotropic casting of beryllia appears to be an attractive method for forming large, process-size crucibles. Four thixotropically cast, laboratory-scale crucibles (4-in. OD by 9 in. high) have been ordered from The Brush Beryllium Company with delivery expected in May 1962. This company has thixotropically cast 4 beryllia samples (2- to $2\frac{1}{2}$ -in. OD by $\frac{3}{4}$ to 1 in. high) and subjected them to a thermal shock test. The test consisted of heating the samples to 970 C followed by water quenching. No visible cracks were detected in the cooled samples, indicating that the thixotropically cast samples were relatively stress-free.

3) A crucible constructed of hot-pressed beryllia blocks with ground mating surfaces.

The use of fabricated shapes for constructing a crucible is in conformity with common industrial practice for forming large-size crucibles.

The thixotropically cast and the block-constructed primary crucibles will be jacketed with a metal secondary crucible. The annulus between the primary and secondary crucibles will be packed with high-fired beryllia grain. The purpose of metal jacketing is twofold:

- (1) to minimize the possibility of breakage during remote handling of the ceramic crucible;
- (2) to keep the crucible intact in order to minimize or prevent leakage through any cracks which might develop.

Tests to determine the feasibility of using a metal-jacketed, beryllia crucible assembly will be initiated during the next quarter.

d. Pyrometallurgical Reduction Studies

(1) Behavior of Zirconium during the Reduction of Fissium Oxide
(J. B. Knighton, J. D. Schilb, J. W. Walsh)

After the removal of skull material from melt refining crucibles by oxidation and pouring, small amounts of crucible zirconia are found in the oxide product in the form of powder and small fragments. This material, in addition to the fission product zirconium, must be removed in the subsequent steps of the skull-reclamation process.

Two determinations of the amount of crucible zirconia reduced in about 5 weight percent magnesium-zinc solution in the absence of uranium have been reported previously (ANL-6333, page 60, and ANL-6413, page 47). The results of these determinations can be summarized as follows:

Temperature: 800 C
Crucible: tantalum
Atmosphere: argon

Flux	Mixing Rate (rpm)	Percent Reduc- tion in 5 hr
54.2 m/o NaCl-41.1 m/o MgCl ₂ - 4.7 m/o MgF ₂	500	2
47.5 m/o CaCl ₂ -47.5 m/o MgCl ₂ - 5.0 m/o MgF ₂	600	83

The reason for the marked difference in extent of reduction in these two experiments has not been established with certainty. However, it is believed that the difference in flux composition is probably the major factor responsible for the variance in results.

An additional experiment was performed to determine the extent of zirconium oxide reduction during the reduction of uranium oxide by a magnesium-zinc-molten halide system under conditions typical of the skull-reclamation process. The results are shown in Table 4. Under these conditions, complete reduction of the uranium oxide occurred within one hour, whereas only 38 percent of the zirconium oxide was reduced in the same time. After 5 hr, the reduction of zirconium oxide was 85 percent complete. This percentage agrees with the 83 percent reduction reported previously in 5 hr under similar conditions, but in the absence of uranium (ANL-6413, page 47).

Table 4

BEHAVIOR OF ZIRCONIUM DURING REDUCTION OF SKULL OXIDES

Temperature: 800 C
 Mixing Rate: 600 rpm
 Zinc: 927.0 g
 Magnesium: 48.8 g
 Skull Oxides: 54.7 g (reconstituted from screened fractions)
 Flux: 250.0 g (47.5 m/o CaCl_2 -47.5 m/o MgCl_2 -5 m/o MgF_2)
 Crucible: tantalum
 Atmosphere: argon

Time (hr)	U in Liquid Metal Phase		Zr in Liquid Metal Phase	
	Conc (w/o)	(% of total U)	Conc (w/o)	(% of total Zr)
0.5	3.38	85	0.018	16
1.0	4.04	101	0.042	38
2.0	4.05	101	0.065	60
3.0	3.99	99.8	0.078	73
5.0	4.26	106	0.093	85
At 100% reduction	4.00	100	0.109	100

It appears that a useful separation of zirconium from uranium can be achieved by limiting the time allowed for the reaction. Changing the composition of the flux may also be an effective measure, although experimental verification of this point is needed. Either procedure would be advantageous in lessening the demand on later process steps with respect to efficiency of zirconium removal.

(2) Reduction of Thorium Dioxide
(A. V. Hariharan,* J. B. Knighton)

The direct reduction of thorium dioxide to the metal by zinc-magnesium solution has no direct application to EBR-II fuel processing. It does, however, represent a potential extension of this technique to the preparation of metals for nuclear fuels from refined raw materials.

Previous investigations (see ANL-6477, page 43) have shown that thorium dioxide is reduced to the metal by a zinc-5 weight percent magnesium alloy, using a flux of the composition 38 mole percent calcium chloride-55 mole percent magnesium chloride-7 mole percent calcium fluoride. Magnesium ion proved to be a necessary constituent

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which could not be replaced by substitution of calcium ion. Also, the rates of thorium dioxide reduction were much slower than those observed with uranium dioxide. A minimum period of 3 to 4 hr was required for complete reduction of thorium dioxide.

More detailed investigations of the calcium chloride-magnesium chloride-calcium fluoride system were made to establish the composition regions in which effective reduction occurs. In Figure 9, the percent reduction of thorium dioxide in 4 hr at 750 C is shown as a function of fluoride anion concentration in the flux. These data indicate that a minimum magnesium chloride concentration of about 50 mole percent and a calcium fluoride concentration between 7 and 15 percent are required for complete reduction of thorium dioxide under these conditions. By means of these data, the composition region of effective reduction is mapped in Figure 10, where it appears as the area within the uppermost loop.

Figure 9

EFFECT OF FLUORIDE ION ON THE REDUCTION OF THORIUM DIOXIDE

Temperature: 750 C
 Time: 4 hr
 Mixing Rate: 800 rpm
 Zinc: 380 g
 Magnesium: 20 g
 Flux: 200 g (composition indicated below)
 ThO₂: 4.55 g (concentration of Th in metal is 1.0 w/o on complete reduction)

Figure 10
 EFFECT OF FLUX COMPOSITION ON REDUCTION OF THORIUM DIOXIDE

Temperature: 750 C
 Time: 4 hr
 Mixing Rate: 800 rpm
 Zinc: 380 g
 Magnesium: 20 g
 Flux: 200 g MgCl₂-CaCl₂-CaF₂
 ThO₂: 4.55 g (concentration of Th in metal is 1.0 w/o on complete reduction)

(3) Reactions of Uranium Oxides in Molten Chloride Media
(M. D. Adams)

In the proposed skull-reclamation process for the EBR-II fuel cycle, a mixture of uranium and fission product oxides is suspended in a molten halide flux and reduced to metal by a solution of magnesium in zinc. Although satisfactory reductions are being obtained, the chemistry of the process has not been fully defined. A complex heterogeneous system is involved, with several solid and liquid phases. Previous work (see ANL-6287, page 51) has shown the composition of the molten salt to have a strong effect on the rate and extent of oxide reduction. The purpose of the present effort is to obtain information which will aid in the interpretation of the effects of process variables, as well as contribute to the understanding of uranium oxide chemistry in molten salt systems.

Experiments are being conducted to identify the solid phases and the soluble species that are formed when the various uranium oxides are added to molten mixture of lithium chloride and magnesium chloride. Magnesium uranate, MgUO_4 , has been identified as the solid product formed when uranium trioxide is added to molten lithium chloride-magnesium chloride at 650 C. The reaction was carried out in a quartz tube divided into 2 sections by a sintered quartz filter. While a vacuum was maintained in the tube, the salts were melted and the uranium trioxide was added. After 30 min at 650 C, dry helium was admitted to force the molten salt through the sintered filter. The solid magnesium uranate product removed from the filter was identified by chemical analysis (see ANL-6477, page 68) and by its X-ray diffraction pattern, which is reported in the literature.¹ The soluble product has been tentatively identified as uranyl chloride. It is believed that the following equation describes this reaction, although it has not yet been verified experimentally:

In order to establish the validity of this equation, it will be necessary to verify the identity of the uranium species in solution and to prove the stoichiometry of the reaction. Investigations of the reactions of uranium dioxide and U_3O_8 in the same molten salt medium are also in progress.

e. Development of Processes for Plutonium Reactor Fuels

The second core loading of EBR-II is expected to be a plutonium alloy of approximately the following composition: uranium,

¹Rudorff, V. W., and Pfitzer, F., Z. Naturforsch., 9B, 568 (1954).

70 percent; plutonium, 20 percent; fission elements, 10 percent. One of the principal problems encountered in processing this irradiated fuel by liquid metal techniques is to achieve an adequate separation of rare earth fission products from the plutonium. Two promising methods of achieving this separation are being investigated. One involves selective extraction of the rare earths from a zinc-magnesium solution of plutonium and uranium by a suitable molten halide flux. The other method entails the use of a 64 percent calcium-zinc eutectic solution, at 424 C, in which the rare earths are soluble and the plutonium and uranium are relatively insoluble. Preliminary results indicate that both methods are capable of producing an adequate separation.

(1) Separation of Rare Earths from Uranium and Plutonium by Molten Salt Extraction
(J. B. Knighton, J. D. Schilb, J. W. Walsh)

The objective of this study is to determine the relative distribution coefficients of uranium, plutonium, and rare earth elements between molten metal and molten salt phases. Preliminary results (see ANL-6379, page 61) had shown this distribution in the case of cerium oxide to be dependent on the magnesium chloride concentration in the flux system used and the magnesium concentration in the zinc-magnesium metal phase.

Further experiments have been conducted on the distribution of rare earth elements between zinc-magnesium solution as the metal phase and magnesium chloride as the flux. The rare earth metal was added to the liquid metal-flux mixture at 800 C. After a mixing period of one hour, both metal and flux samples were taken. A specified amount of magnesium was then added to change the composition of the metal phase, and the procedure was repeated. By continuing this operation through several cycles, distribution data were obtained over a range of magnesium concentrations. During the course of the experiments the flux/metal volume ratios varied from about 0.7 to 5.0. Each metal sample was analyzed for magnesium, as well as the rare earth, to verify the magnesium concentration in the metal phase.

Distribution coefficients K_d $\left(K_d = \frac{\text{w/o rare earth in flux}}{\text{w/o rare earth in metal phase}} \right)$ have been obtained for cerium, yttrium, praseodymium (Figure 11), and samarium. The results appear as a family of curves for cerium, yttrium, and praseodymium with minima at about ten percent magnesium concentration. At higher magnesium concentrations, the rare earths tend to transfer back into the flux phase. In the case of cerium, the equilibrium was approached from both directions.

Figure 11

DISTRIBUTION OF RARE EARTHS BETWEEN ZINC-MAGNESIUM ALLOY AND MAGNESIUM CHLORIDE FLUX

Temperature: 800 C
Mixing Rate: 350 rpm
Crucible: tantalum
Atmosphere: argon

In all of the metal samples, the concentration of samarium was below the limit of detection (~ 0.01 percent), indicating that samarium strongly favors the flux phase over the entire range of magnesium concentrations. The flux exhibited the reddish-brown color typical of samarium(II) ion.

Yttrium, cerium, and praseodymium distribution experiments were performed with rare earth concentrations ranging from 0.15 to 1.5 weight percent in the metal phase and 1.0 to 4.0 weight percent in the flux phase. Cerium and praseodymium tracer experiments were also conducted at more realistic process concentrations between 0.003 and 0.4 weight percent in the metal phase and 0.18 to 0.45 weight percent in the flux phase. The distribution coefficients of all 3 rare earths showed no dependence on the rare earth concentration over the concentration ranges investigated.

Similar experiments have been conducted with uranium, plutonium, and neodymium. Although complete analytical results are not yet available, preliminary data indicate that adequate separations can be achieved by this method.

(2) Separation of Rare Earths from Uranium and Plutonium
by Calcium-Zinc Extraction

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

An experiment was carried out and is described below in which material similar to the EBR-II second core loading was processed by the calcium extraction procedure. The experiment (MA-Ca-11) consisted of 3 parts: (1) plutonium and cerium (used as a stand-in for yttrium and rare earths) were coprecipitated with uranium in an intermetallic zinc compound; (2) the supernatant zinc solution was poured off; and (3) calcium was added to the uranium-plutonium-cerium-zinc intermetallic compound to form an insoluble uranium-plutonium alloy, while cerium dissolved in the resultant calcium-zinc solution. The effects of variations in calcium concentration and temperature were studied in Part (3). The experimental procedure was as follows:

1. 49.5 g uranium, 13 g plutonium, and 0.659 g neutron-irradiated cerium (stand-in for yttrium and rare earths) were dissolved in 2800 g of zinc by stirring at 775 to 800 C in a tantalum crucible and in a helium atmosphere. The solution was sampled and then cooled to successively lower temperatures, at each of which the melt was sampled after a 30-min settling period. The supernatant liquid was top-poured, after $3\frac{1}{2}$ hr of settling at 470 C, into a cold, outgassed graphite mold.

2. The ingot from the supernatant liquid was reheated and stirred in its graphite mold at 700 to 730 C for $2\frac{1}{2}$ hr and sampled. This step was included to permit material balance computations. The supernatant fraction weighed 2207 g, or about 79 percent of the original charge after correction for removal of samples.

3. The heel from Part 1 was reheated and stirred in its tantalum crucible while calcium sticks were added over a 30-min period. The sequence of steps followed in this part of the experiment was: (a) addition of calcium metal (345-g, 161-g, and 549-g batches) at 35 degrees or more above the maximum sampling temperature; (b) stirring at temperature for 3 to 6 hr; (c) settling either for 30 min or overnight; and (d) sampling. The temperature was then either raised or lowered, depending on whether step (a) or (b) followed.

Samples were taken by pressurizing the melt through tantalum frits press-fitted into 0.25-in.-diameter tantalum tubing. Duplicate samples for each experimental condition were dissolved in 15 M nitric acid-1 M hydrochloric acid and analyzed for (a) zinc by EDTA titration; (b) uranium by fluorophotometry; (c) plutonium by alpha counting; and (d) cerium by counting cerium-141 gamma activity.

The analytical data are given in Table 5 together with material balance estimates. The material balance computations take into account the removal of samples and assume (a) formation of (U, Pu, Ce)Zn_{11.5} in Part 1; (b) precipitation of uranium and plutonium metals in Part 3; and (c) no solvent evaporation (about 20 g of metal was evaporated during the entire experiment).

Table 5

BEHAVIOR OF PLUTONIUM AND CERIUM DURING COPRECIPITATION WITH URANIUM-ZINC INTERMETALLIC AND DECOMPOSITION OF INTERMETALLIC BY CALCIUM

(Experiment MA-Ca-11)

Conditions: Tantalum crucible and accessories; outgassed graphite mold; helium atmosphere (10 psig except during sampling).

Procedure: 1. 49.5 g U, 13 g Pu, and 0.659 g irradiated cerium dissolved in 2800 g Zn at 775 to 800 C; solution cooled to 470 C with intermittent sampling and supernatant poured into graphite mold.

2. Graphite mold containing supernatant (2207 g) reheated to 728 C and sampled.

3. Calcium added incrementally to residue (573 g) from 1 and solution sampled.

Sampling: Liquid metal pressurized through tantalum frits into tantalum tubes. Data in chronological order.

Temp (±3 C)	w/o Found in Solution					Estimated Percent of Original Charge		
	Zn	U	Pu	Ce	Ca ^a	U	Pu	Ce
<u>Part 1</u>								
771	-	1.67	0.476	0.0232	-	97	105	101
682	-	0.78	0.310	0.0144	-	43	65	60
610	-	0.153	0.104	0.0046	-	8.1	21.0	18.1
540	-	0.026	0.0361	0.0017	-	1.4	7.2	6.8
474	-	0.0022	0.0084	0.00047	-	0.1	1.7	1.8
<u>Part 2</u>								
728	-	0.108	0.054	0.0026	-	4.8	9.2	8.7
<u>Part 3</u>								
727	59.5	4.9 x 10 ⁻⁴	1.08	0.069	39.3	< 0.01	72	90
641	59.6	3.8 x 10 ⁻⁴	1.08	0.068	39.2	< 0.01	72	89
729	50.0	1.6 x 10 ⁻⁴	0.613	0.059	49.3	< 0.01	49	92
644	50.0	1.0 x 10 ⁻⁴	0.547	0.059	49.4	< 0.01	44	92
528	50.1	4.6 x 10 ⁻⁴	0.443	0.059	49.4	< 0.01	35	92
729	32.1	1.1 x 10 ⁻⁴	0.086	0.036	67.8	< 0.01	10.4	87
645	32.1	1.1 x 10 ⁻⁴	0.076	0.037	67.8	< 0.01	9.2	88
528	32.1	1.8 x 10 ⁻⁴	0.047	0.037	67.8	< 0.01	5.7	88
424	36.4 ^b	2.5 x 10 ⁻³	0.022	0.041	63.5 ^b	< 0.1	2.3	86

^aComputed by difference.

^bPrecipitation of calcium inferred.

Discussion of Results

Part 1. The analytical data between 771 and 474 C, although not needed for studying cerium removal by calcium-zinc solutions, served to check earlier work (see ANL-5789, page 89) on solubility and coprecipitation in the zinc-uranium-plutonium system. As expected, the data show a straight-line relationship between log weight percent metal in solution and reciprocal absolute temperature, as seen in Figure 12. Although not shown in this figure, the earlier plutonium "solubility" curve parallels the present curve but is displaced upward. This is to be expected, since original charges in the earlier work contained approximately 2.5 times as much

uranium and plutonium. The uranium "solubility" curves for the 2 experiments, however, are neither coincident nor parallel. The reason for this difference is not clear.

Figure 12
COPRECIPITATION OF URANIUM,
PLUTONIUM, AND CERIUM
FROM ZINC SOLUTION

The data can be used to compute the Doerner-Hoskins coprecipitation coefficients, λ , for coprecipitation of plutonium and cerium with uranium from zinc solution. The values obtained are $\lambda = 0.64$ and $\lambda = 0.62$, respectively. These values are in close agreement with the individual coefficients previously found for coprecipitation of trace concentrations of plutonium and cerium with uranium, namely, $\lambda = 0.66$ (see ANL-5789, page 94; ANL-5924, page 136).

Part 2. The data indicate that about 5 percent of the precipitated particles of intermetallic zinc compound was poured with the supernatant solution at the conclusion of Part 1.

Part 3. Plutonium Solubility. At 39 weight percent calcium, approximately 82 percent of the original plutonium charge can be accounted for: 72 percent in solution, nine percent in the supernatant solution of Part 2, and one percent in samples. The 18 percent not accounted for may be assumed to be present as a solid phase. It is unlikely that plutonium was trapped within the precipitating uranium particles during decomposition of the intermetallic zinc compound, thereby causing an unsaturated condition with respect to plutonium. If this had occurred, a low material balance

would also be expected for cerium, which is not the case. Thus, the concentrations of 1.08 percent found at 727 C and 641 C may be regarded as saturation values. Successive decreases in plutonium concentration of the melt were found upon increasing the calcium concentration from 39 to 49 to 68 percent. Since the dilutions caused by the calcium additions are insufficient to account for the decreases in plutonium concentration, saturation of the melt is inferred. It should be emphasized, however, that the saturated conditions inferred for plutonium do not necessarily represent equilibrium, i.e., the solid phases may not be equilibrium phases.

If one assumes that, during calcium decomposition of the uranium-plutonium-cerium-zinc intermetallic compound, plutonium cannot react with any of the components except uranium, then plutonium will separate as plutonium metal, as uranium-plutonium solid solution, or as a mixture of the two. Experimental conditions, such as temperature, rate of calcium addition, mixing rate, and particle size, will influence the composition of the solid phase obtained. Formation of uranium-plutonium solid solution in the present experiment is suggested by comparison with the data of a previous experiment. In the absence of uranium, plutonium solubility was found to be 0.28 percent in a 64 weight percent calcium-35 weight percent zinc-0.33 weight percent cerium solution in equilibrium with liquid plutonium at 704 C (see ANL-6413, page 61). This condition is closely approximated in the present experiment, in which uranium is present, at 68 weight percent calcium-32 weight percent zinc-0.036 weight percent cerium and 729 C, for which a plutonium solubility of 0.086 percent was found. A lower plutonium activity and, hence, solubility would be expected for a melt in equilibrium with uranium-plutonium solid solution than for one in equilibrium with liquid plutonium.

The plutonium data of Table 5, Part 3 may be summarized as follows. In calcium-zinc solutions containing greater than 39 percent calcium, plutonium solubility decreases with increasing calcium concentration and decreasing temperature. The lowest plutonium solubility attained was 0.022 percent at 424 C in 64 weight percent calcium-36 weight percent zinc.

Cerium Behavior. The cerium data of Table 5, Part 3 may be summarized by stating that, within the analytical error, cerium does not coprecipitate with either uranium or uranium-plutonium from solutions containing 39 or more weight percent calcium in zinc. This result is in accord with previous studies of cerium coprecipitation in the uranium-calcium-zinc system (see ANL-6379, page 71). If the cerium behavior is typical of rare earth behavior, then a method for decontaminating rare earth fission products from uranium-plutonium alloy is available.

Uranium Solubility. The very low uranium solubilities found in the range from 39 to 68 percent calcium in zinc, namely, 0.0001 to 0.0005 percent, are in accord with earlier work (see ANL-6379, page 67). The present data serve to re-emphasize statements previously made regarding the separability of plutonium and uranium by means of calcium-zinc solutions.

Summary

The practical impact of Experiment MA-Ca-11 can be understood by reference to the following flow diagram:

The flow diagram presents data which are not the optimum but which summarize the results of Table 5. As can be seen, better than 97 percent of the plutonium and virtually 100 percent of the uranium charged to the calcium decomposition step were precipitated with little or no cerium coprecipitation. By optimizing process conditions insofar as zinc content is concerned, an even greater plutonium recovery can be achieved.

(3) Cerium Solubility in Calcium-Zinc Solutions (M. Ader, J. T. Feeney)

Solubilities of cerium in various calcium-zinc solutions were reported in ANL-6379, page 70. Recently completed experiments indicate that the solubilities reported are too low. In the region of interest, namely, 50 to 70 percent calcium in zinc, cerium solubility is at least 1.5 percent. The reason for the discrepancy is not clearly understood but may be related to the use of graphite filters in the earlier work.

f. Recovery of Plutonium from EBR-II Blanket Material (I. O. Winsch, T. F. Cannon)

Plutonium will be generated in the depleted uranium blanket material of the EBR-II reactor to a concentration of about one percent before the blanket material is discharged for processing. The blanket processes under investigation for the separation of plutonium from uranium by pyrometallurgical methods are based on the high solubility of plutonium in magnesium-rich zinc alloys and the contrasting low solubility of uranium in these alloys.

Several demonstration runs have shown the feasibility of a process in which blanket uranium containing about one percent plutonium is first dissolved in a 14 weight percent magnesium-zinc alloy and subsequently precipitated by adding magnesium to about a 50 weight percent concentration (see ANL-6477, page 48; ANL-6413, page 56; and ANL-6379, page 75). The plutonium remains in solution during the uranium precipitation and may be separated from the uranium by withdrawal of the supernatant liquid. Evaporation of the supernatant solution will be carried out subsequently to provide a plutonium concentrate for incorporation into the core-fuel cycle.

(1) Process Demonstration

Two additional process demonstration runs have been completed; these follow the procedure outlined above. However, in these runs the stainless steel cladding was dissolved along with the uranium to determine if any adverse effects resulted from the presence of stainless steel. Previous tests (see ANL-6477, page 52) showed that stainless steel is dissolved or is attacked rapidly by the zinc-12 weight percent magnesium alloy. Elimination of the necessity to decan the blanket material is a desirable process simplification. Complete analytical results on these runs are not available, but preliminary results indicate no adverse effects arising from the presence of iron, chromium, nickel, and fission products initially present in the charge. Expected uranium and plutonium concentrations were found in the solutions of the dissolution and precipitation steps.

(2) Engineering Operations - Distillation and Phase Separations

Results of previous demonstration runs show that process principles are fairly well established, and work is now being concentrated on engineering operations and equipment design. Much of the equipment and many of the engineering operations are similar to those encountered in the skull-reclamation operation. However, 2 engineering operations which deserve special attention are the evaporation of magnesium and zinc to produce a plutonium concentrate and the phase separation of magnesium-zinc supernatant from the uranium precipitate.

Since considerable experience has been accumulated over the past several years on the evaporation and distillation of metals, the first of the above operations is considered to be largely one of equipment design. An evaporation unit now under design, which can be operated with large-scale skull-reclamation process equipment, will also permit large-scale demonstration of the blanket process. In recent studies on the evaporation of magnesium-zinc solutions containing cerium as a stand-in for plutonium, there was little difficulty in concentrating the solution, provided that vapor baffles were used to restrict solute entrainment.

Equipment (see Figure 13) has been installed to study the separation of the magnesium-zinc supernatant from the precipitated uranium phase by pressure siphoning. Heating the transfer line is accomplished by an electrical heating element which is wound around the transfer line. An initial supernatant removal of 95 percent (and, therefore, a corresponding plutonium removal of 95 percent) would eliminate the necessity of washing the uranium precipitate, since the arbitrarily established process goal of 90 percent plutonium recovery would have been achieved.

Figure 13

EQUIPMENT FOR INVESTIGATION OF SUPERNATANT REMOVAL FROM PRECIPITATED URANIUM

Phase separations are made near the 54 percent zinc-magnesium eutectic in order to allow maximum cooling and therefore maximum precipitation of the uranium without precipitation of other solid phases. The melting point of the eutectic composition is about 345 C. However, because of the narrow eutectic valley, it is advisable that the solution not be cooled lower than 400 C; otherwise, slight variations in composition on either side of the eutectic can easily result in precipitation of an equilibrium solid magnesium-zinc phase.

Four phase separation runs at $\frac{1}{20}$ th full scale (500 g uranium) have been completed (see Table 6). In these runs, 93.5 to 97.5 percent of the supernatant phase was transferred from the precipitated uranium phase by pressure siphoning at 405 and 415 C. These high percentages of supernatant removal are regarded as very good, particularly at this scale of operation. Since phase separations should improve at higher scales of operation, these results indicate that there should be no problem in achieving satisfactory phase separations at full plant-scale operation.

Table 6

PHASE SEPARATION OF MAGNESIUM-ZINC SUPERNATANT SOLUTIONS
FROM PRECIPITATED URANIUM METAL

Scale: 5.2 to 5.6 kg of 50 weight percent magnesium-zinc and
500 g of uranium

Run No.	Phase Separation Temp (C)	Percent of Supernatant Phase Transferred	Uranium Conc		Percent of Total Uranium Transferred
			In Transferred Phase (w/o) ^{a,b}	In Precipitated Phase (w/o)	
1	415	97.3	0.126	72.5	1.25
2	405	97.5	0.045	71.6	0.50
3	415	97.5	0.069	69.0	0.76
4 ^c	415	93.5	0.052	58.5	0.49

^a Solubility of uranium at transfer temperature is about 0.045 percent.

^b Value obtained by resampling of transferred supernatant at 800 C and includes the uranium in solution at transfer temperature.

^c A shield roughly the area of the tube end was placed $\frac{1}{16}$ in. away from the end to prevent insertion of the tube into the uranium precipitate.

The percentages of uranium in the transferred phase (determined by heating this material to 800 C and sampling) are given in Table 6. It is apparent that in only the first run was a significant amount of uranium entrained in the supernatant phase (0.13 percent uranium versus the solubility value of about 0.04 weight percent). In this run, the transfer tube was jammed into the uranium bed. Care was taken to avoid this in the second run. In the fourth run, a shield was placed over the tube opening as a precautionary measure designed to prevent trapping and entrainment of small particles of uranium at the tube opening. This shield was roughly the area of the tube end and $\frac{1}{16}$ in. from the tube end. In the single run in which the shield was employed, there was very little uranium entrained in the transferred supernatant phase. However, this single result is without great significance since similar results (see Runs 2 and 3) were obtained without a shield. It is not considered worthwhile to obtain data to support the use of such a shield. The shield is regarded simply as a device to circumvent the possibility of tube plugging.

Equipment is now being fabricated for one-half scale phase-transfer operations.

g. Synthesis of Reactor Materials

(1) Process Development Studies

(T. R. Johnson, R. L. Christensen, J. R. Pavlik)

An increasing interest in the potential use of uranium and plutonium carbides as high-performance reactor fuels has led to a consideration of pyrometallurgical methods for the preparation and reprocessing of such fuels. Attention has been directed chiefly at the preparation of uranium monocarbide in liquid metal media. Previous work (see ANL-6477, page 53) has shown that uranium monocarbide can be prepared by the addition of carbon to a solution of uranium in zinc or cadmium. Magnesium is usually added to prevent oxidation by impurities. The preparation of plutonium monocarbide has also been studied previously.

It has been necessary in previous experiments to add excess carbon to the system in order to achieve complete precipitation of the uranium as the carbide. Various types of phase separations have been attempted, with limited success, to remove the surplus carbon.

Effect of Sodium on Carbon-Uranium Reaction

Three exploratory experiments were performed to examine the effect of alkali metals on the uranium carbide precipitation reaction. Sodium appears to be an effective wetting agent between carbon and zinc, thus making it possible to decrease substantially the amount of excess carbon used. In these experiments, alumina crucibles with tantalum agitators and baffles were charged with the metals and carbon. The charge compositions are listed in Figure 14. The carbon was a high-purity grade of powdered graphite.

The results of these experiments are compared in Figure 14 with a typical curve (Run P-4) for a similar system without sodium. Both the rate and extent of the reaction were increased significantly by the presence of sodium. The use of alkali metals as wetting agents appears, therefore, to be a promising procedure which is worthy of further consideration. The curves in Figure 14 do not originate at 100 percent of the uranium in solution because the carbide precipitation reaction begins before the uranium is completely dissolved by the zinc solution. Analytical results for this series of experiments are not yet complete.

Figure 14

EFFECT OF SODIUM ON REACTION OF CARBON WITH URANIUM IN ZINC- MAGNESIUM SOLUTION

Crucible: alumina
Stirrer: tantalum
Carbon: high-purity graphite

Run No.		Charge					Total (g)	Temp (C)	Stirring Rate (rpm)
		Metal Phase (w/o)				C/U (atom ratio)			
		Zn	Mg	Na	U				
X	P-4	73	12	0	15	1.5	3540	800	500
□	CP-40	77	10	6	7	1.3	600	800	500
○	CP-43	77	10	6	7	0.92	330	700	500
△	CP-51	81	10	1	8	1.0	310	700	400

Hydrocarbon-Uranium Reaction

The addition of carbon to a liquid metal solution of uranium in the form of hydrocarbon gases represents a possible alternative method of uranium carbide synthesis. This technique has the potential advantage that excess carbon is not added to the system, provided that pyrolysis of the hydrocarbon does not occur as a side reaction.

Several exploratory experiments were conducted to determine the reaction rate of hydrocarbon gases with uranium dissolved in cadmium. Uranium metal was hydrided and dehydrided before being contacted with a cadmium-one weight percent magnesium solution at 550 C. The purpose of this treatment was to increase the slow dissolution rate of uranium in cadmium. After a dissolution period of 4 to 5 hr, a flow of hydrocarbon gas was started.

The reaction vessel and associated equipment were made of 300 series stainless steel. The gases used were "CP" grades of methane, ethane, propane, and butane and were not further purified.

The gas was bubbled into the liquid metal at about 0.1 mole/hr through a tube extending below the baffles and terminating near the agitator. The agitator speed was about 500 rpm. Filtered samples of the metal were taken periodically, both before and after the gas flow was started.

The results of the runs are shown in Figure 15, along with the results of a blank run in which no gas was added. A small but definite decrease in the uranium concentration in solution is apparent in all the runs. The extent of the reaction was limited to about 30 percent. Because of the large amount of metallic uranium in the product, the reaction ingot was not retorted, and the reaction product was not identified. It was concluded that the reaction is inherently inefficient. No additional work is planned on this particular method; however, related techniques, such as retorting uranium-liquid metal solutions in hydrocarbon atmospheres, are being investigated.

Figure 15

REACTION OF VARIOUS HYDROCARBONS WITH URANIUM-CADMIUM SOLUTIONS

Uranium in Solution		Temp (C)	Gas	Gas Flow Rate (moles/hr)	Stirrer Speed (rpm)
(w/o)	(g)				
0.95	7.2	550	methane	0.11	500
1.03	7.8	555	ethane	0.11	500
0.80	6.0	565	propane	0.09	500
1.14	8.6	560	butane	0.07	500
1.32	10.0	555	none	-	500

(2) Production of Uranium Monocarbide for Fuel
Fabrication Tests

(T. R. Johnson, R. D. Pierce, J. F. Lenc, G. D. White,*
 R. L. Christensen, J. R. Pavlik, M. A. Bowden)

The preparation of large quantities (approximately 400-g batches) of uranium monocarbide has continued. The objectives of this program are to develop the required liquid metal techniques and, through the efforts of the ceramics group of the Metallurgy Division, to evaluate the fabricability of the product and its utility as a reactor fuel.

Analytical results have been obtained for 8 batches of uranium monocarbide that were prepared for fabricability tests. The details of the preparations have been reported previously (see ANL-6477, page 54). In general, activated charcoal or graphite was added to a zinc-12 weight percent magnesium-15 weight percent uranium solution at 800 C, and the system was allowed to react, with agitation, for a period of several hours. In most of the preparations, the supernatant liquid metal was removed to separate as much unreacted carbon as possible. The remainder of the material, which contained most of the carbide product, was then vacuum retorted to remove the zinc and magnesium.

The analytical data are presented in Table 7. The product samples for oxygen, total carbon, and nitrogen analyses were sealed in platinum, tin, and aluminum capsules in a helium-filled dry box. "Free carbon" was determined by dissolving a sample in boiling nitric acid, which converts the carbide to gaseous hydrocarbons, but leaves the uncombined carbon as an insoluble residue.

Table 7
 PRODUCT ANALYSES OF URANIUM CARBIDE

Run No.	Charge		Reaction Time (hr)	Method of Phase Separation	Product Analyses								
	U (g)	C/U (atom ratio)			O ₂ (w/o)	N ₂ (w/o)	Insol. Res. (w/o)	Zn + Mg (w/o)	Fe, Cr, Ni (w/o)	Si (w/o)	U (w/o)	Total C/U (atom ratio)	"Free" C/U ^a (atom ratio)
P-2 ^b	535	1.50	5.3	Supernatant solution transferred after settling period	0.90	0.027	0.20	0.5	0.01	0.02	90.6	1.27	0.35
P-3 ^b	528	1.84	14	Supernatant solution transferred after settling period	1.53	-	0.31	0.4	0.06	0.02	91.5	1.16	0.24
P-4 ^b	530	1.50	20	Frozen ingot cropped	0.79	0.021	0.41	0.4	0.01	0.002	90.7	1.18	0.27
P-5 ^b	528	1.50	4	Carbide transferred as slurry	1.17	0.011	0.35	1.3	0.03	0.02	90.5	1.27	0.36
P-6 ^b	525	1.51	8	Metal partly frozen; supernatant solution transferred	0.83	0.028	0.23	0.6	0.06	0.02	90.3	1.20	0.22
P-7 ^c	530	2.00	13	Supernatant solution poured off	-	0.038	4.6	0.7	0.05	0.002	86.3	2.26	0.26
P-8 ^c	390	2.03	12	Metal partly frozen; supernatant solution transferred	0.39	0.065	3.5	1.0	0.16	0.001	87.1	2.00	0.41
P-9A ^{c,d} P-9B ^{c,e}	527	1.88	14	Carbide partially transferred as slurry	0.49 0.81	- -	7.5 5.8	- -	0.03 0.01	0.001 0.002	- 84.3	1.68 2.56	0.79 1.55

^a Uncombined carbon

^b Carbon source - activated charcoal, -200 mesh

^c Carbon source - pure graphite, -200 mesh

^d Transferred fraction

^e Residual fraction

*Metallurgy Division

This residue was then burned to determine the insoluble material exclusive of carbon. Emission spectra indicated only uranium in the residue that remained after burning. Uranium was determined by a volumetric technique having a standard deviation of 0.5 percent. The zinc and magnesium contents were determined by wet chemical methods. Spectrochemical methods were used for the remaining analyses. X-ray diffraction patterns obtained on material from Runs P-2, P-3, P-4, and P-6 showed only uranium monocarbide.

The carbon/uranium ratios for Runs P-2 and P-3, which were reported previously (see ANL-6477, page 55), were based on estimates and are somewhat lower than the analytical results shown in Table 7. The oxygen content of the products is high and is greater for carbide made from activated charcoal than for carbide made from graphite. It is likely that this problem can be eliminated by degassing the carbon more thoroughly and through improvements now being made in the handling procedures.

Surface area determinations* of the activated charcoal and graphite used as the starting materials gave values of 1100 and 4.6 sq m/g, respectively. The corresponding carbide products had surface areas of 6.3 and 0.9 sq m/g.

The ceramics group of the Metallurgy Division found that the carbide prepared in these runs sintered relatively easily and made excellent fired pellets (approximately $\frac{5}{16}$ in. high and $\frac{5}{16}$ in. in diameter). The particle size of the material was reduced by ball-milling to an average of $5\ \mu$, with a maximum of $15\ \mu$. The specimens were pressed at 15 tsi in a $\frac{3}{8}$ -in. die, using a binder, then vacuum-sintered at 1750 C. When a naphthalene-trichloroethylene binder was used, densities of the sintered material were ordinarily in the range from 80 to 85 percent of theoretical. If a 2:1 mixture of acryloid and stearic acid in carbon tetrachloride was used as a binder and if the pellets were held at 1300 C for one hour to drive off volatile materials prior to sintering at 1750 C, product densities over 90 percent were achieved. From the experience of the Metallurgy Division, it appears that the rate and degree of densification can be increased by decreasing the carbon/uranium ratio and the oxygen impurity content of the product.

So that more suitable handling procedures during preparation of the carbide can be available, a vacuum retort, designed to operate in conjunction with a vacuum glove box, is being developed.

*Performed by G. W. Redding.

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

Materials 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. Methods of fabricating process equipment from materials which have proven to be corrosion resistant to process solutions are being investigated and compared.

(1) Corrosion by Molten Metal and Flux Systems
(M. Kyle, M. Deerwester)

(a) Corrosion of Tungsten by Halide Flux Systems

Previous data (see ANL-6379, page 89 and ANL-6243, page 14) have shown that tungsten is not attacked by zinc-magnesium solutions and fluxes containing magnesium chloride, lithium chloride, calcium chloride, and magnesium fluoride at temperatures near 800 C. Tungsten has now been exposed for 100 hr at 800 C to fluxes containing from 2 to nearly 20 mole percent zinc chloride (no metal phase present) in order to determine the effect of zinc chloride. These tests were also designed to test the corrosion resistance of tungsten fabricated by various means, including sintered and rolled sheet, swaged rod, and heliarc-welded tungsten sheet.

No corrosion attack of tungsten has been detected by metallographic examination for the corrosion media and test conditions used to date. This was confirmed by the fact that sample dimensions were unchanged within the accuracy of measurement (0.3 mils). Figure 16 shows a tungsten specimen after exposure to flux of composition (in mole ratios) 47.5 magnesium chloride, 47.5 lithium chloride, 5 magnesium fluoride, and 20 zinc chloride for 100 hours at 800 C. No attack of the tungsten can be discerned. However, the possibility exists that corrosion may have been overlooked because of the laminar grain structure of the wrought tungsten specimens.

In addition to metallographic examination, some of the physical properties of specimens are being studied before and after exposure to corrosive conditions to obtain a measure of the extent of corrosion. In particular, the specimens are subjected to a transverse bend test (see bend test apparatus in Figure 17). In this test the sample is supported between 2 rollers. A constantly increasing force is exerted on the center of the sample until rupture occurs. At this time the force exerted

on the sample and the deflection of the center of the sample from its initial position are recorded. The modulus of rupture is obtained by calculating the flexure stress exerted on the sample at the time of failure. This method has been used to evaluate (see Table 8) the corrosion of tungsten after exposure for 100 hr at 800 C to halide fluxes of composition (in mole ratios): 47.5 magnesium chloride, 47.5 lithium chloride, 5 magnesium fluoride, and 2 or 20 zinc chloride.

