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SUMMARY

CHEMICAL ENGINEERING DIVISION
SEMIANNUAL REPORTI. Chemical-Metallurgical Processing (pages 43 to 196)

The melt refining process will be used for the recovery of the enriched uranium fuel material which constitutes the first core loading of EBR-II. Development work on this process is essentially complete, and plant equipment has been installed at the EBR-II site in Idaho. In the EBR-II Fuel Cycle Facility, the melt refining crucible will be covered with a Fiberfrax fume trap to collect the volatilized iodine activity, as well as other volatile materials such as sodium from the thermal bond.

Several laboratory investigations dealing with the behavior of fission product iodine in the melt refining process have been completed, and the results have been evaluated. These investigations involved fuel charges varying from 7 to about 400 g, and irradiation levels ranging from zero to nearly two total atom % burnup. In all cases, over 99% of the iodine present either as a fission product or as a spiked charge was removed when the fuel was melt refined. The deposition pattern of volatilized iodine activity in the laboratory experiments proved to be dependent primarily upon the temperatures of nearby surfaces during melt refining. In general, the iodine was found deposited as CsI on surfaces that had been at temperatures between 400 and 1000°C. These results suggest that in plant operation, most of the iodine will be collected on the fume trap, although a significant fraction may appear on the upper wall of the melt refining crucible.

Experiments were also performed to determine the amount of iodine activity that will be released to the Argon Cell of the EBR-II Fuel Cycle Facility when the Fiberfrax fume trap is removed from the melt refining furnace. Under conditions simulating the fission product decay heat associated with highly irradiated fuel, a slow flow of argon was passed over a 1-in. dia. Fiberfrax plug containing deposited iodine activity. Under the most severe conditions anticipated, it appears that the iodine activity would be released to the argon at a rate of less than 0.2% per hour. With appropriate operating procedures, it should be possible to limit the release of iodine from the Fiberfrax to negligible amounts.

Preparations have been made for a study of the melt refining of plutonium alloys under a molten halide flux. To permit work with large quantities of plutonium (50 to 100-gram batches), a melt refining furnace which opens into a glove box has been reactivated. Preliminary experiments have been made with uranium.

The purification of argon from nitrogen is frequently desired and may, for future processing operations, be required for the argon atmosphere of the EBR-II Fuel Cycle Facility. The construction of two experimental systems for study of the gettering of nitrogen on hot titanium sponge is nearly complete. Shakedown experiments are being made in an apparatus built to determine the kinetics of the nitrogen-titanium reaction in argon containing nitrogen at initial concentrations between 50 and 50,000 ppm. A 10-cfm pilot plant designed to provide information on component design and reliability for large-volume purification systems is nearly ready for operation.

Work was continued on the development of the skull reclamation process, a process in which molten metal (zinc-magnesium systems) and halide salt solvents are employed as processing media for recovery of melt refining crucible residues. These residues, which are called skull material, are converted by controlled oxidation to oxide powders which may be dumped from the melt refining crucibles. Analyses of melt refining crucibles, which are discarded after the skull oxides have been dumped from them, show the residual or unrecovered uranium content of these scrap crucibles to range between 1 and 3 1/2% of the uranium in the skull material. Although these losses are somewhat higher than expected, they represent a maximum of only 0.2 percent of the uranium in the original melt refining charges, and therefore are not cause for concern.

A series of small-scale (100 to 150 grams of uranium) demonstration experiments of the skull reclamation process has been completed. The results of these small-scale runs, in which several process difficulties were pinpointed and resolved, showed that adequate fission product removal and uranium recovery can be achieved in the skull reclamation process. In other work related to the skull reclamation process, a brief laboratory study showed that EBR-II fuel pins of the first core which cannot be decanned, and, therefore, cannot be melt refined, can be accommodated in the skull reclamation process. The Type 304 stainless steel cladding on the first core fuel pins is readily dissolved in zinc, as is the contained fuel material. The uranium may be subsequently transferred from the metal phase to a molten halide salt phase by oxidation to the trichloride. The feasibility of recovering uranium from other nonsoluble or slightly soluble cladding materials, such as tungsten or a niobium-1% zirconium alloy, by a "chop-leach" procedure was also shown.

With the completion of small-scale demonstrations of the skull reclamation process, work has been advanced to 2-kilogram-scale operations

in a pilot plant. The major objectives of the early pilot plant runs have been the development of operating techniques and the improvement of equipment performance. Particular attention has been given in this early work to the removal of waste molten metal and salt phases and to the mixing of immiscible metal and salt phases, which are important operations in certain steps of the process.

Development work has continued on liquid metal separation processes for fast reactor fuels consisting of uranium-plutonium alloys or carbides. Various head-end steps by which carbide fuels could be accommodated by liquid metal processing are being investigated. The head-end procedures investigated thus far have involved either oxidation of the carbide by reagents such as NaOH or NaNO_3 in a molten chloride flux, or chlorination of the carbide with HCl or chlorine in the same type of flux. Both techniques result in the formation of uranium and plutonium compounds that are readily reduced to the metals by zinc-magnesium solutions.

Liquid alloys of the ternary system cadmium-zinc-magnesium are being considered in place of binary magnesium-zinc alloys for use as process solvents. The addition of a high percentage of cadmium results in lower operating temperatures and smaller zinc concentrations, which may permit the use of stainless steels instead of refractory metals for process equipment. Uranium solubility measurements in the cadmium-rich region of the ternary alloy indicated maximum values of about 1.5 a/o at 600°C , which should be sufficient for process use. The uranium solubility increased with increasing zinc concentration and with decreasing magnesium concentration. On the basis of previous distribution coefficient measurements, it is expected that adequate uranium-plutonium-fission product separations can be achieved by contacting solutions in the ternary alloy with appropriate molten salts. Additional measurements are being made to investigate this point further. An engineering program has been started for the purpose of developing the necessary technology for countercurrent extraction operations with molten salts and metals.

Experimental work relating to the use of a calcium-zinc extraction process for the separation of fission products from plutonium and uranium has been completed. The separation in this solvent is based on the high solubility of rare earths and low solubilities of uranium and plutonium in the calcium-rich region. The solubility of uranium at 750°C was found to decrease sharply from a maximum of 3.0 w/o in zinc - 12.5 w/o calcium to 10^{-3} w/o in zinc - 38 w/o calcium, and to continue to decrease to extremely low values at higher calcium concentrations. The decrease in plutonium solubility with increasing calcium concentration was much less pronounced. At 750°C the plutonium solubility decreased from 6.5 w/o in zinc - 41 w/o calcium to 0.2 w/o in zinc - 75 w/o calcium. Because of the low but significant solubility of plutonium under these conditions, the possibility of achieving 99% plutonium recovery in a single-stage precipitation process appears marginal.

The development of a blanket process for concentrating the plutonium bred in EBR-II blanket material was continued. In this process the plutonium is separated from the bulk of the uranium and is present in dilute concentration (about 0.1 w/o) in a 50 w/o magnesium-zinc product solution. Evaporation of the magnesium and zinc solvent metals to yield a plutonium concentrate is being studied. Evaporation experiments conducted with about 10 kg of the 50 w/o magnesium-zinc alloy have shown the desirability of reflux within the still pot to prevent the deposition of a solute material, such as plutonium, along the walls of the still pot.

Because evaporation or distillation of volatile metal solvents is an important operation in the liquid metal processes under development, this operation has received special attention. A large-scale cadmium distillation unit (distillation rates of up to 100 kg/hr) has been operated intermittently over the last several years as part of a program to develop engineering technology for the metal distillation or evaporation steps. During the last report period, work with the large-scale cadmium distillation unit was completed. A de-entrainment device installed in the vapor space of the still pot considerably reduced entrainment of liquid cadmium drops in the flowing cadmium vapor stream (from several percent without the de-entrainment device to as low as 0.9 percent with the device). An eddy-current liquid level induction probe was used to measure continuously the cadmium level in the still pot, and gave promise of being an effective and accurate instrument for monitoring the metal liquid level in a remotely operated distillation unit. Measurement of the temperature distribution within the vertical axis of the cadmium pool indicates that boiling probably takes place only within the upper inch of the liquid cadmium.

In a study of the mechanism of mercury vaporization from the liquid-vapor interface without vapor bubble nucleation within the pool, it was found experimentally that a steep and constant temperature gradient exists in a thin surface liquid layer (about 0.2 in. thick). The largest value of this gradient measured to date is 115°C/inch. Below this thin surface layer, the pool temperature was almost constant with depth. The vaporizing liquid surface was superheated an average of 30°C above the vapor space saturation temperature.

Work has been started to determine the critical constants of alkali metals. Densities of the vapor and liquid phases of an alkali metal containing a radioactive isotope of the alkali metal will be measured from room temperature up to the critical point of the metal. This will be accomplished by measuring the gamma radiation emanating from the vapor and liquid regions of the alkali metal held within a small capsule.

Preliminary development work and tests are reported on an eddy-current induction probe for remote determination of molten-metal levels and possibly molten salt levels. The probe consists of dual wound, primary and secondary, Nichrome coils on a ceramic core. The output of the secondary coil is strongly affected by the presence of a surrounding conductor, such as a liquid metal. A particular advantage of the eddy current

induction probe is that it operates within a well similar to a thermocouple well and therefore may be easily removed for repair or replacement.

Materials for the containment of molten uranium and its alloys and of the various molten metal and halide salt systems are being evaluated. Both tungsten and tantalum were shown to be unsuitable for containing molten uranium systems. Tungsten, however, possesses excellent resistance to corrosion by the molten zinc-magnesium and halide salt solutions of the skull reclamation and blanket processes, but is difficult to fabricate into large vessels or complex shapes. For this reason the feasibility of using plasma-sprayed tungsten coatings on various substrate materials is being examined. To date, relatively large tungsten-coated crucibles of silicon carbide and Type 410 stainless steel (10-1/2-in. OD by 16 and 21 inches high, respectively) have each withstood eight thermal cycles between room temperature or 300°C and 800°C. They have not yet been employed for the containment of process solutions. In small coupon tests, good adherence of a plasma-sprayed tungsten coating on tantalum was shown in thermal cycling tests. Plasma-sprayed tungsten coatings on type 304 stainless steel coupons failed to provide protection to the stainless steel during exposure to process systems.

Additional information has been obtained on a soluble uranyl (V) species, UO_2Cl , that is formed on the addition of UO_3 , U_3O_8 or UO_2Cl_2 to molten chloride solvents. The thermal decomposition of UO_2Cl_2 produces this species via the reaction:

The equilibrium constant for this reaction at 650°C in the LiCl-KCl eutectic is $1.2 \pm 0.6 \times 10^{-6}$ atm. At temperatures above about 750°C, the thermal decomposition proceeds further, producing solid UO_2 as a product:

The effects of changes in the solvent composition and the temperature on the absorption spectrum of UO_2Cl were investigated. Variations in the spectrum are attributed to the influence of the environment on the axial U-O bonds in the UO_2Cl molecule and resulting changes in the energy level splitting.

Additional work has been done on pyrometallurgical methods for the preparation of refractory fuel materials. Seven preparations of UC on a 200- to 500-g scale have been completed, using a liquid metal precipitation process. This process involves the addition of carbon to uranium dissolved in a zinc-magnesium solution, reaction for about 8 hr at 800°C, removal of the supernatant solution, and retorting of the precipitated UC to remove residual zinc and magnesium. The product has been shown to have good pressing and sintering properties. Current efforts are devoted to decreasing the oxygen impurity content below the best value of 0.29 w/o obtained thus far, and to approaching more closely the stoichiometric carbon/uranium ratio for UC. The minimum carbon/uranium atom ratio obtained to date is 1.16.

Scouting studies have shown that a variety of carbides can be prepared by the reaction of magnesium carbides (MgC_2 or Mg_2C_3) with halides or oxides of different metals in molten chloride salts. This technique was used successfully for the preparation of Pu_2C_3 from PuCl_3 .

Nine batches of US with slightly varying sulfur/uranium ratios were prepared on a 100- to 300-g scale by the reaction of H_2S with hydrided-dehydrided uranium metal. The products were homogenized under vacuum at 1900°C . X-ray data showed the lattice parameter of the products to remain essentially constant at 5.489 to 5.490 Å as the sulfur/uranium ratio varied from 0.99 to 1.02, but to decrease at higher and lower sulfur/uranium ratios. Small concentrations of impurities in the product had no discernible effect on the lattice parameter. The amount of insoluble residue (UO_2 , UOS) formed during the dissolution of US in dilute H_2SO_4 solution proved to be an unreliable index of the total oxygen content of the material.

In a demonstration experiment, 30 g of plutonium metal was produced by the direct reduction of PuO_2 with zinc-magnesium solution in the presence of a CaCl_2 - MgCl_2 - MgF_2 flux. The product was recovered by separating the flux phase and retorting the zinc-magnesium-plutonium ingot. The product yield exceeded 99%, and spectrochemical analyses showed the plutonium metal to contain lower levels of metallic impurities than did the PuO_2 used as the starting material.

Work is continuing on the installation, testing, and corrective repair of equipment in the EBR-II Fuel Cycle Facility.

Eighty thousand standard cubic feet of argon was used to purge 95% of the air from the 66,000-cu ft Argon Cell. Nine days after the argon purge, the argon purification system had reduced the impurities in the cell atmosphere to about 4.3% nitrogen, less than 50 ppm oxygen, and less than 200 ppm water vapor. The rate of air in-leakage was 0.005 scfm.

New bearings were installed in the compressor for the argon purification system after one bearing failed due to inadequate lubrication. These bearings were lubricated with greases recommended for service in dry atmospheres.

The pressure control system for the Argon Cell was modified so that either a constant temperature or a constant pressure could be maintained in the cell.

After the Argon Cell was filled with argon, one fan motor in the Argon Cell cooling system failed, and rapid wear was noted on the piston rings in the high pressure argon compressors. The fan motor was repaired and reinstalled. Replacement of the worn piston rings is planned. Both problems are being studied to determine the best long-range solution.

Direct repair work on the Argon Cell manipulators became necessary after the argon fill, and was carried out by personnel in supplied-air masks.

A total of 2200 cu ft of air was introduced into the cell atmosphere as a result of personnel entering the Argon Cell; however, after four days operation of the purification system, the oxygen concentration in the cell was 10 ppm and the water concentration was 40 ppm.

The bridge drives on four Argon Cell manipulators and one Air Cell manipulator failed due to shearing of a roll pin used in the drive clutch. Calculations of the dynamic loading of the roll pins and an examination of the pins showed that impact loading on the pins caused metal fatigue failure. To prevent future failure of the bridge drive pins, the roll pins have been replaced with solid pins, and the armature voltage of the drive motor has been reduced. Further modifications of the bridge drive clutch are planned.

In the Argon Cell, approximately 8 kg of unirradiated, uranium-fissium fuel pins have been processed in a melt refining furnace with a resultant pour yield of 90.4%. Preliminary operations of a fuel pin decanner and a fuel pin injection casting furnace have begun. Minor adjustments are needed on the injection casting furnace to correct the length of the pin castings.

Two racks have been installed in the Air Cell floor pits for the storage of fuel subassemblies. Coolant air for the two racks will be supplied by two lobe-type blowers. Tests have shown that the system will provide adequate cooling for the subassemblies.

Performance tests of the battery used to drive the blower on the interbuilding transfer coffin show that the battery will perform satisfactorily for eight hours between charges. The usual fuel subassembly transfer operation is expected to require less than four hours.

Heat removal performance tests have shown that the cooling system of the Argonne-fabricated interbuilding transfer coffin is adequate to maintain the maximum fuel element temperature in a core subassembly below 600°F. A core subassembly, with electric heaters in the fuel element cans, was used for the tests. A commercially fabricated interbuilding coffin is being modified to conform to the design of the Argonne-fabricated coffin.

Examination of the drive motors for the manipulator grips showed that excessive brush wear had occurred during operation in the dry cell atmosphere. Preliminary tests of alternative brushes in a similar atmosphere have disclosed a superior type of brush. The testing of brushes in a dry atmosphere with a low oxygen content is being continued to determine the factors that affect brush life. A grip drive motor is being utilized in the tests.

Two portable sample can cappers have been built and tested. The cappers will press-fit a lid into the type of small can used for transfer of small objects from either of the two EBR-II process cells.

Construction of the skull oxidation furnace for the Fuel Cycle Facility has begun. A skull oxide dumper has been tested. This unit dumps the skull from the melt refining crucible into a storage container after the skull has been oxidized in the oxidation step.

Experiments are continuing to develop a satisfactory condenser and collector for the collection of metal vapors in the distillation step of the skull reclamation process. Tests of a butt-type seal between the graphite collector and the graphite crucible cover have been successful. Tests of a one-piece, mild steel condenser-distillate collector unit in distillation runs with zinc-14 w/o magnesium have shown that corrosion of the steel prevents its use. A plant-scale distillation unit which can handle 36 kg of distillate has been designed.

The solubility of plutonium in liquid cadmium is given by the equations:

$$(335 - 399^{\circ}\text{C}) \log (\text{atom percent}) = 6.223 - 4282 T^{-1}$$

$$(399 - 632^{\circ}\text{C}) \log (\text{atom percent}) = 5.148 - 5277 T^{-1} + 1.156 \times 10^6 T^{-2}$$

Below 399°C the equilibrium solid phase is PuCd_{11} , while between 399 and 632°C it is PuCd_6 .

The technetium-rich phase in the technetium-zinc system has been shown to be TcZn_6 , with a face-centered cubic structure and with $a_0 = 7.588 \text{ \AA}$.

The solubility of argon in liquid sodium is 2.4×10^{-7} atom percent at 480°C and one atmosphere pressure. The solubility is directly proportional to the pressure, i.e., Henry's law is followed. The heat of solution of argon in liquid sodium is 16 kcal/mole.

The analysis of sodium for oxygen using an activation method involving the reaction $^{16}\text{O}(n,p)^{16}\text{N}$ has been tested for interference by possible impurities. Only fluorine and possibly boron were found to interfere. The dry oxidation method for the analysis of sodium for carbon has been shown to have low blanks (3-4 μg carbon) and good recovery of carbon from standard samples. Analyses of samples, ranging from 0.1 to 0.8 g, taken from the same sodium source showed that the amount of carbon found was directly proportional to the weight of sample. Variations in composition caused by segregation have been greatly reduced by sampling from the liquid phase.

Studies are under way on the thermodynamics of binary mixtures of the alkali metals using an optical absorption method. A Kovar cell with sapphire windows has been found to be resistant to sodium vapor to at least 220°C .

The decomposition pressure of TcZn_6 has been measured using the continuous weighing effusion method. The free energy of formation of TcZn_6 is given by the equation

$$(470 - 570^{\circ}\text{C}) \Delta G_f^{\circ} (\text{cal/g.-atom}) = -7823 + 6.43T.$$

Extrapolation of these data indicate that TcZn_6 will decompose peritectically into technetium metal and solution at 944°C . Thermal analysis data indicate the peritectic temperature is 950°C .

The thermodynamics of PrCd_{11} is being studied using a galvanic cell method. Preliminary data indicate that the free energy of formation is -34.2 kcal/mole at 500°C .

II. Fuel Cycle Applications of Volatility and Fluidization Techniques (pages 197 to 296)

Fluid-bed fluoride volatility processes are being developed for the recovery of both uranium and plutonium from spent nuclear fuels. High density uranium dioxide pellets, clad in either Zircaloy or stainless steel, are typical of the power reactor fuels which can be processed by this means.

Laboratory support work for the fluid-bed fluoride volatility processes is continuing with a study of the fluid-bed fluorination of U_3O_8 - PuO_2 mixtures. This study is directed toward determining the reaction conditions and procedures which would result in a high degree of removal of uranium and plutonium as hexafluorides from the alumina fluid bed. Mixtures of U_3O_8 and PuO_2 are being used in this work to represent the product which is formed by the oxidation of UO_2 - PuO_2 fuel pellets. The U_3O_8 - PuO_2 powder, mixed with alumina, is carried into the alumina bed in the fluidizing nitrogen stream at a rate of 3 to 6 g of U_3O_8 - PuO_2 per minute. Fluorine is brought into the bed just above the point at which the U_3O_8 - PuO_2 powder enters and the fluorination reaction occurs as they mix.

In the initial experiments the effect of the presence of fission product oxides in the U_3O_8 - PuO_2 mixtures on the retention of uranium and plutonium on the alumina fluid bed was investigated. The U_3O_8 - PuO_2 mixtures contained about 84 w/o uranium and 0.4 w/o plutonium, and the fission products, when present, comprised about 0.9 w/o of the mixture. Experiments were performed in which the U_3O_8 - PuO_2 was fed into the bed at 500°C and 20 v/o fluorine was used as the fluorinating agent; this was followed by a five-hour recycle-fluorination period at 500°C using 100% fluorine. In these experiments, the presence of fission product oxides did not materially change the uranium content of the alumina; in all cases the quantities of uranium retained represented less than 1% of that fed to the reactor. However, the concentration of plutonium retained on the alumina increased from a value of 0.033 w/o in experiments in which fission products were not present to a value of 0.057 w/o in experiments in which fission products were present. An experiment was performed in which the temperature during the U_3O_8 - PuO_2 feeding-fluorination period was 450°C . This was then followed by recycle-fluorination periods of five hours at 450°C , five hours at 500°C , and ten hours at 550°C . The plutonium concentration on the alumina was 0.007 w/o.

A means of analyzing PuF_6 in UF_6 will be required in laboratory and pilot plant investigations of problems associated with the fluid-bed fluoride volatility processes. In typical experiments performed on the fluorination of mixtures of U_3O_8 and PuO_2 in the 1 1/2 inch laboratory fluid-bed reactor, the effluent contains about 350 g UF_6 and about 1.4 g of PuF_6 . Traps cooled to -80°C are used to remove the UF_6 and PuF_6 from the nitrogen-fluorine stream. It would be difficult to obtain a homogeneous sample of the products collected in the cold traps. It would also be difficult and hazardous to hydrolyze such a large quantity of a mixture of UF_6 and PuF_6 in order to use aqueous analytical methods. Some means is needed to separate the plutonium from the bulk of the UF_6 and leave the plutonium in a form which can be readily dissolved in aqueous media. Plutonium hexafluoride is reduced by SF_4 while UF_6 is not. By reaction of a mixture of PuF_6 and UF_6 with SF_4 , the PuF_6 is quantitatively reduced to PuF_4 . A small amount of UF_6 is reduced to lower nonvolatile uranium fluorides by α decomposition which occurs during the time the UF_6 and PuF_6 are in contact. The UF_6 decomposed does not affect the results. After volatilizing the UF_6 , excess SF_4 , and SF_6 from the reaction mixture, the PuF_4 and the nonvolatile lower uranium fluorides can be dissolved in an aqueous solution of 6 N HNO_3 and 0.1 M $\text{Al}(\text{NO}_3)_3$ and an aliquot can be taken for radiochemical determination of the plutonium content.

Several mixtures containing about 0.5 w/o PuF_6 in UF_6 were made which were each reacted with SF_4 in order to determine the optimum reaction conditions. These demonstrations were performed at $85 \pm 5^\circ\text{C}$ in order to liquify the mixture of UF_6 and PuF_6 to facilitate the SF_4 - PuF_6 contact. The plutonium concentration determined by dissolution and analysis of the PuF_4 was compared to the amount of plutonium in the original PuF_6 used to make the mixture. An 11.5-fold stoichiometric excess of SF_4 , heated for one hour with occasional shaking, gave $99.1 \pm 0.5\%$ plutonium recovery. When similar SF_4 excesses were used for 2 and 29 hours, recoveries of plutonium of 101.7 and 98.8%, respectively, were obtained. A 1.90 stoichiometric excess of SF_4 heated for 22 hours resulted in $100 \pm 2\%$ plutonium recovery. Twofold excesses of SF_4 with one or two hours of heating proved to be insufficient for complete reduction of the PuF_6 .

This information is now being applied to the analytical determination of plutonium in PuF_6 - UF_6 mixtures obtained in the operation of the 1 1/2-inch fluid-bed fluorination reactor.

A study of the decomposition of PuF_6 by gamma radiation has been completed with an investigation of the effect that krypton has on the decomposition of PuF_6 . A pronounced enhancement of the decomposition of PuF_6 occurs at an exposure dose of 1×10^8 rads when the addition of krypton to PuF_6 is such that the fraction of electrons contributed by krypton is between 0.65 and 0.75. At an electron fraction of 0.73 for krypton, the G value is 19 (based on energy absorbed in PuF_6 alone), whereas it is 7.5 for PuF_6 alone. When the exposure doses were increased to 2×10^8 rads, no increase in G values with increasing electron fractions of krypton were

observed; instead, there was a steady decrease in the G value with increased values of the electron fraction of krypton.

A study of the factors influencing the rate of alpha decomposition of PuF_6 is in progress to provide information useful to the fluid-bed fluoride volatility processes. Experiments have been carried out in prefluorinated nickel spheres having volumes of 127 ± 2 cc. Plutonium hexafluoride at 100 mm pressure at $26 \pm 2^\circ\text{C}$ was introduced into the spheres where it was held for various times. The undecomposed PuF_6 and the fluorine were then removed from the nonvolatile PuF_4 . The average rate of PuF_6 decomposition for each decomposition time was calculated from the weight of PuF_4 .

The rate of PuF_6 decomposition during a 75-day decomposition period was determined to be $0.19 \pm 0.03\%$ per day as the average result of eleven experiments. An experiment lasting 229 days showed a PuF_6 decomposition rate of 0.16% per day. Further rate decreases were observed in experiments of longer decomposition times, for example, a rate of 0.076% per day was obtained in a 386-day test.

No significant difference was observed in the rate of decomposition when the initial pressures of PuF_6 were 50 mm and 100 mm at $26 \pm 2^\circ\text{C}$ for a 229-day decomposition period. This result differs from previously reported results for shorter decomposition times; earlier, the decomposition rate was slightly less for 50 mm of PuF_6 than for 100 mm of PuF_6 when both were allowed to decompose for the same length of time.

The presence of PuF_4 at the beginning of the decomposition decreased the decomposition rate of PuF_6 to 0.14% PuF_6 per day from 0.19% PuF_6 per day for pure PuF_6 (no PuF_4 present initially) when the initial PuF_6 pressure was 100 mm Hg and the duration of the decomposition was 75 days. In these experiments, 12 to 349.2 mg of PuF_4 (obtained from a previous alpha decomposition of PuF_6 in the sphere) was present at the start of the decomposition. The decrease in PuF_6 decomposition rate was also found to be independent of the amount of PuF_4 initially present.

When fluorine was added to initially pure PuF_6 at 100 mm Hg pressure, the PuF_6 decomposition rate for three different experiments decreased to values between 0.054 and 0.13% per day for 75 days of decomposition. In two different experiments, the average decomposition rates of PuF_6 decreased to values of 0.029 and 0.026% per day during 230 days of decomposition. The decrease in PuF_6 decomposition rate was found to be practically independent of the fluorine pressure, which ranged from 138 mm to 3610 mm.

Oxygen also decreased the PuF_6 decomposition rate. Values of 0.095, 0.099, and 0.113% per day were obtained for the 75-day experiments and values of 0.060 and 0.077% per day were obtained for the 231-day experiments. The decomposition rates were found to be independent of the oxygen pressure, which ranged from 148 mm to 2610 mm.

Helium at 680 mm and 2230 mm partial pressures and krypton at a partial pressure of 3720 mm had little effect on the PuF_6 decomposition rate. These decomposition rates (0.11 to 0.14% per day) were similar to the rates obtained with PuF_6 alone for the same time interval (0.16% per day). At lower krypton pressures of 673 mm and 695 mm, however, the PuF_6 decomposition rates decreased to 0.081 and 0.073% per day, respectively.

High PuF_6 decomposition rates were found in PuF_6 -nitrogen mixtures and are due to a slow reaction which produces NF_3 and PuF_4 . Experiments carried out for 75 days with PuF_6 -nitrogen mixtures indicated an increase in the PuF_6 decomposition rate with an increase in nitrogen pressure. Values obtained for the 75-day decomposition of 100 mm of PuF_6 were 0.45, 0.47, 0.55, 0.62 and 0.71% per day when the PuF_6 was mixed with 88 mm, 119 mm, 382 mm, 1080 mm, and 2670 mm of nitrogen, respectively.

At the request of the Oak Ridge Gaseous Diffusion Plant, samples of alloys of aluminum and of titanium were tested for stress-corrosion in an atmosphere of PuF_6 . Four samples of 7075 aluminum alloy were stressed to $61,000 \pm 600$ psi and two samples of B-120 VCA titanium alloy were stressed to $140,000 \pm 1,100$ psi. The stressed samples were placed in a quartz vessel, and the PuF_6 (52 mm Hg) was added. The temperature of the quartz vessel was held at 28°C for 15 hours, after which the temperature was increased to $65 \pm 3^\circ\text{C}$. At some time between three days and $5 \frac{3}{4}$ days, the two titanium samples ruptured. The vessel was maintained at $65 \pm 3^\circ\text{C}$ for 30 days. At the end of this time and an additional 14 days at $25 \pm 2^\circ\text{C}$, the aluminum alloy samples were still intact.

Work on the evaluation of the two-zone oxidation-fluorination technique for the processing of stainless steel-clad UO_2 pellets was continued. In this scheme, the UO_2 pellets are oxidized in a fluidized-packed bed, the oxidation taking place through openings at the ends or in the sides of short segments of the cladding. The oxidation results in the formation of U_3O_8 powder, which is then fluorinated to UF_6 .

Chopped, clad fuel rods were simulated by placing 0.42-in. dia. x 0.42-in. long cylindrical UO_2 pellets inside 15/16-in. lengths of type 304 stainless steel tubing. In one run, in which these segments were used to form a 3-in. deep fluidized-packed bed, 87% of the uranium charge was removed from the cladding in 12 hr. The oxidation was carried out at 400 and 500°C with 88% oxygen in nitrogen. The remaining uranium was removed by recycle fluorination at 500°C with 64% fluorine in nitrogen. In two other runs which used longer clad segments (10.3-in. long pieces, each with a continuous, longitudinal slit, and 11.6-in. long pieces with holes perforated longitudinally in the cladding), uranium removal from the cladding was essentially complete in 9.5 and 7.5 hr, respectively. In the runs with the long fuel segments, a fluorination cleanup of the alumina bed, after removal of the cladding, was required to recover all the uranium charge as UF_6 product; however, the requirement of a cleanup fluorination step is not considered to be a problem. In these runs, no mechanical means were needed

to complete the uranium removal from the longer clad segments. The perforated cladding (0.020-in. thick) was completely split open by the oxidation of UO_2 to U_3O_8 . During the first six hours of a two-zone oxidation-fluorination run with the perforated cladding, collection rates averaged 30 lb UF_6 / (hr)(sq ft), and the fluorine utilization efficiency based on UF_6 collected was 88%. These values are the highest obtained thus far in two-zone, oxidation-fluorination runs with clad UO_2 pellets.

The separation of UO_2 fuel from stainless steel-clad fuel elements was also studied in experiments in which only oxidation (no fluorination) was carried out in a fluidized-packed bed. In this process, short segments (approximately 1 in. long) of chopped fuel rods were simulated by inserting UO_2 fuel pellets into pieces of stainless steel (type 304) cladding. Separation of the fuel material from the cladding was accomplished in these experiments by reacting the exposed UO_2 with air at a temperature of about 450°C to form U_3O_8 powder. The air also served to fluidize the alumina grain in the voids of the packed bed of fuel segments.

This oxidation technique resulted in a separation of approximately 70% of the UO_2 from the cladding. The separation was increased to 95% by mechanical vibration applied internally to the fuel segments and by the use of gas-pulsing of the fluidized-packed bed.

An engineering-scale high-alpha facility is being built to study process steps in the fluid-bed fluoride volatility process for the recovery of plutonium and uranium from spent uranium dioxide-plutonium dioxide fuel. The contractor's work on the general facility has been completed. The installation of the fluorinator and its services is completed. Preparations are underway to place the fluorinator system into operation.

A program investigating the cleanup of exhaust air from alpha facilities used in fluoride volatility work is in progress. As part of the program, the behavior of PuF_6 and UF_6 released to simulated glove-box atmospheres is being studied. It had been previously found that the release of pure PuF_6 or UF_6 into moist air results in rapid reaction of the hexafluorides with the water to produce a solid reaction product (PuO_2F_2 or UO_2F_2) which is effectively removed by high efficiency (AEC) filters.

In recent hydrolysis experiments, UF_6 has been diluted with dry nitrogen before mixing with moist nitrogen. Under these conditions of release, the hydrolysis reaction is not as rapid as with release of pure hexafluoride into moist nitrogen, and the reaction is found to occur primarily on solid surfaces instead of in the gas phase. These experiments showed that, when hydrolysis is not complete, a large percentage of the released uranium can pass through a high efficiency (AEC) filter. Continuing work with UF_6 will include the study of the kinetics of the surface reaction in order to provide a basis for the design of filter units with surface areas large enough to ensure completion of the hydrolysis reaction. The surface reaction kinetics will also be studied with PuF_6 .

A study was made of heat conduction in the lateral direction in fluidized-packed beds in order to gain further information on heat transfer in certain fluidized-bed systems. The results of this study are of interest in the fluidized-bed fluoride volatility process, wherein heat transfer is accomplished by particles fluidized in the voids of UO_2 pellet beds undergoing exothermic chemical reactions. In this study, the effects of various sizes of (fixed) packing, several sizes of fluidized particles, and two different fluidizing gases (helium and air) on the effective thermal conductivities of fluidized-packed beds were determined. The effective thermal conductivities ranged from 1 to 40 Btu/(hr)(sq ft)(°F/ft) as determined from the average values of the temperature gradients on either side of a centrally located heater in the column.

It was found that the effective thermal conductivities could be correlated by the equation:

$$\frac{k_{\epsilon}}{\rho C_p} = (0.0075) \left[0.0558 D_p (V - V_{mf}) / V_{mf} \right] \text{ ft}^2/\text{sec}$$

where k_{ϵ} = effective bed thermal conductivity, Btu/(sec)(sq ft)(°F/ft)

ρ = density of fluidized particle, lb/cu ft

C_p = fluidized particle heat capacity, Btu/(lb)(°F)

D_p = diameter of fixed packing, ft

V = fluidizing gas velocity corrected for packing void fraction, ft/sec

V_{mf} = minimum fluidization gas velocity corrected for packing void fraction, ft/sec

A study has been carried out to determine the characteristics of the longitudinal (axial) movement of particulate solids in fluidized-packed bed reactors. The study is important to the understanding of the two-zone, oxidation-fluorination process for UO_2 pellets, since longitudinal transport of particulate solids (both the fluidized alumina bed and the U_3O_8 fines) occurs during processing.

The study of longitudinal transport in a fluidized bed was made in simple test columns with mixtures of copper and nickel shot of -40 +50, -100 +120, -140 +170 mesh sizes. Although dissimilar materials were used, the system is considered homogeneous because the densities of these materials are equal and their fluidization properties should therefore be similar. In fines transport experiments, fine nickel powder (avg. dia., 24μ) with fluidized particles of -100 +120 mesh copper or -40 +70 mesh alumina grain was used. Tests of the fluidized-packed bed were conducted with 3/8-in. or 1/2-in. dia. steel spherical packing in a 2-in. ID Lucite column. In all of this work, magnetic separation provided a convenient means of analyzing bed samples. It was demonstrated that the mixing of the fluidized copper and

nickel particles followed a diffusion model and that diffusion coefficients could be used to describe mixing rates. The effects on longitudinal mixing diffusivities of the particulate solids were determined for varying conditions of gas flow rate, bed height, and size of packing and of fluidized material.

Significant results from these solid transport studies which can be used for the design of fluidized-packed bed reactors are as follows:

(1) The rates of mixing with mixtures of -100 +120 mesh copper and nickel particles were higher than those with either the larger (-40 +50 mesh) or smaller (-140 +170 mesh) particle size mixtures.

(2) With increasing gas flow, the longitudinal mixing diffusivities increased to a maximum and then dropped off. For a fixed bed of 3/8-in. dia. steel spheres and after correcting the gas velocity for packing voidage, the maximum diffusivities for -140 +170, -100 +120, and -40 +50 mesh copper-nickel mixtures were, respectively, 12.6×10^{-3} ft²/sec at a gas velocity of 1.5 ft/sec, 17.5×10^{-3} ft²/sec at 1.5 ft/sec, and 9.2×10^{-3} ft²/sec at 4.2 ft/sec. In these tests, the bed height (static) of the fluidized mixtures was 24 in.

(3) Mixing rates increased by a factor of 3.5 as the height (static) of the fluid bed was increased from 8 to 24 in.

(4) The solids mixing diffusivities for open tube fluidization (no packing) and for fluidization in the voids of 1/2-in. dia. spheres were, respectively, about 140 and 1.7 times as great as the mixing diffusivities for fluidization in the voids of 3/8-in. dia. spheres.

(5) In several tests which were carried out to determine the effect of void structure in the fixed bed, diffusivities obtained with a -100 +120 mesh copper-nickel mixture fluidized in the voids of several random-packed beds of 3/8-in. dia. spheres varied by less than a factor of 2.

(6) To avoid accumulations of oxide fines in the lower (oxidation) zone of a two-zone, oxidation-fluorination reactor, the oxidation rate should not be allowed to exceed the fines transport rate. The following transport diffusivities were obtained in a 3-in. dia. column at the indicated conditions.

Gas Velocity (ft/sec)	Spherical Packing Diameter (in.)	Fluidized Particles	Static Height of Fluid Bed (in.)	Fines Transport Diffusivity (ft ² /sec)
0.33	3/8	-100 +120 mesh copper	12	-4.4×10^{-3}
0.80	3/8	-40 +170 mesh alumina	36	8×10^{-3} to 14×10^{-3}
0.33	None	-40 +170 mesh alumina	26	2.5×10^{-3}

Development of a fluid-bed volatility process for the recovery of uranium from highly enriched uranium-alloy fuels is continuing. Full application of the process to aluminum-based fuels as well as zirconium-based fuels appears feasible, according to current results. The process scheme involves a hydrochlorination step which effects volatilization and removal of the cladding and alloying material, and a fluorination step to recover the uranium as the hexafluoride. A hydrofluorination step between these two to displace the bulk of the chloride and convert the uranium chlorides to the tetrafluoride is also being used, but is an optional process step. The reactions are conducted in an inert fluidized bed, which serves as a heat transfer medium. Work is in progress in both bench-scale (1 1/2-in. dia.) and pilot-scale (6-in. dia.) facilities.

A total of six runs were carried out in the 1 1/2-in. dia. fluid-bed system on nonirradiated fuel. Two of the experiments were made with Zircaloy-clad, uranium-Zircaloy alloy and four were made with aluminum-clad, uranium-aluminum alloy. The fuel charges were in the form of small multiplate assemblies, except in one run in which aluminum-based fuel chips were used. Each experiment included hydrochlorination, hydrofluorination, and fluorination steps. The major difference in the processing of these two alloys is the temperature of hydrochlorination, which was about 400°C for Zircaloy and about 200°C for aluminum.

Current studies showed that a less expensive type of alumina, sintered alumina rather than fused alumina, is suitable both as a fluid-bed and packed-bed filter material. This material remained free-flowing, showed little or no size degradation, and most important, its retention of uranium was low. The concentration of uranium in the final beds was 0.01% or less, which was similar to that obtained with fused aluminas. Fluorinations were initiated at 250°C with low (~5%) concentrations of fluorine and completed at 500°C with high (~90%) concentrations of fluorine. Residual uranium values in the case of aluminum fuels were generally lower than for Zircaloy fuels.

In the current studies, it was found that varying the depth of the packed-bed filter in the range 6 to 12 in. had an effect on the quantity of uranium lost during hydrochlorination of aluminum-based fuels. An acceptable loss, about 0.1% of the uranium in the initial charge, was obtained only when the bed depths were greater than nine inches; in contrast, only a 6-in. depth was required in the case of Zircaloy-based fuels.

Up to 1100 ppm water added to the HCl stream was found to have a negligible effect on alloy reaction rates and overall HCl requirements. This system was tested as a simulation of a simple HCl recycle scheme in which a room temperature condenser would be used. The presence of hydrogen (20 v/o) in a moist HCl stream also appeared to be without effect.

The stability (freedom from caking) of the two types of alumina (RR-type, Norton Company and sintered alumina, Aluminum Co. of America) was investigated under severe conditions in two runs. Information on fission product disposition was also investigated in these runs. A group of eleven

fission product elements were added to the inert bed material along with the alloy charge (one experiment with Zircaloy, the other with aluminum). Planned interruptions simulating emergencies, such as power failures and periods during which the main fluidizing gas stream was turned off (thereby allowing the fluid bed to become static), were carried out during and between the several steps of the reaction sequence. During the periods when the main gas flow was turned off, the temperature of the bed was cycled between room temperature and 600°C. It was found that the bed was readily refluidized upon each return to "normalcy". The bed remained free-flowing and was readily drained from the reactor upon completion of the runs (total time under static conditions about 180 hr). The disposition of fission products and also of the minor constituents of Zircaloy throughout the reaction cycle corresponded, generally, with the behavior expected from the higher valent chlorides and fluorides of the individual elements.

Shakedown tests in the pilot plant that has been installed to demonstrate the fluid-bed volatility process for enriched uranium-alloy fuels indicate that satisfactory operation of the pilot plant can be expected. In the current experiments, all of the equipment involved in the hydrochlorination and hydrofluorination steps was operated. Other components (for example, the diaphragm compressor and the UF_6 cold trap system) have been given preliminary tests but require additional shakedown under conditions which more nearly simulate actual operating conditions. Multiplate assemblies, which were fabricated from Zircaloy or aluminum and which did not contain uranium, were processed in three successive experiments. Two of these assemblies were 3-ft long Zircaloy assemblies which weighed 17.75 kg and 13.6 kg; the third was a 4-ft long aluminum assembly which weighed 13.65 kg). These assemblies were reacted to completion in hydrochlorination periods of 8.25, 5.0, and 11.7 hr duration, respectively, while submerged in beds of alumina (4-ft deep, static, and weighing about 40 kg). During the hydrochlorination of Zircaloy, the fluid-bed temperature ranged from 400 to about 545°C, while the reactor wall was maintained at about 395°C. During the hydrochlorination of aluminum, fluid-bed temperatures were in the range 300 to 320°C, while the reactor wall temperature was maintained at about 270°C. Overall average efficiencies of HCl utilization were about 40, 43, and 55% in the three cases.

The fluid-bed hydrolysis reactor, which is an integral part of the pilot plant, was operated at temperatures of 375°C and 330°C during the Zircaloy and aluminum experiments, respectively. Sand was used as a starting bed material in the runs with Zircaloy, and alumina was used as the bed material in the run with aluminum. Very little deposition of the product oxide on the surface of the starting bed material was noted, particularly during the Zircaloy runs, the bulk of the material being converted to fines (-230 mesh). Nevertheless, bed temperatures remained uniform (indicative of good operation), the pressure drop across the sintered metal filters remained at a modest level, and product was readily withdrawn during the run at a rate to maintain the bed level constant.

Improvements and modifications to the pilot plant are being made according to the dictates of the shakedown work. Provision for pulse-blowback of the packed-bed filter has been made; also, an improved gas sampling apparatus for use with the thermal conductivity cells has been installed.

Bench-scale equipment has been fabricated for a high-activity-level study of the fluid-bed volatility process for highly enriched uranium-alloy fuels. The equipment will be test-assembled outside of the cave facility, operated briefly, and finally installed in the hot cell. Installation in the hot cell is now planned for early 1964.

Corrosion studies aimed primarily at the evaluation of nickel as a material of construction for the fluid-bed volatility processes are in progress. Several types of welded and nonwelded specimens are being subjected to simulated process conditions of reactant concentrations and temperatures. Corrosion tests involving flow of fluorine through nickel filter media at 400°C are also in progress. An exploratory study was completed on the resistance of a solid, flexible, closed-cell plastic (Armaflex 22, product of the Armstrong Cork Co., Lancaster, Pa.) to 10% and 50% fluorine in nitrogen and to undiluted fluorine. This material was considered for use as an insulating material for fluorine-containing equipment; however, 24-hr tests at room temperature disclosed that some reaction occurred even in the test with the lowest concentration of fluorine. Surface-hardening, which became more severe with the higher fluorine concentration, was noted. Complete reaction of the material occurred in the test with undiluted fluorine after an incubation period of about two hours.

Studies were continued on a fluid-bed process for the preparation of high-density, spheroidal particles of uranium dioxide directly from UF_6 . Results of these studies will be applied to subsequent work on the preparation of dense UO_2 - PuO_2 particles from mixed hexafluoride feeds. The process involves reaction of the hexafluoride with a mixture of steam and hydrogen in the presence of a product oxide bed. The process scheme is currently being studied in a 3-in. dia. Monel column at temperatures of 650°C to 700°C. Studies with mixed uranium-plutonium hexafluorides are planned for a 2-in. dia. unit now in design. This unit will be installed in the High-Alpha Engineering Facility.

Current studies were made with the filter vessel surmounting the fluid-bed zone. Previously, the unit operated with a separate filter chamber, thereby permitting fines formed in the system to be elutriated out of the fluid-bed zone. With the new arrangement, fines were returned directly to the bed upon blowback of the filters. No unusual effects of this equipment change were observed. Conditions similar to those used in previous studies resulted in a similar product, UO_2 particles having a density of about 9.5 g/cc.

Current work showed that the productivity of the system could be increased without sacrifice of product quality by employment of deeper beds. A hexafluoride feed rate of 50 g/min and a 17-in. bed height (static) gave a product with a higher density than the same feed rate with a 9-in. bed, the corresponding density values being 9.1 and 8.8 g/cc.

Preparation of dense UO_2 particles in a smaller size range than those made previously was demonstrated. Starting with a 3.7-kg bed of -170 +325 mesh particles having a density of 8.6 g/cc, a product having over 50% of the material in the desired size range, 140 + 170 mesh (88 to 105 μ) was produced; previously -80 +100 mesh material had been prepared. Further, the density of the product (9.8 g/cc) was the highest thus far attained at 650°C.

III. High Temperature Fuels and Materials Development (pages 297 to 304)

A program for the development of high temperature fuels and materials is under way. The general area of study is concerned with the chemical stability and chemical reactions of potential high temperature fuels (such as uranium oxides, phosphides, sulfides, arsenides, nitrides, and possible solid solutions) with possible reactor environments (hydrogen and possible contaminating gases) and with supporting refractory components (such as tungsten, rhenium, molybdenum, tantalum, and certain alloys). The objective is to build up a reservoir of basic data from which needed information for evaluation studies may be drawn. The approach is to study the relevant chemical systems in a quantitative manner leading to thermodynamic evaluations. Selected systems are to be investigated in an integrated way using five primary methods of high temperature study which are mutually supporting. These are (1) effusion vapor pressure measurements, (2) mass spectrometric measurements of effusing species, (3) transpiration vapor pressure measurements, (4) phase diagram measurements, and (5) interdiffusion measurements.

Definition of the experimentation was initiated during this report period and the main efforts to date have been devoted to the planning, acquisition, installation, and adaptation of equipment for the projected measurements. Studies of the vapor-condensed state equilibria in the uranium-uranium dioxide system are in progress. Exploratory studies of the nature of the condensed state phase diagrams of uranium monosulfide with several of the refractory metals have been carried out. A time-of-flight mass spectrometer with provision for high temperature effusion studies is nearly operational.

IV. Calorimetry (pages 305 to 325)

The technique that was developed for combustions of zirconium and uranium in fluorine has been used for combustions of niobium, tantalum, and ruthenium. The following standard enthalpies of formation of the pentafluorides in kcal mole⁻¹ were obtained: NbF₅, -433.5; TaF₅, -455.1; and RuF₅, -213.4.

Additional measurements have been made of the energy of combustion of zirconium diboride in fluorine. Attempts were made to obtain more accurate results. Final interpretation of the results is incomplete. The same technique used for the studies with zirconium diboride was also used for a series of combustions of niobium diboride in fluorine. Preliminary determinations of the heat of combustion of niobium diboride in fluorine are presented in the text.

A method has been developed for combustions of silicon carbide in fluorine, in which method the sample is confined to the center of a flat nickel disk by a nickel ring. Calorimetric combustions have been started. Several approaches are being considered for the auxiliary determination of the enthalpy of formation of tetrafluoromethane.

A new technique for the combustion of thorium in fluorine was developed which appears to be satisfactory: The sample is suspended at the top of the bomb during the initial stage of combustion. After combustion has proceeded to the point that the suspension wire parts, the burning sample falls onto a 1/2-inch layer of compacted fluoride powder on the bottom of the bomb.

Preliminary experiments are being carried out for the combustion of uranium monosulfide in fluorine. Several different means are being investigated for preventing premature reaction of the sample.

Assembly and testing of the 1500°C drop calorimeter is continuing. Shielding for the furnace is being redesigned; a copper block calorimeter has been built and is being put into operation; the gate system has been assembled; and work is in progress on the assembly of the drop mechanism.

Design of the complete furnace and drop mechanism for the 2500°C drop calorimeter is complete, and construction has been started.

V. Reactor Safety (pages 326 to 402)

The experimental program to determine rates of reaction of molten reactor fuel and cladding metals with water is continuing. One method uses the energy contained in the light beam from a ruby laser to heat single particles of metal in a water environment. The experiment is designed to study not only the chemical reaction of particles with water, but also to study the transient energy exchange and associated hydrodynamic effects. The technique has now been developed so that small metal foil squares of zirconium, stainless steel, platinum, and aluminum can be reproducibly heated to form molten spheres. The extent of chemical reaction is determined by microanalysis of the quantity of hydrogen generated in a closed quartz cell and by metallographic determination of the oxide film thickness. The rates of reaction and heat transfer will be determined from transient temperature measurements using an electronic two-color optical pyrometer and from transient measurements of the thickness of the steam-hydrogen film from high-speed motion pictures.

Laboratory studies of the kinetics of isothermal metal-steam reactions have been extended to include uranium from 1200 to 1600°C and molybdenum from 1100 to 1700°C. Both studies were performed by a method in which steam, at one atmosphere, was passed over induction-heated cylindrical specimens. The progress of reaction was observed by continuous measurement of the volume of hydrogen generated. Uranium, which is molten above 1133°C, was supported on a quartz pedestal and retained its shape because of the strength of an oxide film which formed. Reaction rates for uranium followed the parabolic rate law and yielded an activation energy of 25 kcal/mole. The results, however, were complicated by the poor thermal conductivity of the oxide film, which resulted in a large temperature gradient across the oxide film.

The studies of the kinetics of the molybdenum-steam reaction were undertaken to determine the suitability of molybdenum as a structural material for experimental apparatus to be operated at high temperatures in steam. The molybdenum-steam reaction, unfortunately, was found to be very rapid at the higher temperatures studied. The reaction followed a linear rate law with an activation energy of 54 kcal/mole. The reaction occurs with the evolution of volatile MoO_3 .

Laboratory studies of the high-temperature combustion of aluminum and magnesium in water were also carried out. Aluminum, when heated to 1750°C in air, ignites and burns vigorously by a vapor phase mechanism. Burning pellets dropped into water continue to burn beneath the water surface and later at the water surface. A series of experiments were performed to determine the combustion rate of aluminum as a function of pellet size. The consumption time was found to be a linear function of pellet diameter. Reaction under water occurred at a rate of 0.96 g Al consumed/(sq cm) (min).

Experiments with magnesium were performed by heating a bottom-tapped crucible of magnesium to 700°C and discharging the molten metal through an argon atmosphere into a water pool. The reaction rate was determined by taking motion pictures of the displacement of water level (in a gas burette) that resulted from the chemical generation of hydrogen. If the magnesium-water reaction is compared with the aluminum-water reaction at equal metal vapor pressures, a physical similarity of the reactions is apparent. Both appear to be vapor phase combustion processes, although the magnesium reaction rate is much the faster.

Studies of metal-water reactions initiated by a nuclear transient have been continued. In these studies, small fuel specimens were submerged in water in high-pressure autoclaves which were then placed at the center of TREAT and subjected to severe nuclear transients. Four experiments were performed with small plates of 89.35 w/o zirconium-10.65 w/o uranium (93% enriched). Two of these experiments were performed with a nuclear energy input sufficient only to heat the plates to their melting point (1840°C). One of these experiments was conducted in room temperature water and one in water heated to 285°C (1000 psi vapor pressure). The extent of metal-water reaction was 5.3 and 2.3%, respectively. In the other two experiments, one at each of the water temperatures given above, the energy addition was sufficient to fully melt the plates. In one of these experiments (in room temperature water), the extent of reaction was 6.3%, and in the other (in heated water), the extent of reaction was 13.1%. The results showed that, in general, there was only a minor effect of water temperature and steam overpressure. This was in contrast with the marked effect of water temperature noted previously with aluminum-uranium alloy material.

An experimental program has begun in which specimens of pre-irradiated fuel are melted and dispersed in water by a nuclear transient in the Transient Reactor Test Facility (TREAT). The purpose of the program is to determine the effect of preirradiation on the extent of metal-water reaction and on the dispersion behavior during fuel meltdown. One experiment has been completed with a 93.5 w/o uranium (20% enriched)-5 w/o zirconium-1.5 w/o niobium fuel pin which had been preirradiated in the Materials Testing Reactor (MTR) to 1.5% burnup of the uranium-235 atoms present. The experimental results were nominally identical to previous results obtained with clean non-preirradiated fuel samples. Extensive particle formation and 22.6% reaction occurred.

The fidelity with which transient pressure was recorded by a pressure transducer located at a distance from an autoclave containing a TREAT experiment was studied briefly. The results showed that a transducer located at the end of a tube 15 ft long would satisfactorily record pressure-time events in TREAT experiments. It is expected that this procedure will greatly decrease spurious pressure signals resulting from the response of commercial pressure transducers to transient neutron pulses.

Studies of the oxidation and ignition of plutonium are continuing. Isothermal oxidation studies were extended to a higher temperature range in order to interpret ignition results. Previous studies had been limited to a maximum of 480°C because of excessive self-heating. In the present series of experiments, two small (1/8-in.) stainless steel plates were clamped on the plutonium cube samples to act as heat sinks and thereby inhibit self-heating. Experiments have now been performed up to 550°C with negligible self-heating. The reaction initially followed a parabolic rate law and subsequently followed a linear rate law at these high temperatures.

Isothermal oxidation studies with a plutonium-2 a/o aluminum alloy were initiated because of the beneficial effect of aluminum addition (i.e., a higher ignition temperature) noted in previous ignition studies. Experiments conducted over the range from 240 through 490°C indicated that the oxide which was formed on the aluminum alloy was more protective than the oxide formed on unalloyed plutonium. The effect was more marked at lower temperatures.

Isothermal oxidation experiments were also carried out with electrolytic high purity plutonium (99.84 a/o Pu) prepared by the ANL Metallurgy Division. Results were identical with those obtained with Hanford plutonium, which had nearly ten times the impurity content of the electrolytic material.

Previous studies of the isothermal oxidation of plutonium had shown that a change of oxidation mechanism occurs between 300 and 400°C, so that there is a minimum in the oxidation rate at approximately 420°C. It was postulated that a second protective oxide film is formed above 420°C. It was considered of interest, therefore, to determine whether the protective oxide film formed at high temperatures would afford subsequent protection at lower temperatures. A specimen was oxidized at 438°C to form the protective oxide, the temperature was then reduced in steps, and the reaction rate was determined at each step. Results indicated that oxidation rates were lowered by a factor of 9 to 50 at temperatures between 150°C and 350°C.

A series of experiments were completed to determine the effect of moisture on the ignition and oxidation behavior of plutonium in air. Ignition temperatures were determined by burning curve experiments for two plutonium samples in air saturated with water vapor at room temperature (air with greater than 20,000 ppm moisture content). The plutonium samples were a 5-mm cube and a 0.11-mm thick foil. The ignition temperatures were essentially identical to those found previously in dry air. Determinations of the effect of moisture on the isothermal oxidation rate have been performed at 150 and 190°C. Marked effects were observed with water contents of 21, 180, and 510 ppm. The oxidation rate of ~20 $\mu\text{g}/(\text{sq cm}) (\text{min})$ between 100 and 200°C, previously referred to as the

third stage and which showed no temperature dependence, is apparently due to the presence of greater than 180 ppm moisture in the oxygen. The oxidation rate at 190°C in oxygen containing less than 5 ppm moisture reached a maximum of only 1.4 $\mu\text{g}/(\text{sq cm}) (\text{min})$.

Two programs of research on the ignition behavior of alloys have been completed. In one of the programs, binary alloys consisting of plutonium and about 2 a/o of another element were studied. Typical impurities and elements of varied valence were used as the second constituent in the plutonium alloys. The alloys, containing Al, C, Ce, Cr, Co, Fe, Mn, Ni, and U, were formed into a series of 5-mm cubes and foils of various sizes. The ignition temperature of these specimens was then determined by the burning curve method. Major effects were shown by the Al, Ce, C, and Co additives, which raise the ignition temperatures of foil specimens (high specific area) from 150 to 250°C above that of unalloyed plutonium.

The other program was concerned with ternary alloys containing about two parts of uranium to one part of plutonium and about 6 a/o of a third element. Interest in these alloys is based on the need for a 2:1 uranium-plutonium alloy for zero power critical experiments. Binary alloys of this type have a tendency to crumble and, as a result, are extremely pyrophoric. Ternary alloys, which were prepared by the ANL Metallurgy Division, contained Al, C, Cu, Fe, Mo, and Zr as the third element. Alloys containing Al, Cu, C, and Zr were found to have undesirable ignition behaviors, although none were as poor as the behavior of a sample of uranium-plutonium alloy without a third component. Good resistance to ignition was achieved with alloys containing iron or molybdenum; however, the ignition characteristics of the iron alloy were adversely affected by the presence of moisture in the air.

An investigation of the thermal conductivity of metal powders has been initiated in order to achieve a better understanding of powder ignition phenomena. Measurements were accomplished using a line source heating method. Preliminary results have been obtained with spherical powders of nickel and uranium. Experimental variables included particle size, pressure, temperature, and extent of oxidation. The latter variable was of particular interest in the interpretation of ignition data. Nitrogen was used as a substitute for air in most of the experiments. Some studies were performed with air, helium, and argon. The conductivity at one atmosphere decreased about 40% as the average particle size was reduced from 1000 μ to 50 μ . There was about a 30% decrease in the conductivity of uranium powders resulting from an oxidation of 12%.

Studies were resumed of the aluminum- U_3O_8 thermite reaction. Experiments were performed with cold-pressed compacts of aluminum- U_3O_8 , containing 30, 45, 60, 75, and 90 w/o U_3O_8 and with unenriched Argonaut

fuel plates which contain 39 w/o U_3O_8 . Two experimental methods were used, one in which pellets were heated at 25°C per min and one in which pellets were heated rapidly by insertion into a 1250°C furnace. Results showed that a maximum thermal effect occurred for specimens in the composition range 60 to 75 w/o U_3O_8 . For both experimental methods, sample temperatures peaked at about 400°C above the furnace temperature in the 60 to 75 w/o U_3O_8 composition range. Results showed that there was no effect of environment, air or argon, or of 3 w/o water added to the pellets. A maximum self-heating rate of 150°C per second was measured with an electronic two-color pyrometer. Results of a series of chemical analyses performed on the residue from pellets after heating indicated that UAl_3 is the favored reaction product.

VI. Energy Conversion (pages 403 to 423)

Work on the development of methods for the conversion of heat into electrical energy was continued. The major effort was devoted to thermally regenerative emf cells. Work on the thermocouple effect was limited to experiments needed for the rounding out of the thermoelectricity program, which is being terminated.

Thermodynamic analysis of the emf-temperature-composition data for the lithium-bismuth system has been completed.*

Emf-temperature-composition data on the lithium-tin system have also been obtained. Compositions from 0.10 to 0.50 atom fraction of lithium in tin over a temperature range of 760 to 1120°K have been studied. A thermodynamic analysis of the data is in progress.

Solid-liquid equilibrium data for the binary salt system LiH-LiBr have been analyzed and large (about 400 cal/mole) positive excess chemical potentials have been found for lithium hydride.

A study was made of the heat of fusion of LiH , since this value is the least accurately known parameter needed for calculations of thermodynamic functions in the LiH-LiCl and LiH-LiBr systems.

The results of this study were in close agreement with a literature-based value of 5240 cal/mole for the heat of fusion of LiH and indicated that earlier values of about 7000 cal/mole are in error.

Regeneration of the binary metal alloy systems, Li-Bi , Li-Sn , and Na-Sn , has been demonstrated. Detailed mass spectrographic studies of the Li-Bi system have been made; Li^+ and Bi^+ were the predominant vapor

*Since the completion of this work, it has been found that Li_3Bi and possibly LiBi intermetallic species are soluble to an appreciable extent in the fused lithium-salt electrolyte. The effect of this solubility on the cell data is currently being investigated.

species. A value of -46.0 kcal/mole was calculated for the free energy of formation of Li_3Bi . This value is in good agreement with the value of -43.2 kcal/mole obtained in bimetallic cell studies. However, the vapor pressure of the lithium is relatively low while the bismuth vapor pressure increases rapidly at temperatures above 900°C , thereby making good separations of lithium from bismuth difficult. Separations of lithium from tin and sodium from tin were demonstrated with 50 a/o alloys sealed under vacuum in long stainless steel tubes. Ninety percent of the total sodium and 16.7 percent of the total lithium distilled from their respective alloys when the alloys were heated at 950°C and the alkali metals condensed at 450°C . Although cell performance and regeneration of tin binary systems appear to be favorable, corrosion problems due to tin may be difficult to solve, especially at high regenerative temperatures. A sodium-bismuth bimetallic cell appears to be the system best suited for initial engineering studies since adequate corrosion data on both sodium and bismuth metals are available. Studies of this system are in progress.

Electrical resistivity measurements for a series of US-ThS solid solutions of varying composition ratios show only a very slight dependence on temperature in the 0 - 1100°C range. A maximum in the resistivity occurs at a mole ratio of US to ThS of about $75/25$. Figure of merit values have been calculated using the resistivity data, previous Seebeck coefficient data, and thermal conductivity data available. The figure of merit values do not change appreciably with temperature. However, they are too low by approximately a factor of ten for useful high temperature thermoelectric power generation.

VII. Nuclear Constants (pages 424 to 428)

Monoenergetic neutron capture data are reported for rhenium and gadolinium for neutron energies between 0.15 and 2 Mev, and neutron total cross sections are given for rhenium for energies between 2 kev and 2 Mev. Preparations are described for the forthcoming measurement of capture to fission ratios of uranium and plutonium isotopes in EBR-II.

CHEMICAL ENGINEERING DIVISION SEMIANNUAL REPORT

July-December, 1963

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 lower costs are their simplicity, compactness, low-volume dry wastes, and capability for handling short-cooled fuels, with an attendant reduction in fuel inventories. Since pyrometallurgical processes do not at present provide high decontamination from fission products, their use in a fuel cycle requires remote refabrication of the fuel. For plutonium-bearing fuels of high burnup, this problem is present to some extent in any process because of the radiation associated with the higher plutonium isotopes.

Among the pyrometallurgical processes under development are melt refining (a simple melting procedure for metallic fuels) and various 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, such as carbides.

The melt refining process is presently in the most advanced state of development, and it will be used for the recovery of enriched uranium from the first core loading of the second Experimental Breeder Reactor (EBR-II),** located in Idaho.

A. Pyrometallurgical Development

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

The fuel for the first core loading of EBR-II is approximately 50% enriched uranium alloyed with 5 w/o noble metal fission product elements (fissium) which improve the irradiation stability of the alloy. The fuel pins are clad with stainless steel, which is thermally bonded to the pins by a small amount of sodium in the annulus. To process the fuel, the pins are declad mechanically, chopped, and charged to a lime-stabilized zirconia crucible in which they are melted and liquated under an argon atmosphere at 1400°C for a period of three to four hours. During this treatment,

*A summary of this section is given on pages 17 to 25.

**Melt refining will be performed in the Fuel Cycle Facility, which is adjacent to the EBR-II reactor building.

approximately two-thirds of the fission products are removed through volatilization and through selective oxidation by the crucible. The purified metal is top-poured into a mold to form an ingot from which new fuel pins are prepared by an injection-casting procedure. A mixture of oxidized material and unpoured metal remains in the crucible as a skull; uranium is recovered from the skull by a separate process (see Skull Reclamation Process) employing liquid metal solvents.

In the melt refining operation, volatilized sodium and condensable fission products are collected by a Fiberfrax* fume trap on top of the zirconia crucible. Additional experimental work has been carried out during the past six months in order to determine with more certainty the behavior of fission product iodine that is released during melt refining, and to obtain more information on the release of iodine activity from the fume trap when the melt refining furnace is opened in the Argon Cell (an argon-atmosphere process cell) of the EBR-II Fuel Cycle Facility. Preparations have been made for an investigation of the melt refining of plutonium alloys under a molten halide salt phase.

Because of a possible future need to remove nitrogen from the argon atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility, a study is in progress on the removal of nitrogen from argon by gettering the nitrogen on hot titanium sponge. The kinetics of the nitrogen-titanium reaction are being determined, and a pilot plant to demonstrate the removal of nitrogen impurity from argon on an engineering scale has nearly been completed.

a. Distribution of Fission Product Iodine in the Melt Refining Process
(N.R. Chellew, D.M. Meyer)

The behavior of fission product iodine in the EBR-II melt refining process was first investigated in a series of small-scale experiments with unirradiated and low-activity synthetic uranium-fissium alloys.¹ Further information was obtained in four melt refining experiments with 400-g charges of uranium-5 w/o fissium alloy that had been irradiated to burnups ranging from 0.56 to 1.75 total atom percent (ANL-6696, Table 5, p. 22). These experiments confirmed the results from the earlier work with synthetic charges in that melt refining at 1400°C removed over 99% of the iodine activity from the product ingot. Additional results were then obtained in two supplementary experiments in which 7-g charges of highly irradiated uranium-5 w/o fissium alloy were melt refined for one hour at 1400°C;

*A product of the Carborundum Corporation prepared from amorphous fibers and colloidal silica binder. The reported composition in weight percent is: Al₂O₃ (51.2), SiO₂ (47.4), B₂O₃ (0.7), and Na₂O (0.7).

¹Chellew, N.R., and Ader, M., Nucl. Sci. Eng., 9, 82 (1961).

the purified alloy was not poured from the crucible (ANL-6569, p. 26). In these experiments, the melt refining crucible was contained in assemblies that were designed to collect condensable fission products volatilized from the molten fuel alloy. After melt refining, about 1.3% of the initial iodine activity was found in the combined ingot and skull and approximately the same amount was found in the crucible. Most of the iodine activity that could be accounted for was condensed on portions of the assembly that had been at temperatures between about 400 and 1000°C. Comparison of the relative gram atom amounts of elements found in the condensate indicated that the iodine was present primarily as CsI. Less than one-half of the iodine activity initially present in the charge was recovered in these experiments. The low activity balances have been attributed mainly to losses incurred during the remote handling of the apparatus.

Because of the unknown fate of the iodine activity not accounted for in the melt refining process, two additional experiments were performed, the main objective being to obtain satisfactory iodine material balances along with iodine distribution data. Synthetic charges were prepared by spiking uranium-fissium alloy with iodine in order to avoid the remote handling required for highly irradiated fuel. Fuel specimens weighing about 20 g were prepared by inserting cesium metal and either KI or CsI labeled* with I^{131} in separate holes in a uranium-5 w/o fissium capsule and sealing the holes with tapered plugs made of the same alloy. In order to simplify the handling procedures and subsequent analytical determinations, the cesium and iodine were added in concentrations that were, respectively, about 3 and 14 times greater than those that would be present in EBR-II fuel at a total burnup of 2 a/o.

Melt refining was carried out in an induction-heated quartz tube furnace located behind temporary shielding in a hood. The apparatus is illustrated in Figure I-1. A closed tantalum tube was employed as a collector for the volatilized material, and the inner furnace parts were arranged so that the charge and the entire lime-stabilized zirconia crucible would be at the same temperature. Prior to each experiment, the temperature profile of the collector was determined by measuring the temperature at various locations along the collector with a thermocouple. The relationship between the reference and charge temperatures was also determined by simultaneous measurements with the reference thermocouple and another thermocouple located inside the crucible.

The fuel (about 20 g) was charged to the zirconia crucible (height, 1 1/16 in.; OD, 9/16 in.), which was placed in the apparatus as shown in Figure I-1 and was outgassed at 200°C for 20 min. (The cap assembly

*The labeled compounds were prepared by R.J. Popek of the Analytical Group. An aqueous solution of the inactive compound was mixed with I^{131} in a basic solution of Na_2SO_3 , and the labeled compound was precipitated by the addition of isopropyl alcohol and was vacuum dried.

Figure I-1

APPARATUS FOR COLLECTION
OF IODINE-131 VOLATILIZED
DURING MELT REFINING
EXPERIMENTS
(not to scale)

108-6260 Rev.

was raised off the tantalum collector during this step.) Argon was then added to the system, the spring-loaded cap was placed on the tantalum collector, and the charge was melt refined for one hour at 1400°C. When the furnace had cooled, the sealed collector tube was removed from the furnace, and the I^{131} activity along the length of the tube was measured with a counter equipped with a 1/8-in. wide collimator. The collection apparatus was then dismantled and analytical samples of activity in the condensate, the crucible, and the combined skull and ingot were obtained by dissolution or leaching with acid. The I^{131} gamma activity in the samples was measured in a deep-well scintillation counter and confirmed with a 256-channel analyzer. The crucible was counted intact after its surface had been treated with acid to remove adhering portions of the skull.

Analytical results for the two experiments are presented in Table I-1. Within the estimated limits of analytical error, all of the I^{131} activity in the original charge was accounted for. In each case, over 99% of the activity was found on the collector tube. The combined ingot and skull contained a maximum of 0.6% of the activity, and the crucible a maximum of 0.1%. The I^{131} distribution along the collector tube as a function of the temperature of the tube during melt refining is shown in Figure I-2. The iodine activity that was added in the form of KI (b.p. 1325°C) was distributed over a wide temperature range, and about one-half was in the zone that had been heated to 1400°C. Most of the iodine that was added as CsI (b.p. 1280°C), however, was found in a relatively narrow zone that had been at temperatures between 790 and 1020°C. These results suggest that the I^{131} activity was collected primarily as KI in Experiment I and as CsI in Experiment II.

Table I-1

DISTRIBUTION OF IODINE AFTER MELT REFINING URANIUM-FISSIUM
ALLOY SPIKED WITH I¹³¹ ACTIVITY

Charge: In Experiment I, 19.490 g of U-5 w/o fissium alloy was spiked with 0.132 g of cesium metal and 0.040 g of iodine as KI labeled with 61.1 μC of I¹³¹.

In Experiment II, 19.859 g of U-5 w/o fissium alloy was spiked with 0.122 g of cesium metal and 0.029 g of iodine as CsI labeled with 112 μC of I¹³¹.

Apparatus: See Figure I-1.

Crucible: Lime-stabilized zirconia.

Conditions: Melt refining for 1 hr at 1400°C under argon atmosphere.

Experiment	Melt Refining Fraction	% of Initial I ¹³¹ Activity ^a
I	Ingot and Skull ^b	0.01
	Crucible ^c	0.1
	Condensate	99
II	Ingot and Skull ^b	0.6
	Crucible ^c	0.03
	Condensate	106

^a The estimated precision of the analyses, $\pm 5\%$ relative, includes variations observed during the preparation of the labeled compounds.

^b The charges were allowed to solidify in the crucible after melt refining was completed.

^c The crucible surfaces were treated with acid to remove adhering skull material prior to analysis for iodine activity.

Figure I-2

DISTRIBUTION OF IODINE-131 VOLATILIZED TO COLLECTOR TUBES
EMPLOYED DURING MELT REFINING EXPERIMENTS

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The deposition pattern of iodine added as CsI showed a close resemblance to that of fission product iodine in the earlier experiments with highly irradiated uranium-fissium alloy. In both cases, the I^{131} activity was deposited in a narrow temperature zone, although in the experiments with irradiated fuel the temperature of this zone was somewhat lower (ANL-6569, Table 1, page 28).

On the basis of these experiments, it was concluded that the low material balances obtained in the earlier work resulted from inadequate handling and collection techniques. The results substantiated previous data which indicated that melt refining at 1400°C for one hour removes nearly all of the fission product iodine from the product ingot and the skull. Although the results obtained on the distribution of I^{131} activity cannot be applied directly to the plant-scale melt refining process, they show that the deposition pattern of iodine on components near the melt refining crucible depends mainly on the temperature of the components. In the plant equipment, a substantial fraction of the iodine activity is expected to collect on the upper wall of the melt refining crucible and on the Fiberfrax fume trap, since these surfaces will be well below the melt refining temperature of 1400°C.

b. Release of Iodine Activity from a Fiberfrax Fume Trap
(N.R. Chellew, D.M. Meyer)

During the melt refining operation in the EBR-II Fuel Cycle Facility, a Fiberfrax fume trap will be positioned on top of the melt refining crucible to collect volatilized sodium (sodium from the annulus between fuel pins and cladding) and condensable fission products. This trap is described in ANL-6605, p. 67. Much of the iodine activity that is volatilized during melt refining is expected to condense on the fume trap.

When the melt refining operation has been completed, the furnace will be allowed to cool to an equilibrium temperature, and the argon atmosphere in the furnace, which will contain Xe^{133} and Kr^{85} , will be pumped from the furnace. Fresh argon will be added before the furnace is opened to the argon atmosphere of the Fuel Cycle Facility. The temperature of the fume trap during these operations will depend on the procedure that is followed. If the 7/8-in. thick Fiberfrax cover remains on top of the crucible after the pour, fission product decay heat from the highly radioactive skull in the crucible will raise the temperature of the fume trap to about 700°C on the inner surface that faces the skull, and to about 350°C on the outer surface. If the fume trap is tilted away from the crucible, however, it is expected to be at a temperature of 150 to 200°C . In order to estimate the amount of I^{131} activity that would be released from the Fiberfrax to the argon atmosphere of the process cell during removal and disposal of the fume trap, the rate of iodine release from Fiberfrax was measured under the two temperature conditions mentioned above.

Previous work with synthetic EBR-II type fuel (ANL-6725, p. 32) had indicated that I^{131} would be released from a Fiberfrax fume trap having a temperature gradient from about 700 to 300°C at a rate of about 0.2% of the iodine present per hour of exposure to argon. With the trap heated to a maximum temperature of 150°C , the release rate appeared to be much slower; however, this observation was based on limited data. Of the total amount of I^{131} activity released by the Fiberfrax to a flowing argon atmosphere, more than one-half disappeared from the gas phase, presumably through the deposition of CsI on the walls of the apparatus.

The primary objective of the present study was to obtain additional information on the rate of release of I^{131} from a Fiberfrax fume trap to an argon atmosphere under the lower of the two temperature conditions described above. A secondary objective was to determine the effect of a small increase in the oxygen impurity content in the argon atmosphere on the rate of I^{131} release from the Fiberfrax.*

The apparatus that was used in the experiment has been described previously (ANL-6725, Figure I-1, page 33). Briefly, it consisted of an induction furnace in which a uranium-fissium charge containing tracer-

*The atmosphere in the Argon Cell of the EBR-II Fuel Cycle Facility is circulated through a purification system that provides heat removal and maintains the oxygen level below 20 ppm and the moisture level below 5 ppm. If an emergency occurred, such as failure of the gas-cooling system, the oxygen and water vapor concentrations would increase slowly. The moisture content of the argon was not varied in this experiment, since the reaction of water with sodium and cesium forms a basic solution which itself is an effective trap for most forms of gaseous iodine.

level iodine activity was melt refined. A Fiberfrax plug was located above the charge so as to have a temperature gradient about like that of the fume trap in the plant equipment (bottom surface, 1000°C; top surface, 540°C). Provision was made for raising the Fiberfrax plug into a separate quartz tube furnace where it could be isolated and could be heated to simulate fission product decay heating. Iodine that was released from the Fiberfrax and transported by an argon stream (at a flow rate corresponding roughly to the anticipated flow rate of the atmosphere in the Argon Cell) was collected in a series of charcoal beds with AEC filters at the inlet and outlet.

A melt refining charge was prepared by placing UI_3 and cesium metal in separate holes in a 20-g piece of uranium-5 w/o fissium alloy capsule and sealing the holes with plugs of the same alloy. The plugs were sealed in place by electron-beam welding. The capsule was then lightly irradiated to produce I^{131} and Cs^{134} activity for analytical purposes, and it was cooled for 22 days. This charge, along with 0.2 g of sodium to simulate sodium from the thermal bond, was placed in a lime-stabilized zirconia crucible, covered with the Fiberfrax plug (dia., 1 in.; depth, 1 in.), and melt refined for one hour at 1400°C under argon. After the system had cooled, the furnace was evacuated to remove the Xe^{133} and Kr^{85} activities, and the Fiberfrax was withdrawn into the quartz tube furnace, which was isolated from the melt refining furnace by closing a connecting gate valve.

Argon containing less than 25 ppm nitrogen, 5 ppm water vapor, and either 2.2 or 175 ppm oxygen was passed over the surface of the Fiberfrax plug at a flow rate of 6.6 ft/min and then through the AEC filter-activated charcoal assemblies. The Fiberfrax was heated to 170°C, which is approximately the temperature that the fume trap will reach when it is in the open position in the plant melt refining furnace. The amount of activity released as a function of time was determined by periodically removing one of the three charcoal traps in the collection system and counting the gamma activity with a 256-channel gamma spectrometer. The activity was collected continuously, except for overnight periods when the Fiberfrax was cooled to room temperature and held in a static argon atmosphere. Upon completion of the experiment, the activity remaining in the Fiberfrax and the activity condensed on the quartz furnace tube were determined by leeching these components with acid and counting the activity in the solutions.

The analytical results from this experiment are presented in Table I-2. Of the 307.8 μc of I^{131} accounted for, about 99.84% was retained by the Fiberfrax. Of the 0.16% that was released, the amount found on the walls of the apparatus was much larger than the amount that had been transported in the argon stream to the AEC filter-charcoal assemblies. These data provide further support for the expectation that most of the iodine activity escaping from the fume trap in the EBR-II Fuel Cycle Facility will condense on cool surfaces of the furnace and will not appear in the atmosphere of the Argon Cell.

Table I-2

DISTRIBUTION OF IODINE AFTER REHEATING OF FIBERFRAX
FUME TRAP USED IN MELT REFINING EXPERIMENT

Experimental ConditionsMelt Refining Step

Crucible: Lime-stabilized zirconia.

Charge: 19.858 g of U-5 w/o fissium alloy was spiked with 0.175 g of cesium metal, 0.034 g of iodine as UI_3 , and 0.2 g of sodium metal.

Conditions: Alloy heating, 1 hr at 1400°C; atmosphere, Ar.

Fiberfrax Temp: Bottom area (facing melt), 1000°C; top area, 540°C; Fiberfrax outgassed at 1000°C prior to use.

Iodine Collection Step

Argon Flow through Filter Assembly: 34 ft/min.

Argon Flow over Sides of Fiberfrax: 6.6 ft/min.

Impurities in Argon: H_2O vapor, 5 ppm; N_2 , < 25 ppm; O_2 , indicated below.

Initial Iodine Activity in Fiberfrax: 307.8 μC .

Fiberfrax Temperature	Time (hr)	Oxygen Conc. in Argon (ppm)	Iodine Distribution, % of Initial Activity ^a		
			Collected by Filter Assembly (cumulative)	Volatilized to Walls of Apparatus	Retained by Fiberfrax
Constant at 170°C	30.2	2.2	3×10^{-3}	0.15	99.84
Constant at 170°C	30.9	175	7×10^{-3}		
Varying ^b	14	89 (av.)	3×10^{-3}		

^a Appropriate corrections for decay have been applied.

^b Cooled to room temperature for overnight holding periods and reheated to 170°C.

Figure I-3

IODINE ACTIVITY COLLECTED IN ACTIVATED CHARCOAL ASSEMBLIES
DURING REHEATING OF FIBERFRAX
USED IN MELT REFINING EXPERIMENT

108-7303

The rates of I^{131} collection by the AEC filter-activated charcoal assemblies are shown in Figure I-3. In the argon atmospheres containing either 2.2 or 175 ppm oxygen, the I^{131} collection rates were each nearly constant after an initial period during which the rate was somewhat higher. The 80-fold increase in the oxygen concentration of the argon increased the collection rate by a factor of about 2.5. However, this higher rate with the Fiberfrax at 170°C was only about 10^{-3} of that obtained in the earlier work in which the Fiberfrax had a temperature gradient from 685 to 315°C.

In general, these results confirmed earlier observations which indicated that the temperature of the fume trap will be the main factor determining the rate of I^{131} release to the atmosphere of the Argon Cell of the Fuel Cycle Facility when the melt refining furnace is opened. It should therefore be possible to minimize the release of fission product iodine by lifting the fume trap away from the crucible after the melt refining operations are completed and the furnace is opened. It also appears that the total amount of iodine released is proportional to the time that the fume trap is exposed to the argon atmosphere.

Increasing the oxygen content of the argon to a level about nine times greater than the maximum concentration (20 ppm) expected in the Argon Cell had only a minor effect on the rate of iodine release.

c. Use of Salt Fluxes in Melt Refining
(G.A. Bennett, W. Spicer, and W. Pehl)

Melt refining of uranium-fissium* alloys under a molten chloride salt was previously investigated in a few experiments (ANL-6648, pp. 35-38). The potential advantages of this process as compared to the present melt refining process (ANL-6605, p. 61) are a lower operating temperature (1150 versus 1400°C), a shorter liquation time (1/2 versus 3 hours), higher product yields (estimated to be about 99% versus 90 to 95%), and operation in beryllia crucibles which give promise of being more reliable and durable than zirconia crucibles. Use of a flux of calcium chloride containing 7 w/o magnesium fluoride as a rare earth oxidant resulted in excellent cerium removal (about 99%) in one hour at 1100 to 1300°C without apparent attack of a beryllia crucible. Yields of purified metal were high (95 to 98%) for the small scale of operation (700 g of uranium-fissium alloy).

Preparations have now been made to evaluate this procedure for plutonium-containing metal fuels. By careful control of the amount of magnesium chloride or fluoride oxidant added, it is hoped that preferential oxidation of the rare earth metals and extraction into the salt phase can be accomplished without significant oxidation and extraction of the plutonium. The major objectives will be to determine the percentages of plutonium removed from the product metal by extraction into the salt phase and by vaporization, probably as the trichloride. A melt refining furnace with an integral glovebox (see Figure I-4) designed for experiments with plutonium alloys has recently been reactivated, and several shakedown experiments with uranium have been performed.

Experimental work with plutonium alloys will be started in early 1964. Initially, plutonium-uranium-fissium alloys of the type contemplated for future core loadings of the EBR-II reactor will be employed. These alloys are expected to contain between 10 and 20 percent plutonium, about 10 percent fissium, and the balance uranium. Cerium will be added to a concentration of about 0.5% to represent all rare earth elements.

d. Removal of Nitrogen from Argon with Titanium Sponge
(M. Kyle, J. Arntzen)

A method is under development for removing nitrogen contamination from argon by gettering the nitrogen on hot titanium sponge metal (see ANL-6648, pp. 38 to 40, and ANL-6725, pp. 39 to 41). Although this method will have general utility for removing nitrogen from argon, the major incentive for its development is a possible future need to remove nitrogen from the argon atmosphere in the Argon Cell of the EBR-II Fuel

*Fissium is a mixture of the relatively noble fission products: ruthenium, molybdenum, palladium, rhodium, and zirconium.

Figure I-4

INDUCTION FURNACE WITH INTEGRAL GLOVE BOX

108-7133

Cycle Facility. Two sets of experimental equipment are presently being constructed: (1) equipment for a study of the kinetics of nitrogen removal from argon on hot titanium sponge and (2) a pilot plant for obtaining overall process performance data and information on component reliability. Studies will be conducted with argon containing initial nitrogen concentrations between 50 and 50,000 ppm.

(1) Kinetics of Nitrogen Removal from Argon with Titanium Sponge

A schematic diagram of the equipment which has been built for a study of the kinetics of nitridation of titanium sponge by argon-nitrogen mixtures is shown in Figure I-5. An argon-nitrogen mixture of carefully controlled composition is continuously circulated through a series of eight small (3 grams) test beds containing titanium sponge. The circulation rate (50 to 1500 liters/hr) is such that only a small fraction of the nitrogen present in the gas stream reacts with the titanium in a single pass through the series of beds. The entire nitrogen content of the gas (as well as any oxygen and water vapor inleakage) is removed after each pass by a large titanium bed which is in the closed loop. Nitrogen is slowly bled into the system just ahead of the titanium test beds, the nitrogen concentration being controlled by careful regulation of the nitrogen and argon flow rates.

Figure I-5

APPARATUS FOR DETERMINATION OF THE KINETICS
OF NITROGEN REMOVAL FROM ARGON WITH TITANIUM SPONGE

The purpose in maintaining the circulation rate such that only a small fraction (less than 5%) of the nitrogen present in the gas stream reacts during any given pass is to approximate a differential titanium bed in order to facilitate interpretation of the data. The extent of reaction of the titanium test material will be determined at intervals during the run by successively and permanently removing the top titanium test bed, and determining its nitrogen content by Kjeldahl analysis.²

For analysis of the data, it will be assumed that each test bed in the series reacted with gas having the same nitrogen concentration. As a result, a correction for decrease in nitrogen content of the gas between the beds should not be necessary. Before rate data are taken, however, it will be necessary to establish that the series of small titanium beds do, in fact, perform as an overall differential bed.

The system (Figure I-5) operates as follows: Argon gas is circulated in a closed loop by a reciprocating diaphragm pump. A pump bypass loop is utilized to produce a constant flow rate through the reaction loop, the flow rate being controlled by the pressure drop across the flow control valve. Both the inlet and outlet pressures of this valve may be set by pressure regulators (No. 1 and No. 2,

²Thompson, J. M., Anal. Chem., 25, 1231-5 (1953).

Figure I-5) on the pump discharge. This system allows the pressure drop across the flow control valve, and consequently the circulation rate through the loop, to remain constant despite wide variations in the pump outlet pressure. The flow rate of the argon gas is metered and recorded by a pressure transducer connected across a calibrated orifice plate. A third pressure regulator (No. 3) provides additional argon for the loop when required.

The argon gas next passes through a 40-lb bed of titanium sponge, maintained at 950°C, in which all of the nitrogen, oxygen, and water vapor contaminants present in the argon are removed. The desired nitrogen concentration in the argon is then re-established by mixing the purified argon gas with a constant flow of nitrogen entering the loop. Before this nitrogen is mixed with the argon flow, it is passed through a molecular sieve bed operated at room temperature and a copper bed maintained at 600°C to remove water and oxygen contaminants.

The flow rate of the nitrogen is controlled by the pressure drop across a "standard leak" (normally used for calibration of vacuum system leak detectors) which consists of a flattened length of tubing in which there is a small hole, or "leak". The pressure on the inlet side of the "standard leak" is controlled by pressure regulator No. 4.

The gas mixture then passes into the test chamber where it is heated to reacting temperature (850°C to 950°C is the range to be studied) before passing through the series of eight test beds. Each test bed consists of 3 to 10 g of -1/2 in. +20 mesh titanium sponge contained in a 2-in. OD by 0.5-in. high circular tray, the bottom of which is constructed of two layers of 70 mesh stainless steel (Type 310) screen. After passing through the test chamber, the gas is cooled and recirculated through the flow control equipment.

A test bed is removed by opening the slide valve on the test chamber, lifting the test bed into the cooling chamber (argon atmosphere), reclosing the slide valve, and allowing the test bed to cool to room temperature before removing it from the chamber.

Preliminary Performance of Experimental Equipment

Operating characteristics of the experimental equipment have been determined in a series of equipment shakedown runs. These have revealed the following problems which must be corrected before accurate data can be obtained:

- 1) To date, the series of test beds has not performed as an overall differential bed. Reaction rates are low in the first few beds.

Gas may be entering the series of test beds at a considerably lower temperature than the desired 900°C. The result would be that the first few beds would serve mainly to bring the gas up to operating temperature. This difficulty has stemmed from inaccurate gas temperature measurements, which have been higher than the true measurements because of radiation from the hot (hotter than the gas) pipe walls. Radiation-shielded thermocouples will be installed to overcome this problem.

To ensure that the gas is at the proper temperature before it enters the first test bed, a gas preheater consisting of a heated packed bed is being installed in front of the test beds.

- 2) An oxide film forming on the titanium sponge as a result of oxygen contamination of the argon gas would interfere with the titanium-nitrogen reaction.^{3,4} The extent of oxygen reaction which is deleterious was not specified. Therefore, considerable effort is being taken to keep the oxygen concentration in the test gas as low as possible. Ultimately, the effect of oxygen will be determined by deliberately adding known oxygen concentrations to the circulating gas. In one 96-hr run in which the test beds were not removed, the average oxygen content of the titanium sponge in the test beds increased from an initial value of 0.02% to 0.18%. From the amount of oxygen which had reacted with the titanium bed material, the oxygen concentration in the argon-nitrogen gas was calculated to be 0.6 ppm. While it is not known whether this oxygen concentration is deleterious, an effort will be made to reduce the oxygen concentration further by installation of an oxygen-gettering bed (possibly titanium sponge operating at about 550°C, at which temperature titanium is effective for gettering oxygen but not nitrogen).⁴

The following positive results have been noted with respect to loop performance:

- 1) Maintenance of the argon-circulation and nitrogen-addition rates at levels within 1% of the desired values has been demonstrated. Results of analyses of the gas composition,⁵ made at frequent intervals during the runs, have in general agreed with concentrations calculated from preset flow rates of the nitrogen and argon within 3%.

³ Gibbs, D. S., Svec, H. J., Harrington, R. E., Ind. Eng. Chem., 48, 289-296 (1956).

⁴ Gulbransen, E. A. and Andrew, K. F., Trans. AIME, 185, 741-748 (1949).

⁵ Dombrowski, H. S., Anal. Chem., 26, 526-528 (1954).

- 2) Reaction rates were essentially the same for two fractions of titanium sponge particles, one fraction of 0.072 ± 0.007 -in. dia. and the other 0.148 ± 0.054 -in. dia. These particle size fractions were used in alternate test beds. Titanium sponge conversions (fractional) were 0.518 ± 0.045 and 0.513 ± 0.018 for the smaller and larger particle sizes, respectively.
- 3) The Kjeldahl analysis of the nitrogen content of titanium sponge has been satisfactory. Analytical accuracies are estimated to be $\pm 1\%$. In past runs, only a small fraction of a 3-g test bed (usually a single particle of titanium sponge) has been analyzed for nitrogen. In the future, an entire test bed will be dissolved and analyzed to guard against the selection of particles having abnormal reactivities and to decrease the effect of such abnormal reactivities.

(2) Pilot Plant for Nitrogen Removal from Argon

A pilot plant scale unit designed to demonstrate the removal of nitrogen impurity from argon gas on an engineering scale is presently under construction. This unit will operate at a gas circulation rate near 10 cfm and with argon containing a nitrogen concentration which will be varied between 50 and 50,000 ppm. The unit is designed to provide information on component design and reliability for large-volume purification systems.

Figure I-6

SCHEMATIC DIAGRAM OF PILOT PLANT EQUIPMENT FOR REMOVAL OF NITROGEN FROM ARGON

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Figure I-7

PILOT PLANT EQUIPMENT FOR REMOVAL OF NITROGEN FROM ARGON

(The titanium sponge bed and the two trickle heaters are contained in a furnace (not visible) located above the pebble bed heat exchangers.)

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The equipment layout of the unit is diagramed in Figure I-6 and shown in Figure I-7. The gas will be circulated from a surge tank (11 cu ft) by means of a blower. The flow rate will be controlled by a butterfly valve on the blower inlet and by adjustment of blower speed. The pressure drop across a calibrated orifice plate is to be used to determine flow rate. The gas will be passed through a four-way valve and into one of the two pebble-bed regenerative heat exchangers. These heat exchangers are made of type 310 stainless steel pipe, 8-in. nominal OD and 48 in. long, filled with 1-in. OD chrome steel balls. These vessels will be used alternately to cool the reacting gas and store heat on the discharge side of the titanium sponge bed and to preheat the reacting gas on the inlet side of the sponge bed.

After leaving a pebble bed, the gas will pass into one of two trickle heaters which are located in a large resistance furnace. The trickle heaters are 8-in. OD by 20-in. high Hastelloy "X" (trade name of Haynes Stellite Division of Union Carbide) pipes filled with 0.25-in. OD by 1-in. long

steel rods. The trickle heaters are designed to bring the reacting gas up to reacting temperature (900°C) before the gas enters the titanium sponge bed, where the nitrogen is removed. The titanium sponge bed is contained in a Hastelloy "X" pipe 8 in. OD by 26 in. high, lined with Type 316 stainless steel which possesses good resistance to reaction with the sponge. The sponge bed consists of approximately 40 lb of -1/2 in. +20 mesh titanium sponge.

The gas will then be passed through the second trickle heater (now off) and into the second pebble bed regenerative heat exchanger, where the gas will be cooled and the heat content of the gas stored for future use. The gas will then flow through the four-way valve into a water-cooled gas cooler, where its temperature will be reduced to room temperature, and then into the surge tank for recirculation. Nitrogen will be fed into the argon stream, immediately before the surge tank, through a standard rotameter. Makeup argon will also be added at this point.

The pressure drop around the system is expected to be between 1 and 2 psi. The blower used to circulate the gas is designed to operate at inlet pressures of from 0 to 2 psig and, by variation of the blower speed, at outlet pressures of from 1 to 12 psig. At the expected system pressure drop, the circulation rate can be varied from 0 to 50 cfm. The blower, which was manufactured by M-D Blowers Inc., is of special design to prevent air and oil leakage into the circulating gas.

It is intended to operate the four-way valve on a time cycle so that at a predetermined time, the valve will change position and reverse the flow of gas through the purification system in order to recover the sensible heat stored in the pebble bed regenerative heat exchanger.

2. Processes Employing Liquid Metal Solvents

Several processes are being developed which employ liquid metals and salts as processing media. The skull reclamation process is under development for recovery of the fissionable material remaining in the crucible residue (skull) after a melt refining operation. Small-scale runs for demonstration of this process have been completed. Process operations are also being conducted in engineering-scale equipment (about one-half of full plant scale). Preliminary work has been done on a process modification which permits the handling of nondecladdable EBR-II fuel pins by the skull reclamation process.

Work was continued on the development of a liquid metal process for the extraction of plutonium from EBR-II blanket material. Emphasis is presently being given to work related to the concentration of the plutonium product solution by evaporation of the solvent metals.

Laboratory work is also under way on recovery processes for fuel materials which contain plutonium as a fissionable material. Engineering studies have been started in support of these processes.

a. Development of the Skull Reclamation Process

The skull reclamation process is being developed as an auxiliary process to melt refining for processing the first fuel loading of the EBR-II reactor. The process has two purposes: (1) recovery of uranium from the skull remaining in the crucible after melt refining, and (2) separation of fission products from the uranium. The recovered and purified uranium will be returned to the main EBR-II fuel cycle. The skull reclamation process provides for all disposal of nonvolatile fission products in the EBR-II fuel cycle.

Figure I-8

FLWSHEET FOR SKULL RECLAMATION PROCESS

The flowsheet for the skull reclamation process is presented in Figure I-8. This is essentially the same flowsheet as the one presented earlier (ANL-6725, page 42), except that the present flowsheet has been modified to permit use of the same crucible for all steps except for the final solvent evaporation and product melting step.

(1) Removal of Uranium Skull Material from Melt Refining Crucibles by Oxidation
(R.D. Pierce, J.T. Hepperly)

The first step in the proposed skull reclamation process is oxidation of the skull to permit the subsequent removal of oxide powder from the crucible by pouring. Prototype skull oxidation and oxide dumping equipment has been built and tested in the fuel cycle mockup facility (ANL-6477, page 87, ANL-6725, p. 93). A number of melt refining crucibles from which the skull material was removed in the prototype oxidation and dumping equipment have been processed to evaluate the efficiency of uranium removal from the crucibles. A jaw crusher and ball mill were used to pulverize the crucibles to facilitate sampling of the pulverized crucibles.

Acid leaching of the pulverized samples does not extract all of the uranium. A fusion-dissolution of a small (0.2-g) sample works well, but is time-consuming and requires that especially good sampling be achieved. Direct X-ray fluorescence of a pulverized sample has proved to be a suitable procedure for these samples. Uranium analyses by X-ray fluorescence and by the fusion-dissolution technique have been performed on waste crucibles from ten runs. The results are presented in Table I-3.

The amount of uranium remaining in the waste zirconia crucibles following oxidation and removal of the skull oxide ranged between 1 and 3 1/2% of that in the total skull material. These results, although obtained in runs made for the development and testing of the oxidation and dumping equipment, cast considerable doubt on the possibility that the low losses previously expected (less than one percent of the uranium in the skull) can be achieved in this step. The earlier estimates of about one percent loss were based on acid leach samples which are now known to give low results. The higher results, which now seem probable, represent no more than 0.2 percent of the original melt refining charge and are acceptable for the present process.

(2) Small-Scale Studies of the Skull Reclamation Process
(R.D. Pierce, K.R. Tobias, N. Quattropani)

A program of small-scale demonstrations of the skull reclamation process was completed in equipment located inside an argon-atmosphere glove box (shown in ANL-6543, pp. 32 to 35). These demonstrations (scale: 100 to 150 g of uranium) were made to establish permissible ranges of process variables and to expose and rectify any process difficulties. The establishment of flowsheet conditions in these runs will permit emphasis to be given to process mechanics and equipment performance in the larger scale process studies discussed in a following section of this report.

Table I-3

URANIUM LOSS IN MELT REFINING CRUCIBLES AFTER
REMOVAL OF SKULL BY OXIDATION

Skull Oxidation Run No. ^a	Original Melt Refining Charge (g)	Composition of Original Melt Refining Charge	Weight of Unoxidized Skull (g)	Uranium Loss in Waste Zirconia Crucible		
				(g)	(percent of uranium in skull)	(percent of uranium in melt refining charge)
SOF 26	8361	U-5% Fissium- 0.7 % Ce	619	18	3 1/2	0.2
SOF 29	8252	U-5% Fissium- 0.7 % Ce	510	11	2 1/2	0.14
SOF 30	8888	U-1.3% Fissium	634	12	2	0.14
SOF 31	9675	U-5% Fissium	834	9	1.2	0.10
SOF 32	9532	Uranium	562	20	3 1/2	0.2
SOF 33	8552	U-5% Fissium	246	8	3 1/2	0.10
SOF 34	10,288	U-5% Fissium	195	5	3	0.05
SOF 35	8334	U-2.5% Fissium	318	6	2	0.07
SO 74	9543	U-5% Fissium- 0.7 % Ce	460	3.5	0.9	0.04
SO 75	8860	U-4.5% Fissium- 0.7 % Ce	578	12	2 1/2	0.14

^aThe skulls were oxidized completely in the SOF runs and were oxidized partially (~25%) in the SO runs.

Three demonstration runs (Runs BJ-21, BJ-22, and BJ-24) were completed. In the first of these, Run BJ-21, 10 percent of the charge was skull oxide and the remaining 90 percent was an unoxidized skull. In both of the other two runs, all of the new charge material was completely oxidized skull material. A recycled heel was present in Run BJ-24. In the final run, the modified process presented in Figure I-8 was followed. It differs from the older flowsheet presented in ANL-6725, p. 42, in that the precipitation steps are performed in the same tungsten crucible as is used for the noble metal extraction and reduction steps rather than in a separate beryllia crucible. This modification would eliminate from plant equipment one processing furnace as well as a large beryllia crucible.

The modified flowsheet also provides for dissolution of the uranium cake present after the decomposition step in zinc-12 percent magnesium in order to transfer the uranium to a relatively small beryllia crucible for retorting. In the original flowsheet, removal of the uranium product for transfer to the retorting equipment was effected by lifting the uranium out of the large beryllia crucible. This procedure was followed in the small-scale demonstration runs except in the final run, as noted above. However, for remote operation (the technique to be used with plant equipment), the removal of a solution is easier than the handling of a solid cake. When uranium is removed in a solution, the quantity of solvent to be evaporated for each kilogram of uranium product is increased from the range of 0.4 to 1 kg of 50 w/o magnesium-zinc alloy to at least 7.3 kg of 12 w/o magnesium-zinc alloy.

Table I-4

URANIUM MATERIAL BALANCES FOR SKULL RECLAMATION RUNS

	Uranium Content (g)		
	<u>Run BJ-21</u>	<u>Run BJ-22</u>	<u>Run BJ-24</u>
<u>Charge</u>			
Skull Oxide	13.6	101	103
Skull	125.4	0	0
Heels	<u>0</u>	<u>0</u>	<u>12</u>
Total Charge	139	101	115
Product	116	86	75
Heels and Samples	11.1	12.6	37
<u>Waste Streams</u>			
Noble Metal Extraction	0.16	0.04	0.04
Reduction Flux	0.24	0.71	0.81
Intermetallic Compound			
Precipitation	1.8	0.59	4.5
Intermetallic Compound			
Decomposition	<u>0.8</u>	<u>0.29</u>	<u>1.2</u>
Total Uranium in Waste Streams	3.0	1.6	6.6
Total Uranium Accounted For	130.1	100.2	118.6

Uranium Material Balances. The uranium material balances for the three demonstration runs are presented in Table I-4. No heels were introduced in either of the first two runs to compensate for the heels remaining after the runs; however, the uranium in heels and samples is considered to be recoverable and on this basis the uranium losses are only 2.2 and 1.6 w/o for the first two runs. In Run BJ-24, a large heel of

uranium product solution was left after product dissolution and transfer of the solution to a beryllia crucible. This made uranium recovery low in this run. The large heel left after the dissolution and transfer is abnormal and should not constitute a process problem.

The uranium losses in the waste streams were all small, except for the intermetallic compound precipitation step of Run BJ-24. In this run, uranium-zinc intermetallic compound was entrained in the waste and nine times the amount of dissolved uranium (solubility limit of 0.03 w/o) was transferred. Entrainment, which has been a frequent problem in this step (ANL-6725, pp. 44-45), will be studied in the large-scale engineering equipment.

Fission Product Removals. The overall fission product removals for the three runs are shown in Table I-5. The recycle of heel

Table I-5

CHARGE AND PRODUCT COMPOSITIONS FOR SKULL RECLAMATION
RUNS BJ-21, BJ-22, AND BJ-24

Element(s)	Run BJ-21		Run BJ-22		Run BJ-24	
	Charge ^a (g)	Product (g)	Charge ^b (g)	Product (g)	Charge ^b (g)	Product (g)
Uranium	139	116	101	86	115	75
Cerium	11.0	2.1	5.4	0.47	6.5	0.7
Total Rare Earths	1.6×10^{10c}	2.6×10^{9c}	--	--	--	--
Molybdenum	3.1	0.51	2.5	0.20	2.5	0.07
Ruthenium	2.6	0.9	1.6	0.20	1.6	0.11
Zirconium	3.2 ^d	1.4	2.4 ^e	0.3	2.7 ^e	0.25
Cesium	1.0	nil	—— Not Present in Run ——			
Strontium	0.53	0.0013	—— Not Present in Run ——			

^aCharge contained irradiated uranium tracer which had been cooled one year.

^bCharge contained ruthenium-106 tracer.

^cTotal β counts, principally cerium activity.

^dComposed of 2.6 g in crucible fragments, 0.38 g in ZrO_2 reagent, and 0.2 g in fission.

^eRepresents about 0.2 g from fission; the balance was crucible fragments.

solutions will increase the uranium content of a product stream much more than the fission product content.

Cerium is removed in two steps of the process, the uranium reduction step and the intermetallic compound decomposition step. Between 10 and 15 percent of the cerium remains in the waste flux after a reduction step and the balance dissolves in the 50% magnesium-zinc solution of the decomposition step. In the latter step, a fraction of the cerium that is equivalent to the phase transfer efficiency is removed with the waste supernatant phase. The results for cerium in Runs BJ-22 and BJ-24 are as expected, but the cerium removal in Run BJ-21 is somewhat lower than would be expected from the phase transfer achieved following the decomposition step. This poorer removal is believed to have resulted from incomplete decomposition of the intermetallic compound and incomplete liberation of coprecipitated cerium.

The charge in Run BJ-21 contained irradiated uranium tracer which had been cooled one year. The behavior of total rare earths determined by beta counting in this run, therefore, mainly reflects cerium and some yttrium activity. The behavior of these elements, as determined by beta counting, is in reasonable agreement with the results of chemical analyses for cerium. In general, these runs again demonstrate that adequate removals of rare earth elements are achieved in the skull reclamation process.

The removals of the relatively noble elements molybdenum and ruthenium were satisfactory in all three runs. Major decontamination from these elements is accomplished in the noble metal extraction step, in which these noble metals are reduced by zinc from skull oxide which is suspended in flux at 800°C. At the metal phase transfer temperature of 525°C (which was selected to be below the flux melting point in order to immobilize the skull oxide-flux phase), the molybdenum and ruthenium are largely insoluble and must be transferred in suspension. In Run BJ-21 the melt was agitated more gently during the transfer than in BJ-22 and BJ-24 (100 rpm in Run BJ-21 versus 150 and 200 rpm, respectively, in Runs BJ-22 and -24). A resultant poorer suspension of the noble metal precipitates in Run BJ-21 probably explains the slightly lower decontamination in that run.

Zirconium behavior continued to be somewhat erratic in these runs. The only significant zirconium removal occurred in the intermetallic compound precipitation step. The poor removal of zirconium in Run BJ-21 and the good removals in Runs BJ-22 and BJ-24 were more extreme than would be expected from the phase separations of 83, 83, and 70 percent accomplished after the respective intermetallic compound precipitation steps. Zirconium behavior is being studied further.

Cesium chloride and strontium oxide were added to Run BJ-21 with the charge as carriers for the radioactive cesium and strontium in the irradiated uranium used in this run. The cesium and the strontium both remained in the flux phase during the reduction step and were discarded in this phase.

With the three experiments just discussed, the small-scale demonstrations of the complete skull reclamation process have been concluded; however, experiments on this scale will be performed to evaluate specific chemical problems such as the present uncertainty in zirconium behavior. The investigation of the overall process will be continued in the larger pilot plant discussed in a following section.

(3) Special Skull Reclamation Process Studies

Sampling of Zinc for Ruthenium Analysis. Concentrations of ruthenium in zinc solutions of the skull reclamation process have been difficult to determine (ANL-6725, p. 45) because of a sampling problem. The problem has resulted from the reaction of dissolved ruthenium with the tantalum sample tubes, particularly the tantalum frits, to form an insoluble phase. No satisfactory substitute has been found for tantalum, but a substantial reduction of the reaction of tantalum with ruthenium has been effected by use of a modified sampler.

Both the sample tube which was used previously and the alternative design are shown schematically in Figure I-9. In sampling, a tube of either type is inserted into the melt and held for a period of time to

Figure I-9
TANTALUM SAMPLE TUBES

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reach melt temperature, after which the furnace pressure is increased by about 20 psi to force a sample into the tube. The tube is then withdrawn and the sample is allowed to freeze under pressure. A period of about 2 min is allowed for collection of filtered samples, but it has been found that a sample can be obtained in 5 sec with the alternative design.

A series of samples were taken at 800°C with fritless tubes at sampling times (preheat and under pressure) of 5 to 90 sec. In each case a satisfactory sample was obtained. Ruthenium present in the zinc at a concentration of 0.056 percent was spiked with Ru¹⁰⁶ tracer to permit determination of the interaction of ruthenium with the tubing. In all samples taken in less than 30 sec, between 2 and 6 percent of the total ruthenium in the sample interacted with the tantalum. This seemed to be a lower limit, probably controlled by the time required for the sample to freeze. The results for all the samples obtained by means of fritless tubes, with allowance being made for the amount of interacted material, were in good agreement. With filtered samples (obtained with the original sampling tube), the extent of interaction has been variable and has involved as much as two-thirds of the total ruthenium.

In the light of these results, it appears that unfiltered samples which are withdrawn in less than 30 sec can be analyzed for ruthenium with useful accuracy by a chemical procedure. Test runs with tracer ruthenium can be used in estimating the uncertainty resulting from the tantalum-ruthenium interaction.

Control of Flux Heel. With the present skull reclamation process (see flowsheet, Figure I-8), all process steps are conducted in a single tungsten crucible except the final step of evaporation of solvent to recover the uranium product from solution in a magnesium-zinc alloy. These steps include the noble metal extraction, the uranium reduction, two uranium precipitations, and the product dissolution step. In pilot plant studies, it has been observed that a portion of the flux heel, which remains after the flux transfer at the conclusion of the uranium reduction step, transfers with the product solution that is to be evaporated. Since this flux contains some nonvolatile materials, especially magnesium oxide, its presence results in contamination of the uranium product remaining after evaporation of the solvent.

In a small-scale experiment, a technique was successfully employed to avoid transfer of this flux with the product solution. In a simulated product-dissolution step in which an appropriate amount of flux was still present, an amount of magnesium fluoride was added which was equivalent to that which would be added for the noble metal extraction step when the crucible was re-used for the next run. Because of the relatively large amount of magnesium fluoride compared to the amount of flux heel and because of the high melting point of magnesium fluoride (1225°C), the salts formed an agglomerated sludge which did not transfer when the melt was poured. When this technique is used, a flux heel will be present for the noble metal extraction step of the next run.

This technique of immobilizing the salt phase will be tried in future pilot plant runs.

(3) Pilot Plant Studies of the Skull Reclamation Process
(I.O. Winsch, D.E. Grosvenor, G. Rogers, P. Mack,
J. Hepperly)

A pilot plant for the skull reclamation process is currently being operated for equipment demonstration as well as process demonstration purposes. The scale of operation is about 2 kg of skull oxide (containing about 75 percent uranium), which compares with the full-plant scale of about 7 kg of skull oxide (5 kg of uranium) for equipment to be installed in the EBR-II Fuel Cycle Facility.

A description of the pilot plant was presented previously in ANL-6687, p. 35. All process operations up to the final retorting step are now being performed in one large tungsten crucible (about 12-in. OD by 19 in. high) which is centrally located within a large mild steel bell jar (24-in. OD by 36 in. high). (In early runs, unsuccessful attempts were made to use a large beryllia crucible of about the same size for the uranium precipitation steps.) The tungsten crucible is heated by radiation from a 5/8-in. thick graphite susceptor which, in turn, is heated by radiation-cooled induction coils.

Enclosure of the furnace within a bell jar allows an argon atmosphere to be maintained in the system and permits pressurization of the furnace for transfer of molten metals or salts through a pipe to either a waste container or, in the case of the product solution, a retorting crucible. The bell jar cover has three nozzles, one of which is used for a stirrer, the other two of which are used for insertion of transfer pipes and other equipment used for sampling, liquid level measurement, and temperature measurement.

The equipment is now being operated in an open glovebox. After equipment operation and operating procedures have become sufficiently reliable, the glovebox will be closed, and a dry air atmosphere will be maintained within it. Eventually, an argon or nitrogen atmosphere may be used within the glovebox.

Seven runs (SKR-1 through SKR-7) have now been made, but the first three were not carried to completion because of equipment difficulties; one difficulty was the failure of two large beryllia crucibles which were used in the second and third runs. The next three runs (SKR-4 through SKR-6) were made in a single tungsten crucible according to the basic flowsheet shown in Figure I-8. In the seventh run, a slight modification of this flowsheet was explored. The removal of waste flux, which is normally done after the reduction step, was not carried out until the magnesium-zinc supernatant solution of the final uranium precipitation step had been removed. The major objectives of these runs have been the

development of operating techniques and familiarization with and improvement of equipment performance. The method of operation, the equipment performance, and the general results are discussed for each step of the process.

Noble Metal Extraction. The noble metal extraction step is performed in the tungsten crucible at 800°C by contacting a slurry of skull oxides in a halide flux with zinc, which extracts the noble metal fission product elements molybdenum, ruthenium, technetium, rhodium, and palladium. The materials charged to this step are 2 kg of oxidized skull material, 8.8 kg of halide flux,* and 35 kg of zinc.

The phases are mixed for four hours at 800°C, after which the system is cooled to about 525°C to freeze the flux phase. The zinc phase, which remains liquid at this temperature, is then transferred by pressure through a heated transfer line to a waste container. Since the solubilities of molybdenum and ruthenium are exceeded at the transfer temperature, it is necessary that the zinc phase be stirred during the transfer to suspend the precipitated molybdenum and ruthenium particles. However, in some of these runs, it was not possible to keep the stirrer rotating prior to and during transfer of the zinc. To overcome this difficulty, it will be necessary to use a more powerful stirrer motor than that which is presently used.

The percentages of zinc transferred in the last four runs were 88, 91, 89, and 89. These values are regarded as satisfactory. Although argon is passed through the transfer tube into the zinc phase as the flux is being frozen in order to keep the transfer tube open and to maintain a vent through the flux layer, it was found that the frozen flux appreciably slows the transmission of gas pressure required to force the molten zinc out through the tube. A high-resistance route for the gas exists along the agitator shaft, which is rotated slowly during freezing of the flux. Consequently, a pressure of about 12 psig was required to effect zinc transfer, rather than the 7 psig calculated to be necessary. It was shown that, if desirable, the gas pressure required to effect transfer could be decreased by maintaining an opening through the flux by means of an open-end pipe having its top opening above the flux phase and its bottom opening in the zinc phase. If vanes were employed on the agitator shaft, which is rotated slowly while the flux is solidifying, a satisfactory opening through the flux phase might also be maintained along the agitator shaft.

*Composition of flux: 47.5 m/o MgCl_2 , 47.5 m/o CaCl_2 , and 5 m/o MgF_2 . When uranium metal was present in the charge, or when uranium and magnesium were present in a crucible heel from the preceding run, zinc chloride was also added to the flux to prevent loss of uranium in the zinc.

Reduction Step. The reduction of uranium oxides from the flux phase also is effected at 800°C in the tungsten crucible. The flux phase is vigorously mixed with a 5 percent magnesium-zinc alloy, and, as the uranium oxides are reduced by magnesium, the uranium metal dissolves in the zinc-magnesium phase. The uranium concentration in the zinc-magnesium phase approaches 4 w/o at complete reduction. The reductions were performed without difficulty, and in Runs SKR-4, SKR-5 and SKR-6 were essentially complete (i.e., 99 percent or more) in less than four hours.

Following the reduction, a high temperature (800°C) transfer of the flux phase to a waste container was made in each run, except Run SKR-7, by raising the heated transfer line so that the inlet was above the metal phase and in the flux phase. A gas pressure of 3 to 5 psi was used to transfer the flux phase. This pressure effected a transfer of the flux phase (density of about 2) but not of the metal phase (density of about 5.7). As the transfer of flux progressed, the line was slowly lowered until the flow of flux ceased, thereby indicating that the inlet end of the transfer line was in the metal phase. In Runs SKR-4, SKR-5, and SKR-6, the phase transfer efficiencies for removal of the waste flux were 62, 94.5, and 93 percent, respectively. No reason can be given for the low efficiency in Run SKR-4. Flux separation efficiencies of at least 90 percent are desired.

The above procedure generally has provided a good transfer of flux, but it necessitates vertical movements of the transfer line. In Run SKR-7, the flux transfer was not carried out until the final metal waste solution was removed in order to avoid changing the position of the transfer line to effect the transfer of the flux. The use of a fixed transfer line is considered very desirable for remote operation of plant equipment. However, a transfer of only 60 percent of the flux phase was realized. In the following step, over one-third of the residual flux was transferred with the product metal solution. Such transfer of flux with the uranium product solution cannot be allowed because of the large quantity of nonvolatile material (mainly magnesium oxide) present in the flux phase. This nonvolatile material would remain with the uranium metal product after retorting. Therefore, if delayed removal of the flux phase is to be practical, the efficiency of flux removal must be increased. A small flux heel can probably be immobilized by the addition of magnesium fluoride (by the procedure described in a preceding section of this report), but this is not a practical solution for a large flux heel. Further work will be devoted to the development of the delayed flux removal procedure.

Uranium Precipitation Steps. After the reduction step, the uranium-zinc product solution is cooled from 800°C to between 500 and 525°C in order to precipitate uranium as a uranium-zinc intermetallic compound (as the epsilon phase, which is approximately U_2Zn_{23}). The supernatant liquid is then pressure-siphoned to a waste container. Next, sufficient magnesium is added to the precipitated uranium-zinc intermetallic compound to decompose the compound and thereby liberate uranium metal. The resultant supernatant metal, a 50 percent magnesium-zinc solution, is then removed by pressure siphoning.

The efficiency of removing the supernatant solution following the intermetallic compound precipitation step ranged between 60 and 70 percent in Runs SKR-4 through SKR-6. Because of the low supernatant removals experienced through Run SKR-6, special runs, PT-7 through PT-12, were made in order to study and improve the phase separation efficiencies of this step of the process. In these runs, a 5% magnesium-zinc solution was charged to the furnace with 1.5 kg of depleted uranium rod. The solution was maintained at 800°C for one hour while it was mixed at approximately 350 rpm to dissolve the uranium rod. The solution was then cooled to about 500°C to precipitate the uranium-zinc intermetallic compound. In Run PT-7, the procedure employed for cooling was identical to that employed in the skull reclamation process Runs SKR-1 through SKR-6, that is, the solution was simply cooled without stirring from 800°C to between 500 and 525°C. In Runs PT-8 through PT-12, the solution was stirred slowly at 40 rpm during cooling from 800°C to 600°C; when 600°C was reached, stirring was discontinued and the solution was cooled to 500 or 525°C.

Table I-6

SUPERNATANT REMOVAL EFFICIENCIES AND URANIUM
CONCENTRATIONS IN TRANSFERRING SUPERNATANT SOLUTION
FROM INTERMETALLIC PRECIPITATION STEP

Run No.	Temp. of Transfer (°C)	Percent of Supernatant Solution Transferred	Percent Uranium* in Grab Samples of Transferring Supernatant		
			Start	Middle	End
PT-7	500	70.0	--	--	--
PT-8	500	86.6	0.03	--	0.032
PT-9	500	84.1	0.04	0.043	0.35
PT-10	500	88.5	0.073	0.043	0.21
PT-11	525	87.2	0.041	0.033	1.10
PT-12	525	87.8	0.122	0.055	2.16

*Theoretical solubility of uranium in a 4 w/o Mg-Zn solution is 0.017% at 500°C, and 0.03% at 525°C.

As shown in Table I-6, the efficiency of supernatant removal was markedly improved (to between 84 and 88 percent) by mild stirring while most of the uranium was being precipitated. This improvement is attributed to the formation of a compact cake in the bottom of the crucible as a result of the stirring. It is believed that the mild stirring eliminated temperature gradients at the wall and thus prevented the formation of a precipitate along the walls.

Grab samples were taken of the transferring supernatant solution during Runs PT-8 through PT-12 and analyzed for uranium. As shown in Table I-6, uranium contents were slightly greater than the uranium solubility during most of the transfer, but increased to rather high values near the end of the transfer operation. The average uranium content of the transferred solution was not determined in these runs since the transferred solution was used again in the succeeding run. However, it is clear that the concentration of uranium in the grab samples taken during the transfer did not represent the average concentration of uranium in the supernatant. To obtain reliable samples of a transferred supernatant solution, it will be necessary to remelt all of the transferred material and to sample it at a temperature of 700 to 800°C. The high uranium concentrations present near the end of a transfer are of concern. However, it is not yet known to what extent the average concentration is influenced by a high concentration in any single grab sample.

The 50% magnesium-zinc supernatant solutions present after decomposition of the intermetallic compound were transferred with efficiencies of 87, 81, 94 and 70 percent in Runs SKR-4 through 7. Except for the poor efficiency in SKR-7, these removals are considered to be satisfactory. In Run SKR-7, the run in which all of the flux phase was still present at the time that the 50% magnesium-zinc supernatant solution was removed, it was found that a considerable portion of the metal supernatant phase (at least 11 percent) had been trapped in the flux phase and was subsequently transferred with the waste flux. This undoubtedly resulted from the fact that the flux phase is only slightly more dense than the metal phase (estimated as a few tenths of a density unit in g/cc). It is believed that this problem can be avoided by decreasing or even eliminating the mild agitation (60 rpm) which has been used during cooling of the supernatant solutions from 800°C to the transfer temperature following the intermetallic decomposition step.

Uranium Cake Dissolution. The product uranium is dissolved in the tungsten crucible by adding sufficient zinc (and magnesium, if necessary) to produce a 12 w/o magnesium-zinc alloy (final concentration after dissolution of the uranium) and then is transferred by pressure-siphoning. The saturation concentration of uranium in this solution is about 16 w/o at 800°C. The uranium concentration in the product solution to date has been about 9 w/o because the final solution volume has been dictated by the weight of supernatant solution left as a heel after the previous uranium precipitation step and supernatant transfer. The product solution has had a rather small volume (about 4 liters); therefore, the height of the solution in the crucible has been only about 4 in., and it has been possible to remove only 65 to 75 percent of the product solution. By incorporating a sump in the bottom of a tungsten crucible, it should be possible to increase considerably the yield of product solution. No sump was provided in the present crucible but one could be provided in crucibles obtained in the future.

Equipment Modifications. During the runs now completed, a number of modifications have been made to the furnace and auxiliary equipment to overcome the difficulties encountered during the runs:

- 1) Mixing was inadequate in the reduction step in Runs SKR-1 and SKR-2, as indicated by low uranium oxide reductions (about 65% complete). This was improved in SKR-3 by increasing the stirrer speed from 575 to 1300 rpm. A further improvement in the oxide reduction was achieved in Run SKR-4 by increasing the diameter of the 3/4-in. high impeller from 3 in. to 5 in., even though the stirring rate was reduced to about 500 rpm. (Mixing power input is proportional to the third power of the speed and the fifth power of the impeller diameter.) Since these changes were made, uranium oxide reductions have been about 99 percent complete. Subsequently, a second impeller was installed on the agitator shaft. It is 1 3/4 in. from the crucible bottom and provides mixing in the low-volume product solution without the necessity of lowering the agitator shaft to bring the single impeller (normally located 3 3/4 in. from the bottom of the crucible) into the solution.

In early operations, the agitator shaft (30% tungsten-molybdenum) often was frozen in the lower graphite guide bearing of the agitator support assembly by salt and metal vapors which had deposited in the bearing. This was eliminated by installing three tungsten heat shields just below the bearing. Except for six centering projections, the agitator bearing assembly was reduced in diameter to leave an annular space between it and the bell jar nozzle in which it fits. A slight buildup of flux or metal in this space is now less likely to freeze the assembly in the nozzle.

- 2) The original insulation retainer in the top of the bell jar furnace was a flat stainless steel plate which was bolted in place. After a short period of use, this plate became badly warped. A new insulation retainer is being used which consists of a central disc of stainless steel located above the crucible in the high temperature zone and an overlapping, flat stainless steel doughnut (15-in. ID by 25-in. OD). Both the disc and doughnut are made of 1/4-in. thick type 304 stainless steel. The doughnut is located above the central disc and is bolted to it. The new retainer has worked well.
- 3) Three types of transfer line failures have been experienced: (a) electrical heater failure, (b) breakage of the somewhat brittle 30% tungsten-molybdenum alloy which is the transfer pipe material, and (c) plugging of the transfer tube. The electrical heaters are 600-watt, magnesia-insulated, stainless steel-

sheathed, 1/8-in. OD heating cables which are wound on the transfer tube.* The frequency of heater failure has been markedly reduced by increasing the number of heaters from 3 to 5 and lowering the power input to each. Discussions are in progress with several heater manufacturers to develop a heater design that has a long life at high temperatures, will withstand thermocycling, and is more easily installed on the transfer tube than is the present heater.

Because of problems with limited heater life, several arrangements of heating and insulating materials were tested. In these tests a 1/8-in. OD heating cable was wrapped on a 15-in. section of 5/8-in. OD molybdenum-tungsten tube with the same heater pitch as was used on the pilot plant transfer lines (one turn every 3/8 in.). Exterior insulation consisting of 1 in. of Fiberfrax was used in all tests. Results were as follows:

	<u>Watts Required to Reach Temperature of 850°C Within Pipe</u>
Heaters on stainless steel sheath over Mo-W tube (Presently used on transfer tubes)	276
Heater wound directly on Mo-W tube	287
Heaters imbedded in Thermon** directly applied to Mo-W tube	>540
Double stainless steel sheath - one over the heater and one between the heater and tube	360
Heaters wound on stainless steel sheath and imbedded in copper spray coating	340

The best of the above arrangements is the heater-transfer tube arrangement presently used. The power required to reach 800 to 850°C is much less than anticipated and is less than has been

*The 30% tungsten-molybdenum alloy tube is protected from air oxidation by sheathing it in stainless steel (see Figure I-3, ANL-6687, p. 37). The stainless steel sheath and heaters are extended into the furnace to a point 4 to 6 inches above the solutions in the crucibles. The electrical heaters are wound on the outside of the stainless steel sheath.

**A proprietary product of Thermon Manufacturing Co., Houston, Texas, for improving heat transfer.

used in pilot plant transfer operations. Therefore, a longer heating period at lower power will be allowed in future pilot plant operations.

Breakage of the molybdenum-tungsten transfer tubes has been partly the result of excessive handling (frequent repositioning in furnaces or removal from furnaces for repair), which has imposed severe mechanical stresses. This problem is being overcome by operating with the tubes in a fixed position and by design changes made to strengthen the tubes.

Tube plugging has resulted from cold spots in the transfer line. Most cold spots have been eliminated by the addition of more electrical heaters. One troublesome area has remained; this is a 4 to 6-in. unheated section above the liquid in the crucible. Additional heat to this area has been provided by increasing the height of the induction coil used to heat the crucible and by increasing the number of turns of the coil from 4 to 6, thereby increasing the temperature of the upper portion of the crucible. This has also had the beneficial effect of preventing the buildup of solid masses of flux or metal on the upper crucible walls.

The operation of the equipment has been improved considerably by the above modifications. Additional modifications may be necessary to ensure the durability and reliability of components and systems for plant equipment.

(4) Study of Uranium Recovery from Clad Fuel Pins
(V.G. Trice, L.F. Dorsey)

To provide for the contingency that some of the EBR-II fuel pins may not be decladdable for melt refining⁶ (for reasons of cladding failure, swelling of the fuel pins, or reaction of the uranium-5 w/o fissium alloy with the stainless steel clad), a brief study has been made which shows that the noble metal extraction step of the skull reclamation process⁷ can be adapted to the recovery of uranium from stainless steel clad fuel. In addition

⁶The decladding operations and the melt refining process are described in ANL-6605, "Description and Proposed Operation of the Fuel Facility for the Second Experimental Breeder Reactor (EBR-II)", pp. 59-72.

⁷ibid., pp. 115-122. See also p. 61 of this report. The skull reclamation process provides for the recovery of uranium from residues (skull) remaining in melt refining crucibles. In order to remove the skull from a crucible, it is oxidized to convert it to a free-flowing oxide powder.

to the study of the extraction of uranium from fuel pins clad with stainless steel, experiments were conducted with uranium-5 w/o fissium fuel pins clad with materials that are being considered as possible future cladding materials, i.e., niobium-1 w/o zirconium, tungsten-lined type 304 stainless steel, and tungsten-lined Hastelloy X.