Figure 16

PHOTOMICROGRAPH OF SINTERED-AND-ROLLED TUNGSTEN SHEET
AFTER 100-HR EXPOSURE TO A HALIDE FLUX SYSTEM AT 800 C

Flux Composition (mole ratios): 47.5 magnesium chloride, 47.5 lithium chloride,
5 magnesium fluoride, and 20 zinc chloride

Etchant: 10 percent KOH
10 percent $K_3Fe(CN)_6$ aqueous solution

250X

Figure 17

SCHEMATIC OF BEND TEST APPA-
RATUS USED FOR TUNGSTEN
PHYSICAL PROPERTY
MEASUREMENTS

Table 8

SUMMARY OF BEND TEST DATA FOR TUNGSTEN SPECIMENS

Static test conducted in alumina crucible in argon atmosphere

Samples were 90 ± 3 mils by 90 ± 3 mils by 1.5 in. in size (except as noted otherwise) and were prepared by electrical discharge cutting of the parent material.

The bend test specimens were supported on rollers set on 1.25-in. centers. The ram exerted a force on the center of the sample (no-load speed 0.33 in./min) until rupture occurred. Deflection and applied force were recorded at rupture.

Breaking stress was calculated by the following relationship:

$$S = \frac{3}{2} \frac{Fl}{ab^2}$$

where

S = Flexure stress, psi

F = Applied force, lb

l = Distance between supporting rolls, in.

a = Sample width, in.

b = Sample thickness, in.

Material	Treatment			No. of Samples Tested	Mean Deflection (mils)	Mean Breaking Stress (psi)	Std Deviation (psi)
	Temp (C)	Time (hr)	Flux Composition (mole ratios)				
Sintered Rolled Sheet			As Received	7	8	155,000	16,000
Sintered Rolled Sheet	800	100	None	4	7	133,000	36,000
Sintered Rolled Sheet	800	100	47.5 MgCl ₂ 47.5 LiCl 5 MgF ₂ 2 ZnCl ₂	4	7	129,000	14,000
Sintered Rolled Sheet	800	100	47.5 MgCl ₂ 47.5 LiCl 5 MgF ₂ 20 ZnCl ₂	4	6	145,000	11,000
Swaged Rod			As Received	3	5	81,000	11,000
Swaged Rod	800	100	None	4	5	80,000	8,000
Swaged Rod	800	100	47.5 MgCl ₂ 47.5 LiCl 5 MgF ₂ 20 ZnCl ₂	4	5	92,000	17,000
Sintered Rolled Sheet (control for welded sheet) ^a			As Received	4	8	155,000	28,000
Welded Sheet ^a			As Received	2	3	66,000	17,000
Welded Sheet ^a	800	100	None	2	3	48,000	17,000
Welded Sheet ^a	800	100	47.5 MgCl ₂ 47.5 LiCl 5 MgF ₂ 2 ZnCl ₂	2	3	48,000	6,000

^aSamples were 90 ± 2 mils wide by 98 ± 1 mils thick by 1.5 in. long.

Three forms of tungsten have been tested: sintered and rolled sheet, $\frac{3}{4}$ -in. swaged rod, and 90- to 100-mil-thick heliarc-welded, sintered- and-rolled sheet. The data present in Table 8 show sintered-and-rolled sheet tungsten to have an initial modulus of rupture of $155,000 \pm 16,000$ psi. The values obtained for the modulus of rupture on samples which had been heat treated and exposed to the halide fluxes were insignificantly lower than those obtained for "as received" material. Corrosive attack to a depth of 5 mils would have decreased the modulus of rupture by 30 percent (calculated by the equation in Table 8) as compared with the observed decrease of 3 percent. In view of the large standard deviation of the measurements, the 3 percent decrease is not considered significant.

As expected, the 90-mil-thick sintered-and-rolled sheet had a higher modulus of rupture than the $\frac{3}{4}$ -in.-diameter sintered-and-swaged rod because of the greater amount of cold working done on the rolled sheet. The strengthening obtained by cold working was not lost during the heat treatment at 800 C for 100 hr.

Heliarc-welded tungsten was also examined by the above tests. Results obtained showed that the welded material was approximately one-third as strong as the parent sintered-and-rolled material. Metallographic examination of the welds showed excessive grain growth and porosity in the vicinity of the weld. All samples failed in the heat-affected zone. Figure 18 shows a heliarc tungsten weld after heat treatment at 800 C for 100 hr in an argon atmosphere.

Figure 18

MACROGRAPH OF TUNGSTEN WELD AFTER BEING
BROKEN IN BEND TEST SHOWING POROSITY AND
GRAIN GROWTH IN VICINITY OF WELD

Thus, based on both metallographic examination and measurements of physical properties, it appears from these tests that tungsten has very high corrosion resistance to the zinc-magnesium and flux systems encountered in the skull-reclamation process, including flux systems containing zinc chloride. Cold working improves the strength and deformation limit of tungsten. Tungsten welds are presently unsatisfactory because of excessive weakening of the material in the vicinity of the weld.

(b) Corrosion of Molybdenum-30 Percent Tungsten Alloy in Zinc and Zinc-Magnesium Systems

Re-examination of samples of a molybdenum-30 percent tungsten alloy exposed to zinc, zinc-5 percent magnesium, and zinc-50 percent magnesium alloy for 300 hr at 850 C has led to some clarification of the corrosive attack of zinc on this alloy (see ANL-6477, page 63). No significant corrosion attack was noted for essentially the entire surface after exposure to zinc for 300 hr at 850 C, as shown in the photomicrograph of Figure 19 of a typical area along the surface. An atypical 3-mil-deep pit caused by extraction of a grain was noted in an area not shown on the photomicrograph. **Because adjacent grains appear intact, there is a strong possibility that this was a defect in the original material.** No attack was detected on samples exposed to zinc-magnesium solutions.

Figure 19

MOLYBDENUM-30 PERCENT TUNGSTEN ALLOY EXPOSED TO
ZINC AT 850 C FOR 300 HOURS

The possibility of molybdenum leaching from the alloy is still being investigated. Since this alloy appears to have good corrosion properties and is readily machinable, more extensive corrosion testing of this alloy is planned.

(c) Corrosion of Tantalum and Tantalum-10 Percent Tungsten by Halide Flux Systems

A run has been conducted at 800 C for 100 hr to test the corrosion resistance of tantalum and tantalum-10 percent tungsten alloy to the flux of composition (in mole ratios): 47.5 lithium chloride, 47.5 magnesium chloride, 5 magnesium fluoride, and 2 zinc chloride. The data, which are reported in Table 9, showed that both tantalum and the tantalum-tungsten alloy are considerably weaker and less ductile after exposure to the flux containing zinc chloride.

Table 9

SUMMARY OF TRANSVERSE BEND TEST DATA FOR TANTALUM AND TANTALUM-10 PERCENT TUNGSTEN ALLOY

(Static test in alumina crucible under argon atmosphere unless otherwise noted)

(Sample size: 0.030 x 0.75 x 1.5 in.)

Material	Treatment			No. of Samples Tested	Mean Deflection ^a (mils)	Applied Force ^b (lb)	Remarks
	Time (hr)	Temp (C)	Flux				
Ta	100	800	None	3	>200	73	Samples were ductile
Ta	100	800	A ^c	3	54	50	Samples ruptured
Ta ^d	100	850	B ^c	1	>200	78	Sample was ductile
Ta-10% W	100	800	None	3	83	86	Samples cracked
Ta-10% W	100	800	A ^c	3	26	37	Samples ruptured

^a Mean deflection given is in mils deflection of the center of the sample from horizontal taken at the time of sample rupture. The distance between the rollers was 1.25 in.

^b Applied force is the maximum force required to cause rupture, cracks, or deformation of the sample beyond its elastic limit.

^c Flux composition in mole ratios: A. 47.5 LiCl: 47.5 MgCl₂: 5 MgF₂: 2 ZnCl₂
B. 47.5 LiCl: 47.5 MgCl₂: 5 MgF₂

^d Test reported previously (see ANL-6379, page 89) in which a coupon was contained in a tantalum capsule which was rotated 180° at 2 cycles per minute.

Tantalum specimens were still ductile after exposure to the flux which did not contain zinc chloride (see ANL-6379, page 89). Therefore, attack by zinc chloride is suspected to be the cause of embrittlement. This conclusion is supported by observation of tantalum accessories used in the tungsten work reported on page 73. A tantalum secondary crucible developed holes and cracks after 100 hr during exposure to zinc chloride vapors. The data of Table 9 also show that weakening and embrittlement resulting from exposure to the flux was more serious for the tantalum-tungsten alloy than for tantalum.

(2) Tungsten Crucible Testing
(G. A. Bennett, L. F. Dorsey, W. A. Pehl)

Runs have been performed under processing conditions in agitated tungsten crucibles in order to determine corrosion effects on a larger scale and to obtain other information not obtainable by capsule corrosion tests. These tests were carried out in crucibles which were approximately 5 in. in diameter by 8 to 12 in. high, and which were made by various means of fabrication. Noble metal-leaching experiments and skull oxide-reduction experiments were conducted at 800 to 850 C in runs lasting from 24 to 72 hr. Samples of the metal phase were taken at intervals throughout the run.

The crucibles were tested to obtain the following information:

- 1) confirmation of the corrosion data obtained by capsule tests for the crucible materials;
- 2) verification of the inertness of the container material (including impurities) to dissolved uranium;
- 3) measurement of the extent of permeability of the crucible to zinc vapor under processing conditions;
- 4) evaluation of the ability of the crucible to withstand repeated freezing and remelting of the crucible contents;
- 5) an indication of the crucible strength and integrity by its ability to withstand normal handling procedures.

Tungsten crucibles have been tested that were made by (1) plasma-arc spraying tungsten powder on a mandrel, followed by sintering, and (2) isostatic pressing of tungsten powder, followed by sintering. Two plasma-arc-sprayed-and-sintered crucibles performed well, except that, after repeated usage, cracks developed which were attributed to handling (see ANL-6413, pages 65 to 67).

During the past quarter, a large number of tests were conducted with two pressed-and-sintered crucibles measuring $5\frac{1}{4}$ in. in diameter by 12 in. high by $\frac{1}{2}$ -in.-thick wall. Both crucibles performed well with respect to each of the requirements listed above. In no case was there any evidence of corrosion or other adverse effect on the tungsten crucibles.

In addition to many test runs, the pressed-and-sintered tungsten crucibles underwent a number of remelts for the purpose of removing the charge from the crucible by pouring in a tilt-pouring furnace. With these remelts included, one of the crucibles sustained about 25 freezing and remelting cycles and about 300 hr of operation above 800 C. As evidence of the inertness of the crucible to these conditions, the tool marks from the initial machining of the inside of the crucible appeared to be unchanged after this treatment.

During these runs, the dissolved uranium appeared to be inert to the tungsten crucibles and the crucibles appeared to be impermeable to zinc vapor, as discussed in ANL-6477, page 57.

In summary, pressed-and-sintered tungsten crucibles are considered to be adequate for the skull-reclamation process with regard to the requirements listed above. However, because of uncertainties in the severity of handling to be expected in the remotely operated processing cell, other methods of fabrication, such as forging, are being investigated in the hope of obtaining a full-scale crucible which has greater impact strength than a pressed-and-sintered crucible. The problems involved in the fabrication of process equipment are discussed further in the next section. Capsule corrosion tests will be conducted over longer periods of time in order to determine the usable lifetime of the crucible. Tests in crucibles with agitation will be conducted in the future only to determine the degree to which uranium reacts with impurities in the charge materials to form insoluble compounds.

The tests described above provided an opportunity to test agitators. One of the agitators tested was machined from molybdenum-30 weight percent tungsten alloy swaged rod. Total operating time for this easily machinable alloy has reached approximately 169 hr at temperatures varying between 700 and 850 C. Erosion of the agitator shaft due to rubbing on the harder tungsten heat shields had occurred, but there was no visible or photomicrographic evidence of corrosion of the lower end of the agitator, which had been immersed in the molten flux and metal.

(3) Fabrication of Process Equipment (P. A. Nelson, G. A. Bennett)

Corrosion tests, solution stability runs, and process runs have demonstrated that tungsten, molybdenum-10 percent tungsten,

and beryllia have adequate corrosion resistance for skull-reclamation process equipment. Suitable means for fabricating process equipment from these materials are, therefore, being evaluated.

(a) Noble Metal Leach and Oxide Reduction Crucible

Designed for a capacity of 5 kg of skull oxide, these crucibles will have an inside diameter of 13 to 14 in. and an inside height of 26 to 28 in. The best choice of material for the crucible to be used in the noble metal leach and reduction steps appears to be tungsten, although a final decision has not been reached. Beryllia, the second choice at present, is not as strong as tungsten nor as easily fabricated into full-scale monolithic crucibles. Construction of beryllia reduction crucibles from beryllia tiles is being considered. This type of construction has the advantage of permitting the construction of very large crucibles.

Many methods of fabricating tungsten crucibles have been considered. Isostatic pressing and sintering is thought to be the most appropriate because the sizes obtainable are not seriously limited. The crucible made by this method should have adequate strength, and the cost is expected to be less than for crucibles made by any other method. By isostatic pressing and sintering, it is possible to fabricate crucibles with vertical mixing baffles which are formed as integral parts of the crucible during the pressing operation. A moderately large (approximately 11-in. OD x 20 in. high) crucible of this type has been ordered for the integrated process-demonstration equipment. It is hoped that any unforeseen difficulties entailed in fabricating the full-scale crucible will be discovered during fabrication of this smaller crucible.

The only other methods of fabricating tungsten crucibles which are still being considered are forging from a pressed-and-sintered billet and plasma arc-spraying powdered tungsten on a mandrel followed by sintering.

(b) Fabrication of Agitators and Transfer Tubes

The promising corrosion data obtained for the molybdenum-30 percent tungsten alloy (reported on page 68) have focused attention on this alloy for fabrication of agitators and transfer tubes. The alloy not only shows good corrosion resistance to zinc and flux media, but the usefulness of the alloy is enhanced by its good machining characteristics and acceptable low-temperature ductility.

Arc-cast and swaged bar is available for agitator shafts, and agitator propellers can be cut from swaged rod or forged billets. This alloy can be threaded, which simplifies the problems of joining the propeller to the shaft and joining the top of the shaft to a steel shaft extending through the process equipment shell.

Until the present time, tantalum has appeared to be the best choice of material for transfer tubes because of the ease of fabrication and the fair corrosion resistance of tantalum to zinc. However, the poor resistance of tantalum to attack by fluxes containing zinc chloride and to attack by nitrogen (which will probably be present in the cell atmosphere) indicates that tantalum would not be a suitable material for transfer tubes. Molybdenum-30 percent tungsten is now being considered for this application. Tubing can be fabricated from this alloy in lengths up to 5 ft long by gun drilling of swaged rod. Elbows would be required at the corners. By this method, a 12-ft-long transfer line with $\frac{1}{4}$ -in. inside diameter, $\frac{3}{16}$ -in. wall, and including 2 elbows, can be fabricated for about \$1500 (not including the heating elements and insulation required for heated tubes). Five-foot lengths of tubing of this type have been ordered for testing.

(4) Argon Purification for Inert Gas Welding Facility
(M. Kyle, M. Deerwester)

Some experience has been accumulated with the inert-gas-purification system of the inert gas welding facility described in ANL-6413, page 69. This purification system is similar to that designed for the inert-atmosphere glove box (see page 33). The welding facility was constructed to provide a dry argon atmosphere in which to load, weld, and unload corrosion capsules with reactive metals and hygroscopic salts.

A schematic diagram of the argon purification system is shown in Figure 20. The gas leaving the glove box passes through a

Figure 20

SCHEMATIC DIAGRAM OF ARGON-PURIFICATION SYSTEM FOR DRY BOX WELDING FACILITY

catalyst bed (1) in which hydrogen is converted to water vapor by reaction with oxygen (an impurity present in ample concentration for this reaction). The water vapor is removed in a bed of Molecular Sieves* (2), which is followed by a filter (3) to remove any dust from the Molecular Sieves. The Molecular Sieves bed is placed on the suction side of the pump to prevent the temperature rise of the gas during pumping from impairing the efficiency of water vapor removal by the Molecular Sieves. The vane (carbon-impregnated Teflon) pump (4) develops a pressure of 7 psi at a pumping rate of 1.2 cfm (3 glove box volumes per hour). The discharge from the pump is filtered (5) to remove eroded vane material. Oxygen and nitrogen are

*Product of the Linde Company.

removed by reaction with titanium sponge ($-\frac{1}{2}$ in. to +20 mesh) heated to 900 C in 304 stainless steel vessels (6 and 7). The argon leaving the titanium beds is cooled to room temperature in a water-cooled heat exchanger (8), and is then filtered at the inlet to the dry box by a filter (9) capable of removing particles one micron and larger which may have become entrained in the gas during its passage through the titanium beds.

Preliminary analyses of the gas showed that after sustained operation (4 hr at temperature) the oxygen content of the box decreased from an initial oxygen value (obtained by purging) of greater than 100 ppm to a value near 7 ppm. The water content of the box dropped from greater than 200 ppm to a value of about 20 ppm. No quantitative nitrogen data have been obtained, but examination of titanium sponge removed from the gettering vessels has revealed a large amount of brown coloration throughout the sponge particles. This is indicative of reaction with nitrogen.

The pump used in this facility failed after 200 hr of operation because of seizing of the pump bearings. A spare pump was installed and failed after 20 hr of operation because of poor pump alignment. When these pumps were opened, a black deposit was found in both the pump inlet and the pump bearings. Spectrochemical analysis of the inlet residue showed high concentrations of aluminum, calcium, iron, molybdenum, and silicon, thereby indicating that the residue probably contained dust from the Molecular Sieve bed. On the basis of this evidence, a filter was installed at the pump inlet to prevent Molecular Sieve dust from abrading the vane material.

A corona effect from the welding cable to the bottom of the box has been noted. This corona is noted during the time the welder is supplying high-frequency ac current to initiate the welding arc. Once the welding arc has started, the corona disappears as the high-frequency cut-out activates. This corona appears because the voltage gradient at the gas-insulation interface is too great for a gas with a low dielectric strength such as argon.

i. Supporting Engineering Studies in Liquid Metal Systems
(L. Burris)

(1) Power Requirements for Mixing of Liquid Metals
(R. D. Pierce and D. Armstrong*)

A number of runs have been completed in a dynamometer for measuring mixing power in liquid metal systems. The apparatus has been designed to permit stirring of liquids under an inert atmosphere

*Co-op Student from Northwestern University.

and at temperatures up to 800 C. The dynamometer allows 2 means of measuring the mixing torque: that of the transmitted torque by measuring the twist of a torque wire coupling shaft, and that of the reactive torque by measuring the applied torque on a low-friction torque table. A third method, that of measuring the reactant torque on a suspended motor, is expected to supersede the others.

In the first runs, the power required to stir mercury at room temperature was measured on the torque table. Data were taken with both baffled and unbaffled $4\frac{7}{8}$ -in.-ID crucibles.

Some of the preliminary results obtained in baffled crucibles are compared in Figure 21 with earlier data obtained calorimetrically. The new apparatus permits more rapid determination of data and increases the power and temperature ranges which can be studied.

Figure 21

POWER RELATIONSHIPS IN MIXING OF MERCURY

(15.8 kg of mercury in 4-7/8-in.-ID, flat-bottom, cylindrical tank containing four 1/2-in. baffles)

Both lines have a slope of 3, which is in agreement with the theory² that power should be proportional to the cube of the agitator speed. The break at the upper part of the line made with the 3 x 1-in. paddle mixer is a result of the mixing of air into the mercury at high power inputs. When additional data have been obtained, correlations involving dimensionless groups will be attempted.

(2) Metal-distillation Studies

(J. Lenc and R. Paul)

Operation of the large-scale cadmium-distillation unit was resumed during the past quarter. As reported in ANL-6477, page 74, the original induction coil fabricated from $\frac{3}{8}$ -in. solid copper rod

burned out. This coil was replaced with a new coil formed from $\frac{1}{2}$ -in. wide by $\frac{3}{4}$ -in. high solid copper bar. The function of the induction coil is to heat the distillation crucible. A total of 640 kg of cadmium has been distilled in 3 runs conducted to date with the new coil. No major problems were encountered in operating the unit during these 3 runs.

²Miller, F. D., and Rushton, J. H., Ind. Eng. Chem., 36, 499 (1944).

Pertinent data for these recent tests are listed in Table 10 along with comparable information for 2 tests made previously with the original coil. Comparison of these data indicates the new coil is less efficient than the original coil. This lower efficiency is attributed to the increased gap between the coil and the susceptor and a sizable reduction in the amount of heat radiating from the coil to the stainless steel distillation crucible, due to the presence of an insulating liner that was inserted between the new coil and the crucible. The purpose of this liner, $\frac{1}{2}$ -in.-thick molded "Fiberfrax," was to prevent the new coil from being short-circuited to the crucible. To increase the efficiency of the new coil, the liner will be absent in future runs.

Table 10

DISTILLATION OF CADMIUM IN LARGE-SCALE
CADMIUM DISTILLATION UNIT

Run No.	Distillation Temp (C)	Condenser Pressure (mm)	Induction Power Level (kw)	Distillation Rate (kg/hr)	Weight of Cd Distillate (kg)	Power Calculation from Distillation Rate (kw)	Power Efficiency (%)
18	587	60	20	31.4	274.3	8.3	41.5
19	555	30	22	38.6	264	10.1	46.2
20	555	30	20	36.5	101.6	9.6	48.0
14 ^a	550	30	24	66.8	323	17.6	73.2
8 ^a	562	42	21.2	52.2	107	13.7	64.8

^aRuns conducted with original induction coil (formed from $\frac{3}{8}$ -in. solid copper rod).

At one point in Run No. 20, the distillation chamber was inadvertently filled with liquid cadmium to a height approximately 8 in. above the tapered metal-to-metal seal located at the top of the crucible. In spite of the crucible being overfilled, distillation of the liquid cadmium was successfully completed. Inspection of the internal components of the distillation vessel after cooling revealed that leakage of liquid cadmium past the tapered seal was negligible. The reliability of this seal design may be of significant value in large-scale equipment for processing liquid metals.

A series of runs is planned to determine the extent of entrainment of several elements in cadmium vapor at various distillation rates.

B. FUEL PROCESSING FACILITIES FOR EBR-II

A direct-cycle fuel-reprocessing plant using pyrometallurgical procedures was designed and is being 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.

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

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

Because of the very low rate of construction during the past several months, all work uncompleted by January 12, 1962, was deleted from the construction contract of Diversified Builders, Incorporated. This contractor is still required to turn over to the Atomic Energy Commission all remaining data, drawings, manuals, and operating instructions which had not previously been furnished. In addition, the contractor is required to assign to Argonne National Laboratory all on-site material which is required for installation or construction. The remaining work in this contract is to be done by the J. F. Pritchard Company under a cost-plus-fixed-fee contract. The contract with the J. F. Pritchard Company was originally established for equipment installation. The work is being done under the direct supervision of Argonne National Laboratory personnel.

Work by Diversified Builders, Incorporated just prior to January 12, 1962, included instrument installation, adjustment, and cleaning of electrical and mechanical equipment, and painting. Reworking of the service sleeve flanges was a major effort and consisted of refinishing the flanges to remove corrosion pits. This was followed by welding of backup flanges to the flanges made undersized by the refinishing operations.

As of January 12, 1962, the reported completion figure for the Fuel Cycle Facility was 98 percent; however, some major items included in this figure were found to be unsatisfactory. These are being repaired or corrected. Corrective work and completion work in progress during this quarter included the cleaning of the Argon Cell liner, refacing of the bottom flange of the 6-ft-diameter transfer lock, disassembly and cleaning of in-cell cranes and manipulators, painting of the sub-cells, and repair of window liner sealing surfaces. The corrective work involves a large effort and will considerably delay the bringing of the Facility into operating condition.

Installation of process equipment began on January 15, 1962, and includes construction and installation of electro-pneumatic control cabinets in the sub-cell area, installation of window shutter drive brackets in the Argon Cell, and installation of a jib crane on the Argon Cell roof.

b. Fuel Cycle Facility Equipment

(G. Bernstein, A. Chilenskas, L. Coleman, J. Graae, T. Eckels, M. Slawewski, H. Stethers)

Fabrication of the service sleeve feed throughs is progressing satisfactorily. An inspection trip was made to the vendor on December 21, 1961, to observe the leak-testing and tensioning methods used on the feed throughs. When installed in the Fuel Cycle Facility, the top flange of the feed through seals against a gasket on the service sleeve. The force required to effect the seal is applied by placing the entire feed through in tension through an arrangement of springs and bolts at the bottom end of the service sleeve. Two of the 2-in. vacuum feed throughs were placed under 40,000-lb tension by means of a hydraulic unit, and leak tested while in tension. Since the inspection all units have been leak tested. Completion of delivery is scheduled for the end of March.

The installation packet for the emergency diesel generator has been completed and issued to the Idaho Field Engineer for transmittal to the installation contractor. This generator will supply power to the important items in the Fuel Cycle Facility if both normal power and the power from the existing emergency system fail.

The monitoring system for the suspect stack has been ordered. The installation of the system has been divided into 2 parts; one part consists of the flange installation on the stack for the isokinetic sampling nozzles; the second part consists of the required piping, electrical, and electronic equipment installation. The first part of the job has been issued to the field engineer; the second portion of the job will be detailed as soon as required information on the electronic equipment is received from the vendor. Specifications for a small building to house the above system have been written and issued for bids.

The specifications for the off-gas monitor have been prepared and issued for bids. The system is to monitor continuously the activity of the gas discharged from the off-gas holdup tank. Gases released in the melt refining and skull-oxidation steps will be stored in this holdup tank until favorable meteorological conditions permit discharge through the site stack. The off-gas monitor will measure the activity and this, with knowledge of existing meteorological conditions, will be the basis for the determination of permissible discharge rate. The principal activity in the gas from the hold-up tank is xenon-133, and the concentration will vary from 10 to 10,000 c.

Installation instructions for the de-gas furnace system have been issued to the installation contractor.

Tests are being performed to determine the feasibility of monitoring the performance of the operating manipulators which will be used in the Argon and Air Cells by listening to the sounds generated by the manipulators. There are 2 main purposes for performing these tests. First, changes in sound levels from the various drive units in the manipulator carriages could indicate that maintenance is required. These changes in sound level could be caused by bearing or brush wear. Second, the sound levels could give an operator, using the manipulator, a better orientation of the various drives in operation. This is particularly advantageous in operating the grip drives, since a definite change in sound level occurs when the grip pressure is changing. To date, various methods have been tested and all have met with some success, but none are successful to the degree required for in-cell service. The first monitors tested were intercom systems with wires between stations. This system is probably best, but it is limited inasmuch as conductors are not available on the manipulators for this purpose. There is also a large amount of noise inherent in this system resulting from electrical interference generated by the copper brush take-off for the carriage.

The second system tested was a wireless-type intercom which transmits back over the conductors providing power to the unit. This system was unacceptable because of the noise level.

A third system, which is being tested, utilizes a frequency-modulated transmitter mounted in the carriage. This transmits a signal to a remotely located frequency-modulated receiver. The power for the transmitter is taken from the dc field supply for the drive units. This system has reduced the electrical noise somewhat, but it is extremely sensitive to such things as antenna location and orientation and to the effects of surrounding steel structures. The transmitter is transistorized and may require shielding for protection from radiation damage. The main effort at present is to make the system operate satisfactorily on the manipulator in the mock-up area. Actual system operation, however, cannot be demonstrated until the system is tried on the manipulators in the Argon Cell.

c. Manipulators and Cranes
(J. Graae, R. Vree, W. Voss)

The 5-ton pillar jib crane is being installed on the roof of the Fuel Cycle Facility so that it can service the roof hatches for both the Air and Argon Cells. The crane has an 18-ft boom and headroom of 13 ft under the boom. A special structural steel base will be fastened to the concrete roof and the jib crane will be mounted on this base.

Abrasive dust which was generated in grinding operations performed by the construction contractor is being removed from the cranes. Bearings are being cleaned and relubricated with radiation-resistant grease. Many bearings show signs of damage and are being replaced.

The manufacturer of the electromechanical manipulators has provided the drive units on one carriage with new drive unit locating pins designed at Argonne National Laboratory. There is now no tendency for the pins to bind in the locating bushings, even if the drive units are lifted or lowered in a slanting position. The new pins cannot be subjected to a bending moment under normal handling procedures. The manipulator manufacturer is providing the same type of locating pins for the other drive units.

The Model 150 articulated arm has been modified and retested (see ANL-6477, page 79). The motor that rotates the arm burned out in previous tests. This motor operates off the same power supply as the arm rotation motor of the operating manipulator. To satisfy the requirements of the latter motor, the supply voltage is about 110 v, dc. This voltage is excessive for use with the motor on the Model 150 arm. Tests were made with resistors in series with the armature of the Model 150 arm, but this method of reducing the armature voltage proved impractical because no single series resistor was adequate for both the starting and running periods. The method which proved successful consisted of installing a 100-ohm resistor in parallel with the power supply and connecting the armature of the Model 150 arm motor to one side and to the center of the resistor. A switch was installed in the electrical connector for the Model 150 arm so that installation of this arm on the operating manipulator de-energizes the rotation motor on the operating manipulator. The resistor is so located in the circuit that the voltage reduction only occurs when the Model 150 arm is installed. The voltage to the motor of the Model 150 arm is reduced to a maximum of 47 v. Tests showed that this permitted operation of the motor without difficulties. The rotation speed of the arm was 2 rpm.

A tool rack and changer with capacity of one dual hook, one single hook, and one parallel jaw hand has been modified to allow a better line-up of the manipulator forearm with the adapters on the tools. The inside edges of the spring-loaded collar on the forearm have been deburred and honed smooth. The combined effect is that tools can now be remotely changed without the aid of the second manipulator. These modifications have also made it possible to move the rack to any new position on the cell floor without leveling or bolting the rack in place. The rack will be further modified to provide a place for the removable forearm.

d. Materials Testing

(G. Bernstein, L. Coleman, A. Chilenskas, J. Graae)

The testing of radiation-resistant lubricants for use in bearings was continued during the past quarter. A bearing lubricated with NRRG-159* has been alternately irradiated and run in a test stand (see ANL-6287, page 85). The bearing was given a single heavy coat of grease. No subsequent additions of grease were made and no effort was made to retain the grease in the bearing other than wrapping it in aluminum foil during irradiation. The bearing has accumulated 4.0×10^9 rad and 300 hr of running without visible signs of wear. This performance is equivalent to 4 years of actual operating time in the Fuel Cycle Facility and meets the requirement set for successful performance (see ANL-6333, page 95). In addition, these results correct a testing error which was identified in a previous report of a similar test (see ANL-6379, page 103). In that test, a roller bearing was lightly coated with grease and was then alternately irradiated and run in the test stand. Predicted service life of the bearings is related to both the running time and irradiation dose. The running periods which were selected previously were too short in relationship to the accumulated irradiation. On the basis of the running time selected, the projected life of the bearing appeared to be only one year.

The testing of mixed radiation-resistant greases on roller bearings is also continuing for reasons previously discussed (see ANL-6477, page 80). These tests are designed to indicate the extent to which a grease, which was originally specified for the 5-ton cranes in the Air and Argon Cells, must be diluted with NRRG-159 in order to have a projected useful life approaching 4 years. A mixture of 3 parts of the specified grease and one part NRRG-159 failed after 2.5×10^9 rad and 188 hr of operation. The 1:1 and 1:3 blends of the specified grease and NRRG-159 have received 4×10^9 rad irradiation and 300 hr running time. The 1:1 mixture was very hard and the bearing squealed during the running test. The 1:3 mixture ran well. It may be concluded that replacement of 75 percent or more of the specified grease with NRRG-159 will yield a mixture with a projected life expectancy of better than 4 years. These tests have now been terminated.

Porous impregnated bearings are being investigated for possible use with small experimental equipment and tools. Tests of porous bronze thrust bearings lubricated with either radiation-resistant oil (NRRO-359*) or with the bearing manufacturer's standard lubricant have been completed. Measurements of wear and bearing temperature were made while the bearing was subjected to a 400-lb axial load at 40 rpm. The results were largely nonreproducible and no direct comparison between the 2 lubricating oils is possible at this time. The results indicated that both lubricants when unirradiated performed satisfactorily for at least

*A product of Standard Oil Company of California.

100 hr at the above-stated conditions. The tests with NRRO-359 irradiated to 1×10^9 rad were not reproducible. In one experiment, the bearing suffered destructive wear at the end of 60 hr of testing, while another bearing was still performing satisfactorily at the end of 120 hr. With the NRRO-359 irradiated to 2×10^9 rad, 2 tests showed destructive wear of the bearing after runs of short durations, namely, 2 hr and 20 hr. The temperature measurements taken under test conditions did not appear to be sufficiently reproducible to permit their use as a wear index; however, higher operating temperatures were observed with irradiated NRRO-359 than with un-irradiated NRRO-359. Some of the difficulty which caused the results to be nonreproducible may have stemmed from the inability to maintain precise alignment of the thrust bearing and shaft in the test stand. A large lathe is being modified to permit testing sleeve bearings under radial load. It is anticipated that better alignment of shaft and bearing can be maintained in this equipment. It is possible that work on the sleeve bearing may permit the development of a reliable correlation between bearing temperature and wear rate.

Various elastomers are being tested to determine their suitability for use as possible gasket materials to replace the lead gasket now specified for use on the large transfer lock in the Argon Cell. Irradiation testing of neoprene and gum rubber in the test assembly has been completed. Both materials became permanently set in the test rig following irradiation to 6×10^7 rad, but they were still resilient and judged serviceable. Further irradiation of the neoprene indicated that it would be serviceable for use as gasket material to about 2×10^8 rad, but was judged too hard at 3.2×10^8 rad. The gum rubber was still resilient and considered possibly serviceable at 4×10^8 rad, but exhibited loss of strength (it crumbled and was easily punctured) at 2×10^8 rad. Testing of Adiprene C* is in progress.

e. Shielding Windows and Cell Lighting
(T. W. Eckels)

The installation of the Argon and Air Cell shielding windows was originally started in April 1961 as part of the Package 3 contract, but work was halted in May 1961 because of 3 major difficulties encountered:

1. Some of the tank units were found to be sufficiently oversize in width and height to make insertion into their steel liners impossible.
2. A chemical reaction, apparently between a drying agent in the interior tank coating and the window oil, was producing a substance which was plating out on the various oil-glass interfaces within the tank unit. This resulted in a loss of transmission.

*A product of Minnesota Rubber Company.

3. Some "C" plates, nominally one-inch thick, were found to be as much as 0.090-in. undersize, which was sufficient to make a gastight seal impossible with the gasket and hold-down frame dimensions as designed.

All window components were disassembled and corrective work was performed for Items 1 and 2 in Idaho Falls by the R. V. Harty Company, a subcontractor under the Pittsburgh Plate Glass Company. By late January 1962, all components had been transferred back to the Fuel Cycle Facility, and in early February installation was resumed. Fifteen "C" plates have been installed. For the installation of undersized "C" plates, an additional cushion gasket will be used to compensate for the variation in thickness. Three tank units and outer gas seals were also installed. The outer gas seals were tested for leaks and were found satisfactory. However, 4 uninstalled, oil-filled tank units for the central control room of the Argon Cell were discovered to be leaking oil through the welded steel structure. Subsequent tests of the 3 installed tank units indicated possible oil leaks, and the units are therefore being removed. Other units are awaiting closer inspection to determine their condition. The tank units were delivered to Idaho over a period of time extending from June through November 1960. During the time period from delivery through at least June 1961, not a single unit had developed a leak.

Further installation of the tank units must await satisfactory welding repairs to these 4 units. Since each tank unit weighs more than 6 tons, special equipment was built for accomplishing the installation of the units. The difficulty of access to the central control room (from basement) makes it highly desirable to complete the installation of the room's 8 tank units before proceeding to the installation work in the outer annulus of the Argon Cell and the Air Cell. The window manufacturer has assumed complete responsibility for correcting these difficulties.

Eight 1000-w mercury vapor lamps and luminaires were installed and lighted in a segment of the Argon Cell which contains an installed central control room window tank unit. This was done to evaluate the quality of viewing through the tank unit and "C" plate under actual operating lighting conditions. The viewing quality was judged to be eminently satisfactory. The dimming of lights within the central control room is, as expected, necessary to reduce glare and reflections from the glass on the operator's side.

The zinc coating on the steel lining of the Argon Cell was found to be extremely dirty. In order to increase the lighting efficiency and remove materials which might lead to excessive outgassing, which, in turn, could affect the cell gas purification system, the liner has been thoroughly cleaned.

2. EBR-II Fuel Processing Mockup

a. Melt Refining Furnace (W. E. Miller)

Work on the assembly for the removal and sampling of the ingot from the graphite crucible is nearing completion. A drop hammer is used to break the sample protrusions from the ingot. A rough draft of an operating manual for the apparatus has been completed and submitted to the operating personnel at Idaho. The finished apparatus will be shipped to Idaho during the next quarter.

3. Skull-reclamation Process

a. Skull Oxidation (W. E. Miller, H. Stethers)

After the melt refining step is carried out, a skull remains in the zirconia crucible. Oxidation of the skull, in order to allow its easy removal as a powder, is planned. This operation is being studied in a prototype skull-oxidation furnace (see ANL-6333, page 99; ANL-6477, page 86). In the following, several of the latest experiments are described.

Several runs have been made in the prototype skull-oxidation furnace using an oxygen feed-control system which maintains the oxidation reaction at an essentially constant rate. Skull oxidations made previously (see ANL-6145, page 41) were carried out in an atmosphere of argon and oxygen at nearly constant total pressure. A constant partial pressure of oxygen was maintained in the gas mixture. Both static* and flow systems were studied. Neither of these systems appears to be suitable for use in the Fuel Cycle Facility. Since the skulls will be nitrided to a greater or lesser extent by their contact with the atmosphere of the Argon Cell, the use of a static system does not appear feasible because the rate of oxidation progressively decreases as nitrogen is liberated into the furnace atmosphere. In flow systems utilizing a constant partial pressure of oxygen, the rate of oxidation also decreases with time. At high partial pressure of oxygen, the initial oxidation rate is excessively high and undesirable sintered agglomerates of the oxides are produced. At lower partial pressures of oxygen, the time required for the reaction to go to completion is inordinately long, and the process is thereby made impractical.

*No gas was exhausted from the system. As the reaction progressed, oxygen was added to maintain the total pressure constant.

The use of the control system which feeds oxygen to the furnace in such a manner that a nearly constant rate of oxidation is maintained overcomes the difficulties described above. With this system, the prototype oxidation furnace is first filled with argon. In the initial stages of the oxidation reaction, oxygen is fed to the furnace at a constant rate. After a time, the rate of consumption of oxygen becomes less than the feed rate, thereby causing a rise in pressure. This change in pressure is used as a signal for the discharge of a small amount of gas from the reaction chamber. A repetition of this cycle results in oxygen enrichment of the furnace gas and keeps the reaction rate nearly constant. The furnace is kept at a nearly constant temperature by automatic control of an immersion-type heater.

In 2 skull-oxidation runs carried out with the oxygen feed-control system, the oxygen feed rate used in the first run was equivalent to a conversion rate of one gram of uranium per minute, and the feed rate in the second run was equivalent to 2 grams of uranium per minute. The product from the first run had some pieces of about $\frac{1}{4}$ -in. diameter, which fell apart at a touch. The product from the second run contained larger pieces which were more difficult to break. The products from both runs were better than any previously produced in the prototype furnace, inasmuch as no hard agglomerates were present.

In another run, the same method of oxidation was applied to a skull which had previously been nitrided. In the nitridation portion of the run, a skull containing 420 g of uranium was 50 percent nitrided in 25 hr. This skull was then oxidized with the continuous-oxygen-enrichment method described above. An oxygen rate equivalent to the conversion of 2 g of uranium per minute was used. Oxygen consumption ceased after about 5 hr of operation. The product from this run was acceptable in that there were no hard agglomerates and no apparent unoxidized material.