The noble metal extraction step of the skull reclamation process provides for the removal of elements less electropositive than zinc by contacting a suspension of skull oxides in a molten salt with zinc. These elements include the relatively noble fission products, principally molybdenum, ruthenium, rhodium, palladium, and technetium, and also constituents of many cladding materials, e.g., tungsten, iron, and nickel. To accommodate clad fuel, the noble metal extraction step was modified by the addition of sufficient zinc chloride to the salt phase to oxidize uranium to the trichloride and thereby to provide for its extraction into the flux phase.

In preliminary scouting experiments, the direct reaction of uranium-5 w/o fissium with zinc chloride contained in a LiCl-KCl eutectic salt* was found to be too vigorous for practical use. The temperature was difficult to control, and excessive frothing occurred. Therefore, it was decided to employ a two-phase molten salt-zinc system. In such a system, the fuel pins sink to the bottom of the zinc and the rate-controlling step becomes the rate of dissolution of uranium in zinc. The relatively noble elements are retained in the zinc phase as the uranium is oxidized and extracted into the flux phase.

The major objective of the present experimental program was a comparison of the percentage of uranium extracted from clad and unclad fuel pins under relatively standard processing conditions. Because the program was in the nature of a feasibility study, extensive experimental variations were not made. A standard dissolution time of four hours was employed. Temperatures of 750 and 800°C and amounts of zinc chloride 20 and 120 percent in excess of the theoretical amount required to oxidize the uranium were employed.

Eight experiments were made, four of which were control experiments using unclad fuel pins, and four of which were made with clad fuel pins. The progress of each extraction was observed by

*At the time these preliminary experiments were conducted, the composition of the flux for the noble metal extraction step was indefinite. The KCl-LiCl eutectic was selected because its phase diagram was known, because it has a relatively low melting point, and because of the possibility of identifying uranium species in it. Insofar as uranium oxidation by zinc chloride is concerned, it would be expected that a similar result would be realized in the present noble metal extraction flux (47.5 m/o MgCl_2 , 47.5 m/o CaCl_2 , and 5 m/o MgF_2).

periodically sampling the salt phase to determine its uranium concentration. Information was also obtained on the amount of dissolved and undissolved uranium in the metal phase after four hours and on the percentage of zinc chloride in the salt phase as a function of time. Zinc chloride can disappear from the salt phase by two mechanisms: (1) reduction by uranium and (2) volatilization.

First, the amount of uranium in solution in the zinc phase at the conclusion of an experiment was determined from filtered metal samples obtained in tantalum tubes fitted with tantalum frits. Then the total amount of uranium in the zinc phase at the end of a run was determined by dissolving the entire zinc phase in aqua regia and analyzing a sample of the resulting solution for uranium.

The fused salt used in the experiments was the mixture which is currently favored for use in the skull reclamation process. The composition of the mixture (exclusive of zinc chloride) was: 47.5 m/o calcium chloride, 47.5 m/o magnesium chloride, and 5.0 m/o magnesium fluoride. Before use in the extraction studies, the salts were purified to remove moisture and other impurities that might react with uranium. The calcium chloride and magnesium chloride were first blended together and premelted in air to remove some of the water and to separate the bulk of the insolubles. The premelted product was then placed in a quartz vessel, melted, held molten at 800°C and sparged with hydrogen chloride, and filtered through a quartz frit. The zinc chloride was premelted and treated similarly but in a Pyrex vessel at 500°C. Magnesium fluoride was treated separately because it was difficult to dissolve completely in molten calcium chloride-magnesium chloride salt and undissolved magnesium fluoride would have been separated out of the molten salt when the molten salt was filtered. Because of the high melting point of magnesium fluoride (~1225°C), it was not practical to melt the magnesium fluoride; therefore, it was treated by heating to 500°C under hydrogen chloride gas and maintaining these conditions until water was no longer observed in the off gas.

The fuel pins used in the extraction experiments were prepared by inserting 0.144-in. diameter uranium-5 w/o fissium fuel pins about one inch long individually into appropriate lengths of cladding sheath and peening the ends of the sheaths to hold the fuel pins in place. In all experiments, the charge consisted of about 20 g of uranium (net weight with the weight of the cladding and fissium elements excluded), 200 g of salt, and 200 g of zinc. The constituents were placed in a Coors alumina crucible and heated to 750 or 800°C under argon. The system was held at the run temperature for four hours, and the phases were mixed with a flat-blade tungsten paddle operated at 800 rpm. The experimental conditions and results are given in Table I-7.

The control experiments with unclad pins (Experiments A, B, C, and D) indicate that 97 percent or more of the uranium charged was dissolved, oxidized, and extracted into the flux in 4 hr. The fact that a

Table I-7

DISSOLUTION OF CLAD AND UNCLAD EBR-II FUEL PINS IN LIQUID METAL-SALT MEDIA

Fuel Pins: 1- to 1 1/2-in. long segments of 0.144-in. diameter pins of uranium-5 w/o fissium alloy in indicated cladding. Net uranium per experiment = 20 g.

Salt Phase: 200 g total consisting of 47.5 m/o CaCl_2 , 47.5 m/o MgCl_2 , and 5.0 m/o MgF_2 plus ZnCl_2 in proportion to amount of uranium present as indicated below.

Metal Phase: 200 g of zinc.

Conditions: Phases mixed under argon at temperature of experiments for 4 hr with 1/2-in. wide x 1-in. diameter impeller operated at 800 rpm.

Experiment	Cladding	Excess Zinc Chloride in Flux (%)	Temp (°C)	Zinc, as ZnCl_2 in Salt Phase (w/o)			U Conc. (w/o) in Salt Phase after 1/2 hr	Uranium Retained In Metal Phase after 4 hr (percent of U charged)		
				Initial	After 1/2 hr	Final		Total ^a	Undissolved ^b	In Solution ^c
A	none	20	750	4.95	0.5	d	7.2	0.3	0.2	0.1
B	none	20	800	4.95	0.04	(7.21%) ^e	7.4	3.1	2.2	0.8
C	none	120	750	9.2	d	0.3	8.9	1.2	1.0	0.2
D	none	120	800	9.2	2.2	0.3	7.2	0.6	0.6	0.044
E	304 stain- less steel	20	750	4.95	d	d	4.5	10.0	d	d
F	Tungsten- coated	20	750	4.95	d	d	4.0	15.7	0.6	15.1
G	Hastelloy-X Internal tungsten coating on 304 stain- less steel	120	750	9.2	6.0	1.7	0.5	24.4	24.2	0.2
H	Niobium-1 w/o zir- conium	120	750	9.2	4.1	0.9	0.01	34.8	34.7	0.11

^a The total amount of uranium in the metal phase was determined by analyzing an aqueous sample of the solution obtained by dissolving the entire metal phase in aqua regia.

^b The amount of undissolved uranium was determined by difference.

^c The amount of uranium in solution in the metal phase was determined from filtered metal samples. The concentration of uranium in the metal phase in weight percent is approximately equal to 1/10 of the datum given.

^d Data were not obtained.

^e Analysis may not be representative of the salt phases because the sample may have been contaminated with metallic zinc.

small percentage of uranium remained undissolved after 4 hr indicates that, even for unclad pins, a 4-hr dissolution time is not quite long enough. No variation of dissolution rate with increase of temperature from 750 to 800°C is discernible. The low zinc chloride concentrations remaining in the salt phase indicate considerably greater disappearance of zinc chloride than can be accounted for by oxidation of the uranium. Thus, appreciable zinc chloride was volatilized from the melt, and the more rapid vaporization of zinc chloride at 800°C than at 750°C may have largely negated any potential benefits of the higher operating temperature. In Experiment B, for example, essentially all of the zinc chloride had disappeared from the salt phase after 1/2 hour with the result that appreciable unoxidized uranium (0.83 percent of that charged) was present in zinc solution at the end of the experiment.

In the clad pin experiments (Experiments E, F, G, and H), the cladding prevented, at least in the early stages of dissolution, contact of the fuel pin with the zinc solvent except at the ends of a pin, and dissolution rates were slowed. This can be seen by the relatively low percentages of uranium in the salt solution after one-half hour in the clad pin experiments, compared with similar data for the unclad experiments. In Experiment G (pin clad in type 304 stainless steel, internally coated with tungsten), 24% of the uranium was undissolved after four hours, and in Experiment H (pin clad in niobium-1% zirconium), 35 percent of the uranium was undissolved. The low concentration of uranium in metal solution at the end of most of the clad-pin experiments indicates that the uranium was being oxidized as rapidly as it was dissolved. However, in these experiments, in which a 120 percent excess of zinc chloride was initially present, there was insufficient zinc chloride remaining to oxidize the remaining undissolved uranium, indicating that most of the zinc chloride had volatilized. Since no sample of the final metal solution was obtained in Experiment E (stainless steel-clad pin), the data show only that at least 90 percent of the uranium had been dissolved. In Experiment F (tungsten-coated Hastelloy-X), essentially all the uranium had dissolved after four hours, but 15 percent remained in zinc solution, indicating that the zinc chloride oxidant had been completely lost from solution by volatilization and reaction (only a 20 percent excess of zinc chloride was employed in this experiment).

Figure I-10 is a photograph of tungsten coating fragments that remained in the zinc phase after the processing of fuel pins clad with tungsten-coated 304 stainless steel. The tungsten fragments were exposed by leaching away some of the zinc with aqua regia. Stainless steel cladding (Experiment E) and niobium-1% zirconium cladding (Experiment H) were either dissolved or disintegrated and dispersed in the zinc solvent phase.

Because substantial dissolution of the uranium from clad fuel pins (65 to 90 percent) was realized in the experimental time of four hours, it is concluded that dissolution of uranium out of small segments of clad fuel pins is a feasible procedure. However, on the basis of the experiments reported above, the following changes are recommended:

- 1) A time longer than four hours must be allowed for complete dissolution of the uranium, or pin segments must be shorter than the 1- to 1.5-in. segments used in these experiments. Unless the claddings are dissolved or disintegrated by the zinc, the required dissolution time should be proportional to pin lengths.
- 2) To avoid excessive vaporization of the zinc chloride, the zinc chloride should be added slowly or incrementally as needed, rather than all at the beginning of a run as was done in the above experiments. It may also be feasible to reduce the vaporization rate of zinc chloride by lowering the temperature of operation.

Figure I-10

TUNGSTEN FRAGMENTS REMAINING AFTER THE LIQUID METAL-SALT
EXTRACTION OF URANIUM FROM EBR-II FUEL PIN SEGMENTS
IN STAINLESS STEEL CLADDING INTERNALLY COATED
WITH TUNGSTEN

108-6291

(Experiment G, experimental conditions given in Table I-7.)

The photograph shows the tungsten coating fragments imbedded in the zinc ingot. The fragments were exposed by dissolving away a portion of the zinc solvent with aqua regia. A piece of undissolved fuel pin is visible adjacent to the center tungsten fragment.

(5) Mixing Studies in Liquid Metals and Salts
(D. Grosvenor and J. Hansen*)

The degree of mixing of liquid halide salt and magnesium-zinc metal phases is an important variable in the reduction of thorium dioxide or uranium dioxide suspended in the salt phase. The densities of the two phases differ widely (being about 2 g/cc and 6 g/cc), making it difficult to disperse the two phases in each other. As an aid in determining effective methods of agitation, mixing patterns and intensities of agitation were observed in glass vessels with immiscible liquids having an even greater

*Student Aide.

difference in densities than the salt-metal systems. The test system consisted of water and Cerrolow-117,* an alloy melting at 47°C (117°F) and having a density of 8.1 g/cc. The volume ratio of metal to water was 1.67 to 1, and the total water-metal volume was 1350 cc. The container was a flat-bottom glass vessel 4 1/2 in. in diameter and 10 in. high. Four, 1/2-in. wide tantalum baffles were spaced 90° apart on split tantalum bands to form an assembly which fits snugly in the glass container.

The agitators and shafts were made of a 30 w/o tungsten-molybdenum alloy. Because this material is difficult to machine, simple agitator shapes were employed as shown in Figure I-11. The agitators were

Figure I-11

SIMPLE AGITATOR SHAPES USED
IN MIXING STUDIES

(All agitators were 2.0 in. wide
and 5/8 in. high.)

108-7287

2-in. diameter pitched paddles deflecting either upward or downward by blades pitched 30° from horizontal (impellers a and b in Figure I-11) and a flat paddle (impeller c) with a height equal to the projection of the pitched blade impellers.

*The composition of Cerrolow-117 (manufactured by Cerro Corporation, New York) in weight percent is: bismuth-44.7, lead-22.6, indium-19.1, tin-8.3, and cadmium-5.3.

Figure I-12

IMPELLER SHAFT WITH SPACERS AND BLADE

108-7270

Figure I-12 shows an assembly of the impeller shaft and an agitator which was designed so that the position of the agitator could be varied relative to its distance from the bottom of the glass container and relative to its distance from the metal-water interface. The mixing power input was measured with the dynamometer designed and used by Armstrong (ANL-6596, p. 84). The agitator motor was a 1/3-hp, d-c motor equipped with variable voltage speed control. The rotational speed was indicated on a scaler actuated by a photocell which counted the revolutions of a small segment of the shaft, one-half of which was silvered, the other half of which was black. The photocell was energized by light intermittently reflected from the silvered half of the rotating shaft.

One additional bearing was installed under the flange of Armstrong's equipment, below which flange the glass vessel sat, to reduce the whip at the tip of the agitator shaft. This was a graphitar bearing which added slightly to the no-load power, but was carefully aligned with the shaft assembly to develop a minimum of bearing load. The bearing power requirement, which remained reasonably constant once proper shaft and bearing tolerance and alignment were achieved, was a small fraction (less than 10 percent) of the mixing power.

Photographs were taken of mixing patterns and intensity at various speeds (about 550, 950, 1300, and 1700 rpm) with the agitator at five different locations relative to the interface:

- (1) Top edge of blade one-half inch below metal-water interface
- (2) Top edge of blade at interface
- (3) Center of blade at interface
- (4) Bottom edge of blade at interface
- (5) Bottom edge of blade one-half inch above interface

The photographs in Figure I-13 show the effect of impeller speed and resultant mixing power on the intensity of agitation. The impeller was an upward-deflecting impeller (impeller b of Figure I-11) positioned across the interface. A homogeneous mixture was not produced, even at the highest speed (1740 rpm), although the degree of dispersion of the phases was fairly good at the higher speeds.

The effect of impeller location for an upward-deflecting impeller is shown in Figure I-14. The best mixing at intermediate speeds (1325 to 1478 rpm) was realized with the agitator located across the interface or just below the interface. While the rotational speeds were about the same in this series, the power input was relatively low when the agitator was in the water phase because of the low density of this phase. The position of the agitator would become relatively unimportant when sufficient power is introduced to create a homogeneous mixture.

Figure I-13

EFFECT OF IMPELLER SPEED ON INTENSITY OF MIXING

Speed: 530 rpm
Power: 2.2×10^{-3} hp

Speed: 955 rpm
Power: 9.5×10^{-3} hp

Speed: 1380 rpm
Power: 2.5×10^{-2} hp

Speed: 1740 rpm
Power: 4.5×10^{-2} hp

108-6918

Upward deflection provided by impeller b (Figure I-11)
which was positioned with midpoint at interface

Figure I-14

EFFECT OF IMPELLER DEPTH ON INTENSITY OF MIXING

Bottom of impeller 1/2 inch above interface.
 Speed: 1478 rpm. Power: 4.8×10^{-3} hp.

Midpoint of impeller at interface.
 Speed: 1348 rpm. Power: 2.4×10^{-2} hp.

Top of impeller at interface.
 Speed: 1325 rpm. Power: 2.4×10^{-2} hp.

Top of impeller 1/2 inch below interface
 Speed: 1390 rpm. Power: 2.8×10^{-2} hp.

Upward deflection provided by impeller b of Figure I-11.
 Mixing speeds were approximately the same at each impeller
 depth, ranging between 1325 and 1478 rpm.

Figure I-15

EFFECT OF DIRECTION OF FLOW (UP OR DOWN) ON MIXING INTENSITY

Impeller b - upward deflection - with bottom of impeller at interface. Speed: 915 rpm. Power: 6.9×10^{-3} hp.

Impeller a - downward deflection - with bottom of impeller at interface. Speed: 1040 rpm. Power: 2.6×10^{-3} hp.

Impeller b - upward deflection - with midpoint of impeller at interface. Speed: 1348 rpm. Power: 2.4×10^{-2} hp.

Impeller a - downward deflection - with midpoint of impeller at interface. Speed: 1371 rpm. Power: 2.7×10^{-2} hp.

The effect on intensity of agitation of upward or downward deflection of the stirred phases is shown in Figure I-15. Superior mixing occurred with upward-deflecting paddles. Again, power requirements were strongly dependent on whether the light or heavy phase was being pumped.

Photographs are not presented for the flat-blade paddle. However, for a given speed, the power input was about two times higher than that realized with the pitched-blade agitators. The same effects as those shown in Figures I-13 and I-14 were realized at somewhat lower rotational speeds.

Wedge-shaped agitators (a combination of two 30° pitched units--impellers (a) and (b) in Figure I-11) were tested with the apex at the interface, both with the apex as the leading edge and as the trailing edge. Runs were made with the blades together, separated 1/8 in., and separated 1/2 in. Mixing was comparable to that realized with the flat-blade impeller; at a given speed, about twice the power input was required for the flat-blade impellers as was required with the pitched-blade impellers. The best mixing with the double impellers occurred with no spacing between blades and with the apex as the leading edge. However, the wedge-shaped agitator has no advantage over the simpler vertical flat-blade or pitched-blade paddles.

These qualitative observations indicate that the best mixing of the immiscible phases with flat or pitched-blade paddles occurred when the agitator was located across or just below the interface. When a pitched-blade paddle was employed, the best results were realized with upward-deflecting blades.

A series of experiments is now in progress to define the mixing conditions required for complete reduction of uranium dioxide by a magnesium-zinc alloy while the dioxide is suspended in a halide salt. Complete reduction of uranium dioxide in such a system is essential in the skull reclamation process.

b. Processes for Plutonium Reactor Fuels
(R. K. Steunenbergh, L. Burris, Jr.)

Fuels containing both uranium and plutonium are being developed for use in fast breeder reactor cores and blankets. Alloys, oxides, carbides, sulfides, and other forms of uranium and plutonium are receiving consideration as potential reactor fuels. It appears that pyrometallurgical fuel processing concepts might be applied to any of these materials with relatively minor variations in the process flowsheet.

Studies have been initiated on various head-end steps through which carbide fuels could be accommodated by processes utilizing liquid metal solvents.

A critical separation in the processing of fast breeder fuels by pyrometallurgical methods is the extraction of rare earth fission products from plutonium, as well as uranium. Two possible methods for achieving this separation have been investigated. One method takes advantage of the high solubilities of rare earths and the low solubilities of uranium and plutonium in molten calcium-zinc alloys. The other method involves the selective extraction of rare earths from uranium and plutonium in zinc-magnesium solutions. The possibility of adding a high percentage of cadmium to the zinc-magnesium solution is being investigated, since this modification of the process may permit the use of stainless steel instead of refractory metals such as tantalum or tungsten for process vessels.

(1) Head-end Treatments for Uranium-Plutonium Carbide Fuels

(J. B. Knighton, D. A. Wenz, E. D. Johanson*)

In an effort to develop head-end procedures for reprocessing uranium-plutonium carbide fuels by pyrochemical methods, a preliminary investigation of reactions between UC and various reagents in molten salt solvents has been conducted. The objective of this effort is to convert the carbides into a form that is amenable to processing in liquid metal and molten salt media. To accomplish this end, it appears that two basic requirements must be fulfilled: (1) the uranium and plutonium must be converted to a soluble form either in a salt flux or in a molten metal phase, and (2) the presence of free carbon must be avoided. Two general approaches to the problem have been explored in scouting studies. The first involves oxidation of the UC in a molten salt to form a uranium oxide or a uranate that can be reduced by zinc-magnesium alloy, producing a solution of metallic uranium in the liquid alloy. The other approach consists of chlorination of the UC in a molten chloride salt to form soluble uranium chlorides.

Exploratory Investigations. Scouting studies were first carried out on reactions of UC with a variety of molten salts. The procedure consisted simply of adding a pellet of UC to an open crucible containing the molten salt at the indicated temperature and observing the reaction for a period of one to two hours. The qualitative results of this study are presented in Table I-8. The reaction products were identified by X-ray diffraction. Several salts such as ZnCl_2 and CdCl_2 reacted only slowly with the carbide and were given no further consideration. The reaction with Na_2CO_3 was complete after less than 10 minutes, and was too rapid for process use. Dilution of the Na_2CO_3 with an equimolar NaCl-KCl mixture decreased the reaction rate, but also led to incomplete reaction. Undiluted KClO_4 and KClO_3 each resulted in a very rapid and complete reaction of the UC, but the reaction was accompanied by ignitions

*Co-op Student, Northwestern University.

Table I-8

REACTIONS OF URANIUM MONOCARBIDE WITH VARIOUS MOLTEN
SALTS IN AIR ATMOSPHERE

Salt	Temp. (°C)	Visible Reaction		Gas Evolution	X-Ray Identification of Product
		Rate	Extent		
ZnCl ₂	350	slow	incomplete	no	--
CdCl ₂	575	slow	incomplete	no	UO ₂
NaCl-KCl	775	no reaction		no	--
Na ₂ CO ₃	900	very rapid	complete	yes	Na ₂ U ₂ O ₇ , UO ₃ , NaOH·H ₂ O, "Na ₂ UO ₆ "
Na ₂ CO ₃ -NaCl-KCl	725	slow	incomplete	no	UC, UO ₂
KClO ₃	425	very rapid	complete	yes	K ₂ U ₂ O ₇
KClO ₄	500	very rapid	complete	yes	K ₂ U ₂ O ₇
MgCl ₂	800	moderate	complete	yes	MgO, MgUO ₄
MgCl ₂ -CaCl ₂ -MgF ₂	950	slow	incomplete	yes	MgUO ₄
NaOH	500	rapid	complete	yes	Na ₂ U ₂ O ₇ ^a
NaOH-NaCl-KCl	925	rapid	complete	yes	^a Al ₂ O ₃ , UO ₂ , ^b other
NaNO ₃	400	very rapid	complete	yes	Na ₂ U ₂ O ₇

^a Possible phase.

^b Unidentified phase.

and splattering of the melt. Both KClO₄ and KClO₃ are known to decompose at the temperatures of process interest (~800°C). The UC reacted completely with MgCl₂ to form MgUO₄ and MgO, the oxygen being supplied by the air atmosphere. When the MgCl₂ was diluted with CaCl₂ and MgF₂, however, this reaction was slow and incomplete. Both NaOH and NaNO₃ reacted readily with UC, producing Na₂U₂O₇ as a solid product, and eliminating carbon through the formation of CO₂.

Since these results led to the conclusion that NaOH and NaNO₃ are promising oxidizing agents for UC in molten salt media, further studies were made of each of these reagents in equimolar NaCl-KCl solutions.

Reaction of Uranium Monocarbide with Sodium Hydroxide. The reaction of UC with NaOH in molten salt solution appeared to produce solid Na₂U₂O₇ and a gaseous mixture of CO₂ and hydrogen. Several experiments were performed in which UC pellets were added to molten NaCl-KCl containing various concentrations of NaOH at temperatures of 725 to 810°C, and the reaction was observed for a period of one hour. The experimental observations are listed in Table I-9. The reaction was characterized by occasional ignition of the off-gases in the air atmosphere,

Table I-9

REACTION OF UC WITH NaOH IN NaCl-KCl UNDER AIR ATMOSPHERE

Time: 1 hr								
Wt. Ratio of NaOH to UC	NaOH (g)	UC (g)	NaCl-KCl (g)	Temp. (°C)	Visible Reaction		Gas Evolution	Color of Product ^a
					Rate	Extent		
0.32	0.6	1.9	50	810	moderate	incomplete	yes	black, trace of yellow
0.33	0.5	1.5	50	725	moderate	incomplete	yes	black, trace of yellow
0.60	1.2	2.0	50	800	rapid	incomplete	yes	black, trace of yellow
1.56	2.8	1.8	50	800	rapid	incomplete	yes	green-yellow
1.58	3.0	1.9	25	725	very rapid	complete	yes	yellow
3.14	6.9	2.2	50	810	very rapid ^b	complete	yes	yellow
3.12	5.3	1.7	50	725	very rapid ^b	complete	yes	yellow

^aThe black UC is easily distinguishable from the characteristic orange or yellow color of uranates and the higher uranium oxides.

^bThe reaction rate in these experiments became so rapid that some material overflowed from the crucible.

suggesting the presence of hydrogen. For NaOH to UC equivalent ratios of 10 to 1, the reaction was complete in less than one hour. The NaOH concentration in the salt proved to have a considerable effect on the extent of reaction. Whereas 3.0 g of NaOH and 1.9 g of UC in 25 g of NaCl-KCl resulted in complete reaction of the UC, 2.8 g of NaOH and 1.8 g of UC in 50 g of NaCl-KCl resulted in a reaction that was estimated to be only about 50% complete. Where the reaction had proceeded to completion, all of the carbon appeared to have been removed in the off-gases. As the NaOH concentration in the salt was increased, the solid product of the reaction changed from a brownish-black color to the clear yellow color that is characteristic of the uranates.

Reaction of Uranium Monocarbide with Sodium Nitrate.

Sodium nitrate is believed to offer the greatest promise of the reagents investigated for the oxidation of UC in molten salt media. Apparently absent are the disadvantages of concentration effects, the need for high NaNO_3 :UC ratios, and complexity of products. Experiments were conducted in which UC pellets were treated with varying amounts of NaNO_3 in molten NaCl-KCl at temperatures of 775 and 800°C. The results are summarized in Table I-10. At NaNO_3 -UC weight ratios of about one or above, the reaction proceeded mildly to completion, producing $\text{Na}_2\text{U}_2\text{O}_7$ as a product.

The $\text{Na}_2\text{U}_2\text{O}_7$ product is readily converted to MgUO_4 through the addition of MgCl_2 to $\text{Na}_2\text{U}_2\text{O}_7$ in the NaCl-KCl system. Magnesium uranate is easily reduced by magnesium-zinc alloy to produce a solution of uranium in the metal phase. A disadvantage of this procedure as a head-end treatment for carbide fuels is that solid MgO is produced as a by-product of

Table I-10

REACTION OF URANIUM MONOCARBIDE WITH SODIUM NITRATE^a IN SODIUM CHLORIDE-POTASSIUM CHLORIDE UNDER AIR ATMOSPHERE

Time: 1 hr								
Wt. Ratio of NaNO ₃ to UC	NaNO ₃ (g)	UC (g)	NaCl-KCl (g)	Temp. (°C)	Visible Reaction		Gas Evolution	Color of Product
					Rate	Extent		
0.33	0.5	1.5	50	775	rapid	incomplete	yes	orange
0.37	0.6	1.6	25	800	rapid	incomplete	yes	orange
0.67	1.2	1.8	50	800	rapid	nearly complete	yes	orange
1.06	1.7	1.6	50	800	rapid	complete	yes	orange
1.70	2.9	1.7	50	775	rapid	complete	yes	orange
3.43	7.2	2.1	50	775	rapid	complete	yes	orange

^aSodium nitrate is probably present primarily as Na₂O at these temperatures.

the reduction of MgUO₄. Although the MgO could be eliminated from subsequent process steps by discarding the molten salt at this stage of the process, this procedure has the drawback that it would add to the volume of radioactive salt wastes. Work is therefore being done on chlorination procedures in an attempt to convert UC to soluble uranium chlorides in oxygen-free flux systems.

Chlorination of Uranium Monocarbide in Molten Salt

Media. The objective of the chlorination procedure is to convert UC to a soluble uranium species in molten salt solution and simultaneously to remove carbon from the system. Several scouting experiments were performed in which either HCl or chlorine was sparged through molten salts containing UC pellets. Hydrogen chloride was used with the NaCl-KCl-MgCl₂ eutectic* at 500 to 600°C, and with equimolal NaCl-KCl at 750°C. Chlorine was used with the LiCl-KCl eutectic** at 450°C and with equimolal NaCl-KCl at 750°C. In all cases the UC reacted completely to form a soluble uranium species having the characteristic color of uranium (IV). However, free carbon also was present in the salt. Although it may be possible to separate carbon from the salt by filtration, it would probably be more desirable to remove it as a gaseous product if possible.

Attempts were made to remove the carbon from the system by the reaction with CO₂ to form CO. Varying proportions of gaseous HCL and CO₂ were sparged through NaCl-KCl melts containing UC pellets at 750 to 850°C. However, little carbon removal was evident in experiments up to 3 or 4 hours in duration. Although removal of carbon by this technique is

*Eutectic composition, 30 m/o NaCl-20 m/o KCl-50 m/o MgCl₂;
m.p. 396°C.

**Eutectic composition, 59 m/o LiCl-41 m/o KCl; m.p. 352°C.

thermodynamically possible, the reaction appears to be slow in the molten salt environment. Experimental work is being continued on this general approach.

(2) Molten Salt Extraction Process

(J.B. Knighton, R. von Ammon*, J.D. Schilb,
J. W. Walsh)

Cadmium-zinc-magnesium alloys are being investigated as process media for plutonium-bearing reactor fuels. Addition of a high percentage of cadmium to the zinc-magnesium alloys that were previously being considered for this purpose (ANL-6725, p. 53) is an attractive possibility, since this would permit operation at lower temperatures and low zinc concentrations and thus series 400 stainless steels could be used as container materials instead of tantalum or tungsten. The principal criteria governing the selection of a solvent are (1) adequate solubility of the fuel constituents, (2) acceptable corrosion rates of the process equipment, and (3) distribution coefficients that will permit the extraction of fission products from plutonium and uranium when the liquid metal solvent is equilibrated with a molten salt.

Addition of zinc to cadmium has been shown to increase the solubility of uranium. Addition of small amounts of magnesium to either zinc or cadmium causes the uranium solubility to increase, but at high magnesium concentrations it decreases again. From the standpoint of uranium solubility, the composition region of interest in this ternary alloy would be one of low magnesium and moderate zinc concentrations.

Whereas alloys of high zinc concentration are very corrosive to stainless steels, cadmium and magnesium can be contained without difficulty. An alloy that is low in zinc with cadmium and magnesium in any proportions would therefore be the most satisfactory from a corrosion viewpoint.

Finally, favorable distribution coefficients** between the alloy and a molten salt are essential for an efficient separation of fission products from uranium and plutonium. In particular, the extraction factor*** for rare earths should be greater than unity, and it should be less than unity for uranium and plutonium. The distribution coefficients of the pertinent elements have been found to depend upon the compositions of the salt and

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**The distribution coefficient, K_d , in these studies has been defined as $K_d = (w/o \text{ of element in flux}) / (w/o \text{ of element in metal})$.

***The extraction factor, E.F., for an element is defined as $E.F. = K_d (w_s / w_m)$ where K_d is the distribution coefficient and w_s and w_m are the respective weights of the salt and metal phases.

metal phases and the temperature. The separation factors* between the rare earth elements and plutonium, however, remained essentially constant as the composition of the molten chloride salts was varied. Thus by changing the composition of the salt phase, it is possible to vary the absolute values of the pertinent distribution coefficients without significantly affecting their ratios. These changes in the composition consist of variations in the proportions of different alkali and alkaline earth cations in the chloride salt. In this connection, it should be noted that the operating temperature is restricted by the melting point of the salt.

The zinc to cadmium ratio in the metal phase also affects the distribution coefficients, which are about an order of magnitude larger for a cadmium-magnesium system than for a comparable zinc-magnesium system. Very low magnesium concentrations in the metal phase are undesirable, since minor variations in the magnesium concentration cause large changes in the distribution coefficients. In order to operate in a stable region, it is necessary that adequate magnesium concentrations be used.

It appears that composition regions exist in the cadmium-zinc-magnesium system where the uranium solubility is adequate, the corrosion rates of stainless steel are low, and the distribution coefficients are favorable. The objective of the present study is to define these regions, particularly with respect to uranium solubility and distribution behavior.

Solubility of Uranium in Cadmium-Zinc-Magnesium

Alloys. The solubility of uranium in the cadmium-rich portion of the cadmium-zinc-magnesium system is being determined at temperatures of 350 to 700°C. For the solubility determinations, the alloy was contained in a Morganite (recrystallized alumina) crucible inside a tantalum secondary crucible. This assembly was placed in a stainless steel furnace tube that was heated by a resistance furnace. Auxiliary equipment provided for a high-purity argon atmosphere, temperature measurement to $\pm 1^\circ\text{C}$, stirring with a tantalum agitator, and withdrawal of liquid metal samples through tantalum frits into tantalum tubes. A layer of flux (LiCl-KCl eutectic, m.p. 348°C) on top of the molten metal served two purposes: (1) to minimize the vaporization of cadmium in extended runs, and (2) to maintain the metal in a more nearly isothermal condition by reducing the heat loss from the surface. In the absence of the flux, a temperature drop of about 2 to 3°C was observed near the surface of the metal. At least 6 hours was allowed for equilibration at temperature before each sample was taken. In each run, one-half of the samples were taken when equilibrium had been approached from a higher temperature, and one-half when it had been approached from a lower temperature. Since the results are consistent, it is believed that the data represent equilibrium conditions. The precision of the analyses (standard deviation) was as follows: uranium, $\pm 1.8\%$; magnesium, $\pm 0.67\%$; zinc, $\pm 2.26\%$.

*The separation factor, S.F., for elements A and B is defined as the ratio of the distribution coefficients, $\text{S.F.} = K_d(\text{A})/K_d(\text{B})$.

Ten runs have been completed to date using solvents of the following nominal compositions.

<u>Run Number</u>	<u>Mg (a/o)</u>	<u>Zn (a/o)</u>	<u>Cd (a/o)</u>
II	10	6	84
I	10	10	80
III	10	13	77
V	10	20	70
IX	10	30	60
IV	13	13	74
VIII	13	20	67
VII	20	13	67
VI	20	20	60
X	20	30	50

Complete analytical data are available for the first seven of these runs at the present time. The results are presented in Figures I-16 through I-19, where

Figure I-16

SOLUBILITY OF URANIUM
IN Cd-Zn-Mg ALLOY:
CHANGES IN ZINC AND
MAGNESIUM CONCENTRATIONS
WITH TEMPERATURE

Nominal Composition of Solvent

<u>Run</u>	<u>Cd (a/o)</u>	<u>Zn (a/o)</u>	<u>Mg (a/o)</u>
IV	74	13	13

Figure I-17

SOLUBILITY OF URANIUM
IN Cd-Zn-Mg ALLOY:
EFFECT OF ZINC
CONCENTRATION

Figure I-18

SOLUBILITY OF URANIUM
IN Cd-Zn-Mg ALLOY:
EFFECT OF MAGNESIUM
CONCENTRATION
AT 13 a/o ZINC

Figure I-19

SOLUBILITY OF URANIUM
IN Cd-Zn-Mg ALLOY:
EFFECT OF MAGNESIUM
CONCENTRATION
AT 20 a/o ZINC

the logarithm of uranium solubility in a/o is plotted against $1/T(^{\circ}\text{K})$. In Figure I-16, typical changes in zinc and magnesium concentrations with temperature are shown. In Figures I-20 and I-21, the uranium solubility at a fixed temperature (600°C) is shown, first at constant magnesium and varying zinc concentrations and then at constant zinc and varying magnesium concentrations.

Because of the complexity of this ternary system, these data alone are insufficient to provide a complete interpretation of these solubility curves. However, a few definite trends have become apparent. (1) In the high-temperature region, uranium exhibits retrograde solubility, a feature that is well known in the binary system uranium-cadmium⁸ and in the ternary systems uranium-cadmium-magnesium and uranium-cadmium-zinc. Only in Runs V and VI, where the solvent had a high zinc content (20 a/o Zn, 10 a/o Mg; 20 a/o Zn, 20 a/o Mg, respectively), was this feature

⁸ Martin, A. E., Johnson, I. and Feder, H. M., Trans. Met. Soc. AIME., 221, 789 (1961).

absent in the temperature region that was investigated. (2) The uranium solubility increased with increasing zinc concentrations in the solvent (Figures I-17 and I-20). (3) The uranium solubility decreased with increasing magnesium concentrations in the alloy (Figures I-18, I-19 and I-21). (4) The uranium solubility curves as a function of temperature showed definite breaks, indicating the precipitation of uranium, intermetallic compounds of uranium, or both. Since the zinc concentration curves always showed breaks at the same temperatures as the high-temperature breaks in the uranium solubility curves, it appears that precipitation of the delta uranium-zinc phase ($\sim U_2Zn_{17}$) begins at this point. This conclusion is supported by the fact that the temperature range between the two breaks in the uranium solubility curve increased with increasing zinc concentration in the solvent. In Runs IV, V, and VI (13 a/o Zn, 13 a/o Mg; 20 a/o Zn, 10 a/o Mg; 20 a/o Zn, 20 a/o Mg, respectively), the zinc concentration curve showed a second break

Figure I-20

EFFECT OF ZINC CONCENTRATION
ON SOLUBILITY OF URANIUM
IN Cd-Zn-Mg ALLOY

Mg concentration held constant
at 10 a/o
Temperature: 600°C

108-7296

Figure I-21

EFFECT OF MAGNESIUM
CONCENTRATION ON SOLUBILITY
OF URANIUM IN Cd-Zn-Mg ALLOY

Zn concentration held constant
at 13 a/o
Temperature: 600°C

108-7277

corresponding to the low-temperature break in the uranium solubility curve. At temperatures below this break, the zinc curve had a decreased slope. This observation suggests that either a uranium-cadmium phase (probably UCd_{11}) was precipitated in this region along with small amounts of the delta

uranium-zinc phase, or the decrease in zinc concentration resulted from substitutional solution of zinc in the UCd_{11} phase. Substitutional solution of cadmium in the delta phase and of zinc in the UCd_{11} phase was inferred from X-ray diffraction data on some of the crystals that had been isolated from the matrix by selective dissolution, using CrO_3 as an etchant. The lattice parameters of the two intermetallic compounds appeared to change, although definitive information was not obtained. (5) The composition curve for magnesium showed no significant breaks. Only at the lowest temperatures did a sharp decrease in magnesium concentration take place. This decrease was attributed to the precipitation of MgZn_2 , which was expected on the basis of the ternary phase diagram for cadmium-zinc-magnesium.⁹ Substitutional solution of magnesium in either the delta uranium-zinc phase or in UCd_{11} is unlikely and did not occur to a detectable extent. This result was verified by chemical analyses of the intermetallic phases.

Calculations of activity coefficients and solubilities of all four components in this system from available thermodynamic data have been undertaken by Prof. G.M. Brown.* To complete these calculations, it is necessary to determine the compositions of the intermetallic phases in equilibrium with the solution. A series of quenching experiments has been started in order to obtain this information. This technique consists of equilibrating a solution with the solid at a fixed temperature and with stirring for a period of at least 15 hours. Stirring is then discontinued for one hour to permit solid material to settle and form a bed of crystals at the equilibrium temperature; the system is then quenched with cold water. It was possible, upon metallographic examination of the ingot, to distinguish the crystals that had settled at the equilibrium temperature from those that were formed during quenching.

Although samples of the ingots have been submitted for electron probe microanalysis, the results are not yet available. Metallographic results, however, were consistent with the conclusions that were drawn from the solubility measurements. In the region of retrograde solubility, metallic uranium was the only solid phase detected. In the intermediate region between the two breaks in the uranium solubility curve, both the delta uranium-zinc phase and apparently unreacted uranium were observed. The samples that had been equilibrated at the higher temperatures within this region contained needle-like crystals typical of the delta phase, while those equilibrated at the lower temperatures contained crystals that were more nearly rectangular in shape. This observation may represent further evidence for the substitutional solution of cadmium in the delta uranium-zinc phase. In the low-temperature region below the second break in the uranium solubility curve, uranium, the delta uranium-zinc phase, and UCd_{11} were found in metallographic specimens. It is suspected that the

⁹Smithells, C. J., Ed., Metals Reference Book, Vol. I, p. 523, Butterworth Inc., Washington (1962).

*Resident Research Associate, Northwestern University.

uranium and the delta phase in this case represented unconverted solid particles that were coated with a layer of UCd_{11} and were not actually in equilibrium with the solution.

The results of these studies thus far indicate that the uranium solubilities in the composition regions of interest are high enough to use this ternary alloy as a solvent in a fuel reprocessing flowsheet. Work is continuing on the identification of the solid uranium-bearing phases in equilibrium with the solutions.

Distribution of Elements between Cadmium-Zinc-Magnesium Alloy and Molten Salts. Concurrent with the measurements of uranium solubility reported above, the codistribution behavior of uranium and praseodymium between cadmium-zinc-magnesium solutions and a flux of the composition 30 m/o NaCl -20 m/o KCl -50 m/o MgCl_2 is being investigated. Results of these experiments are not yet available. Further distribution measurements will be made with various fluxes when the composition of the metal phase has been defined.

(3) Calcium-Zinc Extraction Process (M. Ader, J. T. Feeney)

Uranium and plutonium solubilities in calcium-zinc solutions have been determined in connection with processes for the recovery of fast breeder reactor fuels. The work with uranium extends the range of solubility data reported earlier (ANL-6687, p. 44). The plutonium solubility data reported here were obtained both for their own value and for comparison with previous plutonium solubilities that were measured in calcium-rich zinc solutions containing uranium. The results indicate that uranium-plutonium fuels could be reprocessed by this method, in which rare earth fission products are separated by selective precipitation of uranium and plutonium from the calcium-rich solution. However, process application of this separation appears to be somewhat unfavorable because of plutonium losses arising from a small, but significant, solubility of plutonium in the liquid metal solution. The experimental work on the calcium-zinc extraction process has therefore been discontinued in favor of the molten salt extraction process.

Solubility of Uranium in Calcium-Zinc Solutions.

Uranium solubilities in calcium-zinc solutions containing 0 to 25 w/o calcium at 700, 750 and 800°C were reported previously (ANL-6687, Table I-3, p.46). Further work (Experiment MA-Ca-16) has extended the solubility measurements to calcium concentrations of up to 50 w/o. Most of the data were obtained at 700, 750 and 800°C, with a few additional measurements at 650 and 850°C. The experimental and analytical procedures were essentially the same as those described in ANL-6687, p. 44.

An attempt was made to determine the solubility of uranium in solutions containing 50 to 100 w/o calcium (Experiment MA-Ca-15). Because of the very low solubilities involved (from 10^{-4} to less than

Table I-11

SOLUBILITY OF URANIUM IN CALCIUM-ZINC SOLUTIONSExperiments: Ma-Ca-14^a, Ma-Ca-16Procedure: Uranium (excess) dissolved in liquid zinc;
calcium added incrementallyConditions: Equipment, tantalum; atmosphere, argon;
1.5-hr minimum equilibration periodSampling: Melt pressurized through tantalum filters into tantalum
tubes

Temp. (°C ± 1)	Calcium (w/o)	Uranium (w/o)	Temp. (°C ± 1)	Calcium (w/o)	Uranium (w/o)
850	27.4	0.032	751	23.7	0.046
850	40.8	0.021	750	27.5	0.015
			751	34.4	0.0026
799	3.42	2.51	750	40.9	0.0005 ₆
799	4.95	1.95	748 ^b	48.5	0.0001 ₅
800	6.10	1.93			
800	7.27	2.09	700	0	1.14
801	8.43	2.38	697	0.58	0.97
800	9.7	3.33	700	1.10	0.87
800	10.6	4.29	700	2.05	0.67
801	11.7	4.24	700	9.8	0.192
800	12.9	2.67	699	11.1	0.38
800	14.8	1.28	700	12.1	0.61
800	16.3	0.75	700	12.7	0.76
800	20.6	0.17	701	13.2	0.88
800	23.1	0.091	700	13.7	1.04
800	27.5	0.021	699	14.2	1.04
799	28.5	0.021	700	14.8	1.00
801	34.0	0.0052	701	15.4	0.90
801	40.8	0.0011	700	15.8	0.72
			700	16.5	0.45
750	0	2.89	701	17.4	0.38
749	2.04	1.63	700	20.4	0.094
750	3.61	1.03	701	23.2	0.040
753	5.26	0.79	700	27.6	0.0082
751	6.31	0.67	701	34.1	0.0014
752	7.64	0.71	700	40.8	0.0001 ₈
751	9.0	0.97	701 ^b	51.1	0.00002
750	10.7	1.45			
751	11.6	2.03	644	0	0.48
750	12.3	3.04	649	0.62	0.39
750	12.7	2.50	649	0.90	0.30
752	14.9	1.12	650	15.9	(0.30)
750	16.4	0.55	650	17.4	0.28
750	20.3	0.14			

^aPreviously reported in ANL-6687, p. 44.^bExperiment Ma-Ca-15 (see text).

Figure I-22
SOLUBILITY OF URANIUM
IN CALCIUM-ZINC SOLUTIONS

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10^{-6} w/o), U^{233} was used as the solute and the samples were analyzed for uranium by alpha counting. Although most of the results were rejected because of excessive scatter of the data, it was established that the uranium solubility is extremely small ($<10^{-4}$ w/o) at these calcium concentrations.

A complete tabulation of the uranium solubility data for calcium-zinc solutions containing up to 50 w/o calcium is given in Table I-11. This tabulation includes results that were reported previously. In Figure I-22, uranium solubilities at 700, 750, and 800°C are shown as a function of the calcium concentration. These curves represent isotherms on the liquidus surface of the uranium-calcium-zinc phase diagram. The similarity between the shapes of these curves and those representing the solubility of uranium in magnesium-zinc solution (ANL-6477, p. 93) has been mentioned previously. By analogy with the more thoroughly studied uranium-magnesium-zinc system, the equilibrium solid phase in the region to the left of the solubility peaks in Figure I-22 is believed to be a uranium-zinc intermetallic phase (probably the same as the delta phase, $\sim U_2Zn_{17}$, in the U-Mg-Zn system), and in the region to the right of the peak the equilibrium solid phase is probably uranium. The uranium solubility at 700°C in the composition

region of 2 to 10 w/o calcium was not determined, since the isotherm should intersect the boundary of the crystallization field of calcium-zinc intermetallic compounds (not shown).

Solubility of Plutonium in Calcium-Zinc Solutions. The procedures and apparatus used in determining the solubility of plutonium in calcium-zinc solutions were generally similar to those used for the uranium solubility measurements. Plutonium and calcium metals with weight ratios of either 1:3 or 1:7 were heated and stirred in a tungsten crucible (tantalum paddle and accessories) at 850°C under an argon atmosphere for three or more hours. The melt was allowed to settle for 15 to 30 minutes and then sampled by pressurizing the liquid metal through a tantalum frit into a preheated tantalum tube. Stepwise additions of zinc were made, and the procedure of stirring, settling, and sampling was repeated at various temperatures. In most cases, equilibrium was approached from a falling temperature. Duplicate samples were taken simultaneously. The samples were dissolved in HCl solution and analyzed for plutonium by alpha counting, and for zinc by an EDTA titration method. Samples containing more than 67 w/o zinc were analyzed for calcium by EDTA titration, and the zinc content was obtained by difference.

The plutonium solubilities were determined in two separate experiments (MA-Ca-17 and MA-Ca-18) at temperatures of 400 to 850°C and at zinc concentrations varying from 0 to 90 w/o. The most reliable solubility data from both experiments are listed in Table I-12. The plutonium solubility is shown as a function of calcium concentration at various temperatures in Figure I-23. The solubility curves represent isotherms on the liquidus surface of the ternary phase diagram. An effort was made to restrict the solubility measurements to composition regions where precipitation of calcium and calcium-zinc intermetallic compounds would not occur. The calcium-zinc binary phase diagram¹⁰ was therefore used as a guide for selecting the experimental calcium/zinc ratios and temperatures. Although the existence of ternary plutonium-calcium-zinc intermetallic compounds is possible, it is likely that the solid phases in equilibrium with the solutions were only plutonium metal or plutonium-zinc intermetallic compounds, since plutonium-calcium intermetallic compounds apparently do not exist. However, since the equilibrium solid phases were not identified, it is possible that some of the reported plutonium solubilities do not represent single solute solubilities, but represent instead plutonium concentrations in equilibrium with a mixture of two phases. This type of behavior is frequently found in ternary systems where the melt follows a eutectic or peritectic line as the temperature is changed. In the present experiments there were instances when, after the experimental conditions were changed, the relative changes in zinc and plutonium concentrations suggested the possibility that calcium-zinc, as well as plutonium-zinc compounds, were precipitated.

¹⁰Messing, A. F., Adams, M. D., and Steunenberg, R. K., Trans. Quarterly, A.S.M. 56(3), 345 (1963).

Table I-12

SOLUBILITY OF PLUTONIUM IN CALCIUM-ZINC SOLUTIONS

Experiments: MA-Ca-17, MA-Ca-18

Procedure: Plutonium (excess) dissolved in liquid calcium;
zinc added incrementallyConditions: Tungsten crucible, tantalum accessories; argon
atmosphere; 3-hr minimum equilibration periodSampling: Melt pressurized through tantalum filters into
tantalum tubes

Temp. (°C ± 1.5)	Zinc (w/o)	Plutonium (w/o)	Temp. (°C ± 1.5)	Zinc (w/o)	Plutonium (w/o)
848	0	0.079	653	56	2.52
850	23.6	0.303	651	58	2.81
849	40	1.09	648	60	2.65
851	51	3.16	651	64.5	2.04
851	55	4.9	650	65	1.80
850	57	7.0			
852	66	4.7	598	50	1.11
851	67 ^a	5.3	598	55	1.52
852	71 ^a	4.8	599	59	1.39
			600	63	0.60
750	21.4	0.164			
750	40	0.73			
747	51	2.12	548	40	0.22
749	55	4.01	548	50	0.82
750	59	6.5	549	55	0.84
753	66	4.9	552	58	0.66
751	68 ^a	5.2	552	58.5	0.45
750	71 ^a	4.8	551	59	0.22
751	75 ^a	4.25			
751	78 ^a	3.61	492	39	0.123
749	81 ^a	3.23	493	50	0.44
751	84 ^a	2.70	494	54.5	0.31
751	86 ^a	2.30			
750	90 ^a	1.59	465	50	0.293
651	23.8	0.090	450	40	0.095
650	40	0.44	449	50	0.232
649	51	1.47	450	53	0.064
			438	50	0.188
			401	40	0.053

^aCalcium in sample determined by analysis; zinc value calculated by difference.

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Figure I-23

SOLUBILITY OF PLUTONIUM
IN CALCIUM-ZINC SOLUTIONS

The general shapes of the plutonium solubility curves in the calcium-rich region (from about 40 to 100 w/o calcium) in Figure I-23 resemble those of the uranium solubility curves in Figure I-22. However, the solubility of plutonium is about 10^3 to 10^4 times greater than that of uranium at similar temperatures and calcium concentrations. For example, the respective solubilities of plutonium and uranium in zinc-50 w/o calcium at 750°C are 1.6 w/o and 0.0001 w/o. The fact that the maxima in the plutonium solubility curves occur at higher calcium concentrations than those for uranium reflects the more negative free energy of formation of plutonium-zinc intermetallic compounds than of uranium-zinc intermetallic compounds.

Further information can be derived from the data in Table I-12 by plotting the weight percent plutonium solubility as a function of reciprocal absolute temperature at various zinc concentrations, as shown in Figure I-24. The 24 and 40 w/o zinc curves and the upper portion of the 51 w/o zinc curve show a straight-line, near-parallel relationship, implying that the same solid phase is in equilibrium with these solutions. The break in the curve for 51 w/o zinc at about 535°C implies a change in the solid phase that is in equilibrium with the solution (possibly, a change from plutonium metal to PuZn_2 as the temperature is decreased).

The curves representing the logarithm of the plutonium solubility as a function of reciprocal absolute temperature become complex at high zinc concentrations. Additional data would be required before a

Figure I-24
SOLUBILITY OF PLUTONIUM
IN Ca-Zn SOLUTIONS

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meaningful interpretation could be made of the results in this region. Although the results for the 55 w/o zinc solution are shown in Figure I-24 as a smooth curve, a discontinuous curve would probably be more valid. The complex nature of the zinc-rich region of the plutonium-zinc-calcium system is apparent in Figure I-23. This complexity probably arises from the formation of plutonium-zinc intermetallic compounds, such as PuZn_2 , PuZn_9 , and $\text{Pu}_2\text{Zn}_{17}$. In Figure I-23 the data of Chasanov (ANL-6725, p. 100) were used to locate the end points of the plutonium solubility curves at zero percent calcium. Results of earlier unreported measurements of plutonium solubility at about 800°C indicated that increasing the calcium concentration from zero to 5 w/o resulted in a minimum plutonium solubility followed by a maximum. Thus, it is likely that the 750°C solubility curve shown in Figure I-23 up to 8.5 w/o calcium goes through a minimum, a maximum, and another minimum before reaching its end point at zero percent calcium. The curves at the lower temperatures would be expected to intersect the boundaries of the crystallization fields of calcium-zinc intermetallic compounds (not shown).

The present plutonium solubility data are in reasonable agreement with earlier results (ANL-6413, p. 61) that were obtained in solutions containing about 0.4 w/o cerium and 11 to 35 w/o zinc. On the other hand, the present data differ significantly from those obtained (see ANL-6543, p. 51) after the stepwise addition of calcium to a uranium-plutonium-zinc intermetallic compound having a uranium/plutonium ratio of 4 to 1 and containing a negligible amount of cerium. In general, the solubility of plutonium in the presence of uranium was about 25 to 75% of that in the absence of uranium. This effect is attributed to the formation of solid solutions of plutonium and uranium, which would lower the activity of the plutonium in equilibrium with the liquid metal solution. Coprecipitation of

plutonium with the uranium was ruled out because the uranium concentration after the first addition of calcium to the solution was too low, 5×10^{-4} w/o, (ANL-6543, p. 51) to have affected the plutonium in solution as the temperature and calcium concentration were varied.

Since no further work is anticipated on this subject, a brief survey of the objectives, results, and status of the calcium-zinc extraction studies is given below.

Evaluation of the Calcium-Zinc Extraction Process.

Upon consideration of various liquid metal processes for the recovery of plutonium and uranium from fast breeder reactor fuels, it was recognized that the removal of rare earth fission products from plutonium and uranium is a critical step. For the purpose of flowsheet studies, it was assumed that the fuel would contain 15 to 20 w/o plutonium, 75 to 80 w/o depleted or natural uranium, about 5 to 10 w/o fission (noble metals), and approximately 2 w/o fission products. Although the fuel was not specified, it was recognized that it might be either a metallic alloy or solid solutions of oxides or carbides. In order to concentrate on the basic plutonium-rare earth separation by calcium-zinc extraction, it was assumed that existing techniques for decladding the fuel and removing noble metal fission products could be used. For example, noble metal removal is effected in the EBR-II skull reclamation process by extraction of noble metals with liquid zinc from a suspension of U_3O_8 in a molten chloride flux. The pyrometallurgical process steps leading up to the plutonium-rare earth separation would probably result in a mixture of uranium, plutonium, and rare earths in a molten chloride salt, or in a liquid zinc alloy, or possibly coprecipitated as metal-zinc intermetallic compounds. Addition of calcium or calcium-rich zinc to any of these systems would result in the precipitation of uranium and plutonium, while the rare earths would remain in solution. The supernatant solution containing the rare earths would be removed as a waste stream, and residual zinc and calcium in the uranium-plutonium product would be removed by vacuum distillation.

The feasibility of this separation was examined in experiments on both the individual and mutual behavior of uranium, plutonium, and rare earths in calcium-zinc solutions of varying concentrations. Cerium was used as a stand-in for yttrium and the rare earths because of its high fission yield and the belief that it would be more difficult to extract into calcium-zinc solution than the higher rare earths. Cerium removals of 90% or more from uranium and plutonium were shown to be feasible. No evidence was found for the coprecipitation of cerium with uranium (ANL-6379, p. 71) or with uranium-plutonium mixtures (ANL-6543, p. 51). The solubility of cerium in calcium-rich zinc solutions, although not measured, was shown to be sufficient so that it would not limit the extent of rare earth removal.

The solubility of uranium in calcium-zinc solutions containing 30 w/o or more calcium is so low (see Figure I-22) that complete precipitation of uranium is assured in a single batch precipitation step. There is no discernible influence of plutonium on the solubility of uranium.

An over-all process objective of 99% plutonium recovery was assumed in studies of possible flowsheets for reprocessing fast breeder reactor fuels. Since the calcium-zinc method for plutonium-rare earth separation involves precipitation and since the scale of the operation would be relatively small, a single-stage batch precipitation becomes attractive. Thus the plutonium solubility must be low enough so that the calcium-zinc solution need not be recycled to avoid excessive plutonium losses. To achieve low plutonium solubilities, the precipitation would be carried out with the solvent composition near the low-melting calcium-zinc eutectic (62 w/o calcium-38 w/o zinc, m.p. 394°C) in order to take advantage of the temperature coefficient of plutonium solubility (see Figure I-24).

Several conceptual batch-type flowsheets for the recovery and decontamination of uranium and plutonium were devised in order to evaluate the merits of the calcium-zinc extraction technique for rare earth removal. In general, it was found that plutonium losses of 3 to 5% would be incurred, depending on the particular flowsheet under consideration. These losses might be reduced by incorporating additional steps, such as evaporation of most of the zinc prior to the precipitation, and by utilizing the tendency of uranium and plutonium to form solid solutions that decrease the solubility of plutonium. However, the likelihood of obtaining 99% plutonium recovery in a single precipitation step is marginal. Although there is a reasonable possibility of meeting the process requirements by this type of separation, it was concluded that the molten salt extraction method of rare earth removal offers greater advantages in terms of versatility and adaptability to plant-scale operation. For this reason, the effort on the calcium-zinc extraction method has been terminated.

(4) Development of Engineering Equipment and Procedures (V. Trice, T. Johnson, L. Dorsey)

Preparations are being made for the study of certain engineering problems associated with pyrometallurgical methods of reprocessing plutonium-bearing fuels. The critical step in such processes is the separation of rare earth fission products from the actinide elements. Experimental data (ANL-6569, pp. 39-43) indicate that this separation can be achieved by an extraction operation based on favorable distribution of the elements between a liquid metal and a liquid salt. Continuous or semicontinuous extraction operations are being considered since potentially large quantities of fuels will be handled from future reactors.

This program is starting with an investigation of equipment for contacting liquid metals and liquid salts. The goal is the construction and operation of a small-scale countercurrent extraction column using high-temperature liquid systems that are compatible with common materials of construction but that are chemically and physically similar to those which may be used in actual processes. The work of Knighton (ANL-6596, p. 65) has shown favorable distribution coefficients for the separation of plutonium from the lanthanides in a system of cadmium-

magnesium and a chloride salt containing 50 mole percent magnesium chloride. A cadmium-base metal phase and a salt phase of 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl have been chosen since there are sufficient data and experience available to permit construction of equipment with some degree of confidence. These liquids can be contained reasonably well at temperatures to about 650°C in mild steel or stainless steel.

A low-temperature facility is being built first to study briefly the flow patterns of a heavy metal phase flowing countercurrent to a much lighter phase in a packed column. Wood's metal (50 w/o Bi, 25 w/o Pb, 12.5 w/o Sn, 12.5 w/o Cd, melting point 70°C) and water will be used initially. Various designs of equipment can be tested on this facility and the information then applied to the high-temperature unit.

The high-temperature unit will be used to demonstrate engineering techniques for circulating metal and salt countercurrently through a simple packed column, to indicate problem areas, and to provide a facility for evaluating new ideas and equipment. It is hoped that measurements of extraction rates can also be made with the equipment. With the experience gained from this engineering demonstration unit, and with process requirements better defined, process demonstration on a pilot-plant scale can be undertaken.

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

In the presently proposed blanket process (ANL-6477, p. 47), uranium blanket material from the EBR-II reactor, containing about one percent plutonium, is dissolved in a 12 to 14 w/o magnesium-zinc alloy at 800°C to produce a 12 to 14 w/o uranium solution. The subsequent addition of magnesium to an approximately 50 w/o concentration precipitates the uranium from solution while the plutonium remains in solution. By cooling to 400°C , the uranium solubility in the supernatant phase is further decreased and then the plutonium-bearing supernatant phase is removed. Isolation of the plutonium from this latter phase is to be accomplished by evaporating the magnesium and zinc solvent.

(1) Concentration of Plutonium Product Solution by Evaporation

The concentration of plutonium in the 50 w/o magnesium-zinc product solution is only 0.08 w/o. The plutonium will be concentrated to between 1 and 10 w/o by evaporating most of the magnesium and zinc.

Four previous distillation runs (ANL-6725, pp. 63-66) in which cerium was used as a substitute for plutonium showed that a large fraction of the cerium was deposited as a solid film on the still pot wall. In these runs, the temperature of the exposed wall of the still pot was higher than that of the boiling metal. Consequently, magnesium and zinc were

Table I-13

EFFECT OF INDUCED REFLUXING IN STILL POT ON NET DEPOSITION
OF TIN^a ON STILL POT WALL

Charge: 8 to 10 kg of 50 w/o magnesium-zinc alloy containing about 0.5 w/o tin

Still Pot: 8 3/4-in. diameter by 8 in. high

Distillation

Conditions: Pressure: 36-40 mm

Temperature: 710-770°C

Run No.	Length of Heated Section of Still Pot (in. from bottom)	Distillation Rate (kg/hr)	Heel Weight (kg)	Distribution of Tin ^a (% of that charged)		
				Heel	Still Pot Wall	Vapor Baffle
1	5	0.92	0.87	62.4	32.4	b
2	5	0.95	0.67	55.4	29.0	b
3	3	0.70	2.4	140	0.2	0.05
4	3	0.87	0.2	73	1.4	0.5

^aThe plutonium product solution of the blanket process is concentrated by evaporation. Tin is currently being used as a stand-in for plutonium.

^bInformation not obtained.

"flashed" from any solution that splashed onto the still pot wall above the solution level, thereby leaving behind a solid deposit of cerium.

In the next few runs (Table I-13), the induction heating coil was repositioned to provide most of the heating near the bottom of the crucible. This was done in an attempt to effect partial condensation of some of the vaporized zinc and magnesium on the exposed still pot wall and thereby to prevent deposition of solute material (e.g., plutonium or substitutes for plutonium) on the wall and also to dissolve and wash back into the liquid any solute which may have deposited on the vessel wall. The still pot charge in these runs was a 50 w/o magnesium-zinc alloy containing about 0.5 w/o tin as a substitute for plutonium. Tin was used rather than cerium because both plutonium and tin are liquids at still pot temperatures (710-770°C) while cerium is not. In the first two runs, the heat input was concentrated in the lower 5 to 6 inches of the 8-in. high still pot and in the third and fourth runs in the bottom 3 inches. Considerable refluxing in Run 3 was indicated by a tinned appearance of the still pot wall at the completion of the run, a condition which was not apparent after the first two runs. As a result of the extensive

refluxing in Run 3, the net evaporation was only about one-half that of previous runs in which the heat input was spread over the full height of the still pot. Smaller amounts of tin were deposited on the still pot in Runs 3 and 4 than in the first two runs. This is evident even though material balances in these runs were not good. The large heel in Run 3 as compared with the heels in Runs 1, 2, and 4, could be an indication that less tin was deposited on the still pot wall because spattering of liquid is likely to increase as dryness is approached. This is supported by the results of Run 4 in which dryness was approached and in which somewhat larger amounts of tin were deposited on the still pot wall and vapor baffle.

The above experiments show the advantage of reflux along the still pot wall to prevent deposition of the plutonium solute. Therefore, provision for some reflux of the solvent metals, zinc and magnesium, will be incorporated in the design of large scale evaporation equipment.

(2) Flux Blanket Process (I.O. Winsch, J. Bartos*)

Some additional work has been done on an alternative blanket process using molten salt flux and zinc chloride for processing EBR-II blanket material. In this process, uranium and plutonium are first oxidized into a flux phase by zinc chloride and subsequently are reduced out of this phase with excess magnesium. The reduced plutonium dissolves in the magnesium (which should float on the flux phase) while the reduced uranium (which is insoluble in magnesium) would settle to the bottom of the vessel. Previous work (ANL-6687, pp. 47-49) showed that the oxidation and reduction reactions went to completion as expected. However, poor separation of magnesium from the precipitated uranium occurred in the reduction step. Therefore, subsequent efforts have been devoted to improving the separation of these metals.

The requirements of the carrier salt phase are: nonreducibility of its constituents by magnesium, a density as high as practicable to promote floating of the excess magnesium, and good separation from the metal phases. In previous work, the carrier flux was a $\text{BaCl}_2\text{-KCl-LiF}$ (75-23-2 weight percent) salt. Because the presence of fluoride ion has promoted good separation of metal and salt phases, the concentration of fluoride salt was increased in a few runs to as high as 50 weight percent. No beneficial effects were noted.

To date, the best separation of magnesium from uranium has occurred when FeCl_3 has been added in the reduction step to form a low-melting ($\sim 730^\circ\text{C}$) uranium-10 w/o iron alloy. The presence of iron in the uranium phase is undesirable, but its use showed that good

*Co-op student from Illinois Institute of Technology.

coalescence of the uranium phase is promoted by lowering the melting point of the uranium phase. No further work on this alternative blanket process is planned at this time.

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

Studies are in progress to evaluate equipment items and various materials for the containment of liquid metal and liquid salt systems of the types contemplated for reprocessing fast reactor fuels. The main objective of the work is the selection of materials and equipment items for EBR-II processes, but information of more general interest is also being accumulated. Included in this section are a study of materials for containing molten uranium and its alloys, a study of the performance of plasma-sprayed tungsten coatings on various substrate materials, and a description and tests of an eddy-current induction probe for measurement of liquid metal levels.

(1) Materials for Containment of Molten Uranium and Its Alloys
(G.A. Bennett, N. Quattropani, W. A. Pehl)

Various materials are being investigated for containing uranium and uranium alloys at temperatures ranging from near their melting points to several hundred degrees above their melting points. Preliminary experiments have been completed in which both tungsten and tantalum have been tested as container materials for molten uranium and for uranium-iron eutectic (66 a/o uranium; melting point, 725°C).

The experimental procedure consisted of suspending either a tungsten rod or a tantalum rod in a relatively large volume of either uranium or the uranium-iron alloy, which was contained in a ceramic crucible in an argon atmosphere. The volume of molten metal was large in order to avoid saturation of the uranium with dissolved tungsten or tantalum.* First the uranium was heated to 1200°C (melting point, 1133°C) or the uranium-iron eutectic was heated to 900°C; then the rod under test was lowered into the molten metal to a depth of 1/4 to 3/4 inch for a period of six hours. At the conclusion of this period, adhering uranium was removed from the tungsten rods with dilute hydrochloric acid and from the tantalum

*Attack of the tungsten or tantalum, if by a simple solution mechanism, would stop or be sharply decreased when the molten metal became saturated. The effect of saturation was graphically demonstrated when a small tungsten crucible (1 in. in diameter by 1 in. high) made from swaged tungsten rod suffered only minor corrosion while containing uranium at 1200°C for 50 hours. Calculations showed that the uranium had become saturated with tungsten by only very slight attack of the tungsten crucible.

Figure I-25

ATTACK OF TUNGSTEN AND TANTALUM RODS BY MOLTEN URANIUM
AND URANIUM-IRON EUTECTIC ALLOY

108-6673A

rods with dilute nitric acid, after which the rods were examined for evidence of corrosion and for changes in dimensions and weights.

Both visual observation (Figure I-25) and the weight change values (Table I-14) indicate extensive corrosion of both tungsten and tantalum by uranium at 1200°C. Severe attack of tungsten occurred even at 900°C. With tungsten, the attack mechanism appears to be simple dissolution. With tantalum, penetration of the tantalum by the uranium appears to have occurred. On the basis of these results, neither tungsten nor tantalum can be considered a suitable container material for molten uranium.

This work is being extended to include tests of carbides, nitrides, and borides of the highly refractory metals such as titanium, zirconium, hafnium, niobium, tantalum, and chromium.

(2) Testing of Plasma-Sprayed Tungsten Coatings
(G.A. Bennett, I.O. Winsch, P. Mack and W. Pehl)

Although pressed-and-sintered tungsten crucibles have been shown to be satisfactory for containing the liquid metal and salt systems of the skull reclamation process, such crucibles are expensive and the size of tungsten crucibles fabricated by pressing and sintering is limited. A

Table I-14

ATTACK OF TUNGSTEN AND TANTALUM RODS BY
MOLTEN URANIUM AND URANIUM-IRON EUTECTIC

Conditions: Temperature of Molten Uranium, 1200°C
 Temperature of Molten U-Fe Alloy, 900°C
 Exposure Time, 6 hr
 Length of Submerged Portion of Rod,
 1/4 to 3/4 inch

<u>Material Tested</u>	<u>Solvent Metal</u>	<u>Test Temperature (°C)</u>	<u>Weight Change (g)</u>	<u>Calculated Percent Weight Change of Submerged Section</u>
5/32-in. Dia. Rod Swaged from Single Crystal Tungsten	Uranium	1200	-3.26	-79
1/2-in. Dia. Rod Swaged from Sintered Tungsten	Uranium	1200	-11.28	-31
5/32-in. Dia. Rod Swaged from Single Crystal Tungsten	U-Fe Eutectic Alloy ^a	900	-0.18	-9
1/4-in. Dia. Tantalum Rod	Uranium	1200	+1.75	+14
1/4-in. Dia. Tantalum Rod	Uranium	1200	+3.78	+32

^a66 a/o uranium.

possible method of overcoming these limitations is by plasma-spraying tungsten coatings on less expensive materials which can be fabricated into large shapes. The possibility of using stainless steel coated with tungsten for certain equipment items in the skull reclamation process is also receiving consideration. Such equipment items are crucible housings, vapor baffles, insulation retainers, and liquid metal or salt transfer lines.

Large Tungsten-Coated Silicon Carbide and Stainless
Steel Crucibles

In ANL-6725, pp. 74-76, survey experiments were reported on the condition of plasma-sprayed and sintered coatings of tungsten, beryllia, tantalum monoboride, and zirconium diboride on various

substrate materials after cycling 12 times between 300 and 800°C. The coatings were applied to one side of thin, 1 3/4-inch square coupons of the substrate materials. Among the promising combinations of coating and substrate materials were tungsten sprayed directly on silicon carbide in air and tungsten on type 430 stainless steel. Good adherence of the tungsten coating to the stainless steel was effected by spraying on an intermediate nickel-chromium-boron alloy layer (Nicrobraz No. 120*) before spraying on the tungsten layer. Both of the layers sprayed on stainless steel were deposited in an argon atmosphere. The material of the intermediate layer diffuses into both the substrate and tungsten during final sintering.

In order to test these materials further, relatively large crucibles of silicon carbide (10 1/2 in. OD by 15 in. high with 5/8 in. wall) and of type 410 stainless steel (10 1/2 in. OD by 21 in. high with 1/8 in. wall) were plasma-spray coated** with tungsten by the techniques described above. Silicon carbide was selected for further testing because of its availability in large sizes, its low cost, and because its coefficient of thermal expansion closely matches that of tungsten. A 400 series stainless steel was selected because of the easy fabricability of stainless steels in general and because the coefficient of thermal expansion of 400 series steels more closely matches that of tungsten than does the thermal expansion coefficient for the 300 series stainless steels.*** Although for the coupon tests type 430 stainless steel was coated with tungsten (ANL-6725, p.75), type 410 was employed for fabrication of the large crucible because it is easier to weld than type 430 stainless steel. However the change is considered minor.

On both crucibles, the tungsten coating was 30 to 35 mils thick. Tungsten particles less than 12 microns in diameter were employed for the plasma spraying. The coated crucibles were sintered by the vendor at 1150°C for 10 hours – the silicon carbide crucible in argon and the stainless steel crucible in hydrogen.

Both crucibles were then subjected to a series of eight thermocycles in an argon atmosphere. The temperatures were alternated between room temperature and 900°C, and between 300 and 900°C (four cycles between each pair of temperatures). At the conclusion of the

*A product of Wall Colmonoy Corporation, Detroit, Michigan.

**By the Western Gear Corp., Lynwood, California.

*** Mean coefficients of thermal expansion,
 Type 304 SS - $20.2 \times 10^{-6} / ^\circ\text{C}$ (0 to 1000°C)
 Type 410 SS - $13.7 \times 10^{-6} / ^\circ\text{C}$ (0 to 1000°C)
 Tungsten - $4.6 \times 10^{-6} / ^\circ\text{C}$ at 27°C and $5.2 \times 10^{-6} / ^\circ\text{C}$ at 1027°C
 Silicon Carbide - average of $4.5 \times 10^{-6} / ^\circ\text{C}$ to $5.3 \times 10^{-6} / ^\circ\text{C}$,
 depending on material (25 to 1000°C)

temperature cycling operations, both coatings were intact and apparently undamaged (See Fig. I-26). The only changes noted were (1) the tungsten coating on the silicon carbide had acquired a reddish-brown cast, which is believed to be the result of slight surface oxidation of the tungsten by oxygen or water contaminants in the argon atmosphere and (2) a number of dark-colored spots, possibly also due to oxidation, appeared on the bottom of the stainless steel crucible.

Figure I-26

TUNGSTEN-COATED SILICON CARBIDE AND STAINLESS STEEL
CRUCIBLES AFTER THERMAL CYCLING

Cycling Conditions: Argon Atmosphere
4 cycles - RT to 900°C
4 cycles - 300 to 900°C

108-6697-T

Both coated crucibles will be tested further by using them to contain the molten zinc-magnesium-uranium and halide salt systems of the skull reclamation process.

Coupon Tests of Plasma-Sprayed Tungsten Coatings

Thermal Cycling Tests. The survey experiments on various combinations of plasma-sprayed coatings and substrate materials were continued. Plasma-sprayed tungsten coatings on two tantalum coupons were tested by thermal cycling. Both coupons were prepared

similarly,* except that tungsten was sprayed directly on the surface of one coupon, while a graded tungsten-tantalum coating was deposited on the second coupon. That is, the coating composition was varied from 100% tantalum at the substrate surface to 100% tungsten at the outer surface in seven approximately equal steps.

The test coupons were then thermal cycled 12 times under argon. The temperature cycles alternated between room temperature and 930°C and between 200°C and 930°C. Visual observation at the conclusion showed no deterioration of the tungsten coating which had been sprayed directly on the tantalum substrate. The graded coating was chipped around the outer edges. Because of its slightly better adhesion and much lower spraying cost, the direct spray technique appears preferable; however, more definitive tests would be necessary before a choice between the two coating techniques could be made.

Corrosion Tests. Two stainless steel (type 304) coupons (1 1/2 in. square by 1/4 in. thick) were completely plasma-spray coated with tungsten by personnel of the Oak Ridge Gaseous Diffusion Plant. The coupons were subjected to in-process corrosion tests in the skull reclamation process pilot plant. One of the coupons was submerged in a 4 w/o magnesium-4 w/o uranium-zinc solution for one hour at 800°C. The other coupon was suspended in the vapor space above the tungsten crucible in the skull oxide reclamation furnace during a complete process demonstration run. At the conclusion of the tests, both of the tungsten coatings had separated from the stainless steel substrate, and the stainless steel coupon in the metal solution had been severely attacked. These results confirm earlier results (ANL-6725, p. 75). In the earlier tests, either the brazing or graded coating technique was necessary to insure sufficiently good adhesion of tungsten to a stainless steel to survive thermal cycling, which is a less severe test than exposure to process systems.

(3) Testing of Ceramic Crucibles (I. O. Winsch, T. F. Cannon)

Ceramic crucibles of various materials are often used in experimental work for the containment of liquid metal and salt systems. Such crucibles may ultimately be used also in processes under development which utilize liquid metal and liquid salt systems. Therefore, new types of crucibles are being tested in a continuing program in order to keep abreast of new developments in the manufacture of crucibles.

*By the Western Gear Corp. of Lynwood, Calif. as follows: tungsten particle size, 100% less than 12 microns; final coating thickness, 30 to 35 mils; spraying conducted in 5% hydrogen-argon atmosphere; coating sintered at 1150°C for 6 hours in argon.

Beryllia Crucibles. One of the alternative operational procedures of the skull reclamation process involves performing the uranium precipitation steps (ANL-6725, p.51) in a large beryllia crucible after which a solid uranium concentrate would be physically removed and transferred to retorting equipment. The ability to remove physically the solid concentrate requires that the crucible be unwetted by the process metal solutions. However, large, thixotropically cast beryllia crucibles received for use in the pilot plant were wetted and penetrated by the process metal solutions, a behavior contrary to that previously experienced with smaller crucibles (see ANL-6725, pp. 47 and 48). New large beryllia crucibles are on order, but the manufacturer is attempting to discover the reason for the recent wetting of crucibles before manufacturing new crucibles.

The manufacturer furnished two truncated beryllia cones, about 3 in. high with a large diameter of 3 in., which had been thixotropically cast and fired. The material used in these cones was the beryllia mix proposed for new large beryllia crucibles which are on order. Within a 6-hour exposure at 800°C to zinc-magnesium solutions of the skull reclamation process, these were also wetted and penetrated. The manufacturer believes that the beryllia "fines" did not migrate to the surface in these particular test specimens. Further work is being done to correct this fault by increasing the percentage of fines in the original mix and by applying a spray coating of fines to the inside of the crucible wall prior to final firing.

Coors Beryllia and Alumina Crucibles. A thixotropically cast beryllia crucible (3 5/16-in. OD x 3 3/4-in. high with a 5/16-in. wall) manufactured by the Coors Porcelain Company has also been tested by holding zinc-magnesium alloys at temperatures of 700°C to 800°C for a total time of 21 hr. Slight wetting by the metal solutions occurred in the vicinity of the gas-liquid interface, and several long hairline cracks formed above the melt level.

A thixotropically cast alumina crucible, having the same size as the above beryllia crucible and also manufactured by the Coors Porcelain Company, was similarly tested by holding a molten zinc-halide salt system and later a magnesium-halide salt system for periods of 8 and 4 hr, respectively, at 800°C. The crucible was not undercut or wetted, and in each case the solidified contents were loose and could be shaken out of the inverted crucible. However, hairline cracks formed in the base and extended up the walls of the crucible. The test was repeated, using the same crucible, and slight penetration by the molten salt occurred but it was still possible to remove the solidified contents. There was no evidence of further cracking or penetration into the cracks by the melt.

The crucibles manufactured by the Coors Porcelain Company were made from very fine powders. As a result, they were of high density and more subject to thermal and mechanical shock than are less

dense crucibles. Further efforts by the Coors Porcelain Company will be in the direction of producing less dense products which it is hoped will retain the characteristic of not being wetted by metal solutions.

(4) Use of Eddy Current Induction Probe for Liquid Level Measurements

(I. O. Winsch, D. Benzing)

In liquid metal processes, a method is needed for the remote determination of levels of molten salts and molten metals and, if both are present, the interface between the two. Equipment has been installed to test the feasibility of using an eddy current induction probe of the type developed by Davidson.¹¹ A particular advantage of an eddy current induction probe is that it operates within a well similar to a thermocouple well and therefore may be easily removed for repair or replacement.

The probe consists of dual wound coils of 20 gauge Nichrome wire on an alumina rod; the coils are insulated from each other and from contact with the well by Melbond* ceramic adhesive. The liquid level probe operates on the principle that the inductance of a coil supplied with high-frequency alternating current is reduced when the coil is in the vicinity of a closed loop of conducting material.

Use of a single coil in a bridge circuit to measure the change of inductance would lead to difficulties in the design of the electronic circuit, since the resistance is larger than the reactance and is temperature-dependent. Use of a dual wound coil system minimizes these difficulties. The effect may be regarded as one of changing mutual inductance between the two coils. If a constant current is fed into one coil, and the emf induced in the other is measured, the resistance of the coils does not enter into the measurement. The high-frequency alternating current induces electrical eddy currents in the surrounding liquid metal which, in turn, set up a magnetic field opposing the current produced in the second coil, thereby changing its inductance. The strength of the magnetic field is dependent on the height of the liquid metal around the coil.

The penetration of the eddy currents into the surrounding conducting medium is a function of the resistivity of the medium and

*Product of Melpar, Inc., Falls Church, Va.

¹¹D. F. Davidson, Measurement of Liquid-Metal Levels by the Effect of Eddy Currents on Inductance, British Report IGR-R/CA-255, United Kingdom Atomic Energy Authority, December 1957.

the frequency of the alternating current. The relationships are given by the following equation:

$$d = \frac{2}{\pi} \sqrt{\frac{\rho}{f}}$$

where d = effective depth of penetration, cm,

ρ = resistivity, $\mu\text{ohm-cm}$

f = frequency, kc/sec.

The frequency chosen must be low enough to penetrate through the stainless steel tube wall in order that a change of inductance will occur when metal is outside the tube. If the frequency is too low, however, the mean radius of the eddy currents in the liquid metal is large and their magnitude is small, giving a smaller coupling with the coil. The ceramic adhesive and the surrounding atmosphere have such high resistivities that their effect is negligible. For a frequency of 50 kc/sec and a value of resistivity of $70 \mu\text{ohm-cm}$ for stainless steel, the depth of penetration in stainless steel would be $d = \frac{2}{\pi} \sqrt{\frac{70}{50}} = 0.76 \text{ cm}$. This should be adequate penetration for a stainless steel well having a 1/2-in. OD and a 1/32-in. wall thickness.

Figure I-27

CIRCUIT DIAGRAM FOR EDDY CURRENT LIQUID LEVEL PROBE

A circuit diagram for the probe is shown in Fig. I-27. Fig. I-28 is a photograph of a completed probe unit and of one with the outer insulation stripped away to show the coils.

Initial testing is being done using cadmium contained in stainless steel equipment. Cadmium is easier to handle than zinc systems because it may be contained in stainless steel, whereas the more corrosive zinc systems require the use of tungsten or tantalum vessels.

Figure I-28

EDDY CURRENT INDUCTION PROBES

(Outside diameter of probe is about 3/8 in. Coil length is about 4 in.)

However, work will be done with zinc-based systems and two-phase molten metal-salt systems after the techniques of liquid level measurements have been perfected with molten cadmium-salt systems.

Calibration of the probe for determination of liquid metal levels has shown the probe to have very satisfactory characteristics. A change in cadmium level of one inch produced a change in signal of approximately 0.9 mv. This change was linear throughout the length of the 4-in. probe. A uniform spacing of the coils is required to give a linear response.

Two methods of coil operation can be employed: (1) a movable coil could be used to locate the interface by the sharp change in output voltage of the secondary coil which occurs at a gas-metal interface as the coil is lowered into the metal or (2) a fixed probe having a coil length in excess of the maximum anticipated liquid level could be employed to give a continuous record of liquid level. In the latter case, a calibration of each probe would be required for temperature, liquid level, and for the particular liquid metal system being used.

The effect of temperature on a 4-in. long coil with coils spaced about 1/32 in. apart is illustrated in Fig. I-29. In the

Figure I-29

EFFECT OF TEMPERATURE ON OUTPUT VOLTAGE OF EDDY
CURRENT LIQUID LEVEL PROBE

Readings obtained with a 4-inch coil completely immersed in cadmium.

108-7282

liquid region, the change in signal is nearly linear at about 0.002 mv per degree Centigrade. Since the temperature effect is proportional to the length of coil immersed in the liquid metal, it is appropriate to express the result as mv per degree Centigrade per inch of "immersed" coil. For the 4-in. probe, this is 0.00047 mv per degree Centigrade per inch of coil immersed in cadmium. Measurements have not yet been made in other metals.

Future work will be directed towards determination of the effects of (1) various compositions of the metal and (2) the presence of an immiscible salt phase.

e. Supporting Chemical Investigations
(R. K. Steunenberg)

Fundamental studies dealing with molten salt and liquid metal systems are being conducted to supply supporting data for process use and to elucidate the chemical aspects of various process steps. During the reporting period, further investigations of uranium oxide reactions with molten chloride solvents have been completed. This work has a bearing on the noble metal extraction and oxide reduction steps of the skull reclamation process.

Reactions of Uranium Oxides in Molten Chloride Media
(M. D. Adams, D. A. Wenz)

It has been reported previously (ANL-6569, p. 54) that a soluble uranium (V) species, UO_2Cl , is formed on the addition of UO_3 , U_3O_8 or UO_2Cl_2 to molten chloride solvents. Further evidence for the identification of this species as UO_2^+ ion was provided by the similarity between its absorption spectrum in molten salt solution and that of the isoelectronic species NpO_2^{2+} (ANL-6725, p. 76). A method was also described in ANL-6725 by which preliminary values of the molar absorptivity for UO_2Cl in LiCl-KCl and in NaCl-KCl-MgCl_2 at 650°C were determined. Subsequent measurements have been made in different molten chlorides at various temperatures.

A diagram of the apparatus that was used in these studies was given in ANL-6725, p. 77. Briefly, the measurements were made with a Cary Model 14 Recording Spectrophotometer equipped with a cell furnace in the sample compartment. Standard fused-quartz cells (1-cm square) were attached to a vacuum line via a stopcock.

The UO_2Cl was formed in the cell by the thermal decomposition of UO_2Cl_2 that had been added to the salt solution:

The chlorine gas evolved by reaction 1 was condensed in a liquid nitrogen cold trap on the vacuum line, isolated from the spectrophotometer cell by closing the stopcock, then measured by allowing it to expand into a calibrated volume at room temperature and observing the pressure. At the same time, the absorption spectrum of the molten salt solution was obtained. It was then possible to calculate molar absorptivities for the UO_2Cl , using the following information: (a) the stoichiometry of reaction 1, (b) the quantity of chlorine collected, (c) the optical absorbance, and (d) the density of the salt solution. In the wavelength region of interest, the absorption resulting from the undecomposed UO_2Cl_2 was negligible.

Having determined molar absorptivity values, it was possible to determine the equilibrium constant for reaction 1 by simultaneous measurement of the UO_2Cl absorbance and the pressure of chlorine in equilibrium with the salt solution. Chlorine pressures over the range of 2 to 15 torr were measured directly by means of a Booth-Cromer pressure transmitter that was connected to a mercury manometer. Because of the low value of the equilibrium constant, it became desirable to extend the measurements to pressures below the useful range of the pressure transmitter. These low pressures, in the range of 0.03 to 0.7 torr, were fixed by placing a low-temperature slush bath around the cold trap so that the equilibrium chlorine pressure over the solution would be equal to the vapor pressure of solid chlorine in the cold trap. Slush baths consisting of 2-methyl butane and 2, 3-dimethyl butane were maintained at known

temperatures, and the chlorine pressure was calculated from its vapor pressure equation. Equilibrium constants obtained by this method of pressure measurement and those obtained by direct pressure measurement with the transmitter were in good agreement. The results are shown in Table I-15. The value for the equilibrium constant

Table I-15

URANYL CHLORIDE DECOMPOSITION EQUILIBRIUM CONSTANT
IN LiCl-KCl AT 650°C

Run	<u>Molar Concentration</u>		<u>Cl₂ Pressure</u> (atm.)	<u>K_{eq}</u> (atm.)
	<u>UO₂Cl₂</u>	<u>UO₂Cl</u>		
159-3	0.143	0.0041	2.6×10^{-3}	2.1×10^{-6}
160-4	0.158	0.0023	2.6×10^{-3}	5.6×10^{-7}
160-5	0.158	0.0017	1.7×10^{-2}	1.9×10^{-6}
163-1	0.179	0.0183	1.6×10^{-4}	1.7×10^{-6}
163-2	0.172	0.0247	4.0×10^{-5}	8.2×10^{-7}
163-3	0.195	0.0023	9.9×10^{-3}	1.4×10^{-6}
164-1	0.138	0.0108	1.2×10^{-4}	7.3×10^{-7}
164-3	0.133	0.0161	4.0×10^{-5}	5.9×10^{-7}

Av. 1.2×10^{-6}

Standard Deviation = 0.6×10^{-6}

$$K_{eq} = \frac{(UO_2Cl)^2 (P_{Cl_2} \text{ [atm]})}{(UO_2Cl_2)^2}$$

in the LiCl-KCl eutectic at 650°C was $1.2 \pm 0.6 \times 10^{-6}$ atm. ($\pm$ value = standard deviation).

A second reaction involving further thermal decomposition was observed when solutions of UO₂Cl₂ and UO₂Cl were held under vacuum for extended periods of time at temperatures above 750°C:

This reaction became evident from the precipitation of black UO₂ from the molten salt solutions. The precipitate was identified by X-ray diffraction analysis of a portion of the solid that had been separated from the salt by filtration. A small amount of a uranium (IV) species in solution was also indicated by a slight absorption peak in the wavelength region of 1100m μ .

By carrying out the experiments at temperatures below 750°C and using reasonably brief periods of time, it was possible to avoid reaction 2 in the investigations of UO_2Cl_2 .

The evidence obtained in this study indicates that reaction 1 represents the initial step of the thermal decomposition of UO_2Cl_2 in molten chloride solvents. The reaction appears to be easily reversible and to reach a measurable equilibrium at temperatures of about 600 to 650°C. At temperatures of about 750°C and above, further decomposition to UO_2 and chlorine occurs, as indicated by reaction 2. The fact that UO_2 suspended in a molten chloride solvent can be converted to UO_2Cl_2 by passing chlorine through the mixture indicates that reaction 2 is also reversible.

Effects of Solvent and Temperature on the UO_2Cl_2 Spectrum.

Most of the experimental work on the UO_2Cl_2 spectrum involved the use of either LiCl-KCl solutions or the NaCl-KCl-MgCl_2 eutectic as the solvent. The effects of temperature changes on the UO_2Cl_2 spectra in these two solvents are shown in Figures I-30 and I-31. In all of the solvents, the

Figure I-30

URANYL (V) SPECTRA IN LiCl-KCl SOLVENTS

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spectra were influenced at the shorter wavelengths by the absorption of UO_2Cl_2 and by a shift of the charge-transfer absorption edge to longer wavelengths with increasing temperature.

Figure I-31

URANYL (V) SPECTRUM IN NaCl-KCl-MgCl₂ EUTECTIC

108-6681 Rev. 3

To investigate the effect of solvent composition on the UO_2Cl spectrum, data were also obtained in the following solvents: MgCl_2 at 750°C; equimolar LiCl-MgCl_2 at 650°C; LiCl-KCl-MgCl_2 (mole ratio 50:35:15) at 450°C. These results are presented in Figure I-32.

Figure I-32

URANYL (V) SPECTRA IN THREE MOLTEN CHLORIDE SOLVENTS

108-6682 Rev.

It is apparent from Figures I-30, -31, and -32 that the UO_2Cl spectrum is strongly influenced by variations of the temperature and solvent, especially in the shorter wavelength regions. The linear O-U-O group appears to give rise to the spectra of uranyl (V) and (VI) compounds.¹² Factors that affect the O-U bonds will change the overlap of the bonding orbitals involved, and can thereby alter the energy levels of the molecule. The shorter the U-O bond, the greater is the axial field on the uranium atom and the larger is the splitting of the energy levels. Thus, changes in absorption energies in the shorter wavelength regions would correspond to changes in the energy level splitting resulting from variations in the axial field in the molecule. It is postulated that these variations in the axial field are caused by differences in attraction between the cations in the various molten salt solutions and the oxygen atoms in the UO_2^+ complex.

f. Supporting Engineering Studies
(L. Burris, Jr.)

During the past reporting period, engineering studies were conducted in the general area of liquid metal boiling. Work was also begun on the determination of the critical constants of alkali metals.

(1) Studies in Large-Scale Cadmium Distillation Unit
(I. G. Dillon, P.A. Nelson, J. Arntzen,
N. Quattropiani)

The large-scale cadmium distillation unit (see Figure I-33) is an engineering test facility which was built to demonstrate the distillation of a liquid metal on a large scale and to evaluate the performances of components within the system. The unit has been operated intermittently during the past three years. The latest and final series of tests in this equipment were made to study the efficiency of a de-entrainment device, to evaluate the performance of an eddy-current induction probe for determination of the liquid level in the still pot, and to determine the vertical temperature profile in the still pot.

De-entrainment Studies

The entrainment of liquid cadmium droplets in cadmium vapor has previously been determined to be as high as 8% (ANL-6648, p. 84). In an attempt to reduce the quantity of liquid entrained in the vapor, a de-entrainment device was installed in the still pot vapor space as shown in Figure I-34. This device consists of two perforated plates made of 16-gauge stainless steel and spaced 1 in. apart. The perforations are 3/8-in. diameter holes spaced 1/2 in. apart (center-to-center distance).

¹²McGlynn, S. P., and Smith, J. K., J. Mol. Spectr., 6, 164 (1961).

Figure I-33

LARGE-SCALE CADMIUM DISTILLATION UNIT

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

108-3948-A

The 1-in. space between the plates is packed with coarse steel wool. A baffle arrangement forces all vapor from the still pot to flow through the de-entrainment device.

To determine the extent of liquid entrainment occurring after the de-entrainment device was installed, lead (which is nonvolatile relative to cadmium) was added to the still pot in the most recent tests to give a nominal lead concentration in the cadmium of about two percent.* Tin had been used for this purpose in previous runs, in which no de-entrainment device was present. As a result of extensive entrainment occurring in those runs, tin had been transported to the condensate receiver, where sampling is done to determine the extent of liquid

*The amount of cadmium in the still pot at any time was approximately 100 kg. The condensate from one run was fed intermittently to the still pot in the succeeding run.

Figure I-34

CROSS SECTION OF STILL OF LARGE-SCALE CADMIUM DISTILLATION
UNIT SHOWING DE-ENTRAINMENT DEVICE

entrainment. Therefore, it was not feasible to use tin as an entrainment tracer in the present study, in which high de-entrainment factors were expected.

Five runs were made, at successively higher distillation rates up to a maximum of about 90 kg/hr. The first three runs were made at 7.5 mm Hg cadmium receiver pressure. In the next two runs, the receiver pressures were 15 (Run ID-9) and 30 mm Hg (ID-10) and the distillation rates were kept constant at 90 kg/hr. The data given in Table I-16 show that the amount of liquid cadmium in the cadmium vapor increased from 1.2 to 2.3% when the distillation rate was increased from 40 kg/hr to 90 kg/hr at a constant receiver pressure of 7.5 mm Hg. When the receiver pressure was increased from 7.5 mm Hg to 30 mm Hg at a distillation rate of about 90 kg/hr, the entrainment of liquid cadmium in cadmium vapor decreased from 2.3% to 0.9%. In the two runs with and without the de-entrainment device that can be compared directly (ID-10

Table I-16

ENTRAINMENT OF CADMIUM IN LARGE-SCALE DISTILLATION UNIT

Run No.	Cadmium Receiver Pressure (mm Hg)	Boiling Point (°C)	Liquid Temperature in Still Pot (°C)	Power (kw)			Apparent Rate of Distillation (kg/hr)	Apparent Power Efficiency (%)	Liquid Entrainment (% of Cd ^a Collected)
		Corresponding to Pressure in Cadmium Receiver		Calc. from	Calc.				
				Rate of Dist.	Loss				
<u>Present Data</u> (with de-entrainment device)									
ID-6	7.5	472	543	30	9.6	20.4	39	32.1	1.2 ^b
ID-7	7.5	472	542	30	11.9	18.1	48	39.5	1.6 ^b
ID-8	7.5	472	545	40	21.3	18.7	86	53.3	2.3 ^b
ID-9	15	504	557	40	22.7	17.3	92	56.8	1.8 ^b
ID-10	30	537	575	40	22.0	18.0	89	55.0	0.9 ^b
<u>Previous Data</u> (without de-entrainment device) ^c									
26	30	537	553	20	9.6	10.4	36.7	48	2.5 ^d
30	30	537	568	30	18.2	11.8	69.5	61	0.4 ^d
32	30	537	563	40	23.7	16.3	90.0	59	5.0-8.0 ^d

^a Tin was used as a monitor of entrained liquid in runs made without a de-entrainment device; lead was used as a monitor in runs made with the de-entrainment device (see Figure I-34).

^b Precision: $\pm 10\%$ for colorimetric lead analyses.

^c ANL-6648, p. 48.

^d Order of magnitude precision only for spectrochemical tin analyses.

and 32), the level of entrainment was a factor of 7 lower with the de-entrainment device than found previously when a de-entrainment device was not present. However, the general level of entrainment was disappointingly high (0.9 to 2.3%) in the five runs made with the de-entrainment device present. Since operation of the cadmium distillation unit is being discontinued, it will not be possible to investigate alternative de-entrainment devices or procedures.

The distillation temperatures in these runs (see Table I-16) were, in general, considerably higher than those which correspond to the pressure measured in the condensate receiver. A large part of this difference may be accounted for by a large pressure drop through the de-entrainment device. However, as will be pointed out later, some of this difference may be accounted for by a temperature drop which occurs near the surface of the cadmium pool. The pressure drop between the vapor space in the still pot and the condensate receiver, the major part of which should be the drop occurring in the de-entrainment device, was determined to be about 15 mm Hg in a run in which the cadmium distillation rate was 48 kg/hr. This was determined by comparison of the measured pressure in the condensate receiver with the cadmium vapor pressure corresponding to the temperature in the vapor space.

Still Pot Liquid Level Measurements with Eddy-Current Induction Probe

In several of the runs, an eddy-current induction probe was used to measure continuously the liquid level in the still pot. This device is believed to have promise for remote measurement of liquid metal levels.

The eddy-current induction probe consists of two separate coils, a primary and a secondary, wound alternately for a distance of 14 in. on a 1/4-in. OD ceramic core (8 turns per in. for each coil). The output of the secondary coil is affected by the presence of nearby conductors, such as a liquid metal. The probe was operated in a 7/16-in. ID stainless steel well which had a wall thickness of 1/32 in. and which extended well below the level of cadmium in the still pot. Calibration of the probe was accomplished in the feed tank adjacent to the still pot (see Figure I-33). The calibration showed a change in the output signal of the secondary coil of 1.1 mv/in. Cd and a temperature coefficient of 0.0067 mv/°C.

Figure I-35

TYPICAL TRACING OF STILLPOT LIQUID LEVEL READING
DURING LARGE-SCALE CADMIUM DISTILLATION RUN

108-7278

A typical tracing of liquid level during a run is shown in Figure I-35. This plot shows the instrument deflections representing the sharp increase in level during charging of cadmium from the feed tank to the still pot, the gradual decrease in level with distillation, and the level fluctuations that occurred during distillation. The change in liquid level on charging each new quantity of cadmium agreed with that expected for the size of the charge made. The relationship between cadmium level in inches and the probe signal was:

$$\text{Cadmium Level (in.)} = 8 + (\text{output signal (mv)}/1.1).$$

Some difficulty with probe operation was experienced; the probe shorted out to the stainless steel well as a result of abrasion or chipping of ceramic insulating coating on the coils (see Figure I-28). This is regarded as a minor problem. Therefore, it is felt that the eddy-current induction probe shows considerable promise for providing remote continuous measurement of liquid metal levels.

Temperature Distribution in Still Pot

In several runs, the vertical temperature profile near the center of the still pot was determined by moving a thermocouple up and down within a thermocouple well fabricated from 1/2-in. pipe. Because of the dampening effect of the thermocouple well, an observed temperature cannot be regarded as a point temperature, but rather as an integrated temperature over the distance from about 1/2 in. above to 1/2 in. below the thermocouple tip. The major observation from the data shown in Figure I-36 is that the temperature in the liquid region is essentially

Figure I-36

TYPICAL TEMPERATURE DISTRIBUTION ALONG THE VERTICAL AXIS OF THE STILL POT OF THE LARGE-SCALE CADMIUM DISTILLATION UNIT DURING DISTILLATION

108-7267

Conditions

Cadmium Receiver Pressure, 7.5 mm Hg

Distillation Rate, 48 kg/hr

Power Input, 30 kw

Points 9 and 10 are metal temperatures inside the wall of the stillpot

Point 12 is the temperature of the interior of the metal wall, 1/16 inch from the inside wall (see Fig. I-34).

constant, being 20 to 30°C higher than that in the vapor region, where the temperature was also constant with position. The temperature in the vapor space should be the boiling point of the metal. This temperature corresponds to a pressure of 22 mm of mercury as compared with 7.5 mm in the condensate receiver. From the increase in boiling point with cadmium head (Figure I-36), it is apparent that the temperature of the liquid cadmium was well below the boiling point at all depths except the top one inch of cadmium. Even the temperature of the still pot wall (point 12 of Figure I-36) was below the cadmium boiling point at cadmium depths of greater than about one inch. It may be concluded, therefore, that boiling of cadmium occurs within the upper inch of the liquid cadmium.

General Performance of the Distillation Unit

The relationship between power input and apparent distillation rate is shown in Figure I-37 for all runs reported in Table I-16.

Figure I-37

RELATIONSHIP BETWEEN POWER INPUT AND APPARENT DISTILLATION RATE IN LARGE-SCALE CADMIUM DISTILLATION UNIT

These data indicate that the apparent distillation rate was low in Run ID-7. No explanation can be given for this discrepancy. The power input corresponding to the threshold of distillation was determined by experiment to be 6 kw.

The unit operated smoothly except for two shutdowns. The first interruption was caused by a cadmium leak in the feed tank

pipings. This leak developed as a result of an improperly stubbed-off pipe. The second interruption was caused by failure of the induction coil. It was found that two busbars had separated from the coil because the bolts had been loosened by thermal cycling. This was repaired and the unit put back in operation.

These runs conclude the present program on the large-scale distillation unit. The unit has been shut down and placed in standby condition. A topical report on all work to date is being prepared.

(2) Study of Mechanisms of Liquid Metal Boiling and Entrainment

(J. Wolkoff, J. J. Heiberger)

The mechanism by which the evaporative phase change from liquid to vapor takes place depends in part on the rate at which the transformation occurs. The highest rates are usually obtained in nucleate boiling, where vapor bubbles form and grow at discrete points within the liquid pool, rise through the liquid, and emerge at the interface separating the liquid and vapor zones. Liquid droplets are created by the emerging vapor bubbles, and these may be entrained and carried away by the moving vapor stream.

At a lower rate of phase change, the transformation can occur by forming vapor only at the liquid-vapor interface without creating vapor bubbles within the liquid pool. With this mechanism (here called nonturbulent vaporization), there is no droplet formation or entrainment. Nonturbulent vaporization of most liquids will occur only at low rates of vaporization. However, reasonably high nonturbulent vaporization rates can be expected for many liquid metals because of favorable physical properties, such as high density, high thermal conductivity, and high surface tension. When the heat input and vaporization rates are increased, there is an increased tendency toward vapor bubble nucleation and bumping within the liquid pool.

The conditions necessary to achieve high nonturbulent vaporization rates are being examined with pure mercury in glass equipment. It has been found that active circulation within a liquid metal pool allows higher vaporization rates before nucleation begins (with occasional bumping) than does poor circulation. Induction heating (10 kc), when substituted for resistance heating, improved the circulation in a shallow mercury pool and the dependent nonturbulent vaporization rate (ANL-6648, p. 86). Vaporization rates as high as 905 lb Hg/(hr)(sq ft), equivalent to a heat flux of 115,000 Btu/(hr)(sq ft) through the vaporizing surface, were obtained.

Vertical temperature traverses were taken near the evaporating surface during the nonturbulent vaporization of mercury at low pressure (<5 torr). All traverses were taken at the centerline of the pool.

A 2 5/8-in. dia. x 3-in. deep pool in an all-glass boiling loop (ANL-6648) was in turn inductively and resistively heated during the traverses. The temperature probe used was a 1/16-in. dia. stainless steel-sheathed thermocouple (chromel-alumel elements) whose hot junction end had been bent into a small flat spiral to minimize conduction to or from the thermocouple tip by placing an appreciable length of the thermocouple within a small essentially isothermal area. The hot junction of the thermocouple could be read in the usual way or as a liquid metal thermocouple with the mercury as one element of the couple. The boiling loop previously described (ANL-6648, p. 85) was modified to include a mercury cold junction held at 0°C. The two thermocouples agreed satisfactorily, i.e., within about 2°C.

Table I-17

SUMMARY OF VERTICAL TEMPERATURE TRAVERSES IN A MERCURY POOL DURING
NONTURBULENT VAPORIZATION AT LOW PRESSURE (<5 torr)

(Readings were taken at the pool centerline near the vaporizing surface of
a 2 5/8-in. dia. x 3-in. deep pool.)

Method of Heating and Run No.	Average Heat Flux through the Evaporating Surface ^a [Btu/(hr)(sq ft)]	Liquid Surface Temp. (°C)	Deep Liquid Temp. ^b (°C)	Temperature Gradient in Surface Layer of the Liquid ^c (°C/in.)
<u>Induction (10 kc) with Cylindrical Coil</u>				
NTV-43	64,000	173	184	63
NTV-43	86,000	176	189	76
NTV-43	114,000	181	199	115
<u>Cylindrical External Resistance Heater</u>				
NTV-44	64,000	160	176	70
NTV-44	75,000	164	185	97

^aDivide by heat of vaporization of mercury (~127 Btu/lb) to obtain lb Hg/ (hr)(sq ft).

^bMeasured well below the surface layer at an average depth of 1/2 in.

^cThe average thickness of the layer having this gradient was 0.17 in.

The results are summarized in Table I-17, and a plot of one of the traverses is shown in Fig. I-38. The outstanding characteristic of these traverses was the existence at the vaporizing surface of a narrow zone in the liquid which had a steep and constant temperature gradient. Under the experimental conditions which were employed, the values of this gradient ranged from 63 to 115°C /in. This zone existed with both induction heating and resistance heating. The thickness of the zone averaged 0.17 in. Below this layer, the pool temperature was almost constant with depth. The temperature gradient, the surface temperature, and the deep liquid temperature each increased with increased vaporization rate.

Figure I-38

TEMPERATURE TRAVERSE IN MERCURY POOL DURING
NONTURBULENT VAPORIZATION

2 5/8-in. dia x 3-in. deep pool
10 kc induction heating
Avg heat flux 114,000 Btu/(hr)(sq ft)
Run NTV-43

108-7286

As shown in Fig. I-38, one technique for locating the vaporizing surface was graphical (the intersection of the temperature traverses above and below the interface). The vapor space of the boiling loop was kept hotter than the liquid pool to prevent condensation. Location of the vaporizing surface by visual observation was hindered by surface motion during the vaporization process. In general, however, the locations of the surface as determined visually and graphically agreed to within 1/32 in.

If it is assumed that the gradients listed are the same over the entire surface of the liquid as at the centerline, a molecular conduction process can account for an average of only 14% of the heat passing through the surface. With resistance heating, molecular conduction accounted for a slightly higher percentage of the heat passing through the surface than with induction heating, but the difference was small. At the moment, the mechanism for transfer of the remaining heat has not been elucidated. However, since heating takes place at the walls, a radial temperature gradient, presumed to exist but not yet measured, can modify the calculation of the percentage of heat transferred by conduction. In addition,

there were two sources of errors inherent in the thermocouple used thus far: (1) physical disruption of the liquid temperature gradient and of the flow of metal by the thermocouple, and (2) averaging of the temperature over the area of the thermocouple tip. A smaller thermocouple (now being tested) may reduce these errors and thereby increase the measured gradient.

The pressure in the vapor space of an externally resistance-heated tubular glass boiler (1-in. dia. x 12 in. deep) was measured during nonturbulent vaporization of pure mercury at low pressure (<5 torr) to determine the degree of superheating present at the vaporizing liquid surface. At the same time, the surface temperatures were obtained by centerline temperature traverses as described above. The surface of the pool was found to be superheated an average of about 30°C higher than the vapor space saturation temperature. A large superheat is considered to be an important part of the mechanism of nonturbulent vaporization at high rates. The driving force for this vaporization process depends on the superheat which can be attained before vapor bubble nucleation takes place.

(3) Determination of Critical Constants of Alkali Metals (I. G. Dillon*)

Study of the nature of liquid metals indicates that their behavior may be expected to be considerably different from that of the so-called "normal" liquid used as the basis of the original theorem of corresponding states. However, many thermodynamic and physical properties of a metal can be calculated or estimated from their critical constants for the entire range of temperature from the boiling point to the critical point.

Thermodynamic properties of alkali metals are of particular interest because of the use of these metals as heat exchange media. For most alkali metals, vapor pressures and liquid and vapor densities are generally known up to the vicinity of the boiling point. While many estimates have been made of the critical constants of alkali metals, no actual measurements of the critical constants, vapor pressure, vapor density, and liquid density are known for the entire range of temperature from the boiling point to the critical point. Therefore, it is proposed to make measurements of vapor and liquid density as a function of temperature for the alkali metals, sodium, potassium, rubidium, and cesium from room temperature up to the critical point. Density will be determined by measurement of gamma radiation from the liquid and vapor phases of radioactive tracer-containing metal held in a bomb.

Initial measurements will be made on cesium and rubidium, since their estimated critical temperatures (about 1900°C) are

*Ph.D. Candidate from Illinois Institute of Technology.

much lower than those estimated for sodium and potassium (2200-2500°C). Density measurements on sodium and potassium may be limited to temperatures attainable with presently available materials of construction.

Other investigators^{13, 14} are presently obtaining vapor pressure data for the alkali metals in the medium pressure range ($1 < P < 15$ atm). Initially, it is proposed to estimate the critical pressure by extrapolation of these data to the critical temperature obtained by the method outlined above. When critical temperature measurements have been completed, an attempt will be made to solve the difficult problem of measuring pressure at these high temperatures in order to obtain actual measurements of critical pressures.

Table I-18

ESTIMATED CRITICAL CONSTANTS OF THE ALKALI METALS;
CRITICAL CONSTANTS FOR MERCURY

Metal	Molecular Weight	P_c (atm)	T_c (°K)	D_c (g/cc)	V_c $\left(\frac{\text{liters}}{\text{g mole}}\right)$	Compressibility
						Factor $\left(Z_c = \frac{P_c V_c}{RT_c}\right)$
Rb	85.48	190 ^a	2190 ^b	0.32	0.267	0.282
Cs	132.91	180 ^a	2150 ^b	0.42	0.316	0.322
Na	23.00	490 ^a	2780 ^b	0.18	0.128	0.275
K	39.10	240 ^a	2440 ^b	0.18	0.217	0.260
Hg	200.61	1587	1733	4.7	0.043	0.477

^a $P_c = \pm 10\%$.

^b $T_c = \pm 300^\circ\text{C}$.

¹³ P.F. Young and D.E. Deutsch, Design and Operation of 1800°F Pumped Boiling Rubidium Loop System and Determination of Density and Vapor Pressure of Rubidium between 174 and 1800°F, USAEC Report AGN-8034, March 1962.

¹⁴ C.F. Bonilla, D. L. Sawhney, and M.M. Makansi, Vapor Pressure of Alkali Metals, Rubidium, Cesium, and Sodium-Potassium Alloy (NaK) up to 100 psi, Transactions Quarterly, American Society for Metals (ASM), 55, No. 3, 877-890 (September 1962).

Based on the best current data, estimates¹⁵ are given in Table I-18 for the critical constants of the alkali metals sodium, potassium, rubidium, and cesium (mercury, which is included also, is to be used for calibration purposes because data are known for it over the entire range from melting point to the critical temperature).

Figure I-39

APPARATUS FOR DETERMINATION OF CRITICAL TEMPERATURES OF ALKALI METALS

Proposed Work

It is proposed to use the equipment shown in Figure I-39 to measure the critical temperature and critical density of rubidium and cesium. The density of the liquid and of the vapor will be measured by the amount of gamma radiation from appropriate radioactive isotopes (see Table I-19). The critical temperature, that temperature at which the gamma ray measurements will indicate equal vapor and liquid densities, will be measured by a tungsten-5% rhenium/tungsten-26% rhenium thermocouple if a suitable calibration can be made; if not, by an optical pyrometer reading of the temperature of the molybdenum-tungsten block (a 2-in. diameter x 5-in. long cylinder of molybdenum-30 w/o tungsten alloy). Heating will be accomplished by inductively heating the molybdenum-30 w/o tungsten block.

¹⁵ A. V. Grosse, The Liquid Range of Metals and Some of Their Physical Properties at High Temperatures, USAEC Report NP-10795, September 5, 1960.

Reaction of the block with the tungsten carbide insulation will be prevented by means of a tantalum can. The assembly, consisting of the tungsten carbide insulation, molybdenum-tungsten block, and container crucible, will be mounted in an evacuated furnace. The electronic counting equipment and the optical pyrometer will be outside the furnace. Radiation measurements will be made through collimation holes. Since critical constants and density data are known for mercury, this metal will be used to compare values obtained with this equipment with previously reported values.

Table I-19

RADIOACTIVE ISOTOPES TO BE USED IN DETERMINING
CRITICAL CONSTANTS OF ALKALI METALS

<u>Isotope</u>	<u>Half-life</u>	<u>γ energy (Mev)</u>	<u>Precursor (n, γ reaction)</u>	<u>Relative Abundance of Precursor (%)</u>
Rb ⁸⁶	18.7 d	1.08	Rb ⁸⁵	72.15
Cs ¹³⁴	2.1 y	0.605	Cs ¹³³	100
K ⁴²	12.5 hr	1.53	K ⁴¹	6.88
Na ²⁴	15 hr	2.75	Na ²³	100
Hg ^{203^a}	47 d	0.28	Hg ²⁰²	29.8

^aTo be used for calibration purposes, since critical data for mercury have been determined experimentally.

Preliminary experiments have been made to determine the temperature distribution in the bomb, which is a molybdenum-30 w/o tungsten cylinder, 2 in. in diameter by 5 in. long. The configuration used is shown in Figure I-40. An induction coil has been designed and constructed that gives 80% transmission of power from the 30-kw generator to the Mo-30 w/o W cylinder. The temperatures obtained to date indicate there will be no difficulty in obtaining the desired temperatures of 1900-2500°C. Temperatures have been measured using both an optical pyrometer and tungsten-5% rhenium/tungsten-26% rhenium thermocouples. At present, the two methods of temperature measurement agree at high temperatures (>1900°C) within 25°C. The initial configuration used had an outside diameter of 4 1/2 in. and a length of 7 1/2 in. Initial temperature measurements showed that there were large temperature gradients in both axial and radial directions in the molybdenum-30% tungsten block, and indicated that more insulation was needed in both the axial and radial directions. Use of a larger configuration (5 3/4-in. OD x 9 1/2-in. long) has given a more uniform, but yet not completely satisfactory, temperature distribution.

Figure I-40

PROPOSED DESIGN OF ASSEMBLY FOR DETERMINATION OF
TEMPERATURE DISTRIBUTION IN AN INDUCTIVELY
HEATED Mo-30 w/o W CYLINDER

A test capsule has been designed, as shown in Figure I-41. This capsule is sealed initially by driving the tapered plug through the tantalum gasket. The plug is then welded to the capsule to complete the closure. One test capsule has been sealed merely by driving the tapered plug through the tantalum gasket. A leak test by means of a helium mass spectrometer indicated no leak through the tantalum gasket seal. Initial sealing by means of the tapered plug will allow charging of the capsule with alkali metal under high vacuum, and then removing the capsule to an inert atmosphere for welding.

A 1-in. long by 1/2-in. OD molybdenum-30 w/o tungsten cylinder was irradiated in the CP-5 reactor for 14 days at 10^{12} n/(cm²)(sec). This was done to indicate the background contribution of the container metal to the total activity of an irradiated alkali metal in

Figure I-41

TEST CAPSULE FOR CONTAINMENT OF ALKALI METALS

a capsule of nearly the same outside dimensions. The data shown in Figure I-42 indicate that 30 days cooling will be required for sufficient decay of radiation from the capsule to permit contact handling, although after 21 days the material could be handled with tongs. The shape of the curve indicates that the activity is due primarily to two isotopes - namely, tungsten-187 having a half-life of 24 hours and molybdenum-99 having a half-life of 66 hours.

Figure I-42

GAMMA RADIATION FROM AN IRRADIATED MOLYBDENUM-30 w/o TUNGSTEN CYLINDER

Cylinder 1/2-in. OD x 1 in. long.
Irradiated 14 days at a flux of 10^{12} n/(cm²)(sec)

108-7302

High-purity cesium has been received, and the manufacturer's analysis is as follows:

<u>Element</u>	<u>w/o</u>	<u>Element</u>	<u>w/o</u>
K	0.014	Mn	ND<0.0001
Na	0.008	Ni	ND<0.0001
Li	0.013	Si	<0.0001
Rb	0.018	Tl	ND 0.0005
Al	0.002	Ti	ND 0.0001
Ca	ND ^a <0.0001		
Cr	<0.0001	Total	0.056
Cu	<0.0005		
Fe	<0.0001		
Pb	ND <0.0001		
Mg	<0.0001		

^a ND = not detectable. The number following ND is the limit of detection.

This analysis was undoubtedly on an oxygen-free basis. Since the amount of oxygen present is important from the standpoint of both corrosion and the determination of critical temperature, an oxygen analysis of the sample was made by the mercury extraction method used for sodium. The oxygen content was found to be 0.0127 weight percent. This is larger than is desirable, but may not be high enough to cause great difficulty.

It is hoped that the data obtained in the proposed work will give greater insight into the nature of metals and that it will be possible to develop a reduced equation of state applicable to metallic fluids.

3. Reactor Materials (R. K. Steunenberg)

Pyrometallurgical methods for the preparation of nuclear fuel materials are being investigated. Refractory compounds of the actinide elements that are of interest as high-performance reactor fuels are being prepared for fabricability evaluations and irradiation testing. A second objective is to develop techniques by which the metallic products of liquid metal fuel processes can be reconverted to refractory compounds such as uranium and plutonium carbides. By combining these techniques with the head-end procedures and the liquid metal separations processes described in preceding sections of this report, there is a possibility of developing a complete processing cycle for uranium-plutonium carbide fuels.

Metallic fuel materials can be prepared by the direct reduction of actinide oxides or halides from a molten salt flux with liquid metal solutions containing magnesium.

Experimental results that were obtained during the reporting period concern the preparation of uranium and plutonium carbides, uranium sulfides, and plutonium metal.

a. Preparation of Uranium Monocarbide
(E. J. Petkus, M. A. Bowden)

The liquid metal process for the preparation of UC involves the following steps: (1) dissolution of metallic uranium in a zinc solution containing 14 to 18 w/o magnesium, (2) addition of a degassed carbonaceous material (usually activated charcoal) somewhat in excess of the stoichiometric requirement to form UC, (3) reaction of the constituents with stirring for about 8 hr at 800°C, (4) a phase separation to remove the bulk of the supernatant liquid metal and excess carbon from the precipitated UC, and (5) vacuum distillation to remove residual magnesium and zinc from the product. It has been demonstrated that UC prepared by this method has good pressing and sintering properties. The main objective of the present work was to produce carbide having a carbon content near the theoretical value of 4.80 w/o (for UC) and as low an oxygen content as possible.

Seven preparations on a scale of 200 to 500 g each have been completed to date, using the equipment described in ANL-6725, p. 79. Two of these products have been transferred to the Metallurgy Division for evaluation. Analytical results are available for the products of the first five runs and are presented in Table I-20. The lowest oxygen content was 0.29 w/o in Run UC-5. The total carbon content varied between about 5.4 and 5.9 w/o. Since in early runs some of the added carbon did not react with the uranium, an excess quantity of carbon was used in the charge. This excess is being decreased in current runs in an attempt to approach the theoretical carbon content of the UC product more closely.

In an attempt to determine the main sources of oxygen contamination, the starting materials were analyzed for oxygen. These results are presented in Table I-21. As expected, the major source of oxygen contamination was the activated charcoal, which contributed about 73% of the total oxygen in the starting materials. Although the activated charcoal that was used in these runs had been degassed by heating under vacuum, it was thought that the handling procedures were inadequate to assure the absence of air contamination. Improvements in the apparatus and techniques used for the charcoal degassing step are reflected in the lower oxygen content of the UC from Run UC-5 (Table I-20). An effort is also being made to reduce the oxygen contamination by using other forms of finely divided carbon that have lower surface areas for the adsorption of gases. However, it is suspected that a decreased surface area may result in a slower reaction of the carbon with the uranium in the solution.

The helium-vacuum glove box, in which the starting materials were charged and the UC product recovered, was evacuated every night and recharged with fresh helium in order to reduce the amounts

Table I-20

PREPARATIONS OF UC BY THE LIQUID METAL PRECIPITATION METHOD

Reaction Temperature:	800°C				
Duration of Reaction:	8 hr				
Mixing Speed:	350-400 rpm				
Solvent:	14-18 w/o Mg in Zn				
	Run UC-1	Run UC-2	Run UC-3	Run UC-4	Run UC-5
Charge (atom ratio, C/U)	1.20	1.20	1.20	1.20	1.20
Method of Phase Separation	none	pour	pour	pressure siphon	pressure siphon
Product Yield (g)	456	393	233	474	398
<u>Chemical Analyses of Products</u>					
Uranium Content (w/o) ^a	87.5	92.0	90.0	92.5	93.8
Total Carbon Content (w/o)	5.60	5.40	5.40	5.86	5.56
Free Carbon Content (w/o)	3.1	0.80	1.2	1.32	1.06
Total C/U (atom ratio)	1.27	1.16	1.19	1.26	1.18
Free C/U (atom ratio)	0.70	0.17	0.26	0.28	0.22
Oxygen (w/o)	2.52	0.39	0.60	0.61	0.29
Nitrogen (ppm)	700	380	380	60	10
Magnesium (w/o)	0.16	0.19	1.02	0.20	0.15
Zinc (w/o)	0.37	0.52	1.49	0.58	0.31
<u>X-Ray Diffraction Result</u>					
Species	UC	UC	UC, UO ₂ ^b	UC	UC
Lattice Parameter (Å) ^c	4.959	4.959	4.959	4.959	4.959
Surface Area (m ² /g)	2.95	2.73	1.86	1.49	0.28

^aTheoretical value for UC, 95.2 w/o.

^bMinor phase.

^cTheoretical value for UC, 4.961 Å.

of moisture, oxygen, and nitrogen in the glove box atmosphere. Calculations based on the levels of these impurities in the helium indicated that less than 0.01 w/o oxygen contamination of the UC product could result from this source of moisture and oxygen.

Contamination of the product by residual zinc and magnesium, which varied from 0.46 to 2.51 w/o total for both elements, resulted from flakes of these metals dropping off the retort cover when the product crucible was removed. This problem is not considered to be serious, as it could be eliminated by changes in the equipment design.

Table I-21

POSSIBLE CONTRIBUTION OF STARTING MATERIALS TO OXYGEN
CONTAMINATION OF URANIUM MONOCARBIDE

<u>Material</u>	<u>Oxygen Content by Analysis</u>	<u>Grams of Starting Material in Typical Run</u>	<u>Total Oxygen (g)</u>	<u>Percent of Total Contribution</u>
Charcoal	1.92 w/o	30.4	0.582	73
Magnesium	64 ppm	510	0.032	4
Zinc	34 ppm	3160	0.107	13
Uranium	157 ppm	500	0.078	10
Total			0.801	100

(Assuming that stoichiometric uranium monocarbide is formed, and that 500 grams of uranium and 25 grams of charcoal are used:

$$\text{w/o oxygen from starting materials} = \frac{0.801 \times 100}{525} = 0.15)$$

In future preparations, emphasis will be placed on decreasing the oxygen contamination, approaching the stoichiometric carbon/uranium ratio for UC, and determining some of the physical properties of the product.

b. Development of New Methods for Carbide Preparation
(J. P. LaPlante, H. E. Griffin, R. D. Wolson)

It was reported previously that UC had been prepared by the reactions of magnesium carbide (MgC_2 or Mg_2C_3) with UF_4 in molten salt media (ANL-6725, p. 78). Subsequent studies have been made to determine if this type of reaction can be used for the preparation of metal carbides in general. Various compounds of several different metals were treated with magnesium carbide in the presence of a molten salt (35.0 m/o LiCl -65.0 m/o MgCl_2). The magnesium carbide was prepared by the reaction of commercial-grade CaC_2 with MgCl_2 .¹⁶ Starting with the reactants UF_4 , U_3O_8 , MgUO_4 , ZrO_2 , SiO_2 , NaWO_3 , V_2O_5 , $\text{V}_2\text{O}_2\text{Cl}_4$, TaO_2 , and NaMoO_4 , the following products were found by X-ray diffraction: UC, UC_2 , ZrC, β -SiC, WC, α - W_2C , VC, TaC and Mo_2C . No attempt was made at the time to isolate the pure carbides.

¹⁶A. Schneider and J. F. Cordes, Z. anorg. u. allgem. Chem. 279, 94 (1955).

A single experiment was performed to establish whether uranium carbides could be prepared in the molten salt flux by addition of magnesium and carbon, rather than MgC_2 or Mg_2C_3 . A negative result from this experiment indicated that the presence of magnesium carbide is necessary for the reaction to occur.

Because of the unavailability of high-purity CaC_2 to be used as a starting material for the preparation of MgC_2 or Mg_2C_3 , the preparation of magnesium carbides by the reactions of magnesium metal with acetylene or pentane¹⁷ is being investigated. The yield of MgC_2 from the magnesium-acetylene reaction was low, and a large amount of free carbon was formed. The preparation of Mg_2C_3 by the reaction of magnesium metal with pentane is currently being investigated.

c. Preparation of Plutonium Carbides
(J. F. Lenc, J. R. Pavlik, J. D. Schilb)

The objective of this study is to evaluate various methods for the preparation of plutonium carbides. Initially, consideration was given to liquid metal precipitation processes, since such a procedure might permit simultaneous precipitation of uranium and plutonium carbides as solid solutions. Three scouting experiments were performed, in which cerium was used as a stand-in for plutonium. In the first two experiments, a cerium carbide was precipitated on the addition of activated charcoal to cerium dissolved in zinc-magnesium solutions. In the third experiment, spectrographic-grade graphite was added instead of activated charcoal. It was thought that less oxygen contamination of the product might result from the use of graphite because of the lower surface area that would be available for adsorption of air and moisture. The graphite, however, failed to precipitate the cerium. Apparently, the reduced surface area retarded the rate of reaction with dissolved cerium. X-ray diffraction analyses of the products from the two experiments with activated charcoal showed only the presence of CeC_2 . In a similar experiment performed earlier (ANL-6333, p. 75), X-ray analyses showed Ce_2C_3 as the principal phase, with indications that traces of CeC_2 and alpha cerium might have been present.

The current effort is being concentrated on the reaction of Mg_2C_3 with PuCl_3 . The initial studies of the Mg_2C_3 - PuCl_3 reaction have been limited to scouting experiments in a low-purity nitrogen atmosphere, this being the only facility that was available at the time. In the first experiment (Run PC-1), about 5 g of plutonium metal was dissolved in 600 g of zinc at 800°C in the presence of 300 g of a 35 m/o LiCl -65 m/o MgCl_2 salt phase. After dissolution of the plutonium, the melt was cooled to 500°C. Sufficient ZnCl_2 was added at this point to oxidize the plutonium to PuCl_3 on reheating to 800°C. Analyses of samples of the metal and salt phases showed that approximately 97% of the plutonium had been oxidized and extracted into the salt. The salt phase, after solidification, was separated from the zinc and divided into two portions, designated A and B. Portion A weighed 124 g and contained about 2.2 g of plutonium. Portion B weighed 161 g and contained about 2.65 g of plutonium.

¹⁷F. Irmann, *Helv. Chim. Acta*, 31, 1584 (1948).