The off-gas from the oxidation furnace will at some times contain an appreciable concentration of oxygen. For safety reasons, this cannot be tolerated in the furnace off-gas system of the Fuel Cycle Facility. An oxygen conversion unit will, therefore, be required to remove the oxygen from the oxidation-furnace effluent. Design of a conversion unit and an adaptation of the previously described oxygen-control system for use with plant equipment are proceeding.

The possibility exists that some batches of fuel may become inadvertently contaminated with iron and nickel, which are not removed by melt refining. Such batches will be fed directly to the skull-reclamation process for removal of the contaminants. Since relatively large charges will be involved, an oxidation experiment with a 7-kg ingot of uranium was undertaken to test the feasibility of this procedure. After 18 hr of reaction,

the ingot was 48 percent converted to the oxide. The atmosphere used initially was 30 percent oxygen in argon. The burning was very irregular, as indicated by the oxygen consumption rate which decreased to nearly zero at times. It was necessary, therefore, to enrich the mixture in oxygen in order to accomplish the oxidation within a reasonable amount of time. At other times the rate of oxygen consumption was excessive, as evidenced by a temperature rise. The rate was then reduced with an argon quench. The contents of the crucible increased in volume as the ingot metal converted to the oxide. The oxide at the heater surface sintered into a hard mass which pushed against and deformed the heater. Some alterations in the furnace are being considered, so that the furnace may be used to burn large pieces of metal as well as crucible skulls.

The skull-oxide dumper has been tested. The function of the dumper is to pour the oxidized skull from the zirconia melt refining crucible to metal storage containers and to dump the used, emptied zirconia crucibles into waste containers. The tests showed that the design is satisfactory and that the dumper will be adequate after a few minor modifications.

b. Collection of Metal Vapors
(W. E. Miller)

Uranium coated with magnesium-zinc is the product from the uranium precipitation step of the skull-reclamation process. A convenient method for removing the magnesium-zinc alloy from the uranium is to distill off the alloy. Sorption of magnesium-zinc on molded Fiberfrax fume traps is being investigated as one means of collecting the vapors evolved in the distillation.

The first experiments (see ANL-6477, page 84) were done in the melt refining furnace in standard furnace equipment. The standard size fume trap efficiently sorbed vapors from charges as large as 225 g of magnesium-zinc, but the efficiency decreased with a larger charge. Traps have now been obtained which have an outside height of $8\frac{3}{4}$ in. and a wall thickness of $1\frac{3}{4}$ in. The weight of these traps is about 2400 g compared with 1200 g for the standard trap, which was $5\frac{1}{4}$ in. high and had a $\frac{7}{8}$ -in. wall thickness. Two runs have been made with the large traps.

In the first run, the crucible was charged with 500 g of 50 weight percent magnesium-zinc. The metal was distilled at a rate of about 20 g/min at one atmosphere pressure. In this run, the inverted molded Fiberfrax trap was placed on the furnace top ring as in melt refining practice (see ANL-6145, page 32, Figure 2). Eighty-three percent of the charge was trapped. There was evidence of leakage at the junction formed by the furnace top ring and the trap (see Figure 22, unsealed trap).

Figure 22
MAGNESIUM-ZINC VAPOR ABSORBED ON
SEALED AND UNSEALED TRAPS

In the second run, a trap seal was used. The seal was prepared by placing a ring of soft Fiberfrax felt in a groove machined in the rim of the trap. The soft felt conformed to the contour of the furnace top and filled any gap at the junction of the trap and the furnace top. For run conditions identical with those of the first run, 95 percent of the charge was trapped as compared with 83 percent trapped in the first run. The trap seal was effective, as can be seen in Figure 22. A cross section of the sealed trap is shown in Figure 23. From a study of the trap used in the second run, it would appear that the 5 percent of the charge not recovered in the run probably did not leak through the Fiberfrax. It is believed that the vapors escaped from the crucible assembly by permeating through the zirconia crucible and the cylindrical graphite susceptor.

Figure 23
CROSS SECTION OF SEALED TRAP AFTER RUN
WITH MAGNESIUM-ZINC

A steel liner is being constructed to fit between the crucible and the furnace susceptor. The trap seal would be made on this liner and hence eliminate the escape of vapors through the body of the furnace. When the liner is completed, more runs will be made.

An adaptation of the seal described above may be used in conjunction with disposable metal fume condensers. Experiments are being planned to explore this as an alternative means of collecting the magnesium-zinc vapors.

c. Remote Operations Equipment Development
(G. Bernstein, A. Chilenskas, L. Coleman, T. Eckels,
W. Miller, H. Stethers)

The first model of a skull oxide-processing furnace is being fabricated. Designs are being developed for equipment to be used in charging the oxide and removing the reclaimed uranium product.

A heated transfer line (see ANL-6413, page 17) has been used to transport liquid magnesium and cadmium. When an attempt was made to use the tube to transport magnesium vapor, the tube plugged. The tube was modified at the flanges to reduce the heat losses and raise the temperature at these points. When the modified tube was used to transport vapors, the tube plugged at the end closest to the receiver. Adding auxiliary heat at this point did not solve the problem. Investigation of this problem is continuing.

d. Induction Heating and Mixing
(A. A. Chilenskas)

Low-frequency induction heating is being investigated as a means of heating and mixing the metal-salt charges used in the skull-reclamation process (see ANL-6379, page 46). This method has several apparent advantages for equipment design and maintenance, since it replaces a rotating stirrer with a stationary induction coil. Preliminary results obtained with the use of 60-cycle power and a zinc charge (see ANL-6477, page 88) have been sufficiently encouraging to extend the work to metal-salt systems. Apparatus has been assembled to permit further experimentation in a closed, recirculating inert gas atmosphere. Mixing and heating tests are in progress to determine the adequacy of this method for the leaching and reduction steps of the skull-reclamation process.

C. Chemistry of Liquid Metals
(I. Johnson, H. M. Feder)

Investigations of the chemistry of liquid metal systems are being conducted to provide basic concepts and data for the design of methods for

the reprocessing of reactor fuels. In addition, the results of these studies provide ideas and data for the formulation and testing of theories of liquid metal solutions.

1. 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 that 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.

Solubility of Uranium in Liquid Indium (M. G. Chasanov and P. D. Hunt)

The solubility of uranium in liquid indium was determined with a scale-down apparatus (see ANL-6413, page 88). High-purity indium (99.999 percent, Consolidated Mining and Smelting Company) and reactor-grade uranium were used in this study. The uranium concentrations were determined fluorometrically.

The experimental data are given in Table 11 and are shown graphically in Figure 24. These values are about half as large as those of Hayes and Gordon³ (quoted in ANL-6413, page 95).

Table 11

SOLUBILITY OF URANIUM IN LIQUID INDIUM

Temp (C)	Uranium (atom. %)	Temp (C)	Uranium (atom. %)
339 ^a	$7.5_2 \times 10^{-5}$	611	$7.7_2 \times 10^{-3}$
374 ^a	$9.0_7 \times 10^{-5}$	618	$1.0_2 \times 10^{-2}$
455	$4.5_5 \times 10^{-4}$	650	$1.5_5 \times 10^{-2}$
470	$8.2_0 \times 10^{-4}$	663	$2.0_2 \times 10^{-2}$
509	$1.5_0 \times 10^{-3}$	710	$3.1_5 \times 10^{-2}$
557	$4.1_7 \times 10^{-3}$	720	$4.4_9 \times 10^{-2}$
567	$5.1_1 \times 10^{-3}$		

^aNot employed in computation of the solubility equation.

³Hayes, E. E., and Gordon, P., J. Met. and Cer., TID-65, 130-141 (1948).

Figure 24
SOLUBILITY OF URANIUM IN
LIQUID INDIUM

The data of Table 11 were used to compute the following solubility equation:

$$(455 \text{ to } 720 \text{ C}) \text{ uranium: } \log (\text{atom percent}) = 3.78 - 5150 T^{-1}$$

The relative standard deviation for this equation is 12 percent.

Metallographic examination of the furnace-cooled solubility ingot revealed the presence of an intermetallic phase, which was identified as UIn_3 by X-ray diffraction.⁴ This phase is well-known and has been characterized by several investigators.^{5,6}

⁴Schablaske, R., and Tani, B. S., private communication.

⁵Iandelli, A., and Ferro, R., *Ann. Chim. (Rome)* **42**, 598-608 (1952).

⁶Maskrey, J. T., and Frost, B. R. T., *J. Inst. Metals* **81**, 171-181 (1953).

Solubility of Praseodymium in Liquid Zinc
(I. Johnson and K. E. Anderson)

Additional measurements have been made on the solubility of praseodymium in liquid zinc. In earlier work reported in ANL-6477, page 92, it was discovered that the solubilities below 592 C were too low to be determined accurately by wet chemical analysis of the samples. A radiochemical method was used in the present experiment. Praseodymium metal was irradiated in the CP-5 reactor. The praseodymium-141 (100 percent abundance, 11.2-b cross section) yields the 19.2-hr beta-gamma-active praseodymium-142 on neutron irradiation. The daughter of praseodymium-142 is neodymium-142, which is stable and, therefore, does not interfere with the counting.

A charge consisting of 3.84 g of activated praseodymium (99.5 percent) and 402 g of zinc (99.99 percent) was melted in a high-purity alumina crucible. After 15 hr of stirring at 713 C, sampling was started. Tantalum sample tubes fitted with porous tantalum filters were used.

The data obtained in this experiment together with the valid previous results are given in Table 12 and shown graphically in Figure 25. These data may be represented by the empirical equation

$$\log (\text{atom percent praseodymium}) = 6.447 - 6764 T^{-1}$$

over the temperature range from 430 to 725 C.

Table 12

SOLUBILITY OF PRASEODYMIUM IN LIQUID ZINC

Temp (C)	Praseodymium	
	Weight Percent	Atom Percent
725	1.11	0.518
713	0.823	0.383
• 681	0.554	0.258
637	0.208	0.0966
614	0.160	0.0742
592	0.081	0.0376
557	0.0424	0.0197
507	0.0132	0.00612
454	0.00306	0.00142

Figure 25
SOLUBILITY OF PRASEODYMIUM
IN LIQUID ZINC

Solubility of Beryllium in Liquid Zinc
(I. Johnson and K. E. Anderson)

The solubility of metallic beryllium in liquid zinc was measured by the conventional method. A charge consisting of 5.15 g of beryllium metal (99.0 percent, Beryllium Corporation Grade UC-50) and 501 g of zinc (99.99 percent) was stirred at 700 C for 21 hr. Samples were taken with sample tubes fitted with filters. Examination of the beryllium metal after the experiment showed little evidence of attack; however, spectrographic and later chemical analysis of the samples showed significant amounts of beryllium. The solution composition was also found to vary with temperature, suggesting that equilibrium may have been attained.

The solubilities of beryllium found in this experiment are given in Table 13. It is seen that the spectrographic analyses agree in most instances with the more accurate chemical analyses. The solubility data are shown in Figure 26. The data may be represented by the empirical equation

$$\log (\text{atom percent beryllium}) = 3.211 - 3233 T^{-1}$$

Experiments are underway to determine the composition of the equilibrium solid phase.

Table 13

SOLUBILITY OF BERYLLIUM IN LIQUID ZINC

Temp (C)	Solubility of Beryllium (w/o)	
	Chemical	Spectrographic
696	0.080 ₅	0.08
630	0.060 ₂	0.08
611	0.053 ₆	0.08
571	0.037 ₈	0.04
512	0.020 ₆	0.02
486	0.015 ₂	0.01
453	0.018 ₅	0.02
429	0.0064 ₄	0.006

Figure 26
SOLUBILITY OF BERYLLIUM IN
LIQUID ZINC

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

The solubility of uranium was measured in 2 additional zinc-magnesium melts as a function of temperature by the usual procedure. The data for these 2 solubility experiments are shown in Figure 27, with the uranium solubility plotted against the reciprocal of the absolute temperature. The magnesium contents of the samples are shown in parentheses adjacent to the experimental points on the curve. The figure illustrates

particularly well that, in both experiments, the data at higher temperature, which were collected in a temperature region in which uranium was the solid phase in equilibrium with the melts,

Figure 27

THE SOLUBILITY OF URANIUM IN ZINC-MAGNESIUM MELTS

show very low temperature coefficients of solubility. The figure also shows that at lower temperatures the data of the 2 experiments together define a binary eutectic line in the zinc-magnesium-uranium system. The portion of this eutectic line at higher temperature, which is also shown in the figure, was established in previous experiments (see ANL-6477, pages 93 and 94). The data shown in this figure will later be presented in a ternary plot along with other data obtained for this system.

2. Coprecipitation Studies

The degree of separation of a fissionable element from impurities which may be achieved by recrystallization from metallic solvents is often limited, not by a lack of a sufficient difference in

solubility, but rather by the extent of coprecipitation. Thus, even though the solubility of an impurity is not exceeded when the temperature is lowered, a large fraction of the impurity present may crystallize with the fissionable metal.

Coprecipitation of Ruthenium by Uranium from Liquid Magnesium-Zinc Solutions

(I. Johnson and K. E. Anderson)

Coprecipitation of ruthenium by uranium when the latter is precipitated from liquid magnesium-zinc solutions was demonstrated by the results of experiments reported in the last quarterly report (see ANL-6477, pages 95 and 97). These results also indicated that the coprecipitation coefficient of ruthenium when carried by gamma uranium was higher than the coprecipitation coefficient when carried by beta uranium. The present experiments were undertaken to study further the coprecipitation of ruthenium by gamma and beta uranium.

The experiments were done as follows: A homogeneous solution of uranium and radioactive ruthenium in a 12 percent magnesium-zinc solution was prepared at the temperature of the experiment. After the solution was sampled, additional magnesium was added. This caused the precipitation of some of the uranium metal. Further additions of magnesium were made, bringing about precipitation on each addition. The liquid phase was sampled after each addition by means of tantalum tubes fitted with graphite filters. The samples were analyzed for uranium, ruthenium, and zinc. In the first experiment, the temperature was 810 C, and gamma uranium was most likely the precipitating phase. The temperature of the second experiment was 752 C, and beta-uranium was most probably the precipitating phase.

The results of the 2 experiments are given in Table 14. It is seen that the ruthenium concentration decreased as magnesium was added to precipitate uranium.

Table 14

COPRECIPITATION OF RUTHENIUM BY URANIUM

Sample No.	Zinc (w/o)	Magnesium ^a (w/o)	Ruthenium (w/o)	Uranium (w/o)
Experiment I: Temperature, 810 C Precipitate: gamma uranium ^b				
1	79.4	(11.0)	30.6×10^{-3}	9.6
2	64.2	(35.0)	6.60×10^{-3}	1.30
3	55.4	(44.3)	3.70×10^{-3}	0.35 ₄
4	45.4	(54.5)	1.95×10^{-3}	0.062
5	35.4	(64.6)	-	0.0099
Experiment II: Temperature, 752 C Precipitate: beta uranium ^b				
1	81.6	(14.0)	2.65×10^{-2}	4.33
2	65.4	(32.8)	1.72×10^{-2}	1.86
3	54.7	(44.8)	1.06×10^{-2}	0.47 ₈
4	46.6	(53.3)	0.77×10^{-2}	0.12 ₆
5	38.9	(61.1)	0.56×10^{-2}	0.04 ₀

^aMagnesium obtained by difference.

^bThe precipitating form of uranium is assumed from phase-diagram information and was not definitely identified.

Since the solubility of ruthenium in zinc is increased by the addition of magnesium in the absence of a coprecipitating agent, it must be concluded that ruthenium does coprecipitate with uranium. The data in Table 14 also indicate that the extent of coprecipitation is greater with gamma than with beta uranium.

Examination of the uranium solubility data shows a discrepancy. The solubilities at the lower temperature are greater than the solubilities at the higher temperature. Comparison of these data with the results previously reported (see ANL-6477, page 95) for the solubility of uranium in magnesium-zinc solutions suggests that the values found for the 3 lowest magnesium concentrations (14.0, 32.8, and 44.8 weight percent) at 752 C and the initial sample at 810 C are probably correct. All other values are probably low. These low results were probably caused by reaction between the uranium in the sample and the graphite filters.

Since the uranium values given in Table 14 are not trustworthy, values of the correct uranium solubility at each composition were estimated from the previously reported data (see ANL-6477, page 95). This procedure permits the computation of provisional values for the coprecipitation coefficients. Doerner-Hoskins plots for the 2 experiments are shown in Figure 28. The coprecipitation coefficients computed from the slopes of the straight lines are 0.3 at 752 C and 0.8 at 810 C.

Figure 28

COPRECIPITATION OF RUTHENIUM
BY URANIUM FROM MAGNESIUM-
ZINC SOLUTIONS

3. Liquid-Liquid Distribution Studies

Distribution coefficients for a number of elements which occur in nuclear fuels were measured in the lead-zinc system.* These measurements, which were made with only one distributing solute, showed that some separations are possible in this solvent system. A series of experiments have been performed to determine whether or not the presence of 2 or more distributing solutes in a melt will sensibly affect the coefficients obtained for single solutes. Codistribution coefficients between lead and zinc of plutonium in the presence of uranium and of cerium and ruthenium in the presence of uranium have been previously reported (see ANL-6477, page 98). The codistribution coefficients of uranium, plutonium, strontium, and cesium in the same system are now reported.

The Codistribution of Uranium, Plutonium, Strontium, and Cesium between Lead and Zinc (F. Cafasso and J. Vincenzi)

Lead, zinc, and a sample of Chalk River uranium** were charged to an alumina crucible and heated to a desired temperature. The melt which resulted was stirred with a tantalum paddle for one hour and allowed to settle for 2 hr at temperature. Three or four samples of the upper and lower phase were taken at each of the following temperatures: 701 ± 2 C, 733 ± 2 C, and 761 ± 2 C. The sampling pipets were quartz tubes equipped with graphite filters and coated internally with magnesium oxide. The concentrations of strontium and cesium in the samples were determined by beta-counting methods, while the plutonium concentration was determined by alpha-counting methods.

The analytical results are given in Table 15 and the distribution coefficients for each element are given in Table 16. Figure 29 shows the logarithm of the distribution coefficient of uranium and plutonium plotted against $1/T$. The codistribution coefficients measured earlier for the uranium-plutonium system (see ANL-6477, page 98) are also shown. It can be seen that a reasonably good agreement exists between the 2 separate experiments. The concentration of uranium was about the same in both experiments, but the concentration of plutonium was lower by about a factor of 15 in the present experiment. At these low levels of plutonium, no concentration dependence of its distribution coefficient would be expected and no such dependence was found.

*Measurements for uranium, cerium, strontium, and palladium may be found in ANL-6231, page 74; for cerium and palladium in ANL-6333, page 113; and for cerium and strontium in ANL-6413, page 92.

**The Chalk River uranium was irradiated from January 18, 1951, to September 24, 1951. The burnup was determined to be 0.1 ± 0.01 percent of the total uranium atoms.

Table 15

THE CODISTRIBUTION OF URANIUM, PLUTONIUM, STRONTIUM, AND CESIUM BETWEEN LEAD AND ZINC

Crucible: Alumina
Stirrer: Tantalum

Temp (C $\pm$ 2°)	Upper Layer					Lower Layer				
	w/o U	w/o Pb	Pu(c/m/mg)	Sr(c/m/mg)	Cs(c/m/mg)	w/o U	w/o Zn	Pu(c/m/mg)	Sr(c/m/mg)	Cs(c/m/mg)
702	0.25	5.0	180	2.9	4.2	3.8×10^{-3}	11.4	10.2	22	5.2
701	0.26	14.2	186	5.1	8.5	3.3×10^{-3}	11.2	9.4	21	4.9
700	0.24	14.2	180	5.6	7.2	4.1×10^{-3}	11.3	11.3	24	8.2
734	0.26	19.7	153	5.3	23	8.6×10^{-3}	14.5	15.2	13	8.6
734	0.30	19.5	166	7.1	40	1.0×10^{-2}	14.7	16.8	16	6.1
732	0.29	19.0	162	4.2	27	1.0×10^{-2}	14.4	17.3	15	14
730	0.29	19.0	169	3.9	22	1.0×10^{-2}	14.4	16.6	13	6.6
763	0.24	27.1	140	6.9	17	2.5×10^{-2}	20.1	28.4	22	10
760	0.25	26.1	146	7.5	14	2.2×10^{-2}	19.3	27.6	49	11
760	0.21	26.2	134	5.3	5.8	2.0×10^{-2}	19.0	27.5	58	8.5

Table 16

CODISTRIBUTION COEFFICIENTS OF URANIUM, PLUTONIUM,
STRONTIUM, AND CESIUMDistribution Coefficients
($\frac{\text{concentration in upper layer}}{\text{concentration in lower layer}}$)

Temp (C $\pm$ 2°)	Uranium	Plutonium	Strontium	Cesium
702	66	18	0.1	1
701	79	20	0.2	2
700	59	16	0.2	1
734	30	10	0.4	3
734	30	9.9	0.4	7
732	29	9.4	0.3	2
730	29	10	0.3	3
763	9.6	4.9	0.3	2
760	11.4	5.3	0.2	1
760	10.5	4.9	0.1	1

Figure 29
EFFECT OF TEMPERATURE ON THE
CODISTRIBUTION OF URANIUM AND
PLUTONIUM BETWEEN LEAD
AND ZINC

Table 15 shows that there was considerable scatter in both the cesium and strontium results. This scatter is principally due to analytical difficulties which arose from the extremely low levels of cesium and strontium activities in the samples. In the light of this difficulty, it is believed that only qualitative conclusions can be drawn from these data. It appears that the distribution coefficient for cesium is around unity from 700 to 760 C and that the coefficients of strontium over this same temperature range are not significantly different from those measured earlier (see ANL-6413, page 92), which were 0.09 at 656 C, 0.11 at 703 C, and 0.15 at 740 C.

The Mutual Liquid Solubility of Lead and Zinc
(F. Cafasso, J. Vincenzi)

The equilibrium diagram for the lead-zinc system has been the subject of numerous investigations.⁷ Below 650 C, this diagram is well established. General agreement exists between the investigations of Waring and his collaborators,⁸ who used liquid sampling methods; Kleppa,⁹ who used electromotive force methods; and Rosenthal *et al.*,¹⁰ who used vapor pressure methods to establish the immiscibility field. Above 650 C, however, wide discrepancies exist in the available data for either side of the immiscibility gap. On the zinc-rich side of the gap, the vapor pressure measurements of Rosenthal *et al.*¹⁰ are in reasonable accord with the data of Hass and Jellinek,¹¹ who sampled lead-rich and zinc-rich phases in the solid state. Waring and his collaborators, however, found larger solubilities of lead in zinc than did Hass and Jellinek and showed that the measurements of the latter were made under non-equilibrium conditions.

It appears that the data of Waring *et al.*⁸ are the most reliable for the lead-zinc system above 650 C. However, there are 2 factors which warranted a re-investigation of the equilibrium diagram in this temperature region. First, in the investigations of Waring *et al.*,⁸ the composition of the lead-rich lower layer was not determined by direct sampling except at 2 temperatures, namely, 693 and 780 C. Second, there is some question

⁷Hansen, M., and Anderko, K., Constitution of Binary Alloys, McGraw-Hill Book Co., Inc., New York (1958).

⁸Waring, R. K., Anderson, E. A., Springer, R. D., and Wilcox, R. L., Trans. A.I.M.E. 111, 254 (1934).

⁹Kleppa, O. J., J. Am. Chem. Soc. 74, 6052 (1952).

¹⁰Rosenthal, F. D., Mills, G. J., and Dunkerly, F. J., Trans. A.I.M.E. 212, 153 (1958).

¹¹Hass, K., and Jellinek, K., Zeit. fur anorg. und allgem. Chemie 212, 356 (1933).

about the equilibration temperatures which they reported, since the temperature of the melts was not measured directly. The techniques used in this laboratory permitted liquid samples of both phases to be obtained in a reasonably reproducible fashion and also permitted the melt temperature to be measured directly.

One of the problems experienced with two-phase liquid systems as the temperature is raised close to the consolute temperature (approximately 800 C in the lead-zinc system) is the emulsification of one solvent layer in the other. As the densities of the 2 layers approach one another, separation of the 2 layers occurs very slowly after agitation. In order to determine the possible influence of this factor on the results obtained, 2 samples of each phase were taken at 2 widely spaced settling periods. The first sample at each temperature was taken after a 2-hr stirring period and a 3-hr settling period. The melt was again stirred for 2 hr and then allowed to stand for 18 hr at temperature before a second pair of samples was withdrawn. This procedure was followed for each pair taken at roughly 650, 702, 734, 763, 784, and 802 C. At each temperature, there was no significant difference measured between samples taken after a 2-hr and an 18-hr settling period. The equilibrium diagram obtained from these measurements is shown in Figure 30. The data of Waring and his collaborators have been included in this diagram. Reasonably good agreement exists between these data for the zinc-rich branch of the gap. The small differences that do exist fall in the range of experimental uncertainty. It is interesting to note that the only 2 points Waring *et al.*⁸ obtained along the lead-rich branch by direct sampling of the lower layer fall exactly on our curve.

Figure 30

EQUILIBRIUM DIAGRAM FOR THE LEAD-ZINC SYSTEM ABOVE 650 C

To determine the consolute temperature of this system, Waring, et al.⁸ used a method which relied upon the difference in absorption of X rays by lead and zinc. When X rays were passed through a melt, the 2 layers were easily identifiable. In a single experiment, they found complete solution in a melt containing 57.5 percent lead at 790 C and 2 layers at 780 C. The large uncertainty in the actual temperature of the melt caused them to report the temperature of complete miscibility to be between 770 and 800 C. Using thermal analysis, Seith and Johnen¹² have determined the consolute temperature to be 798 C. Data from the present study show that at 802 ± 2 C complete miscibility exists in this system, while at 784 ± 2 C segregation into 2 layers occurs. The temperature at which the gap closes must lie between these temperatures. With this limited information, the closure of the miscibility gap can be represented only approximately. To show its arbitrariness, this portion of the solubility curve in Figure 30 has been represented by a broken line.

4. Thermodynamic Studies

Thermodynamic functions for key elements in liquid metal solvents and for the more important solid intermetallic phases are being measured. Two methods are being used. Galvanic cells have proved to be especially useful for the measurement of activities in liquid metal solutions as well as for the determination of the free energy of formation of the equilibrium solid phase in solid-liquid two-phase regions. On the other hand, for systems containing several well-defined intermetallic phases, measurement of the decomposition pressure by the effusion method is proving to be useful. The 2 methods supplement each other.

Thermodynamics of the Uranium-Tin System (Emf Method) (I. Johnson and R. Yonco)

As a part of our systematic study of the thermodynamics of uranium-B subgroup systems* measurements have been made of the emf of the cell

as a function of temperature. The two-phase uranium-tin alloy consisted of a liquid uranium-tin solution and the uranium-tin intermetallic compound

¹²Seith, W., and Johnen, H., Z. Elektrochem. 56, 140 (1952).

*For studies of the uranium-zinc system, see ANL-5924, page 132; for the uranium-cadmium system, see ANL-5996, page 116; for the uranium-lead system, see ANL-6183, page 71; for the uranium-thallium system, see ANL-6231, page 76; for the uranium-indium system, see ANL-6413, page 93; and for the uranium-gallium system, see ANL-6477, page 101.

USn₃. The latter compound has a face-centered cubic structure which is isotopic with AuCu₃ (Ll₂). The overall cell reaction is

On the assumption that 3 faradays are required for the transport of one gram atom of uranium through the cell, the standard free energy of formation of USn₃, ΔG_f° , is given by the equation

$$\Delta G_f^\circ = 3 F E + 3 R T \ln a_{\text{Sn}} \quad ,$$

in which E is the emf of the cell and a_{Sn} is the activity of tin in the saturated uranium-tin solution. The solubility of uranium in tin is very small over the temperature range of the present experiments, and consequently a_{Sn} is very close to unity. The term $3 R T \ln a_{\text{Sn}}$ is, therefore, insignificant and has been neglected.

The experimental data are given in Table 17 and shown in Figure 31.

Table 17

EMF OF URANIUM-TIN CELL

$\text{U} | \text{UCl}_3, \text{KCl-LiCl (eutectic)} || \text{U-Sn (2-phase alloy)}$

Temp (K)	Emf (v)	Temp (K)	Emf (v)
636	0.4624	789	0.4300
642	0.4601	803	0.4280
646	0.4574	808	0.4262
665	0.4547	825	0.4230
672	0.4543	832	0.4204
688	0.4506	843	0.4193
705	0.4461	849	0.4171
713	0.4458	868	0.4138
723	0.4445	873	0.4117
727	0.4434	884	0.4104
749	0.4394	890	0.4086
752	0.4383	908	0.4054
764	0.4358	913	0.4034
786	0.4313	927	0.4012
788	0.4308	950	0.3964

Figure 31

EMF OF CELL: $\text{U}|\text{UCl}_3, \text{KCl-LiCl}(\text{eutectic})|$
 $\text{U-Sn}(2\text{-phase alloy})$

These data may be represented over the the temperature range from 373 to 677 C by the quadratic equation

$$E \text{ (v)} = 0.5662 - 1.373 \times 10^{-4} T - 4.425 \times 10^{-8} T^2$$

to within 0.7 mv.

The free energy (ΔG_f°), enthalpy (ΔH_f°), and entropy (ΔS_f°) of formation of USn_3 may be represented by the equations

$$\Delta G_f^\circ \text{ (cal mole}^{-1}\text{)} = -39,180 + 9.499 T + 3.062 \times 10^{-4} T^2$$

$$\Delta H_f^\circ \text{ (cal mole}^{-1}\text{)} = -39,180 - 3.062 \times 10^{-4} T^2$$

$$\Delta S_f^\circ \text{ (cal deg}^{-1} \text{ mole}^{-1}\text{)} = -9.499 - 6.124 \times 10^{-4} T$$

At 500 C, $\Delta G_f^\circ = -31.6_5$ kcal/mole, $\Delta H_f^\circ = -39.0_0$ kcal/mole, and $\Delta S_f^\circ = -9.97$ cal/deg-mole.

Thermodynamics of the Uranium-Indium System
(I. Johnson)

The emf data for the uranium-indium cell (see ANL-6413, page 93) may be combined with the solubility data reported by Chasanov on page 89 to estimate some of the thermodynamic properties of uranium in saturated indium solutions.

In the galvanic cell, uranium is transferred from solid uranium to a saturated solution in liquid indium. The emf is related to the difference in the free energy (Gibbs) of uranium in solid uranium and saturated solution by the equation

$$-3F E = \bar{G}_U - G_U^\circ = RT \ln a_U \quad , \quad (1)$$

in which it has been assumed that 3 faradays of electricity are required for the transport of one mole of uranium. Here $\bar{G}_U$ is the partial molal free energy of uranium in the saturated solution and G_U° the molal free energy of pure solid uranium; also, a_U is the activity of uranium in the saturated indium solution, the reference state being pure solid uranium. The atom fraction of uranium in saturated indium solutions, $(N_U)_{\text{satd}}$, may be obtained from Chasanov's report, whence

$$RT \ln a_U - RT \ln (N_U)_{\text{satd}} = -3F E - RT \ln (N_U)_{\text{satd}}$$

or

$$RT \ln \gamma_U = -3F E - RT \ln (N_U)_{\text{satd}} \quad , \quad (2)$$

where γ_U is the activity coefficient of uranium in the saturated indium solution. Combination of the emf data and the solubility data leads to the numerical expression

$$RT \ln \gamma_U = -731 - 0.710 T + 3.88 \times 10^{-3} T^2 \quad . \quad (3)$$

This expression may be used to compute the activity coefficient of uranium in saturated indium solutions over the temperature range common to the 2 sets of data (450 to 675 C).

The excess thermodynamic quantities for uranium in saturated indium solutions may also be computed from these data. Excess quantities are defined as the difference between the partial molal quantity for the real solution and the partial molal quantity for an ideal solution of the same composition. When the real solution is ideal, the excess quantities are zero. The ideal partial molal free energy of uranium in an indium solution, $\bar{G}_U^{\text{id}}$, of atom fraction N_U is given by the expression

$$\bar{G}_U^{\text{id}} = G_{U(\text{liq})}^\circ + RT \ln N_U \quad , \quad (4)$$

where $\bar{G}_U^\circ$ is the molal free energy of liquid uranium at the temperature T. Combination of equations (1) and (4) gives

$$\bar{G}_U - \bar{G}_U^{\text{id}} + (G_{U(\text{liq})}^\circ - G_U^\circ) = -nF E - RT \ln N_U \quad (5)$$

or

$$\bar{G}_U^{\text{xs}} + \Delta G_{\text{fusion}} = -nF E - RT \ln N_U \quad (6)$$

in which ΔG_{fusion} is the free energy of fusion of uranium at the temperature T. In the case of saturated solutions of uranium in liquid indium, the right-hand side of Equation (6) is equal to $RT \ln \gamma_U$ as defined in Equation (2); numerical values computed from Equation (3) are given in Table 18. The free energy of fusion was estimated from the numerical data given by Kelley.¹³ From the results of this computation it is concluded that solutions of uranium in liquid indium exhibit small negative deviations from ideal behavior at low temperatures. These deviations become less negative as the temperature increases. Whether or not the reversal in sign of $\bar{G}_U^{\text{xs}}$ at 600 C is real is not certain. One might expect $\bar{G}_U^{\text{xs}}$ to approach closer to zero as the temperature is increased; however, since the temperatures are considerably below the melting point of the solute (uranium), it is possible that a second reversal in trend may occur beyond the temperature range of the present experiments.

Table 18

EXCESS THERMODYNAMIC QUANTITIES FOR
URANIUM-INDIUM SOLUTIONS
(cal/mole)

Temp (C)	$\bar{G}_U^{\text{xs}} + \Delta G_{\text{fusion}}$	ΔG_{fusion}	$\bar{G}_U^{\text{xs}}$
450	783	2154	-1371
500	1037	1931	- 894
550	1311	1699	- 388
600	1604	1485	119

The activity coefficient γ_U [see Equation (2)], which is defined relative to pure solid uranium, is related to the activity coefficient γ_U' defined relative to pure supercooled liquid uranium by the equation

$$\gamma_U' = \gamma_U \exp\left(\frac{-\Delta G_{\text{fusion}}}{RT}\right)$$

¹³Kelley, K. K., Contributions to the Data on Theoretical Metallurgy, XIII: High-temperature Ideal Content, Heat Capacity, and Entropy Data for the Elements and Inorganic Compounds. Bulletin 584, Bureau of Mines (1960).

For the present system the quantity γ_U is more useful in practical computations, since it does not involve quantities, such as ΔF_{fusion} , which cannot be directly measured. However, for theoretical considerations, γ_U is more significant, since it only includes changes in free energy due to the solution process.

Lanthanum-Cadmium System (Effusion Studies)
(E. Veleckis and E. Van Deventer)

A study of the intermediate phases in the lanthanum-cadmium system has been made by Iandelli and Ferro¹⁴ by metallographic and X-ray techniques. In addition to the LaCd compound identified earlier,¹⁵ they have reported a hexagonal LaCd₂ compound and a cubic LaCd₁₁ compound. Attempts to prepare homogeneous alloys of composition LaCd₃ invariably resulted in a mixture of 2 phases.

A study of the phase relations in the lanthanum-cadmium system by means of the recording effusion balance have been made in the

Figure 32

LANTHANUM-CADMIUM SYSTEM: ISOTHERMS AT 370 AND 450 C

Laboratory. The purpose of this study was to verify the stoichiometry of the known phases and to investigate the unexplored regions of the phase diagram.

Two typical $\log P_{\text{mm}}$ versus composition isotherms at 370 and 450 C are shown in Figure 32. Both curves share the same ordinate but the abscissae are as shown on the graph. Sudden pressure descents in the curves indicate the existence of 3 narrow phases corresponding to compositions LaCd₁₁, La₂Cd₉ and LaCd₂. In addition, there is evidence for the existence of another phase, probably with a range of homogeneity, around the composition LaCd₈.

To verify the effusion results, a number of alloys, prepared by stopping effusion at certain preselected compositions, were submitted for X-ray analyses. The results of these analyses, shown in Table 19, identify the compounds LaCd₁₁, LaCd₂, and LaCd and confirm the new phases "E" and "F," of which structural identification was not made because of exceedingly complex diffraction patterns.

¹⁴Iandelli, A., and Ferro, R., Gazz. chim. ital., 84, 463 (1954).

¹⁵Iandelli, A., and Botti, E., Gazz. chim. ital., 67, 638 (1937).

The phases "E" and "F" correspond most probably to the compounds La_2Cd_9 and $\text{LaCd}_{\sim 8}$, respectively, as is apparent from the comparison of the effusion and X-ray results.

Table 19

RESULTS OF X-RAY DIFFRACTION ANALYSES^a OF
SOME LANTHANUM-CADMIUM ALLOYS

Sample	Composition	Phases
E-5	$\text{LaCd}_{17.30}$	$\text{LaCd}_{11} + \text{Cd}$
E-7	$\text{LaCd}_{11.45}$	$\text{LaCd}_{11} + \text{Cd}$
E-8	$\text{LaCd}_{11.00}$	$\text{LaCd}_{11} + \text{Cd}$
G-29	$\text{LaCd}_{9.67}$	$\text{LaCd}_{11} + \text{"F"}^b$
E-17	$\text{LaCd}_{8.38}$	$\text{LaCd}_{11} + \text{"F"}$
E-16	$\text{LaCd}_{7.09}$	$\text{"F"} + \text{"E"}^c$
G-19	$\text{LaCd}_{\sim 6}$	$\text{"E"} + \text{"F"}$
EA-14	$\text{LaCd}_{4.02}$	"E"
EA-11	$\text{LaCd}_{3.44}$	$\text{"E"} + \text{LaCd}_2$
EA-13	$\text{LaCd}_{2.67}$	$\text{LaCd}_2 + \text{"E"}$
EA-12	$\text{LaCd}_{1.71}$	$\text{LaCd}_2 + \text{LaCd}$

^aAnalyses performed by R. Schablaske and B. Tani

^bPhase "F" is probably $\text{LaCd}_{\sim 8}$.

^cPhase "E" is probably La_2Cd_9 .

In this study we have thus confirmed the existence of the known compounds LaCd_{11} and LaCd_2 , obtained an indirect verification of LaCd , and discovered 2 new phases, La_2Cd_9 and $\text{LaCd}_{\sim 8}$. In contrast with the systems cerium-cadmium^{14,16} and praseodymium-cadmium (ANL-6477, page 103), no evidence for the existence of the 1:6 and 1:3 compounds was found in the system lanthanum-cadmium.

¹⁶Elliott, G. R. B., and Lemons, J. F., J. Phys. Chem., 64, 137 (1960).

II. FUEL CYCLE APPLICATIONS OF VOLATILITY AND FLUIDIZATION TECHNIQUES*

A Direct Fluorination Volatility Process has been proposed for the recovery of uranium and plutonium from irradiated nuclear reactor fuels. This process is based on the volatilities of uranium and plutonium hexafluorides. In this process fluidization techniques are also used to advantage. Progress continues to be made in application of this process to uranium oxide and zirconium-matrix fuels.

Recovery of uranium and plutonium from spent uranium oxide is accomplished by decladding with 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 from volatile fission products by distillation and separated from one another by thermal decomposition of the plutonium hexafluoride.

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

1. Fluorination of Plutonium-Uranium Dioxide (R. L. Jarry, T. D. Baker, J. J. Stockbar)

Laboratory development work for the Direct Fluorination Process has been concentrated on experiments designed to elucidate the factors involved in the removal of plutonium, by fluorination, from mixtures of alumina, uranium oxide, plutonium oxide, and fission product element oxides. The oxide mixtures have been prepared to simulate the feed material in the fluorination step of the process. In the conceptual flowsheet of the Direct Fluorination Volatility Process, uranium and plutonium are removed, as the hexafluorides, from oxide fuels by fluorination at 450 C in a fluid-bed reactor. A typical process charge for a fluid-bed reactor would consist of 100 kg of uranium, 0.4 kg of plutonium, 30 kg of Alundum, and about 0.8 kg of fission product elements. All of these components of the charge would be present as the respective oxides. If in such a processing scheme 99 percent of the charged plutonium were removed as plutonium hexafluoride, then the residual plutonium concentration on the Alundum inert solids would be 0.013 weight percent.