Portion A of the salt was charged into a graphite crucible-condenser assembly inside a stainless steel retort together with about 0.25 g of Mg_2C_3 . The charge was heated to 650-675°C to permit the Mg_2C_3 to react with the PuCl_3 in the salt. After one-half hour, the retort was evacuated to less than 0.1 torr to remove the volatile components of the system (mainly LiCl and MgCl_2) by vacuum distillation. The distillation required about three hours and was completed at a temperature of 890°C and a pressure below 0.03 torr. X-ray diffraction analysis of the residue indicated only PuOCl , with no evidence for plutonium carbides. Failure of the reaction to produce plutonium carbides was attributed to the presence of moisture in the hygroscopic salts that were used in the experiment.

Portion B of the salt was used in a second experiment, which was conducted in substantially the same manner, except that the amount of Mg_2C_3 was increased by a factor of about eight (from 0.25 to 2 g) in an attempt to eliminate the oxygen-bearing species in the salt first, then to bring about the reaction of PuCl_3 with Mg_2C_3 . The product from this experiment was identified by X-ray diffraction as being primarily Pu_2C_3 with the possibility of minor amounts of PuOCl .

Plans have been made for future experiments in high-purity inert atmospheres in which attempts will be made to prepare mixed carbides of uranium and plutonium through the reaction of Mg_2C_3 with mixtures of the respective trichlorides in the 35 m/o LiCl -65 m/o MgCl_2 molten salt medium.

d. Preparation of Uranium Monosulfide (S. Vogler, J. A. Trischan)

The objective of this work is to prepare US that is suitable for evaluation as a reactor fuel material. A product of known composition and controlled impurity content is desired. In order to achieve this objective, characterization of the US by appropriate chemical and physical methods is necessary.

The preparative method of Eastman and coworkers¹⁸ was used to produce US in batches of 100 to 300 g. This procedure consists of three steps: (1) bulk uranium metal is hydrided and dehydrided to produce finely divided uranium metal powder, (2) the uranium powder is treated at 400 to 500°C with the stoichiometric quantity of H_2S required to form US, and (3) the resulting mass of metallic uranium and higher uranium sulfides is ground, sieved, mixed, and heated in vacuum to about 1900°C to form homogeneous US. All steps of the preparation are conducted in vacuum or under high-purity inert atmospheres to avoid contamination of the product.

Previous preparations of US on a smaller scale had produced a product of inadequate purity, as indicated by chemical analyses and

¹⁸E. D. Eastman, et al., J. Am. Chem. Soc., 72, 4019 (1950).

lattice parameters obtained by X-ray diffraction. These impurities, mainly nitrogen and carbon, proved to be contaminants of the H_2S that was used. By condensing the H_2S in a liquid nitrogen cold trap under vacuum, it was found that the levels of these impurities were reduced substantially.

Table I-22

ANALYSES OF URANIUM MONOSULFIDE PREPARATIONS

Scale: 100-300 g (Material prepared by the reaction of H_2S with hydrided-dehydrided uranium. Product is then ground, sieved, mixed, and homogenized under vacuum at $1900^\circ\text{C}.$)

Run No.	Total Uranium ^a (w/o)	Total Sulfur ^b (w/o)	S/U (atom ratio)	X-Ray ^c (Å)	Insolubles (w/o)	Oxygen (w/o)	Nitrogen (w/o)	Carbon (w/o)
52	87.50	12.20	1.04	5.485	<0.01	0.088	<0.0010	0.038
51	87.96	12.06	1.02	5.490	0.03	~0.2	0.0053	0.017
57	87.90	12.10	1.02	5.490	0.19	0.09	<0.001	0.013
58	87.89	12.03	1.016	5.490	0.13	0.12	0.011	0.042
59	87.95	11.88	1.003	5.489	0.09	0.075	0.0024	0.063
62	88.02	11.86	1.00	5.489	0.01			
54	87.98	11.73	0.99	5.489	0.03	0.21	0.007	0.028
55	88.10	11.62	0.98	5.485	0.19	0.13	0.009	-
56	88.42	11.29	0.95	5.484	1.3	0.13	0.006	-

^aDetermined by ignition of the sulfide to U_3O_8 .

^bDetermined gravimetrically, after oxidation of sulfide to sulfate.

^cLattice parameter.

Analytical data for the current preparations of US are listed in Table I-22. The variations in sulfur/uranium ratio from 0.95:1 to 1.04:1 should provide a reasonable range for determinations of the effect of this parameter on the sintering characteristics of the material. Lattice parameters of 5.489 or 5.490 Å were obtained for products in which the sulfur/uranium ratios were between 0.99:1 and 1.02:1. At both higher and lower sulfur/uranium ratios, the lattice parameter was decreased. This result confirms the data of other investigators,¹⁹ who reported a range of solubility in this region of the uranium-sulfur system.

Since UC and UN have the same structure as US, but much smaller lattice parameters, the presence of these impurities as solid solutions should result in a decreased lattice parameter of the product. The effect of oxygen contamination is more obscure. However, the results from Runs 51, 57, and 58, which all show sulfur-uranium ratios of 1.02:1, indicate that the limited variations in the impurity content did not affect the

¹⁹A value of 5.490 Å for US is reported by Cater, E. D., P. W. Gilles and R. J. Thorn, J. Chem. Phys. 35, 608 (1961).

lattice parameters appreciably. The data in Table I-22 suggest that the sulfur/uranium ratio has a greater effect on the lattice parameter of the US product than do the impurities at these concentrations.

The US product is readily soluble in 3.6 N H_2SO_4 , with the evolution of H_2S . However, UO_2 and UOS are insoluble in this reagent. Dissolution of US in H_2SO_4 solution is therefore used frequently as a method of determining the UO_2 and UOS as an insoluble residue. The data in Table I-22 suggest that the insoluble residues in H_2SO_4 solution constitute an unreliable index of the oxygen content of US. This conclusion is exemplified by a comparison of the results from Runs 51 and 57. It is suspected that oxygen which is present as a solid solution in US does not form an insoluble phase in H_2SO_4 solution.

A few additional preparations of US by this method are being made to provide material for fabricability testing by the Metallurgy Division.

e. Direct Reduction of Plutonium Dioxide to Metallic Plutonium
(J. B. Knighton, J. D. Schilb)

A demonstration experiment has been performed in which PuO_2 suspended in a molten halide flux was reduced to plutonium metal by means of a magnesium-zinc alloy. The charge consisted of a total of 600 g of metal (540 g of zinc and 60 g of magnesium), 300 g of flux (47.5 m/o CaCl_2 -47.5 m/o MgCl_2 -5.0 m/o MgF_2), and 35.65 g of PuO_2 (sufficient to produce 30 g of plutonium metal upon complete reduction). The reactants were heated to 800°C and agitated at 800 rpm for 2 hr in a tantalum crucible. At the end of the reduction period, the contents of the crucible were poured into a graphite mold. The metallic ingot was cleaned to remove adhering flux, combined with a magnesium-zinc wash ingot (used to remove any unpoured plutonium remaining in the tantalum crucible), and charged to a cone-shaped tantalum distillation crucible.

The system was evacuated overnight at about 20_μ pressure; then heat was applied. The bulk of the zinc was removed by vacuum distillation at 500°C . Final removal of the zinc and magnesium was then attempted at 700°C . Examination of the residue showed that an unconsolidated irregular metallic product remained in the conical crucible. The weight of the residue was considerably greater than 30 g, probably because of the presence of a plutonium-zinc intermetallic compound as well as plutonium metal. Additional magnesium was added, and the distillation was repeated at 700°C . After this treatment, the residue weighed 30.15 g, a value in reasonable agreement with the 30 g of plutonium that would have been formed upon complete reduction of the PuO_2 in the original charge. Analysis of the flux for plutonium indicated a reduction yield in excess of 99%.

A 7.5-gram sample of the product was removed from the crucible and submitted for spectrochemical analysis. The results are shown in Table I-23. It appears that plutonium metal of good purity can be produced

in high yield by this method. A process based on this technique would have the advantage that the oxide, rather than the fluoride of plutonium, can be used as a starting material, thereby decreasing greatly the radiological hazard associated with the (α , n) reactions involved in handling plutonium compounds.

Table I-23

ANALYSIS OF PLUTONIUM METAL PRODUCED BY Mg-Zn
REDUCTION OF PuO₂

Sample taken from 30 g of Pu
metal prepared by Zn-Mg
reduction of PuO₂ in 47.5 m/o
CaCl₂-47.5 m/o MgCl₂-5.0 m/o MgF₂

<u>Element</u>	<u>Conc'n. in PuO₂ Starting Material (ppm)</u>	<u>Conc'n. in Pu Metal Product (ppm)</u>
Al	180	100
B	1	<2
Ba	1	<1
Ca	140	25
Cr	100	1
Fe	100	75
K	10	<5
Mg	300	85
Mn	30	10
Na	50	<5
Ni	90	25
Pb	8	10
Sn	<5	10
Sr	<0.5	<0.01
Zn	<5	15

B. Fuel Processing Facilities for EBR-II
(J. H. Schraidt, M. Levenson, L. F. Coleman)

A direct-cycle fuel reprocessing plant based on pyrometallurgical procedures was designed and is being constructed as part of the Experimental Breeder Reactor No. II (EBR-II) Project. 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. Status of Fuel Cycle Facility

a. Building and Building Services

(J. O. Ludlow, M. A. Slawewski, H. L. Stethers)

(1) Preparation for Argon Filling of Argon Cell

During the time that the Argon Cell was filled with nitrogen for air in-leakage tests, a bearing started to fail in the nine-stage centrifugal compressor after about 1000 hours of operation in the argon purification system. The difficulty was indicated by a rise in temperature measured by a resistance thermometer and an increase in bearing noise measured by a microphone. (A resistance thermometer and a microphone are permanently mounted on each bearing of essential equipment in the Fuel Cycle Facility.) The compressor was dismantled and examination of the bearing indicated that inadequate lubrication was the cause of the difficulty. This could have been caused by either incorrect initial lubrication or degradation of the lubricant as a result of high service temperature and the extreme dryness of the nitrogen atmosphere in which the bearing had been operated.

The two bearings on the compressor as well as the two bearings on the drive motor were replaced with new ones. Visplex EP1 grease* was used to lubricate one bearing on the compressor and one bearing on the motor, whereas Sinclair EP1 grease** was used to lubricate the other two bearings. Both greases are recommended for use at high temperatures in atmospheres where the water vapor content may be low. The Visplex grease has been used successfully in dry helium atmospheres of low-oxygen content in the Fuel Fabrication Facility at Argonne National Laboratory, Lemont. After lubricating the new bearings, the compressor and drive motor were returned to service and have been in operation for about 1600 hours without evidence of bearing deterioration.

The removal of the compressor (and drive motor) from its enclosure for repairs was difficult. The enclosure has been modified to overcome the difficulty in removing these equipment items. Fittings and valves have been installed to permit the installation of a second compressor and enclosure at a later time, without interrupting the operation of the argon purification system.

Installation of a 0-1000 ppm range oxygen analyzer in the Argon Cell gas purification system was completed. This instrument will supplement the present 0-100 ppm oxygen analyzer and will be particularly useful during start-up and leak hunting operations.

*A product of the Viscosity Oil Co.

**A product of the Sinclair Refining Co.

The argon pressure control system²⁰ was modified so that the Argon Cell could be maintained at either constant pressure (constant difference between the cell absolute pressure and atmospheric pressure) or at a constant temperature. Maintaining the cell at a constant, high (about 100°F) temperature may prove desirable in order to limit the damage to the shielding windows from disruptive discharges of the stored electrical charge in the glass which is induced by high gamma dosages. The system was modified after the nitrogen in the Argon Cell had been replaced with air. After this modification to the argon pressure control system, the Argon Cell was sealed, and the control system was operationally tested. The control system operated satisfactorily with either temperature or pressure as the controlled variable.

While maintaining the cell at a pressure less than atmospheric, tests to check the air in-leakage rate by the cell gas inventory method (see ANL-6687, p. 63) were carried out. The test results indicated higher air in-leakage rates than could be allowed. Leak testing of cell penetrations disclosed a number of small air leaks which were repaired.

(2) Argon Filling of Argon Cell

On August 6, 1963, argon gas was introduced into the Argon Cell of the EBR-II Fuel Cycle Facility. However, only 80,000 standard cubic feet of argon gas, instead of the 110,000 standard cubic feet, was delivered for this purpose, owing to difficulties that the vendor experienced with his equipment. The air concentration was reduced to about 5 percent as a result of the argon fill. After the fill had been completed, the argon purification system was started. (In this purification system, the oxygen is removed from the atmosphere by catalytically reacting the oxygen with added hydrogen and removing the resulting water by means of a desiccant.) The flow rate through the purification system was 175 scfm. After nine days, during which the purification system was usually operated only on the day shift, the concentrations of impurities in the argon gas were as follows: nitrogen, about 4.3 percent; oxygen, less than 50 ppm; and water, less than 200 ppm.

Periodically, the rate of in-leakage of air was determined by noting the rate of increase in the oxygen concentration during an overnight period. During these air in-leakage test periods, the addition of hydrogen to the catalyst bed was stopped so that there was no oxygen removal, and the pressure in the cell was maintained at a negative pressure

²⁰ Schraidt, J. H., Coleman, L. F., Holcomb, W. F., Levenson, M., and Ludlow, J. O., "Establishing and Maintaining a High Purity Atmosphere in EBR-II Fuel Cycle Facility Argon Cell," Proceedings of the Eleventh Hot Laboratories and Equipment Conference, New York, N. Y., November 18-21, 1963, pp. 181-190.

of 2 to 4 inches of water. By mid-September, the test results showed that the rate of air in-leakage was reduced to 0.0048 scfm. At that time, the impurity concentrations in the cell argon were as follows: oxygen, 45 ppm; water, 45 ppm; and, nitrogen, 5.15 percent.

The purification system is usually operated only on the day shift; therefore, the oxygen concentration in the cell argon rises every night and over the weekend. It is this intermittent operation of the purification system that causes the minimum oxygen concentration to be about 50 ppm. However, if the purification system were operated continuously with the addition of the stoichiometric requirement of hydrogen and if the in-leakage rate were to remain at 0.0048 scfm, calculations show that the concentration of oxygen in the cell could be reduced to 6 ppm and maintained at this level. The advantages of maintaining such a low level of oxygen would not, however, compensate for the additional work which would arise from continuous operation of the purification system.

(3) Argon Cell Entry by Personnel

Personnel wearing self-contained air masks have entered the Argon Cell while the cell contained argon gas in order to carry out repairs on the cell manipulators. An air bottle having a capacity of 40 cubic feet of air was carried by each individual entering the cell. With this air supply, the useful working time per entry averaged 14 minutes. Each entry into and exit from the cell required 4 minutes. Thirteen entries were made; these introduced approximately 2200 standard cubic feet of air into the cell. This resulted in a maximum water vapor concentration of 250 ppm; and maximum nitrogen and oxygen concentrations (estimated) of 7.9 and 0.8 percent, respectively. Four days after the last entry, the argon atmosphere contained 7.2 percent nitrogen, 10 ppm oxygen, and 40 ppm water vapor.

(4) Failure of Fan Motor in Argon Cell Cooling System

The Argon Cell cooling system consists of two subsystems, each subsystem containing refrigerated coils and a 15,000 cfm direct motor driven vaneaxial fan. The fan in one of the subsystems failed after being in operation for several weeks in the argon atmosphere. The subsystem was isolated by closing two 24-in. butterfly valves (which sealed without detectable leakage), and the fan and motor were removed for inspection and repair. Inspection of the motor showed that arcing, which had occurred in one of the field coils of the field winding, destroyed most of the coil and shorted the winding. The motor was then rewound and reassembled. The fan and motor were reassembled, adjusted, and tested electrically and vibrationally. These units were then reinstalled in the cooling system.

The failure of the fan motor might have been due to some factor unique to the dry argon atmosphere in which the motor was run. It is known that dry atmospheres cause deterioration of many electrical insulations

and that argon is less efficient than air when used as a heat transfer agent or an electrical insulator. However, the exact effect that a dry argon atmosphere will have upon a conventional electric motor is not known. The resistivity of the winding insulation on each of the motors of the two cooling system fans is being measured weekly in order to detect deterioration of the insulation. If such deterioration is detected, examination of the insulation, prior to complete failure, may reveal the cause of the deterioration.

(5) Dry Argon Compressor System

Two 2-stage reciprocating compressors, each providing 80 scfm at 100 psig, are installed on the service floor to provide compressed argon for the operation of various equipment items in the Argon Cell such as valves and pneumatic cylinders. Argon for the compressors is supplied from the Argon Cell. The compressors and their associated controls have been in operation since the Argon Cell was filled with argon (August 6, 1963). The operation of the system has proved satisfactory. However, rapid wear of the piston rings (Teflon impregnated with carbon) in the argon compressors has occurred. (In the two-stage compressors, there are two piston rings in the low pressure stage, and one piston ring in the high pressure stage.) The particles worn from the piston rings have been transmitted into the high pressure argon system and have caused malfunction of some of the pressure reducing valves in the system. The carbon-impregnated Teflon piston rings were recommended and supplied by the compressor manufacturer for use in a dry argon atmosphere of low oxygen content.

One compressor has been operated for about 760 hr, during which time one piston ring had worn to within 0.007 in. of the piston wall. Measurements of the piston rings after 600 and 760 hr showed that the maximum wear rate was about 2.5×10^{-5} in./hr. The second compressor has been operated for about 640 hr. After 490 hr of operation, one of the piston rings on this compressor had worn to within 0.017 in. of the piston wall.

The piston rings in both compressors are to be replaced; one compressor will have Fiberglass-impregnated Teflon rings and the other will have new rings of carbon-impregnated Teflon. At the Fuel Fabrication Facility at Argonne National Laboratory, piston rings of Fiberglass-impregnated Teflon have provided good service in compressors which handle dry helium of low oxygen content (see ANL-6677, p. 398). The useful life of Fiberglass-impregnated Teflon piston rings was 7800 hr or more, and the wear rate was 1.3×10^{-6} in./hr. New piston rings of Fiberglass-impregnated Teflon will be installed in one of the argon compressors. New carbon-impregnated Teflon piston rings will be installed in the other argon compressor to determine if the previously observed high wear rate was due to some factor which was specific to the start-up of the system. The wear rates of the piston rings in both compressors will be periodically determined.

b. Air Cell and Argon Cell Cranes
(J. Graae, W. Voss, R. Vree)

One 5-ton crane is installed in the Air Cell and two are installed in the Argon Cell. The design of the Air Cell crane differs from that of the crane in the Argon Cell in that the movement of the bridge in the Air Cell is rectilinear, whereas the movement of each bridge in the Argon Cell is radial about a center pivot. Electrical connections to the Air Cell crane are through bus bars which hang from the ceiling and through spring-loaded sliding collectors mounted on the crane bridge. Electrical connections to the Argon Cell cranes are through slip-rings mounted around the center post of the Argon Cell and through spring-loaded brushes mounted on the crane bridges. The trolleys for the cranes in both cells are identical in design and are interchangeable.

The crane bridges in the Argon Cell are numbered 1 and 2. The crane bridge in the Air Cell is numbered 3. The crane trolleys are numbered 1, 2 and 3. Since the trolleys are interchangeable, a crane sometimes has a bridge with one number and a trolley with another number.

Time meters are used to record the total accumulated running time of each motor. By September 30, 1963, the total accumulated running times (in hours) were as follows:

<u>Motor</u>	<u>Crane Bridge No. 1</u>	<u>Crane Bridge No. 2</u>	<u>Crane Bridge No. 3</u>
Drive Motor No. 1	16.0	31.6	31.1
Drive Motor No. 2	34.6	26.0	—

<u>Motor</u>	<u>Crane Trolley No. 1</u>	<u>Crane Trolley No. 2</u>	<u>Crane Trolley No. 3</u>
Hoist	92.7	71.4	112.2
Drive	27.7	22.8	30.8

Each Argon Cell crane bridge has two drive motors, each of which alone can drive the crane bridge. Each motor is independently controlled from the Operations Control Room and only one of the motors on a crane bridge is in use at a time. There is only one drive motor on the Air Cell crane bridge.

Once reprocessing of radioactive fuel has commenced, direct personnel access to these cells will be virtually impossible. Therefore, a considerable effort has been spent on making the cranes (and all other mechanical equipment in the cells) reliable and remotely maintainable. As a consequence, modifications to the cranes have been made in the field when

operating experience revealed the need for a change. Changes which have been made include the following:

- (1) Electrical sliding collector assemblies have been modified to permit free movement and alignment with the bus bars (see ANL-6569, page 68 and ANL-6596, page 94).
- (2) Electrical bus bar supports have been modified to improve bus bar-collector alignment.
- (3) Guide-ins, lifting bails, and similar components have been modified to facilitate the remote removal and replacement of trolley and hoist motor drive units.
- (4) Redesigned bridge drive units with new types of gear reducers have been installed (see ANL-6648, page 100). The redesigned drive units included a locating pin system of a new type which facilitates installation of the drive unit.
- (5) The electrical control circuits have been modified to improve the operations of the controls (see ANL-6569, page 69 and ANL-6648, page 100).
- (6) The limit switches for the bridges and the trolleys have been modified to permit their remote replacement.

In addition to the above changes, all moving parts on these cranes have been reworked, regreased and carefully adjusted.

The No. 2 trolley and hoist drives became inoperable when a short circuit occurred in the seven-conductor mineral-insulated cable which connects the two sets of pick-up brush assemblies on the underside of the trolley. The cable has been replaced, and the trolley is again in operation on the bridge of the Air Cell crane.

The No. 3 trolley has been removed from the bridge of the Air Cell crane because of noise in the hoist gear reducer. When the gear reducer was dismantled, considerable damage was found. The hoist drum shaft extending into the gear box was bent; the inner race of the ball bearing for this shaft was splintered; and the gear case was gouged by the gear on the bent shaft. The hoist cable was flattened as a result of the hoist block having become wedged between the hoist drum and the equalizer pulley.

The damage was caused by a malfunction of the up-limit switch circuit. The limit switch-actuated relay originally installed in the circuit required a high inrush current (6 amp) for its operation. The inrush current of the relay caused an appreciable drop in the circuit wiring and, occasionally, the 24-volt supply of the control system could not provide

sufficient current to actuate the relay. This relay has been replaced with one requiring much less current for its operation, and the failure of the up-limit switch circuit should not recur.

Without the protection of a circuit limit switch, the shaft and shaft bearings for the hoist drum were subject to high overload conditions as a result of the full stalling torque of the hoist motor and the impact from the motor armature which has a gear reduction of about 1700 to 1. The originally furnished gear reducer and drum-shaft were evidently not designed to take such a load. To prevent this overload condition from recurring because of failure of the limit switch circuit, additional measures for protecting the three crane hoists are being studied.

The three crane trolleys, including their hoists, are now operating satisfactorily.

c. Air Cell and Argon Cell Manipulators
(J. Graae, W. Voss, R. Vree)

There are two electromechanical manipulators in the Air Cell and six in the Argon Cell. The designs are basically the same except that the movement of the bridge in the Air Cell is rectilinear, whereas the movement of the bridge in the Argon Cell is radial about a center pivot. Electrical connections to the Air Cell manipulators are bus bars mounted on the cell walls and through spring-loaded sliding collector assemblies. Electrical connections to the Argon Cell manipulators are by means of multiconductor cables which are suspended from a pivot tower in the center of the cell ceiling and plugged into the manipulator bridges.

A large effort has also been spent on making the manipulators reliable and remotely maintainable. However, the field modifications and corrective rework that were performed on the manipulators have not been as extensive as those done on the cranes. To a large extent, major field changes on the manipulators were avoided by incorporating in the final design information developed while operating the prototype manipulator in the mock-up facility of the Chemical Engineering Division. Most of the field work involved has consisted of correcting faulty workmanship and making minor changes in dimensions and materials. Recent changes that have been made to the manipulators include the following:

- (1) The square drive tubes inside the telescoping arm showed gall marks which indicated that these tubes might have been the cause of the occasional sticking of the spline tubes. Two of the four square steel drive tubes in each manipulator were replaced with brass tubes so that a set of drive tubes consisted of steel tubes alternated with brass tubes.

- (2) Many bearings were found to be almost dry of lubricant; thus, all bearings were inspected. Those requiring lubricant were relubricated. It is believed that the lack of lubricant noted in the bearings was due to inadequate lubrication at the time of initial assembly of the bearing.
- (3) The worm-gear drive on top of the arm of each manipulator was provided with a grease shield, and grease was added to the drive housing. The grip now has the specified power (750 lb lift with the dual hook) and operates smoothly.
- (4) All solenoid-operated clutch mechanisms for bridge and carriage drives were reworked to relieve the binding between plunger and solenoid housing, the binding of clutch yoke, and the binding of clutch on drive shaft. To free some of the moving parts of the tendency to stick, they were lapped together with grinding compound. During assembly, all parts were carefully aligned in order to assure free and rapid operation.

Manipulator bridge drives failed on four Argon Cell manipulators (No. 2, 3, 4, and 5) and on one Air Cell manipulator (No. 7) soon after the corrective work on the solenoid clutch mechanisms was completed. The smooth operation of the reworked clutches probably accelerated the deterioration of the bridge drives by increasing the impact loading on the clutch. The failures in the bridge drives occurred in the driven half of the clutch mechanism and were found to be due to shearing of the roll pin (slotted cylindrical spring pins) which connects the driven clutch half to its shaft. The cause of the failure of these pins has been attributed to metal fatigue. Although the pins on the No. 1 and No. 6 Argon Cell manipulators did not fail, examination of the roll pins showed that they were near failure.

When originally installed, the roll pins appeared to be adequate for the intended service. The roll pins are rated for a 7700-lb force in double shear. The gear motor has a rated output torque of 206 in.-lb and a starting torque of about 800 in.-lb. The diameter of the driven clutch shaft is $3/4$ in. The maximum shear force is then, $\frac{800}{1/2 \times 3/4} = 2100$ lb. The safety factor is then, $\frac{7700}{2100} = 3.7$.

However, the operation of the bridge drive mechanism introduces high impact loads which momentarily cause a substantial increase in the torque. The solenoid operated four-jaw clutch in the drive mechanism disengages when power to the bridge is turned off (this allows a manipulator to be pushed by an adjoining manipulator). When the power to the bridge is turned on again, the clutch is usually not in position to engage (the clutch

jaws are riding on top of each other). The drive motor accelerates very rapidly; thus, the clutch jaws may re-engage when the drive motor is turning at full speed, subjecting the drive mechanism to the combined effects of torque and impact.

Calculations based upon drive motor characteristics and the inertia of the bridge indicate that the maximum torque on the clutch may be as high as 1400 in.-lb. The shearing force on the roll pin is increased to 3740 lb, and the safety factor is thus reduced to two, which is not adequate for a reversible type of load. Since roll pins are particularly subject to flexing under load, their failure is attributed to metal fatigue.

The roll pins have been temporarily replaced with solid alloy steel pins which are rated at 14,000 lb in double shear. The pins for the manipulators in the Argon Cell were replaced (while the cell contained high-purity argon) by personnel who entered the cell wearing self-contained air masks, as described earlier in this section of the report.

To prevent future failures of the bridge drives, the following changes are being made in the bridge drive motor and the clutch:

- (1) The armature voltage on the drive motor has been reduced from 115 volts to 80 volts. This change reduces the motor speed from 1725 rpm to 1400 rpm and reduces the torque by one-third.
- (2) The diameter of the driven clutch shaft extension will be increased to 1 in., and a square key (1/4 in. x 1/4 in. x 0.875 in. long) will be used in addition to the pin to secure the driven clutch half to the shaft.

d. Process Equipment Installation
(J. O. Ludlow, M. A. Slawewski)

The spiral decanner²¹ and pin chopper, which removes the stainless steel cans from the fuel pins and cuts the fuel pins to required lengths, is being used to prepare charges for the testing of melt refining furnaces. Unirradiated fuel elements, consisting of depleted uranium-fissium alloy pins which are sodium-bonded to the stainless steel fuel element cans, have been provided for this purpose.

The processing of a charge of approximately 8 kg of un-irradiated, depleted uranium-fissium alloy fuel pins has been carried out

²¹ Simon, J. P., and White, J. R., "Mechanical Decanning of EBR-II Fuel Elements," Proceedings of the Tenth Conference on Hot Laboratories and Equipment, Washington, D. C., November 26-28, 1962, pp. 91-98.

in one melt refining furnace. The poured yield was 90.4 percent of the metal charged. A second melt refining furnace is being prepared for installation in the Argon Cell.

The core subassembly dismantler²² has been remotely installed in the Air Cell. This machine will be capable of remotely disassembling all seven subassembly types currently planned for use in EBR-II.

A run was made in the injection casting furnace²³ using uranium-fissium material. Mechanical operation of the equipment was satisfactory. The as-cast lengths of the pins from this first run were 2 to 4 inches short, but this condition can be corrected by temperature and pressure adjustments to the equipment.

e. Miscellaneous Cell Service Equipment
(G. Bernstein, J. Graae, M. Slaweki)

(1) Storage Racks for Fuel Subassemblies

Two racks have been installed in the Air Cell floor pits for the temporary storage of spent and refabricated fuel subassemblies (see ANL-6725, p. 91). Each rack consists of a cluster of four tubes and fits into a 1-ft dia., 10-ft deep storage pit. Each tube can hold a single subassembly and is adapted to receive core, blanket and control-type subassemblies.

Coolant air for the two racks will be supplied by two lobe-type, positive displacement blowers located in the basement area adjacent to the Air Cell. Each blower can deliver 135 cfm air at about 2 psig, which will be sufficient for cooling eight subassemblies. The blowers will be operated with one blower unit in stand-by condition. Automatic controls will place the stand-by blower in operation should the other blower fail.

A manifold arrangement at the bottom of each cluster distributes the air to each of the four tubes. A spring-loaded valve at the bottom of the tube is opened automatically by the lower end of the subassembly when it is loaded into the tube. The valve has an orifice which allows air to flow through the tube when no subassembly is in the tube. This orifice arrangement reduces the variation in output pressure on the blower which would exist if the empty tubes were completely closed.

A series of tests were made to determine the rate of air flow which must be passed through each stored subassembly in order to

²² Simon, J. P., and Wehrle, R. B., "EBR-II Fuel Dismantling Equipment," Proceedings of the Tenth Conference on Hot Laboratories and Equipment, Washington, D. C., November 26-28, 1962, pp. 99-110.

²³ Jelinek, H. F., and Iverson, G. M., "Equipment for Remote Injection Casting of EBR-II Fuel," Nucl. Sci. Eng., 12, 405-411 (1962).

limit the fuel pin temperatures to safe values. The heat generated in a 15-day-cooled core subassembly from fission product decay will be about 1000 watts (see ANL-6605, pages 21 and 53). A maximum center pin temperature of 600°F is the design goal for storage or transport of a subassembly. The atmospheric pressure at the Fuel Cycle Facility is 12.2 psia. An electrically heated model of a core subassembly (described in the next section of this report) was used for the tests. The electrical input to the heaters was successively adjusted to 340, 770, 1050, and 1500 watts and the center pin temperature determined at each power input with various rates of air flowing through the subassembly. The results are shown in Figure I-43. It was decided, for the conditions previously noted, that a flow of 15 cfm (12.2 psia) would provide adequate cooling of a stored core subassembly. A control rod subassembly has only two-thirds as many fuel elements as a core subassembly and, therefore, would require an air flow rate of about 10 cfm for cooling.

Figure I-43

AIR COOLING TESTS OF CORE
SUBASSEMBLY

(Resistance-heated core sub-
assembly used to simulate
irradiated subassembly.)

Pressure drop data were determined for various rates of flow through an empty storage tube, a core subassembly, a control rod subassembly, and a storage tube containing a core subassembly. Pressure drops for a storage tube containing a control rod subassembly were extrapolated using the test data. The results and the estimates are shown in Figure I-44. The pressure drop through a storage tube containing a core subassembly will be less than 3 in. H₂O when the rate of air flow is 15 cfm (12.2 psia) and the pressure drop through a storage tube containing a control subassembly will be less than 5 in. H₂O when the rate of air flow is 10 cfm (12.2 psia). The rack cooling, which is capable of providing air at a pressure up to 2 psig, will therefore supply adequate cooling for any combination of empty tubes and tubes containing core or control subassemblies.

Figure I-44

PRESSURE DROP FOR AIR FLOW
THROUGH STORAGE TUBES FOR
FUEL SUBASSEMBLIES

108-7261

2. Service Equipment Development

a. Interbuilding Fuel Transfer Coffins (G. Bernstein, A. Chilenskas, M. Slaweki)

Fuel subassemblies containing spent or reconstituted fuel will be transported between the Reactor Building and the Air Cell of the Fuel Cycle Facility in two 20-ton interbuilding fuel transfer coffins (see ANL-6687, p. 65).

One coffin was designed and built by Argonne National Laboratory. This coffin is undergoing final testing at Idaho. The coffin is shown suspended from its lifting yoke in Figures I-45 and I-46. The principal external mechanical features are indicated in the figures.

The body of the coffin consists of a steel cask, approximately 10 ft high and 32-in. OD, in which there is an internal tube, 6-in. ID, that is surrounded by 13 in. of lead shielding. The shielding will reduce the radiation at the surface of the coffin to less than 10 mr/hr. The fuel subassembly is contained in an insert tube which fits the center tube of the coffin.

The fission heat generated in a subassembly which has been irradiated to 2 w/o burnup in 135 days and cooled for 15 days will be approximately 1 kw*. This heat is removed by circulating a gas stream (which may be air or argon) through the subassembly. The gas is cooled in a heat exchanger which surrounds the center tube and which is bonded to the lead body of the coffin. Due to the heat capacity of the large mass of shielding lead, the temperature rise in the lead is less than 4°F per hour.

*Approximately 300 watts of additional heat is developed directly in the shielding lead due to absorption of gamma radiation which escapes from the fuel subassemblies.

Figure I-45

INTERBUILDING FUEL TRANSFER COFFIN - FRONT VIEW

108-7159

The circulation of gas is maintained by a lobe-type blower (on the coffin) shown in Figure I-45. The blower is driven by a 1 1/4 hp, 32-volt d-c motor, which is powered by a 25-cell nickel-iron alkaline battery rated at 30 volts and 300 ampere-hours (the battery is rated for an initial voltage of 35 volts and a final voltage of 25 volts when discharging 300 amp-hr over a 6-hr period). Performance tests on this equipment showed that a fully charged battery can drive the blower at speeds which range from about 1450 rpm initially to about 1100 rpm after 8 hours. These blower speeds are equivalent to blower deliveries of about 32 and 22 cfm of gas, respectively.

Figure I-46

INTERBUILDING FUEL TRANSFER COFFIN - REAR VIEW

108-7158

The usual fuel subassembly transfer operation is expected to require less than four hours. During loading and unloading operations in the Reactor Building, the coffin is also equipped to permit cooling of the subassembly from an external source of coolant. Coolant gas lines are attached to three-way plug valves (shown in Figure I-45), which permit gas circulation from the external source, the blower, or simultaneously from both systems.

Tests have been carried out to demonstrate the heat removal capability of the coffin. A resistance-heated core subassembly was

constructed in order to simulate fission product heating of an irradiated subassembly. In place of the 91 fuel pins contained in a subassembly core, resistance heaters* which were placed in the fuel element cans were used. The 91 resistance heaters were each 14 in. long and 1/8-in. diameter. They were arranged in seven parallel circuits, each consisting of 13 elements connected in series. Each resistance element was rated at 15 watts at approximately 8.5 volts. Temperatures of three elements (center, middle and outer row) were measured by attaching thermocouples to the cans in place of the usual spacer wires. Gas stream temperatures at the inlet and outlet of the subassembly were also measured to establish heat balances. As anticipated, it was found that the temperature of the center pin was highest. A maximum surface temperature of 600°F on the center pin has been chosen as a specification for the operation of the coffin. (This temperature is a conservative value, since pin temperatures in the reactor are approximately 1200°F.)

Separate tests with either air or argon as the coolant gas were conducted in which the removal of heat from a subassembly was measured at several heat input rates and at gas circulation rates of 20 and 30 scfm. The power input to the subassembly core and the flow rate of the gas circulating were held constant until steady state conditions were achieved. Center pin temperatures attained under these conditions are shown in Figure I-47. The lower heat capacity of argon results in higher pin temperatures at given flow rates. The tests demonstrated that the cooling system of the coffin was more than adequate to remove the fission product heat from a spent fuel subassembly.

It is necessary to remove a thin film of sodium which coats the irradiated fuel subassembly when it is discharged from the EBR-II reactor. The sodium will be removed while the fuel subassembly is contained within the transfer coffin. The removal of the sodium will be carried out at the sodium removal station which has been constructed between the Reactor Building and the Fuel Cycle Facility. The procedure (see ANL-6687, page 66) involves the conversion of the sodium to sodium hydroxide and the removal of the sodium hydroxide with a water wash. The transfer coffin cavity and the subassembly is then dried by means of air.

The mechanical operations of this procedure have been successfully demonstrated. However, this procedure has not yet been carried out with a sodium-covered subassembly.

Helium leak tests using a mass spectrometer have been performed on the coffin. The results of these tests indicate that with the coffin pressurized to 2 psig, no measurable leaks were present.

*The resistance heaters were magnesia insulated and stainless steel sheathed and swaged.

Figure I-47

HEAT REMOVAL PERFORMANCE TESTS ON INTERBUILDING
FUEL TRANSFER COFFIN USING AIR OR ARGON AS COOLANT

(Resistance-heated core subassembly used to
simulate irradiated subassembly.)

The second fuel transfer coffin (commercially designed and fabricated) employs an external gas-to-air heat exchanger to remove heat from the circulating coolant gas stream. This system requires a separate air blower for the heat exchanger. In addition to its greater complexity, this system imposes an excessive power drain upon the storage batteries. The coffin is being modified to conform to the Argonne design.

b. Materials Testing

(G. J. Bernstein, P. Kelsheimer, M. A. Slaweki,
H. L. Stethers)

At the conclusion of the nine-week period during which the Argon Cell was filled with nitrogen, the drive motors (direct current; 1/4 hp) for the manipulator grips were examined. An extremely high rate of brush wear was discovered. Although the total running time of these motors in the dry nitrogen atmosphere (as low as 5 ppm water and 8 ppm oxygen) was an hour or less, brushes were worn more than 0.218 in., which is the maximum

allowable wear. These brushes (Stackpole grade 56*) are made of electrolytic graphite and are treated with barium fluoride for high altitude use. The results of earlier brush tests (see ANL-6029, page 21; ANL-6068, page 25; and ANL-6101, page 23) made in an argon atmosphere indicated that the wear rate of these brushes should have been much less than that found. The earlier tests, however, were conducted in a small volume test chamber in which it was difficult to maintain an atmosphere of low moisture content for long periods of time. Apparently, the slow drying of the brushes in the Argon Cell during the extended period of exposure to a low moisture content atmosphere created the condition for rapid brush wear.

Brush tests are now being conducted in a large volume, controlled argon atmosphere box in which the argon atmosphere is continually monitored for oxygen and moisture. Brushes are being tested in a pair of motors which are coupled together so that one motor drives the second one, which acts as a generator. The load on the generator is adjusted to impose a controlled load on the driving motor. These motors are identical to those currently being used in the Argon Cell manipulators and those used in previous tests (1/4 hp, d-c Eemco** motors; model no. C-743-c). An automatic control circuit operates the motor on cycles of 5 sec on and 5 sec off with reversal of direction on alternate cycles. This mode of operation is designed to approximate the operation of the manipulator grip drive motor during its usual use in the Argon Cell.

Tests of the Stackpole grade 56 brushes were made at moisture levels between 9.7 and 11.4 ppm and oxygen levels of less than 20 ppm in order to verify that low levels of moisture and oxygen were indeed the cause of the rapid brush wear in the nitrogen atmosphere of the Argon Cell. A high rate of wear of 0.296 in./hr was found under these experimental conditions. Though the differences in properties, such as dielectric strength and heat transfer characteristics, between nitrogen and argon are considerable and may affect the rate of brush wear, it is believed that the primary cause of fast brush wear in either atmosphere is the low oxygen and moisture contents. If dielectric strength and heat transfer characteristics of the atmosphere have a significant deleterious effect upon the wear rate of the brushes, operation in argon should cause greater rates of brush wear than operation in nitrogen.

Preliminary tests on several other types of brushes were conducted. A resin-bonded carbon-graphite brush containing 5 percent molybdenum disulfide (Stackpole grade 660) gave the best test results, i.e., showed the least wear. In atmospheres containing 1.7 to 21 ppm moisture and less than 20 ppm oxygen, the highest wear rate was 0.0189 in./hr for this grade brush.

*A product of Stackpole Carbon Co., St. Mary's, Penn.

**Electrical Engineering and Manufacturing Corporation, Los Angeles, Calif.

Additional tests are being carried out with the Stackpole grade 660 brush. In these tests, an attempt will be made to correlate brush wear with motor operating characteristics and to determine the effect on brush wear rate of different concentrations of oxygen and moisture (in the concentration range 0 to 100 ppm).

c. Miscellaneous Service Equipment Development
(G. J. Bernstein, W. E. Miller)

Before any small object is removed from the Air Cell or the Argon Cell, it will be sealed in a small sample can. This procedure is necessary to prevent the spread of radioactivity when transferring an object from either cell and to minimize the hazards of pyrophoricity when transferring an object from the inert atmosphere in the Argon Cell to the air atmosphere in the Air Cell. Sample cans, 3/4-in. ID by 2 in. long, will be used to contain the small objects. The sample can will be sealed by pressing a dished cap into the opening of the can.

Two portable sample can cappers of the same design have been built and successfully tested. One of the cappers is shown in Figure I-48. The main components of the sample can capper are the cap magazine, operating arm, capping mechanism, sample can carrier, and a cart. All operations of the sample can capper (in either process cell) are performed with an electromechanical operating manipulator.

In a typical operation of the capper, the sample can carrier containing six loaded sample cans is placed in the cart by means of an electromechanical manipulator which operates special tongs that are designed for handling the sample can carrier. The cart is then slid under the capping mechanism, where the cart is positioned by means of a recess in the track and a V-guide rail. A slide bar, not visible in the figure, moves the two rear sample cans so that they are rigidly positioned with respect to the sample can carrier and hence are positioned with respect to the capping mechanism. The electromechanical manipulator is used to lift the operating arm which feeds caps from each side of the cap magazine to the capping mechanism. When the operating arm is moved down, the capping mechanism forces caps into the two rear sample cans. The operating arm is then moved to a neutral position, and the cart moved out from under the capping mechanism. The sample can carrier is rotated 120 degrees, and the procedure repeated. If it is desired to cap one can at a time, only one side of the cap magazine is loaded and the sample can carrier is rotated 60 degrees between cappings.

3. Process Equipment Development

a. Skull Oxidation Equipment
(G. Bernstein, W. Miller, M. Slawewski, H. Stethers)

After the melt refining step is carried out, a skull remains in the zirconia crucible. The skull contains significant quantities of fission-

Figure I-48

SAMPLE CAN CAPPER

108-6677A

able material which will be recovered by means of the skull reclamation process. The skull will be removed from the crucible by converting the metallic skull to an oxide powder that will be poured out of the crucible. Equipment is being developed for the oxidation of skulls and the transfer of oxide powders and includes the following: an oxidation furnace, a control system for the furnace oxidizing process, and a mechanism (dumper) for transferring the oxide powder from the melt refining crucible to a storage container.

The design of the skull oxidation furnace has been completed, and the drawings have been released for its construction. Preliminary designs and the design concepts of the oxidation furnace are given in previous reports (ANL-6725, page 93, ANL-6477, page 86, and ANL-6333, page 99). Plans and procurement of equipment items are proceeding for the installation of the oxidation furnace control system (ANL-6687, p. 70) in the Fuel Cycle Facility.

Figure I-49

SKULL OXIDE DUMPER

108-6611A

A skull oxide dumper (Figure I-49) has been developed which separates the oxide from the zirconia crucible, transfers the oxide to a storage container, and then discards the used crucible into a waste can. All the manipulations are carried out by means of the electromechanical manipulator. Operation of the dumper is described below.

After the melt refining step, the melt refining crucible is placed in a crucible container, and, thereafter, the crucible container is handled rather than the crucible. After the skull is oxidized in the oxidation furnace, the crucible container is placed in the crucible container receptacle of the dumper (see Figure I-49). A crucible hold-down ring and an oxide receiver (storage container) are then added to the crucible container. The crucible hold-down ring is recessed at the top so that the oxide receiver fits into it and rests against a shoulder. The bottom of the hold-down ring is

Figure I-50

DRIVE MECHANISM

108-6624A

machined so that the upper lip of the crucible container fits into a recess and the ring rests upon the lip of the crucible. The hole through the ring has the same diameter as the inside diameter of the crucible.

In the first step of the dumping operation, the crucible container, crucible hold-down ring, and oxide receiver are clamped together by the clamping arms (see Figure I-50). These clamping arms rotate about a shaft that is fastened to the crucible container receptacle. The clamping arms are spring loaded so that they are open (see Figure I-49) when the crucible container is in the upright position. With the clamping arms in the open position, access to the crucible container receptacle for purposes of loading and unloading is provided. The crucible container receptacle is mounted on a horizontal shaft which has a pinion gear and which is rotated when the rack is moved (see Figures I-50 and I-51).

Figure I-51

BEGINNING OF OXIDE DUMP

108-6622A

When the rack starts to move down, the resulting rotation of the crucible container receptacle moves the three clamping arms against the cam plate (see Figure I-50), causing the clamping arms to close on the receptacle-receiver assembly. As the arms close, a spring force is transmitted from the clamping arms to the skull oxide receiver and the crucible holding ring, forcing these and the crucible toward the bottom of the crucible container receptacle.

As the rack continues its downward motion, the receptacle-receiver assembly is rotated (see Figure I-51) until the rack reaches the bottom of its stroke, at which point the receptacle-receiver assembly is completely inverted. Thus, the skull oxide is dumped from the crucible into the skull oxide receiver. The manipulator handle attached to the rack is then turned 90 degrees. This opens the clamping arm (see Figure I-52) which

Figure I-52

OPERATION OF OXIDE RECEIVER RELEASE MECHANISM

108-6617A

holds the oxide receiver against the hold-down ring, and the oxide receiver drops to a platform. The other manipulator handle is then operated to pivot the oxide receiver platform (see Figure I-53) to a position where the skull oxide receiver may be picked up with tongs. The manipulator handle which is attached to the rack is rotated back to its original position in order to close the clamping arm, and the rack is raised to the top of its stroke.

To dump the crucible from the crucible container, the crucible hold-down ring is first removed with tongs (see Figure I-54). The dumping procedure (the skull oxide receiver platform is in the position shown in Figure I-53) is then repeated, but the holding arms now restrain only the crucible container. At the end of the dump stroke, the crucible, no longer held by the hold-down ring, falls out of the crucible container into a waste can. The waste can containing the crucible is then removed from beneath the dumper as shown in Figure I-55.

Figure I-53

FINISH OF ROTATION OF OXIDE RECEIVER PLATFORM

108-6614A

The use of the existing skull oxide receiver has two inherent disadvantages. First, the use of a re-usable skull oxide receiver would require a special mechanism to transfer the oxide from the receiver to the skull reclamation furnace. Secondly, if the receiver is made of conventional metals, such as steel or stainless steel, the uranium chips or buttons in the skull might become contaminated with iron, owing to alloying at local hot spots. To overcome these difficulties, zinc cans will be used to receive the skull oxide. The zinc cans containing the skull oxide will be sealed with press-fit, zinc lids, and then charged into the skull reclamation furnace to be melted. An average of approximately 6 kg of zinc, as cans and lids, will be added in this manner for each kilogram of uranium in the skull oxide. Since the noble metal extraction step of the skull reclamation process requires the addition of 14 kg of zinc for each

Figure I-54

REMOVAL OF CRUCIBLE HOLD-DOWN RING

108-6620

kilogram of uranium (see ANL-6818), the addition of 6 kg of zinc as cans is permissible. One hundred zinc (>99 percent pure) cans with lids have been obtained.

A re-usable receptacle, similar to the existing skull oxide receiver, and a modified version of the crucible hold-down ring are being fabricated so that the zinc cans may be used in the skull oxide dumper.

b. Collection of Metal Vapors
(W. E. Miller, H. L. Stethers)

One of the final steps in the skull reclamation process is the distillation of Mg-Zn alloy from the uranium product. A maximum of 36 kg of Zn-12 w/o Mg (see ANL-6818) will be associated with 5 kg of uranium, which

Figure I-55

REMOVAL OF CRUCIBLE RECEIVER

108-6615A

is the anticipated batch size. A number of distillation experiments have been performed (see ANL-6687, page 73, and ANL-6725, page 98) in which designs of equipment for the remote operation of the distillation step have been evaluated. The equipment described in these previous reports was sized for 2 to 3 kg of distillate, which was based upon previous flow sheet requirements. A plant-scale distillation apparatus, suitable for handling 36 kg of distillate, has been designed (see Figure I-56) and built, but has not yet been tested. The main components of this apparatus are a graphite condenser, graphite distillate collector, process crucible, graphite secondary (crucible enclosure), and graphite secondary cover. Except for the distillate collector, all of these components are re-usable. The purpose of the graphite felt insulation inside the distillate collector and the insulation between the distillate collector and the secondary cover is to prevent reboiling of the collected distillate.

Figure I-56

MAGNESIUM-ZINC DISTILLATION APPARATUS
36 KILOGRAM SCALE

The distillation apparatus shown in Figure I-56 has two features, other than size, which make this apparatus significantly different from the distillation equipment described in previous reports. First, the seal between the distillate collector and the secondary cover has been changed to a butt joint. This type of joint has been tested in smaller-scale equipment in eight runs in which 1 to 6 kg of magnesium-zinc distillate have been collected. The butt joint prevented leakage and was easily separated after each experiment. Secondly, in the earlier version of the distillation apparatus, a cover was fitted directly onto the graphite crucible. In the new apparatus, a graphite secondary cylinder has been added to contain the process crucible, and the cover fits onto the secondary. This feature retains the high-quality seal that is possible when readily machinable graphite parts are mated, but now permits the use of a crucible fabricated from materials other than graphite. The graphite secondary is shorter than the crucible to permit pouring from the crucible, if it is found desirable to consolidate the uranium left in the crucible by melting the residual uranium and pouring it into a mold.

The possibility of replacing the graphite condenser and graphite distillate collector with a single unit made of mild steel was investigated. Six runs were carried out with such an apparatus. Three 1-kg charges and three 3.5-kg charges of Zn-14 w/o Mg were each distilled at one mm Hg absolute pressure until a final crucible temperature of 1200 to 1250°C was reached. There was no measurable leakage of distilled zinc-magnesium in any of the runs; and, at the end of each run, the steel condenser-collector unit could be readily lifted off the crucible cap spout without sticking. After the six runs were made, the steel condenser-

Figure I-57

SECTIONS OF SINGLE PIECE CONDENSER-COLLECTOR UNIT
SHOWING CORROSION AFTER SIX DISTILLATIONS
OF ZINC-14 w/o MAGNESIUM ALLOY

(Material of construction: mild steel)

108-6374A

collector unit was sectioned for examination (see Figure I-57). It was observed that considerable corrosion or iron dissolution had taken place in the standpipe and at the seal between the steel condenser-collector and the graphite crucible cap. Since the dissolved iron washes back into the crucible containing the uranium, the iron would contaminate the product. Since steel has proved to be an unsatisfactory material for the condenser-collector unit, subsequent runs will be made using graphite as a material of construction for the condenser and collector.

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

The chemistry of liquid metal systems is being investigated to provide basic concepts and data for the design of methods for the reprocessing of

nuclear fuels and to provide a basis for the development of liquid alkali metal technology. The results of these studies also provide data for the testing of theories of liquid metal solutions.

1. Solubilities in Liquid Metals

Of prime importance in the design of fuel-reprocessing methods utilizing liquid metal solvents are the solubilities of the metals whose separations are being attempted. These solubilities need to be known as a function of both temperature and solvent composition. The solubility of a metallic solid in a liquid metal solvent is related to the difference between the free energy of formation of the solid and the partial excess free energy of the solute in the saturated solution. Therefore the temperature coefficient of the solubility gives information on the corresponding enthalpy and entropy differences. The systematization of such data for a wide variety of different systems will furnish the empirical relations which will aid in the resolution of the factors governing the energetics of formation of liquid metal solutions. For these fundamental applications of solubility data, it is necessary to know the constitution and the thermodynamics of the solid phase in equilibrium with the liquid phase.

Solubility of Plutonium in Liquid Cadmium

(M. G. Chasanov, P. D. Hunt, and R. Yonco)

The solubility of plutonium in molten cadmium was determined by direct sampling of the saturated solution, using tantalum sample tubes fitted with tantalum filters. The results of this experiment, in which 30.6 g of plutonium (99.85% Pu) was added to 300 g cadmium (99.95% Cd) contained in a magnesia crucible, are given in Table I-24. The data may be represented by the empirical equations:

$$\begin{aligned} (335 \text{ to } 399^\circ\text{C}) \log (a/o \text{ Pu}) &= 6.223 - 4282 T^{-1}, \\ (399 \text{ to } 632^\circ\text{C}) \log (a/o \text{ Pu}) &= 5.148 - 5277 T^{-1} + 1.156 \times 10^6 T^{-2}. \end{aligned}$$

The relative standard deviations for these two equations are 5 and 1%, respectively. These data are compared in Figure I-58 with earlier solubility data reported by Winsch, Nelson, and Paul (ANL-5959, p. 120). Both sets of data agree reasonably well. Winsch and coworkers observed a break in the solubility curve at 404°C; the newer data has the break at 399°C.

The break in the solubility curve at 399°C indicates a peritectic reaction. The equilibrium solid phase below the peritectic temperature was prepared by the slow electrolysis of plutonium into an initially unsaturated liquid plutonium-cadmium alloy at 380°C. The cadmium-rich alloy produced was found to have an X-ray diffraction pattern similar to UCd_{11} . Thus, it appears that the most cadmium-rich intermetallic phase in this system is PuCd_{11} .

Table I-24

SOLUBILITY OF PLUTONIUM IN LIQUID CADMIUM

(Data in chronological order)

<u>Temp. (°C)</u>	<u>Plutonium (w/o)</u>
335	0.332
351	0.470
373	0.888
388	1.16
408	1.63
425	1.92
443	2.28
488	3.59
504	3.90
554	5.86
569	6.71
603	8.42
632	10.9
669	9.29 ^a

^aUnsaturated solution, 9.26 w/o Pu charged.

Figure I-58

SOLUBILITY OF PLUTONIUM IN LIQUID CADMIUM

108-7143

An alloy with a cadmium to plutonium atom ratio of 7 was prepared by heating the metals in a tantalum crucible to 650°C and then annealing for two weeks at 600°C. Metallographic examination of this alloy after quenching showed an intermetallic phase and some free cadmium. X-ray examination of the intermetallic phase yielded a pattern similar to the rare earth-cadmium compounds of the MCd_6 type. Thus, the break at 399°C can be ascribed to the peritectic reaction

Zinc-Techneium System

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

Studies (ANL-6648, p. 116) of the technetium-zinc system by means of differential thermal analysis and X-ray analysis indicated the existence of at least two intermediate phases. Measurements of the solubility of technetium in liquid zinc gave evidence for a peritectic reaction at about 544°C. Further studies have been made in an attempt to fix more exactly the composition of these intermediate phases.

The two intermetallic compounds were readily prepared by heating technetium and excess zinc in a rocking furnace - the more zinc-rich phase, below 544°C; the other phase, above 544°C and below 950°C. While the two phases could be identified by X-ray diffraction, the excess zinc interfered with the characterization of these compounds. Attempts to free these phases from the zinc matrix by leaching with a variety of reagents proved unsuccessful. In every case the crystalline structure of the intermetallic compound was affected by the leaching.

The compositions of these intermetallic phases were bracketed using alloys prepared by powder metallurgical methods. One series of such compacts were heated at 420 to 490°C for a period of two weeks. X-ray diffraction indicated that the more zinc-rich phase, designated "L" phase, has a zinc to technetium atom ratio between 15 and 18. Another series of alloys were heated at 600 to 630°C for two weeks; examination of these alloys indicated that the more technetium-rich phase has a zinc to technetium atom ratio between 5 and 7 (most likely 6). Table I-25 lists the alloys prepared, the annealing temperatures, and the phases found.

Results of an effusion experiment (which is described later) indicated that the technetium-rich phase has a zinc to technetium atom ratio of 5.5. However, the effusion residue was found to be slightly contaminated with oxide; this implies that the actual value of the ratio is somewhat larger than 5.5. Spectrochemical analysis of a sample of the technetium-rich phase obtained by the effusion technique yielded the composition 20.8 w/o technetium and 79.6 w/o zinc. The composition of TcZn_6 corresponds to 20.2 w/o technetium and 79.8 w/o zinc.

Table I-25

PHASES PRESENT IN ANNEALED Zn-Tc ALLOYS
PREPARED BY POWDER METALLURGY

Atom Ratio, Zn/Tc	Annealing Temp. (°C)	Phases Present (major phase listed first)
31	490	Zn, L ^a
20	491	Zn, L
18	420	Zn, L
15	490	L, TcZn ₆
10	475	L, TcZn ₆
7	630	TcZn ₆ , Zn
6	600	TcZn ₆
5	630	TcZn ₆ , Tc

^aL represents an unidentified diffraction pattern which is believed to represent a single phase.

The X-ray diffraction pattern of the technetium-rich phase has been indexed* on the basis of a face-centered cubic cell with $a_0 = 7.588 \text{ \AA}$. With twenty-eight atoms in the unit cell ($4 \times \text{TcZn}_6$), the calculated density of the intermetallic is 7.5 g/cm^3 ; the density of this material was found experimentally to be 7.4 g/cm^3 .

An alloy containing 66 a/o technetium was prepared by the effusion method and was found to contain only TcZn₆ and technetium. Thus, no additional compounds between TcZn₆ and the technetium terminus are indicated. There was no evidence of solid solution at either end of the diagram in alloys prepared either by effusion or by direct combination of the elements.

These findings are compatible with the following ternary phase equilibria:

*X-ray studies were carried out by R. Schablaske of the X-ray Diffraction and Spectroscopy Group.

Solubility of Argon in Liquid Sodium (S. K. Dhar)

An experimental investigation of the solubility of rare gases in liquid alkali metals is under way. The data will be used to gain a better understanding of the factors that determine solubilities in liquid metals. The rare gases are expected to dissolve in liquid metals as unexcited atoms, since the promotional energy to the p^5s configuration is very large (ranging from 156 kcal/mole for Rn to 383 kcal/mole for Ne). The electrons of the rare gas atoms will therefore not be available for metallic binding and the principal interaction will be between neutral rare gas atoms and metal ions. The energetics of this interaction can be estimated from the temperature coefficient of the solubility.

Figure I-59

SCHEMATIC OF GAS SOLUBILITY APPARATUS

The solubility of argon in liquid sodium has been measured over the temperature range 340 to 480°C. The apparatus, shown schematically in Fig. I-59, consists of three interconnected stainless steel (type 316) vessels (A, B, and C) of about 4-liter capacity. Vessel C was used to transfer sodium from the bulk supply. The outlet tube of vessel C was equipped with a metallic filter; oxide formed by cooling the sodium could be removed before the sodium was transferred to vessel A. In vessel A, the liquid sodium was saturated with argon, while in vessel B the dissolved argon was stripped from the sodium. All vessels were treated with molten sodium at 450°C for about two hours prior to use.

The experimental procedure consisted of three steps.

Step 1: About three liters of sodium were saturated with argon in vessel A in the pressure range 3-9 atmospheres and between 340 and 480°C. The saturation step consisted of circulating argon through the molten metal at a rate of approximately 400 cc/min. for 3 hr. This was followed by a slow agitation of the metal for 2 hr. by means of a magnetically coupled stirrer. The saturated metal was then allowed to stand at the given temperature and pressure for 3 hr. The latter two steps were carried out to free the solution of entrapped gas bubbles.

Step 2: Two-thirds of the saturated metal was transferred to vessel B, where it was stripped of dissolved argon by sparging with helium at 1-atm pressure. The transfer of the metal from vessel A to vessel B took place at a rate of about 150 cc/min. If no argon was added to the saturator during transfer, the pressure in the saturator fell to about one-half its original value during the transfer. In other experiments, the gas pressure in the saturator was maintained nearly constant during the transfer by the addition of argon. No difference in the solubility was found between the two methods of transferring the sodium metal to vessel B. The transfer required approximately 15 minutes. The slow rate of transfer eliminated turbulent flow in the metal, and thus reduced the possibility of admixture of the bottom layer (which was being transferred) with the top layer which has an adsorbed layer of argon. The slow rate of transfer also reduced the possibility of dislodging and transferring small bubbles which would have become trapped on the dispersion assembly. The transfer time was varied between 20 and 12 minutes without a difference in the solubility being noted. The possibility of a gas-metal interface between the inner wall of the container and the contacting metal was also reduced by the fact that the vessel was wetted by sodium.

Step 3: Stripping of the saturated metal in vessel B was done by sparging the metal with helium at one atmosphere. Sparging was accomplished by circulating the helium through a micrometallic disperser disc located near the bottom of vessel B. The sparging was done at 160-200°C for a period of about 35 minutes. During the last 10 minutes of this period, the gas was passed through the liquid nitrogen-cooled activated carbon trap where all of the argon and some of the helium were absorbed. The trap was made of copper and contained 7 g of carbon. Following the adsorption, the trap was pumped out to 35 mm pressure to remove most of the helium, and was subsequently heated to about 390°C to desorb the argon. The argon was partly collected in a 110-cc sample bulb and was analyzed with a mass spectrometer. From a knowledge of the pressure and the total volume of the trap, the connecting line, and the sample bulb, the total quantity of displaced argon may be calculated.

The solubility of argon in liquid sodium was measured at 480°C at argon pressures ranging from 3.4 atm to 9.1 atm. The data given in Table I-26 and shown on Figure I-60 indicate that the solubility is directly proportional to the argon pressure, as required if Henry's law is to apply. The demonstration that the solubilities are directly proportional to the

pressure indicates that the experimental method is valid for measuring solubilities, that is, the procedures for saturation, sampling, and analysis are satisfactory.

The temperature dependence of the solubility was determined by measuring the solubility at constant pressure at temperatures ranging from 340°C to 480°C. The data given in Table I-27 and shown in Figure I-61 indicate a heat of solution of 16 kcal/mole.

There are no reported experimental measurements of the solubility of argon in liquid sodium with which to compare the present data. Several theories have been reported by which the solubility and heat of solution of argon in liquid sodium can be calculated. Calculations have been made using the theories proposed by McMillan²⁴ and by Johnson and Shuttleworth.²⁵ The calculated solubilities are several orders of magnitude larger than those found experimentally. The calculated heats of solution are smaller than those observed experimentally. Both theories required an estimation to be made of the work necessary to make a cavity in the metallic solvent to accommodate the rare gas atom. Each theory would be in approximate agreement with the experimental results if the radius of the cavity were assumed to be from 25 to 50% larger than the normal radius of the rare gas atom.

Figure I-60

HENRY'S LAW PLOT OF THE SOLUBILITY OF ARGON IN SODIUM AT 480°C

108-7139 Rev.

²⁴ W. G. McMillan, BNL-353 (T-63)(1955).

²⁵ G. W. Johnson and R. Shuttleworth, Phil. Mag. 4, 957 (1959).

Table I-26

DEPENDENCE OF THE SOLUBILITY OF ARGON
IN LIQUID SODIUM ON PRESSURE

Temperature: 480°C

<u>Pressure,</u> <u>(psia) (atm)</u>		<u>Solubility</u> <u>(atom fraction)</u>
135		2.9×10^{-8}
134.5		1.5×10^{-8}
132		1.5×10^{-8}
136		3.3×10^{-8}
131.5		2.6×10^{-8}
135.5		1.9×10^{-8}
Avg. 9.1		Avg. 2.3×10^{-8}
103		1.5×10^{-8}
101		1.4×10^{-8}
104		1.5×10^{-8}
Avg. 6.9 ₄		Avg. 1.45×10^{-8}
78.5		1.6×10^{-8}
73.5		1.3×10^{-8}
72		0.85×10^{-8}
Avg. 5.1 ₇		Avg. $1.2_5 \times 10^{-8}$
46.5		0.72×10^{-8}
53		0.88×10^{-8}
43.5		0.60×10^{-8}
Avg. 3.4		Avg. $0.7_3 \times 10^{-8}$

Table I-27

DEPENDENCE OF THE SOLUBILITY OF ARGON
IN LIQUID SODIUM ON TEMPERATURE

Pressure: 9 atm

<u>Temperature</u> <u>(°C)</u>	<u>Solubility</u> <u>(atom fraction)</u>
Avg. 480 ^a	Avg. 2.3×10^{-8}
435	1.67×10^{-8}
432	1.0×10^{-8}
432	1.02×10^{-8}
Avg. 433	Avg. 1.26×10^{-8}
380	0.36×10^{-8}
380	0.41×10^{-8}
385	0.42×10^{-8}
385	0.57×10^{-8}
Avg. 383	Avg. 0.44×10^{-8}
340	0.26×10^{-8}
340	0.25×10^{-8}
340	0.23×10^{-8}
341	0.19×10^{-8}
Avg. 340	Avg. 0.23×10^{-8}

^aSee Table I-26.

Figure I-61
DEPENDENCE OF SOLUBILITY
OF ARGON IN LIQUID
SODIUM ON TEMPERATURE

(Argon pressure, 9 atm.)

108-7288

2. Liquid Sodium Coolant Chemistry

The utilization of liquid alkali metals as heat transfer media in high-power-density fast nuclear reactors as well as in other power sources makes essential a continuing advancement in alkali metal technology. To insure a sound technological advance, a fundamental research program is needed. A program is under way to elucidate the chemistry of the reactions that occur in liquid alkali metal solutions; special emphasis will be given to liquid sodium, since its importance is presently greatest.

Sodium of high, known purity is required for significant research. Therefore, studies are being made in the closely related areas of purification, analysis, and metal handling. Liquid sodium contaminated with oxygen and carbon has been found to be more corrosive to structural materials than pure sodium. When the two impurities are both present, extensive carbon transfer occurs under some conditions. Basic studies are being started to determine the mechanism of carbon transfer in liquid sodium solutions.

a. Sodium Purification

(G. Lutz, D. Neil, K. Anderson)

For the experiments planned in this study, very high purity sodium will be required. This high purity material will initially be used in the standardization of the analytical methods for the determination of trace amounts of carbon and oxygen in sodium. Several methods of purification are currently being investigated. For the preparation of pound quantities of sodium, an all-metal vacuum still (capacity one liter per day) has been designed and constructed. This apparatus is currently being leak-tested and will be vacuum degassed prior to use. Provisions have been made for transferring the sodium distilled in this unit to the various pieces of experimental equipment without contamination.

To prepare small samples (50-150 g) of sodium of low carbon and low oxygen content, hot gettering with zirconium is being used. Several samples have been prepared, and a carbon content in the sodium of 25 ppm has been found (by analysis using the dry oxidation method). By further development of this method it is believed that lower carbon contents can be obtained.

Another preparative method being investigated involves the decomposition of sodium azide. This material is readily available and is easily purified by recrystallization. Thermal decomposition of sodium azide proceeds smoothly at about 320°C. After decomposition, the residual material is filtered (at 110°C) to separate the sodium from the undecomposed azide. Preliminary results are most promising, and the optimum conditions for the decomposition and subsequent filtering and sampling are now being established. A carbon analysis of a sample prepared using this method indicated zero carbon within the uncertainty of the analytical method, which was ± 2 ppm.

Since the interest is in a material that is free of trace impurities, well-defined methods of handling, transferring and sampling of liquid sodium are necessary in order to prevent contamination. Experiments designed to establish such procedures are currently in progress.

b. Sodium Analysis

(1) Oxygen

(G. Lutz, K. E. Anderson)

For the routine analysis of sodium samples containing 100 ppm of oxygen or greater, the amalgamation procedure is used. The technique used is based on that reported by Pepkowitz and Judd.²⁶ The apparatus used has been constructed so that the amalgamation may be accomplished under a vacuum of 10^{-4} torr or less. All stopcocks with which the mercury comes in contact are of a nonlubricated type, thus avoiding possible contamination of the mercury. All parts of the apparatus may also be baked out prior to use.

To analyze samples of sodium containing less than about 100 ppm of oxygen, two different activation methods are under development. In the first method, the sample is irradiated with 14.5-Mev neutrons produced from a Cockroft-Walton generator. Nitrogen-16 (7.3-sec. half-life) is produced from the oxygen in the sample by the reaction $O^{16}(n,p)N^{16}$. The active nitrogen isotope emits a 6.1-Mev gamma ray which is measured with two 4-in. x 4-in. NaI (Tl) detectors and a multichannel analyzer. Samples are transferred from the generator to the counting equipment in about 2 sec with a pneumatic transfer system.

Irradiations were made at a flux of $\sim 1.5 \times 10^8$ n/(cm²) (sec) for 30 sec (93.7% of saturation). Measurements on standard oxygen samples yielded about 225 counts per milligram of oxygen. Samples containing magnesium, aluminum, phosphorus, silicon, cobalt, potassium, nickel, manganese, and iron, all of which are possible impurities in sodium, were irradiated and their gamma spectra examined. None of these elements were found to interfere; however, fluorine, which yields N^{16} via an (n, α) reaction, and boron, which yields Be^{11} via an (n, p) reaction, would interfere in the analysis. Neither of these elements are likely impurities in sodium.

The major problem in this method is concerned with obtaining a container with a low oxygen content for the sample. Polyethylene from various sources was irradiated and found to contain 200-400 ppm of oxygen. An effort is being made to obtain polyethylene which is low in oxygen. It is also planned to test some metals as potential container materials.

²⁶ L. P. Pepkowitz and W. C. Judd, Anal. Chem. 22, 10 (1950).

The counting efficiency of the system used is about 5%. A few experiments with a small anthracene crystal and pulse height analyzer indicate that the counting efficiency may be improved by counting the 10.5-Mev beta radiation associated with 28% of the N^{16} disintegrations.

The second activation method being investigated involves the production of F^{18} from O^{16} by triton irradiation. The tritons are produced in situ by thermal neutron irradiation of the sample to which a small amount of lithium has been added; tritons are produced by the reaction $Li^6 (n, \alpha) H^3$. Methods for adding lithium to the sample are under development.

(2) Carbon

(C. Luner and P. D. Hunt)

The carburization studies planned (see section c which follows) will require a reliable method for analyzing the carbon content of sodium. The dry oxidation method has been chosen. In this method, the sodium is first burned under oxygen at low pressure and then the residue is heated to 1100°C in a stream of purified oxygen at atmospheric pressure. The carbon dioxide produced by the oxidation of the carbon in the sample is collected in a cold trap (maintained at -180°C using liquid oxygen coolant) and subsequently is measured manometrically. In blank runs with reagents, low carbon contents (3 to 4 μg of carbon) were obtained. Quantitative recoveries of the carbon in standard samples have been obtained (see Table I-28). Variations in the carbon content of the sodium were obtained when the samples were taken from solid sodium. It appears that segregation of carbon occurs readily during freezing of the liquid. It was observed, however, that sampling variations can be minimized by sampling from the liquid phase. Using this sampling technique, an approximately linear relation has been obtained between the carbon found and the weight of the sodium sample (see Fig. I-62). The sodium sample contained approximately 76 ppm of carbon. Experiments are now in progress to determine the recovery of carbon as carbonate and graphite from sodium of known carbon content.

Table I-28

RECOVERY OF DIFFERENT FORMS OF CARBON BY THE DRY OXIDATION METHOD

Form of Carbon	Carbon Added (μg)	Carbon Found (μg)
Sucrose	82.0	85.0
Sodium Carbonate	56.6	56.5
Sodium Carbonate	10.3	10.7
Graphite	44.5	46.0
Graphite	12.2	13.0

Figure I-62

RELATION BETWEEN CARBON
RECOVERY AND SODIUM
SAMPLE WEIGHT

(Carbon content: 76 ppm)

108-7283

c. Carburization Reaction in Liquid Sodium
(C. Luner and D. Neil)

A potentially serious problem associated with the use of liquid sodium in nuclear reactors is the tendency of metals to carburize or decarburize. This is caused by the basic instability of many metallic systems with respect to graphite. Thus, ordinary steel is a metastable system of ferrite (α -Fe) and cementite (Fe_3C). The thermodynamically stable system would consist of ferrite containing a smaller concentration of carbon and graphite. Liquid sodium can act as a path for the transformation of the metastable to the stable system, thus effecting a decarburization. Similarly, many ferrous alloys containing nickel and chromium are not stable if carbon is available for reaction with the alloy. Thus, sodium may also act as a medium for the transport of carbon to the alloy to form the more stable carbide system. In either case, whether it be carburization or decarburization, undesired changes in the mechanical properties of the container materials result.

The mechanism of carbon transport in liquid sodium is not understood. In addition, the role of dissolved oxygen is not known, although it is believed to be significant.

A basic study of the transport of carbon by liquid sodium has been started. The initial experiment will be the determination of the solubility of graphite in liquid sodium as a function of both temperature and oxygen content. An apparatus to equilibrate graphite and sodium has been assembled and is undergoing testing.

3. Thermodynamic Studies

Thermodynamic functions are being measured for elements that are of importance to pyrometallurgical separations processes and for elements that are particularly useful for the testing of theories of metallic systems. Galvanic cells have proved to be especially useful for the measure-

ment 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 alloys. For systems composed of several well-defined inter-metallic phases, measurement of the decomposition pressure by the Knudsen effusion method is proving to be very useful. Systems in which only a small difference in electrochemical potential of the components exists and in which both components have nearly the same vapor pressure are not readily studied by either the galvanic cell method or effusion method. For such systems, a vapor phase optical absorption method is being developed.

The galvanic cell method is being used to systematically study binary plutonium alloys with the low melting B-subgroup metals and the most cadmium rich compounds in rare earth-cadmium systems. Some preliminary results for the praseodymium-cadmium system are reported below. The effusion method is being used to study binary systems involving zinc or cadmium as the second (volatile) component. Results of a study of the thermodynamics of TcZn_6 are reported below. The optical method is being used to study the thermodynamics of binary alkali metal systems.

Thermodynamics of Binary Alkali Metal Solutions
(Optical Absorption Method)

 (F. Cafasso, V. Khanna, and R. Murray)

A vapor pressure method which employs the principles of absorption spectrophotometry is to be used to determine the thermodynamic properties of binary alkali metal solutions. In this method, light that is characteristic of one of the alkali metals (resonance radiation) is passed through the vapor phase over the pure alkali metal and through the vapor phase over one of its binary solutions. The absorption of this radiation by the vapor over both liquids is measured at the same temperature. The ratio of these two absorbances is, in principle, a measure of the activity of the metal in the solution. A more detailed discussion of the principles of this technique was given in a previous report (see ANL-6725, p. 107).

Much of the preliminary work in this study was devoted to refining instrumentation and to testing absorption cells for resistance to attack by sodium vapor. An absorption cell made entirely of quartz and one made of glass to which sapphire windows were sealed had poor resistance to sodium vapor in the temperature range 120°-160°C. However, a Kovar (Ni 29%, Co 17%, Fe 54%) cell to which sapphire windows were sealed by a special metallizing process²⁷ showed good resistance to sodium at temperatures as high as 220°C. Consequently, this cell was used to measure the temperature coefficient of absorption by equilibrium sodium vapor in the range 180-220°C. The enthalpy of vaporization for the reaction $\text{Na(l)} \rightleftharpoons \text{Na(g)}$ calculated from these preliminary data is 26.7 kcal. This value is in reasonable agreement with the best literature value²⁸ of 25.9 kcal at 200°C.

²⁷Advanced Vacuum Products, Inc., Stamford, Connecticut.

²⁸W.H. Evans, R. Jackson, T.R. Munson and D.D. Wagman, J. Research NBS 55, 83 (1955).

Thermodynamics of Technetium-Zinc System:
 Decomposition Pressure of TcZn_6
 (E. Valeckis and E. VanDeventer)

Studies of the technetium-zinc system (see a preceding section of this report) have revealed the existence of two intermediate phases: a zinc-rich phase which contains about 5.5 a/o technetium and a technetium-rich phase which corresponds to the formula TcZn_6 . The thermodynamics of formation of this latter compound have been investigated by the measurement of the zinc vapor pressures in the equilibria

over the temperature range of 470 to 570°C. The vapor pressures were measured by means of a continuous weighing effusion balance. A tantalum effusion cell with two orifices (approximately 0.01 cm diameter) was used for all of the measurements.

Approximately 150-mg alloy samples were used in each experiment. To prepare the alloy, arc-melted technetium-99 and high purity zinc (99.999%) were heated together at 600°C for 31 days. The alloy contained approximately 15 a/o Tc. In a typical experiment zinc was evaporated isothermally until no further changes in sample weight were observed. The weight loss vs time graph had one sharp break at the sample weight which corresponded to TcZn_6 . The break was followed by a straight-line portion which corresponded to the heterogeneous region TcZn_6 -Tc. The rate of weight loss in this region is proportional to the decomposition pressure of TcZn_6 by the Knudsen equation:

$$P_{\text{mm}} = 17.14 (\text{KA})^{-1} (T/M)^{1/2} (\Delta w/\Delta t) \quad (2)$$

in which P_{mm} is the vapor pressure of zinc in mm, K the Clausing short-channel correction factor, A the orifice in cm^2 area, T the absolute temperature, M the gram atomic weight of zinc, and $\Delta w/\Delta t$ the rate of weight loss in grams per second. The effective orifice area, KA, of the cell was determined by calibration with pure zinc. From the known vapor pressure of zinc²⁹ and the measured rate of weight change, a value of $\text{KA} = 0.162 \times 10^{-3} \text{ cm}^2$ was computed.

Because of the low volatility of technetium, only zinc is found in the vapor phase. Mass spectrometric³⁰ and torsion effusion³¹ studies have shown that zinc vapor consists mainly of monatomic zinc.

No evaporation coefficient correction was applied to the data. The small area of the orifice of the cell relative to the area of the sample renders such a correction negligible.

²⁹R. F. Barrow et al., Trans. Faraday Soc., 51, 1354 (1955).

³⁰K. H. Mann and A. W. Thickner, J. Phys. Chem., 64, 241 (1960).

³¹G. M. Rosenblatt and C. E. Birchenall, J. Chem. Phys. 35, 788 (1961).

The results of eleven experiments in the temperature range 470 to 570°C are shown in Table I-29. The decomposition pressures are also shown in Fig. I-63 where $\log P$ is plotted against $1/T$. These data may be represented to within $\pm 5\%$ of the empirical equation

$$\log P \text{ (mm)} = 9.853 - 8242 T^{-1} \quad (3)$$

Table I-29

DECOMPOSITION PRESSURE
AND STANDARD FREE ENERGY OF FORMATION OF TcZn_6

Temp (°C)	$\frac{\Delta w}{\Delta t} 10^6$ (g/sec)	P mm	P° mm	$-\Delta G_f^\circ$ (kcal/g-atom)
470.0	0.165	0.0592	0.640	3.02
480.0	0.217	0.0778	0.826	3.03
488.4	0.306	0.110	1.02	2.89
500.0	0.429	0.156	1.36	2.85
510.0	0.554	0.203	1.72	2.86
520.0	0.813	0.299	2.17	2.68
530.0	0.988	0.366	2.72	2.75
541.7	1.59	0.594	3.52	2.47
552.4	2.10	0.789	4.42	2.43
560.0	2.42	0.914	5.15	2.46
570.0	2.94	1.114	6.34	2.50

In spite of the relatively high vapor pressures (above 1 mm) reached at the highest temperature, the data show no evidence of deviating from molecular flow conditions. At 570°C the ratio of the mean free path to the orifice diameter is about 1.5. Vapor pressure measurements for mercury³² have demonstrated the persistence of the molecular flow at similar ratios.

The standard free energy of formation of TcZn_6 , listed in column 5 of Table I-29 was computed by means of the relation ΔG_f° (cal/gram atom) = $x_{\text{Zn}} RT \ln (P/P^\circ)$, in which x_{Zn} is the atom fraction of zinc (6/7) in the compound, P the decomposition pressure, and P° the vapor pressure of pure liquid zinc. Values of P° were calculated using the equation given by

³²K.D. Carlson, P.W. Gilles and R.J. Thorn, J. Chem. Phys., 38, 2725 (1963).

Figure I-63

DECOMPOSITION PRESSURE OF TcZn_6

108-7141 (Rev)

Barrow and his coworkers²⁹ and are tabulated in column 4 of Table I-29. The free energy may be represented by the empirical equation

$$\Delta G_f^\circ (\text{cal/g-atom}) = -7823 + 6.43T \quad (4)$$

to ± 75 calories.

TcZn_6 is reported to decompose peritectically into pure technetium metal and a saturated liquid zinc solution at about 950°C . Extrapolation of Equation 4 indicates $\Delta G_f^\circ = 0$ at 944°C , which, in view of the long extrapolation involved, is in satisfactory agreement with the thermal analysis result.

The partial molal excess free energy of technetium in saturated solutions may be computed from the free energy of formation of TcZn_6 and the solubility of technetium in liquid zinc. At 500°C the partial molal excess free energy of technetium in a saturated liquid zinc solution is -3.2 kcal/mole Tc, indicating moderate deviations from ideal solution behavior. Thus, the low solubility of technetium in liquid zinc (6×10^{-3} a/o at 500°C) is due to the great stability of TcZn_6 (at 500°C , $\Delta G_f^\circ = -20.0$ kcal/mole) rather than large negative deviations of the solution from ideal behavior.

Thermodynamics of the Praseodymium-Cadmium System
(I. Johnson and R. Yonco)

The thermodynamics of the praseodymium-cadmium system is being studied by emf measurements using the galvanic cell:

The cell reaction consists of the dissolution of praseodymium into the fused salt at the pure praseodymium electrode and deposition of praseodymium into the saturated liquid alloy electrode. The two phase alloy consists of a dilute solution of praseodymium in liquid cadmium and the intermetallic phase PrCd_{11} .

The cell assembly used for these studies is similar to that described in ANL-6687, p. 80 for the plutonium-zinc galvanic cell. The KCl-LiCl eutectic contained 0.3 w/o PrCl_3 . Crucibles made from tantalum were used to contain the eutectic and the alloy electrode.

Preliminary data obtained with this cell indicate that the free energy of formation of PrCd_{11} is -34.2 kcal/mole at 500°C.

products remain in the alumina bed and are discarded with the bed material as solid waste. The UF_6 and PuF_6 are then fed to a distillation tower for removal of the remaining fission products and for separation into two fractions, one composed of pure UF_6 and the other composed of a mixture of PuF_6 and UF_6 . The latter fraction is then reconverted to oxides by reaction with a mixture of steam and hydrogen in another fluidized-bed reaction vessel.

In the development of the fluid-bed fluoride volatility process for uranium dioxide-type fuels, additional studies were made of the removal of UO_2 pellets from stainless steel-clad fuel segments utilizing the two-zone reactor. In this process, a major part of the UO_2 is removed by oxidizing the pellets to U_3O_8 . The remaining uranium is removed by fluorination.

Studies were continued of the separation of UO_2 from stainless steel-clad fuel elements in experiments in which only oxidation (no fluorination) was carried out in a fluidized-packed bed. In this process, the separation of the fuel material from the cladding is achieved by reacting the exposed UO_2 with air at an elevated temperature to form U_3O_8 powder which is removed from the cladding.

Construction was continued of an engineering-scale alpha facility. This facility will be used to study the process steps in the fluid-bed fluoride volatility process for the recovery of UO_2 - PuO_2 fuel.

The study of the cleanup of exhaust air from alpha facilities used in fluoride volatility work was continued.

In supporting studies of fluidized-bed systems, the heat conduction in the lateral direction and the characteristics of the longitudinal (axial) movement of particulate solids in fluidized-packed beds were studied.

Studies were continued on a fluid-bed volatility scheme for the recovery of uranium from highly enriched uranium-alloy fuels. Application of the process to uranium-zirconium alloy and uranium-aluminum alloy fuels is being evaluated. In this process scheme, separation of the uranium from the alloying material and the cladding, since these are the same material, is carried out by means of a hydrochlorination step. The uranium is subsequently recovered as the hexafluoride during a fluorination step.

Shakedown tests are now in progress in the pilot plant that has been installed to demonstrate the fluid-bed fluoride volatility process for recovering uranium from highly enriched uranium-alloy fuels. In these tests, the hydrochlorination and hydrofluorination reaction steps were carried out with fuel subassemblies composed only of Zircaloy or of aluminum (no uranium present). During the hydrochlorination step, the fluid-bed hydrolysis reactor was operated to convert the volatile zirconium tetrachloride or the aluminum trichloride to its respective solid oxide.

A process for the direct fluid-bed preparation of high-density spheroidal particles of uranium dioxide by the simultaneous reaction of uranium hexafluoride with steam and hydrogen continued to be investigated. The results of this investigation will be used for subsequent work on the preparation of dense UO_2 - PuO_2 particles from mixed hexafluoride feeds.

Corrosion studies were initiated for the evaluation of the suitability of nickel and other materials of construction for the fluid-bed volatility processes.

Laboratory-scale fluorinations of mixtures of U_3O_8 - PuO_2 and of U_3O_8 - PuO_2 containing selected fission product oxides were carried out in a 1 1/2-in. diameter fluid-bed fluorinator.

The selective reduction of plutonium hexafluoride to the tetrafluoride with sulfur tetrafluoride was studied as a possible means of analyzing PuF_6 in a mixture with UF_6 .

The study of the decomposition of plutonium hexafluoride by gamma irradiation has been completed with an investigation of the effect that krypton has on the decomposition of PuF_6 .

Additional studies were made of the effect of various factors (such as time, temperature, additives and container volume) on the rate of decomposition of gaseous PuF_6 caused by the alpha radiation from the plutonium.

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

1. Fluid-Bed Fluorination of U_3O_8 - PuO_2 Mixtures (R.L. Jarry, A.V. Hariharan,* G. Pierini,** J.J. Stockbar, T.D. Baker)

In the fluid-bed fluoride volatility process, the declad fuel elements are reacted with oxygen and then with fluorine at about 500°C to convert the oxides to the volatile compounds, uranium hexafluoride and plutonium hexafluoride.

In previously reported work (ANL-6742, ANL-6766, page 82), small-scale, boat experiments were performed in order to develop a fluorination procedure applicable to mixtures of uranium dioxide, plutonium dioxide, and alumina, which would result in a high degree of removal of uranium and plutonium from the alumina. In these experiments synthetic mixtures made up to simulate a process charge for a fluidized-bed reactor (100 kg U, 0.4 kg Pu, ~1 kg fission products, and 30 kg alumina) were used. This study

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defined a set of experimental conditions which resulted in the removal of essentially all of the uranium and greater than 99% of the plutonium from such mixtures by fluorination. The experimental technique employed oxidation of the UO_2 - PuO_2 solid solution to produce a mixture of U_3O_8 - PuO_2 followed by a two part fluorination procedure to convert the uranium and plutonium to their respective hexafluorides. The first part of the fluorination, in which the major portion of the uranium was removed, was performed at 450°C using 10 v/o fluorine in nitrogen. The second part of the fluorination, to remove the plutonium, was performed at 550°C using 75 v/o fluorine. When both fluorination periods were of 10-hour duration, the residual plutonium concentration on the alumina was 0.007 w/o, which corresponds to a removal of 99.5 percent of the plutonium contained in the solid mixture.

The next step in the laboratory development work in support of the fluid-bed fluoride volatility process was a study of the fluid-bed fluorination of U_3O_8 described in the topical report, ANL-6763. The oxide, U_3O_8 , is obtained upon oxidizing UO_2 pellets prior to fluorination.

The present report gives the results of initial fluorination experiments performed in fluid beds of alumina using mixtures of U_3O_8 and PuO_2 . The purpose of these and future experiments is to provide information for the evaluation of the following: (1) the level of plutonium retention in the alumina bed under various reaction conditions, (2) the relative rates of fluorination of U_3O_8 and PuO_2 , (3) plutonium retention on the filters and surfaces of the reactor, and (4) comparison of fluorination rates of U_3O_8 - PuO_2 mixtures prepared by the oxidation of UO_2 - PuO_2 solid solutions with those prepared by mechanically mixing U_3O_8 and PuO_2 .

Mixtures of U_3O_8 and PuO_2 , containing about 0.4 w/o plutonium, were prepared by adding commercially produced U_3O_8 (specifications for this material are given in a previous report, ANL-6763) to the oxidation product of pellets of UO_2 - PuO_2 solid solution which contained about 4 w/o plutonium. About 1000 g of U_3O_8 was blended with 100 g of the U_3O_8 - PuO_2 mixture produced by the oxidation of the UO_2 - PuO_2 pellets. In some of the mixtures of U_3O_8 - PuO_2 a blend of 11 fission product element oxides was added. The specific fission product oxides used and the weight percent of each in the mixture are listed in Table II-1. The fission product elements chosen are those which produce nonvolatile fluorides (with the exception of molybdenum). The U_3O_8 - PuO_2 mixtures were blended for about 10 hours. Samples were then taken of the mixtures for uranium and plutonium analyses. The analytical results for a representative batch showed 0.386 ± 0.001 w/o plutonium and 80.5 ± 0.2 w/o uranium. The fission product oxide concentration in the mixture based on the weight of oxides added was 0.86 w/o.

Commercial grade fluorine, which was passed through a sodium fluoride trap at 100°C to remove HF , was used. The nitrogen, which was used as the fluidizing gas and also as a diluent for the fluorine, was passed through a trap containing Molecular Sieves to remove water. High-purity fused alumina was employed as the inert fluidized material.

Table II-1

COMPOSITION OF U_3O_8 - PuO_2 -FISSION PRODUCT OXIDE MIXTURE^a

<u>Material</u>	<u>w/o of Mixture</u>
La_2O_3	0.050
CeO_2	0.090
Pr_6O_{11}	0.042
Nd_2O_3	0.173
Sm_2O_3	0.040
Eu_2O_3	0.002
Gd_2O_3	0.0004
Y_2O_3	0.026
BaO	0.058
ZrO_2	0.182
MoO_3	0.187
PuO_2	0.4
U_3O_8	Balance

^aRepresentative of spent Dresden-type fuel after 10,000 Mwd/ton burnup, 4 yr in reactor, 30-day cooled. Two-day discharge from reactor; 100 kg U (as UO_2), 0.4 kg Pu (as PuO_2), and ~0.9 kg fission product elements as their respective oxides. Relative quantities of fission products as calculated by R. K. Steunenberg (see ANL-6742, p. 14).

The fluid-bed apparatus used in this work was similar to that which was used for the fluorination of U_3O_8 and which was described in a previous report (ANL-6763). The apparatus consisted of the following major components: (1) a 1 1/2-in. fluid-bed fluorinator, (2) a powder feeder, (3) a system of cold traps, which was used to condense the UF_6 - PuF_6 product, (4) a Lapp diaphragm pump employing a remote head, which was used to circulate the gas phase, (5) activated alumina traps for the disposal of fluorine, and (6) manifolds supplying fluorine, nitrogen, and vacuum service. All of the apparatus was contained within an alpha glove box and manipulation of the apparatus was accomplished through glove ports. The alpha glove box, the detailed description of which has been published,¹ was three modules in length and 1 1/2 modules in height. A module is a cube 40 inches on edge. Figure II-2 is a photograph of one face of the alpha box

¹Malecha, R.F. et al. TID-7599 (1960).

showing the placement of the apparatus before all the windows and gloves had been put in place. In Figure II-3, a close-up view of the fluid-bed reactor is shown.

Figure II-2

THE 1 1/2-INCH DIAMETER FLUID-BED REACTOR SYSTEM
IN ALPHA GLOVE BOX

108-6080

Procedure

The fluorinations of the U_3O_8 - PuO_2 mixtures were performed using two reaction periods. In the first period, which will be referred to as the feeding-fluorination period, the U_3O_8 - PuO_2 powder was injected into the fluid bed. During this period, about 99% of the uranium was converted to UF_6 and part of the plutonium, between 40 and 70 w/o, was converted to PuF_6 using a gas mixture of 20 v/o fluorine in nitrogen. The feeding fluorinations, with the exception of one done at 450°C, were carried out at 500°C. In the second period, which will be referred to as the recycle-fluorination period, the fluorine content was raised to about 100% and the gas was cycled through

Figure II-3

THE 1 1/2-INCH FLUID-BED REACTOR

108-6077

the Lapp pump and returned to the fluidized bed. This recycle-fluorination period was intended to remove essentially all the remaining uranium and plutonium.

The general operating procedure for the fluorinations was as follows: About 400 g of 120 mesh fused alumina was placed in the fluid-bed fluorinator, which was then heated to the operating temperature, 450 or 500°C. During the heating period, the nitrogen flow, sufficient to fluidize the bed, was started. A charge of a mixture of 300 g of U_3O_8 - PuO_2 and 150 g of alumina was placed in the powder feeder. (Alumina was mixed with the U_3O_8 - PuO_2 to improve the flow characteristics of the oxide powder.) When the reactor reached the proper operating temperature, the fluorine flow was started into the bed through a gas distributor cone (see ANL-6763, Figure II-3). The fluorine, which was 20 v/o of the total flow, was diluted with an

equal quantity of nitrogen before it entered the bed. The U_3O_8 - PuO_2 -alumina mixture was introduced into the fluidizing nitrogen stream, and then into the fluid bed at a point below the fluorine inlet, at a rate of about five grams of U_3O_8 - PuO_2 mixture per minute. The gas velocity in the 3/8-in. dia. fluidizing-nitrogen inlet line into which the U_3O_8 - PuO_2 mixture was fed was 5 ft/sec. Total flow rate through the fluid bed was 12 liters per minute with the fluidizing nitrogen contributing approximately seven liters per minute and the mixture of fluorine and nitrogen contributing approximately five liters per minute. The superficial gas velocity in the fluid bed was about 0.6 ft/sec at room temperature (about 1.5 ft/sec at 500°C).

The effluent gas stream from the fluorinator, during the feeding-fluorination period, passed through three cold traps and a sodium fluoride trap (in order to remove the UF_6 and PuF_6), and then through an activated alumina trap, which reacted with and removed the excess fluorine before discharging the effluent gas to the glove box atmosphere. After the feeding-fluorination period, the fluorine content of the gas phase was increased to approximately 100% and the recycle period was started. During the recycle period the gas was passed only through the cold traps. After the reaction period had been completed, the sodium fluoride trap and the cold traps (which were maintained at -78°C) were evacuated to remove the noncondensable gas from the cold traps and the unreacted gas from the sodium fluoride. The traps were then warmed to room temperature and weighed to obtain the amount of UF_6 and PuF_6 collected. The alumina, which was used as the fluid-bed medium, was removed from the reactor and samples were taken for uranium and plutonium analyses. The small amount (about 1-2 grams) of a mixture of uranium and plutonium fluorides and alumina which was retained in the disengaging section was removed and submitted for uranium and plutonium analyses.

Prior to the tests with U_3O_8 - PuO_2 mixtures, experiments using U_3O_8 alone were made to determine the efficiency of the cold traps for collection of UF_6 . Nine experiments were performed in which the feeding-fluorination period at 500°C, using 20 v/o fluorine, was followed by a recycle-fluorination period of five hours at 500°C, using 100% fluorine. The average results for these experiments showed a conversion of $99.7 \pm 0.1\%$ of the U_3O_8 to UF_6 and a cold trapping efficiency of 99.3%.

Results and Discussion

The first experiments involving plutonium were made using U_3O_8 - PuO_2 mixtures which did not contain fission product oxides. In all of the experiments, the feeding-fluorination period was performed at 500°C, using 20 v/o fluorine in nitrogen. A mixture of 300 g of U_3O_8 - PuO_2 and 150 g of Al_2O_3 was fed into a 400-gram bed of Al_2O_3 at a rate of about five grams of U_3O_8 - PuO_2 per minute. Each feeding-fluorination period was followed by a recycle-fluorination period at either 500 or 550°C for 5 or 15 hours using 100% fluorine. In one experiment, which was terminated after the feeding-fluorination period, the alumina bed contained 0.043 w/o uranium and 0.063

w/o plutonium. The results for experiments in which the feeding-fluorination period was followed by a recycle-fluorination period are listed in the first part of Table II-2. After a recycle fluorination at 500°C for five hours, the

Table II-2
FLUORINATION OF U_3O_8 - PuO_2 MIXTURES

<u>Experimental Conditions</u>					
Feeding-Fluorination Period:					
Bed Temperature	500°C				
Total Gas Flow	12 liters/min				
F ₂ Concentration	20 v/o				
Alumina in Bed	400 g				
Alumina in Feed	150 g				
U ₃ O ₈ -PuO ₂ Feed	300 g				
U ₃ O ₈ -PuO ₂ Feed Rate	-5 g/min				
Recycle-Fluorination Period:					
Total Gas Flow	8 liters/min				
F ₂ Concentration	100 percent				
Recycle Fluorination Period		Concentration in Al ₂ O ₃ Bed			
Temp (°C)	Time (hr)	w/o U	Wt. U (g)	w/o Pu	Wt. Pu (g)
Part 1, No fission products present. ^a					
500	5	0.021	0.120	0.033	0.187
550	5	0.003	0.016	0.022	0.124
500	15	0.007	0.041	0.030	0.157
550	15	0.014	0.075	0.011	0.056
Part 2, Fission products present. ^b					
500	5	0.016	0.069	0.057	0.330
550	5	0.017	0.096	0.038	0.220
550	15	0.021	0.117	0.029	0.165
500-550 ^c	15	0.015	0.085	0.007	0.040

^a U_3O_8 - PuO_2 mixture contained 253 g U and 1.05 g Pu.

^b U_3O_8 - PuO_2 -F.P. oxides mixture contained 241 g U, 1.13 g Pu and 2.58 g of a mixture of fission product oxides containing the following oxides: La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Y_2O_3 , BaO, ZrO_2 , and MoO_3 (see Table II-1).

^cFeeding-Fluorination Period 3 hr at 450°C
Recycle-Fluorination, 5 hr at 500°C and
10 hr at 550°C

uranium and plutonium concentrations on the alumina were 0.021 w/o and 0.033 w/o, respectively; after a recycle fluorination at 550°C for five hours, the uranium and plutonium concentrations on the alumina were 0.003 w/o and 0.022 w/o, respectively. Extending the recycle-fluorination period to 15 hours resulted in concentrations on the alumina of 0.007 w/o uranium and 0.030 w/o plutonium at 500°C, and 0.14 w/o uranium and 0.011 w/o plutonium at 550°C. In these fluid bed experiments the alumina to uranium ratio has been about 1:2, while in the boat experiments reviewed earlier the alumina to uranium ratio was 3:1. A plutonium concentration of 0.01 w/o on the alumina in these particular fluid-bed experiments represents about five percent of the plutonium fed to the reactor for a single use of alumina while for the boat experiments a plutonium concentration of 0.01 w/o on the alumina represented about one percent of the plutonium involved in the experiment.

A second set of experiments were performed using U_3O_8 - PuO_2 mixtures containing fission product (F.P.) oxides. In one experiment, which was terminated after the feeding-fluorination period, the alumina bed contained 0.149 w/o uranium and 0.106 w/o plutonium. The results for experiments in which the feeding-fluorination period was followed by a recycle-fluorination period are listed in the second part of Table II-2. These results show concentrations on the alumina of 0.016 w/o uranium and 0.057 w/o plutonium after five hours of fluorination at 500°C, and 0.017 w/o uranium and 0.038 w/o plutonium after 5 hr of fluorination at 550°C. After 15 hr of recycle fluorination at 550°C, the uranium and plutonium concentrations on the alumina bed were 0.021 w/o and 0.029 w/o, respectively.

In these experiments the presence of fission product oxides in the U_3O_8 - PuO_2 mixtures did not materially increase the uranium retention on the alumina; in all cases the quantities of uranium retained represented less than one percent of that fed to the reactor. The presence of fission products in the U_3O_8 - PuO_2 mixture did, however, result in a substantial increase, about twofold, in the plutonium retention on the alumina. These results are remarkably similar to results previously obtained for the boat reactor experiments (ANL-6742, page 15). In the boat experiments, the plutonium concentration in the alumina for non-fission product and fission product experiments were 0.027 w/o and 0.065 w/o, respectively.

An experiment was performed to investigate the effect on the plutonium concentration of the alumina bed when an alumina bed was re-used for several fluorinations of U_3O_8 - PuO_2 mixture containing fission product oxides. Three fluorinations of 300 g of U_3O_8 - PuO_2 -F.P. oxide mixture, containing 241 g of uranium, 1.13 g of plutonium, and 2.58 g of fission product oxides, were made, using in each a feeding-fluorination period at 500°C followed by a recycle-fluorination period at 500°C of

five hours. The alumina bed was removed from the reactor after each fluorination and sampled--then split into two portions, 400 g to be re-placed in the reactor and 150 g to be mixed with the next 300 g charge of U_3O_8 - PuO_2 -F.P. oxides mixture. After the initial fluorination, the plutonium concentration on the alumina was 0.057 w/o. The concentration of plutonium on the alumina after the second fluorination was 0.114 w/o. After the third fluorination, the concentration was 0.167 w/o. The plutonium concentration on the alumina in this experiment increased almost linearly with each additional fluorination. The uranium concentration on the alumina remained at less than 0.1% of the total uranium fed in any of the three fluorinations. The re-use of the alumina bed did not result in a lower overall retention of plutonium on the alumina than that which would have resulted if a fresh batch of alumina had been used with each of the three batches of oxide mixture. The conclusion obtained from the result of this fluid-bed fluorination experiment is identical to that for a similar experiment performed using the boat reactor (ANL-6742, page 13). However, further work will be carried out to determine the conditions which will allow re-use of alumina.

In a single experiment, a lower temperature, 450°C, was used both during the feeding-fluorination period and in a 5-hr recycle-fluorination period. These two periods at 450°C were followed by recycle fluorinations of 5 hr at 500°C and 10 hours at 550°C. The fluorine concentration was 20 v/o during the feeding-fluorination period and 100% during the recycle-fluorination period. During the feeding-fluorination period, 300 g of a U_3O_8 - PuO_2 -F.P. oxides mixture, containing 254 g of uranium, 1.18 g of plutonium, and 2.58 g of fission product oxides, was fed into the reactor at a rate of about two grams per minute. The alumina bed after this series of fluorinations contained 0.015 w/o of uranium and 0.007 w/o of plutonium. The choice of reaction conditions used in these experiments was made on the basis of results obtained in a series of boat reactor experiments (ANL-6742, page 17). In the boat experiments a low concentration of plutonium resulted on the alumina as a result of a two-step fluorination procedure. During the first step, in which the major portion of the uranium is removed, a low temperature (450°C) and a low concentration of fluorine (10 v/o in nitrogen) was used. In the last step, a higher temperature (550°C) and a higher fluorine content (75 v/o in nitrogen) was used to effect the removal of plutonium.

Future experimental work will be concerned with the following types of investigations. The extended recycle use of an alumina bed; the alumina to U_3O_8 - PuO_2 ratio of 2:1 being used in these experiments would allow, in process operation as many as 10 re-uses before the self-heating due to fission product accumulation would require the alumina to be discarded. The effect of substituting U_3O_8 - PuO_2 mixtures prepared by mechanical mixing of the two components for mixtures prepared by the oxidation of UO_2 - PuO_2 solid solution on the plutonium retention in alumina will also be evaluated. The use of mechanically prepared mixtures in the pilot plant studies would result in an economy in material costs.

2. Selective Reduction of Plutonium Hexafluoride in Uranium Hexafluoride Using Sulfur Tetrafluoride
(R. Wagner, W. Shinn)

In laboratory and engineering development work on the fluid-bed fluoride volatility process, it is necessary to determine the quantity of plutonium in mixtures of PuF_6 and UF_6 collected from the effluent of fluidized bed, fluorination reactors. A typical fluorination experiment on mixtures of U_3O_8 and PuO_2 with the 1 1/2-in. dia. laboratory-scale fluidized bed apparatus yields a mixture containing 350 g UF_6 and 1.4 g PuF_6 . Traps cooled to -80°C are used to remove the UF_6 and PuF_6 from the nitrogen, fluorine stream.

It would be very difficult to obtain a representative sample or to hydrolyze the entire UF_6 - PuF_6 mixture. Good mixing of the UF_6 and PuF_6 would be required to make a sample representative. Because of the low vapor pressures (90 to 150 mm Hg) of UF_6 and PuF_6 at room temperatures, an inordinate volume, about 1500 l, would be required to mix, as gases, the UF_6 and PuF_6 obtained from a typical fluidized bed experiment. Mixing the UF_6 and PuF_6 as liquids and taking a liquid sample would require the liquid-vapor phase diagram to make corrections for any differences in PuF_6 concentrations in the liquid and in the vapor over the liquid. The liquid-vapor phase diagram has not yet been determined. Plutonium tetrafluoride and lower uranium fluorides are formed by alpha decomposition. The solubility of PuF_4 in liquid UF_6 - PuF_6 is not known, hence the possibility of precipitating PuF_4 exists. The volatilities and reactivities of UF_6 and PuF_6 make homogenization of the solid compounds impractical. Hydrolysis of such large mixtures of UF_6 and PuF_6 would also be hazardous. A separation of most of the uranium from the plutonium would reduce the amount of material to be hydrolyzed and decrease any interference by uranium in the plutonium analysis. It has been shown by Steindler and Steidl (ANL-6145, page 99, ANL-6183, page 94, and ANL-6231, pages 94, 96) that SF_4 will reduce PuF_6 quantitatively to PuF_4 with the formation of SF_6 and that UF_6 is not reduced by SF_4 .

A series of experiments was performed to demonstrate that PuF_6 present to the extent of only 0.5 w/o in liquid UF_6 could be quantitatively reduced to the nonvolatile PuF_4 by gaseous SF_4 . Optimum operating conditions were sought by investigating the effects of shaking the mixtures, varying the SF_4 to PuF_6 mole ratios, and varying the reaction times.

Mixtures were made by adding weighed amounts of purified PuF_6 to prefluorinated nickel reaction vessels. Uranium hexafluoride, in quantities to produce mixtures of about 0.5 w/o PuF_6 in UF_6 , was then added and weighed in the vessels. Sulfur tetrafluoride, in either a twofold or tenfold mole excess of the PuF_6 was condensed on the solids at -196°C . The reaction vessels were then heated to $85 \pm 5^\circ\text{C}$ to facilitate SF_4 - PuF_6 contact and were permitted to remain at this temperature for periods from one to 29 hours. The vessels, except one, were shaken intermittently during heating. The reaction vessels were reattached to the vacuum service manifold and the volatile components were transferred to a storage vessel cooled to -196°C . The reaction vessels were cut open and the solids were dissolved in 500 cc of 6 N HNO_3 , 0.1 M $\text{Al}(\text{NO}_3)_3$ for radiochemical and amperometric

analysis of the plutonium. An additional portion of 100 cc of acid solution was used to rinse the vessels thoroughly to make certain that the dissolution was complete.

The results of these experiments are summarized in Table II-3. Two experiments (the first two tests in Table II-3) indicated an insufficient quantity of solid upon weighing the product of the SF_4 reaction to justify dissolution and analysis. A 2.08 SF_4/PuF_6 mole ratio was used in one experiment, in which a 0.59 w/o PuF_6 in UF_6 mixture was heated for 1.7 hr without shaking. Only 65.7 percent of the expected solid was obtained. In

Table II-3

SELECTIVE REDUCTION OF PuF_6 IN UF_6 BY SF_4

Reaction Temperature: $85 \pm 5^\circ\text{C}$

Initial Mixture (g)		moles SF_4 / mole PuF_6	Heating Time (hr)	% Pu Recovery	U in Solid Product (g)
PuF_6	UF_6				
1.950	328.3	2.08	1.7	-- ^a	-- ^a
1.987	289.4	1.90	1.0	-- ^a	-- ^a
1.810	353.5	1.90	22	100.0 ^b	0.018
1.830 ± 0.012	354.4	11.5	1.0	99.1 ^c	0.125
2.047	291.7	9.26	29	98.8 ^c	0.165
4.011	912.2	11.3	2.0	101.7 ^b	0.310

^aNo analysis was made

^bDetermined by radiochemical counting of Pu alphas ± 2 percent

^cDetermined by amperometric titration of Pu to ± 0.5 percent

another experiment, using a 0.51 w/o PuF_6 - UF_6 mixture and reacting this with a 1.90 mole excess of SF_4 for 1.0 hr with shaking, only 43.6 percent of the expected solid was recovered. When a 22-hr heating period and intermittent shaking were employed, a 1.90 stoichiometric excess of SF_4 was sufficient to obtain complete reduction of PuF_6 to PuF_4 . The use of about a tenfold mole excess of SF_4 in tests of 1-, 2-, and 29-hr durations gave recoveries of 98.9, 101.7 and 97.7% plutonium, respectively. These values are within the ± 2 percent uncertainty of the radiochemical analytical method. The plutonium contents in the solutions from the 1-hr and 29-hr experiments above were also determined by amperometric titration. These determina-

tions, which have uncertainties of $\pm 0.5\%$, indicated plutonium recoveries of 98.8% for the 29-hr heating and 99.1% for the 1-hr heating. Less than 4 mg of plutonium was found in each of the 100 cc of acid solution used for the additional rinses used to check the dissolution procedure.

Steindler and Steidl have shown that UF_6 decomposes when in the presence of PuF_6 (ANL-6231, p. 99). Uranium hexafluoride has also been shown to decompose to lower uranium fluorides in the presence of alpha radiation from radon.² In the SF_4 experiments it was not possible to ascertain exactly how long the UF_6 was exposed to the alpha radiation from plutonium, because of the varying lengths of time necessary to remove the volatile products. The acid solutions of the solids from the $\text{PuF}_6\text{-SF}_4$ reduction were analyzed for uranium. The largest amount of uranium found was 0.31 g. Although quantitative evaluation of the amount of uranium expected from radiation decomposition is not possible, it is believed that the formation of solid uranium product results from radiation decomposition of UF_6 . The small quantities of uranium found indicate that no appreciable reduction of UF_6 is caused by SF_4 .

During these experiments it has been observed that after the addition of SF_4 , heating, and the reduction of PuF_6 to PuF_4 , the UF_6 transfers out of the reaction vessel slowly. No explanation is presently available to account for the reduced UF_6 transfer rate.

In summation it has been demonstrated that SF_4 gas can be used to quantitatively reduce PuF_6 to nonvolatile PuF_4 in a liquid mixture of PuF_6 in UF_6 . Using an elevenfold stoichiometric excess of SF_4 , one hour of heating at 85°C , with intermittent shaking, was sufficient to convert $100 \pm 1\%$ of PuF_6 to PuF_4 in a 0.5 w/o mixture of PuF_6 in UF_6 . A twofold excess of SF_4 is sufficient at 85°C , but the heating time must be extended to about 22 hr. The small quantity, 0.31 g, of uranium deposited in the reaction vessel is believed to be due to alpha radiation decomposition of the UF_6 .

3. The Decomposition of Plutonium Hexafluoride by Gamma Radiation in the Presence of Krypton

(M. J. Steindler, D. V. Steidl, W. Gunther)

The volatility of PuF_6 is utilized in the fluid-bed fluoride volatility process to effect a separation of plutonium from most of the fission products. During the fluorination step, and in subsequent operations, plutonium compounds are exposed to radiation from fission products. A study of the decomposition of PuF_6 by gamma radiation has been undertaken to obtain information concerning the extent of decomposition, the products of the decomposition, and the fundamental processes involved in the radiation chemistry of PuF_6 .

²C. H. Shiflett et al., J. Inorg. Nucl. Chem., 7, 210 (1958).

Plutonium hexafluoride decomposes under the influences of gamma radiation to elemental fluorine and PuF_4 (see ANL-6477, p. 118). In the absence of added gases, the G value* for the decomposition of PuF_6 has been found to be 7.5 ± 1.7 (see ANL-6687, p. 106). Helium added to PuF_6 does not influence the decomposition appreciably and a G value of 6.6 ± 1 has been obtained (see ANL-6725, p. 128). The experiments reported at this time are designed to study the influence of gaseous krypton on the G value for the decomposition of PuF_6 by gamma radiation.

The experimental procedure used in these experiments has been outlined previously (ANL-6477, page 118). Briefly, the experimental procedure was the following. Samples of purified PuF_6 were introduced into nickel vessels which had been pretreated with elemental fluorine and PuF_6 . The samples were irradiated in the Argonne High-Level Gamma Irradiation Facility to the desired dose. After irradiation, the contents of the vessel were analyzed to determine the residual PuF_6 and the quantity of fluorine and PuF_4 formed. The amount of energy absorbed by PuF_6 and by krypton was calculated from dosimetry data based on the Fricke dosimeter and the ratio of the electron densities of liquid water and the gas in question.

The results of experiments carried out to an exposure dose of approximately 1×10^8 rads are shown in Table II-4 and Figure II-4. The results of experiments carried out at an exposure dose of approximately 2×10^8 rads are shown in Table II-4 and Figure II-5. A number of comments apply to both sets of data. G values indicated in Table II-4 were obtained from single experiments, and thus differ from the G value cited for the decomposition of PuF_6 in the absence of other gases. In the latter instance, the G value for the decomposition was obtained from the slope of a plot of absorbed energy versus moles of PuF_6 decomposed. Further, although the added krypton contributes to the total energy absorbed in the system, the G values for the present experiments were calculated on the basis of only the energy absorbed in PuF_6 . This method of calculation permits direct comparison of these data to the G value of 7.5 noted earlier for the decomposition of PuF_6 alone. Finally, the disparity between the amount of PuF_6 lost and the PuF_4 formed is believed to be the result of experimental errors rather than the result of some significant deviation from the cited stoichiometry of the decomposition.

The results obtained at an exposure dose of approximately 1×10^8 rads ($\sim 1.5 \times 10^{20}$ ev absorbed in PuF_6) are unusual in that a marked enhancement of the decomposition of PuF_6 is observed at an average electron fraction of krypton** of approximately 0.73. There are sufficient experimental

*G = molecules decomposed per 100 ev absorbed.

**Average electron fraction is the number of e^- due to Kr in the system divided by the average number of all e^- in the gas phase. The PuF_6 content used in the calculations is the average of the initial and final amounts of PuF_6 present. The average electron fraction of Kr may most easily be obtained from:

$$\frac{\text{dose absorbed in Kr}}{\text{dose in Kr} + \text{dose in PuF}_6}$$

Table II-4

DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE IN MIXTURES WITH KRYPTON
BY GAMMA RADIATION

Temperature: 60-70°C
 Average gamma energy: 0.75 Mev
 PuF₆ pressure: 80-100 mm Hg at 25°C

Experiment No.	Initial PuF ₆ (millimoles)	Initial Krypton (millimoles)	Absorbed Dose (ev x 10 ⁻²⁰)		PuF ₄ Formed (millimoles)	PuF ₆ Lost (millimoles)	Electron Fraction of Krypton	G ^a
			in PuF ₆	in Kr				
Exposure dose: ~1 x 10 ⁸ rads								
112	0.996	0.295	14.8	1.2	0.149	0.170	0.075	6.5
166	1.030	1.552	15.2	6.0	0.165	0.149	0.283	6.2
101	1.000	2.376	15.2	9.5	0.161	0.138	0.385	6.0
156	1.024	3.304	16.4	14.2	0.191	0.189	0.464	7.0
70	0.984	4.753	14.8	19.7	0.141	0.195	0.571	6.8
94	1.042	5.408	15.1	21.1	0.198	0.191	0.583	7.8
15	1.074	8.146	15.1	32.9	0.332	0.313	0.685	12.9
30	1.006	9.238	13.8	37.5	0.352	0.346	0.731	15.2
18	1.005	9.157	14.0	39.5	0.480	0.423	0.738	19.4
26	0.979	10.05	13.1	38.9	0.337	0.302	0.748	14.7
164	1.021	14.04	15.5	55.1	0.120	0.109	0.780	4.5
62	0.998	17.64	15.4	73.1	0.145	0.166	0.826	6.1
192	0.537	17.79	16.0	154.7	0.148	0.167	0.906	5.9
Exposure dose: ~2 x 10 ⁸ rads								
8	0.991	0.446	25.8	3.6	0.295	0.286	0.122	6.8
12	1.011	0.870	26.3	6.6	0.295	0.270	0.201	6.4
10	0.999	0.949	25.9	7.0	0.235	0.216	0.213	5.2
188	1.006	1.327	29.1	11.2	0.312	0.316	0.278	6.5
194	1.007	1.977	30.3	16.9	0.257	0.269	0.358	5.2
186	1.035	2.931	29.5	23.8	0.235	0.280	0.447	5.2
176	1.049	4.877	32.4	41.4	0.208	0.203	0.561	3.8
174	1.003	7.063	31.6	60.5	0.222	0.223	0.657	4.3
103	1.023	8.427	32.9	73.6	0.160	0.198	0.691	3.3
114	1.032	8.575	24.6 ^b	55.1	0.112	0.185	0.691	3.6
90	1.007	8.575	29.7	70.0	0.185	0.218	0.702	4.1
198	1.001	18.23	32.1	156.3	0.131	0.160	0.830	2.7

^aG value based on the average of PuF₆ lost and PuF₄ formed, and calculated on the basis of energy absorbed in PuF₆ only.

^bExposure dose ~1.5 x 10⁸ rads.

results to conclude that the enhancement of the decomposition represents a real phenomenon.

In the absence of additional data, it is not possible to present a conclusive mechanism which accounts for all of the experimental results. No study found in the literature parallels this study with PuF₆. The data which are available in the literature normally refer either to the use of very small additions of rare gases to systems for the purpose of studying the sensitization of a process or to the addition of large quantities of rare gases in order to study the charge transfer processes induced by radiation. Results

Figure II-4

DECOMPOSITION OF
PLUTONIUM HEXAFLUORIDE
IN MIXTURES WITH KRYPTON
BY GAMMA RADIATION

(Pressure of PuF_6 : ~80 mm Hg (1 millimole); Pressure of krypton: variable; Total Exposure dose: $\sim 1 \times 10^8$ rads ($\sim 15 \times 10^{20}$ ev absorbed in PuF_6); Dose rate: 1×10^4 to 4×10^4 rads/min; Temperature: $60-70^\circ\text{C}$; Average gamma energy: 0.75 Mev; G calculated only from energy absorbed in PuF_6 .)

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Figure II-5

DECOMPOSITION OF
PLUTONIUM HEXAFLUORIDE
IN MIXTURES WITH KRYPTON
BY GAMMA RADIATION

(Pressure of PuF_6 : ~80 mm Hg (1 millimole); Pressure of krypton: variable; Total exposure dose: 0.2×10^8 rads ($\sim 30 \times 10^{20}$ ev absorbed in PuF_6), $\Delta 1.5 \times 10^8$ rads; Dose rate: 1×10^4 to 4×10^4 rads/min; Temperature: $60-70^\circ\text{C}$; Average gamma energy: 0.75 Mev; G calculated only from energy absorbed in PuF_6 .)

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of experiments reported in the literature on the addition of reactive components to gases in order to study the variation of G values are not relevant to the present work.

Even though a comparison with results in the literature is not possible, it may be instructive to examine the possible reactions which could contribute to the observed effects. If the data obtained at an exposure dose of 1×10^8 rads is considered, the results may be interpreted as being caused by several competitive processes each of which becomes important in turn as the concentration of, and hence the energy absorbed in, krypton increases. The initial drop in G for the decomposition may be assigned to processes such as those illustrated in Equations 1 and 2:

Equation 1 represents the deactivation of an excited PuF_6 molecule by transfer of excitation energy to krypton. No data are available on the energy levels of PuF_6 . If it is assumed that the first ionization potential of PuF_6 is similar to that of UF_6 ,³ a value of approximately 15 ev is obtained. The lowest excited state of krypton is 9.915 ev above the ground state.⁴ Thus, excitation energy can be transferred between krypton and PuF_6 without ionization of either species if the energy available is less than the ionization potential of krypton³ (13.999 ev). Reaction 2 represents a charge transfer process which may proceed as written except that approximately 1 ev of excitation energy must be distributed between the krypton ion and the PuF_6 molecule. The absorption spectrum of PuF_6 ⁵ shows several bands at frequencies both greater than and less than 8100 cm^{-1} (1 ev), indicating that partition of the excess energy to PuF_6 is at least possible. Both Equations 1 and 2 result in the deactivation of excited (or ionized) PuF_6 which, in turn, should result in a lowering of the G value for the decomposition.

A second process which may become important as the energy input to krypton increases, i.e., as the electron fraction of krypton increases, is shown by Equation 3

In this case, the activated species of krypton has been identified as $\text{Kr}^{*'}$ in order to emphasize the difference between Reaction 3 and Reaction 1. Further the reaction has been written to show complete decomposition, but it is recognized that intermediates of unknown composition or energy content may be present. As the energy absorbed by krypton is increased, Reaction 3 should

³Warren, V.L. and Horton, J.C., K-1429 (1959).

⁴Moore, C.E., Atomic Energy Levels, NBS Circular 467, Vol. II (1952).

⁵Steindler, M.J., ANL-6687.

become increasingly important and would result in an increase in the G value for the decomposition. Finally, at very great krypton concentrations, and hence at very great energy contents of krypton, reactions 4 and 5 may be operative.

Equation 4 represents the deactivation of a highly excited species of PuF_6 or the deactivation of an ionic form of PuF_6 . If this reaction is to become important, the PuF_6 species must be short-lived. No direct evidence for Reaction 4 exists. Enhancement of the back-reaction has been demonstrated in the absence of krypton (ANL-6596, p. 130) and it has been shown that irradiation of mixtures of PuF_4 and fluorine can produce quantities of PuF_6 in excess of those anticipated from thermodynamic considerations of the equilibrium alone.⁶ Although Equation 5 represents a three-body collision, adsorption of fluorine on PuF_4 is likely and the energy of the reaction is considerably below the energy of the first excited state of krypton. Further, the mechanism of the back reaction may be the activation of F_2 or PuF_4 by Kr^* with subsequent formation of PuF_6 . This process does not require three-body collisions.

While the series of reactions proposed above may account for the results observed at an exposure dose of 1×10^8 rads, the same scheme is not applicable directly to the data obtained at 2×10^8 rads. That the difference between data obtained at a difference of exposure of a factor of only two should be so striking is very unusual. The complete lack of enhancement of the decomposition on simple extension of time of irradiation* is in contrast to most phenomena observed in the radiation chemistry of gases. A process must be operative which reduces the decomposition of PuF_6 as the irradiation time is increased. Not considered in the previous discussion of the mechanism is the role of krypton fluorides. No evidence for the formation of krypton fluorides has been obtained in the present experiments. On the basis of the few data which have been reported on the preparation and properties of KrF_4 , it appears unlikely that appreciable quantities of KrF_4 would remain in the reaction vessel after irradiation owing to the thermal instability of

⁶Trevorrow, L.E., Shinn, W.A. and Steunenbergh, R.K., J. Phys. Chem. 65, 398 (1961).

* Experiments were carried out in identical fashion with the only variation being in the time of exposure. The dose rates, materials of construction, methods of analysis, methods of calculation of the results, etc., were identical. In addition, experiments were done without attention to the sequence of either Kr concentration or irradiation time.

KrF_4 .^{7,8} Further, the formation of KrF_4 would enhance the decomposition of PuF_6 if the reaction leading to the formation of KrF_4 and its subsequent decomposition proceed according to Equations 6 and 7

The reaction shown by equation 7 has been reported in the literature by Grosse.⁷ It may also be possible that the product of Reaction 6 is not the tetrafluoride of krypton but the difluoride, reasoning by analogy with the xenon system. In either case, the result of Reactions 6 and 7 would be an enhancement of the G values for the decomposition. Thus it may be that the enhancement observed at a dose of 1×10^8 rads results from the formation of krypton fluorides. It is difficult to see why such enhancement of the decomposition of PuF_6 should decrease sharply with increasing exposure dose and also how such a sharp decrease is effected, unless the importance of the back reaction is as great as has been indicated.

In summary, the effect of krypton on the decomposition of PuF_6 has been studied at several exposure dose levels. At an exposure dose of 1×10^8 rads, a pronounced enhancement of the decomposition of PuF_6 is observed at an average electron fraction of krypton of 0.73. No such enhancement of the decomposition is observed at an exposure dose of 2×10^8 rads and at the latter dose, all additions of krypton to PuF_6 decrease the G value for the decomposition. While several reactions have been proposed to account for the enhanced decomposition of PuF_6 , including possible formation of krypton fluorides, the mechanism which would correlate the data obtained at all exposures remains obscure. No further work on this system is planned.

4. Alpha Radiation Decomposition Rate of Plutonium Hexafluoride (R. Wagner, W. Shinn)

In order to provide information useful for the quantitative manipulation of PuF_6 , studies of the decomposition of gaseous PuF_6 by alpha radiation from the plutonium are in progress. Plutonium hexafluoride offers an opportunity to study conveniently the radiation chemistry of an inorganic vapor. The number of publications reported in the literature on the radiation chemistry of inorganic gas systems is small. A study was reported on the alpha decomposition of UF_6 .⁹ The decomposition produced a multitude of lower uranium fluoride products. Since PuF_6 decomposes only to PuF_4 and F_2 , PuF_6 is a much simpler system to study. Since plutonium itself emits alpha radiation and has a high specific activity, no external source of alpha

⁷Grosse, A.V. et al., Science 139, 1047 (1963).

⁸Turner, J.J. and Pimentel, G.C., Science 140, 974 (1963)

⁹Shiflett, C.H., J. Inorg. Nucl. Chem. 7, 210 (1958).

radiation is needed. The alpha radiation is therefore homogeneously distributed in PuF_6 gas.

The present studies are aimed at the determination of the rates of PuF_6 decomposition under different conditions and environments. Effects of time, PuF_6 pressure, temperature, container volume and material, surface, and additives (such as PuF_4 , fluorine, oxygen, nitrogen, krypton or helium gas) on the PuF_6 decomposition rate are being determined. This information will also be helpful in making corrections for PuF_6 decomposition in other laboratory studies.

Radiation chemistry results are usually expressed in terms of G values, that is, the number of molecules decomposed per 100 ev absorbed. No direct way, however, is known to measure the energy dose for a self-induced alpha decomposition. As in the case of UF_6 , the energy absorbed by the system must be calculated. Steindler (see ANL-6596, p. 133) has calculated the alpha energy dissipated in PuF_6 at various PuF_6 pressures and the decomposition rates expected for PuF_6 , assuming the G value obtained for the gamma radiation decomposition of PuF_6 to be applicable to the alpha radiation system. Steindler has also shown that the reaction $\text{PuF}_4 + \text{F}_2 \rightarrow \text{PuF}_6$ takes place in a gamma field (see ANL-6596, p. 130). The decomposition of PuF_6 measured is the overall decomposition and includes the decomposition and recombination. Therefore, if the rate of decomposition of PuF_6 can be measured for very short times, that is, before much PuF_4 is formed, a G value could be obtained for the decomposition of pure PuF_6 . There should be an equilibrium state where the rate of decomposition is equal to the rate of recombination. From the equilibrium conditions and from the G value for the decomposition of PuF_6 , a G value can be calculated for the recombination reaction. Attempts are being made to determine the equilibrium concentrations of PuF_6 , F_2 and PuF_4 , and the time required for the system to approach equilibrium.