Data on the amounts of uranium and plutonium retained on residues resulting from the fluorination at 450 C of mixtures of uranium-plutonium oxides and Alundum have been reported previously (see ANL-6477; page 109). Data from experiments in which compounds of fission products were added to the uranium oxide-plutonium oxide-Alundum mixture were included in the report. Plutonium retention of about 0.03 weight percent

*A summary of this section is given on pages 6 to 11.

was found on Alundum residues without the addition of fission products. However, with the addition of fission products, the plutonium retention on the Alundum residue increased to about 0.06 weight percent. The uranium content of Alundum residues has usually been less than 0.02 weight percent, and there was no significant change in retention upon the addition of fission products. The value of 0.02 weight percent uranium in Alundum corresponds to only 6×10^{-3} percent of the original uranium content of the solid reactant. Since the removal of uranium does not present a problem in this process, the discussion of experimental results has been mainly concerned with the subject of plutonium retention on fluorination residues. In the preceding quarterly (ANL-6477), results were also presented for experiments in which pyrohydrolysis and refluorination were used to reduce the plutonium content of Alundum residues not containing fission products. The pyrohydrolysis treatment followed by fluorination was effective in reducing the plutonium content of the residues to between 0.02 and 0.03 weight percent. Refluorination alone was found to be as effective as refluorination combined with prior pyrohydrolysis for residues containing less than about 0.1 weight percent plutonium.

The present report contains experimental results of (1) the pyrohydrolysis and refluorination of Alundum and nickel fluoride residues containing fission products; (2) the refluorination at 550 C of an Alundum residue containing fission product element oxides; (3) fluorination of uranium-plutonium oxide-Alundum mixtures containing mixtures of fission product element oxides or fluorides; and (4) a prefluorination treatment using hydrogen fluoride followed by direct fluorination.

A detailed description of the reaction system used for these experiments was given in a previous report (see ANL-6379, page 139). The general procedure for the experiments was described in a previous report (see ANL-6477, page 107) and is summarized below. A nickel boat containing the solid reactant was placed in a horizontal tubular reactor through which the gaseous reactant was circulated. The gaseous fluorination mixture was made up in a 4.5-liter ballast volume which is part of the reaction system volume and which is in series with the tubular reactor. After the evacuated reactor had been heated to the desired temperature, the fluorination gas mixture in the ballast vessel was slowly admitted to the reactor. When the pressure had equalized throughout the reaction system, at about 750 mm, a circulating flow of 800 ml/min was started. After the prescribed reaction period, the fluorinating gas was removed by pumping, and the reactor was flushed with helium and allowed to cool to room temperature. The reaction residue was then removed from the reactor, weighed, and sampled for analysis.

Several experiments were performed in which fluorination residues containing fission product elements were refluorinated in an attempt to lower the plutonium content of the residues. These residues

were from experiments in which a 4 weight percent plutonium containing uranium-plutonium mixed oxide had been fluorinated for 10 hr at 450 C. In 2 experiments, the residues were pyrohydrolyzed at 1000 C for 2 hr and then fluorinated at 450 C for 10 hr. In one of these experiments, the residue contained Alundum as the inert solid, and in the other the residue contained nickel fluoride as the inert solid. The data for these experiments are listed in Table 20. The plutonium content of the Alundum residue after this treatment was 0.018 weight percent, as compared with an initial concentration of 0.287 weight percent (see Experiment 111). In the case of the residue containing nickel fluoride (see Experiment 115), the plutonium concentration resulting from this treatment was 0.177 weight percent, as compared with an initial concentration of 0.366 weight percent. In the third experiment listed in Table 20, an Alundum residue was re-fluorinated at 550 C for 10 hr without a prior pyrohydrolysis step. The plutonium concentration in the residue after this treatment was reduced from an initial value of 0.105 to 0.010 weight percent.

Table 20

THE REMOVAL OF URANIUM AND PLUTONIUM FROM
FLUORINATION RESIDUES BY PYROHYDROLYSIS
AND/OR ADDITIONAL FLUORINATION

Pyrohydrolysis: 1000 C for 2 hr
Fluorination Gas Mixture: 75 v/o F_2 , 25 v/o O_2
Fluorine Recycle Rate: 800 ml/min
Fluorination Time: 10 hr
Analysis of Uranium-
Plutonium Oxide Mixture: 81.7 w/o U, 3.8 w/o Pu

Exp No. ^a	Temp (C)	Residue of Exp	Inert Solid	Initial Sample				Residue	
				Fission Product Mixture	U (w/o)	Pu (w/o)	Pyro- hydrolyzed	U (w/o)	Pu (w/o)
111	450	98	Al_2O_3	FP-1 ^b	0.007	0.287	yes	8×10^{-4}	0.018
115	450	90	NiF_2	FP-1 ^b	0.003	0.366	yes	3×10^{-3}	0.177
107	550	101	Al_2O_3	FP-2 ^c	0.008	0.105	no	3×10^{-3}	0.010

^aFor previous work on pyrohydrolysis see Table 27, page 109, ANL-6477.

^bFission product mixture FP-1 contains: BaF_2 , SrF_2 , YF_3 , ZrF_4 , $NdCl_3$, $CsCl$, La_2O_3 , Sm_2O_3 , Ce_2O_3 , and Pr_6O_{11} .

^cFission product mixture FP-2 contains: La_2O_3 , Sm_2O_3 , Ce_2O_3 and Pr_6O_{11} .

The effect of the addition of fission product elements as the oxides or fluorides on the retention of plutonium by Alundum was studied in several fluorination experiments. The fission product oxide mixture was prepared to conform to the distribution of fission product elements expected for a Dresden-type fuel element after a burnup of about 10,000 Mwd/ton. A list of the fission product element oxides which

would form nonvolatile fluorides upon fluorination, and therefore remain in the residue, was given in a previous report (see ANL-6477, page 110). The fission product mixture, designated FP-3, contained BaO, ZrO₂, La₂O₃, CeO₂, Y₂O₃, Nd₂O₃, Sm₂O₃, Pr₆O₁₁, Eu₂O₃, and Gd₂O₃. Analyses furnished by the suppliers showed purities of greater than 99.9 percent for all the oxides. A portion of fission product mixture FP-3 was fluorinated to produce a mixture containing the corresponding fluorides and is designated FP-3F. These fission product mixtures were added to the reaction mixture of uranium-plutonium oxide containing about 4 weight percent plutonium and Alundum. The specifications for the high-purity Alundum and for the uranium-plutonium oxide solid solution containing about 4 weight percent plutonium were given in previous reports (see ANL-6413, page 110; ANL-6477, page 107). The data for these experiments are listed in Table 21. In the experiments in which the fission product oxide mixture was used, the weight percents plutonium found on the residues were 0.065 for Experiment 109 at 450 C and 0.040 for Experiment 114 at 550 C. When, however, the fission product mixture containing the fluorides was used, the retention of plutonium on the Alundum was markedly reduced. This is shown by the results of Experiments 113 and 126 in which the amounts of plutonium (weight percent) on the Alundum residues were 0.012 and 0.017, respectively. These results would seem to indicate some interaction between the fission product element oxides, the plutonium oxide, and the Alundum during the fluorination period.

Table 21
FLUORINATION OF URANIUM-PLUTONIUM OXIDE MIXTURE CONTAINING FISSION PRODUCT OXIDES OR FLUORIDES

			Fluorination Gas Mixture:		75 v/o F ₂ , 25 v/o O ₂									
			Gas Recycle Rate:		800 ml/min									
			Fluorination Time:		10 hr									
			Analysis of Uranium-Plutonium Oxide Mixture:		81.7 w/o U 3.8 w/o Pu									
Exp No.	Temp (C)	Fission Product Mixture ^a	Initial Sample							Residue				
			Total Weight (g)	Weight Inert Solid (g)	Weight Fission Products (g)	Weight U (mg)	Weight Pu (mg)	U (w/o)	Pu (w/o)	Weight Recovered Solids (g)	Weight U (mg)	Weight Pu (mg)	U (w/o)	Pu (w/o)
109	450	FP-3	4.00	3.00	0.08	915	40.4	22.9	1.61	3.22	0.29	0.29	0.009	0.065
113	450	FP-3F	3.76	2.65	0.07	857	38.0	22.8	1.61	2.77	0.16	0.33	5.6 x 10 ⁻³	0.012
126	450	FP-3F	3.76	2.65	0.07	857	38.0	22.8	1.61	2.73	0.15	0.46	5.6 x 10 ⁻³	0.017
114	550	FP-3	3.76	2.65	0.07	808	33.8	21.5	0.90	2.95	0.30	1.18	0.010	0.040

^aFP-3 contains: BaO, ZrO₂, Y₂O₃, La₂O₃, CeO₂, Pr₆O₁₁, Nd₂O₃, Sm₂O₃, Eu₂O₃, and Gd₂O₃.

FP-3F contains: BaF₂, ZrF₄, YF₃, LaF₃, CeF₄, PrF₃, NdF₃, SmF₃, EuF₃, and GdF₃ and was prepared by fluorination of FP-3 mixture.

A group of experiments were performed with uranium-plutonium oxide mixtures containing 0.3 to 0.4 weight percent plutonium and about one weight percent of fission product oxide mixture FP-3. These mixtures were prepared by adding the proper quantities of uranium dioxide and of fission product oxide mixture FP-3 to the previously

prepared 4 weight percent plutonium mixture. The uranium dioxide was prepared by the reduction of uranium hexafluoride with a steam-hydrogen mixture. These mixtures approximated the composition of the fuel charge to a fluid-bed fluorinator. The actual reaction charge used was 3.42 g of the uranium-plutonium oxide mixture, which contained about 0.03 g of fission product oxides, and 0.9 g of Alundum. Experiments were performed to show the effect of the concentration of fluorine in the fluorinating gas mixture and of prefluorination of the solid reactants with hydrogen fluoride on the retention of plutonium in the residues.

Table 22 lists the experimental results obtained. For a fluorine concentration of 10 volume percent, the plutonium concentration in the Alundum residue averaged about 0.1 weight percent at 450 C (Experiments 119 and 123) and increased to an average of about 0.4 weight percent at 550 C (Experiments 122 and 132).

Table 22

HYDROFLUORINATION AND/OR FLUORINATION OF URANIUM-PLUTONIUM MIXTURES FROM ALUNDUM INERT SOLIDS

Solid Reaction Mixture: (1) (U-Pu)O₂, 3.42 g which contains;
 Batch I 2930 mg U, 9.9 mg Pu
 Batch II 2950 mg U, 9.9 mg Pu
 Batch III 2990 mg U, 14.4 mg Pu
 (2) Al₂O₃, 0.90 g
 (3) Fission Products, 0.03 g
 Fluorinating Gas Flow: 800 ml/min

Exp No.	Temp (C)	(U-Pu)O ₂ Batch No. ^a	Fluorinating Gas Mixture				Time (hr)	Weight Recovered Solids (g)	Residue				Downstream Al ₂ O ₃ Blank	
			v/o F ₂	v/o HF	v/o N ₂	v/o O ₂			Wt U (mg)	Wt Pu (mg)	U (w/o)	Pu (w/o)	U (w/o)	Pu (w/o)
119 ^b	450	II	10	-	65	25	10	0.91	0.25	1.00	0.028	0.110	3.4 x 10 ⁻³	9 x 10 ⁻⁴
123 ^b	450	II	10	-	65	25	10	0.96	0.71	0.80	0.074	0.083	5 x 10 ⁻³	2 x 10 ⁻³
122 ^b	550	II	10	-	65	25	10	2.77	1299	8.20	46.9	0.296	0.11	4 x 10 ⁻³
132 ^b	550	II	10	-	65	25	10	1.69	517	8.62	30.8	0.514	-	-
134	450	II	75	-	-	25	10	- ^c	-	-	0.260	0.058	-	-
135	450	III	75	-	-	25	10	0.985	0.99	1.59	0.100	0.162	0.20	4.5 x 10 ⁻³
120 ^b	450	II	{ 10	-	65	25	1	0.94	0.12	0.55	0.013	0.059	6 x 10 ⁻⁴	2 x 10 ⁻³
			{ 75	-	-	25	9							
121 ^b	550	II	{ 10	-	65	25	1	- ^c	-	-	0.043	0.034	0.022	3 x 10 ⁻³
			{ 75	-	-	25	9							
133	450	II	75	-	-	25	10	0.98	0.25	0.15	0.025	0.015	-	-
	550		75	-	-	25	10							
128 ^d	450	II	-	25	75	-	2	0.94	0.12	0.35	0.013	0.037	-	-
			75	-	-	25	10							
129 ^d	350	I	-	25	75	-	1	0.92	0.16	0.24	0.017	0.025	-	-
	450		-	25	75	-	2							
	450		75	-	-	25	7							
137 ^d	350	I	-	25	75	-	1	0.955	0.25	0.24	0.236	0.028	-	-
	450		-	25	75	-	2							
	450		75	-	-	25	7							

^aPrepared by the addition of UO₂ and FP-3 mixture to (U-Pu)O₂ mixture containing about 4 w/o Pu. Batch I was oxidized at 550 C for 2 hr and then reduced at 550 C for 2 hr.

		w/o U	w/o Pu
Analyses:	Batch I	85.8	0.29
	Batch II	86.3	0.29
	Batch III	87.2	0.42

^bIn these experiments the 10 v/o fluorine was added to the nitrogen-oxygen mixture slowly over the first hour of reaction time.

^cWeight of fluorinated residue not determined.

^dIn these experiments the 25 v/o hydrogen fluoride was added to the nitrogen slowly over the first hour of reaction time.

In these experiments the fluorine concentration of the gas mixture was slowly brought up to 10 volume percent over the first hour of reaction time. High plutonium retentions on the residues of the experiments performed at 550 C were matched by correspondingly high uranium retentions. The amounts of uranium on the Alundum residues were 46.9 and 30.8 weight percent for Experiments 122 and 132, respectively. These residues had a hard surface crust and were of a yellowish color, indicating the presence of uranyl fluoride. Increasing the fluorine concentration to 75 volume percent in Experiment 134, which was carried out at 450 C, resulted in a plutonium concentration on the Alundum residue of about 0.06 weight percent.

In other experiments, in which the uranium-plutonium oxide mixtures containing 0.3 to 0.4 weight percent plutonium were used, the volume percent fluorine and, in some cases, the temperature were changed during the 10-hr reaction period. The initial fluorine concentration of 10 volume percent was achieved slowly over the first hour of reaction. Experiment 120 at 450 C and Experiment 121 at 550 C were performed with 10 volume percent fluorine for one hour and 75 volume percent fluorine for the remaining 9 hr. The plutonium contents of the residues were 0.059 weight percent for the experiment at 450 C and 0.034 weight percent for that at 550 C. A single experiment (Experiment 133) was made in which 75 volume percent fluorine was used in 2 fluorination periods of 10 hr each, one at 450 C and the other at 550 C. The plutonium concentration of the residue from this experiment was 0.015 weight percent.

In some of the experiments (Experiments 119, 120, 121, 122, 123, and 135) described in the preceding paragraphs, a nickel boat containing Alundum was placed downstream of the boat containing the uranium-plutonium oxide mixture. This was done to determine whether plutonium hexafluoride would be removed from the gaseous reaction products by the Alundum. The results of these experiments are listed in the last 2 columns of Table 22. In all cases, the weight percent plutonium in this Alundum did not exceed a value of 5×10^{-3} . The uranium pickup by the Alundum in the downstream boat was also low except in those cases (Experiments 121 and 135) in which the uranium content of the reaction residue was high. These results seem to indicate that, under the conditions of fluorination, plutonium hexafluoride would not be reduced in passing over an Alundum surface.

In Experiments 128, 129, and 137, listed in Table 22, a pre-fluorination step with 25 volume percent hydrogen fluoride in nitrogen was employed. This preliminary treatment was then followed by a direct fluorination with a mixture of 75 volume percent fluorine with oxygen. The uranium-plutonium oxide mixtures containing 0.3 to 0.4 weight percent plutonium were used in these experiments. In 2 experiments (129 and 137), the uranium-plutonium oxide mixture was oxidized at 550 C for 2 hr with 25 volume percent oxygen in nitrogen, followed by a reduction at 550 C for

2 hr with 25 volume percent hydrogen in nitrogen. In Experiment 128 at 450 C, the mixture was hydrofluorinated for 2 hr and then fluorinated for 10 hr; a plutonium content on the Alundum residue of 0.037 weight percent resulted. In Experiments 129 and 137, the hydrofluorination was started at 350 C and then continued at 450 C for 2 hr, followed by fluorination, also at 450 C, for 7 hr. Hydrogen fluoride was added to the nitrogen slowly during the first hour of reaction time. The amounts of plutonium (weight percent) in these residues were 0.025 and 0.028 for Experiments 129 and 137, respectively. The hydrofluorination procedure does not seem to offer any advantage over the two-step direct fluorination procedure.

At this point in the experimental program, several generalizations can be made about the problem of removing plutonium from inert solids.

(1) Plutonium is retained on Alundum residues to about 0.03 weight percent; with the addition of fission product element oxides, the retention is increased to between 0.05 and 0.06 weight percent. When fission product elements are present initially as the fluorides, they do not increase the plutonium retention in Alundum residues.

(2) Plutonium retained on Alundum residues can be effectively removed, leaving less than 0.020 weight percent plutonium on the residue, by either pyrohydrolysis followed by fluorination at 450 C or by a refluorination alone at 550 C. The presence of fission product element compounds does not hinder the effectiveness of these procedures.

The development of a laboratory-scale fluid-bed reactor is continuing. This unit will be incorporated into the presently available plutonium facility. Experimental work with this equipment will provide data which will more realistically approximate the conditions for the projected pilot-plant study. For this work, uranium-plutonium dioxide pellets containing 5 weight percent plutonium dioxide and about one weight percent of a mixture of 19 fission product element oxides will be fabricated by an outside contractor.

An experimental study has been started which is designed to show any interaction between plutonium and fission product element compounds. Such interactions, if any, would be of great importance to the problem of minimizing the retention of plutonium on inert solids in the presence of fission products. The initial experimental program will be concerned with the fluorination of mixtures of plutonium and fission product oxides and fluorides. A study of the products of these reactions will be made by means of chemical and X-ray diffraction analyses.

2. Separation of Mixtures of Uranium and Plutonium Hexafluorides by Selective Thermal Decomposition of Plutonium Hexafluoride
(L. Trevorrow, R. Wagner, J. Riha, W. Shinn)

After spent oxide fuel has been declad, it will be converted into a mixture of uranium hexafluoride and plutonium hexafluoride in the fluorination step of the Direct Fluorination Volatility Process. A separation of the components of the mixture will be carried out in order to obtain pure compounds of uranium and plutonium. Selective thermal decomposition of plutonium hexafluoride is being considered as a means of separating the mixture, since plutonium hexafluoride is much less stable than uranium hexafluoride at elevated temperatures. The mixture of uranium and plutonium hexafluoride vapors would be passed through a decomposition vessel at some optimum temperature, at which the rate of decomposition of plutonium hexafluoride is rapid and the rate of decomposition of uranium hexafluoride is very slow. The plutonium would remain in the vessel as plutonium tetrafluoride, and the uranium hexafluoride would pass on in the gas stream to be condensed and collected, free of plutonium. Previous experimental results (see ANL-6333, page 145) showed that the rate of decomposition of plutonium hexafluoride was enhanced in the presence of plutonium tetrafluoride. Therefore, a decomposition vessel would initially be charged with some plutonium tetrafluoride to increase the rate of separation.

Two sets of experiments have been carried out to explore the feasibility of this separation scheme. Mixtures of plutonium and uranium hexafluorides were circulated through a heated, nickel vessel containing plutonium tetrafluoride. Figure 33 is a schematic drawing of the apparatus used. Samples of the gas were taken after various intervals and analyzed for plutonium and uranium. A chemical analysis was also carried out on the solids deposited in the heated vessels.

The decomposition vessels, 2 in. in diameter and 2 in. in length, were packed with 25 to 28 g of nickel wool to increase the interior surface area (geometric) to about 1500 sq cm. The temperature of the vessels was monitored by a thermocouple in a $\frac{1}{4}$ -in.-diameter well which extended down a distance of one inch into the nickel wool. Temperatures at the bottom of the vessels were 6 to 10 degrees lower than at the top.

A single vessel was used for all of the experiments in the first set, whereas a new vessel was used for each of the experiments in the second set. The treatments of the vessels prior to use in the separation experiments differed in each of the 2 sets of experiments. In the first set, fluorine gas at 1 atm pressure was circulated through the vessel for $2\frac{1}{2}$ hr at 300 C, after which fluorine was allowed to remain in the vessel at room temperature for several days. In the second set of

experiments, fluorine gas at 1 atm pressure was circulated through the vessel for 6 hr at 300 C. A quantity of plutonium tetrafluoride was deposited in all of the vessels prior to use in the separation experiments. This was accomplished by circulating plutonium hexafluoride through the vessels at 250 C, whereby several grams of plutonium tetrafluoride were deposited in each vessel. The initial quantity of plutonium tetrafluoride deposited in each vessel was determined by weighing.

Figure 33

APPARATUS USED FOR SEPARATION OF URANIUM
HEXAFLUORIDE-PLUTONIUM HEXAFLUORIDE
MIXTURES BY THERMAL DECOMPOSITION

Apparatus Used for Set 1

Sampling procedure: Diaphragm pump is stopped. Valves 1, 2, and 3 are closed. To collect a sample in trap A, valve 4 is opened so that gas in the sample volume is expanded into trap A. Trap A was evacuated prior to the experiment.

Apparatus Used for Set 2

Sampling Procedure: Diaphragm pump is stopped. Valves 5 and 6 are closed and valve 7 is opened. Next, valves 1 and 2 are closed, and valves 3 and 4 are opened. In order to circulate gas through the initial sample trap, valve 8 is closed, and valves 9 and 10 are opened, and the diaphragm pump is started again.

The mixture for each experiment was prepared by adding uranium hexafluoride and plutonium hexafluoride to a ballast tank of 8530-ml volume, determined by PVT measurements. The hexafluorides were allowed to stand overnight in the ballast tank to insure mixing. The combined pressure of uranium and plutonium hexafluorides in the mixture was 100 ± 2 mm. Helium was added to the mixture to make the total pressure 760 ± 10 mm. The mixture was recycled through the system, about 10 times at room temperature, bypassing the reaction vessel, after which an initial sample of the gas mixture was taken. The mixture was

then recycled through the heated nickel vessel, at a flow rate of 800 ml/min, by means of a Lapp Pulsafeeder pump with a Monel diaphragm.*

The gas-sampling procedure also differed in the 2 sets of experiments. In the first set of experiments, the circulating gas was sampled by isolating a portion of the gas in a section of the system bounded by valves. A portion of this gas sample was then expanded into an evacuated trap containing a frozen, aqueous solution of aluminum nitrate and nitric acid cooled in liquid nitrogen. Immediately after the expansion the trap was closed. Only a fraction of the sample originally isolated was collected. This technique resulted in the collection of samples of unequal size. Only in the experiment at 300 C (see No. 86, Table 23), in which the expansion was carefully controlled to the same pressure each time, were all the samples approximately equal in size. The variation of sample sizes is reflected in the variation of the quantity of uranium in the samples shown in Table 23. This method of sampling did not permit predetermined total quantities of uranium and plutonium to be isolated in the sample volume, but did permit determination of the ratio of plutonium to uranium, which is essential to the interpretation of the experiments. In the second set of experiments, a larger portion of the gas mixture was isolated and then circulated through the trap containing the frozen, aqueous solution. In the first set of experiments, gas samples were taken initially and at various intervals during a 10-hr period. In the second set, gas samples were taken only initially and finally after 4 hr of circulation. After collecting the sample by either method, the frozen mixture was melted, the trap was thoroughly shaken to hydrolyze the plutonium hexafluoride and uranium hexafluoride, and the resulting solution was analyzed for uranium and plutonium.

The solids deposited in the decomposition vessels were completely dissolved for an analysis of their uranium and plutonium contents. The vessels were cut into pieces and immersed together with the nickel wool packing in a solution of aluminum nitrate and nitric acid. The nickel wool was completely dissolved and the other parts of the vessels were thoroughly etched by the solution. In some experiments the resulting solution contained some suspended solid, which was filtered off. To determine whether this solid contained any uranium or plutonium, the solid was dried at room temperature and examined with an X-ray spectrometer. The major constituent was a nickel compound, and the presence of neither uranium nor plutonium was detected. It was assumed, therefore, that the clear filtrate contained all of the uranium and plutonium deposited in the decomposition vessel. The solution was analyzed for uranium and plutonium.

In evaluating the results of the separation experiments, the most important things to consider are the concentration of uranium in the plutonium tetrafluoride deposited, the rate of decrease of the ratio of plutonium to uranium in the gas phase, and the minimum ratio of plutonium to uranium obtained in the gas phase.

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

Table 23

SEPARATION OF GASEOUS MIXTURE OF URANIUM HEXAFLUORIDE AND PLUTONIUM HEXAFLUORIDE BY THERMAL DECOMPOSITION

Mixtures were circulated through nickel vessels (2-inch dia., 2-inch length) packed with nickel wool.
Initial partial pressures of the constituents of the gas were: UF_6 , ~90 mm; PuF_6 , ~10 mm; He, ~660 mm.
The total volume of the gas mixture was 9300 ml.

The weight of plutonium was obtained by weighing PuF_4 in the vessel using an analytical balance.

Set I includes run numbers 73, 78 and 86; Set II includes run numbers 129, 120 and 137.

No.	Temp Decomp Vessel (C)	Calc Geometric Internal Surface Area ^a (sq cm)	Circulation Time (hr)	Analysis of Gas Sample			Removal Factor (Pu/U) Initial/ (Pu/U) Final	Wt Pu Initially in Vessel as PuF_4 (g)	Analysis of Solids Deposited From Gas Mixture		
				Wt U (mg)	Wt Pu (mg)	Ratio (Pu/U)			Wt Pu Deposited (g)	Wt U ^c Deposited (g)	Percentage U ^d in Solid
73 ^b	150 ± 3	1.6×10^3	0	34.9	3.3	9.4×10^{-2}		2.95			
73	150 ± 3		1.25	45.1	3.96	8.78×10^{-2}					
73	150 ± 3		5	37.6	2.22	5.90×10^{-2}					
73	150 ± 3		10	30.6	0.76	2.5×10^{-2}	3.76				
78 ^b	195 ± 4	1.6×10^3	0	38.2	2.62	6.86×10^{-2}		3.67			
78	195 ± 4		0.5	40.9	0.47	1.2×10^{-2}					
78	195 ± 4		1.25	37.0	9.39×10^{-3}	25×10^{-5}					
78	195 ± 4		5	52.8	2.4×10^{-3}	4.5×10^{-5}					
78	195 ± 4		10	49.9	3.1×10^{-3}	6.2×10^{-5}	1.1×10^3				
86 ^b	292 ± 5	1.6×10^3	0	37.0	2.45	6.62×10^{-2}		4.43			
86	292 ± 5		0.5	39.5	1.4×10^{-3}	3.5×10^{-5}					
86	292 ± 5		1.25	35.7	5.0×10^{-3}	14×10^{-5}					
86	292 ± 5		5	34.7	1.5×10^{-3}	4.3×10^{-5}	0.91×10^3				
86	292 ± 5		10	35.7	2.6×10^{-3}	7.3×10^{-5}					
129	200 ± 4	1.4×10^3	0	429	28.3	6.60×10^{-2}	1.6×10^2	3.13	0.66	0.0044	0.67
129	200 ± 4		4	411	0.164	3.99×10^{-4}					
120	250 ± 5	1.4×10^3	0	440	20.1	4.57×10^{-2}		4.83	0.503	0.0064	1.3
120	250 ± 5		4	404	0.195	4.83×10^{-4}	0.95×10^2				
137	300 ± 5	1.6×10^3	0	445	37.4	8.4×10^{-2}		3.53	0.84	0.0030	0.36
137	300 ± 5		4	406	0.147	3.62×10^{-4}	2.3×10^2				

^aIncludes area of nickel wool.

^bExp 73, 78, 86 done in same vessel - the final solid analyzed was that which accrued from the 3 experiments listed plus a 10-hr unlisted experiment at 250 C.

^cThe weight of uranium was obtained by fluorophotometric analysis.

^dPercentage U = $\frac{(\text{Wt U in solid}) \times 100}{(\text{Wt U in solid}) + (\text{Wt Pu deposited from mixture})}$

Table 23 shows the analysis of the solids deposited. The concentration of uranium in the solids is evaluated by the percentage, defined by

$$\text{Percentage Uranium} = \frac{(\text{wt U in solid}) \times 100}{(\text{wt U in solid}) + (\text{wt Pu deposited from mixture})}$$

The first solid which was analyzed had accumulated during the first 3 experiments listed in Table 23 and also during an unlisted, 10-hr experiment at 250 C. The concentration of uranium in this first solid was 0.7 weight percent. The concentrations of uranium in the solids deposited in the last 3 experiments were of the same order of magnitude, even

though the total time of exposure to uranium hexafluoride vapor was only 4 hr for each experiment as compared with 10 hr in each of 4 experiments carried out in the first vessel. The quantities of uranium deposited in all the vessels were quite small. Since the rate of thermal decomposition of uranium hexafluoride should increase with temperature, the concentration of uranium in the solids should increase regularly with the temperature of deposition. However, Table 23 does not show a regular increase in the concentration of uranium in the solids when the deposition temperatures increased from 200 to 300 C. Probably, the rate of thermal decomposition of uranium hexafluoride is too slow at these temperatures to be readily detected and accurately measured by the techniques of these experiments.

The analyses of the gas phase are also shown in Table 23. The composition of the solids deposited showed that the concentration of uranium hexafluoride in the gas phase remained essentially constant during any experiment. Therefore, the change in the plutonium-to-uranium ratio is a measure of the rate of removal of plutonium from the gas phase. In the graphs of plutonium-to-uranium ratio versus circulation time in Figure 34, the slopes of the curves indicate the rates of plutonium removal. Such curves were not obtained for the second set of experiments, since only initial and final gas analyses were obtained. The removal of plutonium from the gas phase during 4 hr of circulation differed by about a factor of 10 from that obtained in the first set of experiments. This difference might be the result of rate effects. The rate of removal of plutonium from the gas phase is expected to be proportional to the internal surface area of the vessel. Possibly the internal surface area in the vessel and packing used in the first set of experiments was higher than that in the other vessels because of surface roughness. In order to obtain additional information on the minimum ratio of plutonium to uranium obtainable in the gas phase, a set of experiments is being planned similar to the second set reported here except that the total circulation times will be 10 hr rather than 4 hr.

The rate of removal of plutonium from the gas phase at 150 C (No. 73, Figure 34) is probably too slow for process application. The rates of removal at 200 and 300 C, however, were much faster. As indicated in Figure 34, when the vessel was at 300 C, the ratio of plutonium to uranium in the gas reached its minimum limit after the whole gas mixture had cycled through the vessel only about 10 min. The recycle rate was estimated from the total system volume of 9300 ml and the volume flow rate of 800 ml/min. Thus, the whole gas mixture passed through the decomposition vessel every 12 min.

Figure 34

RATIO OF PLUTONIUM TO URANIUM IN
GASEOUS URANIUM HEXAFLUORIDE-
PLUTONIUM HEXAFLUORIDE MIXTURES
AS A FUNCTION OF THE NUMBER OF
TIMES A MIXTURE IS CYCLED
THROUGH A HEATED VESSEL

The average total residence time for the whole gas mixture in the decomposition vessel can be calculated from the total flow time and the ratio of volume of the decomposition vessel to the total volume of the system:

$$\begin{aligned}
 \left(\frac{\text{average residence time of whole sample in vessel}}{\text{sample in vessel}} \right) &= \left(\frac{\text{residence time per cycle}}{\text{per cycle}} \right) (\text{number of cycles}) \\
 &= \frac{(\text{vessel volume})}{(\text{flow rate})} \times \frac{(\text{total flow time})(\text{flow rate})}{(\text{total system volume})} \\
 &= \frac{(\text{vessel volume})(\text{total flow time})}{(\text{total system volume})}.
 \end{aligned}$$

The volume of the decomposition vessel was 100 ml and the total volume of the system was 9300 ml; therefore, the average total residence time is $(100/9300) \times (\text{flow rate}) = (1.1 \times 10^{-2}) \times \text{total flow time}$. Thus, at 300 C (No. 86, Table 23), the ratio of plutonium to uranium in the gas phase had reached its minimum value after a total flow time of about 2 hr, which corresponds to a total average residence time for the whole gas mixture in the decomposition vessel of about $(1.1 \times 10^{-2}) \times (2) = 2.2 \times 10^{-2}$ hr or 1.3 min.

A theoretical limit for the ratio of plutonium to uranium in a plutonium hexafluoride-uranium hexafluoride mixture obtained by circulation of the mixture through a vessel can be calculated from the initial ratio and the equilibrium constant for the reaction $\text{PuF}_4(\text{s}) + \text{F}_2(\text{g}) \rightleftharpoons \text{PuF}_6(\text{g})$ at the temperature of the vessel. For this calculation it is assumed that the change of the ratio of plutonium to uranium in the gas phase is caused by the change in the concentration of plutonium only. This assumption is supported by the low concentration of uranium found in the solid deposited in the decomposition vessels. The theoretical limit is

$$\left(\frac{\text{plutonium}}{\text{uranium}} \right)_{\text{limit}} = \left(\frac{\text{plutonium}}{\text{uranium}} \right)_{\text{initial}} \times \frac{K}{(K + 1)},$$

where K is the equilibrium constant for the reaction.

Equilibrium constants for the reaction were reported in ANL-6101, page 81. From the mean vessel temperatures and their average deviations, the calculated limit of the ratio for the experiment at 200 C (No. 78, Table 23) is $(5.5 \pm 0.7) \times 10^{-5}$ (195 ± 4 C). The experimental value of the minimum ratio agrees with this. It lies somewhere between 4.5×10^{-5} and 6.2×10^{-5} . The calculated limit of the ratio for the experiment at 300 C (No. 86, Table 23) is $(1.55 \pm 0.07) \times 10^{-4}$ (292 ± 5 C). The experimental value of the minimum ratio at 300 C is somewhat lower than this. It lies between 4.3×10^{-5} and 7.3×10^{-5} , which would be characteristic of an equilibrium state at a temperature between 184 and 223 C. This probably indicates that in the experiment at 300 C the plutonium hexafluoride vapor did not reach the temperature of the vessel and packing. The calculated limits of the plutonium-to-uranium ratios may also be compared with the experimental minimum ratios in Figure 34.

It is assumed that the minimum concentrations of plutonium hexafluoride in the uranium hexafluoride vapor is an equilibrium concentration of plutonium hexafluoride in the presence of its decomposition products, plutonium tetrafluoride, and fluorine. Experiments are being planned to determine whether the concentration of plutonium hexafluoride in the uranium hexafluoride can be decreased further by removing the fluorine and recycling the hexafluoride through the hot vessel. The fluorine will be removed by condensing the hexafluorides and evacuating the system.

The experiments reported above have shown that the circulation of gaseous mixtures of uranium hexafluoride and plutonium hexafluoride through nickel vessels at 200 to 300 C reduced the ratios of plutonium to uranium by factors varying between 10^2 and 10^3 . The residence time of the gas in the heated vessel necessary to accomplish this reduction was of the order of one minute. The concentration of uranium in the plutonium, deposited as plutonium tetrafluoride in the vessel, varied from 0.4 to 1.3 percent. Additional experiments are being planned to check the results reported here and also to attempt to reduce further the ratio of plutonium to uranium in the gas mixture.

3. Plutonium Particulate Filtration from Exhaust Systems (R. Kessie, T. Gerding)

The exhaust ventilation air from a facility handling plutonium hexafluoride should be filtered to prevent the discharge of plutonium particles into the atmosphere should an accidental release of plutonium occur within the facility. A program was initiated to determine the efficiencies of filter material which might be used to handle the exhaust ventilation air from this type of facility.

a. Studies of Particle Sizes of Uranium Hexafluoride Hydrolysis Products

In order to develop techniques which might be later used in the plutonium hexafluoride release studies, the behavior of uranium hexafluoride upon hydrolysis was investigated. The investigations involve the development of techniques for particle examination of uranium hexafluoride hydrolysis product.

An electrostatic precipitator, sketched in Figure 35, was used to collect particles formed from the vapor-phase hydrolysis of uranium hexafluoride.

Figure 35

ELECTROSTATIC PRECIPITATOR

The electrostatic precipitator was made from a piece of Lucite tubing $4\frac{1}{2}$ in. long by $2\frac{1}{4}$ -in. diameter. Two holes, located midway between the ends, were drilled through the tube wall directly opposite each other. A single-hole rubber stopper was placed in each end of the unit to provide an entrance and exit for the gas stream. Two rubber stoppers, one holding a brass rod which served as the collection electrode and the other holding a hypodermic needle which served as the discharge electrode, were located in the 2 holes drilled through the tube wall. An 11,000-v potential was applied across the electrodes. Air containing the particulate material from the vapor-phase hydrolysis of uranium hexafluoride was passed through the unit and the sample collected on an electron microscope grid which was covered by a thin carbon film. The grid was located at the end of the collection electrode.

Figures 36 through 39 are photographs taken with an RCA electron microscope. Figure 36 is a sample of clean AEC-type filter medium.

Figure 36

AEC FILTER MEDIUM

(Measurement of fiber diameter from several photographs indicate; 10 percent smaller than $0.029\ \mu$, 10 percent larger than $3.3\ \mu$. Median diameter $0.31\ \mu$. Calculated average fiber diameter $1.5\ \mu$).

4,200X

2.3 μ

Figure 37

PARTICLES FROM THE VAPOR-PHASE HYDROLYSIS
OF URANIUM HEXAFLUORIDE COLLECTED
BY AEC FILTER MEDIUM

(Particle size range 0.1 to 0.007 μ .)

48,000X

0.2 μ

Figure 38

PARTICLES FROM THE VAPOR-PHASE HYDROLYSIS
OF URANIUM HEXAFLUORIDE COLLECTED
BY THE ELECTROSTATIC PRECIPITATOR

(Particle size range 0.3 to 0.02 μ .)

48,000X

0.2 μ

Figure 39

FILTERED PARTICLES FROM THE VAPOR-PHASE
HYDROLYSIS OF URANIUM HEXAFLUORIDE
COLLECTED BY THE ELECTROSTATIC PRECIPITATOR

(Particles had passed through one AEC filter.
Particle size range 0.05 to 0.01 μ .)

96,000X

0.10 μ

The median value of measurements of the diameters of 181 fibers was 0.31 μ , with one percent smaller than 0.029 μ and one percent greater than 3.3 μ . The average fiber diameter was calculated as 1.5 μ . This picture represents a sample taken from the surface of the filter.

Figure 37 shows particulate matter from the vapor-phase hydrolysis of uranium hexafluoride collected by the AEC filter medium. Figure 38 is the same material collected by the electrostatic precipitator. The samples were collected at the same time by dividing the gas stream so that equal quantities flowed through the filter and the electrostatic precipitator. The particles, excluding agglomerates, collected by the AEC filter medium had a particle size range from 0.1 to 0.07 μ . The sample collected by the electrostatic precipitator had a particle size range from 0.3 to 0.02 μ . There are small particles present in the sample collected by the electrostatic precipitator which are not apparent in the material collected by the filter. This suggests the possibility that some fine material had passed through the AEC filter medium. Figure 39

was made from a sample of the particles formed by the vapor-phase hydrolysis of uranium hexafluoride collected by the electrostatic precipitator after passing through one AEC filter. These particles had a size range from 0.05 to 0.01 μ .

b. Filter Experiments with Plutonium Hexafluoride and Its Hydrolysis Products

Particle penetration data were obtained from experiments in which small-scale controlled releases of plutonium hexafluoride, 25 mg or less, were made into an atmosphere of known moisture content. A miniature motor-driven fan was located in the mixing chamber to insure complete mixing of the gases therein. Air mixtures were passed through 2 or more AEC filters, a water bubbler, and 2 Millipore filters in series at a controlled flow rate. Gamma and/or alpha counts of the filters and bubbler were used to determine penetration for individual and combinations of filters. Each filter sample had an area of 8.6 sq cm exposed to the gas stream. A more detailed description of the equipment and experimental procedures have been reported previously (see ANL-6477, pages 113 to 115).