The amount of PuF_6 decomposed was determined by weighing the PuF_4 formed. The weighing procedures used were described in ANL-6687, p. 149. The present experiments were carried out in prefluorinated nickel spheres having volumes of 125 to 129 cc. However, the prefluorination procedure has been changed from those reported previously. The spheres are now treated with 1200 mm of ClF_3 at 26°C for 1/2 hr, then with 700 mm of fluorine at 40°C for 1/2 hr, and finally with 620 mm of fluorine at 100°C for 24 hr.

All the spheres were filled with 100 mm of purified PuF_6 at 26°C except two, which contained 50 mm of PuF_6 . Three spheres also contained nickel wool to increase the surface area. Some decompositions were carried out in spheres which contained PuF_4 from previous PuF_6 alpha decomposition experiments.

In experiments in which a second gas was mixed with PuF_6 , the 100 mm of PuF_6 was introduced first and weighed. If the pressure of the

second gas was to be more than 200 mm, the gas was expanded into the sphere from a higher pressure. However, if the second gas pressure was to be less than 200 mm in the decomposition sphere, the PuF_6 was condensed using a bath at -80°C before expanding the second gas into the sphere. In no experiment was the PuF_6 maintained in a condensed state for more than 20 min. Since the alpha decomposition rate of solid PuF_6 is higher than that of gaseous PuF_6 , a correction appeared to be necessary. The correction, however, was found to be smaller than the experimental uncertainties for the determination of gaseous PuF_6 decomposition rates, and, therefore, was not applied. In all cases, the second gas was added within seven days after the PuF_6 filling. The times indicated in this report refer to the time that the PuF_6 was in its sphere. The residence time of the second gas was always less.

Samples of 100 mm of PuF_6 were allowed to decompose for 75.6 ± 1.0 , 229, 327 or 386 days. In 75.6 days, a decomposition rate of 0.19% of the initial PuF_6 per day with a standard deviation of 0.03% per day was obtained by averaging the results from eleven experiments. The result of an experiment of 229-day duration indicated that 0.16% of the PuF_6 initially present decomposed per day. In two experiments of 327-day durations, values of 0.083 and 0.091% PuF_6 decomposition per day were obtained. Extending the time to 386 days reduced the rate still further, the rate being 0.076% per day. The data reported here substantiate the conclusions reported in ANL-6687, p. 150, namely, that the PuF_6 decomposition rate decreased with time.

The PuF_6 decomposition rates (0.16 and 0.19% per day) obtained in two experiments of 229-day duration with 50 mm of PuF_6 were not very different from the PuF_6 decomposition rate (0.16% per day) obtained in an experiment, also of 229-day duration, but with 100 mm of PuF_6 . Previous data (ANL-6687, p. 105), but for shorter times, showed a slight decrease in decomposition rate when 50 mm of PuF_6 was used instead of 100 mm.

The choice of a constant time period, volume, and initial PuF_6 pressure allows the direct observation of the effect of such variables as surface area and PuF_4 content on the PuF_6 decomposition rate. For these experiments, a decomposition period of about 75 days was arbitrarily chosen and an initial pressure of 100 mm of PuF_6 in 127 ± 2 -cc nickel spheres was used.

Under the conditions of a constant period of time (75 days), constant volume (127 ± 2 cc), and constant initial PuF_6 pressure (100 mm), the rate of decomposition of PuF_6 was $0.19 \pm 0.03\%$ per day at $26 \pm 2^\circ\text{C}$. However, when the geometrical surface area was increased tenfold in each of three spheres by placing nickel wool in the spheres, the rate increased to $0.30 \pm 0.03\%$ per day. These data indicated a rate dependence on nickel surface area.

The results of a single experiment that was carried out in a non-prefluorinated 127-cc nickel sphere for 75.0 days indicated a PuF_6 decomposition rate of 0.22% per day. This rate was higher than the rate (0.19% per day) obtained when prefluorinated spheres were used, but was lower than the rate (0.30% per day) obtained in spheres which were packed with nickel wool and prefluorinated. These data indicate the existence of surface effects.

A series of 25 experiments was performed in which samples of 100 mm of PuF_6 were decomposed for 75.2 ± 0.6 days in spheres which also contained between 12.0 and 92.0 mg of PuF_4 , and in one sphere which contained 349.2 mg PuF_4 from previous alpha decompositions of PuF_6 . The average of the decomposition rates was 0.14% per day with a standard deviation of 0.03% per day. The results are shown in Figure II-6. The decomposition rates (0.19% per day) obtained in spheres which had no previous exposures to PuF_6 are also indicated in Figure II-6, as well as the results (0.30% per

Figure II-6

RATE OF DECOMPOSITION OF PuF_6 VERSUS QUANTITY OF PuF_4
INITIALLY PRESENT

Vessels: Nickel spheres
Volume: 127 ± 2 cc
Decomposition Time: 75.2 ± 0.6 days
Temperature: $26 \pm 2^\circ\text{C}$
Initial PuF_6 Pressure: 100 mm

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day) obtained in the spheres packed with nickel wool. It can be seen that there is no obvious correlation between the amount of PuF_4 initially present and the rate of PuF_6 decomposition above the PuF_4 .

The presence of fluorine decreased the PuF_6 decomposition rate. This may be caused by an enhancement of the recombination or back reaction. When fluorine was added to the 100 mm of PuF_6 in spheres containing no PuF_4 initially, the PuF_6 decomposition rates for periods of 74.7 days and 230 ± 1 days were less than those found for the same periods when only PuF_6 was present at the start of the decomposition. During a decomposition period of 74.7 days, the PuF_6 decomposition rates were 0.19, 0.082, 0.13, and 0.054% per day for 0 mm, 138 mm, 395 mm, and 3610 mm of fluorine, respectively. The pressure dependence indicated is not reliable because of the large deviations and the small number of experiments. When the duration of the experiment was 230 ± 1 days, fluorine reduced the PuF_6 decomposition rate from 0.16% per day for pure PuF_6 to 0.026 and 0.029% per day for a 100 mm PuF_6 -2280 mm fluorine mixture and 100 mm PuF_6 -682 mm fluorine mixture, respectively.

Addition of oxygen also decreased the PuF_6 decomposition rate appreciably. Average decomposition rates of 0.099, 0.095 and 0.113% PuF_6 per day were obtained in the presence of 148 mm, 430 mm, and 2610 mm of oxygen, respectively, during 74.7-day tests. This is to be compared with the 0.19% per day decomposition rate obtained with PuF_6 alone in the 75-day experiments. In two experiments of 231-day duration, in which about 660 mm of oxygen was used, the PuF_6 decomposition rate decreased in value from 0.16 for pure PuF_6 to 0.060 and 0.077% per day in the presence of oxygen. X-ray diffraction analysis was performed on the solids remaining after the 231-day decomposition. The diffraction pattern showed the solid to be amorphous PuF_4 . In the experiment utilizing 2610 mm oxygen, no oxygen-fluorine compounds were found by an infrared scan of the gases which were not condensable at -80°C . Since there was no evidence of any reaction with oxygen, the decreased rate might be explained on the basis that oxygen changed the energetics of the PuF_6 -fluorine- PuF_4 system, either by absorbing some of the alpha energy or by deactivating any existing species of PuF_6 .

Helium present to the extent of 677 mm, 680 mm, and 2230 mm in 100 mm of PuF_6 in experiments of 230 ± 1 -day durations resulted in values of PuF_6 decomposition rates of 0.12, 0.14, and 0.11% per day, respectively. When krypton pressures were 673 mm and 695 mm, PuF_6 decomposed at rates of 0.081 and 0.073% per day during 231 days. These rates were about the same as those obtained for oxygen at nearly the same pressures. When the krypton pressure was 3720 mm, the decomposition rate (0.11% per day) was close to the value obtained with PuF_6 alone (0.16% per day).

The presence of nitrogen was found to increase greatly the extent and rate of PuF_6 decomposition. The 75.9 to 76.6-day decompositions showed that the amount of PuF_6 decomposed (0.45, 0.47, 0.55, 0.62 and 0.71% per day) increased with increasing nitrogen pressure (88, 119, 382, 1080, and 2670 mm). These results are shown in Figure II-7. These results are to be compared with the 0.19% per day decomposition rate obtained with PuF_6 alone in the 75-day experiments.

Figure II-7

DECOMPOSITION OF PuF_6 GAS VERSUS PRESSURE OF
NITROGEN GAS

Vessel: Nickel sphere
 Volume: 127 ± 2 cc
 Decomposition Time: 76.2 ± 0.4 days
 Temperature: $26 \pm 2^\circ\text{C}$
 Initial PuF_6 Pressure: 100 mm

During 231 days, samples of 100 mm of PuF_6 in the presence of 649 mm and 653 mm of nitrogen decomposed at the rates of 0.40 and 0.42% per day, respectively. In an experiment of 229-day duration 2250 mm of nitrogen caused 100 mm of PuF_6 to decompose at the rate of 0.34% per day. The lower nitrogen pressures gave the higher rates of decomposition. These results are much higher than the 0.16% per day decomposition rate obtained with PuF_6 alone in the 229-day experiment. These data are summarized in Tables II-5 and II-6.

The very high PuF_6 decomposition rates found in PuF_6 -nitrogen mixtures were due to a slow reaction between nitrogen and PuF_6 or nitrogen and the fluorine formed. The reaction products were NF_3 and PuF_4 .

In three of the 76.2-day experiments with nitrogen present, the gases remaining at the end of the decomposition period were passed through several traps cooled to -80°C to remove the undecomposed PuF_6 , and then were passed through a trap cooled to -196°C to remove any condensable compounds. The fluorine and nitrogen were removed by pumping. On warming the -196°C trap, a gas was found. An infrared spectrum of this gas showed it to be NF_3 , which is characterized by a strong peak at 1032 cm^{-1} and a very strong peak at 905 cm^{-1} .¹⁰ Nitrogen trifluoride was also

¹⁰Wilson, M. K. and Polo, S. R., J. Chem. Phys. 20, 1716 (1952)

found in the 100 mm PuF_6 -2250 mm nitrogen mixtures after 229 days. An X-ray diffraction pattern was obtained for the solid formed in this experiment. The pattern was similar to those obtained for amorphous PuF_4 or PuF_4 of small crystalline size. Not enough information is available to determine if the nitrogen reacts with the PuF_6 or if the nitrogen reacts with the fluorine formed by the decomposition; the latter reaction would remove fluorine and prevent the fluorine- PuF_4 recombination.

In summary, it has been shown that the decomposition rate of gaseous PuF_6 due to alpha radiation from the plutonium is not a linear function with time. When fluorine is added to the PuF_6 , the PuF_6 decomposition rate is lowered considerably. These facts indicate that a recombination of fluorine and PuF_4 takes place. The increased PuF_6 decomposition rate when nitrogen is present is due to the formation of NF_3 . The formation of NF_3 decreases the amount of fluorine available for the recombination reaction. Helium, krypton and oxygen decrease the PuF_6 decomposition rate, but only slightly.

The rate of a PuF_6 decomposition for 75-day tests carried out in a nonprefluorinated nickel sphere was slightly higher (0.22% per day) than the rate obtained in prefluorinated spheres (0.19% per day). However, even if the surfaces are prefluorinated, the rate of PuF_6 decomposition is increased with increased surface areas, indicating some surface dependent reaction. The rate of PuF_6 decomposition in spheres containing PuF_4 from previous decompositions is lower than the rate of PuF_6 decomposition in spheres used for the first time. However, no correlation is found between the rate of PuF_6 decomposition and the amount of PuF_4 initially present.

Experiments now in progress include a series which will be sampled after 570 days of PuF_6 decomposition. This length of time should be sufficient for the PuF_6 -fluorine- PuF_4 system to attain equilibrium concentrations. In this series of experiments, the initial PuF_6 pressures are 50 mm, 75 mm, and 100 mm and should indicate whether the equilibrium concentrations are dependent on PuF_6 pressure. Some of the 127 cc spheres in this series contained some PuF_4 from previous experiments. In order to determine the effect of volume on the decomposition of PuF_6 , that is, the effect of longer alpha radiation paths through PuF_6 gas, a nickel sphere having a volume of 22.5 liters and containing 100 mm of PuF_6 at ambient temperatures will be sampled when the PuF_6 residence time becomes 570 days so that a comparison can be made with the decomposition that has taken place in the 127 cc sphere during the same time period.

Another series of experiments is in progress in which the PuF_6 decomposition time will be 75 days. All experiments in this series except one are being carried out in nickel spheres of 127 ± 2 cc volume. One sphere being used in this series has a volume of 5.96 liters and contains 100 mm of PuF_6 . Results from this experiment will also be used to determine the effect of a larger volume.

Table II-5

DECOMPOSITION OF PuF₆ BY ITS ALPHA RADIATION

Spherical Nickel Vessels: 125 to 129 cc

Storage Temperature: 26 ± 2°C

Initial PuF₆ Pressure: 100 mm unless otherwise indicated

Prefluorination Conditions: 1200 mm ClF₃, 26°C, one-half hr then with
 700 mm F₂, 40°C, one-half hr then with
 620 mm F₂, 100°C, 24 hr

Initial Weight of PuF ₆ (mg)	PuF ₆ Decomposed (mg)	Average Rate of PuF ₆ Decomposition (percent per day)			
		No. of Days			
		74.6-75.5	229	327	386
235.3 ^a	38.8	0.22	-	-	-
226.1	40.0	0.24	-	-	-
227.7	37.2	0.22	-	-	-
214.3	30.1	0.19	-	-	-
218.6	30.8	0.19	-	-	-
227.4	24.4	0.14	-	-	-
234.3	26.7	0.15	-	-	-
226.6	28.6	0.17	-	-	-
234.2	30.9	0.18	-	-	-
223.7	31.6	0.19	-	-	-
233.2	38.7	0.22	-	-	-
226.5	38.1	0.22 ^b	-	-	-
227.6	56.7	0.33 ^b	-	-	-
230.4	51.4	0.30 ^b	-	-	-
228.0	46.6	0.27 ^b	-	-	-
249.9	88.5	-	0.16	-	-
136.6 ^c	51.5	-	0.16 ^c	-	-
142.7 ^d	62.7	-	0.19 ^d	-	-
234.0	63.5	-	-	0.083	-
235.8	69.8	-	-	0.091	-
239.4	70.7	-	-	-	0.076

^aThis nickel sphere was not prefluorinated.^bThese spheres were packed with nickel wool to increase the geometrical surface tenfold. They were prefluorinated by the same treatment as described above.^cInitial PuF₆ pressure was 50 mm instead of 100 mm.^dInitial PuF₆ pressure was 50 mm instead of 100 mm; 232 days instead of 229 days.

Table II-6

RATES OF ALPHA DECOMPOSITION OF GASEOUS PuF_6 MIXTURES

Spherical Nickel Vessels: 125 to 129 cc

Storage Temperature: $26 \pm 2^\circ\text{C}$ Initial PuF_6 Pressure: 100 mmInitial Weight of PuF_6 : 215 to 250 mg

Second Gas Component	Pressure of Second Gas Component (mm Hg)	Average Rate of PuF_6 Decomposition (percent per day)	
		No. of Days	
		74.7-76.6	229-231
None	--	0.19	0.16
Fluorine	138	0.0082	--
	395	0.13	--
	3610	0.054	--
	682		0.029
	2280		0.026
Oxygen	148	0.099	--
	430	0.095	--
	2610	0.113	--
	658	--	0.060
	660	--	0.077
Nitrogen	88	0.45	--
	119	0.47	--
	382	0.55	--
	1080	0.62 ^a	--
	2670	0.71 ^a	--
	649	--	0.40
	653	--	0.42 ^b
	2250	--	0.34 ^b
Krypton	673	--	0.081
	695	--	0.073
	3720	--	0.11
Helium	677	--	0.12
	680	--	0.14
	2230	--	0.11

^a An infrared scan of the product gases after removal of PuF_6 showed NF_3 to be present.

^b An infrared scan showed NF_3 to be present. X-ray analysis of the solid suggested it to be amorphous PuF_4 .

The three spheres which contain nickel wool were refilled with 100 mm of PuF_6 . These spheres now also contain some PuF_4 from previous radiation decomposition of PuF_6 . The average rate of PuF_6 decomposition over a 75-day period will be compared with the 0.30% per day decomposition rate obtained when no PuF_4 was initially present.

A set of 127-cc nickel spheres, some containing PuF_4 and others containing only PuF_6 initially, were filled with 100 mm of PuF_6 and are being stored for 75 days at 80°C to determine the effect of this temperature on the rate of PuF_6 decomposition. These experiments should indicate how much thermal decomposition takes place at 80°C .

A series of experiments has been started to determine the rate of PuF_6 decomposition over short periods of time (from 12 hours to 5 days). These data are expected to yield the initial rate of PuF_6 decomposition and indicate any chemical reaction of the PuF_6 with the vessel wall.

5. Stress-Corrosion Studies of Aluminum Alloy and Titanium Alloy in Plutonium Hexafluoride
(R. Wagner, W. Shinn)

At the request of the Oak Ridge Gaseous Diffusion Plant, stressed samples of alloys of aluminum and of titanium were exposed to PuF_6 . The samples were received already stressed in individual nickel plated steel jigs, which subjected each specimen to tension on one side and compression on the other side. Four of the samples were 7075 aluminum alloy loaded to $61,000 \text{ psi} \pm 600 \text{ psi}$. The other two were B-120 VCA titanium alloy loaded to $140,000 \text{ psi} \pm 1,100 \text{ psi}$. The six samples were placed within a cylindrical, 2.5-liter quartz vessel constructed of 85 mm tubing which was mounted vertically in a furnace, the lower part of which could be lowered for sample observation.

The vessel containing the samples was filled with 2.35 g of PuF_6 to a pressure of 52.0 mm Hg at 28°C . The B-120 VCA titanium samples ruptured at some time between 3 and $5 \frac{3}{4}$ days at $65^\circ\text{C} \pm 3^\circ\text{C}$. The 7075 aluminum alloy samples which were maintained at $65 \pm 3^\circ\text{C}$ for 30 days and for 14 additional days at $25 \pm 2^\circ\text{C}$ did not rupture.

B. Engineering-scale Investigation of Fluid-Bed Fluoride Volatility Process
(A. A. Jonke)

1. Development of Fluid-Bed Fluoride Volatility Processes for the Recovery of Uranium and Plutonium from Uranium Dioxide Fuels
(W. J. Mecham)

Development of a fluid-bed fluoride volatility process for the recovery of uranium and plutonium from spent UO_2 fuels has continued. In this process, uranium and plutonium oxides are reacted with fluorine to produce volatile hexafluoride products. Because the fluorination reactions

are highly exothermic, fluidized beds of inert solids are used to improve heat transfer from packed beds of fuel element segments or unclad pellets which are themselves too large to be fluidized.

Development studies on an engineering scale have been directed toward optimization of conditions for the processing of UO_2 pellets. These studies have been carried out in a 3-in. ID, air-cooled reactor using fused alumina grain as the inert bed material. The major objectives of the program have been to demonstrate short processing times (less than 20 hr) for batch operations and satisfactory overall fluorine utilization efficiencies (about 75%) for 12-in. deep fluidized-packed beds of uranium dioxide pellets. These objectives have been demonstrated in experiments which utilized the two-zone oxidation-fluorination method.

In the two-zone method of operation, a mixture of oxygen and nitrogen is admitted to the bottom of the reactor and passed through a fluidized-packed bed (a bed containing the fuel charge with inert solids filling the voids). Oxidation of UO_2 to U_3O_8 occurs in this zone (oxidation zone). The U_3O_8 spalls off the surface of the pellets as fine particles (10 to 20 μ dia.) which have a high specific surface area. Fluorination of these fines to uranium hexafluoride (UF_6) is carried out in a fluidized bed (fluorination zone) which is contiguous with and located above the fluidized-packed bed. Transport of the fines from the oxidation zone to the fluorination zone is aided by pulsing the inlet gas. Processing times of 12.5 hr and fluorine utilization efficiencies of 75% have been achieved with 12-in. deep fluidized-packed beds (ANL-6687, p. 112 and ANL-6725, p. 137).

The two-zone method of operation offers several advantages over direct fluorination of the pellets (see ANL-6596, p. 136). One advantage is that caking due to solids formation by the reaction of UF_6 with uranium oxides is eliminated. Another advantage is that improved heat removal can be obtained. The highly exothermic fluorination of uranium oxides takes place in the unhindered fluidized bed where heat transfer coefficients are a factor of 10 higher than those in fluidized-packed beds.

Studies were made of the removal of UO_2 pellets from stainless steel-clad fuel segments utilizing the two-zone reactor. In this process, a major part of the UO_2 is removed by oxidizing the pellets to U_3O_8 . The remaining uranium is removed by fluorination. The method was found to be effective in removing UO_2 from both slit and perforated stainless steel tubing.

The contractor's work on the engineering-scale alpha facility has been completed. This facility will be used to study the process steps in the fluid-bed fluoride volatility process for the recovery of UO_2 - PuO_2 fuel. Equipment is being installed in the facility and preparations are under way to place the fluorination equipment into operation.

A program investigating the cleanup of exhaust air from alpha facilities used in fluoride volatility work is in progress. As part of the

program, the behavior of PuF_6 and UF_6 released to simulated glove-box atmospheres is being studied. The work also includes evaluation of cleanup devices, such as high efficiency (AEC) filters.

A study was made of the heat conduction in the lateral direction in fluidized-packed beds. Various sizes of fixed packing and fluidized particles were studied. An equation relating the effective thermal conductivities to the density and heat capacity of the fluidized particles, the diameter of the fixed packing, and fluidizing gas velocities was derived.

A study was carried out to determine the characteristics of the longitudinal (axial) movement of particulate solids in fluidized-packed beds. Data obtained from these studies will be of significant value in the design of fluidized-packed bed reactors.

- a. Separation of Uranium Dioxide Fuel from Stainless Steel Cladding by Oxidation and Fluorination Reactions
(L. J. Anastasia, R. V. Kinzler, R. Mancini,* B. Kullen, and A. Rashinskas)

Laboratory studies have recently demonstrated the feasibility of oxidative decladding of UO_2 pellets from stainless steel tubing. In these studies, the UO_2 was exposed to oxygen by means of either punched holes¹¹ or milled slots (ANL-6725, p. 122) in the cladding. Oxidation of the UO_2 to U_3O_8 ruptured the cladding and pulverized the pellets, thereby permitting complete removal of uranium from the cladding. In separate oxidative decladding studies (discussed in a subsequent section), 15/16-in. long, stainless steel-clad segments have been reacted in a fluidized-packed bed configuration similar to that described above for the two-zone oxidation-fluorination process. In these tests, some difficulty was encountered in obtaining complete separation of the uranium from the cladding by oxidation alone.

In two previous decladding experiments which utilized the two-zone method of oxidation-fluorination (ANL-6725, p. 142), complete removal of UO_2 from the cladding was achieved with a 1.5-in. deep fluidized-packed bed (Run UOF-71) and 95% removal was achieved with a 6-in. deep fluidized-packed bed (Run UOF-72) in total processing times of 8.5 and 13.5 hr, respectively. The charges for these runs consisted of 15/16-in. long segments of type 304 stainless steel tubing (0.010-in. wall thickness) which contained two pellets each. These segments, with the cladding open at both ends, simulated chopped or sheared fuel rods. In both runs, the oxidation step was carried out at 450°C with 22% oxygen in nitrogen (total gas rate, 1.1 cfm); however, in both runs, a final fluorination period with fluorine alone was required in order to achieve the UO_2 removals indicated.

*Co-op Student, University of Detroit.

¹¹Guon, J., et al., Low Decontamination Reprocessing Studies on Irradiated UO_2 Fuel, NAA-SR-7136 (Nov. 30, 1962).

Recent two-zone decladding experiments have been carried out with a 3-in. deep fluidized-packed bed of 15/16-in. clad segments. Runs were also made with vertical bundles of tubes (10 in. and 12 in. long) in which the cladding had been slit or perforated longitudinally. For purposes of comparison, an experiment was carried out with a 3-in. deep fluidized-packed bed of 15/16-in. clad segments using single zone oxidation-fluorination (i.e., exposure of the clad sections to a mixture of oxygen and fluorine). The operating conditions and results for these runs, UOF-73 through UOF-76, are shown in Table II-7.

Table II-7

OPERATING CONDITIONS AND RESULTS OF FLUID-BED OXIDATION-FLUORINATION
EXPERIMENTS WITH STAINLESS STEEL-CLAD UO_2 PELLETS

Equipment:	3-in. ID, air-cooled reactor				
UO Pellets:	0.42 in. x 0.42 in. right cylinders				
Inert Material:	Fused alumina ^a				
Pulsing Conditions:	Duration 0.04 sec				
	Frequency 2 pulses/min				
	Pressure 20 psig ^b				
	Gas Volume 0.016 cu ft/pulse				
		UOF	UOF ^c	UOF	UOF
		73	74	75	76
<u>Materials Charged</u>					
Weight of UO ₂ pellets	(g)	2886	1710	1704	3249
Weight of cladding (type 304 stainless steel)	(g)	204	275	274	497
Al ₂ O ₃ : weight	(g)	7100	6800	6100	6100
size range	(mesh)	-40 +170	-40 + 170	-80 +200	-80 +200
<u>Cladding</u>					
Length of segments	(in.)	10.3	0.94	0.94	11.6
Thickness	(mil)	10	20	20	20
Number of segments charged		12	85	85	12
UO ₂ pellets per segment		24	2	2	27
Simulated fuel rod treatment		Slit	Chopped	Chopped	Perforated
		Cladding			Cladding
Fixed-bed height	(in.)	10.3	3	3	11.6
Fixed-bed configuration		Bundle of Tubes	Packed-Bed	Packed-Bed	Bundle of Tubes
<u>Once-Through Gas Flow (Two-Zone Operation)</u>					
Duration	(hr)	9.5	-	12.0	7.5
<u>Oxidation Zone:</u>					
Temperature	(°C)	450 (5.5 hr) + 500 (4 hr)	-	400 (8.5 hr) + 500 (3.5 hr)	475
Oxygen Concentration	(%)	6.6 to 23.3	-	88	88
Diluent		N ₂	-	N ₂	N ₂
Total gas rate	(cfm) ^d	1.1	-	0.3	0.3
<u>Fluorination Zone:</u>					
Temperature	(°C)	500	-	500	475
Fluorine feed diluent		Process	-	Process	Process
		Off-Gas	-	Off-Gas	Off-Gas
Diluent recycle rate	(cfm) ^d	0.25	-	0.65	0.65
Fluorine concentration	(%)	5-10	-	3-14	9.3-24
Total gas rate	(cfm)	1.5	-	1.0	1.0
<u>Off-Gas Recycle (Single-Zone Operation)</u>					
Duration	(hr)	4.4	6.5	5.0	-
Temperature	(°C)	500	500	500	-
Oxygen concentration	(%)	-	0-29	-	-
Fluorine concentration	(%)	90	9-42	64	-
Diluent		N ₂	N ₂	N ₂	-
Total gas rate	(cfm) ^c	0.8	0.7-1.2	0.7	-
<u>Total Processing Time</u>	(hr)	13.9	6.5	17.0	7.5
<u>Results</u>					
Fluorine utilization efficiency	(%)	38	38	42	72
UO ₂ removal from cladding	(%)	100	59	≈100	100

^aBlue Label Alundum, a product of the Norton Co., Worcester, Mass.

^bIn Run UOF-74 pulse gas manifold pressures of 30 and 40 psig were also used.

^cSingle-zone oxidation-fluorination was used in this run.

^dAt 25°C and 1 atm.

Processing of Simulated Chopped or Sheared Fuel Segments

In Run UOF-74, which utilized the single-zone oxidation-fluorination scheme, 59% of the original UO_2 was removed from the clad fuel segments in a 3-in. deep fluidized-packed bed in 6.5 hr. During the course of the run, the concentrations of oxygen and fluorine and the manifold pressure of the pulse nitrogen gas were increased (see Table II-7) in order to increase the production rate of UF_6 . No experimental difficulties were encountered during the run. However, because of low collection rates [average of 6 lb UF_6 /(hr)(sq ft)] and low fluorine utilization efficiency (38%), the run was voluntarily terminated without attempting to completely remove uranium from the cladding. These results were poorer than those obtained in comparable two-zone oxidation-fluorination experiments (see Run UOF-75 below).

In Run UOF-75, the two-zone, oxidation-fluorination scheme was used to process a 3-in. deep fluidized-packed bed composed of short lengths (~1 in.) of fuel segments. The operating conditions are listed in Table II-7. During the fourth hour of operation, a production rate of 35 lb UF_6 /(hr)(sq ft) was achieved. Since this rate was considered reasonably high, the two-zone technique of operation was continued for an additional 8 hr. The clad fuel segments were then removed from the reactor according to their positions in the upper, middle, and bottom thirds of the packed-bed charge. The distribution of uranium found in these portions of the packed bed is shown in Table II-8.

Table II-8

URANIUM DIOXIDE DISTRIBUTION IN STAINLESS STEEL-CLAD FUEL SEGMENTS AFTER TWO-ZONE OXIDATION-FLUORINATION, RUN UOF-75

Operating Conditions:	See Table II-7			
Fixed Bed Height:	3 in.			
Charge:	Chopped Fuel Rods (simulated), two UO_2 pellets per segment			
Segment Length:	0.94 in.			
Total Weight of Stainless Steel:	274 g			
Run Duration:	12 hr			
<u>Approximate Bed Position</u>	<u>Upper</u>	<u>Middle</u>	<u>Bottom</u>	<u>Composite</u>
<u>Number of Clad Fuel Segments</u>	28	28	29	85
<u>Initial Weight of UO_2 in Clad Segments</u>	(g) 561	561	582	1704
<u>Approximate Weight of UO_2 Retained in Clad Segments After Processing</u>	(g) 41	67	115	223
<u>Indicated UO_2 Removal</u>	(%) 93	88	80	87

Uranium removal from the cladding was greatest in the upper third of the packed bed and less in the lower portions of the packed bed. (Similar results were obtained in Run UOF-74.) This effect of position on the removal of uranium from cladding is probably due to the action of the gas pulses which imparts greater movement to the uppermost sections of the bed, thereby aiding the removal of loose material from the clad fuel segments that are located in the upper parts of the packed bed. Similar results have been obtained in oxidative decladding experiments which also utilized pulsed, fluidized-packed beds (see ANL-6725, p. 154).

The residue of uranium oxide in the cladding tubes appeared to be loosely packed U_3O_8 . Since about 87% of the uranium charge had been removed from the cladding by the two-zone technique, it seemed likely that complete removal of the oxide from the cladding could be achieved by continuing the run using a direct fluorination (single-zone) step (See Table II-7). After this final fluorination step, only a small quantity (0.4 g) of uranium compounds remained in the cladding tubes; the overall uranium removal was greater than 99.9%.

Run UOF-75 differed from previous two-zone decladding runs in two respects. First, a high concentration of oxygen (88% rather than 22%) was used for the oxidation. Secondly, the fuel segments were removed from the fluid-bed reactor following completion of the two-zone operation to determine the extent of UO_2 removal. The segments were then recharged to the reactor for the direct (single-zone) fluorination step. The handling of the fuel segments may have influenced overall uranium removal, so an additional run would be required to verify that complete removal of uranium can be achieved with a final in situ fluorination of the fuel segments.

Although the results of Runs UOF-71, -72, -74 and -75 are not conclusive, it appears promising that uranium can be completely removed from clad fuel segments of chopped fuel elements by suitable reaction with oxygen and fluorine in a fluidized-packed-bed system. For conditions of complete removal of uranium, the problems of maximum allowable bed height, minimum processing time, and the extent of fluorination of the stainless steel require further investigation. Extensive fluorination of the stainless steel cladding is not desirable because this reaction would result in the formation of volatile chromium fluorides which would be collected as a contaminant in the UF_6 product.

Removal of UO_2 from Simulated Stainless Steel-Clad Fuel Rod Bundles

The two-zone method of oxidation and fluorination has also been applied to the removal of UO_2 from 10 and 12-in. long clad segments of simulated fuel rods which had been either slit or perforated longitudinally. These segments were charged to the reactor as a vertical bundle of rods. For Run UOF-73, a continuous slit along the length of the clad fuel segments (10.3 in.) was made by means of a 1/16-in. wide carborundum grinding wheel. (A typical specimen of a slit segment was shown in Figure II-10,

ANL-6725, p. 143). For Run UOF-76, the tubing was perforated by means of a spiked wheel device. This device readily perforated the 0.020-in. thick stainless steel tubing (packed with UO_2 pellets) to form a line of holes about 1/16 in. wide by 3/16 in. long by 3/32 in. deep. The holes were spaced approximately 11/32 in. between centers.

In Run UOF-73 (see Table II-7 for the operating conditions), virtually all of the uranium charged to the reactor was converted to UF_6 in 9.5 hr. Fluorine utilization efficiency, based on conversion to the hexafluoride, was 55.4%; the average UF_6 production rate was 18 lb UF_6 / (hr)(sq ft). The cladding tubes were then removed from the fluid-bed reactor prior to a cleanup fluorination step of the alumina bed. This cleanup step reduced the uranium concentration in the alumina from 0.28 to 0.08 w/o. As a result of the inclusion of the cleanup step, the overall fluorine utilization efficiency for the run was reduced to 38%.

In Run UOF-73, the uranium was completely removed from the 10.3-in. lengths of fuel clad segments by the two-zone oxidation-fluorination process; hence, direct fluorination (single-zone operation) was needed only to effect a cleanup of the alumina bed and not to complete the removal of UO_2 from the cladding as was necessary in the run (Run UOF-75) made with short fuel segments. Although the uranium was removed from cladding with a wall thickness of only 0.010 in., it is believed that uranium removal would also be complete from cladding several times thicker if the slits in the cladding were sufficiently extensive. A continuous, longitudinal slit in the cladding partially destroys its physical integrity and exposes large portions of the pellet surface area to reaction with oxygen. However, as shown by the results from a subsequent run (Run UOF-76), it appears that adequate exposure of the pellets to oxygen can be achieved through perforations in the cladding.

In Run UOF-76, the charge consisted of twelve 11.6-in. lengths of 0.020-in. thick type 304 stainless steel tubing which had been packed with UO_2 pellets and which had then been perforated by the spiked wheel device described above. Twelve of these simulated fuel-rod segments were charged as a bundle to the fluid-bed reactor and were processed by means of the two-zone oxidation-fluorination technique (the operating conditions are given in Table II-7). The operating conditions for this run were similar to those used for Run UOF-75 in which the fuel charge consisted of short lengths of stainless steel-clad segments. As in Run UOF-75, the oxygen concentration used in Run UOF-76 was 88%. This concentration was about a factor of four higher than that used in Run UOF-73 in which the cladding had been slit longitudinally. In Run UOF-76, UO_2 was completely removed from the cladding in 7.5 hr.

A photograph of typical specimens of cladding which had been completely split open by the oxidation of UO_2 to U_3O_8 is shown in Figure II-8. On some of the cladding tubes there was a metal fluoride film which indicated corrosive attack by fluorine during the run. Since these tubing pieces were

Figure II-8

CLADDING TUBES RUPTURED BY THE OXIDATION
OF UO_2 TO U_3O_8 DURING
RUN UOF-76

(Type 304 stainless steel tubing, 0.020-in. thick wall).

located below the fluorine introduction point, the corrosive attack may have occurred by diffusion or back mixing of fluorine into the oxidation zone.

The UF_6 production rates observed in Run UOF-76 were quite uniform; more so than might have been expected for a process which depends on the rupture of stainless steel cladding. The bar graph in Figure II-9 indicates the degree of uniformity in the UF_6 production rate. For the

Figure II-9

URANIUM HEXAFLUORIDE PRODUCTION RATE FOR RUN UOF-76,
A TWO-ZONE OXIDATION-FLUORINATION
OF STAINLESS STEEL-CLAD UO_2 PELLETS

(For Run Conditions, see Table II-7)

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first 6 hr of operation, the UF_6 production rates averaged 30 lb UF_6 /(hr)(sq ft). At this point in the run, 96% of the uranium charge had been collected as UF_6 at a fluorine utilization efficiency of 88% (based on UF_6 product collection). The overall fluorine utilization efficiency for the 7.5-hr long run was 72%. The average rate of UF_6 production and the overall fluorine efficiency obtained in this run are the highest which have yet been achieved in two-zone oxidation-fluorination process runs with clad UO_2 pellets.

Run UOF-76 also demonstrated that 0.020-in. thick stainless steel cladding which had been perforated with a longitudinal line of holes could be ruptured by oxidation of the contained UO_2 pellets. The pulverized pellets were completely removed from the cladding tubes without the use of external mechanical attachments for vibration of the cladding. It should also be noted that, in contrast to the runs with short lengths of chopped fuel segments (Runs UOF-74 and -75) exposure of the cladding to a fluorine

cleanup step was not required to complete the removal of UO_2 from the cladding. However, additional fluorination of the alumina in the fluid bed is required to recover all of the uranium as UF_6 . This requirement is not considered to be a problem.

b. Oxidative Separation of UO_2 Fuel from Stainless Steel Cladding in a Fluidized-Packed Bed
(M. Baerns, L. Marek, R. Kinzler)

The study of the oxidative separation of UO_2 fuel from stainless steel cladding was continued. The work was carried out in a fluidized-packed bed. The oxidation product in the form of U_3O_8 fines is removed from the unreacted cladding and may then be fluorinated and recovered as UF_6 as discussed in the preceding section of this report.

In this fluidized-packed bed method, simulated fuel segments form a randomly packed bed (nonfluidized) and alumina grain which serves as an inert fluid-bed material is fluidized in the voids of the packed bed. At temperatures above 350°C , oxidation of the dense UO_2 pellets results in the formation of pulverized U_3O_8 as a result of a large reduction in density effected in the material. At lower temperatures, intermediate oxides are formed¹²⁻¹⁶ and generally no fines are produced.

In previous experiments (see ANL-6687, p. 124 and ANL-6725, p. 148) separation of the U_3O_8 from the cladding was inadequate when the fuel segments were not agitated. Oxide removal from the cladding amounted to about 60 to 80%. With agitation by gas pulsing, the separation was improved to approximately 95%.

During the present work, mainly the effect of vibration combined with gas pulsing was investigated as a means of further improvement of the separation of the oxide from the cladding.

Experimental Conditions and Results

The experiments were carried out in a 2-in. dia. nickel reactor. A general description of the apparatus and the results of the first 16 runs were given in the previous quarterly reports cited above. The experimental conditions and results of the present experiments (Runs XO-17 to XO-25) are summarized in Table II-9.

¹²De Marco, R.E., Teller, H.A., Abbott, R.C., Burkhardt, W., Am. Cer. Soc. Bull., 38, 360 (1959).

¹³Hoekstra, H.R., Santoro, A., and Siegel, S., J. Inorg. Nucl. Chem. 18, 166 (1961).

¹⁴Scheibe, H., Ermischer, W., Some Studies of Uranium Dioxide at Temperatures of About 300°C , Zentral-Institut f. Kernphysik, Rossendorf, Germany, Report ZfK-WF-14.

¹⁵Scott, K.T., Harrison, K.T., J. Nuclear Material 8(3), 307 (1963).

¹⁶Aronson, S., Roof, R.B., Belle, J., J. Chem. Phys. 37, 137 (1957).

Table II-9

OPERATING CONDITIONS AND RESULTS OF RUNS FOR OXIDATIVE SEPARATION OF URANIUM
DIOXIDE FROM STAINLESS STEEL CLADDING

Equipment: 2-in. ID nickel column

Inert Bed Charge^a: 1500 g alumina grain (-40 +170 mesh)

Bed Height (Static Condition):

Packed Section: 7 cm (Run XO-18); 15 cm (Runs XO-19 to XO-23, Run XO-25); 22 cm (Run XO-24)

Total Bed: 7 cm (Run XO-18)^a; 35 cm (Runs XO-19 to XO-23, Run XO-25); 28 cm (Run XO-24)

Oxidizing Gas: air^b

Run No.	Weight of UO ₂ Pellets ^c (g)	Number of Clad Fuel Segments	Gas Flow Rate (scfm)	Temperature ^d (°C)	Process Time (hr)	Elutriated U ₃ O ₈ Fines (g)	UO ₂ Removed (%)
XO-17 ^e	632	32	0.4	445	7.33	60	68
XO-18 ^a	400	20	0.39	370 to 510	11.75	0	47
XO-19 ^f	798	40	0.86	440	5.75	83	75
XO-20 ^{b, f}	806	40	0.88	440	8.2	124	62
XO-21 ^f	806	40					
Oxidation			0.85	450	5.75		
Reduction			0.90	600	2.00		
Reoxidation			0.85	450	2.33		
				Total	10.08	395	92.5
XO-22 ^f	805	40					
Oxidation			0.85	20 → 450	2.0		
				450	3.5		
Reduction			0.90	450 → 600	1.25		
				600	1.5		
Reoxidation			0.86	600 → 450	0.6		
				450	2.7		
				Total	11.55	370	95.6
XO-23 ^f	805	40	0.85	20 → 350	1.42		
				350 → 400	0.5		
				400	2.0		
				400 → 450	0.5		
				450	4.25		
				Total	8.67	202	98.7
XO-24 ^f	1209	60	0.85	20 → 375	1.0		
				375 → 400	0.5		
				400	3.0		
				400 → 450	0.5		
				450	3.0		
				Total	8.0	100	77
XO-25 ^f	805	40	0.85	20 → 300	1.0		
				300 → 415	0.5		
				415	2.5		
				415 → 450	0.5		
				450	3.0		
				Total	7.5	197	93

^a Run XO-18 was carried out in the absence of inert fluid-bed material.

^b In Run XO-20, air was diluted with nitrogen resulting in 7.5 v/o oxygen.

^c Added as random-packed pieces of simulated sheared fuel segments which were made by placing two UO₂ pellets (0.45-in. dia. and length) in close fitting stainless steel tubes. These tubes were open at both ends.

^d Averaged over process time and bed height.

^e Packed bed was divided into four individual 1.5-in. high sections, each section containing eight fuel segments.

^f Gas pulses were introduced into bottom of reactor column (frequency, 2 pulses per min; duration, 0.5 sec) and mechanical vibration was transmitted to the fuel pieces.

For the current experiments, a magnetic-type vibrator (60 cpm, 440 watt) was added to the equipment. In two experiments (Runs XO-19 and XO-20), the vibrator was connected to the bottom flange of the reactor. In subsequent experiments, Runs XO-21 to XO-25, the vibrator was connected to a transmittance rod which was introduced into the reactor so that the fuel segments could be directly vibrated. The last arrangement is shown in Figure II-10.

Figure II-10

EQUIPMENT FOR TRANSMITTANCE OF VIBRATION TO FLUIDIZED-
PACKED BED

Simulated fuel segments were made by inserting two cylindrical UO_2 pellets (0.42-in. dia. by 0.42 in. long) into stainless steel tubes (15/16 to 1 1/16 in. long by 0.43-in. ID). The tubes used in Runs XO-17 to XO-20 had 0.01-in. thick walls, whereas the thickness of the tubing in Runs XO-21 to XO-25 was 0.02 in.

The fluidized-packed bed was fluidized with nitrogen while being heated to operating temperature. At operating temperature, the nitrogen was replaced by air. (As an alternative method in some experiments, air was used during the heating-up period.) In the experiments in which the U_3O_8 residues in the cladding were given a reduction treatment with hydrogen, a mixture of approximately 5% hydrogen in nitrogen was used as fluidizing gas.

In several experiments, oxygen consumption in the reaction gas was measured by means of a gas thermal conductivity cell. Although the course of the reaction could be followed by means of the cell, its primary function was to indicate the end of the period of oxygen consumption. When gas pulsing was used, the gas velocity fluctuated in the conductivity cell, and the oxygen concentration could not be quantitatively measured.

A description of Runs XO-17 to XO-25 is given below. Runs XO-17 and XO-18 were carried out to supplement some earlier experiments (Runs XO-15 and XO-16) which were described in the preceding quarterly report (see ANL-6725, p. 153). In Runs XO-19 to XO-25, the effect of mechanical vibration on the separation of UO_2 from the stainless steel cladding was studied.

Run XO-17. In Run XO-17, the experimental conditions were similar to those of the oxidation portion of previously reported Run XO-15 (ANL-6725, p. 153), except that gas pulsing was not applied in the current run. In this way, a comparison of the results of these runs indicates the influence of gas-pulsing on the removal of UO_2 . The fluidized-packed bed in this run of the current series consisted of four sections separated from each other by perforated support plates. Each section contained eight fuel segments and was 1.5 in. deep. The fluidized alumina was continuous through the four sections. The removal of UO_2 was 68%.

Run XO-18. In Run XO-18, no inert fluid-bed material was added to the packed bed of fuel segments. Thus, the effect of the presence of the inert fluid-bed material on the separation process could be evaluated. In the absence of fluidizable material in the voids between the fuel segments, a temperature gradient occurred along the bed; the temperature at the bottom of the bed was 370°C and at the top of the bed was 510°C . The removal of UO_2 amounted to only 47%. The results of this run show that the presence of inert fluid-bed material is necessary for this type of process.

Runs XO-19 and XO-20. Vibration was used in Runs XO-19 and XO-20 with the vibrator mounted on the bottom flange of the reactor. In this way the vibrations were directly transmitted to the reactor column and indirectly to the fuel segments. A uniform temperature was maintained throughout the bed in both runs. In Run XO-19, air was used for the oxidation; in Run XO-20, a mixture of air and nitrogen (oxygen concentration 7.5%) was used. The lower oxygen concentration did not significantly affect the removal. Final removals of UO_2 in Runs XO-19 and XO-20 were 75% and 62%, respectively.

Run XO-21. In Run XO-21, the vibration was directly transmitted to the fuel pieces by means of the transmittance rod (see Figure II-10). This method of vibration was more effective than the one applied in Runs XO-19 and XO-20. The reduction-reoxidation scheme and gas pulsing were also used. The final removal was 92.5%.

Runs XO-22, XO-23, XO-24, and XO-25. The experimental conditions of Runs XO-22, XO-23, XO-24, and XO-25 were, in general, similar to those of Run XO-21; however, no reduction and reoxidation steps were used in Runs XO-23 to XO-25 and the start-up procedure was changed. This new start-up procedure was as follows: the bed was heated with air as fluidizing gas (instead of nitrogen) and the temperature was slowly increased (see Table II-9) to the final reaction temperature. In Run XO-24, a fluidized-packed bed of 60 fuel segments (instead of 40 segments as in Runs XO-21, XO-22, XO-23 and XO-25) was employed to study the influence of the height of the packed section. The final removals of UO_2 for Runs XO-22, XO-23, XO-24 and XO-25 were 95.6, 98.7, 77, and 93%, respectively.

Discussion of Experimental Results

The oxidative separation of the UO_2 from the cladding is, in general, governed by the mechanical removal of the oxidation product rather than by the chemical reaction. This was indicated by measuring the oxygen consumption in the reaction gas and by the final chemical composition of the oxide residues in the cladding (see Table II-10). The chemical reaction was frequently nearly complete, while the physical separation was still incomplete. Also, in general, separations were increased when the vigor of mechanical agitation of the fuel segments was increased.

Table II-10

CHEMICAL COMPOSITION OF URANIUM OXIDE RESIDUES IN CLADDING^a

Run No.	Residue Composition (w/o)		Run No.	Residue Composition (w/o)	
	UO_2	U_3O_8		UO_2	U_3O_8
XO-1	55	45	XO-16	0	100
XO-2	40	60	XO-17	0	100
XO-3	20	80	XO-18	0	100
XO-4	47	53	XO-19	0	100
XO-6	4	96	XO-20	52	48
XO-9	0.6	99.4	XO-21	0	100
XO-10	0	100	XO-22	0	100
XO-11	40	60	XO-23	0	100
XO-12	18	82	XO-24	6	94
XO-13	0	100	XO-25	25	75
XO-14	0	100			

^aIt was assumed that the uranium oxide residue only consisted of UO_2 and U_3O_8 and that there were no intermediate oxides.

The summarized results of this investigation are discussed below in terms of the effects of the various means used to enhance the separation process. Data that were obtained in previous work (see ANL-6687, p. 124 and ANL-6725, p. 148) are also included in the discussion to present a comprehensive review of this investigation.

Effect of Gas Pulsing. The first series of runs (Runs XO-1 to XO-6, see ANL-6687, p. 124) was concerned with the determination of the rate of UO_2 removal and the influence of gas pulsing on the rate of removal. These results are presented by curve (a) in Figure II-11. Without gas pulsing, the rate of removal was approximately constant until about 70

Figure II-11

EFFECT OF GAS PULSING
ON REMOVAL OF UO_2 FROM
STAINLESS STEEL CLADDING

108-7289

to 80% of the fuel was removed from the cladding. Then, removal stopped. Not more than about 70 to 80% of the UO_2 could be separated from the fuel even when the reaction time was extended to approximately 15 hr.

Gas pulsing, which was used to provide some agitation of the fuel pieces, did not significantly improve the removal. An increase of the rate of removal was observed, but the final removal did not exceed approximately 70 to 80%, as indicated by curve (b) in Figure II-11.

Difficulties in maintaining a uniform temperature throughout the bed were encountered because of the presence of large quantities of U_3O_8 fines. Caking of the fines and channelling occurred. However, by maintaining gas pulsing and increasing the gas velocity and the inventory of the inert fluid-bed material (alumina), a slight improvement in uniformity of bed temperature was achieved. The increase in gas velocity, which resulted in a greater elutriation of the fines from the beds, and the increase in alumina inventory both resulted in decreasing the fines concentration of the beds. With lower fines concentrations, the caking tendency was relieved.

Effect of Reaction Temperature. As reported previously (see ANL-6725, p. 153), the optimum reaction temperature for the oxidative separation process is between 400 and 500°C. At lower temperatures, the oxidation reaction is too slow to achieve separation of UO_2 in reasonable processing times. At higher temperatures, the rate of the oxidation reaction is much higher than the rate of uranium oxide removal resulting in a rapid volume increase of the uranium oxide which causes trapping of the uranium oxide in the cladding.

Effect of Reduction and Reoxidation. Since it seemed likely that caking of U_3O_8 was limiting its separation from the cladding, the U_3O_8 was subjected to a reduction step in an attempt to break up the cake or otherwise improve the conditions for its separation in a subsequent reoxidation step. However, no significant improvement in the removal of uranium oxide from the cladding was obtained when reduction and reoxidation steps were carried out.

Effect of Packing. In all the experiments performed without mechanical vibration but with gas pulsing in a fluidized-packed bed (except in the run utilizing the multi-stage fluidized-packed bed), the removal of uranium oxide from the cladding was always greater in the upper part of the bed than near the bottom of the bed (see ANL-6725, p. 149). The movement of the bottom segments is restricted because of the weight of the upper segments on them. This result is consistent with visual observations of a fluidized-packed bed in a glass column, which indicate that the packing is more vigorously moved in the upper part of the bed by the gas pulsing. The motion of the fuel segments results in loosening of the U_3O_8 and allows better separation of the U_3O_8 from the cladding.

Fluidized-packed beds in which the packed bed was divided into four individual shallow sections of fuel segments (each section 1.5 in. deep) resulted in good removals of more than 90% (Runs XO-15 and XO-16, ANL-6725, p. 153). However, even with the shallow beds, good removal is only possible if motion of the clad fuel pieces is achieved. If the bed is not pulsed (Run XO-17) or if the fuel segments become wedged in the reactor and immobilized, the advantage of the shallow bed arrangement is lost.

Effect of Mechanical Vibration. The separation of UO_2 fuel from the cladding was significantly improved by applying mechanical vibration to the fluidized-packed bed (see Table II-11). The best results (a maximum removal of 98%) were obtained by vibrating the fuel segments directly (Runs XO-22 to XO-25) rather than by vibrating the reactor column (Runs XO-19 and XO-21). The lesser removal of UO_2 (77%) obtained in Run XO-24 was apparently due to the greater number of fuel segments (60) used in this run as compared with the number of segments (40) used in the other runs. This indicates that the mechanical vibration available was less effective for the larger bed of fuel segments. In general, vibration was effective in minimizing channelling in the bed and caking of the U_3O_8 fines. As a result, fairly uniform bed temperatures were maintained.

Table II-11

EFFECT OF MECHANICAL VIBRATION ON THE OXIDATIVE REMOVAL OF
UO₂ FROM CLADDING

<u>Run</u>	<u>Vibration Applied</u>	<u>Reaction Time (hr)</u>	<u>Percent UO₂ Removed</u>
XO-3 ^a	no	7.0; 12.5	52; 80
XO-11 ^b	no	9.0	71
XO-23 ^b	yes	8.7	98.7
XO-25 ^b	yes	7.5	93

^aIn Run XO-3, no gas-pulsing was applied.

^bIn Runs XO-11, XO-23, and XO-25, gas pulsing was applied.

Miscellaneous Effects

Temperature Programming. Some improvement in UO₂ removal was noted when the temperature was increased slowly and air (rather than nitrogen) was used during the heating-up period. This procedure allowed the oxidation reaction to proceed initially at a low rate (compare Runs XO-21 and XO-22, Table II-9).

Thickness of the Cladding. Different wall thicknesses of cladding were tested: 0.01 in. (Runs XO-9 to XO-20), 0.02 in. (Runs XO-21 to XO-25) and 0.035 in. (Runs XO-1 to XO-6). It was thought that the thinner cladding might split by the pressure buildup in the cladding during the oxidation reaction. However, no splitting of the cladding occurred.

Conclusions

Separation of about 95% of the UO₂ from stainless steel-clad fuel segments can be achieved by oxidation in a fluidized-packed bed when mechanical vibration of the fuel segments and gas pulsing combined with a programmed temperature increase were used.

The information gained in this investigation will be used in future studies of the oxidation-fluorination scheme for processing UO₂ fuels. Movability or agitation of the clad fuel pieces has the most important influence on the removal. Of the two methods used, vibration directly transmitted to the fuel segments was the most effective in promoting agitation of the fuel segments.

A programmed temperature increase during the oxidation reaction step combined with mechanical vibration and gas pulsing resulted in a removal of approximately 95% of the UO_2 fuel from the stainless steel cladding. If the design of a system for transmitting sufficient mechanical vibration to a fluidized-packed bed can be solved for a large-scale reactor, then the separation of UO_2 from cladding could probably be achieved to a satisfactory degree, especially if a final fluorination step of the fuel segments were included.

Other reactor designs which would assure the agitation of the fuel segments are certainly possible; but most of them, as for instance a rotary drum, would not allow carrying out the oxidation of the uranium dioxide and fluorination of the U_3O_8 in a single vessel.

c. Design and Construction of an Engineering-scale Alpha Facility

(G. J. Vogel, E. L. Carls, W. Murphy, A. Rashinskas, B. Kullen)

An engineering-scale alpha facility is being built to study various steps in the fluid-bed fluoride volatility process for recovery of fissionable values from spent nuclear reactor fuel of the uranium dioxide-plutonium dioxide type. An investigation of the three basic steps of the process is to be undertaken. These are the following: (1) fluorination of the oxides of uranium-plutonium to their respective volatile hexafluorides, (2) distillation of the uranium-plutonium hexafluorides, and (3) conversion of the mixed uranium and plutonium hexafluorides to the dioxides by reaction with steam and hydrogen. Because of the toxicity of plutonium, the process and auxiliary equipment is housed in two alpha-containment boxes of a modular type. The principal features of the facility have been described previously (see ANL-6569, p. 110). The process equipment is being installed in a large glovebox inside a cell area. The auxiliary equipment is contained in a smaller glovebox located outside the cell area. In this glovebox, equipment for cleaning up the exhaust air from the larger glovebox is also housed. The cleanup treatment for the exhaust air involves scrubbing the air in a water spray tower and passing it through three filters before combining it with the exhaust air from the room. The combined air exhaust is then scrubbed and filtered again before being discharged to the atmosphere. The fluorination equipment is being installed and will be operated first. The equipment for the conversion of the hexafluorides to the oxides is being designed.

Uranium-plutonium dioxide pellets will be fluorinated in a 3-in. dia. two-zone fluidized-bed reactor. In the processing scheme, oxygen is fed into the lower (oxidation) zone, which contains the pellets and alumina particles in the voids of the pellet bed. The oxygen reacts with the UO_2 to form U_3O_8 , which is transported together with PuO_2 particles into the upper (fluorination) zone. In this zone, which is a fluidized bed of alumina, the U_3O_8 fines and PuO_2 particles react with fluorine which is admitted to the

fluidized bed at a point just above the fluidized-packed bed. Process off-gas from the reaction zones is cooled rapidly to minimize the amount of plutonium tetrafluoride (PuF_4) formed by the thermal decomposition of plutonium hexafluoride (PuF_6). The process off-gas which contains the mixed product hexafluorides is then passed through porous metal filters. (The solids which build up on the filter can be blown back into the fluorinator.) The plutonium and uranium hexafluorides are separated from the noncondensable gases (fluorine, oxygen, and nitrogen) by means of two series-connected condensers (4-in. dia.) which are cooled to about -60°C . The noncondensable gas is then either recirculated to the fluorinator by means of a diaphragm pump or passed through series-connected sodium fluoride (NaF) and activated alumina traps before being exhausted from the large glovebox to the cleanup equipment in the smaller glovebox. At the end of a run, the mixed product hexafluorides in the condenser are heated and vapor-transferred to storage pots. The small amount of PuF_4 which will be formed by radiation and thermal decomposition of PuF_6 will be deposited in equipment and lines. These portions of the equipment can be heated to 350°C to facilitate refluorination of PuF_4 deposits. After certain hand-operated shut off valves have been set in the proper position, process control during experimental operation is carried out from a panelboard located outside the cell. The panelboard and top of small alpha box is shown in Figure II-12.

Figure II-12

ENGINEERING-SCALE ALPHA FACILITY: VIEW OF OPERATING AREA
SHOWING REMOTE PROCESS CONTROL PANEL BOARD AND 30-IN.
DIA. BAGOUT PORTS ON TOP OF AUXILIARY GLOVE BOX

108-6725

Nearly all of the equipment components and the inter-connecting lines and valves for the fluorinator system have been installed. The installation of the fluorinator into the large glovebox through one of the top bagout ports is shown in Figure II-13. The installed fluorinator is

Figure II-13

ENGINEERING-SCALE ALPHA FACILITY: FLUID-BED FLUORINATOR
BEING LOWERED INTO LARGE GLOVEBOX
THROUGH A 30-IN. DIA. BAGOUT PORT

108-5794

shown in Figure II-14. To make the equipment in the 17-ft high alpha box easily accessible, lifts are provided (see Figure II-15).

Current work is mainly concerned with completing the installation of the process piping and incorporating modifications required by the specialized and stringent requirements of glovebox operation.

A major portion of the sub-contract work for the installation of electrical, refrigeration, ventilation, and instrumentation systems was completed by October 21, 1963. Additional work on the ventilation and electrical systems and final check-out testing of all the services installed by the contractor remain to be done. Final preparations are underway to place the fluorinator system in operation.

Figure II-14

ENGINEERING-SCALE ALPHA FACILITY: FLUID-BED FLUORINATOR
INSTALLED IN LARGE GLOVEBOX

108-6721

- d. Cleanup of Cell Exhaust Air Contaminated with Plutonium Hexafluoride
(R. W. Kessie)

A program investigating the cleanup of exhaust air from alpha facilities used in fluoride volatility work is in progress. As part of the

Figure II-15

ENGINEERING-SCALE ALPHA FACILITY: LIFT FOR PERSONNEL
TO PROVIDE ALL-LEVEL ACCESS OF ONE SIDE
OF LARGE GLOVEBOX

108-6321

program, the behavior of PuF_6 and UF_6 released to simulated glovebox atmospheres is being studied. This work also includes evaluation of cleanup devices, such as high efficiency (AEC) filters.

Previous work (see ANL-6596, p. 123), in which small quantities (1 to 25 mg) of pure PuF_6 were released into air of controlled humidity, indicated that the hydrolysis reaction rapidly went to completion in the gas phase to produce a gas suspension of small solid particles (smoke). Less than 0.02% of this air-borne plutonium passed through an AEC filter when there was an excess of moisture present in the air. The results of the overall penetration were presented and analyzed from the standpoint of removal of solid particles from the gas stream by filtration (see ANL-6596, p. 123 and ANL-6725, p. 157). However, it is also important to evaluate

quantitatively the extent to which small quantities of unhydrolyzed material may contribute to the total penetration of the filter.

In the reaction between PuF_6 and water, the over-all reaction is believed to yield the hydrolysis product plutonyl fluoride (PuO_2F_2), according to the equation

A similar reaction for uranium hexafluoride (UF_6), in which uranyl fluoride (UO_2F_2) is produced, is well known. In neither case, however, does the over-all reaction indicate the actual chemical steps involved. The actual reaction mechanism is believed to be complex, possibly involving intermediate compounds.

In order to obtain a more positive identification of the compound resulting from the hydrolysis of PuF_6 in the controlled release experiments mentioned above, a sample of the hydrolysis product was removed from the wall of the reaction chamber (mixing vessel) for analysis by X-ray diffraction.*

A photograph of the X-ray diffraction pattern of hydrolyzed PuF_6 is shown in Figure II-16. Reference patterns for uranyl fluoride and

Figure II-16

X-RAY POWDER PATTERNS FOR UO_2F_2 , HYDROLYZED PuF_6 AND PuF_4

108-6414

*The work of Robert V. Schablaske of this Division is gratefully acknowledged in the preparation and evaluation of these diffraction patterns.

plutonium tetrafluoride are included for comparison. The UO_2F_2 diffraction pattern used for reference in this comparison is that of the anhydrous form.¹⁷ The use of the UO_2F_2 diffraction pattern for purposes of comparison is based on the work of Florin, Tannenbaum, and Lemons,¹⁸ who obtained a solid product by exposing PuF_6 to moist air in a fluorothene tube. X-ray diffraction studies of the solid showed it to be isomorphic with UO_2F_2 and it was, therefore, presumed to have the analogous formula PuO_2F_2 . The relatively weak, diffuse lines of the pattern of hydrolyzed plutonium hexafluoride produced in the present experiments is believed to be due to the small crystallite size of the material formed. Crystallite size much smaller than the mean particle diameter of 170 Å is also consistent with the smooth physical appearance of product particles observed under the electron microscope.

The diffraction patterns depicted in Figure II-16 show the following correspondences:

1. At least five major lines of the hydrolysis product correspond to those of UO_2F_2 ;
2. At least five major lines of PuF_4 are not matched with the hydrolysis product or with UO_2F_2 ;
3. At least five major lines of the hydrolysis product and UO_2F_2 are not matched with PuF_4 ;
4. There is no major line of the hydrolysis product which does not match with a major line of UO_2F_2 ;
5. Major lines of PuF_4 which match with the hydrolysis product also match with UO_2F_2 ;
6. Major lines of PuF_4 not matched by UO_2F_2 also do not match with the hydrolysis product.

The above analysis does not constitute a rigorous proof; however, a high degree of similarity does exist between the patterns of UO_2F_2 and the hydrolyzed PuF_6 . Other investigators of the UF_6 -water vapor interaction have observed six distinct powder diffraction patterns corresponding to various hydrates and hydrofluorinated hydrates of pure UO_2F_2 .¹⁹ The formation of a mixture of these compounds in the hydrolysis experiment may be the reason why precise correspondence between the diffraction pattern of UO_2F_2 and that of hydrolyzed PuF_6 could not be obtained.

¹⁷Zachariasen, W.H., *Acta Cryst.* 1, 277 (1948).

¹⁸Florin, A.E., Tannenbaum, I.R., and Lemons, J.F., *J. Inorg. Nucl. Chem.*, 2, 368 (1956).

¹⁹Brooks, L.H., Garner, E.V. and Whitehead, E., IGR-TN/CA-277 (1958).

On the basis of the above comparisons of diffraction patterns and discussion, it is believed that the major hydrolysis product of PuF_6 is PuO_2F_2 and that in this respect the hydrolysis reaction of PuF_6 is similar to that of UF_6 .