The particles used to determine filter efficiency were obtained from the vapor-phase hydrolysis of plutonium hexafluoride. If there had not been sufficient water vapor to hydrolyze completely the quantity of plutonium hexafluoride released, then any unhydrolyzed plutonium hexafluoride could have passed through the filters as a gas.

An initial mole ratio of plutonium hexafluoride to water was calculated by assuming complete and rapid gas mixing within the mixing chamber. In this series of experiments the mole ratio of plutonium hexafluoride to water vapor was varied from 0.021 to 2.76. All of the plutonium hexafluoride hydrolysis product formed does not reach the filters due to plating of some of the products on the release chamber wall and fan blade.

The data from a series of release experiments with plutonium hexafluoride to determine particle-penetration characteristics of an AEC filter medium are presented in Table 24. In Experiments 5 through 13 the gases were mixed by the mechanical stirrer in the mixing chamber; the gases in others were mixed by natural flow.

The penetrations of the filters were calculated from activity collected on the filters and on subsequent filters, with the assumption that penetration of the last filter is not significant. The final 2 filters of the filter series were Millipore membrane filters. These are absolute-type filters and display excellent collection characteristics for a wide range of particle sizes. The penetration was calculated by taking the

counts which were collected downstream of any particular filter divided by the counts collected on this particular filter plus counts collected downstream on subsequent filters and in the bubbler solution. The filter penetrations were calculated based on the total gamma and/or alpha activity detected on the filters and in bubbler solution. In those instances in which the quantity of plutonium on a filter was low, the sample was alpha counted. Alpha counts obtained from these low-level samples were converted to gamma counts by means of an experimentally determined alpha-to-gamma count ratio of 450. Penetrations were as low as 0.0002 percent for a single AEC filter and 0.0001 percent for 2 AEC filters in series. However, when the mole ratio of plutonium hexafluoride to water was high, 2.66, a single AEC filter had a penetration of 59 percent and 2 AEC filters in series had a penetration of 28 percent. The higher penetrations occurred when there was an excess of plutonium hexafluoride over the water available for the hydrolysis and may be due to gaseous unhydrolyzed plutonium hexafluoride passing through the filters.

Table 24
FILTRATION RESULTS FROM PLUTONIUM HEXAFLUORIDE RELEASE

				Air Velocity at Filter: 0.97 cm/sec				
				Mixing Chamber Volume: 385 ml				
				Air Flow Rate: 0.5 liter/min				
				Area of Filter: 8.6 sq cm				
Exp No.	Humidity (mg H ₂ O/l)	Wt PuF ₆ Released (mg) ^c	($\frac{\text{PuF}_6}{\text{H}_2\text{O}}$) ^a (mole)	γ cpm on 1st AEC Filter	γ cpm Beyond 1st AEC Filter	% Penetration 1st AEC Filter ^e	γ cpm Beyond 2nd AEC Filter	% Penetration 1st and 2nd AEC Filters ^e
PR-4 ^b	9.5	1.5	0.021	1.51×10^4	0.078 ^d	0.00052	-	-
PR-2 ^b	8.2	10.4	0.174	1.39×10^5	0.21 ^d	0.00015	0.087 ^d	0.000063
PR-13	1.61	2.9	0.239	1.73×10^4	2.5 ^d	0.015	0.44 ^d	0.0025
PR-11	1.91	4.2	0.291	3.24×10^4	0.17 ^d	0.0005	0.056 ^d	0.00017
PR-7	1.68	13.9	1.10	4.15×10^5	2.2×10^5	35	2.4×10^3	0.37
PR-9	1.41	12.0	1.13	3.66×10^5	2.9×10^4	7.5	48	0.012
PR-10	1.54	14.7	1.26	4.12×10^5	4.6×10^4	10	5.3×10^2	0.095
PR-5	1.08	23.1	1.42	5.77×10^5	2.9×10^5	34	5.6×10^3	0.64
PR-12	1.08	20.9	2.56	4.70×10^5	4.6×10^5	49	9.9×10^4	11
PR-8	1.24	24.9	2.66	5.56×10^5	9.0×10^5	59	3.8×10^5	28
PR-6	0.896	18.7	2.76	4.64×10^5	6.4×10^5	58	1.7×10^5	16

^aCalculated on the basis of initial moisture content of air in the mixing chamber and the quantity of plutonium hexafluoride released.

^bExperiments 2 and 4 had natural mixing of gases; the others had mechanical stirring.

^cAll of the material released does not reach the filters due to plating of some of the hydrolysis product in the mixing chamber.

^dConverted to gamma count from alpha count based on an alpha-to-gamma count ratio of 450.

$$\% \text{ penetration} = \frac{100 [\text{counts past filter(s)}]}{(\text{counts past filter(s)}) + [\text{counts on filter(s)}]}$$

The data from Table 24 have been used in Figure 40 to show the relationship of percent penetration to mole ratio of plutonium hexafluoride to water. The plot indicates that in the range of low mole ratios, <0.5, the penetration was very small, <0.01 percent, but as the mole ratio value increased there was a sharp rise to higher penetrations, >10 percent.

Figure 40
PENETRATION OF AEC FILTER
MEDIUM BY HYDROLYZED
PLUTONIUM HEXAFLUORIDE

Under experimental conditions of high ratios of plutonium hexafluoride to water vapor, plutonium has passed through filter material of the same type as used in the Chemical Engineering Division plutonium facilities. However, it should be emphasized that these conditions are extreme and would not be encountered in our laboratory work. Thus, in the event of an accidental release of a small amount (10 to 15 g) of plutonium hexafluoride, it can be expected that the filters used in the plutonium facilities would prevent discharge of plutonium to the atmosphere.

Work will be continued to obtain more penetration data for a few other filter media. The particle size distribution of plutonium hexafluoride hydrolysis particles generated under varied conditions will be obtained by electron microscopy.

B. Engineering-scale Investigations of Fluoride Volatility Processes (A. A. Jonke)

1. Direct Fluorination of Uranium Dioxide Fuel
(W. J. Mecham, J. D. Gabor, L. Anastasia, J. Wehrle,
R. Kinzler, A. Rashinskas)

The engineering-scale studies of the direct fluorination of uranium dioxide fuel has been directed toward optimization of process conditions for the complete fluorination of batches of fuel pellets in a single step to form uranium hexafluoride product. The rate of

fluorination is rapid but is readily controlled by the rate at which fluorine is introduced. The fluorination rate in practice is limited by the rate of heat transfer rather than by the chemical kinetics of the system. Fluidization of inert Alundum grain in the voids of the pellet bed has been used as an aid to heat transfer. Evaluation of conditions for the fluorination of uranium dioxide has been chiefly considered in terms of batch fluorination time, efficiency of fluorine utilization, temperature control, and freedom from caking. Experiments have been conducted in an air-cooled, 3-in.-diameter nickel fluorinator.

In a preliminary series of runs (see ANL-6379, pages 159 to 171; ANL-6413, pages 118 to 121; ANL-6477, pages 133 to 136), generally satisfactory fluorinations were carried out with 6-in.-deep pellet beds. In these runs, charges of approximately 4.5 kg of uranium dioxide pellets were fluorinated at 400 to 500 C at total gas rates of about 0.7 cfm (1 atm, 20 C). The shortest fluorination time (7 hr) and the highest overall fluorine efficiency (82 percent) were obtained with input fluorine dilution provided by recycle of process off-gas. In this recycle scheme, the presence of oxygen in the recycle product gas had a pronounced effect on promoting the reactivity of the uranium-bearing solids in the reactor. The mechanism of the oxygen effect appeared to involve the formation of U_3O_8 solid fines. For the gas recycle runs with 6-in.-deep pellet beds, no serious problem with caking appeared even with the relatively high oxygen concentrations in the recycled gas. In later runs with the 18-in. pellet beds, however, caking appeared to accompany high concentrations of oxygen in the recycle gas.

In other experiments, also previously reported, it was found that the reaction of the uranium dioxide pellets was rapid with oxygen-nitrogen mixtures above 400 C. Three-inch-deep pellet beds (about 2 kg uranium dioxide) were virtually completely oxidized in 4 hr at 500 C and 1.3 hr at 600 C. The fine U_3O_8 powder produced in these oxidations appeared very reactive toward subsequent fluorination but was difficult to handle because of caking tendencies. This result confirmed the previously noted effect of oxygen in fluorinations. It also pointed out possible difficulties with caking under the condition of higher concentration of product oxygen in the reactor that would occur with the fluorination of deeper pellet beds, particularly with the use of off-gas recycle.

Because of the practical desirability of using deeper beds, a series of runs was undertaken using 18-in. pellet beds (about 13 kg uranium dioxide). In the initial deep-bed pellet fluorination (reported in ANL-6477, pages 141 to 142), the expected appearance of caking was encountered with the use of the total off-gas recycle scheme as applied previously without difficulty to the 6-in. beds. In a second run (UOF-50), a fluorine-nitrogen gas mixture was used without recycle and the fluorination was carried

to completion without caking. This batch run required 30 hr and the overall fluorine efficiency was 37 percent. For economic reasons, this fluorine efficiency is not considered satisfactory for plant application.

The series of deep-bed runs was continued in the present period with fluorinations of pellet batches carried to completion using 2 different procedures. In one run (UOF-53), a modified gas recycle scheme was used, in which nitrogen was introduced with make-up fluorine. The nitrogen addition was designed to dilute the recycle gas and limit the concentration of oxygen recycled to the reactor. Somewhat higher total gas rates were used to favor good mixing and fluidization. The chief aim in this run was the demonstration of high fluorination rates and efficiencies. This run achieved a high fluorination rate and efficiency, but the elimination of caking was not attained. The economic advantages of a recycle scheme is evident, but further improvement of conditions is required with respect to caking.

Another deep-bed run (UOF-52) was carried to completion without gas recycle but with the introduction of a predetermined amount of oxygen. No caking was encountered. During a major part of the run, an improved fluorination rate was obtained relative to the period in the previously reported nonrecycle run (UOF-50), which involved no oxygen introduction. However, the overall fluorination rate and efficiency was not improved in Run UOF-52, probably due to the higher total gas rate and shorter gas residence time in the reactor. However, the conditions that eliminated caking in this run should serve as a guide for planning subsequent runs.

Analysis of a Gas Recycle Applied to the Direct Fluorination Process

In order to describe quantitatively the operation of the gas recycle scheme in general and to assist in the planning and interpretation of experiments, the following mathematical analysis was developed.

In Figure 41 are shown the process gas streams, their molar flow rates, and compositions in the gas recycle system under consideration for the direct fluorination of uranium dioxide pellets. The quantities used are defined below:

- a = fluorine entering system, mol/hr
- b = nitrogen entering system, mol/hr
- c = recycle gas stream, mol/hr
- d = uranium hexafluoride collection rate, mol/hr
- x = mol fraction fluorine in waste gas

y = mol fraction nitrogen in waste gas

z = mol fraction oxygen in waste gas

E = fluorine overall efficiency

$$= \frac{[(\text{fluorine entering system} - \text{fluorine leaving system}) / \text{fluorine entering system}]$$

E' = fluorine reactor efficiency

$$= \frac{[(\text{fluorine entering reactor} - \text{fluorine leaving reactor}) / \text{fluorine entering reactor}]$$

Figure 41

FLOW SCHEMATIC FOR RECYCLE SYSTEMS

^{*}This equality applies at steady state.

The flow quantities and compositions shown in the figure are for the general case in which the measured quantities are the gas additions (a, b, and c), the uranium hexafluoride product collection (d), and the waste gas composition (x,y,z). These conditions completely determine all gas flows, compositions, and reaction efficiencies.

In addition to the 3 reactions given in Figure 41, other reactions occur, namely,

The product, uranyl fluoride, tends to form fines in the system. Moderate amounts of these fines are considered desirable with respect to enhancing the reactivity and, therefore, the fluorine efficiency. However, large amounts of fines (either of UO_2F_2 or of U_3O_8) tend to produce caking and are undesirable. The chief aim of developing a system for close control of reactant gases is to optimize conditions favoring a moderate and constant level of concentration of the fines in the reactor. A satisfactory level of fines would be considered to be one in which the uranium hexafluoride production rate and the overall fluorine efficiency were high and the fines held below the concentration that would cause caking.

Under satisfactory conditions a steady state would be established with respect to fines formation: that is, the rate of formation of fines would equal the rate of removal of fines by formation of uranium hexafluoride vapor. Under such steady-state conditions, the overall fluorine efficiency is given by

$$E = 1 - x\left(\frac{c}{a} + \frac{b}{ay}\right)$$

and by

$$E = \frac{3d}{a}$$

In the nonsteady case of increase or decrease of the amount of fines, the 2 equations are not identical, and the fines accumulation would be calculated from the difference.

A similar condition holds for the reactor fluorine efficiency, for which the 2 equations are

$$E' = \frac{1 - \left(\frac{b}{a}\right)\left(\frac{x}{y}\right)}{1 + x\left(\frac{c}{a}\right)}$$

and

$$E' = \frac{3\left(\frac{d}{a}\right)}{1 + x\left(\frac{c}{a}\right)}$$

The nonsteady-state accumulation of oxides in the reactor can be measured in terms of reactor oxygen efficiency, defined as

$$E'_0 = [(\text{oxygen entering reactor} + \text{oxygen generated} - \text{oxygen leaving reactor}) / (\text{oxygen entering reactor} + \text{oxygen generated})].$$

In quantities defined above

$$E'_0 = \frac{d - z\left(\frac{b}{y}\right)}{zc + d}$$

The reason for using a recycle system is to improve fluorine economy through high overall fluorine efficiency. The improvement possible by recycle can be shown by comparing the "once-through" fluorine reactor efficiency (E') with the "recycle" fluorine overall efficiency (E). By the material balance shown in Figure 41, the following equation relates these 2 efficiencies at steady state:

$$E^2 - E \left[\left(\frac{3}{2} \frac{c}{a} + 1 \right) E' + \left(\frac{3}{2} \right) \left(\frac{b}{a} + 1 \right) \right] + \frac{3}{2} E' \left(\frac{c}{a} + \frac{b}{a} + 1 \right) = 0.$$

By the usual method of solving a quadratic equation, E may be found explicitly:

$$E = \left(\frac{3}{2} \frac{c}{a} + 1 \right) \frac{E'}{2} + \left(\frac{3}{4} \right) \left(\frac{b}{a} + 1 \right) \pm \frac{1}{2} \sqrt{(E')^2 \left(\frac{3}{2} \frac{c}{a} + 1 \right)^2 + 3E' \left[\frac{b}{a} \left(\frac{3}{2} \frac{c}{a} - 1 \right) - \left(\frac{c}{2a} + 1 \right) \right] + \frac{9}{4} \left(\frac{b}{a} + 1 \right)^2}$$

An illustration of the relation of E to E' for typical cases is shown in Table 25. These values show that higher recycle ratios (c/a) and lower nitrogen dilution factor (b/a) favor fluorine economy.

Run UOF-53

An additional run (UOF-53) was made in the present series of deep-bed pellet batch fluorinations to determine the overall performance of a modified gas-recycle scheme. Previous recycle runs showed the effectiveness of gas recycle in attaining high fluorination rates and

efficiencies, but also showed a tendency toward serious caking, which is probably due to the formation of fines caused by the relatively high concentrations of oxygen in the recycle gas. In the modified recycle scheme which was used in this run, nitrogen was introduced during the run along with fluorine, so that maximum concentrations of all reactive gases were reduced, relative to the case of gas recycle without nitrogen addition. A flow diagram is shown in Figure 41, which gives the various process gas streams and shows their quantitative relationships.

Table 25

CALCULATED GAIN IN FLUORINE EFFICIENCY FOR
TYPICAL CASES OF GAS RECYCLE OPERATION

Gas Recycle Ratio $\left(\frac{c}{a}\right)$	Nitrogen Dilution Factor $\left(\frac{b}{a}\right)$	Fluorine Reactor Efficiency (E')	Fluorine Overall Efficiency (E)	Gain ^a in Fluorine Efficiency (%)
2	1	0.50	0.697	20
2	2	0.50	0.575	7.5
4	2	0.50	0.72	22
4	4	0.50	0.70	20
8	4	0.50	0.74	24
8	6	0.50	0.69	19
8	2	0.33	0.68	35
8	2	0.50	0.81	31
8	2	0.67	0.90	23
0 (no recycle)	$\frac{b}{a} \geq 0$	0.50	0.50	0

^aOverall fluorine efficiency - fluorine reactor efficiency.

The charge in Run UOF-53 consisted of 13.2 kg of $\frac{1}{2}$ -in.-diameter x $\frac{1}{2}$ -in.-long uranium dioxide pellets and 3.3 kg of type 38 refractory grain Alundum. The weight ratio of Alundum to pellets was 0.25, corresponding to a layer of Alundum of 3 in. over the uranium dioxide pellets under static conditions and about 6 in. over the uranium dioxide pellets under operating conditions. This weight ratio is the current flow-sheet value, which is also being used in current laboratory fluorination experiments on the removal of plutonium from Alundum-fission product mixtures.

The temperature in this run was set at 500 C by means of a control thermocouple located in a vertical thermowell at distances of from 2.5 to 6.5 in. above the pellet support plate. The pellet support plate was

located 1.25 in. above the conical gas distributor or 4.25 in. above the bottom of the reactor. External heating was used to maintain reactor temperature, and no forced air cooling was required during the run.

Nitrogen was introduced throughout the major part of the run to control the concentration of fluorine and to limit the accumulation of oxygen in the system, with the aim of maintaining conditions favoring good temperature control and elimination of caking problems. The overall fluorine efficiency of 77 percent was the best thus far obtained in the series of deep-bed pellet fluorinations. High rates of uranium hexafluoride production at about 1000 to 1500 g/hr were also achieved and maintained for a period of 9 hr, or about 40 percent of total run time. However, the heat transfer conditions achieved were not satisfactory. During the high-rate period, temperature control was difficult to maintain and, toward the end of this period, a partial caking of the bed occurred.

At the start of the run, the column was brought to operating temperature under full gas recycle with nitrogen as the fluidizing gas. The recycle pump rate was set at 0.7 cfm and nitrogen input to the reactor was 0.12 cfm for a fluidizing velocity of 0.7 ft/sec. Initially, fluorine was introduced at a rate of 0.125 cfm. Reactor temperatures were uniform during the startup period. After a period of about 1 hr, however, the bare-wire thermocouple indicated an abrupt rise in temperature followed by a stabilization at 600 C. The fluorination rate was maintained under these conditions. In Figure 42 input fluorine and nitrogen rates are shown. Also, the uranium hexafluoride and oxygen produced by the fluorination of uranium dioxide are shown. The relation of these rates determines the gas composition. During the high rates of fluorine input, the nitrogen-to-fluorine ratio introduced to the reactor was approximately 1, and the superficial fluidizing velocity was about 1 ft/sec. Satisfactory fluorination rates are reflected both in the total time required to complete the fluorination and the uranium hexafluoride collection rates, shown in Figure 43. Previous deep-bed fluorinations were completed in about 30 hr of operation; Run UOF-53 was completed (96 percent of the pellet charge fluorinated) in 22.3 hr. Uranium hexafluoride collection began almost immediately in this run (345 g/hr in the first 15 min), whereas in previous runs about 2 hr of operation were required to obtain rates in excess of 300 g/hr. The rates shown in Figure 43 can be classified into 3 separate periods: a moderate production period with an average rate of 540 g uranium hexafluoride/hr for the first 9 hr of operation; a high-rate period averaging 1280 g uranium hexafluoride/hr from the ninth through seventeenth hour, and a low rate period of 170 g uranium hexafluoride/hr for the final 5 hr.

The course of the run is also shown in the curves of Figure 44 as the cumulative moles of fluorine added and uranium hexafluoride collected. The ratios of the slopes of these curves give the fluorine efficiency to form

uranium hexafluoride collected during the run. For the moderate, high, and low uranium hexafluoride production periods, this overall efficiency was 77, 87, and 48 percent, respectively.

Figure 42

AVERAGE NITROGEN AND FLUORINE INPUT RATES
AND URANIUM HEXAFLUORIDE
COLLECTION RATES - UOF-53

Conditions:

3-in. Finned Reactor with Gas Recycle

Temperature: 500 C

UO₂ Pellet Bed Charge: 18 in.Fluidizing Velocity: ≥ 0.8 ft/sec

Total Recycle Gas Rate: 0.7 cfm

Figure 43
URANIUM HEXAFLUORIDE PRODUCT
COLLECTION DURING
RUN UOF-53

Conditions:

3-in. Finned Reactor with Gas Recycle
Temperature: 500 C
UO₂ Pellet Bed: 18 in.
Fluidizing Velocity: ≥ 0.8 ft/sec

Figure 44
FLUORINE INPUT AND URANIUM
HEXAFLUORIDE COLLECTED IN
RUN UOF-53

Conditions:

3-in. Finned Reactor with Gas Recycle
Temperature: 500 C
UO₂ Pellet Bed: 18 in.
Fluidizing Velocity: ≥ 0.8 ft/sec

The uranium material balance for Run UOF-53, shown in Table 26, shows that 11.18 kg of the original 11.64 kg uranium charged to the reactor was collected as the hexafluoride in the condenser and in a secondary cold trap on the waste-gas line, for a uranium material balance of 95.8 percent. Analysis of the waste-gas grab samples showed that, in most of the 15 samples taken, only trace quantities (<0.01 percent) of uranium hexafluoride passed through the coil-trap in the waste-gas line. The maximum uranium hexafluoride detected was contained in the

gas sample taken during the 21st hour of operation, and this amounted to 0.06 percent uranium hexafluoride. Hence, very little uranium was lost from the system in the waste gas. The weight of Alundum recovered from the reactor exceeded that charged by 640 g, and it is assumed that the 460 g of uranium not accounted for had remained in the column.

Table 26

URANIUM MATERIAL BALANCE FOR RUN UOF-53

<u>IN</u>				
Pellet Charge	13,214 g (100 w/o UO_2)	$\times \frac{238}{270} =$	$\frac{\text{Uranium (g)}}{11,640}$	
Alundum Charge	3,470 g			
<u>OUT</u>				
UF ₆ Collected				
Condenser	16,391 g			
Secondary Cold Trap	<u>145 g</u>			
		$16,536 \times 238/352 =$	11,180	
	Net Uranium Not Accounted For		460	
	Uranium Material Balance (%)		<u>95.8</u>	
Alundum + Uranium Compounds Recovered 4110 g				
	Less Alundum Charge	<u>3470 g</u>		
	Net Weight g	640 g		

Upon completion of the run, it was observed that about 60 percent of the solids in the reactor had caked. There were 2 distinct and approximately equal portions in the caked material. One portion was hard and nonporous while the other was a soft, porous material. The harder cake was located relatively high in the bed, about 15 in. above the bottom flange and apparently contained most of the uranium remaining in the reactor as evidenced by areas of various colors (brown, red, orange, yellow, and black), which were attributed to compounds of uranium. This portion of the bed formed a cake during the 15th hour of operation or just after the maximum production rate of 1500 g uranium hexafluoride/hr was achieved. At that time, reactor skin temperatures at the elevation where the cake was found (15 to 25 in. above the bottom flange) increased from about 500 to 600 C. This marked an abrupt increase in the column temperature gradient due to poorer heat transfer. Fluidization pressure drop was not impaired and high production rates continued into the 17th hour of operation.

The second, softer portion of the cake is believed to have formed after 18.7 hr of operation when the pressure drop across the bed dropped to zero. At this time only about 8 percent of the uranium was left in the reactor. During the preceding hour, the hexafluoride production rate had dropped below 100 g/hr and then ceased. External heating and fluorine concentration was increased in an effort to complete the fluorination. A decision was then made to add oxygen to the fluorine; five minutes after oxygen was started, the bed formed the soft porous cake.

The conditions selected for this run were not satisfactory in avoiding caking, even though the fluorination was carried virtually to completion. However, in another run made in this period (UOF-52), an 18-in.-deep pellet bed was completely fluorinated without caking under nonrecycle conditions but with oxygen addition. Using the mathematical analysis of recycle operation given above, it is planned in future runs to adjust gas flows with the aim of eliminating caking conditions while retaining the higher fluorine efficiencies of recycle operation.

UOF-52: Deep-bed Fluorination

The third run in the series of deep-bed fluorinations in the finned reactor (18 in. of pellets) was carried to completion in 31.2 hr. The objective of this run was to demonstrate the operating conditions needed for good temperature control and for elimination of caking problems. This objective was fulfilled since temperature control was satisfactory at 490 ± 10 C and there was a complete absence of the caking problems which were previously encountered in deep-bed fluorinations. However, the overall fluorine efficiency suffered and was low (29.4 percent). The temperature-control thermocouple was located 1.5 in. above the pellet-support plate, which in turn was located 13 in. above the conical gas distributor and inlet. External heating was used to supplement the heat of reaction and no forced air cooling was required. Although this run was made without gas recycle, oxygen was introduced at a concentration of 2 to 7 percent for about half the run.

Some improvement in uranium hexafluoride production rates was also achieved, as compared with those of the previous experiment (UOF-50; see ANL-6477, pages 140 to 143). A production rate >600 g uranium hexafluoride/hr was maintained for about the first two-thirds of the run, with a maximum rate of 1530 g/hr attained during the 16th hour of operation. During Run UOF-50, a maximum production rate of 1330 g/hr, was achieved, and the high rate period did not occur until the latter part of the run.

For Run UOF-52, the reactor was charged with 13.2 kg of $\frac{1}{2} \times \frac{1}{2}$ -in. uranium dioxide pellets and 3.8 kg of type 38 refractory grain

Alundum. This weight of Alundum was sufficient to cover 9 in. of the pellet bed under static conditions and to cover fully the pellets under operating conditions. For this run, recrystallized alumina chips were not used between the pellets and the pellet-support plate; since it was thought that sufficient Alundum (13 in.) was present below the plate to eliminate any problems with fines and pieces of pellets dropping through the support plate. The column was brought to operating temperature by means of the external heaters and the use of nitrogen as the fluidizing gas. At operating temperature, the fluidizing velocity due to the nitrogen alone was 0.6 ft/sec; this flow of nitrogen was kept constant except for 2 periods when the system was put on recycle. The total fluidizing velocity approached 1 ft/sec.

In order to establish steady-state conditions quickly and safely, fluorine was carefully introduced initially at a rate of 3 cfh (cu ft/hr at 1 atm, 25 C) and was gradually increased to a maximum of 22 cfh during the first 10 hr. At maximum input rate, fluorine accounted for approximately 30 percent of the total gas flow. For a major portion of the run, fluorine input was relatively constant at 25 to 30 percent of total gas input. The rate of fluorine introduction for the entire run is shown in Figure 45.

Another difference from the previous deep-bed fluorination (Run 50) was the introduction of oxygen to the reactor in Run 52 for about half the period of operation. Oxygen input varied from a low of 2.3 to a maximum of 6.6 percent of total gas input. The lower level of oxygen input was used from about the 6th through the 13th hour of operation, and the high range from the 14th to the 22nd hour of operation (see Figure 45). The effect of oxygen introduction is shown in the uranium hexafluoride collection rates indicated in Figure 45. During the early portion of the run, the hexafluoride collection rate gradually increased to a maximum of 720 g/hr (5.5 hr). During the 6th hour of operation, oxygen was added to the reactant gases and the uranium hexafluoride rate increased to 1000 g/hr. Shortly after this rate was achieved, oxygen was shut off and the collection rate quickly dropped to 490 g/hr. When oxygen was again introduced, the uranium hexafluoride rate increased to 775 g/hr. A maximum collection rate of 1530 g uranium hexafluoride/hr was reached midway during the run. After this maximum rate was achieved, the rate dropped to 315 g/hr in 4 hr. At this point, 80 percent of the pellet charge had been reacted. The system was then put on recycle and a brief period of improved collection rates resulted. Two hours after recycle was begun, the control temperature suddenly increased to 610 C. Following this increase, control temperature was very sensitive to fluorine introduction, and remained so, even though the system was taken off recycle. During this period (Run time 25 to 28 hr), the control temperature varied between 450 and 545 C. At this point in the run, a sample of the Alundum bed was taken and submitted for uranium analysis. The sample contained 6 weight percent uranium, which indicates that the difficulty with temperature

control was probably due to the presence of a large amount of fines in the bed, resulting from high oxygen concentrations during the total recycle operation. Partial recycle such as used in Run UOF-53 would probably have been more satisfactory.

Figure 45

FLUORINE INPUT RATE AND URANIUM HEXAFLUORIDE PRODUCT COLLECTION DURING RUN UOF-52

3-in. finned reactor
UO₂ pellet bed: 18 in.

Temperature: 490 C
Fluidizing velocity: >0.6 ft/sec

The reactor was shut down and the fluorination resumed on the following day; no further control difficulties were experienced. The run was concluded with the system on recycle for the last $\frac{1}{4}$ hr of operation.

The Alundum removed from the reactor was freely flowing. It contained several small pieces of pellets which were similar in shape to the pellets charged but much smaller in size ($\leq \frac{1}{8}$ in.). The total weight of these pieces was 9 g. The concentration of uranium remaining in the Alundum bed was 0.13 weight percent accounting for a total of 5 g of uranium. The interior sections of the reactor appeared to be free of uranium oxides and intermediate fluorides. A light coating of fines ($\sim \frac{1}{32}$ in. thick) was visible on the column filters. Thus, it appears that the reactor was thoroughly stripped of its uranium charge during the run.

The total moles of fluorine introduced and the total moles of uranium hexafluoride collected are shown in Figure 46 as a function of run time. The slopes of these curves have been used to calculate the fluorine efficiency in forming uranium hexafluoride during the run; these efficiencies are shown in Figure 47. The points shown in Figure 47 are average efficiencies during each hour of operation and are connected by straight lines for illustrative purposes. Except for periods of unstable operation (i.e., the first hour of operation and one recycle period, the 25th hour), these efficiencies ranged from 11 to 56 percent. The overall fluorine efficiency for the run as a whole was 29.4 percent. Since no gas recycle was used, the overall efficiency and the reactor efficiency are identical in this run.

Figure 46

FLUORINE INPUT AND URANIUM HEXAFLUORIDE COLLECTION IN RUN UOF-52

Figure 47

FLUORINE EFFICIENCY TO FORM URANIUM HEXAFLUORIDE IN RUN UOF-52

3-in. finned reactor

Temperature: 490 C

UO₂ pellet bed height: 18 in.

Fluidizing velocity: ≥ 0.6 ft/sec

No recycle except as shown

The uranium material balance for this run is shown in Table 27. There were 13,200 g of pellets charged to the reactor; under the assumption that the pellets were 100 percent uranium dioxide, the total uranium charged into the reactor was 11,642 g. The uranium accounted for in the product collection, pellet remains, and Alundum amounted to 11,296 g, for a total material balance of 96.9 percent.

Table 27

URANIUM MATERIAL BALANCE FOR RUN UOF-52

IN		
Pellet Charge	$13,200 \text{ g (100 w/o UO}_2) \times \frac{238}{270}$	$= \frac{\text{Uranium (g)}}{11,642}$
OUT		
UF ₆ Collected		
Condenser	11,664	
Secondary Cold Trap (Recycle)	25	
	$16,689 \times 238/352$	$= 11,282$
Pellet Remains	$9 \text{ g (100 w/o UO}_2)$	$= 8$
Bed Samples	14 g (6 w/o U)	$= 0.8$
Alundum	$3788 \text{ g (0.128 w/o U)}$	$= 5$
	Total	11,296
	Net uranium not directly accountable ^a	346
	Uranium material balance (%)	96.9

^aIncludes condenser losses.

An additional amount of uranium can be accounted for in the process off-gas by use of the data obtained from analysis of the off-gas grab samples and an overall gas material balance. The uranium contained in the gas samples was relatively constant and averaged 10.9 mg uranium per liter of gas (1 atm 25 C). On the basis of 1680 cu ft of total process off-gas, the uranium loss in this stream would amount to about 500 g, which, when added to the uranium accounted for previously, gives a total uranium material balance of 101 percent. In actual practice, the uranium would be recovered from the off-gas not recycled by use of a secondary condenser.

The overall product collections in the previous deep-bed fluorination, Run UOF-50, and Run UOF-52 are compared in Figure 48. In general, uranium hexafluoride collection rates were higher and more uniform in Run UOF-52; this was probably due to a slightly higher and more uniform temperature of operation with a consequent uniform rate of fluorine introduction and also the use of oxygen to improve the production rate. The lower overall fluorine efficiency in Run UOF-52 (29.4 as compared with 36.8 percent) may have resulted from the more constant rate of fluorine introduction which increased the fluidizing velocity and hence decreased the fluorine residence time in the reaction zone. It is expected that recycle of reactant gases should increase fluorination rates and fluorine efficiencies to more desirable levels. It is planned to continue deep-bed runs with the objective of process optimization.

Figure 48

COMPARISON OF URANIUM HEXAFLUORIDE COLLECTION
RATES IN TWO DEEP-BED URANIUM DIOXIDE
PELLET FLUORINATIONS

3-in. finned tube reactor

UO₂ pellet bed height: 18 in.

	UOF-50	UOF-52
Temperature (C):	450	490
Fluidizing Velocity (ft/sec):	≥ 0.5	≥ 0.6

2. Plutonium-handling Facility (G. J. Vogel)

A plutonium-handling facility is being constructed so that successful volatility processing techniques developed in laboratory-scale fluorination experiments can be studied on a larger, pilot-plant scale. The facility consists of 2 alpha-containment boxes in which equipment will be installed initially to study variables in the fluorination of uranium-plutonium dioxide pellets. Although the process is to be remotely monitored and controlled, the alpha boxes are to be equipped with glass windows and gloves to allow direct manipulations as required. A critical path analysis was applied to the construction and installation phases of the project in order to aid in planning and in minimizing the time required for the project.

Alpha Boxes

Two alpha boxes, the subsections of which are now being assembled, are of the modular construction used previously by the Chemical Engineering Division. The larger of the two boxes is $17\frac{1}{2}$ ft high, 27 ft long and $3\frac{1}{2}$ ft wide; the smaller is 10 ft high, 13 ft long and $3\frac{1}{2}$ ft wide. The larger box will contain the equipment that regularly handles plutonium and will be located inside an enclosed cell that will be held at a negative pressure relative to the operating area.

A photograph of the larger box in an early stage of installation is shown in Figure 49. The outer walls of the cell are visible in the photograph since the cell ceiling has not been constructed.

The smaller box will be located in the operating room and will contain equipment that may become alpha contaminated. Bagout ports, filter, electrical and air line inlets, and sphincter openings are located at the ends of the boxes. Large bagout ports, for larger equipment passage, are situated at the top of the boxes, where they can be used with an overhead crane. Small volumes of filtered air will be passed through each box, and the air from the larger box will be filtered, scrubbed twice and filtered again before being exhausted from the building.

Equipment

Initially, the large box will contain equipment to fluorinate uranium and uranium-plutonium dioxide pellets and recover the hexafluoride products. Later, other equipment may be added for studying the separation of uranium from plutonium. The fluorination reaction will be carried out in a 6-ft-long, 3-in.-diameter fluidized-bed reactor which has provisions for zone heating and cooling. The Calrod heating units and the cooling coils are metallurgically bonded to the reactor walls. The reaction zone is cooled by a 2-phase water-air cooling system; the upper de-entrainment zone is cooled by water. Particulate matter in

the reactor exit gas is removed by 2 metallic bayonet filters in series. The first filter section is integral with the reactor so that particulate can be returned to the reaction zone. The uranium-plutonium hexafluorides in the gas from the reactor will be condensed in 2 series-connected, 4-in.-diameter condensers, each 10 ft long. Parallel fins welded onto a $\frac{3}{4}$ -in. pipe through which chilled trichlorethylene is circulated provide the cooling surface. Off-gas from the condensers can be either heated and recirculated through the reactor or can be purged through 4-in.-diameter, activated alumina traps and then through a wet scrubber. Small cold traps of coiled tubing are provided for the collection of plutonium hexafluoride recovered from the equipment by fluorination of any deposited plutonium tetrafluoride.

Figure 49

LARGE ALPHA ENCLOSURE FOR PILOT-PLANT SCALE PLUTONIUM VOLATILITY PROCESS STUDIES

This view shows the enclosure set in place before the cell roof was installed. The size is indicated by the 3-1/2-ft square window openings.

The smaller alpha box will contain the fluorine-, oxygen- and nitrogen-metering systems, and also the tower for scrubbing process off-gas and exhaust air from the large box.

The process will be monitored and controlled remotely from a central control station located in the operating area near the small alpha box.

Critical Path Method

Steps in the construction and installation of the boxes and equipment are being followed by a critical path analysis.^{17,18} In this method, the jobs are listed in the order of performance and a time duration is assigned to each job. Many different paths exist between the starting and finishing points. That path or job sequence requiring the greatest time to complete is the so-called "critical path," which determines the overall project duration. Attempts to shorten overall project time must focus resources on these jobs. The program for critical path analysis is evaluated monthly with the aid of the IBM 704 computer. Currently, the indications are that the facility may be ready for the plutonium experiments by May 1963. In addition to the above scheduling function, the program has been used to estimate the manpower load and also the amounts of money that must be available for the project in the fiscal years 1962 and 1963.

3. Process Studies on the Recovery of Uranium from Enriched Uranium-Zirconium Alloy Fuels (N. Levitz)

Engineering studies are continuing on a process for the recovery of highly enriched uranium from zirconium alloy-type nuclear fuels. The scheme is based on "separations-by-volatility" methods and employs a hydrochlorination-fluorination reaction sequence. Fluidization techniques are used to advantage since near-isothermal conditions can be maintained while carrying out highly exothermic gas-metal reactions. Fixed beds of granular Alundum (the type used in the fluid beds) are being tested as high-temperature filter devices.

The 2 principal steps of the process are: (1) hydrochlorination of the alloy while it is submerged in a fluidized bed of inert solids, thereby separating the zirconium as the volatile tetrachloride (sublimation point, 331 C at 14.7 psia) from the uranium which remains as a solid (particulate) chloride; and (2) fluorination of the system to volatilize and recover the uranium as the hexafluoride. Engineering studies are attempting to establish reaction conditions which will yield satisfactory uranium recoveries (~99 percent) from the inert solids. Initial results (see ANL-6413, page 136 and ANL-6477, page 146) indicate uranium entrainment losses during hydrochlorination were held to nearly 0.2 percent with the use of fixed-bed filters.

¹⁷Kast, W. G., Critical Path Method Ideal Tool for Plant Construction, Petroleum Refiner 41 No. 2, 123-130 (February 1962).

¹⁸Malcolm, D. G., Roseboom, J. H., and Clark, C. E., Application of a Technique for Research and Development Program Evaluation, Summary Report, Special Projects Office, Bureau of Ordnance, Department of Navy, Washington, D. C., 1959.

Uranium removal from the system during fluorination was nearly 96 percent but actual uranium recovery in the cold traps was low, about 70 percent, which indicated that improved traps were needed.

Currently, results are reported on experimental work on the hydrochlorination-fluorination reaction sequence and on a method for disposing of the zirconium tetrachloride off-gas, namely, by steam hydrolysis to convert the material to the solid dioxide. Design of a pilot plant for processing up to 20 kg of alloy has been initiated. A schematic flowsheet is presented.

a. Hydrochlorination and Fluorination Reaction Studies on Uranium-Zirconium Alloy Fuels and Evaluation of Fixed-bed Filters
(J. T. Holmes, D. Ramaswami, C. Schoffstoll)

The current engineering work involves studies of the hydrochlorination-fluorination reaction sequence and the evaluation of granular Alundum (Norton type RR) fixed-bed filters for retaining the uranium solids entrained by the volatile zirconium tetrachloride stream. The effect of gas velocity, in the range from 0.14 to 0.75 ft/sec, on filtration was reported previously (see ANL-6413, pages 137 to 140). It was shown that, for up-flow filtration, lower gas velocities (below 0.2 ft/sec) gave the best filtration (lowest uranium losses). For down-flow of gas through the filter bed, better filtration was achieved with the higher gas velocities (above 0.25 ft/sec). With either technique, better filtration was achieved with smaller particles (in the range -80 +200 mesh). No appreciable effect of bed depth was noted with down-flow filtration and this scheme, in general, gave equal or better results than up-flow filtration with uranium losses generally near 0.2 percent. The use of both up- and down-flow filter beds in series gave uranium losses only slightly better (down to 0.1 percent) than the down-flow filter only (ANL-6477, page 147). For simplicity, the present filtration scheme employs only the down-flow bed.

Equipment

The principal pieces of equipment are of nickel and include a 1½-in.-diameter fluid-bed column topped by a 3-in.-diameter disengaging section and a separate 1½-in.-diameter filter-bed column section. During hydrochlorination, an air-cooled 4-in.-diameter Pyrex glass pipe section is attached downstream of the filter to serve as a zirconium tetrachloride condenser. The excess hydrogen chloride is scrubbed from the off-gas by water in a packed tower. For the fluorination step, the condenser and scrubber are replaced by a series of 3 coil-type cold traps for uranium hexafluoride collection and a packed column filled with activated alumina or charcoal for excess fluorine disposal.

Experimental Procedure

The uranium-zirconium fuel alloy (~5.0 weight percent uranium) in the form of irregularly shaped chips ($\sim \frac{1}{8}$ to $\frac{1}{4}$ in. on a side) is submerged in the Alundum in the reaction zone. Hydrogen chloride is admitted to the system after heatup to the desired temperature, and the reaction proceeds to completion in 5 to 6 hr. Fluorination of the entire system for uranium recovery is then carried out at the chosen temperature by means of gas flow conditions similar to those used during hydrochlorination. Uranium losses during hydrochlorination are determined by analysis of the condensed phase in the zirconium tetrachloride condenser and the solution in the hydrogen chloride scrub tower. Final evaluation of the run is made after fluorination, when the uranium content of the bed material and cold traps is determined.

Hydrochlorination-Fluorination Results

The object of the current work was to determine the total uranium retention and ultimate recovery achievable when the inert bed material is re-used for a number of hydrochlorination-fluorination cycles. The Alundum charge to the reactor and filter beds was used for 5 runs. Run 18 was made with both an up- and down-flow filter bed; the other runs used only the down-flow filter. Use of the latter system is of advantage because the inventory of inert solids is reduced and column operation is simplified.

Experimental conditions and results of these runs are shown in Table 28. Uranium losses during the hydrochlorination steps were similar for both the down-flow and combined up-flow and down-flow filter systems, and were less than 0.2 percent in each case. These results are consistent with those reported previously (see ANL-6413, pages 137 to 140).

Fluorination results show that, upon re-use of the bed, the residual uranium value tends to become constant. The cumulative uranium loss (residual) for 3 cycles was 1.8 percent of the total uranium charged. Losses were further reduced to 1.0 percent after the fifth use of the bed. Approximately 20 percent of the retained uranium was associated with the filter-bed material. On the basis of these results, re-use of the bed material therefore appears to offer a method for achieving acceptable process losses (~1 percent) if it does not become limited by the buildup of fission product heat and activity. In future work, improved single-experiment recoveries will be sought in order to develop a more adaptable process.

Uranium collection in the cold traps and overall uranium material balances were generally satisfactory. The exception, a material balance of 133 percent for Run-18, is attributed to uranium holdup in the

column from the previous run. A good weight balance on the inert bed material was also achieved for each of the experiments.

Table 28

RECOVERY OF URANIUM FROM INERT ALUNDUM GRAIN

Fuel Charge: 350 g of 4.8 w/o U-Zr Alloy in Runs 18, 19, and 20; 350 g of 5.0 w/o U-Zr Alloy in Runs 21 and 22.
 Reaction Bed: 550 g of 90 mesh RR Alundum
 Up-flow Filter Bed: 1450 g of 90 mesh RR Alundum, Run 18 only.
 Down-flow Filter Bed: 220 g of 90 mesh RR Alundum; 100 to 150 g of 20-36 mesh #38 Alundum

Hydrochlorination

Temperature: Adjacent to fuel: 350 to 450 C
 Beds: 350 to 400 C

Velocity: Fluid Bed: 0.7 ft/sec
 Down-flow Filter: 0.8 ft/sec

HCl Concentration: 5 to 50 m/o in N₂ (excess of 2 to 3 times stoichiometric)

Uranium Loss: <0.2 percent of input

Fluorination

Temperature: 350 C

Velocity: Fluid Bed: 0.6 ft/sec
 Down-flow Filter: 0.7 ft/sec

F₂ Concentration: 15 to 40 m/o

Time: 6 hr

Run	Uranium Charge (g)	Hydrochlorination Time (hr)	Reaction Bed		Down-flow Filter Bed (w/o U) ^C		Percent of U Charge in Final Beds ^C	Percent of U Charge in Cold Traps	Total Uranium Accountable (%)
			(w/o U) ^D	(w/o Zr) ^C	Coarse Fraction	Fine Fraction			
18 ^a	16.3	4.0	0.033	0.4	0.012	0.016	4.4	129	133
19 ^b	16.9	5.5	0.093	1.3	0.021	0.063	2.1	89	94
20	16.6	5.5	0.126	0.9	0.046	0.066	1.8	96	101
21	17.5	6.5	~0.1 ^d	1.4	0.047 ^d	0.060	~1.2	99	104
22	17.5	16.0	~0.1 ^d	1.3 ^d	0.07 ^d	~0.06 ^d	~1.0	98	103

^aRun 18 used both an up-flow and down-flow filter bed; all other runs used down flow only.

^bReactor fluorinated without beds present before Run 19 as a cleanup step.

^cValues are based on the cumulative amount of uranium charged.

^dAnalysis by X-ray spectrochemical method.

In additional studies, efforts are being made to establish whether there is a relationship between the amount of residual zirconium in the bed and uranium retention. Current results show zirconium contents of 0.4 to 1.4 weight percent. In 2 experiments, it was found that higher hydrochlorination temperatures (450 and 550 C as compared with 350 and 400 C) were ineffective in decreasing either the zirconium or uranium retention. Future work will include a study of the effect of hydrogen chloride excess on both zirconium and uranium behavior.

The higher hydrochlorination temperature introduced the problem of excessive pressure drop across the down-flow filter. Apparently, particulate nickel (chloride) corrosion products are elutriated from the fluidized-bed column and are deposited on the surface of the down-flow filter bed, thereby causing an excessive flow restriction. This problem may be alleviated by using lower temperatures at which corrosion should be negligible or by using both the up- and down-flow filter in series to reduce the particulate load on the down-flow filter. An exploratory corrosion study under simulated process conditions is planned.

b. Fluid-bed Hydrolysis of Zirconium Tetrachloride
(K. S. Sutherland, D. J. Raue)

The hydrochlorination reaction in the above scheme for the processing of enriched low uranium-zirconium alloy fuels produces an off-gas containing zirconium tetrachloride vapor. For convenient handling of this waste material, conversion to a water-insoluble solid is being proposed. This may be accomplished by steam hydrolysis of the tetrachloride to the dioxide. This reaction is being studied in a 6-in.-diameter fluid-bed reactor system (see equipment description in ANL-6477, page 149) containing a sublimation furnace, solid zirconium tetrachloride feed, and granular zirconium oxide or other inert materials as starting bed materials. It is intended to find conditions whereby the reaction will occur preferentially on the surface of the bed particles.

This 6-in.-diameter scale of fluid-bed equipment is planned for the pilot plant now being designed (see page 153). It is therefore desirable to operate the unit at flowsheet rates. Preliminary experiments (see ANL-6477, page 149) indicated small batches of zirconium tetrachloride could be sublimed into a carrier stream of nitrogen, continuously fed into the column, and reacted with steam. Up to 400 g of zirconium tetrachloride was fed over a period of an hour from a single 2-in.-diameter sublimation furnace. This was the capacity of the original setup. Modifications made to enlarge the feed system included the use of 2 furnaces in parallel, each with a 500-g capacity. More recently, a Vibra-Screw continuous feeder has also been installed, permitting the desired feed rates, about 2 kg/hr, to be achieved. Solid zirconium tetrachloride is fed into a nitrogen conveyor stream which passes through a $2\frac{1}{2}$ -in.-diameter by 24-in.-long furnace tube filled with ceramic Raschig rings and maintained at a temperature of 500 C. The present feed hopper has only a 4-kg capacity, and runs of 2-hr duration have been made. A hopper of larger capacity is being fabricated.

During the course of the recent runs as well as those made previously, the pressure drop across the sintered nickel, exit-gas filters increased markedly. This buildup may be attributed to one or more of the following causes:

- a) production of fines by attrition of bed material or of the newly deposited coating of zirconium oxide,
- b) production of fines by hydrolysis of the zirconium tetrachloride in the gas phase, instead of deposition on the bed material, and
- c) hydrolysis occurring at the filters which causes oxide to deposit in the pores of the filter material.

One of the main causes of attrition was the use of atomization of a water jet by a high-velocity air stream. Accordingly, steam is now being supplied to the bed directly from a small electric boiler. The latest results indicate, however, that this has not relieved the problem of increased pressure. Chemical analysis of the material held on the filters at the end of one run showed a chloride ion content of about 4 percent, which would correspond to about 10 percent ZrOCl_2 , which is considered a possible intermediate in the conversion to oxide.

In a series of one-hour experiments made this quarter, alumina was used as the starting bed material. The amount of zirconium oxide deposited on the particles and collected as fines could be readily determined by chemical analysis. The same bed was used throughout except for dilution with fresh alumina between Runs 14C and 15A, so that subsequent deposition would be onto a previous coating of zirconium oxide. The results are shown in the following table:

Run No.	Initial Bed Wt (kg)	ZrO_2 Equivalent Fed (g)	ZrO_2 Content of Bed		ZrO_2 Content of Fines (w/o)	w/o Feed Deposited on Bed Particles	Cumulative Deposition on Bed Particles (w/o ZrO_2)
			Before (w/o)	After (w/o)			
CO-14A	6.4	490	0	5.8	43	70	70
CO-14C	6.4	510	5.8	9.9	9	57	63
CO-15A	9.2	510	6.9	8.8	34	36	54
CO-16A	9.2	520	8.8	13.3	69	79	60

Since the experiments were short and therefore subject to possible error, too much emphasis should not be placed upon the actual analytical values; however, it is obvious that a significant amount of zirconium oxide failed to deposit on the bed material in each run. At the end of 4 runs, over half of the total amount of zirconium charged was found in the bed. The concentration of zirconium oxide was also high in the material on the filters in 3 of the 4 runs. These results indicate that conditions will have to be explored further so that greater zirconium retention in the bed may be achieved.

Under the conditions existing for the recent runs with continuous feed of zirconium tetrachloride, the gas flow rates were approximately 3 times those required in the pilot plant, largely because of the use of separate gas streams to transport the zirconium tetrachloride and to fluidize the bed. Since this higher rate reduces the residence time in the bed, the apparatus is being rebuilt to enable the carrier gas stream to be used as the fluidizing medium. Other changes will then be made in the operating conditions in an attempt to reduce fine production and pressure buildup at the filters to a satisfactory level.

c. Pilot Plant for Reprocessing Zirconium-enriched Uranium Alloy Fuels
(J. Barghusen, J. Holmes, N. Levitz)

Results of laboratory work and preliminary engineering studies in a $1\frac{1}{2}$ -in.-diameter fluid-bed reactor have indicated that it is feasible to recover uranium from zirconium-uranium alloy-type nuclear fuels by means of volatility and fluidization techniques. The process is based on the use of hydrogen chloride, at temperatures ranging from 350 to 450 C, to convert the alloy to volatile zirconium tetrachloride and nonvolatile uranium trichloride. The hydrochlorination step is conducted with the fuel alloy immersed in a fluidized bed of inert solids which serves as a heat transfer medium. Uranium is recovered as the hexafluoride by direct fluorination of the residue.

A pilot plant has been designed to demonstrate this process on a 20-kg charge scale. A schematic diagram of the major equipment is presented in Figure 50. Also included is a complete materials flowsheet for all process streams. Automatic control of process conditions will be employed. It is proposed that the hydrochlorination and fluorination reactions be carried out in a single 6-in.-diameter nickel reactor. A fixed-bed down-flow filter in series with the fluid-bed reactor is incorporated to ensure retention of uranium trichloride particulate matter. The zirconium tetrachloride produced during the hydrochlorination step is converted to a high-density, water-insoluble form by conversion to zirconium dioxide with steam in a fluid-bed reactor. Off-gases from this unit are passed through a condenser and scrubber to remove the hydrogen chloride before being fed to the building exhaust system.

Figure 50

PRELIMINARY SCHEMATIC FLOW SHEET FOR RECOVERY OF URANIUM FROM ZIRCONIUM-URANIUM ALLOY FUELS

Recovery of uranium as uranium hexafluoride is achieved by fluorination of the uranium residue on the inert fluid-bed particles at approximately 350 C. The product hexafluoride is collected in a system of refrigerated condensers. The fluorine gas stream is recycled, and a small quantity of the gas is bled to a charcoal trap to prevent accumulation of inerts in the gas stream.

The pilot plant will be operated to demonstrate each of the process steps on a practical scale with unirradiated material. Subsequent tests may be made with low-level irradiated feed to define clearly the disposition of fission products in the process.

C. Conversion of Uranium Hexafluoride to Uranium Dioxide (I. Knudsen, N. Levitz, M. Jones)

A fluid-bed process for the preparation of ceramic-grade uranium dioxide from uranium hexafluoride has been developed for application to the production of nuclear fuel. The process involves either of 2 reaction schemes: (1) a two-step procedure in which uranium hexafluoride is first reacted with steam to form uranyl fluoride, which is then further reacted with mixtures of steam and hydrogen to produce the dioxide, or (2) simultaneous reactions with steam and hydrogen mixtures in a single reactor. Sintering tests on pellets prepared from both types of powder products achieved high densities, 93 to 97 percent of theoretical (see ANL-6183, page 123 and ANL-6231, page 134).

Work this quarter involved an exploratory study of the hexafluoride hydrolysis step at a higher temperature (500 C as opposed to 200 C) and additional studies of the simultaneous reaction scheme, with the aim being the preparation of high-density uranium dioxide particles in a single step.

1. Two-step Process Work - Uranium Hexafluoride Hydrolysis

A possible problem associated with the hydrolysis step in the two-step process is the buildup of solids upon reactor surfaces (see ANL-6477, page 150). Excessive deposition would require frequent shut-down for reactor clean-out. An indication of a possible method for producing a hydrolysis product with "different" properties was a reference¹⁹ to the effect that the formation of uranyl fluoride from uranium trioxide by a high-temperature (350 to 500 C) hydrofluorination rather than at low temperatures affects the physical properties such that the solid exhibits no deliquescence. At 500 C uranyl fluoride reacts with steam to form U_3O_8 , which would have properties quite different from those of the fluoride compound.

¹⁹Katz, J. J., and Rabinowitch, E., NNES, VIII-S, The Chemistry of Uranium, McGraw-Hill Publishing Co., New York (1951), page 569.

To explore this problem, hydrolysis experiments were conducted at 500 C in the 3-in.-diameter Monel column. Continuous runs were made with hexafluoride feed rates of 60 and 100 g/min and with 9-to-1 mole ratio mixtures of steam and hydrogen as well as 100 percent steam. The starting bed was uranyl fluoride, but thereafter the final bed from one run was used as the starting bed for the next experiment. The work also included a batch experiment with a starting bed of uranyl fluoride.

After 14.5 hr of cumulative run time, inspection of the reactor showed only a loose dust layer adhering to the internal surfaces. Product analyses (see Table 29, Run 65C) indicated almost complete conversion to U_3O_8 (83.3 percent total uranium as compared to a theoretical value of 84.8 percent for uranium in U_3O_8) was achieved in the batch experiment in 3 hr. Only 0.4 percent fluoride remained as compared with 12.3 percent in the starting material. The products from continuous runs were multi-colored, and the analysis indicated that some uranium tetrafluoride might have been present, as well as other uranium forms (oxide and unreacted uranyl fluoride). A more dense product was obtained with the hydrogen-steam mixtures than with steam only (compare Runs 65D and 65E, Table 29), as determined by measurements of bulk density. A slightly higher nickel content, 32 ppm, was noted in the products from the current runs as compared with 5 ppm nickel in the uranyl fluoride prepared at 200 C.

Table 29

HIGH-TEMPERATURE HYDROLYSIS OF URANIUM HEXAFLUORIDE

		Equipment:		3-in.-diameter Monel column			
		Reactor Temperature:		500 C			
		Steam-H ₂ Superficial					
		Velocity:		0.75 ft/sec			
		Starting Material:		Uranyl fluoride, 12.3 percent F ⁻ , 77.3 percent total U			
		Bed Height:		20 in. (static)			
Run No.	UF ₆ Feed Rate (g/min)	Duration (hr)	Steam-H ₂ Ratio	Final Product Analyses (w/o)			Bulk Density -60 +100 mesh fraction (g/cc)
				F ⁻	Uranium(IV)	Total Uranium	
65Ca	-	3.0	Steam	0.4	29.8	83.3 ^b	3.0
65A	100	1.5	9:1	10.8	1.4	78.5	3.1
65B	100	2.0	9:1	5.8 9.4 ^c	23.3 29.3 ^c	78.6 80.4 ^c	2.7
65D	60	5.0	Steam only	12.0 12.1 ^c	6.9 7.1 ^c	78.0 76.8 ^c	2.3
65E	60	6.0	9:1	8.6 12.5 ^c	21.7 1.1 ^c	80.1 76.3 ^c	3.1

^aThe starting bed was uranyl fluoride.

^bTheoretical value for total uranium in U_3O_8 is 84.8 percent.

^cOverhead fines fraction.

It thus appears that hydrolysis at 500 C achieves the primary aim of reducing the reactor coating (deposition) problem. Of perhaps some disadvantage, however, is the fact that appreciable fines (also of mixed composition) were formed. These amounted to as much as 50 percent of the product in one case. No interference with fluidization was noted and the fines were, for the most part, elutriated over into the filter vessel during the run. For the reduction step, the fines would be recombined with the main product stream and would be converted batchwise.

The above study completes the work on the two-step process.

2. Simultaneous Reaction Studies

The simultaneous reaction of steam and hydrogen with uranium hexafluoride is being studied in a fluid-bed reactor in an effort to prepare high-density uranium dioxide particulates. The ultimate aim of this work would be to develop a simple, direct process for the preparation of "shot" for dispersion or packed-type fuel elements. In previous studies (see ANL-6183, page 123) material prepared by this reaction scheme was of relatively low density (bulk density ~ 4 g/ml) but was sintered as "shot" to 93 percent theoretical density. Ideally, reaction conditions might be found where an intermediate sintering step would be unnecessary.

Current studies are being conducted in a 3-in.-diameter Monel column. Variables investigated during this period were the hexafluoride feed rate over the range from 10 to 27 g/min, steam-hydrogen ratios of 2 and 0.5, and steam excesses from 90 to 1160 percent over the stoichiometric amount. A solids "seed" recycle rate near 10 percent of the feed rate was used to help maintain uniformity of bed particle size. "Seed" stock was $-60 +200$ mesh. The bed temperature was maintained constant at 650 C and the superficial gas velocity was 0.75 ft/sec.

The run procedure involves alternate periods of feed on-time and periods of (fluoride) clean-up when only steam and hydrogen are fed to the unit. In these studies, these periods were generally 45 and 15 min in duration, respectively. The steam excesses mentioned above refer to the hexafluoride feed time only. Product withdrawal is made after each clean-up interval.

Experimental Results and Discussion

Particle density, as measured by mercury displacement, increased substantially from 6.4 g/ml for the starting bed material (product from the two-step process) to 8.9 g/ml (~ 80 percent theoretical) during the course of these preliminary studies (see Table 30). It is believed that even higher values are attainable. Nominal particle size distribution for the product was as follows:

5% +20
 35% +40
 35% +60
 20% +100
 5% -140

Fines collected overhead ranged from 6 to 16 percent of the feed rate. Residual fluoride content of the product ranged from 150 to 3000 ppm. As a consequence of the density increasing and the bed weight being maintained constant, the bed height decreased from about 12 to only 8 in. This process scheme thus appears attractive from the inventory standpoint.

Table 30

FLUID-BED STUDIES ON THE PREPARATION OF
 HIGH-DENSITY URANIUM DIOXIDE PARTICLES

Equipment: 3-in.-diameter Monel column
 Bed Temperature: 650 C
 Bed Weight: 6 kg^a
 Superficial Fluidizing
 Gas Velocity: 0.75 ft/sec

UF ₆ Rate (g/min)	Steam to Hydrogen Mol Ratio	Steam Excess ^b (%)	UF ₆ Feed On-time to Clean-up Time Ratio (min/min)	Total Run Time (hr)	Particle Density by Hg Displacement (g/ml)	Residual Fluoride Content (ppm)
10	2	1160	$\frac{60}{0}$ and $\frac{50}{10}$ ^c	29	6.6 ^d	150 to 1000
19 and 22	2	450 and 550	$\frac{45}{15}$	40.5	7.6	250
20	0.5	250	$\frac{45}{15}$	50.5	8.1	200 to 250
27	0.5	90	$\frac{45}{15}$	56.5	8.9	3000

^aStarting bed in each case was the final bed from the previous run.

^bRefers only to hexafluoride feed on-time period.

^cFinal 8 hr only.

^dStarting bed was two-step process material; Hg density 6.4 g/ml.

Microscopic examination of particles was made. A very pronounced raspberry-like surface noted on the particles prepared at 10 g/min became much less pronounced as runs at higher rates were made. Reasons for this preferred orientation or nucleation can only be conjectured at this time.

It is planned to continue this investigation in an effort to correlate single-variable effects and establish whether still higher densities can be achieved.

D. Calcination Studies in Small-diameter Columns

(J. W. Loeding, N. Levitz, J. E. Kincinas, D. L. Benzing*)

Development work was continued on a scheme to extend the technique of fluid-bed calcination to systems where equipment size (diameter) is of prime concern, as in situations which require the design of critically safe reaction vessels. The work involves vertical-upward spraying of atomized aqueous feed directly into a heated, fluidized bed of granular material through a nozzle mounted in the base of a small-diameter (currently a $2\frac{1}{4}$ -in.) column. With this technique, the feed atomizing gas and the feed solution vapors and decomposition gases serve as the fluidizing medium, thus eliminating the need for a separate fluidizing gas stream. Bottom-feed introduction may also be applicable to more conventional, large-size calciners and offers a possible means of reducing the large volumes of inert gas now handled in such units.

Previous work in the small-diameter calciner indicates that the operation is feasible. Satisfactory runs of 5- to 7-hr duration at rates near 10 ml/min have been described (see ANL-6413, page 147 and ANL-6477, page 152). A modified, extended-tip nozzle was used (see ANL-6379, page 188).

Current work is involved with the testing of a newly designed nozzle, referred to as a submerged-tip type (see Figure 51) at feed rates greater than twice those used previously. An additional 21 hr of operation was also accumulated with an extended-tip nozzle. Overall objectives include demonstration of reliability of the unit in continuous operation and determination of minimum air-to-liquid feed volume ratios for the system (see equipment diagram in ANL-6413, page 147). Granular aluminum oxide has been used as the starting bed material and 1 M aluminum nitrate solution as the feed in all the work to date.

Figure 51
SUBMERGED-TIP NOZZLE

*Coop student from the University of Detroit.

1. Experimental Procedure and Run Conditions

In the current series of experiments with the new submerged-tip nozzle (see Figure 51 and discussion on page 160), the procedure was to increase gradually the feed rate (and heat input), over the duration of the run, to 23 ml/min, the maximum output of the existing feed pump (a "Mini" Milton Roy). When the maximum feed rate was reached, the atomizing air rate was gradually reduced to decrease further the air-to-liquid ratio. This course of action was followed until a run failure was experienced, usually indicated by erratic readings of bed temperature or unusual response of the bed weight manometer. As a rule, input settings were maintained for a period of 2 hr to allow the system to become stabilized before another change was instituted. The bed temperature was maintained at 450 C for the entire series. The product was semicontinuously withdrawn to maintain a constant bed height.

A shorter blowback cycle, 3 min as compared with 4 min, and a longer blowback pulse, 0.18 sec as compared with 0.12 sec, was tried during this period with some degree of success (see discussion on page 161). Blowback supply pressure was 80 psig.

Two additional runs of 6.9- and 14.0-hr duration were made at a constant feed rate of 9.5 ml/min with an extended-tip nozzle.

2. Experimental Results

The new submerged-tip nozzle has been successfully employed in a short shakedown run and 7 operational experiments (see Runs 51 through 57, Table 31). Runs were up to 12 hr in duration. The minimum air-to-liquid ratio attained was 588 for a period of 21 min in Run 57. It appears that ratios near 600 may be the current operational limit. This is lower by a factor of about 3 than air ratios employed in waste calcination studies in a 6-in. column with similar feed (see ANL-6322). Feed rates near 20 ml/min appear satisfactory in the present system.

Little effort was made to correlate particle size effects in the current work because of continually changing conditions, but significant particle growth was noted in at least one run (Run 57), in which 94 percent of the final bed was greater than 40 mesh as compared with a starting bed of 60 percent - 20 + 40 mesh and 40 percent - 40 + 80 mesh. Future work will include a study of factors which affect particle size.

Reliability of the unit was also demonstrated in 2 runs made with an extended-tip nozzle (see Table 31, Runs 48 and 49). A constant feed rate near 9.5 ml/min was used for periods of 6.9 and 14.0 hr. The disadvantage of operating without a protective cap on the nozzle was clearly demonstrated, since the extended liquid tip was found severely eroded after these relatively short operating periods. No further work with this model is planned.

Table 31

OPERATING CONDITIONS AND RESULTS OF CALCINATION RUNS IN A SMALL-DIAMETER COLUMN

Column: 2 1/4-in.-diameter stainless steel calciner
 Feed: 1 M Al(NO₃)₃
 Bed: 325 g Al₂O₃ (60 percent -20 +40 mesh; 40 percent -40 +80 mesh)

Run No.	Type Nozzle	Duration (hr)	Avg Bed Temp (C)	Avg Feed Rate (ml/min)	Avg Air-to-liquid Volume Ratio	Comments
48	Extended Tip	6.9	425	9.4	1590	Voluntarily terminated. Evidence of erosion on nozzle tip.
49	Extended Tip	14.0	425	9.5	1570	Voluntarily terminated. Severe erosion of nozzle tip.
51	Submerged Tip	12.0	425	12.9	1160	Voluntarily terminated. Purpose was to increase feed rate to point of run failure. Feed rate reached 18.35 ml/min, at which time an air/liquid ratio of 824 was reached.
52-56	Similar to Run 51. Purpose was to attain minimum air/liquid ratio. This ratio was brought down to 625 with no run failures.					
57	Submerged Tip	5.25	450	23.0	609	Involuntarily shutdown after 21 min at air/liquid ratio of 588. Prior to this failure, successful operations maintained for 2 hr at air/liquid ratio of 603. Filter fines amounted to 4.1 percent of final bed. Marked particle growth - 94 percent of final bed > 40 mesh - possibly a contributory cause of run failure.

3. Discussion

a. Nozzles

Problems associated with the concentricity of air and liquid openings in the feed nozzle has led to the latest nozzle design, Mark I, referred to as the submerged-tip nozzle. The earlier model, referred to as the modified extended-tip nozzle, actually had 3 orifices, which required close tolerances of concentricity. In several instances, operational difficulties were encountered when there was misalignment of only ~0.007 in. between the liquid orifice and protective-cap orifice. The new design has only 2 openings and, in addition, internal design was improved to assure proper alignment. Another important feature regarding these nozzles is the air cap. As discussed earlier, severe erosion effects were noted on a nozzle with an extended liquid tip; however, no such effects have been noted in any work where the protective cap was used. Future studies will employ the new submerged-tip nozzle.

b. Filter Blowback Operation

The return of filter fines by blowback to the fluidized bed is a necessary adjunct to stable operation, since this material serves as "seeds" for new growth. Frequent blowback is important, since the quantity of returned material will then be kept small and disturbances to the steady-state "heat balance" in the bed, which result from the solids being relatively cool, should thereby be minimized.

Although frequent blowback (4-min cycle with a 0.12-sec burst) has been in use with the filter system (2 bayonet filters in parallel), increased feed rates have produced larger quantities of fines. Accumulation of solids on the filters has occurred in a few instances, resulting in dumping of excessive amounts of cool material into the bed. This has been of serious enough consequence to cause run termination in a few instances. Some improvement was noted when the filter blowback was reduced to 3 min and the blowback pulse increased to 0.18 sec during the course of this work. In future work, additional attention will be directed to the problem of optimizing blowback conditions.

A method for completely eliminating return of material to the bed is the use of a filter chamber mounted offset from the vertical axis of the fluidized bed. This, on the other hand, introduces the disadvantage of having to handle a separate stream of solids and, therefore, does not appear to be a satisfactory solution to the problem.

c. Future Work

Efforts will be directed toward further demonstration of reliability by operating the unit continuously for longer periods. The unit is being instrumented to facilitate automatic operation. An investigation will be made of particle size distribution (or changes) as a function of air-to-liquid ratios and bed temperatures.

III. CALORIMETRY*

(W. N. Hubbard and H. M. Feder)

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 determine some of these data.

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. To date, heat of formation values have been published for zirconium tetrafluoride, molybdenum hexafluoride, boron trifluoride, and silicon tetrafluoride. The heats of combustion in fluorine of two compounds boron nitride and silicon dioxide, have been determined by fluorine bomb calorimetry. To obtain the heat of formation for boron nitride required use of the heat of formation value obtained previously for boron trifluoride, and that of silicon dioxide required the value for silicon tetrafluoride. Zirconium diboride will be studied soon. It will require use of the values for boron trifluoride and zirconium tetrafluoride.

The heats of formation at 25 C from oxygen or fluorine combustion calorimetry will be combined with the change in enthalpy values 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.

A. Combustions of Cadmium and Magnesium in Fluorine

(E. Rudzitis and R. Terry)

A series of 9 calorimetric combustions of cadmium in fluorine has been completed. Seven additional calorimetric combustions of magnesium in fluorine have been carried out to bring the total number of magnesium combustions to 10.

For the combustions of cadmium and magnesium, the samples were supported by discs of the corresponding metal fluoride, both metal fluorides containing approximately 0.2 percent metal oxide. It was found that thermally significant fluorination of the oxide occurred during the combustion reactions, whereas practically none occurred during deliberate prefluorination

*A summary of this section is given on page 11.

at 600 to 700 C. Successive recovery and re-use of the oxygen-depleted, used discs reduced drastically the thermochemical correction and the uncertainties due to fluorination of the support discs.

A few additional calibration experiments will be run before values of heats of formation are calculated from the results of the cadmium and magnesium combustions.

B. Combustions of Titanium and Hafnium in Fluorine
(E. Greenberg and E. Johanson)

Experimental work on the heats of formation of the tetrafluorides of titanium and hafnium was concluded with the characterization and analysis of the titanium tetrafluoride combustion product. A paper describing the work on titanium and hafnium has been accepted for publication in the Journal of Physical Chemistry.

Because the product of combustion of titanium, the tetrafluoride, did not yield a suitable X-ray diffraction pattern, a small quantity was heat treated at about 300 C for approximately half an hour and cooled slowly. The treatment was carried out in a helium-atmosphere box, with the sample contained in a thin-walled Inconel tube that was sealed by crimping. This annealed material gave an X-ray diffraction pattern which is in general agreement with that reported for titanium tetrafluoride by Vorres and Dutton.²⁰

A sample of the titanium tetrafluoride combustion product was also examined by electron microscopy. The particles observed averaged about 1 micron in diameter, and appeared to be spherical and typical of the amorphous particles found in smokes. This observation accounts for the difficulty in obtaining an X-ray diffraction pattern from the combustion product.

The combustion product was also chemically analyzed for fluorine by pyrohydrolysis of the sample, followed by titration of the recovered hydrofluoric acid with standard sodium hydroxide solution. The fluorine content of the product, corrected for a blank determination, was found to be 61.4 ± 0.3 percent, which is in good agreement with the value calculated for titanium tetrafluoride (61.3 percent). These experiments established with certainty that the product of the titanium combustions was titanium tetrafluoride.

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

Preliminary exploratory experiments have been carried out for combustions of vanadium, niobium, and tantalum in fluorine. The development of satisfactory combustion techniques for niobium and tantalum was

²⁰Vorres, K. S., and Dutton, F. B., J. Am. Chem. Soc. 77, 2019 (1955).

reported in ANL-6333, page 127. A satisfactory combustion technique for vanadium in fluorine has not as yet been developed, and further work on vanadium has been suspended.

Experiments have been carried out to determine the extent of spontaneous surface fluorination of tantalum and niobium samples when exposed to fluorine in the bomb. Preliminary results show a slight amount of fluorination, which will require a thermal correction of approximately one calorie per combustion. It will be satisfactory to apply this correction rather than take precautions to protect the sample from fluorination prior to intentional ignition. Chemical and spectrometric analyses of these samples indicated that they are not as pure as desired. Large impurity corrections would have to be made if they were used. Consequently, samples of higher purity have been ordered from other sources. Calorimetric measurements will be made when samples of sufficient purity are obtained.

D. Further Exploratory Combustion Studies
(E. Greenberg and E. Johanson)

Exploratory noncalorimetric combustion experiments have been started to study the ignition and combustion characteristics of sulfur, zirconium diboride, graphite, and diamond in fluorine. Sulfur and powdered zirconium diboride each react spontaneously with fluorine, whereas graphite and diamond require electrical ignition.

The heat of formation of sulfur hexafluoride was determined some time ago by Yost and Claussen.²¹ Recently, Gross, Hayman, and Levi²² used sulfur as an ignitor for the combustion of various substances in fluorine. In the course of their work, the heat of formation of sulfur hexafluoride was found to differ from the previously accepted value of Yost and Claussen by more than 20 kcal/mole. Because of the relative ease of studying sulfur and the availability of a very high-purity sample, it is desirable to resolve this discrepancy.

A one-gram sample of sulfur was burned in 7 atm of fluorine in the glass combustion bomb, by means of the same technique as used in the study of silicon. The sulfur burned with a rather cool flame, and no evidence of fluorination was found on the nickel sample-support dish. For calorimetric experiments, it will be necessary to reduce the amounts of reactants by a factor of 2 because of the pressure limitation of the special fluorine vessel used for spontaneously combustible materials.

The currently available data from which heats of formation of zirconium diboride can be estimated yield values that vary over a range

²¹Yost, D., and Claussen, W., J. Am. Chem. Soc. 55, 885 (1933).

²²Gross, P., Hayman, C., and Levi, D. L. XVIIth. International Congress of Pure and Applied Chem., Abstracts 1, 90 (1959).

of more than 30 kcal. Our laboratory has already obtained the heats of formation of zirconium tetrafluoride and boron trifluoride, and is in a uniquely favorable position to study zirconium diboride by fluorine bomb calorimetry, provided satisfactory combustion techniques can be developed.

A high-purity sample of zirconium diboride has been made available to this laboratory through the Thermodynamic and Kinetic Studies for a Refractory Materials Program* of the Wright Air Development Division. Approximately one-gram quantities of powdered zirconium diboride were burned in 5 atm of fluorine. Observation of the extent of reaction was somewhat hindered because of severe attack on the nickel sample-support dish. A considerable amount of experimentation is still required to find a suitable sample-support technique and to work out combustion conditions for the calorimetric experiments.

The heat of formation of tetrafluoromethane (CF_4) has been determined by several investigators using different techniques. The results differ by several kcal/mole. Because tetrafluoromethane, like sulfur hexafluoride, is a basic fluoride and will be used repeatedly in thermochemical cycles involved with other compounds, it is desirable to obtain a precise value for its heat of formation by direct combustion of carbon in fluorine.

Both graphite and diamond are being studied in order to determine which variety is most suitable for the measurements. It is only necessary to study one form of carbon calorimetrically, because the heat of transformation between graphite and diamond is well known from studies of the heat of combustion in oxygen. Graphite flake and rod and diamond powder were burned in quantities (about 0.5 g) adequate for calorimetric studies. The major problem with carbon appears to be preventing the formation of significant amounts of fluorocarbons other than tetrafluoromethane. Higher fluorine pressures tend to reduce the amount of other fluorocarbons formed, but increase the problems of sample support or containment. Infrared and mass-spectrometric analyses of the combustion products are being employed to examine the products of combustion.

E. Combustion of Uranium in Fluorine (J. Settle)

When uranium metal is burned in fluorine in a manner suitable for bomb calorimetric study, more than 95 percent of the reacted uranium forms uranium hexafluoride. The remainder of the reacted uranium forms a mixture of uranium trifluoride, uranium tetrafluoride, and intermediates between uranium tetrafluoride and uranium hexafluoride. To determine the heat of formation of uranium hexafluoride, it is necessary to determine amounts of lower uranium fluorides after each combustion.

*Several universities and other laboratories are cooperating in the studies.

The most critical of these determinations are those of residual uranium and of uranium trifluoride. The total amount of uranium reacted is determined by subtracting the weight of uranium metal recovered after a combustion from the weight of uranium originally placed in the bomb. Consequently, the weight of unreacted uranium should be determined to the same absolute error as the mass of sample introduced into the bomb. The analysis of uranium trifluoride is important because uranium trifluoride is the main constituent (about two-thirds) of the lower fluoride product of combustion. Large errors in its determination would therefore lead to large errors in the data derived from the combustions.

Therefore, a method must be developed for accurate determination of the composition of mixtures of uranium metal and uranium trifluoride. Substantial progress has been made in the determination of the uranium metal content, but more research is necessary for the determination of uranium trifluoride. The first step in the analytical procedure is to oxidize selectively the uranium metal to uranium III^+ ion by means of anhydrous hydrochloric acid. The volume of the hydrogen produced is measured. Then the uranium III^+ ion from both uranium trifluoride and oxidized uranium metal is further oxidized with concentrated hydrochloric acid to uranium IV^+ , and the volume of hydrogen evolved is measured.

Table 32 presents the data from the analyses of 2 synthetic mixtures of uranium and uranium trifluoride. As can be seen, the results for the uranium analysis were excellent, but the results for the sum of uranium trichloride and uranium trifluoride were very low and inconsistent. It is apparent that some method must be found for promoting the oxidation of U(III) to U(IV) . When this problem is solved, calorimetric combustions of uranium in fluorine will be resumed. If the problem is not resolved soon, it may be expedient to settle for results with an uncertainty in the range of several tenths of one percent.

Table 32

CHEMICAL ANALYSIS OF URANIUM-URANIUM TRIFLUORIDE MIXTURES

Initial Amounts		H ₂ Recovery from Reaction ^a (%)	H ₂ Recovery from Reactions ^{b+c} (%)
U (mg)	UF ₃ (mg)		
1. 2.65	22.54	102	77.2
2. 2.86	4.92	102	38.3

^a For the reaction $\text{U} + 3\text{HCl}$	anhydrous	$\text{UCl}_3 + \frac{3}{2} \text{H}_2$
^b For the reaction $\text{UCl}_3 + \text{H}^+$	aqueous	$\text{U(IV}^+) + 3\text{Cl}^- + \frac{1}{2} \text{H}_2$
^c For the reaction $\text{UF}_3 + 4\text{H}^+$	aqueous	$\text{U(IV}^+) + 3\text{HF} + \frac{1}{2} \text{H}_2$

F. High-temperature Enthalpy Calorimeter
(D. R. Fredrickson, R. L. Nuttall, R. Kleb)

Work is continuing on the assembly of the calorimetric system to measure changes in enthalpy up to 1500 C. The high vacuum requirements of the drop calorimeter have been met as indicated by tests of both vacuum systems. The vacuum system for the furnace and the vacuum system which will provide a vacuum for both calorimeter and gate have been assembled and tested. The latter system has provisions for evacuating the calorimeter and gate either separately or together.

A large portion of the work has been with the installation of the drop mechanism (see ANL-6477, Figure 46, Page 165) and, in particular, with the design, wiring, and testing of sensing circuits used for detection of the position of the sample within the calorimeter. Appropriate circuits are being designed and tested to sense the position of the iron weight within the drop tube so that circuits can be activated at the proper time. The first method tried was to detect a change in the impedance of a coil wrapped around the brass drop tube when the iron weight passed through it. Because of the low impedance induced in the coil by the brass drop tube, the change in impedance when the weight dropped through the coil was not detectable. The method now being tested uses a permanent magnet in the drop weight; a voltage is induced in the coil when the weight passes through. This induced voltage is used to give a pulse which can be amplified and used to trigger an electronic circuit that activates the eddy current brake magnet.

IV. 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.

An experimental program to determine the rates of reaction of molten reactor fuel and cladding metals with water is continuing. Methods currently being used to examine these reactions are the condenser-discharge and volumetric methods in the laboratory, and in-pile reactor transients in the TREAT reactor.

A. Metal Oxidation and Ignition Kinetics (L. Baker)

The isothermal oxidation of uranium at high temperature is being studied. X-ray diffraction studies of oxidized uranium by means of a diffractometer, rather than by the film technique used in earlier work, have been made. Oxidation and ignition studies of plutonium and its alloys continued.

1. Isothermal Oxidation of Uranium at High Temperature (L. Baker, J. D. Bingle)

Preliminary studies of the isothermal oxidation of uranium at temperatures above 300 C were reported in a previous quarterly (ANL-6413, page 160). Further results are reported for uranium. Recent studies have been extended to include uranium-aluminum and uranium-copper alloys. It is the purpose of these studies to provide the data on isothermal reaction rates needed to develop a quantitative understanding of previously reported ignition data. A quantitative relationship between isothermal oxidation rates and ignition-temperature measurements should exist if the ignitions are purely thermal in character. A thermal ignition is merely an accumulation of heat, in which the reacting system is generating more heat than can be dissipated by heat-loss mechanisms, leading to a rapidly increasing temperature.

a. Experimental

The oxidations were carried out in a massive metal "heat sink" reaction cell described previously (see ANL-6413, page 161). The specimens were nominally one-cm cubes polished through 600 grit silicon carbide paper, followed by polishing with 6- μ and 1- μ diamond paste. The reaction cell was connected to a volumetric apparatus (described in ANL-5974, page 41) which measured the quantity of oxygen consumed by

*A summary of this section is given on pages 11 to 13.

the specimen at constant pressure. A constant-volume apparatus using a strain-gage pressure transducer was used in later studies, particularly when a rapid reaction was anticipated. The strain-gage apparatus, shown in Figure 52, was normally filled with tank oxygen to a pressure of 500 mm. The reaction was initiated by opening a glass stopcock connecting the oxygen bulb to the previously evacuated metal reaction cell containing the specimen. Reaction was followed until the pressure reached about 100 mm. Comparison runs made with the constant-pressure oxygen-metering system and the constant-volume pressure transducer apparatus gave identical results. Indications from the pressure transducer were recorded on a $\frac{1}{4}$ -sec speed, 0- to 5-mv recorder with a chart speed of 2 in./min. The pressure transducer gave accurate readings in a few seconds following the start of the reaction, whereas about one minute of adjustment was required before readings could be obtained with the constant-pressure oxygen-metering system.

Figure 52
FAST-RESPONSE ISOTHERMAL
OXIDATION APPARATUS

b. Results with ANL Uranium

The total impurity content of ANL uranium was about 250 ppm. The detailed analyses may be found in ANL-5974, page 146. The metal was beta quenched prior to machining into specimen cubes. Previous studies over the temperature range from 125 to 300 C showed a slow,

linear first stage followed by a more rapid, nearly linear second stage. Rates decreased slightly in later stages of runs above 200 C. In the work done at higher temperatures, in which the "heat sink" reaction cell was used, rates accelerated as reaction progressed for runs in the range from 350 to 400 C. Rates decreased with time for runs above 500 C. Measured rates are given in Table 33 as a function of temperature and extent of reaction for all of the runs made with ANL uranium. Rates at various stages of the reaction are plotted as a function of reciprocal temperature in Figure 53 for rates measured at 1000, 5000, and 20,000 μg of oxygen consumed per sq cm of surface. The results plotted in Figure 53 show that the change from an autocatalytic reaction to one involving a protective oxide at 450 C is very striking.

Table 33

RATES OF OXIDATION OF ANL URANIUM CUBES AT HIGH TEMPERATURE

Temperature (C)		Reaction Rate [$\mu\text{g O}_2/(\text{sq cm})(\text{min})$] at Indicated Total Oxidation ($\mu\text{g O}_2/\text{sq cm}$)						1/n Slope on log-log plot
Nominal	Average	1,000	2,000	5,000	10,000	20,000	50,000	
300	300	66	51	38	-	-	-	
300	300	63	54	40	45	-	-	
350	350	185	228	260	320	350	-	1.19
350	350	164	208	235	247	272	-	1.32
350	350	171	212	220	240	265	-	1.18
400	400	410	590	720	840	1,060	-	1.30
400	400	700	930	1,090	1,200	1,370	1,450	1.44
400	400	390	410	500	560	650	900	1.13
400	400	420	420	480	530	-	-	1.11
450	450	800	850	870	1,040	1,270	-	1.08
450	450	920	860	820	730	690	-	0.92
450	450	900	800	750	720	640	590	0.90
500	505	-	1,350	1,140	1,000	840	-	0.83
500	505	-	880	820	860	840	-	0.89
500	505	1,460	1,360	1,250	1,020	-	-	0.80
550	565	-	-	1,580	1,470	1,330	1,000	0.88
550	565	5,000	3,000	2,280	2,280	-	-	0.76
600	625	-	-	2,850	3,100	2,840	2,260	0.87
600	625	-	-	2,450	2,730	-	-	0.86
600	625	6,700	4,000	3,070	3,500	2,950	-	0.86
600	625	11,500	5,600	4,350	3,690	3,030	-	0.68
700	750	-	17,200	13,900	11,200	-	-	0.82

^aArithmetic average.

Figure 53

THE EFFECT OF TEMPERATURE AND TOTAL
OXIDE THICKNESSES ON THE RATES OF
OXIDATION OF ANL BASE URANIUM

Specimen temperature rose somewhat during runs at the higher temperatures. Some of the runs were made with specimen cubes having a small hole in one of the faces. A fine thermocouple was inserted in the hole so that the thermocouple junction would be near the cube center. The lead wires were threaded through the steel tubing leading to the reaction cell and brought out through a wax seal in a cold portion of the apparatus. The following table gives some of the recorded temperature rises for typical runs:

Nominal Run Temp (C)	Temperature Rise (C) at Cube Center at Indicated Extent of Reaction ($\mu\text{g O}_2/\text{sq cm}$)	
	2,000	20,000
350	2	8
450	2	10
550	19	28
600	20	39
700	40	a

^aRun terminated at about 15,000 $\mu\text{g O}_2/\text{sq cm}$; the temperature rise had reached 80 C before termination.

Average run temperatures were determined from the measurements of temperature rise and are given in Table 33. The temperature rise in the run at 700 C was so great that there was little of quantitative significance in the kinetic results. The measurements of temperature rise made with runs at 600 C show the effectiveness of the "heat sink" reaction cell. The total temperature rise was less than 40 C. The uranium cubes, however, are known to ignite in oxygen at a temperature of 595 C when only the normal cooling processes of convection and radiation are available to the specimen.

Log-log plots of the data from each run were prepared and the slope determined. The slope of the line on such a plot corresponds to $1/n$ in the following empirical rate law:

$$w^n = kt \quad ,$$

where w is the quantity of oxygen reacted, $\mu\text{g}/\text{sq cm}$, t is time, min, and k is a constant for each temperature. Values of $1/n$ are included in Table 33 for each run. Average values of $1/n$ for duplicate runs are also indicated in the table. The results show considerable scatter for runs which had the accelerating rate ($1/n > 1$) at 350 and 400 C. Runs at 450 C were nearly linear ($1/n = 1$). Runs at 500 C and higher showed less scatter and had an average value of $1/n \approx 0.83$ or $5/6$. It was, therefore, most convenient to correlate the results above 500 C in terms of the following rate law:

$$w^{6/5} = kt; \quad (T \geq 500 \text{ C}) \quad .$$

Values of k obtained in the experimental runs are given in Table 34.

Table 34

DETERMINATION OF RATE LAW CONSTANTS
FOR URANIUM OXIDATION

Average Temp (C)	k [($\mu\text{g O}_2/\text{sq cm}$) ^{6/5} /min]	Average k
505	7,540	6,930
505	5,030	
505	8,210	
565	11,000	13,700
565	16,300	
625	23,300	23,900
625	19,300	
625	25,300	
625	27,700	
750	95,300	95,300

An Arrhenius plot of the average k values is given in Figure 54, from which an activation energy of 14.3 kcal/mole was estimated graphically. The rate law can then be written as follows:

$$w^{6/5} = 7.3 \times 10^7 t \exp (-14,300/RT); (T > 500 \text{ C})$$

Figure 54

EFFECT OF TEMPERATURE ON THE RATE CONSTANT
FOR THE REACTION OF URANIUM WITH OXYGEN
ABOVE 450 C

c. Runs with Battelle Base Uranium and Uranium Alloys

Ignition studies in oxygen with Battelle base as-cast uranium (designated BMI) and with uranium alloys were reported previously (see ANL-5974, page 15). The results showed that there were marked

differences in ignition behavior between the 2 kinds of "pure" uranium, ANL and BMI base, and that alloying additions in some cases had profound effects.* Additions of aluminum decreased the ignition temperature about 200 C, whereas the addition of copper increased the ignition temperature about 200 C. Listed below are the ignition temperatures of 8.5-mm cubes of both uranium base metals and the 1 a/o alloys of copper and aluminum.

Ignition Temperature, C (in oxygen)	Pure Uranium			
	ANL	BMI	1 a/o Al	1 a/o Cu
	595	575	355	770

A limited series of isothermal runs of BMI base metal, and of 1 a/o aluminum and 1 a/o copper alloys was therefore undertaken.

Results of the runs are compared with ANL uranium in Table 35. The results show that rates of the 4 materials are similar at temperatures up to 300 C, but that the rate of the aluminum alloy becomes more rapid at 500 C and above.

Table 35

COMPARISON OF OXIDATION RATES OF URANIUM AND URANIUM ALLOYS IN OXYGEN AT HIGH TEMPERATURES

Temperature (C)	Total Oxidation ($\mu\text{g O}_2/\text{sq cm}$)	Oxidation Rate [$\mu\text{g O}_2/(\text{sq cm})(\text{min})$]			
		ANL Uranium ^a	BMI Uranium	1 a/o Cu Alloy	1 a/o Al Alloy
200 ^b	1,000	7	7	6	6
200 ^b	5,000	5	4	4	4
200 ^b	10,000	-	-	-	-
300	1,000	65	75	-	90
300	5,000	40	50	-	60
300	10,000	45	-	-	-
400	1,000	500	520	720	1,560
400	5,000	690	700	770	1,900
400	10,000	790	730	900	1,800
505	1,000	1,450	1,800	1,200	9,700 ^c
505	5,000	1,050	1,650	1,970	15,100 ^c
505	10,000	915	1,510	1,750	19,800 ^c
625	1,000	5,000	7,500	6,400	11,900 ^c
625	5,000	3,630	3,600	2,000	16,500 ^c
625	10,000	3,160	2,680	1,020	20,300 ^c
750		19,900 ^c	-	14,800	-
750		13,900 ^c	-	6,300	-
750		11,200 ^c	-	4,080	-

^aAverage results.

^bLow-temperature results (see ANL-5974, page 64).

^cValues uncertain because of excessive self-heating.

*Detailed analyses for the pure metals and the alloys can be found in ANL-5974, page 145.

The rate for the BMI base metal is somewhat more rapid than that for the ANL base metal at 500 C. The results at 600 C show that the aluminum alloy reacts much more rapidly than the base metals and that the copper alloy forms a more protective film, i.e., the rate is lower but only after some oxide has built up on the surface.

The reaction rates after 10,000 $\mu\text{g O}_2/\text{sq cm}$ oxidation are compared in Figure 55. The results in Figure 55 indicate that the rates of all 4 metals are very similar below 400 C. The aluminum alloy continues to follow an accelerating reaction up to higher temperatures. The oxidation characteristics of the pure metals and the copper alloy undergo a transition so that the oxide film becomes somewhat protective. The BMI base metal undergoes a rather gradual transition, whereas the ANL metal undergoes a sharp transition. The presence of copper renders the oxide film considerably more protective.

Figure 55

RATES OF OXIDATION OF VARIOUS URANIUM SPECIMENS AS A FUNCTION OF TEMPERATURE AFTER 10,000 $\mu\text{g O}_2/\text{sq cm}$ TOTAL OXIDATION

The character of the results suggests that a transition occurs in the oxide films on uranium at about 450 C. It is not presently known whether there is a change in crystal structure or whether there is a change in crystallite size or some other macroscopic property. The transition does not occur when aluminum is present, but it is promoted in the presence of copper. Some characteristic or impurity in the BMI base metal causes the transition to occur more gradually than it does with ANL metal. It should be emphasized that the ANL metal is beta quenched whereas the BMI metal is as-cast, and this difference might account for the differences in reaction rates.

There was a very distinct difference in the appearance of the oxide from runs made above the transition and from those made at lower temperatures. The oxide was loose and flaky, tending to form well-defined plates in the low-temperature region. Oxide from high-temperature runs appears sintered and was very adherent. X-ray studies of the oxide products are in progress. The difficulty in distinguishing between UO_2 and $\alpha\text{-U}_3\text{O}_7$, $\beta\text{-U}_3\text{O}_7$ and U_4O_9 , however, is well known. Hoekstra *et al.*²³ have shown that the $\beta\text{-U}_3\text{O}_7$ phase is stable only below a temperature of about 350 C. It is replaced by a phase designated as $\text{UO}_{2.3}$ at higher temperatures. More studies are needed to determine if one of these phases might account for the self-accelerating reactions observed below 450 C in the oxidation of uranium.

2. X-ray Diffraction Studies of Oxidized Uranium (L. Leibowitz and J. D. Bingle)

It has been reported²⁴ that only uranium dioxide forms during the oxidation of uranium, a conclusion supported by both X-ray and electron diffraction examinations of the surface oxide. Recent studies of low-temperature UO_2 oxidation²³ have shown that erroneous conclusions can be deduced from film measurements of diffraction patterns. The findings of Hoekstra *et al.*, confirmed by Belbeoch, Piekarski, and Perio,²⁵ led us to repeat the X-ray diffraction examination of oxidized uranium with a diffractometer, rather than by the film technique which had been used in the earlier work. A "second phase is detectable early in the oxidation only as a shoulder on certain of the UO_2 diffraction maxima."²³ This shoulder initially is apparent only as an asymmetry in the UO_2 pattern. Such an effect cannot be observed using film. Oxidations were carried out at 100, 150, 200, and 250 C. Two samples were prepared at each temperature.

²³Hoekstra, H. R., Santoro, A., and Siegel, S., J. Inorg. Nucl. Chem. 18, 166 (1961).

²⁴Leibowitz, L., Schnizlein, J. G., Bingle, J. D., and Vogel, R. C., J. Electrochem. Soc. 108, 1155 (1961).

²⁵Belbeoch, B., Piekarski, C., and Perio, P., J. Nuclear Materials 3, 60 (1961).

One of these was oxidized to the end of the first stage²⁴ and required 15 to 180 $\mu\text{g O}_2/\text{sq cm}$, depending on the temperature. The other was oxidized to well into the second stage.²⁴ This treatment required 550 to 1150 $\mu\text{g O}_2/\text{sq cm}$.

All of the second-stage samples showed evidence of the presence of higher oxides.* Of the first-stage samples, only the one at 200 C showed evidence of higher oxides. The intensity distribution in the region $2\theta = 56$ degrees²³ is shown in Figure 56 for the 100 C second-stage sample. This was the most pronounced asymmetry observed. In the other cases, only a slight asymmetry of the peak could be seen. This would not have been observable at all if film were used.

Figure 56

THE INTENSITY DISTRIBUTION AT
 $2\theta = 56$ DEGREES OF X-RAY DIF-
FRACTION PATTERN FROM AN
OXIDIZED URANIUM SURFACE
SHOWING ASYMMETRY

The exact constitution of the new oxide phase cannot be determined from this information. It seems fairly clear that it is not U_3O_8 , but U_3O_7 or U_4O_9 seem to be possibilities.²³

Some further work is planned to help clarify more exactly when formation of the new oxide phase begins. The difficulties of identification are, of course, considerable.

3. Plutonium Oxidation and Ignition Studies (J. G. Schnizlein and D. F. Fischer)

The experimental program to determine oxidation and ignition behavior of plutonium and its alloys is continuing in the new facilities (see ANL-6413, page 168).

*X-ray analysis and interpretation carried out by M. Homa and R. Schablaske, Chemical Engineering Division.

a. Ignition Studies

Ignition experiments in air and oxygen have been completed on plutonium samples containing the following atomic percent additives: 0.27 silicon, 1.26 nickel, 2.40 copper, 0.40 and 1.03 zinc, and nominally 2 magnesium and chromium. All caused limited increase of the ignition temperature, copper having the greatest effect (of approximately 50 degrees). The data are presented in Table 36.

Table 36

PLUTONIUM ALLOY IGNITION TEMPERATURES

Burning-curve Method:^a 0.5-cm cubes

<u>Alloys</u>	<u>Additive (a/o)</u>		<u>Ignition Temperature (C)</u>	
	<u>Nominal</u>	<u>Analysis</u>	<u>In Oxygen</u>	<u>In Air</u>
Pure Pu	-	-	494	508
Si	1/2	0.27	537	544
Si	1	0.28	537	548
Si	2	0.26	525	548
Mg	2	-	512	520 ^b
Cr	2	-	498	514
Ni	2	1.26	489,509	529
Cu	2	2.40	553,546	555
Zn	1	0.40	503	528
Zn	2	1.03	523	528

^aFurnace temperature increased at a rate of 10 degrees per minute while sample is in flowing oxidizing atmosphere.

^bTemperature program not standard in this experiment.

b. Isothermal Oxidation

In addition to its pertinence to understanding of ignition behavior, it should be important to see the effects of the many different metal phases on the oxidation behavior. The phases, crystallographic structures, densities, and the temperatures of transition are as follows:

Phase	Transformation Temperature (C)	Structure	Density (g/cc)
alpha	120	monoclinic	19.84
beta	210	body-centered monoclinic	17.70
gamma	315	face-centered orthorhombic	17.14
delta	452	face-centered cubic	15.92
delta prime	480	face-centered tetragonal	16.07
epsilon	640 (mp)	body-centered cubic	16.51

Dempsey and Kay²⁶ have reported oxidation experiments in air in each of the beta, gamma, and delta phases. They observed a two-stage oxidation in the beta phase similar to that of uranium, a linear oxidation in the gamma phase, and a parabolic oxidation in the delta phase.

Isothermal oxidation experiments on the thermobalance (described in ANL-6413, page 172) have been conducted in alpha, beta, and gamma phases over the temperature range from 100 to 393 C. One run in each phase is plotted in Figure 57.

Figure 57
PLUTONIUM OXIDATION IN OXYGEN IN ALPHA,
BETA, AND GAMMA PHASES
(Samples approximately 1 sq cm area)

²⁶Dempsey, E., and Kay, A. E., J. of Institute of Metals, 86, 379 (1958).

At 100 C in the alpha phase, the oxidation was of a protective nature, there being no weight gain after 120 min (terminated after 1665 min). Because of the small surface area (about one sq cm) of the sample and the limited sensitivity (a weight gain observed of only 0.3 mg), no test of whether the oxidation rate was parabolic, cubic, or logarithmic was justified. Experiments at this temperature will be postponed until larger samples and a more sensitive method (measuring pressure change in a small system with a strain-gage) are available.

In the beta phase, two-stage oxidations were observed similar to the case for uranium (and as reported by Dempsey and Kay). Duplicate runs at 183 and 185 C in oxygen are compared with Dempsey and Kay data in air at 205 C in Figure 58. Fair reproducibility and agreement are demonstrated.

Figure 58

REPRODUCIBILITY OF BETA PHASE PLUTONIUM OXIDATION IN OXYGEN

(Samples approximately 1 sq cm area)

Another experiment conducted at the lower end of the beta-phase range of temperature also showed 2 stages. Comparison of the first stage rates [$1.25 \mu\text{g}/(\text{sq cm})(\text{min})$ at 139 C and $4.4 \mu\text{g}/(\text{sq cm})(\text{min})$ at 184 C]

shows a reasonable temperature dependence (activation energy of the order of 10 kcal). However, the second stage rates are $17.5 \mu\text{g}/(\text{sq cm})(\text{min})$ at 139°C and 17.3 (average of 15.8 and 18.8) $\mu\text{g}/(\text{sq cm})(\text{min})$ at 184°C , indicating no temperature dependence. The oxides in all 3 experiments were dull green, indicative of PuO_2 .

Two experiments in the lower region of the gamma phase indicated linear rates [$10 \mu\text{g}/(\text{sq cm})(\text{min})$ at 220°C and $12 \mu\text{g}/(\text{sq cm})(\text{min})$ at 237°C]. These rates are lower than observed for the second stage in the beta phase and appear to be consistent with the first-stage rates in the beta phase if one considers the higher temperatures and a similar activation energy. The oxides from these runs were dark grey.

An Arrhenius plot of linear rates (see Figure 59) further indicates the possibility that the same process is rate controlling in the lower gamma-phase temperature region as that which determines the first-stage rate in the beta-phase region.

Figure 59
PLUTONIUM LINEAR
OXIDATION DATA

The continuing isothermal oxidation studies will include sufficient experiments to verify reproducibility and to establish the kinetics at 2 temperatures in each phase. A few experiments will be performed on the stage of the microscope to observe the exterior features of the oxide during oxidation.

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. Isothermal studies of the uranium-steam reaction are being made by a volumetric method in which steam at one atmosphere is passed over a one-centimeter cube of metal at an appropriate temperature. In-pile studies of metal-water reactions in TREAT are continuing.

1. Condenser-discharge Methods (L. Baker, R. Warchal)

The condenser-discharge experiment is an attempt to obtain fundamental rate data under experimental conditions similar to those encountered during a serious accident in a nuclear reactor. Either a nuclear runaway or a sudden loss of coolant during operation of a water-cooled reactor could result in contact of 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.

More runs with stainless steel-316 wires have been carried out. Runs completed to date were made in the high-pressure reaction cell in room-temperature water (pressure 0.5 psi). The high-pressure reaction cell was described in ANL-6231, page 156. Runs were made with 30- and 60-mil wires. Results of the runs are given in Table 37 and Figure 60. Metal temperatures with 60-mil wires were limited to about 1600 C because of energy limitations of the apparatus. The melting point of stainless steel 316 was taken as 1370 C (2500 F).²⁷ Enthalpy data, used for translating energy

²⁷Metals Handbook, Vol. 1 (8th Edition), American Society for Metals, Novelty, Ohio (1961), page 423.

input data to initial metal temperatures, were based on a weighted average of data for iron (70 percent), chromium (18 percent), and nickel (12 percent). The appearance of the residue is reasonably consistent with the calculated physical state of the metal given in Table 37.

Table 37

REACTION OF STAINLESS STEEL-316 WITH ROOM-TEMPERATURE
WATER; CONDENSER-DISCHARGE METHOD

Run	Energy Input (cal/g)	Temp (C) and Physical State	% Reaction ^a	Appearance of Residue
<u>Runs with 30-mil Wires</u>				
303	216	1370, solid	0.0	Distorted
304	220	1370, 10% liquid	0.0	Large Particles
182	284	1370, 100% liquid	4.7	Fine Particles
184	288	1400, liquid	2.6	Fine Particles
302	292	1400, liquid	2.7	Fine Particles
181	292	1400, liquid	4.7	Fine Particles
198	294	1400, liquid	3.1	Fine Particles
180	302	1500, liquid	4.0	Fine Particles
183	310	1500, liquid	4.9	Fine Particles
185	328	1600, liquid	6.3	Fine Particles
308	406	2100, liquid	6.4	Fine Particles
316	454	2300, liquid	5.4	Fine Particles
315	455	2300, liquid	4.5	Fine Particles
264	488	2500, liquid	11.6	Fine Particles
265	597	3100, liquid	17.5	Fine Particles
314	716	3800, liquid	35.9	Powder
<u>Runs with 60-mil Wires</u>				
319	148	1000, solid	0.2	Distorted
311	192	1200, solid	0.1	Bent and Cracked
317	246	1370, 50% liquid	0.6	Large Particles
318	277	1370, 90% liquid	1.6	Fine Particles
322	293	1400, liquid	1.8	Fine Particles
321	321	1600, liquid	3.0	Fine Particles

^aBased on reaction to Cr_2O_3 , NiO , and FeO .

Transient pressure traces obtained in the stainless steel runs to date were generally unsatisfactory. The small quantity of gas generated in the less energetic runs made it difficult to distinguish between electrical

noise caused by the discharging condensers and the true pressure signal. Pressure rises were probably explosive in the very energetic runs reported in Table 37. The explosive pressure rises obtained in these runs were similar to those reported previously in very energetic runs with uranium and zirconium wires. It is evident from the results that there is no significant reaction up to the melting point of the stainless steel.

Figure 60

REACTION OF STAINLESS STEEL-316 WITH WATER
BY THE CONDENSER-DISCHARGE METHOD

A complete analysis of the data requires the determination of particle sizes produced in the runs. A further series of runs will be made in heated water.

2. Isothermal Studies of the Uranium-Steam Reaction by the Volumetric Method
(R. E. Wilson, P. Martin)

A knowledge of the reaction rates of solid metals with steam under isothermal conditions is necessary for theoretical derivations and computer studies for the prediction of metal-water reactions under the conditions of a reactor excursion. This experiment supplements data from the condenser-discharge studies and the TREAT experiments. Studies of this reaction have been undertaken by means of a simple volumetric apparatus in which steam at one atmosphere is passed over a one-centimeter cube of metal at the appropriate temperature. The reaction rate is measured by continuously monitoring the hydrogen swept from the reaction cell. Equipment is described in more detail below.

a. Apparatus

A diagram of the apparatus used is shown in Figure 61 and is modeled on a similar apparatus described by Kubaschewski and Hopkins.²⁸ In this apparatus, the uranium sample cube, with a known surface area, is mounted on the end of a thermocouple, with the bead of the thermocouple extending to the center of the cube. The sample is heated to the desired temperature by means of a 4-kw induction heater. The induction coil is mounted outside the quartz reaction vessel so that the water-cooled coil does not condense the steam. The steam is produced by pumping water through heated tubing. The steam flow rate is determined by adjustment of a micrometer needle valve and is limited by the tube heater.

Figure 61

VOLUMETRIC APPARATUS FOR STUDYING THE URANIUM-STEAM REACTION

Hydrogen, produced by the uranium-water reaction

is swept out of the cell into a condenser by the excess steam. In the condenser, the hydrogen is trapped between drops of condensate and is forced through small-diameter tubing into a graduated collection vessel. The amount of hydrogen evolved is recorded as a function of time.

b. Results

Some preliminary results for the uranium-water reaction are plotted in Figure 62, in which the volume of hydrogen produced per sq cm, corrected to standard conditions, is plotted as a function of time for 2 temperatures. The curves drawn through the experimental points

²⁸Kubaschewski, O., and Hopkins, B. E., Oxidation of Metals and Alloys, Butterworth Scientific Publications, London (1953) p. 115.

have slopes which are nearly parabolic. Preliminary results have shown that the reaction is quite reproducible (as shown by the agreement between runs on Figure 62) and that the oxide is protective. A shiny black oxide is produced which adheres firmly to the metal during the runs. When the temperature reaches about 300 C during cooling of the specimen after completion of a run, the oxide begins to powder and flake off.

Figure 62

HYDROGEN EVOLUTION AS A FUNCTION OF TIME FOR THE URANIUM-STEAM REACTION

3. Metal-Water Reaction Studies in TREAT* (R. C. Liimatainen, R. O. Ivins, F. J. Testa)

The program of studying metal-water reactions initiated by nuclear reactor bursts is continuing. The technique consists of exposing fuel specimens in water to a neutron pulse in the TREAT reactor. The purpose of this experimental work is threefold:

1. to determine the fraction of metal that reacts with water;
2. to determine the temperatures and pressures produced during the excursion; and
3. to determine the structural changes that take place in the fuel as a result of rupture or meltdown; this is accomplished by metallographic and particle size evaluations.

*The cooperation of J. Boland, F. Kirn, and H. Lawroski, of the Idaho Division, for the operation of the TREAT reactor is gratefully acknowledged.

a. Aluminum-Water Reactions

The in-pile studies of the reaction of molten aluminum with water have been extended to a higher energy. A summary of the conditions of the energetic pulse test and the results is given in Table 38; the test was performed with a cermet fuel pin submerged in water. A photograph of the fuel specimen after the meltdown in water is shown as Figure 63.

Table 38

METAL-WATER TRANSIENT CEN-77 WITH ALUMINUM- URANIUM OXIDE-CERMET FUEL PINS

Test Conditions: H_2O at 25 C under 20 psia He pressure.

Fuel Pin: 93 percent enriched, 90 w/o Al, and 10 w/o U_3O_8 ,
unclad, 0.375 in. diameter x 0.50 in. long.

TREAT Transient - CEN-77

Reactor Pulse

Integrated power, Mw-sec	750
Peak power, Mw	4085
Period, msec	39
Calculated energy input, cal/g fuel pin core	760

Results

Peak temperatures of fuel pin, C 1400^a

Peak pressures rise in autoclave, psi 345

Appearance of fuel pin after irradiation

Fuel Specimen: Large globule plus many particles.

Inner walls of autoclave: Covered with grey-white deposit;
also some drops sprayed and
solidified on walls and top plug.

Crucibles: Inner crucible shattered, portion
of rim of stainless steel crucible
distorted.

Extent of Al- H_2O Reaction

percent: 19.0

^aThis was the peak measured temperature; however, observation after the transient showed that the thermocouple had lost contact with the aluminum; hence, the true temperature is, no doubt, higher than 1400 C.

Figure 63

ALUMINUM- U_3O_8 CERMET FUEL PIN
AFTER TRANSIENT CEN-77

The observations summarized in Table 38 indicate that there was considerable dispersion of the molten aluminum within the autoclave; also, there was some evidence (grey-white deposit on walls of autoclave) of a vapor-phase reaction. The aluminum particles formed appear to have an oxide coating, and some are porous; 19 percent of the aluminum reacted with the water, as measured by the hydrogen evolution. The data from this transient are compared with 2 lower energy transients in Figure 64. It is evident that the amount of reaction increased quite sharply with the energy input (linear extrapolation of the 2 previous experiments would predict only about 8 percent reaction). Another transient will be conducted at about 1000 Mw-sec to obtain an additional value for the amount of metal-water reaction at a very high energy input.

Figure 64

EXTENT OF ALUMINUM-WATER REACTION
RESULTING FROM IN-PILE MELTDOWNS OF
ALUMINUM- U_3O_8 CERMET FUEL PINS

b. Stainless Steel-Water Reactions

In-pile study of urania-core, stainless steel-304 fuel pins was continued. Table 39 summarizes the data obtained from the 3 most recent transients in TREAT with those urania-core specimens. The purpose of CEN-72 was to determine the behavior of a sealed, waterlogged core during a reactor transient.

Table 39

BEHAVIOR OF URANIUM DIOXIDE-CORE, STAINLESS STEEL-304-CLAD FUEL PINS IN TREAT (TRANSIENTS CEN-72, CEN-69, CEN-71)

Test Conditions: H₂O at 25 C under 20 psia He pressure.

Fuel Pin: 20 percent enriched UO₂ core; 0.33-in.-diameter x 0.50-in.-long core size, 18-mil SS-304 clad; 1-mil gap between clad and core; UO₂, 98 percent of theoretical density.

	TREAT Transient		
	CEN-72 ^a	CEN-69	CEN-71
<u>Reactor Pulse</u>			
Integrated Power, Mw-sec	76	245	400
Peak Power, Mw	450	1500	3280
Period, msec	110	64	43
Calculated energy input, cal/g fuel pin core	99	319	520
<u>Results</u>			
Peak surface temperature of SS-304 jacket, C:	-	1047	995
Peak pressure rise in autoclave, psi	12	-	-
Appearance of fuel pin after irradiation			
core:	cracked, but contained within clad	fragmented	fragmented
clad:	central hole, darkened area	ruptured; 1/2 melted	ruptured; 1/2 melted
<u>Extent of SS-H₂O Reaction</u>			
percent:	3.7	5.4	11.5

^aThe UO₂ core pellet in CEN-72 was waterlogged and then sealed by welding before the fuel pin was subjected to the reactor pulse.

Figure 65
URANIUM DIOXIDE-CORE, STAINLESS STEEL-304-
CLAD FUEL PIN AFTER TRANSIENT CEN-72

Figure 65 shows the appearance of the fuel pin after CEN-72, which was a 76-Mw-sec (95-cal/g UO_2) energy transient. The stainless steel jacket had a central hole through which some of the urania core was expelled. The darkened zone was the region of high temperature, which had undergone oxidation by the water. When the results from CEN-72 are compared with previous transients (see ANL-6413, page 182) with the same type of fuel pin, it is apparent that the sealed, waterlogged fuel pin had

both more metal-water reaction (3.7 as compared to 0.1 percent reaction for a comparable energy input to a dry urania-core fuel pin) and a lower threshold energy of destruction than did a fuel pin with a dry core. Previous data with dry urania-core fuel pins gave a threshold energy of about 174 cal/g UO_2 . This is an interesting point since it suggests that gases (in this case, steam) trapped inside the fuel pin can promote earlier destruction and more reaction of the fuel pin when the pin, submerged in water, is subjected to a reactor transient.

Runs CEN-69 and 71 (see Figures 66 and 67) were made in order to provide further information on the amount of stainless steel-water reaction that occurs as a function of the energy and period.

Figure 66
URANIUM DIOXIDE-CORE,
STAINLESS STEEL-304-CLAD
FUEL PIN AFTER TRANSIENT
CEN-69

Figure 67

URANIUM DIOXIDE-CORE, STAINLESS STEEL-304-
CLAD FUEL PIN AFTER TRANSIENT CEN-71

Increasing the energy from 245 to 400 Mw-sec (320 to 520 cal/g UO_2) caused the amount of metal reacted to increase from 5.4 percent to 11.5 percent. Transient CEN-71 was on a very short period of 43 msec. The results from CEN-69 and 71, when compared with earlier results (ANL-6413, page 182) with urania-core fuel pins, confirm that increasing the energy does cause more metal-water reaction. Also, these oxide-core fuel pins apparently are not as sensitive to period as are the metal (uranium) fuel specimens. Previous experiments with uranium wires (see ANL-6333, page 237) had indicated that shorter periods tend to promote more reaction of all-metal specimens. For example, uranium wire runs at 554 cal/g uranium gave 33.2 and 55.2 percent metal-water reaction at periods of 440 and 152 msec, respectively.

c. Zirconium-Water Reactions*

At the request of the Metallurgy Division, 2 tests were performed with fuel pins with thoria-urania-molybdenum wire cores and Zircaloy-2 clad. Molybdenum wires were used to improve the thermal

*The assistance of L. Neimark in furnishing the fuel specimens and in interpreting the photomicrographs is appreciated.

conductivity of the core and to monitor the core temperatures. The results are given in Table 40, and in Figures 68 and 69. Photomicrographs established that there was melting of the molybdenum wires in the high-energy transient but only incipient melting at the lower energy input. From the point of view of fuel stability, the data suggest that the allowable peak temperature for the central core of this fuel pin is about 2600 C (threshold temperature) for fuel submerged in room-temperature water. The fuel remains intact below 2600 C; however, if the pulse is energetic enough to cause temperatures above 2600 C, rupture or melting occurs.

From a metal-water reaction standpoint, the 2 transients also differed considerably. In the transient in which the fuel remained intact, only 6 percent of the Zircaloy-2 jacket reacted with the water, whereas in the destructive, high-energy test, 29 percent reaction occurred. The weight of the end caps was not included in the calculation, since they were not appreciably heated during the transient. Finally, these 2 experiments demonstrate that metal wires within a ceramic core function as an effective temperature monitor. A possible modification would be to intersperse in the core 3 or 4 wires of metals with widely varying melting points.

Table 40

BEHAVIOR IN TREAT OF THORIUM DIOXIDE-URANIUM DIOXIDE-MOLYBDENUM CORE ZIRCALOY-2-CLAD FUEL PINS

Test Conditions: Water at 25 C, under 20 psia He pressure

Fuel Pin: 10 w/o Mo (wires) in ThO₂-UO₂ core matrix

	TREAT Transient	
	CEN-78	CEN-86
<u>Reactor Pulse</u>		
Integrated Power, Mw-sec	217	580
Peak Power, Mw	658	1270
Period, msec	98	67
Calculated energy input, cal/(g fuel pin core)	230	400
Fuel Pin Enrichment; w/o U ²³⁵ :	7.15	4.54
<u>Results</u>		
Estimated peak temperature of the central core of the fuel pin, C	2600	3000
Appearance of fuel pin after irradiation		
core:	incipient melting of Mo wires	complete melting of Mo wires
clad:	intact, some swelling	ruptured and melted (except for end caps)
Extent of Zr-H ₂ O Reaction ^a		
percent:	6	29

^aMo-H₂O reaction assumed to have been negligible.

Figure 68
TRANSIENT CEN-78

ThO₂, UO₂, Mo CORE, Zr-2-CLAD FUEL PIN AFTER PULSED IRRADIATION

PHOTOMICROGRAPH OF PORTION OF CORE OF FUEL PIN AFTER PULSED IRRADIATION

Figure 69
TRANSIENT CEN-86

ThO₂, UO₂, Mo CORE, Zr-2-CLAD FUEL PIN BEFORE AND
AFTER PULSED IRRADIATION

PHOTOMICROGRAPHS AFTER PULSED IRRADIATION

V. ENERGY CONVERSION*

Two methods of converting nuclear energy into electricity are being examined. These methods are the regenerative cell and the thermoelectric effect.

A. Regenerative Emf Cell

(C. E. Crouthamel, M. Foster, C. E. Johnson, R. Heinrich,
R. Eppley, S. F. Banaszek)

Studies are continuing leading to the development of a regenerative cell to convert heat into electricity in a closed cyclic system. All of the systems in which we are interested involve fused salt electrolytes and liquid metal systems which are not compatible with an ordinary atmosphere (e.g., N_2 , O_2 , water vapor, and other reactive gases must be in the 1 to 50 ppm concentration range in the inert helium or argon atmosphere). Apparatus for the continuous purification of the helium atmosphere in the box is now being assembled and tested.

Hydrogen-diffusion measurements have been made with pure iron diaphragms which were welded to their holders by electron beam welding instead of by the previously used shear-seal technique of mounting the diaphragms in their holders. The results agree with the previously determined hydrogen-diffusion rates.

The diffusion rate of hydrogen through the pure iron diaphragm is presently the predominant effect limiting the power which can be drawn from the lithium hydride cells. As a possible method of increasing the rate of hydrogen diffusion, the hydrogen behind the iron diaphragm has been ionized strongly by two different intensity levels of alpha sources. At low temperature (400 C), diffusion rates with the alpha sources were twice those in the absence of a source; at 750 C, the rates were 20 percent higher with alpha ionization than without. Increase of the alpha source intensity by a factor of 10 (5×10^8 to 5×10^9 d/m) produced no appreciable additional increase in the diffusion rate.

Other possible methods of circumventing this limitation due to diffusion rate are the use of diaphragms of materials which are compatible with the cell environment and which permit hydrogen to diffuse at the higher rates required. One such diaphragm material which is to be evaluated is niobium metal. The fabrication of cells with this and other diaphragm materials has presented problems which are currently being investigated in the Argonne welding shops.

* A summary of this section is given on page 9.

Investigation of bimetallic liquid metal concentration cells has continued. The experiments have been conducted with liquid lithium metal anodes in each case and with a variety of liquid metal cathodes separated by a third liquid phase of fused salts containing the lithium ion. Metals for cathodes were selected as described in the previous quarterly report (see ANL-6477, pages 209 to 213). In addition to the lithium-tin cell, whose current-voltage characteristics also were reported in the previous quarterly report, lithium-bismuth, lithium-cadmium, lithium-lead, lithium-tellurium, and lithium-zinc have been determined and are reported here.

1. Inert Atmosphere Box Helium Purifier

In the regenerative-cell program, nearly all the experiments involve molten metals and salts which are extremely sensitive to all the chemically active gases. The problem not only concerns the absolute purity of the original charge of blanket gas, but also that of purification of the box atmosphere while cycling it at a reasonably high rate. Water vapor, for example, is continually diffusing into the box through rubber gloves. In normal operations, when new equipment is moved into the box, during heating operations, and from other sources there is continual contamination of the atmosphere by chemically active gases. At least 2 general methods of atmosphere purification are possible: one is the use of hot active metals as a getter, and the second is the use of activated carbon or Molecular Sieves at low temperature. Both methods are capable of removing trace concentration levels of the active gases. The latter procedure, which is useful only with helium, was selected for this application.

The schematic diagram of the helium atmosphere purification unit now being tested is shown in Figure 70. The unit has been designed to operate at a helium flow rate of 3 to 5 cfm, which is considered adequate for boxes 15 to 25 cu ft in volume having a total active gas content, in normal operation, of 10 to 20 ppm by volume. The sequence of steps in the purification train shown in Figure 70 is as follows: the contaminated gas flows into a palladium catalytic unit which burns hydrogen to water. (It is assumed that there will be an excess of oxygen over hydrogen gas in the helium atmosphere.) The next step occurs in a Molecular Sieve dryer, which is operated at room temperature and removes water vapor from the helium stream. All remaining gases in the helium stream are next removed in an activated carbon bed cooled by liquid nitrogen. The incoming helium is cooled by the exit-gas stream in a heat exchanger unit filled with copper spheres wetted with a minimum amount of soft solder. The spheres are fused together and to the inner walls at the points of contact to achieve more rapid heat flow in the copper unit.

Figure 70
HELIUM PURIFIER FOR INERT
ATMOSPHERE BOXES

Analysis and monitoring of the glovebox atmosphere will be by a gas chromatographic technique; however, water vapor will also be monitored continuously by the current flow measurement in a phosphorus pentoxide-covered glass surface with 2 platinum wires embedded in the phosphorus pentoxide. The water is electrolyzed out of the phosphorus pentoxide and the cell is continuously regenerated. Such a cell for operation in the range of 0 to 100 ppm water by volume can be obtained commercially. Recent reports^{29,30} have indicated that gas chromatographic techniques can determine, to one ppm, quantities of oxygen, carbon monoxide, nitrogen, argon, and methane in helium. Hydrogen purified by diffusion through a palladium diaphragm will be used as the carrier gas. A Franklin and Marshall Co. model 500 gas chromatograph has been set up and put into operation for this analysis.

2. Hydrogen-diffusion Measurements

In order to study the problems of hydrogen diffusion through diaphragms in a manner independent of the cell problems, measurements of rates of hydrogen diffusion through metal diaphragms are being made. Previous experiments have been described in ANL-6477, page 204. In an attempt to increase the rate of hydrogen diffusion through metal diaphragms, the effect of ionization by a radioactive source was studied. These experiments are described below.

²⁹ Malgirolio, J., et al., Purification and Gas Chromatographic Analysis of Helium, PWAC-352, (June 1961).

³⁰ Carnahan, C. L., Gas Chromatographic Separations of Rare Gases, USNRDL-TR-535, (Nov 1961).

Several pure iron diaphragms were electron-beam welded into type 316 stainless steel holders. The welds were circular and about 1.0 mm wide. The discs were 23 mm in diameter, as measured from the inner edge of the weld, to give a diffusion area of 4.15 sq cm. The distance between the alpha source and the face of the diaphragm is about 10 cm, and the total alpha track length in hydrogen is of the order of 20 cm. The overall diaphragm assembly is shown in Figure 71. The same diaphragm and holder were used for measurements with and without the alpha source.

Figure 71

DIAPHRAGM ASSEMBLY WITH ELECTRON-BEAM WELDING

- (a) without alpha source
(b) with alpha source

The equation used to correlate the quantity of gas permeating the diaphragm per unit time can be expressed as

$$P = \frac{K}{x} \exp (-E_p/RT) \quad ,$$

where P = volume of gas (STP) permeating the diaphragm per unit time

K = a constant which includes the solubility constant of the gas-metal system, the area of the diaphragm, and the difference of the square roots of the pressures across the diaphragm.

x = thickness of the diaphragm.

T = degrees, Kelvin

E_p = activation energy of permeation [cal/(g-atom)].

The activation energy for the permeation of hydrogen through the diaphragm with no ionization of the hydrogen gas was 10,420 cal/g-atom; with the uranium-233 source behind the same diaphragm, the activation energy was 7880 cal/g-atom. Comparison of the data for rates of diffusion and activation energy are shown in Figures 72 and 73.

Figure 72

DIFFUSION RATES OF HYDROGEN
THROUGH A PURE IRON DIAPHRAGM
WITH AND WITHOUT ALPHA IONIZA-
TION OF THE HYDROGEN

Figure 73
ACTIVATION ENERGY
FOR DIFFUSION WITH
ALPHA SOURCE IONIZA-
TION OF HYDROGEN GAS

Increase of the disintegration rate of the alpha source by a factor of 10 (i.e., from 5×10^8 to 5×10^9 d/m) did not produce an additional increase in diffusion rate when the same iron diaphragm was used. It has also been noted that in experiments with iron diaphragms in the operating lithium hydride cells, diffusion rates were 1.5 times that obtained with an identical one-atmosphere hydrogen differential (1 atm to a vacuum) across the diaphragm. Apparently, when monatomic hydrogen at the iron-fused salt interface is removed as the hydride ion, diffusion proceeds more rapidly than when the process of removal is by the recombination of monatomic hydrogen and diffusion of molecular hydrogen into a vacuum. The combined effects of ionization in the gas and hydride ion removal on the diffusion rate in an operating cell will be measured as soon as possible.

3. Bimetallic Cell

The bimetallic cell may be represented as

where M_1 and M_2 are 2 metals. As pointed out in ANL-6477, page 209, bimetallic cells systems offer the possibility of comparatively high current densities at the electrodes and quite compact systems. In ANL-6477, the current-voltage characteristics of the lithium-tin cell were reported.

The densities of the 3 mutually insoluble phases are such that the density of the fused salts with the M_1 salt in solution is intermediate to those of the 2 liquid metal phases. The fused salts must be thermodynamically stable with respect to M_1 , the more electropositive, low-density metal, so that a spontaneous reaction does not occur. Also to be avoided is an M_2 metal which is appreciably soluble in the fused salt phase, since this would permit an undesirable spontaneous reaction of M_1 with M_2 . In the previous quarterly (ANL-6477, page 211), the results of a survey of various bimetallic combinations were given in which the electropositive metal was arbitrarily limited to lithium. The formation of intermetallic compounds with melting points higher than the melting points of either of the 2 pure metals was taken as an indication of an interaction of the metals and also as an indication of high voltage output.

The cell reaction may be written as

The cell emf, therefore, is

$$E = - \frac{RT}{nF} \ln (a_{M_1} \text{ in alloy})$$

Thus a large voltage will be obtained when the activity of the M_1 metal is very low in the alloy. This is a reflection of the strong interaction between M_1 and M_2 . It is especially true in the case in which M_1 and M_2 form intermetallic compounds with high melting points.

In the cells set up for preliminary current-voltage measurements, the electrolyte consisted of the eutectic composition of lithium chloride and potassium chloride, which melts at 352 C. The cathode metals studied, as well as the highest-melting intermetallic compounds formed between lithium and the various cathode elements, are shown in Table 41. These data were taken from Hansen and Anderko.³¹ All of these systems show a large degree of interaction, as indicated by the large difference between the melting points of the elements and those of the highest-melting intermetallic compounds.

Table 41

BIMETALLIC CELL COMBINATIONS WITH
LITHIUM METAL USED AS THE ANODE

Cathode Material	Highest-melting Intermetallic Compound Formed with Lithium	Melting Point of Compound (C)	Cell Potential (v)
Te	Li_2Te	(not listed)	1.93
Bi	Li_3Bi	1145	0.93
Sn	Li_7Sn_2	783	0.73
Pb	$\text{Li}_{10}\text{Pb}_3$	726	0.69
Zn	Li_2Zn_3	520	0.67
Cd	LiCd	549	0.66

When the cathode material was bismuth, cadmium, lead, or zinc, a tantalum crucible was used to contain the metal and the electrolyte fused salts. The molten lithium metal anode was contained in an Armco iron or tantalum ring as a floating disk on the top of the electrolyte. For a tellurium cathode, the tantalum container was not satisfactory and this container was replaced with one of Vycor. Electrical contact with the tellurium was made with a platinum wire. This container was satisfactory for only about 2 days, after which it cracked in operation, possibly because of lithium attack. The results of these experiments are shown in Figure 74 and Table 42. Figure 74 indicates a high open-circuit voltage in the case of the lithium-tellurium combination. However, the corrosive nature of each of these 2 materials presents a severe container problem. In future experiments, crystalline beryllium oxide vessels will be tested as possible containers.

³¹ Hansen, M., and Anderko, K., Constitution of Binary Alloys, McGraw-Hill (1958).

Figure 74
POLARIZATION CURVE
FOR LITHIUM-METAL
CELLS
(Temperature Range: 468-493 C)

(a) Li-Bi

(b) Li-Cd

(c) Li-Pb

(d) Li-Te

(e) Li-Zn

Table 42

PRELIMINARY CURRENT-VOLTAGE
DATA ON BIMETALLIC CELL COMBINATIONS

Conditions: Lithium anodes
Internal plus lead resistances

System	Temperature Range (C)	Open-circuit Voltage (v)	Current Density (Anode) at 0.3-v output (ma/sq cm)	Calculated Sum of Internal and Lead Resistance ^a (ohms)
Li-Te	496 ± 5	1.9380	475	0.71
Li-Bi	489 ± 2	0.9306	650	0.21
Li-Sn	450 ± 10	0.7891	450	0.23
Li-Pb	483 ± 9	0.6866	270	0.32
Li-Zn	468 ± 6	0.6754	225	0.44
Li-Cd	493 ± 20	0.6594	385	0.25

^a Calculated at 0.05-ohm electrical load resistance.

The sum of the internal and lead resistances under load was calculated for each of the cells studied. These data are summarized in Table 42. These resistances are low, permitting the high current densities shown. The shape of the polarization curves under high resistive loads is seen to vary with the bimetallic combination (see Figure 74) from the expected sharp drop to zero voltage. The explanation for this is not presently clear.

The drop of open-circuit cell voltage with the mole fraction of lithium in bismuth is shown in Figure 75 for a lithium-bismuth bimetallic cell. The decrease observed is thought to be satisfactory for cell operation. Leveling occurs at a point at which the alloy becomes saturated with the compound Li_3Bi . Further addition of lithium does not change the liquid alloy composition, but results in precipitation of the solid intermetallic compound.

Several attempts to measure the temperature coefficient of the lithium-bismuth cell were made. All except one were unsuccessful in that the emf did not return to its original value when the temperature was cycled. In the one experiment which was partially successful, the emf of the cell was originally 0.7356 v at 478 C, then fell to 0.6798 v at 601 C, and returned to 0.7257 v at 476 C. This indicates a temperature coefficient of approximately -0.45×10^{-3} v/deg, which does not make high-temperature electrolytic regeneration appear attractive. Additional measurements, with porous barriers, are planned.

Figure 75
CHARACTERISTICS OF THE
LITHIUM-BISMUTH CELL

B. Thermoelectricity Research (R. K. Edwards, H. M. Feder)

Studies of thermoelectricity are underway to contribute to the technological development of direct conversion of heat energy from nuclear reactors into electrical power by means of the thermocouple effect.

Two limited materials areas have been selected as being of special interest. These are liquid thermocouple systems and refractory solid thermocouple materials. The latter are considered to be of particular interest to reactor energy conversion.

1. Liquid Systems (R. K. Edwards)

The thermoelectric properties of liquid systems are of importance since their study should contribute to the extension of solid-state theory to the liquid state. Solid-state investigations of the transport properties of binary semiconductors are generally limited to very narrow composition

ranges by virtue of narrow ranges of phase stability. Liquid binary systems offer a greater latitude for study of composition dependencies.

From a standpoint of the programmatic objective of efficient energy conversion, the studies of liquid systems are directed toward obtaining systematic data which will lead to correlation and understanding of the factors and methods of altering band structures in metallic or semi-metallic systems toward more favorable thermoelectric properties. A theoretical analysis by Klemens³² has suggested that metallic materials might yield more desirable performance possibilities through alteration of their electronic distributions than in the case of the general semiconductor. A recent study of the solid bismuth-antimony system (which forms solid solutions at all compositions) by Smith and Wolfe³³ has produced alloys with thermoelectric efficiencies (at low temperatures) comparable with the best semiconductors now available.

³² Klemens, P. G., Theoretical Requirements for Thermoelectric Materials, Westinghouse Research Report 929-8904-R2, (July 12, 1961).

³³ Smith, G. E., and Wolfe, R., Thermoelectric Properties of Bismuth-Antimony Alloys, Bell Telephone Laboratories Report, Cases 38788-1 and 38728-15.

In the previous quarterly report (ANL-6477, page 214), a partial study of the liquid indium-antimony system showed that the Seebeck coefficient in indium was increased in magnitude by a factor of 2 (at 630 C) by the addition of 20 atom percent of antimony, and also revealed some interesting detailed structure in the curve at the composition corresponding to the semiconducting solid compound, indium antimonide. Temporary apparatus performance limitations made desirable the postponement of continuation of this study in favor of a system at lower temperature. Consequently, a study of the indium-bismuth system was undertaken. This system may be considered to be isoelectronic with the indium-antimony system and should be interesting in comparison. However, since both indium and bismuth are n-type conductors, whereas the components are of opposite types in the indium-antimony system, we would expect less enhancement in the indium-bismuth system. The data indicate that indium has only a minor influence on the contributing band structure of bismuth in the composition range studied ($X_{\text{In}} = 0$ to $X_{\text{In}} = 0.52$). Measurements will be carried out over the complete composition range.

2. Refractory Solid Thermocouple Systems (M. Tetenbaum, F. Mrazek)

For high-temperature use, a refractory, broad-band semiconductor is required if the thermoelectric properties are to be favorable over a large temperature interval. The lanthanide and actinide sulfide systems are highly refractory and have phases with electron concentrations in the semiconducting range. The uranium and thorium sulfide systems and their solid solutions have been selected for the initial studies.

Room-temperature Hall coefficient measurements* were made with a uranium monosulfide specimen which had yielded a promising figure of merit value. The specimen was in the shape of a small plate fabricated from an arc-melted ingot of uranium monosulfide containing approximately 16 weight percent uranium oxysulfide. The values obtained from these measurements are as follows: Hall coefficient, $R \approx -9 \times 10^{-3}$ cc/coulomb; resistivity, $\rho \approx 200 \times 10^{-6}$ ohm-cm; Hall mobility, $U \approx 45$ sq cm/(volt)(sec); carrier density (assuming electrons carry all of the current), $n \approx 0.7 \times 10^{21}$ cc.

The low mobility and high carrier density obtained with uranium monosulfide are consistent with the room-temperature values reported by Kurnick, Merriam, and Fitzpatrick³⁴ for the promising refractory cerium sulfide system of composition intermediate between Ce_2S_3 and Ce_3S_4 . Their material was also found to be n-type.

* We are indebted to Dr. Manuel Kanter of the Solid State Division for making these measurements possible.

³⁴ Kurnick, S. W., Merriam, M. F., and Fitzpatrick, R. L., Rare Earth Sulfides as High Temperature Thermoelectric Materials, GA-1929, General Atomics Division, General Dynamics Corporation, (January 20, 1961).

Additional measurements of the Hall coefficient are planned as new preparations of uranium monosulfide become available.

An apparatus for the measurement of Seebeck coefficients and resistivity from room temperature to approximately 1500 C is nearing completion. In addition, a Z-Meter apparatus for the direct measurement of figure of merit by application of Peltier heating to the sample is being constructed.

A preliminary study of the thorium sulfide system was initiated during the past quarter. A trial batch of thorium monosulfide was prepared by essentially the same procedure outlined by Cater (see ANL-6140) for the case of uranium monosulfide. X-ray analysis of a sample from an arc-melted ingot of this material revealed thorium monosulfide as the major phase, $a_0 = 5.679 \pm 0.005 \text{ \AA}$, some extra lines of medium intensity not attributable to Th or ThS_2 , and a minor phase - possibly ThO_2 or ThOS . The room-temperature resistivity was found to be approximately $2 \times 10^{-4} \text{ ohm-cm}$. Comparison with the room-temperature resistivity values reported by Eastman *et al.*³⁵ for various sulfides of thorium suggests the presence of higher sulfides as contaminants in the arc-melted ingot. The low density value of 8.5 g/cc obtained with the arc-melted specimen (theoretical density = 9.56 g/cc) also appears to support this view.

³⁵ Eastman, E. D., Brewer, L., Bromley, L. A., Gilles, P. W., and Lofgren, N. L., J. Am. Chem. Soc., 72, 4019 (1950).

VI. DETERMINATION OF NUCLEAR CONSTANTS*

(C. E. Crouthamel)

The neutron-capture cross sections of molybdenum-98, antimony-121, and ytterbium-176 are being determined in the fast-neutron energy range. The major factors contributing to the actual energy spread in neutron flux produced by a charged particle reaction in a Van de Graaff accelerator are being studied.

Fast Monoenergetic Capture Cross Sections

(D. C. Stupugia, E. H. Dewell)

Fast capture cross sections are being studied 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. Neutrons are available with energies between 0.2 and about 2.2 Mev. The neutron flux is measured with a fission chamber which counts fissions in a uranium-235 sample. The irradiated sample is analyzed by the characteristic gamma spectrum of its capture product, and this spectrum is related to the absolute disintegration rate by 4π beta counting.

Targets have been irradiated over a 2.0-Mev range of neutron energy, and gamma-ray spectra have been recorded for molybdenum-98, antimony-121, and ytterbium-176. Details of the particular species being studied follow.

Molybdenum-98: In the previous report, data were given for the capture cross sections of molybdenum-98 as a function of neutron energy. Several more points have been determined, and the curve has the shape shown in Figure 76.

Figure 76

CAPTURE CROSS SECTION OF MOLYBDENUM-98

*A summary of this section is given on page 14.

Following the ideas of compound nuclear theory, it is believed that the peak in cross section around 0.6 Mev is due to the contribution of neutrons of high angular momentum with respect to the target nucleus. For each discrete excited state of the compound nucleus, the capture cross section corresponding to this state is given by the Breit-Wigner formula:

$$\sigma_{n\gamma} = \pi\chi^2 g \frac{\Gamma_n \Gamma_\gamma}{(E - E_0)^2 + \Gamma^2/4} \quad (1)$$

where E = neutron energy

E_0 = neutron energy at peak of resonance

$\chi = \lambda/2\pi$ = Dirac wavelength of neutron

Γ_γ = width of excited level for γ -ray emission from compound nucleus

Γ_n = width of excited level for neutron emission from compound nucleus

$\Gamma = \Gamma_\gamma + \Gamma_n$.

and g is a statistical factor depending upon the angular momenta of the neutron, target nucleus, and compound nucleus. Integrating Equation 1 over the energy range of the resonance, and averaging the result over many energy levels, one gets

$$\bar{\sigma}_{n\gamma}(\ell, J) = 2\pi^2\chi^2 g_J \frac{\Gamma_\gamma}{D_J} \left[\frac{\Gamma_n}{\Gamma_n + \Gamma_\gamma} \right]_J, \quad (2)$$

where D_J is the energy spacing of levels in the compound nucleus, ℓ is the orbital angular momentum of the incident neutrons, J is the angular momentum of the compound nucleus, and the parameters Γ_n and Γ_γ are now averaged over many levels of the compound nucleus. In the case applicable to the present work, the experimental neutron energy spread, ΔE , is much greater than the level spacing, D , and the capture cross section depends upon the width parameters averaged over many levels. The capture cross section is obtained by summing the terms due to different J values for each neutron angular momentum ℓ :

$$\bar{\sigma}_{n\gamma} = \sum_{\ell} \sum_J \bar{\sigma}_{n\gamma}(\ell, J) \quad (3)$$

If suitable information is available, the above equations can be used to calculate the separate contributions to the molybdenum-98 cross section due to neutrons of orbital angular momentum quantum number $\ell = 0, 1, 2, \dots$

Recently, such calculations have been made³⁶ for several species, including molybdenum-100, and the analysis was carried out up to neutrons with $\ell = 1$. When these calculations were carried out, maxima similar to these observed for molybdenum-98 were predicted. It is believed that the present molybdenum-98 data can probably be interpreted by assigning the peak at 0.6 Mev to the effect of neutrons of $\ell = 2$.

Ytterbium-176: Twelve irradiations have been carried out on natural ytterbium oxide targets between the neutron energies 0.25 and 2.2 Mev, and the gamma-ray spectra of ytterbium-177 have been analyzed. In order to calculate the capture cross section of ytterbium-176, it is necessary to relate the gamma spectrum of the capture product to its absolute disintegration rate. Therefore a sample of the 2-hr ytterbium-177 activity was assayed by absolute 4π beta proportional counting and by liquid scintillation counting. An aliquot of the known activity was introduced into ytterbium oxide, which was then made into discs of the same size as the target samples. The gamma spectrum of the resulting disc thus gives the required calibration factor. The data from this calibration are now being analyzed.

Antimony-121: Antimony-121 is activated into the 2.8-day antimony-122 and a 3.5-min isomeric state which decays to the 2.8-day species:

Three monoenergetic neutron irradiations have been carried out in the neutron energy range from 0.57 to 0.79 Mev, which were long compared with 3.5 min. Therefore, the irradiations will yield the sum of the cross sections for the production of both states. With suitably timed irradiations and gamma analyses, it will also be possible to measure the separate cross sections for the production of each state of antimony-122.

Neutron Energy Spreads: Although in principle monoenergetic neutrons can be produced by charged particle reaction in a Van de Graaff accelerator, the actual neutron flux on a given sample can have a substantial energy spread. This is particularly true for measurements of activation cross section since sufficient activity can be induced only by compromising with procedures which minimize variations of neutron energy. The major factors contributing to the energy spread are being studied quantitatively for the current cross-section program. Two results are expected: (a) improved cross-section data, i.e., smaller neutron spreads through better

³⁶Weston, L. W., Seth, K. K., Bilpuch, E. G., and Newson, H. W.,
Ann. Phys. 10, 477 (1960).

optimization of the available experimental parameters; (b) actual computation of the effective incident neutron energy - in contrast with the present custom of reporting the neutron energy as the midpoint between the upper and lower energy limits.

The $\text{Li}^7(p,n)\text{Be}^7$ reaction is being used as a neutron source. The neutron energy from each particular reaction depends only on the energy of the reacting proton and on the angle at which the neutron is given off. However, the lithium target is physically thick enough to degrade the proton energies, and protons of all energies between that of the incident and emergent beam take part in processes of neutron production. The amount of the degradation depends on the lithium target thickness which is, in turn, governed by the neutron-flux requirements for sufficient activation. Targets "40 kev thick to protons" are commonly used in activation work.

In addition to the changes of proton energy, another effect must be included in the calculations of neutron energy. The activated sample subtends a finite angle at the neutron source. For a sample aligned with the proton beam, all angles from zero degrees to a maximum determined by the sample diameter and the distance from the lithium target are encountered. Since the neutron energy changes with angle, a geometry term enters. This is a simple computation if the intercept of the proton beam spot on the lithium can be treated as a point source; however, for activation work "close geometry" exposures are often necessary, and the proton spot should be treated as a rectangular distributed source. Since the resulting iterated integrals for an analytical expression of this geometry are extremely complicated, a close approximation can be obtained by treating the proton spot as a series of point sources and performing the resulting integration graphically.

Figure 77 is an example of the relative neutron energy spectra calculated in this study. This particular case is for a 1.0-cm-diameter target placed 2.0 cm from a proton spot, 3.2×6.4 mm ($\frac{1}{8}$ in. $\times$ $\frac{1}{4}$ in.). The incident proton energy is 2.50 Mev and the lithium target is "45 kev thick." Note that the spectrum is skewed to low energies. This is caused by the predominating influence of the rapid increase in the $\text{Li}^7(p,n)\text{Be}^7$ cross section with decreasing proton energy in this region. Curves of this type have been prepared to date for proton energies from 2.1 to 3.0 Mev in 0.1-Mev intervals. Details of the calculation and the complete set of curves will be presented in a topical report when the study is completed.

Figure 77

RELATIVE NEUTRON SPECTRUM ON A
1.0-cm-DIAMETER CIRCULAR SAMPLE
2.0 cm FROM A $\text{Li}^7(p,n)\text{Be}^7$ NEUTRON
SOURCE

VII. REACTOR DECONTAMINATION*

(W. B. Seefeldt)

The Reactor Decontamination Program seeks to determine what the consequences to reactor operation and maintenance might be if a fuel element in a boiling water reactor failed and released fission products into the water and steam. This includes an attempt to establish experimentally the extent to which the fission products might be deposited through the reactor and steam system and to develop chemical methods for decontaminating the system to an extent where direct maintenance could take place.

Loop Studies

(D. Grosvenor, C. Bally)

A stainless steel type 304 loop which simulates the action of a boiling water reactor has been installed in a shielded cell in order to study the effects of simulated ruptures of a fuel element. It is of interest to know

how much and what kind of fission products will distribute through the system in order to ascertain the degree to which maintenance might be impaired in a practical system should fuel-cladding failure occur. Fuel ruptures are simulated in the loop by introducing irradiated metallic uranium. Fission products are released as the uranium corrodes in the circulating water. Deposition of activity in the steam disengaging space is monitored by inserting a metallic sample strip. This is removed following a run, cut into convenient lengths, and counted in a 256-channel gamma scintillation spectrometer. This is correlated with similar information obtained from liquid and condensed-steam samples. All elevations referred to in the text and tables are measured from a common reference point: the liquid sample line. The elevations of pertinent equipment items are shown in Figure 78.

Figure 78

DISENGAGING SECTION OF LOOP SHOWING ELEVATIONS OF COMPONENTS RELATIVE TO REFERENCE

*A summary of this section is given on page 15.

Emphasis in recent runs has been on the development of deposition information for iodine-131 and barium-lanthanum-140. This has required the use of irradiated uranium which has been cooled for a period of less than 30 days, so that all necessary analytical data from the 256-channel analyzer could be obtained within about 50 days following the removal of the uranium from the reactor.

Loop Runs U6 and U6A were made under identical operational conditions: 200 psi pressure, a steam velocity of 1.2 ft/sec, liquid level of 17 to 20 in., and run length of about 10 days. This steam velocity is greater by about a factor of three than the original design steam velocity of Argonne's Experimental Boiling Water Reactor at 20-Mw power as measured in the steam dome of the reactor. A major difference is that EBWR pressure conditions are 600 psi. The stainless steel type 304 sample strip usually inserted into the steam disengaging section to monitor activity deposition is vertically oriented; in order to have an appreciation of the effect of orientation on such deposition, a number of horizontal sections were used in loop Run U6. The gamma scintillation spectra obtained from these samples were resolved into individual fission product contributions by the computer solution (IBM 650) of simultaneous equations. Results are expressed as microcuries of fission product per square centimeter of surface. Gamma spectra are also obtained from liquid and condensed-steam samples, results from which are subsequently related to deposition data. The term "specific deposition" is used to describe the ratio of the fission product deposition (expressed as microcuries per square centimeter) to the fission product content of either the liquid or condensed steam (expressed as microcuries per gram). It is thought that specific deposition is not likely to be dependent to any great extent on activity level, but is dependent on steam pressure, steam velocity, type of metal, and surface condition.

Fission product deposition data on metal surfaces in the steam disengaging section for Runs U6 and U6A are shown in Tables 43 and 44. Data for Table 43 reflect information obtained at the maximum elevation above the steam-water interface (64 to 66 in. above reference). At this elevation, deposition on horizontal and vertical surfaces was equivalent for most fission products. At somewhat lower elevations (49 to 51 in. above reference), differences in deposition on the 2 types of samples were observed; these are shown in Table 44. Values in Table 43 are in general intermediate to those given in Table 44.

The deposition characteristics of ruthenium, cesium, and zirconium appear to be the best clarified of the 6 fission products included in the study. Zirconium has by far the strongest tendency to plate out, greater by the order of a factor of 100 than in the case of either ruthenium or cesium. However, the actual quantity of ruthenium deposited exceeded that of zirconium in both runs because of the much higher concentration of the former in the steam. The microcurie contribution of ruthenium and zirconium to the steam were the highest and lowest, respectively, of the 6 fission products monitored. Ruthenium adsorbs more strongly than cesium by perhaps a factor of 2.

Table 43

DEPOSITION OF FISSION PRODUCTS ON STAINLESS STEEL TYPE 304

Conditions (Run U6 and Run U6A are separate runs):

Pressure: 200 psi
 Length of Run: 10 days
 Steam Velocity: 1.2 ft/sec
 Liquid Level: 17 to 20 in. above reference
 Sample Position: 64 to 66 in. above reference

Fission Product	Run No.	Composition of Liquid ($\mu\text{c/g}$)	Composition of Vapor ($\mu\text{c/g}$)	Disengaging Factor	Fission Product Deposition on ($\mu\text{c/sq cm}$)	Specific Deposition ($\frac{\mu\text{c/sq cm}}{\mu\text{c/g}}$)	
						Related to Liquid ($\times 10^3$)	Related to Vapor
Ce	U6	$[4.5 \times 10^{-1}]^a$	3×10^{-4}	1.5×10^3	7.0×10^{-3}	[15]	23
	U6A	7×10^{-2}	3.5×10^{-5}	2×10^3	7.0×10^{-3}	100	200
I	U6	1.1	2.1×10^{-3}	5.2×10^2	$[3 \times 10^{-1}]$	[<270]	[<140]
	U6A	3.5×10^{-1}	5.6×10^{-4}	6.2×10^2	$<2.6 \times 10^{-3}$	<6.9	<4.6
Ru	U6	1.3×10^{-1}	3.5×10^{-3}	3.7×10^1	2.7×10^{-2}	210	7.7
	U6A	3.2×10^{-2}	5.6×10^{-4}	5.7×10^1	8.4×10^{-3}	260	15
Cs	U6	0.950	6×10^{-5}	1.58×10^4	2×10^{-4}	0.21	3.3
	U6A	6.8×10^{-1}	7×10^{-5}	9.7×10^3	5.4×10^{-4}	0.8	7.7
Zr	U6	2.6×10^{-2}	1×10^{-5}	2.6×10^3	7.2×10^{-3}	277	720
	U6A	1.9×10^{-2}	1.3×10^{-5}	1.5×10^3	7.4×10^{-3}	390	570
Ba-La	U6	$[4.5 \times 10^{-2}]$	$[1 \times 10^{-4}]$	$[4.5 \times 10^2]$	2.7×10^{-3}	[60]	[27]
	U6A	7.4×10^{-3}	1×10^{-5}	7.4×10^2	1×10^{-3}	130	100

^aNumbers in brackets not considered accurate.

Table 44

DIFFERENCES IN ACTIVITY DEPOSITION ON HORIZONTAL AND VERTICAL SURFACES

Run: U6
 Metal: Stainless Steel Type 304
 Liquid Level: 17 to 20 in. above reference
 Sample Position: 49 to 51 in. above reference

Fission Product	Deposition ($\mu\text{c/sq cm}$)	
	Horizontal	Vertical
Ru	4.8×10^{-2}	2.7×10^{-2}
Ce	2.0×10^{-2}	2.2×10^{-3}
Ba-La	5.7×10^{-3}	8.9×10^{-4}
Cs	5.4×10^{-3}	2×10^{-4}
Zr	1.8×10^{-2}	3.8×10^{-3}

The deposition characteristics of cerium, iodine, and barium-lanthanum are less consistent. Specific deposition ratios related to the steam range from a value near one to several hundred for cerium and iodine, and from 27 to 100 for barium-lanthanum.

The very low disengaging factors obtained for ruthenium in both runs U6 and U6A again suggest that volatilization of this fission product occurs under the operating conditions of the experiment. When disengaging factors generally range from 10^3 to 10^4 , those observed for ruthenium were 37 and 57. It is this volatilization phenomena which causes ruthenium to be one of the principal activities present on the metal surfaces in the steam phase.

Run U6 was the first in which both horizontal and vertical samples of stainless steel type 304 were used. Table 44 shows that deposition on horizontal surfaces was greater by a factor of 1.8 to 9 than that on vertical surfaces, with the exception of cesium, which was 27. It is planned to obtain additional data of this type for both stainless steel and mild steel surfaces.

The loop was decontaminated following Run U6A. A solution of carbonate-bicarbonate-permanganate was applied in 2 steps. This was intended primarily as a uranium dissolvent. A proprietary material, designated CS-100, was subsequently applied in 2 additional steps to effect removal of deposited activities. It should be emphasized that the data obtained reflects decontamination capabilities in the liquid phase of the loop, and may not represent the performance of these solutions in removing activities from the vapor phase. Table 45 shows the composition and conditions of the solutions used.

Table 45

RUN U6A DECONTAMINATION CONDITIONS

- Step 1 (designated effluent 3 in Figures 79 and 80)
 - 30.9 g/l KMnO_4
 - 27 g/l Na_2CO_3
 - 21 g/l NaHCO_3
 - $4\frac{3}{4}$ hr at 90 C
- Step 2 (designated effluent 4 in Figures 79 and 80)
 - Same solution composition as step 1
 - 20 hr at 90 C
- Step 3 Water Rinse
- Step 4 (designated effluent 6 in Figures 79 and 80)
 - Proprietary compound CS-100
 - 16-hr soaking at room temperature
 - 0.5 hr circulating at room temperature
- Step 5 (designated effluent 7 in Figures 79 and 80)
 - Same solution as step 3
 - 5 hr at 85 C

The progress of the decontamination in terms of the percentages of uranium and fission products remaining in the loop is shown on a semi-logarithmic plot in Figure 79. A semilogarithmic scale was chosen since

Figure 79

RUN U6A FISSION PRODUCT AND
URANIUM DECONTAMINATION
FROM STAINLESS STEEL
LOOP SURFACES

cesium, iodine, and zirconium than for barium-lanthanum, ruthenium, and cerium. It is also clear that the proprietary material CS-100 was more effective in removing fission products than uranium, and was more effective as a decontaminant than the carbonate-bicarbonate-permanganate.

Similar conclusions are evident from the same information presented in an alternative form in Figure 80. The upper bar graphs show the percentage of each fission product (or uranium) removed by each effluent, and the lower bar graphs the activity to uranium ratios of the corresponding effluents. The superior ability of CS-100 as a decontaminant is visually evident; this is particularly true for barium-lanthanum and ruthenium. As a uranium dissolvent, the carbonate-bicarbonate-permanganate was moderately useful in reducing the residual uranium to 10 percent after two treatments.

Loop Run U7 was initiated to obtain data at higher steam pressures (600 psi), but the experiment was shut down after 48 hr because of equipment malfunction. This was the first run in which a mild steel sample strip had been inserted in addition to the stainless steel type 304 strip.

for any particular treatment the plots of all fission products and uranium would be parallel if equal percentages of each were removed. An assumption which had to be made in presenting the data in this fashion was that some finite percentage (chosen as 1 percent) of fission products and uranium remained in the loop following the last treatment. From the second application of the carbonate-bicarbonate-permanganate (effluent 4), it is evident that a far greater percentage of uranium was removed than of any of the fission products. It can be inferred from this that the amount of activity associated with the uranium was relatively low. In the preceding treatment (effluent 3 which was also carbonate-bicarbonate-permanganate), the greater slopes for the fission products in relation to that of uranium indicates that most of the removed activity originated not with uranium but from the metal surfaces. The treatment was more effective for

Although the run was not completed on schedule, samples of each metal were counted and assayed in order to determine whether or not gross differences of fission product deposition on the two metals could be observed. The results are shown in Table 46. Differences in general were small for all fission products; however, the quantity deposited on the stainless steel surfaces is observed to be consistently the higher of the 2 metals.

Figure 80
DECONTAMINATION DATA FOR
LOOP RUN U6

Pressure: 200 psi
Length of Run: 10 days
Steam Velocity: 1.2 ft/sec

Effluent Designation

1. Loop Drainings	3. $\text{KMnO}_4 - \text{Na}_2\text{CO}_3$	6. CS-100
2. Rinse	4. $\text{KMnO}_4 - \text{Na}_2\text{CO}_3$	7. CS-100
	5. Rinse	

a. Activity (or Uranium) removed expressed as percent of amount remaining in loop (linear scale)

b. Activity to Uranium ratios for each liquid effluent from loop (log scale)

Table 46
COMPARISON OF ACTIVITY DEPOSITION ON STAINLESS STEEL
AND MILD STEEL SURFACES

Run: U7
Pressure: 600 psi
Steam Velocity: 1.1 ft/sec
Length of Run: 48 hr

Fission Product Deposition, $\mu\text{c}/\text{sq cm}$

Fission Product	Stainless Steel Type 304			Mild Steel		
	Minimum	Maximum	Typical	Minimum	Maximum	Typical
Ce	6.6×10^{-3}	4.0×10^{-2}	1.6×10^{-2}	6.4×10^{-3}	1.3×10^{-2}	9×10^{-3}
I	-	-	3×10^{-4}	6.0×10^{-5}	4.1×10^{-4}	1.6×10^{-4}
Ru	7.2×10^{-3}	8.0×10^{-2}	2.6×10^{-2}	9.6×10^{-3}	2.4×10^{-2}	1.5×10^{-2}
Cs	5.6×10^{-5}	3.5×10^{-4}	1.4×10^{-4}	2.0×10^{-5}	4.5×10^{-5}	3.0×10^{-5}
Zr	5.6×10^{-3}	3.0×10^{-2}	1.1×10^{-2}	5.0×10^{-3}	1.2×10^{-2}	7.8×10^{-3}
Ba-La	1.7×10^{-4}	6.0×10^{-4}	3.1×10^{-4}	1.8×10^{-4}	4.0×10^{-4}	2.7×10^{-4}

VIII. ROUTINE OPERATIONS (H. G. Swope)

A. Waste Processing

(H. G. Swope, J. Harast, K. Bremer, G. Teats and V. Lemke)

There were 24,634 gal of radioactive waste processed during the period January through March, 1962. The volumes processed and methods used were as follows:

Process	Volume (gal)
Evaporation and Concentration	23,080
Flocculation	1,120
Distillation of Organic Wastes	62
Vermiculite Absorption	372
Total	24,634

B. High-level Gamma Irradiation Facility

(H. G. Swope, J. Harast, N. Ondracek, B. Kullen, R. Juvinall and D. Bryant)

A summary of irradiations performed in Racks M-1 and M-2 for January through March, 1962 is given in Table 47.

Table 47

SUMMARY OF IRRADIATIONS PERFORMED IN RACKS M-1 AND M-2 DURING JANUARY THROUGH MARCH, 1962

Month	Rack M-1				Rack M-2		
	No. of Samples ^a	No. of Special Dosimetry Samples	Total Urn Units ^b		No. of Urns	No. of Special Dosimetry Urns	Total Urn Units ^c
			Day	Night			
January	176	128	546	1404	0	0	0
February	175	86	571	2032	0	0	0
March	155	12	440	1230	1	4	4
Totals	506	226	1557	4666	1	4	4

^aEquivalent to a No. 2 sized can.

^b1 urn unit in Rack M-1 = 2×10^6 rad.

^c1 urn unit in Rack M-2 = 2×10^5 rad.