Exploratory hydrolysis experiments have also been carried out in which the UF_6 vapor is diluted with dry nitrogen before being mixed with humidified nitrogen. A study of the hydrolysis behavior of UF_6 is needed to provide information for the clean-up of glovebox air containing UF_6 and PuF_6 . Since it is believed that the hydrolysis mechanism for the hexafluorides of plutonium and uranium are similar, the results of experiments with UF_6 should be useful for the design of subsequent experiments with PuF_6 .

In the present series of experiments, the hydrolysis reaction was carried out in a Plexiglas tube 1.5-in. ID by 51.5 in. long. Two gas streams of equal volumetric flow rate, one containing UF_6 and the other H_2O (see Table II-12), entered one end of the tube. The reactants mixed by diffusion while flowing down the tube and then passed through a high efficiency filter mounted across the discharge end of the tube. The resultant pressure of each reactant in the mixed stream was one-half the pressure of the reactant in the separate reagent streams.

Table II-12

VAPOR-PHASE HYDROLYSIS AND FILTRATION OF UF_6

Reaction time (before reaching filter):	14.5 sec
Filter Media:	AEC Type ^a
Diluent Gas:	Nitrogen
Total superficial gas velocity (1 atm, 25°C):	9.7 cm/sec

Run No.	Partial Pressure ^b (mm Hg)		Filter Penetration ^c (%)
	UF_6	H_2O	
1	0.005	0.08	19
2	0.06	0.9	28
3	0.005	0.8	15
4	0.005	7.6	1

^a Absolute type by Flanders Filter Inc., Riverhead, N.Y.

^b These partial pressures apply to the separate reagent streams. In the combined (mixed) streams, the values are one-half those shown in the table.

^c Percent of uranium incident on filter that passed through filter.

The results of the filter penetration measurements are reported in Table II-12. The high penetrations resulted from incomplete reaction of UF_6 with water in the gas phase before the mixed stream passed through the filter.

Electron micrographs of fibers removed from the incident face of the filter used in each of the runs are shown in Figures II-17 to II-20, respectively. Figure II-17 shows the initial surface reaction at active sites before the deposit has become continuous. Figures II-18 and II-19 show further deposition of a continuous layer. Sections of fibers exposed as a result of mechanical disruption of the deposit during fiber removal are evident. Figure II-20 (Run 4) shows a particulate form of deposition as opposed to the continuous layer form. The continuous layer formed on the filters because of chemical reaction which took place at the fiber surface. The particulate solid is formed by reaction in the gas phase and is then collected by the filter. The filters are efficient for removing solid or liquid particles from a gas stream. However, the large filter penetrations (see Table II-12) indicate that the filters are not efficient for completing the surface reaction or for removing unreacted, gaseous UF_6 . Also, the filters are not suitable for controlled measurement of surface reaction kinetics. Work on the measurement of reaction kinetics using packed beds of known surface area is now under way. This work is not yet in a form suitable for reporting. Equipment is being set up in a new glovebox facility for studying the kinetics of the surface reaction with PuF_6 .

Previously discussed effects of particle agglomeration and filter loading (see ANL-6725, p. 157), together with the chemical reaction kinetics, make a fairly complex over-all picture. Physical mechanisms common to more than one effect are present. These common mechanisms are (1) the diffusion of reacting gas molecules to solid surfaces that are either fixed or air-borne and (2) the diffusion of small solid particles resulting in agglomeration and in collection of particles on filter fibers for removal from the gas phase. In future work, it is planned to continue the general approach of vapor-phase hydrolysis and filtration with the objective of obtaining sufficient information on the mechanisms to design a clean-up system that will provide necessary decontamination of discharge air under any possible type of release that could occur in a process plant.

Figure II-17

URANIUM HEXAFLUORIDE
HYDROLYSIS PRODUCT
DEPOSITED ON FILTER FIBERS
IN RUN 1

108-6686

Figure II-18

URANIUM HEXAFLUORIDE
HYDROLYSIS PRODUCT
DEPOSITED ON FILTER FIBERS
IN RUN 2

108-6687 Rev.

Figure II-19

URANIUM HEXAFLUORIDE
HYDROLYSIS PRODUCT
DEPOSITED ON FILTER FIBERS
IN RUN 3

108-6688 Rev.

Figure II-20

URANIUM HEXAFLUORIDE
HYDROLYSIS PRODUCT
DEPOSITED ON FILTER FIBERS
IN RUN 4

108-6689 Rev.

2. Basic Studies of Fluidized-Bed Behavior Related to Process Operations

a. Lateral Heat Conduction in a Fluidized-Packed Bed (B.E. Stangeland * and J.D. Gabor)

Fluidized-packed beds are being used extensively in the development of fluid-bed fluoride volatility processes. It was originally conceived that particles fluidized in the voids of UO_2 pellets which are undergoing a highly exothermic reaction would increase heat transfer and improve process control. However, there is little heat transfer data available for this system. Therefore, a study has been made of the effects on lateral heat conduction of fixed packing size, fluidized particle size and density, and different gases in fluidized-packed beds for a range of gas velocities that would be used in pilot plant processing.

A rectangular fluidization column was used for this study; a schematic diagram of the equipment is shown in Figure II-21. The column

Figure II-21

SCHEMATIC DIAGRAM OF APPARATUS FOR MEASURING LATERAL HEAT CONDUCTION IN FLUIDIZED-PACKED BEDS

was $1 \frac{11}{16}$ in. wide by $8 \frac{1}{2}$ in. high by 7 in. long. The two narrow sides of the column were made of aluminum plates. Copper cooling coils were bonded to the external surface of the plates with a plastic heat transfer cement (Thermon).** Water was supplied to the cooling coils by a constant head tank. Iron-constantan thermocouples were used for the measurement of water inlet and outlet temperatures. The two wide sides were made of $\frac{1}{2}$ -in. thick Plexiglas. The distributor for the fluidizing gas was made of $\frac{1}{8}$ -in. thick sintered stainless steel. The fluidizing gas flow rate was measured by a

*Resident Student Associate, University of California

**Thermon Manufacturing Company, Houston, Texas

rotameter. A heater (6 in. long, 1 1/2 in. wide, and 1/8 in. thick) was located in the center of the column. An iron-constantan thermocouple was spot welded to one side of the heater for measurement of the heater skin temperature.

Probes for measuring the lateral temperature gradient of the fluidized-packed bed were made from the same size steel balls as those used for the bed packing; the probes were made by drilling holes in the steel balls and soldering thermocouple ends in the holes. Three to four probes were placed in a horizontal line at elevations of 3 or 6 in. on each side of the heater. Because of the larger thermal conductivity in the vertical direction as compared with the horizontal direction, the temperatures were essentially uniform in vertical cross-section.

The packed-bed height for all runs was 6 in. The packing consisted of 1/2-in., 3/8-in., 1/4-in., or 1/8-in. steel spheres. For each run, the amount of fluidized particles was adjusted so that regardless of the velocity of the fluidizing gas, the expanded height of the fluidized bed material in the voids of the packing was maintained at a fluidized-packed bed height of 6 in.

One series of runs was made with helium as a fluidizing gas; all other runs used air. Mixtures of copper and nickel shot with narrow size ranges (-40 +50, -60 +70, -100 +120, and -140 +170 mesh) as well as -60 +70 mesh alumina grain and -40 +50 mesh glass beads were used for fluidizing materials.

Mathematical Analysis of Data

For the case of constant cross sectional area, unidirectional heat conduction in a fluidized-packed bed can be related by:

$$q = -k_e A \Delta t / \Delta x \quad (1)$$

where q = rate of heat transfer, Btu/hr

k_e = effective bed thermal conductivity, Btu/(hr)(sq ft)(°F/ft)

A = cross sectional area, sq ft

$\Delta t / \Delta x$ = temperature gradient, °F/ft

The lateral temperature gradients were determined from the location and temperature of the probes in the bed. The effective bed thermal conductivities were based on the average of the temperature gradients on either side of the centrally located heater in the column. The rate of heat transfer, q , was based upon the heat pickup of the water in the cooling coils. For the conditions used in these experiments, the measured effective thermal conductivity, k_e , ranged from about 1 to 40 Btu/(hr)(sq ft)(°F/ft).

It was determined that the effective thermal conductivities for the various run conditions could be correlated by the expression:

$$\frac{k_e}{\rho C_p} = \alpha' = (0.0075) \left[0.0558 D_p (V - V_{mf}) / V_{mf} \right] \text{ ft}^2/\text{sec}^* \quad (2)$$

where ρ = density of fluidized particle, lb/cu ft

C_p = fluidized particle heat capacity, Btu/(lb)(°F)

α' = thermal diffusivity, ft^2/sec

D_p = diameter of fixed packing, ft

V = fluidizing gas velocity corrected for packing void fraction, ft/sec

V_{mf} = minimum fluidization gas velocity corrected for packing void fraction, ft/sec

The physical characteristics of the fluid-bed material and packing and experimental conditions for the various fluidized-packed bed systems which were tested are presented in Table II-13. A general

Table II-13

MATERIALS AND CONDITIONS USED IN LATERAL HEAT TRANSFER TESTS

6-in. bed height for all runs (See Figure II-22 for graphical presentation of the correlation)							
Fluidized Material	Mesh	Fluidized Particle dia. (in.)	Diameter of Packed Spheres (in.)	Fluidizing Gas	Gas Velocity V_{mf}^a (ft/sec)	Particle Density, e (lb/cu ft)	Particle Specific Heat, C_p [Btu/(lb)(°F)]
Cu-N ₁	-140 +170	0.0038	3/8	Air	0.12	555	0.105
Cu-N ₁	-140 +170	0.0038	3/8	Helium	0.28	555	0.105
Cu-N ₁	-100 +120	0.0054	1/2	Air	0.28	555	0.105
Cu-N ₁	-100 +120	0.0054	3/8	Air	0.28	555	0.105
Cu-N ₁	-100 +120	0.0054	1/4	Air	0.28	555	0.105
Cu-N ₁	-100 +120	0.0054	1/8	Air	0.28	555	0.105
Cu-N ₁	-60 +70	0.00905	3/8	Air	0.71	555	0.105
Cu-N ₁	-60 +70	0.00905	1/4	Air	0.71	555	0.105
Cu-N ₁	-40 +50	0.0141	3/8	Air	1.56	555	0.105
Cu-N ₁	-40 +50	0.0141	1/4	Air	1.56	555	0.105
Alumina	-60 +70	0.00905	3/8	Air	0.36	249	0.217
Glass	-40 +50	0.0141	3/8	Air	0.39	137	0.20

^a V_{mf} = minimum fluidization gas velocity corrected for packing void fraction.

* A theoretical foundation for this equation, and particularly the constant 0.0558 is developed in a separate paper by J.D. Gabor, Lateral Solids Mixing in Fluidized-Packed Beds (to be published in the May 1964 issue of the A.I.Ch.E. Journal).

correlation of thermal diffusivity in spherically packed beds is shown in Figure II-22; the straight line in this figure corresponds to Equation (2). The data points in the correlation deviate up to about a factor of about 3 from the plotted line. However, the correlation covers about three orders of magnitude and is based on the diameter of the fixed packing and the minimum fluidization velocity of the fluidized particles. The minimum fluidization velocity can be estimated from the method proposed by Rowe,²⁰

Figure II-22

GENERAL CORRELATION FOR THERMAL DIFFUSIVITIES
FOR LATERAL HEAT TRANSFER IN A FLUIDIZED-PACKED BED

²⁰Rowe, P.N., Trans. Inst. Chem. Engrs. (London), 39, 175 (1961)

who found that the drag coefficient for a single particle in an array of particles was 68.5 times that of an isolated single particle. Therefore, the minimum fluidization velocity for a bed of particles could be calculated in the same fashion as the terminal velocity for an isolated particle by changing the drag coefficient by a factor of 68.5. Hence, heat transfer estimates for design purposes can easily be made from the physical properties of the fluidized particles and the fluidizing gas.

b. Longitudinal Transport of Particulate Solids in Fluidized-Packed Beds
(J.D. Gabor and J. Savage)

A study was made to determine some of the characteristics of longitudinal solids motion of fluidized particles and of the transport of fines in fluidized-packed beds. Such features are important in the two-zone, oxidation-fluorination scheme for processing uranium dioxide fuel in the fluid-bed fluoride volatility process.

Experiments were designed to allow rates of longitudinal solids mixing to be measured in terms of diffusivities. The effects of changes in experimental conditions were then evaluated by comparing solids mixing diffusivities. The characteristics of the solids mixing of fluidized particles were studied with copper and nickel shot fluidized in the voids of various sizes of spherical packing. Because copper and nickel have similar densities, they constitute a homogeneous fluidizing system, and because only nickel is ferromagnetic, the concentration gradients were conveniently determined by magnetic means. Fine nickel powder of 24μ mean particle size was used for studying rates of fines movement.

A Lucite column 2-in. ID by 4.5 ft high, was used as a fluidization vessel in these tests. Sample ports were installed at 4-in. intervals along the length of the column; samples of the fluidized material were withdrawn through hypodermic needles. Humidified nitrogen was the fluidizing gas. Equal weights of copper and nickel were charged to the column: first, a lower layer of pure copper was charged, and then an upper layer of pure nickel. Runs were also made in which the order of the nickel and copper charged to the column was reversed. The results were similar for the two cases. The bed was fluidized over a measured time period at a desired gas flow rate. To determine the extent of mixing, bed samples were analyzed for the concentration of nickel by magnetic separation.

For the initial runs, bed samples were taken along the length of the column to determine the concentration profile after a known time of mixing by fluidization. From the concentration profile, the longitudinal mixing diffusivities were determined by means of the boundary value solution of the diffusion equation. The solution of this equation is given by Sherwood and Reed:²¹

²¹Sherwood, T.K., and Reed, C.E., Applied Mathematics in Chemical Engineering, McGraw-Hill, New York (1939)

$$C = \frac{1}{2} + \frac{2}{\pi} \left\{ \exp \left[-\left(\frac{\pi}{2}\right)^2 \frac{D\theta}{R^2} \right] \sin \frac{\pi x}{2R} + \frac{1}{3} \exp \left[-9 \left(\frac{\pi}{2}\right)^2 \frac{D\theta}{R^2} \right] \sin \frac{3\pi x}{2R} + \frac{1}{5} \exp \left[-25 \left(\frac{\pi}{2}\right)^2 \frac{D\theta}{R^2} \right] \sin \frac{5\pi x}{2R} + \dots \right\} \quad (1)$$

where, C = concentration, fractional weight

D = diffusivity, ft²/sec

x = distance from center of fluidized bed, ft

R = 1/2 height of fluidized bed, ft

θ = time, sec

The experimentally determined concentration profiles were found to be in good agreement with the profiles expected from this diffusion model. After it had been verified by means of the sample concentration profiles that diffusivities could be used to characterize the mixing rates, a simpler experimental procedure was used for the subsequent runs. In these runs, the upper and lower halves of the bed were withdrawn separately; the average concentration of each component in each half of the bed was then determined. The weight fraction of nickel in the upper half was then averaged with the weight fraction of copper in the lower half. The solids diffusivities were then calculated by means of the following equation:²¹

$$F = \frac{1}{2} + \frac{4}{\pi^2} \left\{ \exp \left[-\left(\frac{\pi}{2}\right)^2 \frac{D\theta}{R^2} \right] + \frac{1}{9} \exp \left[-9 \left(\frac{\pi}{2}\right)^2 \frac{D\theta}{R^2} \right] + \frac{1}{25} \exp \left[-25 \left(\frac{\pi}{2}\right)^2 \frac{D\theta}{R^2} \right] + \dots \right\} \quad (2)$$

where F = concentration of the major component in 1/2 of the bed, fractional weight. Equations 1 and 2 are so related geometrically that, for the same values of D, θ, and R, they describe the same diffusion model.

Figure II-23 gives the results of analysis of an experiment in which both of the above methods were used, that is, profile measurements and analyses of the overall concentrations of the two components in the withdrawn halves of the fluidized bed. After determining the diffusion coefficient by means of Equation 2, the concentration profile was calculated by means of Equation 1 and is shown by the solid line in Figure II-23. The agreement of this line with the experimentally determined points indicated that the simplified method for determining the diffusivities was accurate and that the diffusion equations were adequate for determining the rates of solids mixing.

The parameters which were investigated for their effect on the longitudinal diffusivity of particles fluidizing in the voids of fixed packing were: (a) fluidized particle size, (b) bed height, (c) fixed packing size, and (d) fixed packing array. The effect of gas velocity is shown in all cases by relating the diffusivity of the fluidized particles to the gas flow rate.

Effect of Fluidized Particle Size and Bed Height

Mixing rates were compared for several bed heights and sizes of copper and nickel shot fluidized in the voids of a packed bed (fluidized-packed bed system) of 3/8-in. dia. steel spheres. The initial bed depths (static conditions) of the fluidized material were 8, 16, and 24 in. The copper and nickel particles were -140 +170, -100 +120, and -40 +50 mesh in size. The packed bed extended above the depth of the fluidized material in all

Figure II-23

CONCENTRATION PROFILE FOR LONGITUDINAL SOLIDS MIXING
IN A FLUIDIZED-PACKED BED (Run Sm-97)

Fixed Packing: 3/8-in. dia. steel spheres
 Fluidized material: -100 +120 mesh copper-nickel mixture (2900 g)
 Fluid-bed Height ~24 in. (static)
 42 3/4 in. (expanded)
 Fluidizing gas: Nitrogen (humidified)
 Superficial gas velocity, V_o : 0.88 ft/sec
 Average gas velocity (corrected for packing void fraction, ϵ), V_o / ϵ : 1.99 ft/sec
 Packing void fraction, ϵ : 0.442
 Run duration: 1.75 min

cases. Diffusivities versus gas velocities for the various bed heights and particle sizes are given in Figures II-24, II-25, and II-26. Incipient fluidization is indicated as zero diffusivity (see origin of each diffusivity-gas velocity curve).

With increased bed height, there was an increase in solids mixing and, in general, an increase in slugging and a more violent solids movement in the fluidized phase. Because of the baffling by the fixed packing, the slugging is not as violent for a fluidized-packed bed as it is for an ordinary fluidized bed.

Higher solids diffusivities were obtained with -100 +120 mesh particles than with -140 +170 mesh and -40 +50 mesh particles. Further studies would have to be made with intermediate particle sizes (between -100 +120 mesh and -40 +50 mesh) to determine the size giving the maximum

mixing rate. There was a greater incidence of channeling with -140 +170 mesh particles; this condition resulted in reduced solids movement for the -140 +170 mesh particles. With the larger (-40 +50 mesh) particle size, there is also reduced movement because a greater amount of the energy is dissipated in the moving of the heavy particles.

Figure II-24

EFFECT ON LONGITUDINAL SOLIDS MIXING OF BED HEIGHT
OF -140 +170 MESH COPPER-NICKEL SHOT FLUIDIZED
IN VOIDS OF 3/8-IN. DIAMETER STEEL SPHERICAL PACKING

Fluidizing gas: Nitrogen
(humidified)

Average gas velocity: V_0/ϵ , where
 V_0 = superficial gas velocity
and ϵ = fixed-packing void fraction.
 $\epsilon = 0.442$

108-7291

The Effect of Fixed Packing Size

Runs were made with -100 +120 mesh copper and nickel (an initial static bed depth of 8 in.) which were fluidized in the voids of 3/8-in. or 1/2-in. dia. steel spherical packing and in an open tube (no packing). The results of these runs are plotted as the solids diffusivity versus gas velocity in Figure II-27. As expected, there was a decrease in particle movement with decreased packing void size. The solids diffusivity was much greater for open-tube fluidization (no fixed packing); at a fluidizing gas velocity of about 2 ft/sec the mixing was so rapid during a short time interval (<0.5 min) that it was not possible with the present experimental method to determine diffusion coefficients. With higher gas flows, the slugging became violent, indicating even larger solids movements.

Runs were also made with -140 +170 mesh copper-nickel shot particles (at a static height of 8 in.) fluidized in the voids of 3/8-in. or 1/2-in. dia. steel spheres. The diffusivities for the 1/2-in. dia. spheres were about 1.7 times greater than for the 3/8-in. dia. spheres.

Figure II-25

EFFECT ON LONGITUDINAL SOLIDS MIXING OF BED HEIGHT
OF -100 +120 MESH COPPER-NICKEL SHOT FLUIDIZED
IN VOIDS OF 3/8-IN. DIAMETER STEEL SPHERICAL PACKING

Fluidizing gas: Nitrogen (humidified)

Average gas velocity: V_0/ϵ where, V_0 = superficial gas velocity and ϵ = fixed-packing void fraction.
 $\epsilon = 0.442$

108-7280

Figure II-26

EFFECT ON LONGITUDINAL SOLIDS MIXING OF BED HEIGHT
OF -40 +50 MESH COPPER-NICKEL SHOT FLUIDIZED
IN VOIDS OF 3/8-IN. DIAMETER STEEL SPHERICAL PACKING

Fluidizing gas: Nitrogen (humidified)

Average gas velocity: V_0/ϵ where, V_0 = superficial gas velocity, and ϵ = fixed-packing void fraction.
 $\epsilon = 0.442$

108-7279

Figure II-27

EFFECT OF SIZE OF FIXED PACKING ON LONGITUDINAL SOLIDS MIXING IN A FLUIDIZED-PACKED BED

Fluid-bed particles: -100 +120 mesh copper and nickel shot

Bed Height (static): 8 in.

Fluidizing gas: Nitrogen (humidified)

Average gas velocity in voids of packing V_0/ϵ ,

where V_0 = superficial gas velocity, ft/sec, and

ϵ = fixed packing void fraction (for open tube,
i.e., no fixed packing, $\epsilon = 1.00$)

$\epsilon = 0.442$ (3/8-in. dia. spherical packing)

$\epsilon = 0.451$ (1/2-in. dia. spherical packing)

108-7235

Effect of Variation in the Void Structure of the Fixed Packing

The void structure of the fixed packing depends on the orientation of the individual packing elements in the packed bed. In each of the series of runs made with the same fixed-packing size and fluidized-particle size, the physical arrangement of the fixed packing was not disturbed when the fluidized particles were either drained from or recharged to the column. As a result of this procedure, no information was obtained on the effect of diffusivity of the void structure of the fixed packing. To investigate this effect, four runs were made at fluidized-particle bed heights (static) of 8 in. and 16 in. The fluidized-packed bed consisted of randomly charged 3/8-in. dia. steel spheres and -100 +120 mesh fluidized particles. Two runs were carried out without disturbing the arrangement of the fixed packing, and two runs were made with separate charges of fixed packing. The results of these tests (see Figure II-28) show that there was a factor of 1.8 difference in diffusivities between comparable beds, apparently because of the random variations in the packing void structure.

Figure II-28

EFFECT OF CHANGE IN VOID STRUCTURE OF FIXED PACKING
ON SOLIDS MIXING IN A FLUIDIZED-PACKED BED

Fluid-bed Particles: -100 +120 mesh copper and nickel shot

Fixed packing: 3/8-in. dia. steel spheres

Fluidizing gas: Nitrogen (humidified)

Average gas velocity: V_0 / ϵ , where V_0 = superficial gas velocity and ϵ = fixed-packing void fraction.

$$\epsilon = 0.442$$

108-7299

Effect of Gas Flow Rate

Solids mixing rates, as measured by the diffusion coefficients used in these experiments, appear to pass through a maximum as the gas velocity is increased from the minimum fluidization velocity. This effect is indicated in Figures II-24, II-25, II-26, and II-28 where a maximum diffusivity occurs at approximately 1.5 ft/sec for -100 +120 mesh and -140 +170 mesh copper-nickel shot and at 4.0 ft/sec for -40 +50 mesh copper-nickel shot.

Vertical Transport of Fines

Runs were made to study the transport rate of nickel fines (mean diameter, 24μ) in a fluidized-packed bed consisting of 3/8-in. dia. spherical steel packing and -100 +120 mesh copper shot as the fluid-bed material. The fines transport measurements were made in the 2-in. ID Lucite column used in the longitudinal mixing studies. The column was charged first with approximately 30 g of nickel fines mixed with sufficient copper shot (480 g) to be equivalent to a static bed height of 4 in. Then, a charge of copper shot equivalent to a static bed height of 8 in. was added above the nickel-copper mixture in the column. In order to reduce elutriation losses, 8 in. of copper shot were charged rather than 4 in. as was done in measurements of longitudinal mixing of fluidized particles in a fluidized-packed bed (described on p. 257).

If it is assumed that the nickel at the bottom of the column diffuses into an infinite medium above it, a concentration profile occurs in accordance with the following equation:²²

$$\frac{C}{C_0} = \operatorname{erf} \left[\frac{a - X}{2 \sqrt{D\theta}} \right] + \operatorname{erf} \left[\frac{a + X}{2 \sqrt{D\theta}} \right] \quad (3)$$

where C = concentration of nickel at time θ , fractional weight

C_0 = initial concentration of nickel (in the lower 4 in. of the bed)

D = diffusion coefficient, ft^2/sec

θ = time, sec

X = longitudinal distance, ft

a = initial bed height containing nickel, ft

After the bed had been fluidized for 6 sec, three 4-in. sections of the bed were withdrawn and analyzed for the concentration of nickel. The initial nickel concentration, C_0 , was based on the total amount of nickel recovered in the separation step, rather than on the amount charged. The nickel was recovered from the bed, and from an auxiliary filter chamber. Approximately 85% of the nickel was accounted for after each run. It was assumed that within each section the fines loss by elutriation was uniform. The measured concentration of fines in each section was used to determine a concentration profile, fit by means of Equation 3 with a suitable value of D . By this procedure, the fines transport diffusion coefficients, D , were estimated. In Figure II-29, the diffusion coefficients for fines transport are compared with the diffusion coefficients for mixing of the coarser fluidized particles. The diffusivity for the fines (about 24μ) is one to two orders of magnitude greater than that of the copper shot (about 100μ).

A few exploratory runs were made in which nickel fines were used with alumina grain as a fluidized material. This system is quite similar to the system of uranium oxide fines (U_3O_8) in fluidized alumina, which is employed in pilot plant study of the processing of UO_2 fuel. A 3-in. dia. brass column with sample ports at 4-in. intervals along its length was used; this column diameter is the same as that of the pilot plant fluid-bed reactor. In one run made with 3/8-in. dia. steel spheres for fixed packing, 100 g of nickel fines (mean size, 24μ) were thoroughly mixed with -40 +170 mesh alumina grain (static bed height of 4 in.) and charged to the bottom of the column. Pure alumina grain was then added to the column to give a total bed height (static) of 36 in. The fluidizing gas velocity was 0.80 ft/sec (corrected for packing voidage). Samples were withdrawn and analyzed for nickel fines concentration after various time intervals. Figures II-30 and

²²Carslaw, H.S. and Jaeger, J.C., Conduction of Heat in Solids, Second Edition, Oxford, 1959, page 54. The error function (erf) is defined as

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-z^2} dz$$

Figure II-29

LONGITUDINAL FINES TRANSPORT DIFFUSIVITY
IN A FLUIDIZED-PACKED BED

Fixed packing: 3/8-in. dia. steel spheres

Average gas velocity: V_0/ϵ , where V_0 = superficial gas velocity and ϵ = fixed-packing void fraction.

108-7262

II-31 describe the concentration profile of the bed at various run times. After about 30 sec, virtually complete mixing had occurred, and the equilibrium (final) concentration profile was attained.

By means of Equation 3, the fines transport diffusion coefficient in the fluidized alumina was estimated to be 8×10^{-3} ft²/sec after 10 sec, and from the profile at 20 sec, the fines diffusivity was estimated to be 14×10^{-3} ft²/sec. The differences between the diffusivities measured at these two times could be due to radial concentration variations, which were neglected here because bed samples were withdrawn only along the axis of the column. The differences between the diffusivities at 10 and 20 sec could be attributed also to the fines movement not following a diffusion model. The fines were driven up the column not only by a concentration differential but also by the drag forces associated with the gas flow. Therefore, there would be some time effect on the diffusivities if the fine particle movement were defined by a diffusion model which assumes equal diffusivities in either direction.

The equilibrium concentration profile for the completely mixed fines is shown in Figure II-31. This profile is similar to the fines

Figure II-30

CONCENTRATION OF FINES IN ALUMINA GRAIN BED
AFTER VARIOUS TIME INTERVALS OF FLUIDIZED-PACKED
BED OPERATION

Column: 3-in. dia.

Fixed packing: 3/8-in. dia. steel spheres

Fluidized particles: -40 +170 mesh alumina grain
 -500 mesh nickel fines (mean size, 24μ)
 (Initial concentration of nickel fines in
 nickel-alumina mixture in lower 4 in. of
 bed, 24.3 w/o)

Fluidizing gas: Nitrogen (humidified)

Gas velocity
 (corrected for
 fixed-packing
 voidage): 0.80 ft/sec

concentration profile in fluidized beds reported by Thomas, Grey, and Watkins.²³ The fines concentration is higher toward the bottom and the top of the column than at the center. At the bottom of the column where bubbles are initially forming, fluidization is probably not as vigorous as it is higher in the bed. Less vigorous fluidization may be expected to be associated with a higher fines retention in the fluidized particles. Because of the lighter weight of the fine particles compared to the heavier weight of the larger alumina particles, the fines tend to be carried by the gas to the upper portion of the bed; this effect may account for the higher fines concentration at the top of the bed.

²³Thomas, W.J., Grey, P.J., and Watkins, S.B., Brit. Chem. Eng. 6 (3), 176 (1951).

Figure II-31

EQUILIBRIUM CONCENTRATION PROFILE
OF FINES IN ALUMINA GRAIN RESULTING FROM
FLUIDIZED-PACKED BED OPERATION

Column: 3-in. dia.

Fixed packing: 3/8-in. dia. steel spheres

Fluidizing particles: -40 +170 mesh alumina grain
 -500 mesh nickel fines (mean size, 24μ)
 (Initial concentration of nickel fines in
 nickel and alumina mixture in lower 4 in.
 of bed, 24.3 w/o)

Fluidizing gas: Nitrogen (humidified)

Gas velocity
 (corrected for fixed-
 packing voidage): 0.80 ft/sec

108-7273

A run was made in a fluidized bed (without fixed packing) at a gas velocity of 0.333 ft/sec and an initial bed height (static) of 26 in. The fines diffusivity here was estimated to be 2.5×10^{-3} ft²/sec.

The data for fluidized-particle mixing have the following significance in design of fluidized-packed bed reactors;

- (a) Higher rates of mixing were attained with -100 +120 mesh particles than with larger or smaller size particles;
- (b) Mixing increased with bed height;
- (c) A maximum in the mixing rates was attained with -100 +120 mesh particles at a gas velocity of about 1.5 ft/sec;
- (d) Longitudinal mixing in fluidized-packed beds is much less than for open-tube fluidization (no fixed packing);

(e) Mixing is only slightly faster for 1/2-in. dia. spherical packing than for 3/8-in. dia. spherical packing;

(f) Variations in random arrangements of the fixed packing have some effect on mixing rates, but these effects appear to introduce a variability of less than a factor of two and can be neglected for most design purposes.

The data obtained in this investigation are expected to have utility in specifying operating conditions for fuel reprocessing runs. For example, to avoid accumulation of oxide fines in the lower reaction zone (oxidation) of a reactor designed for the two-zone, oxidation-fluorination scheme, the oxidation rate should not be allowed to exceed the fines transport rate.

The general equation for steady state fines transport in a fluidized bed is given by:

$$N = D \frac{(C_o - C_F)}{z} \quad (4)$$

where N = rate of fines transport, lb/(sq ft)(sec)

D = fines transport diffusivity, sq ft/sec

C_o = fines concentration in oxidation zone, lb/cu ft

C_F = fines concentration in fluorination zone, lb/cu ft

z = transport distance (longitudinal), ft

Thus, the rate of fines transport, N , as calculated from the above equation should not exceed the rate of fines formation by oxidation. If, for example, it is assumed that the diffusivity of 8×10^{-3} ft/sec [for the transport of the nickel fines at a gas (air) velocity of 0.80 ft/sec in a bed of 3/8-in. dia. steel spherical packing and -40 +170 mesh alumina grain] can be applied to U_3O_8 fines transport during pilot plant processing, an estimate can be made of the rate at which the fines would be removed from the oxidation zone to the fluorination zone. The diffusivity was measured for 24.3 w/o nickel in alumina grain or a density of nickel fines of about 32.5 lb/cu ft (corrected for packing voidage). If it is desired that the percent of fines does not exceed 10% (13.4 lb/cu ft) in the fluorination zone at a distance 1 ft away, the fines transport rate can be calculated as follows:

$$N = 8 \times 10^{-3} \frac{(32.5 - 13.4)}{1} = 0.15 \text{ lb/(sq ft)(sec)}$$

For a 3-in. dia. reactor, the limiting rate of fines formation would then be 27 lb/hr. This is well in excess of current reaction rates of about 2 lb/hr (ANL-6687). If it is desired that the rate of fines transport should be at least 3 lb/hr and the fines concentration in the oxidation zone should not exceed 10 w/o, the maximum fines concentration in the fluorination zone can be calculated in a similar manner (with the assumption that the diffusivity is independent of the fines concentration). This calculation yields

a maximum of 8.5 w/o fines in the fluorination zone to obtain the specified fines transport rate. This calculated result appears to indicate also that the longitudinal transport of fines proceeds at a rate high enough to be practical.

Because of limited data, these calculations apply only for a gas velocity of 0.80 ft/sec and 3/8-in. dia. spherical packing. The effect of change in gas velocity and packing diameter as well as the size of the fines and of the fluidized particles has not been determined.

Additional work in this area will be done in support of fluid-bed volatility processing as the need arises.

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

Development work on a fluid-bed volatility process for the recovery of uranium from highly enriched uranium-alloy fuels is continuing. The overall objectives of this program are to develop and demonstrate an economical, high-decontamination, high-uranium recovery process (~99%) that is applicable to a variety of fuels. Currently, process application to both zirconium-based and aluminum-based fuels is being evaluated. The process involves, first, hydrochlorination of the alloy while it is submerged in a fluidized bed of inert solids (high-fired alumina), then, fluorination of the system, with both reactions being conducted in the same vessel. The hydrochlorination step effects a separation of the uranium from the alloying material and also, the cladding, since these are of the same material. The separations occur through the formation of the volatile chlorides of zirconium and aluminum (sublimation points at 1 atm for $ZrCl_4$ and $AlCl_3$ are 331°C and 180°C, respectively), while the uranium remains in the system as particulate chlorides. Entrained uranium and other particulate solids are retained in the system by a packed bed of alumina which serves as a high-temperature filter. The uranium is subsequently recovered as the hexafluoride (sublimation point for UF_6 at 1 atm is 56.6°C) during the fluorination step. The progress of the reactions is followed continuously by measuring the concentration of key components in the off-gas stream by the use of in-line thermal conductivity cells. Since both the hydrochlorination and fluorination reactions are highly exothermic, the use of a fluidized bed, because of its excellent heat transfer characteristics, is of extreme advantage and a nearly isothermal system can be maintained under conditions of high reaction rate.

Process work is now being carried out in two facilities, a 1 1/2-in. dia. reactor system (see ANL-6569, page 114), and a newly installed pilot-scale facility in which a 6-in. dia. reactor system is employed. These facilities are being operated with nonirradiated fuel material. Studies involving highly irradiated material are planned for a bench-scale (1 1/2-in. dia.) unit now being assembled for operation early in 1964. Corrosion studies in support of the fluid-bed volatility program on both high-enriched and low-enriched fuel are also in progress.

Currently, a hydrochlorination-hydrofluorination-fluorination cycle is being used for both uranium-Zircaloy and uranium-aluminum fuels. The work in the "cold" 1 1/2-in. unit is aimed at establishing suitable conditions for each of the steps in the reaction sequence and the evaluation of the packed-bed as a filter. Demonstration of the process on a practical engineering level (20 to 30 kg of Zircaloy alloy or 10 to 15 kg of aluminum alloy) will be the goal of the pilot plant operation. The studies with irradiated material will provide information on the disposition of fission products in each of the steps and the effect of the fission products on alloy reaction rate and uranium recovery.

In recent studies (ANL-6725, pages 178 to 182) in the 1 1/2-in. unit, the use of small assemblies of Zircaloy clad, uranium-Zircaloy alloy plates (instead of 1/8 to 6-in. chips) was initiated in order to simulate more nearly the geometry of the actual process system. Complete hydrochlorination of these assemblies was achieved in reasonable periods of time, about 7 hr, under conditions used earlier, that is, fluid-bed temperatures in the range 400 to 500°C, reactor wall temperatures in the range 300 to 415°C, and HCl concentrations as high as about 76 v/o in nitrogen. Alloy temperatures were mainly in the region of 650°C but a peak temperature of 750°C was also noted during this reaction. The quantity of uranium which was lost as a result of passage through the packed-bed filter during hydrochlorination was maintained at minimal values, less than 0.1% of the uranium in the initial charge. This loss was found to depend on the temperature of that portion of the reactor system that is downstream of the fluid bed. Lower temperatures in the packed-bed filter gave lower uranium losses. Alumina of -14 +20 mesh appeared to be as satisfactory as -40 +60 mesh material for use in the filter bed, that is, losses of uranium through the filter bed were about the same for both sizes of alumina.

A fluorination procedure has been found that achieves satisfactory removal of uranium from the alumina beds when single charges of uranium-Zircaloy alloy are used. In earlier work (ANL-6687, pp. 141-144), a scheme was used in which hydrochlorination of successive charges of alloy was followed by a single fluorination in order to reduce the amount of uranium lost by retention on the inert solids to acceptable values, that is, less than 1% of the uranium in the initial charge. The new fluorination procedure employs a lower initial temperature, 250°C as compared with 350°C, and a relatively high initial fluorine concentration, 50% instead of 5 to 10%. Fluorination was completed at 500°C, using a 90% fluorine concentration. The concentration of uranium in both the fluid bed and filter bed was reduced to a level of 0.01 w/o. Similar low levels of retention were obtained for two types of alumina (Type RR Alundum, and a less costly grade, Type 38 Alundum, Norton Co.).

Additional studies made in the 1 1/2-in. dia. unit on nonradioactive aluminum and Zircaloy fuel to establish the effects on uranium recovery of bed material and variations in the conditions for hydrochlorination, hydrofluorination and fluorination are described in detail below. Also, the results of the first experiments with large multiplate assemblies of aluminum

and Zircaloy, which were carried out during shake-down of the pilot plant facility, are summarized.

- a. Bench-scale Hydrochlorination and Fluorination Reaction Studies on Enriched Uranium-alloy Fuels and Evaluation of Packed-bed Filters
(D. Ramaswami, J. Strand and J. Kincinas)

Development studies on the hydrochlorination and fluorination steps of a fluid-bed volatility process for the recovery of highly enriched uranium from uranium-alloy fuels were continued in a 1 1/2-in. dia. fluid-bed reactor (nickel-200) system. The process is currently being evaluated for uranium-zirconium and uranium-aluminum alloys. In the process, the fuel is reacted while submerged in a fluidized bed of inert solids. Separation of the alloying material is achieved first; uranium is then recovered as the volatile UF_6 . High-fired (fused or sintered) alumina in granular form, which has been found to be inert for all process conditions tested thus far, is used both as the fluid-bed material and as a high-temperature packed-bed filter. The progress of the reactions is followed continuously by measuring the concentration of key reaction products in the off-gas streams by the use of thermal conductivity cells. The apparatus and experimental procedure have been described in detail in an earlier report (ANL-6569, pp. 114-118).

The reaction cycle for the process consists of hydrochlorination, hydrofluorination (optional), and fluorination steps. Nitrogen is used throughout the cycle as a diluent and for purging. The fuel, which is submerged in granular alumina, is first reacted with HCl gas. The uranium is converted to solid chlorides while the alloying agent and the cladding (in the current studies, these are both of the same material) are converted to volatile chlorides. The gas stream containing the volatile chlorides, hydrogen, excess HCl and nitrogen is first filtered by a packed bed of alumina which retains entrained uranium particulate solids, and is then passed to a Pyrex glass condenser cooled by ambient air. The exit gases from the condenser are water-scrubbed and, finally, vented. The reactor system is then hydrofluorinated to remove the bulk of the chlorides from the bed. Reaction with hydrogen fluoride results in conversion of the uranium chlorides to uranium tetrafluoride. The system is then fluorinated with elemental fluorine to convert the uranium tetrafluoride to uranium hexafluoride, which is collected in cold traps. The same reaction sequence and equipment is used for both uranium-aluminum and uranium-zirconium alloy fuels; the major differences between the recovery schemes for the two types of fuel lie in the conditions used for the hydrochlorination. These differences are discussed below.

Current Studies

In the current work, the effects of changes in a number of operating variables were investigated. The scope of this work is summarized in Table II-14, which lists the variables and itemizes specific conditions. The items investigated included:

Table II-14

SUMMARY OF OPERATING VARIABLES USED IN CURRENT BENCH-SCALE
STUDIES ON ENRICHED URANIUM-ALLOY FUELS

Apparatus:	1 1/2-in. dia. fluid-bed reactor system.
Number of Runs:	6 (includes two runs made with fission product elements added to the fluid bed).
Alloy Charge:	Multiplate fuel element subassemblies made of uranium-Zircaloy-2 alloy clad with Zircaloy-2 and uranium-aluminum alloy clad with aluminum; 2 to 4 subassemblies per run; Uranium content: 2.2 to 8.9 g per run.
Bed Material:	<p>Fluid Bed: (a) Type of alumina:</p> <p>(1) RR Alundum (Norton Co.), Run Al-1</p> <p>(2) 38 Alundum (Norton Co.), Runs Zr-39, 40, Al-2</p> <p>(3) Tabular T-61 (Aluminum Co. of America), Runs Al-3, 4</p> <p>(b) Quantity: ~ 320 g in each run</p> <p>(c) Mesh Sizes:</p> <p>(1) -40 +60, Run Al-1</p> <p>(2) -40 +120, Runs Al-3, 4</p> <p>(3) -40 +100, Run Zr-40</p> <p>(4) -80 +100, Runs Zr-39, Al-2</p> <p>Packed-bed</p> <p>Filter: (a) Type of Alumina:</p> <p>(1) Type 38 Alundum, Runs Al-1, Al-2, Al-3, Zr-39 and Zr-40.</p> <p>(2) Tabular T-61, Run Al-4</p> <p>(b) Bed depth: 6 to 12 in. (320 to 640 g)</p> <p>(c) Mesh sizes:</p> <p>(1) -40 +60 and -14 +20, Run Al-1</p> <p>(2) -14 + 20, Runs Al-2, Al-3, Al-4, Zr-39 and Zr-40</p> <p>(d) Re-use of alumina, Run Zr-39</p>
Hydrochlorination Conditions:	<p>(a) Dry hydrogen chloride (~1 ppm H₂O), Run Al-1</p> <p>(b) Hydrogen chloride + ~ 35 ppm H₂O, Run Al-2</p> <p>(c) Hydrogen chloride + ~ 1100 ppm H₂O, Run Al-3, Al-4, Zr-39 and Zr-40</p> <p>(d) Hydrogen chloride + 1100 ppm H₂O + 20 v/o H₂, (Runs Al-3 and Zr-39)</p>
Hydrofluorination Conditions:	<p>(a) Fixed HF concentration (50 v/o) with increasing temperature in the range 200 to 350°C, Al-3</p> <p>(b) Constant temperature (350°C) at two HF concentrations (20 v/o and 50 v/o), Run Zr-39</p>
Fluorination Conditions:	<p>(a) Fluorination at 250°C with gradual increase in F₂ concentration from 5 to 90 v/o, followed by fluorination at 500°C with a similar increase in F₂ concentration, Runs Al-2, Al-3, Al-4, and Zr-40</p> <p>(b) Fixed, low F₂ concentration (10 v/o) with gradual increase in temperature from 250 to 500°C, Run Zr-39.</p>

- 1) type and mesh size of alumina for the fluid bed,
- 2) type, mesh size, and quantity of alumina for the packed-bed filter,
- 3) a variety of HCl feeds: dry HCl, HCl containing about 35 ppm H_2O , HCl containing 1100 ppm H_2O , and HCl containing 1100 ppm H_2O and 20 v/o H_2 (Runs Zr-39, Al-3),
- 4) Hydrofluorination under conditions of fixed HF composition with increasing temperature (Run Al-2) and, also, at a fixed temperature at two concentration levels of HF (Runs Al-3 and Al-4) and
- 5) fluorination at two temperatures with varying fluorine concentration (Runs Zr-40, Al-2, Al-3, Al-4) and, also, at a relatively low, fixed level of fluorine with increasing temperature (Run Zr-39).

The results of six runs are reported. Two runs were made with uranium-Zircaloy-2 alloy and four with uranium-aluminum alloy. The quantity of uranium involved ranged from 2.2 to 8.9 g. Runs were evaluated, primarily, on the basis of the quantity of uranium lost through the filter during the hydrochlorination and the quantity of uranium retained by the alumina beds at the end of the reaction cycle. In two of the runs, fission product elements were added along with the alloy charge to establish their disposition throughout the reaction cycle and to determine their effects on uranium retention and caking tendencies of alumina.

Process Conditions. Two runs (Zr-39 and Zr-40) were made in which multiplate subassemblies of uranium-Zircaloy-2 alloy were reacted. Two of these subassemblies were simultaneously hydrochlorinated in each run. Each subassembly (weighing 145 g) consisted of three plates made of normal uranium-Zircaloy-2 alloy clad with Zircaloy-2. The thickness and spacing of plates (approximately 0.07-in.) was similar to that used in the Shippingport pressurized water reactor.²⁴ The plates (5-in. long and 7/8-in. wide) were joined by inert-arc spot welding²⁵ to the plate spacers. Four runs (Runs Al-1, Al-2, Al-3, and Al-4) were made with aluminum fuel (uranium-aluminum alloy clad with aluminum-1100). The plates were 0.050 in. thick and were similar to those used for MTR fuel assemblies.²⁶ In the first aluminum run, the charge was in the form of chips (1/8 to 1/4 in. wide and 1/8 to 3/8 in. long, total weight 143 g), whereas in the remaining runs, it was in the form of multiplate subassemblies (5 in. long and 7/8 in. wide, average weight 51 g each). As many as four aluminum subassemblies were used per run.

²⁴ The Shippingport Pressurized Water Reactor, Addison-Wesley Publishing Company, Inc. Reading, Massachusetts (1958) p. 586.

²⁵ Kaufman, A. R., Nuclear Reactor Fuel Elements Metallurgy and Fabrication, 1st ed., Interscience Publishers, New York, N. Y. (1962) p. 514.

²⁶ Harrison, L. J., "Mechanical Failures of MTR Fuel Assemblies", *Nucleonics*, 21, No. 10, pp. 78 to 84 (1963).

In two of the runs, Run Zr-40 and Run Al-4, eleven fission product elements were charged to the fluid-bed reactor along with the sub-assemblies. The composition of the fission product mixture was similar to that calculated by Burris and Dillon (ANL-5742, pp. 29-31) for U^{235} undergoing fission with 150 days for the time of irradiation and 30 days for the cooling period. The quantities of inactive fission products added in Runs Zr-40 and Al-4 corresponded to the amounts of the elements formed when 10 and 30 g of U^{235} , respectively, undergo fission. Only those fission product elements with concentrations greater than that of antimony (0.027 g of Sb per 100 g of U^{235}) and specific activity greater than that of molybdenum (2.3 curies/gram) were added. Lanthanum and rare earth elements, except cerium, were not added. The total mass of fission product elements that were added resulted in a concentration of 1.5 w/o of the alumina in the reactor in Run Zr-40 and 4.1 w/o in Run Al-4.

Table II-15

DESCRIPTION OF ALUMINA BEDS USED IN THE BENCH-SCALE FLUID
BED-VOLATILITY PROCESS STUDIES ON URANIUM ALLOY FUELS

Quantity of alumina in the
fluid-bed reactor:

320 g

Alloy charge:

Uranium-Zircaloy-2 alloy clad with Zircaloy-2 for Zr-39 and Zr-40; Uranium-aluminum alloy clad with aluminum for Al-1, Al-2, Al-3 and Al-4.

Run No.	Fluid-Bed Alumina		Quantity (g)	Packed-Bed Filter Alumina	
	Type	Mesh Size		Type	Mesh Size
Zr-39	38 ^a	-80 +100	320	38 ^a	-14 +20
Zr-40	38 ^a	-40 +100	320	38 ^a	-14 +20 _b
Al-1	RR ^a	-40 +60	200	38 ^a	-14 +20 _b
			120	RR ^a	-40 +60 _b
Al-2	38 ^a	-80 +100	320	38 ^a	-14 +20
Al-3	T-61 ^c	-40 +120	430	38 ^a	-14 +20
Al-4	T-61 ^c	-40 +120	640	T-61 ^c	-14 +20

^aFused alumina manufactured by Norton Company.

^bThe -40 +60 mesh fraction was sandwiched between layers of -14 +20 mesh alumina, 170 g on top and 30 g on the bottom.

^cSintered alumina manufactured by Aluminum Company of America.

Information concerning the alumina beds charged to the reactor and filter section are given in Table II-15. The quantity of alumina charged to the reactor was the same in each experiment, 320 g, whereas the quantity of alumina used as a packed-bed filter ranged from 320 to 640 g (6-

to 12-in. depths). Three types of alumina were tested, two grades of fused alumina (Type 38 and Type RR Alundum, Norton Co.) and one grade of sintered alumina (Tabular T-61, Aluminum Company of America).

Hydrochlorination of uranium-Zircaloy-2 alloys was carried out at average temperatures of 380°C for the fluid bed and 350°C for the filter bed. The inlet HCl concentrations were similar to those used in previous runs (ANL-6725, page 179). Before being fed to the reactors, the HCl was bubbled through a humidifier containing a saturated solution of hydrochloric acid which was maintained at 21°C. The moisture content of the exit gas was about 1100 ppm (the equilibrium value). During the first part of Run Zr-39, 20 v/o hydrogen was fed with the HCl. These reactant streams simulate conditions expected when HCl is recycled from a simple condenser system.

Hydrochlorination of uranium-aluminum alloys was carried out while maintaining the temperature of the fluid and filter beds above the sublimation point (180°C, 1 atm) of aluminum trichloride (AlCl_3). Fluid-bed temperatures ranged from 193 to 404°C, while the filter temperature was maintained at 200°C. The overall hydrochlorination conditions were similar for all runs, the major differences being the moisture contents of the HCl gas streams. Moisture contents of the inlet HCl were 1, 35, 1100, and 1100 ppm for Runs Al-1, Al-2, Al-3, and Al-4, respectively. Hydrogen chloride containing 20 v/o hydrogen was fed during the first part of Run Al-3.

The hydrofluorinations in runs with uranium-Zircaloy-2 were carried out at a temperature of 350°C. The durations of the treatments and the concentrations of HF used were as follows: one hour each with 20 v/o and 50 v/o HF in Run Zr-39; one hour with 20 v/o HF in Run Zr-40.

Hydrofluorination in Runs Al-3 and Al-4 consisted of a 1-hr reaction period at 350°C with 20-50 v/o HF; hydrofluorination was not carried out in Run Al-1. During the hydrofluorination period in Run Al-2, with 50 v/o HF, the temperature of the reactor assembly was gradually raised from 200 to 350°C over a period of three hours.

Fluorinations were also carried out in several different ways. In Run Zr-39, 10 v/o fluorine was fed while the temperature was gradually increased from 250°C to 500°C; Run Zr-40 involved two temperature levels, 250°C followed by 500°C, with gradual increase in fluorine concentration from 5 v/o to 90 v/o at each temperature level. Separate fluorination of the fluid and filter beds was carried out during Zr-39. Fluorinations were similar in Runs Al-2, Al-3 and Al-4 and included a low temperature (250°C) period followed by a high-temperature period (500°C). At each temperature level the concentration of fluorine was gradually increased from 5 v/o to 90 v/o over a period of 2 hr. In Run Al-1, fluorination was conducted at 350°C for 1.5 hr and at 500°C for 5.0 hr. A typical reaction cycle for an aluminum run (Run Al-2) is summarized in Table II-16.

Table II-16

REACTION CONDITIONS FOR HYDROCHLORINATION,
HYDROFLUORINATION AND FLUORINATION OF MINIATURE
MULTIPLATE URANIUM-ALUMINUM FUEL ELEMENT SUBASSEMBLIES

Run No.: A1-2

Equipment: 1 1/2-in. fluid-bed reactor assembly

Fuel Charge: Three 4.2 w/o uranium-aluminum alloy subassemblies weighing 55 g each

Fluid Bed: 320 g of alumina, -80 +100 mesh (Type 38 Alundum, Norton Co.)

Packed-bed
Filter: 320 g of alumina, -14 +20 mesh (Type 38 Alundum, Norton Co.)

Gas Velocity in
the fluid and
filter beds: 0.5 to 0.7 ft/sec

Type	Reactant		Time (hr)	Temperature (°C)	
	Concentration (v/o)	Quantity (x Stoichiometric)		Fluid Bed	Filter Bed
HCl	0 to 73	1.1 ^a	2.5 ^b	193 to 404	200
HCl	0 to 73	2.5 ^a	5.0 ^c	201 to 354	200
HF	50	60 ^d	1	200	200
HF	50	73	1	275	275
HF	50	73	1	350	350
F ₂	5 to 90	275 ^e	2	250	250
F ₂	5 to 90	275	2	500	500

^aStoichiometric amount to hydrochlorinate 165 g of aluminum to AlCl₃.

^bTime during which the first assembly was hydrochlorinated.

^cTime during which the second and third subassemblies were simultaneously hydrochlorinated.

^dStoichiometric amount to hydrofluorinate 6.9 g of uranium to UF₄.

^eStoichiometric amount to fluorinate 9.1 g of UF₄ to UF₆.

Results and Discussion

Results are presented and discussed in terms of the variables listed above in Table II-14. Of prime importance are the effects of these variables on uranium recovery and losses, reaction rates, and bed behavior (caking). Important, also, are good uranium material balances. Overall results indicate that (1) a satisfactory reaction cycle has been established for both zirconium-based and aluminum-based fuels, (2) high (99%) recovery of uranium can be achieved, and (3) aluminas used for bed materials are stable (remain free-flowing and fluidizable).

Uranium Material Balances. Very good material balances were obtained for all of the runs. Typical material balances for two of the runs (Runs Zr-39 and Al-3) are illustrated in Table II-17. Moreover, the total recoverable uranium (which includes the uranium associated with samples submitted for chemical analysis) was high, 99.0 percent of the uranium (6.1 g) in the alloy charge for Zr-39 and 99.6 percent of the uranium (8.9 g) in the alloy charge for Al-3.

Material Balances for Minor Constituents of Zircaloy-2 and Fission Products. The distributions of most of the minor constituents of Zircaloy and the fission product elements were in conformity with those that may be estimated from the volatilities of their higher valent chlorides and fluorides. Material balances on these elements were based on the analyses of individual samples by X-ray spectrographic and/or spectrochemical methods. Typical data from processing of uranium-Zircaloy-2 alloy (Run Zr-40) showed that major amounts of three of the minor elements had volatilized during hydrochlorination: aluminum, 79%; boron, 84%; and tin, 97%. The relatively low recovery of aluminum may partially result from the formation of the oxide by reaction of the aluminum chloride with the moisture in the feed gas. Lesser amounts of three other minor elements volatilized during hydrochlorination: silicon, 14%; iron, 22%; and manganese, 36%; the remaining amounts of these elements were retained by the alumina. Of the fission products, molybdenum volatilized throughout the reaction cycle (42% volatilized during hydrochlorination and 51.5% during fluorination). Almost all of the titanium (99.1%) volatilized during fluorination. Of the sixteen elements studied, eight were completely retained by the alumina. These were: silver, 99.7%; barium, 99.7%; cerium, 100%; cadmium, 100%; cobalt, 100%; strontium, 96.4%; and yttrium, 100%. Volatilization of molybdenum and titanium during fluorination indicates that final purification of UF_6 may be needed.

Uranium Distribution Between Packed-Bed Filter and Fluid Bed. By separately fluorinating the filter bed and the fluid bed, an indication of the distribution of uranium in the system after hydrochlorination was obtained. In current studies an average of 17% of the uranium in the initial charge was recovered from the filter bed, the bulk of the uranium being recovered from the fluid bed. As shown by the analysis of the alumina at the end of the run, the uranium was as completely removed from the alumina in the filter as from the alumina in the fluid bed.

Table II-17

URANIUM MATERIAL BALANCES FOR RUNS Zr-39 AND Al-3

Reaction Cycle: Hydrochlorination-Hydrofluorination-Fluorination

Fuel Charge: 296 g of 2.1 w/o uranium-Zircaloy-2 alloy for Run Zr-39,
 172 g of 5.2 w/o uranium-aluminum alloy for Run Al-3

	Uranium Balance ^a (% of U in the Initial Charge)	
	Run Zr-39	Run Al-3
<u>Uranium Recovered</u>		
1. From cold traps (UF ₆)	96.93 ^b	98.96 ^c
2. From the activated alumina trap	0.08	0.12
3. Uranium values (recoverable) in fluid-bed samples	2.08	0.56
4. Total	99.04	99.64
<u>Uranium Lost</u>		
1. Uranium retained by alumina ^d		
a. In fluid bed ^e		
+200 mesh (317.4 g for Zr-39, 321.5 g for Al-3)	0.50	0.11
-200 mesh (2.6 g for Zr-39, 15 g for Al-3)	0.03	0.03
b. In filter bed		
+20 mesh (320 g for Zr-39, 430 g for Al-3)	0.30	0.09
-20 mesh (2.0 g for Zr-39, 4.1 g for Al-3)	0.02	0.01
2. Uranium loss through packed-bed filter during hydrochlorination		
a. HCl + 20 v/o hydrogen (1.9 hr for Zr-39 and 3.3 hr for Al-3)	0.01	0.06
b. HCl alone (8.6 hr for Zr-39 and 4.2 hr for Al-3)	0.02	0.04
3. Total	0.88	0.34

^aSecond decimal places are reported to show the relative insignificance of some of the items.

^bIncludes uranium recovered under three successive sets of fluorination conditions, 79.78% from the first fluid-bed fluorination with 10 v/o fluorine, 1.62% from the second fluid-bed fluorination with 11 to 90 v/o F₂, and 15.53% from the filter-bed fluorination.

^cIncludes 97.39% from the low temperature (250°C) fluorination and 1.57% from the high temperature (500°C) fluorination of both the fluid bed and packed-bed filter.

^dType of alumina given in Table II-15.

^eTotal weight of the residual fluid bed adjusted to account for the samples withdrawn.

Uranium Retention by Alumina. Fluorination conditions have now been established for consistently high removals (minimal retentions) of uranium from alumina. High concentrations of fluorine, perhaps as high as 90 v/o, and final temperatures of 500°C appear necessary to achieve high removals (see typical fluorination conditions and results in Table II-18 and Figure II-32). Results have been satisfactory regardless of the moisture content of the HCl, the presence of fission product elements, or the type of alumina used. The level of uranium was reduced to at least 0.01 w/o of the final alumina beds in all cases. Generally, lower retentions of uranium were sustained in the case of uranium-aluminum alloy, for example, in Run A1-2, the retentions were 0.003 w/o and 0.0016 w/o for the fluid bed and filter bed, respectively.

The effects of mesh size of alumina on the reaction rates during the hydrochlorination and fluorination steps are under study.

Table II-18

RECOVERY OF URANIUM FROM ALUMINA BY FLUORINATION

(Run A1-2)

Equipment: 1 1/2-in. fluid-bed unit
 Fuel Charge: 165 g of 4.2 w/o uranium-aluminum alloy
 Reaction Cycle: hydrochlorination-hydrofluorination-fluorination
 Reaction Bed: 320 g of alumina (Type 38 Alundum, Norton Co.)
 -80 +100 mesh

Fluorination Time (hr)	Temperature (°C)	Quantity (x Stoichiometric ^a)	Maximum Concentration of Fluorine ^b (v/o)	Residual Uranium in Alumina (w/o)
0.5	250	15	20	0.2
1.0	250	52	50	0.03
1.5	250	91	80	0.015
2.0	250	117	90	0.01
2.5	500	15	20	<0.01 ^c
3.0	500	52	50	<0.01 ^c
3.5	500	91	80	<0.01 ^c
4.0	500	117	90	0.003

^aStoichiometric amount to fluorinate 9.1 g of uranium tetrafluoride to uranium hexafluoride.

^bConcentration of fluorine was increased in steps of 10 v/o every ten minutes to the values indicated above.

^cAnalysis by X-ray spectrographic method.

Figure II-32

RECOVERY OF URANIUM FROM ALUMINA BY FLUORINATION

(Run A1-2, see Table II-18 for conditions)

Uranium Loss through the Packed-Bed Filter During Hydrochlorination of Uranium-Aluminum Alloys. The uranium loss during hydrochlorination of uranium-aluminum alloys decreased sharply when the depth of the packed-bed filter was increased from 6 to 8 inches; the loss then appeared to level off. The actual rates of uranium loss were 11.0, 1.2, and 0.7 mg/hr for corresponding filter-bed depths of 6, 8, and 12 in. (Runs A1-2, A1-3, and A1-4, respectively). During these runs, the temperature of the filter bed was maintained at 200°C. The low rates of uranium loss encountered in Runs A1-3 and A1-4 are similar to those encountered previously during the hydrochlorination of uranium-Zircaloy-2 alloys (ANL-6725, p. 181) in which the temperature of the filter bed was maintained at a much higher temperature (350°C). This similarity in rates of uranium loss, even though the levels of temperature of the filter beds were widely different, suggests that a different "form" of uranium chloride is produced when the aluminum alloy is hydrochlorinated than when the zirconium alloy is reacted. The mechanism of filtration may be different in the two cases.

Effect of Hydrogen or Uranium Losses in the Hydrochlorination Step. The presence of hydrogen in the HCl feed did not affect the quantity of uranium lost through the packed-bed filter. Results of Run Zr-39 showed that the uranium losses through the filter (determined by analysis of uranium in the $ZrCl_4$ condenser) were similar for the run in which hydrogen was used and in the run in which hydrogen was not used.

The actual values were 1.3×10^{-5} and 0.6×10^{-5} g of uranium per gram of zirconium condensed for the two parts of hydrochlorination, the 20 v/o hydrogen in HCl and no-hydrogen, respectively. Similarly, for Run Al-3, the loss through the filter was 5.0×10^{-5} and 3.4×10^{-5} g of uranium per gram of aluminum collected in the condenser in the two instances. By effecting reduction of the more volatile uranium tetrachloride to the trichloride, the hydrogen had been expected to give lower losses.

Effect of Moisture on the Hydrochlorination Reaction. Use of moisture in HCl in concentrations up to 1100 ppm did not appear to affect either the overall hydrochlorination rates or the HCl utilization efficiencies. Experiments made with zirconium alloy in which as-received HCl (manufacturer's specification for water content, 35 ppm) was used in one run (Run Zr-38, reported in ANL-6725, page 178), and HCl containing 1100 ppm water was used in another run (Run Zr-39) gave nearly identical alloy reaction rates, 27 and 28 g/hr, respectively. Also, the total stoichiometric amounts of HCl required for complete reaction were similar in the two cases. Runs with uranium-aluminum alloy also showed that moisture had little effect. Runs Al-2 (35 ppm H_2O) and Al-3 (1100 ppm H_2O) gave alloy reaction rates of 23 and 23 g/hr, respectively. Overall amounts of HCl fed for complete reaction were 3.6 and 3.0 times the stoichiometric* requirements in Runs Al-2 and Al-3, respectively.

Effect of Hydrofluorination Temperature. Analysis of alumina bed samples taken at the end of each hydrofluorination period during Run Al-2 indicated that removal of chloride can be achieved at $350^\circ C$, satisfactory removal can be achieved at $275^\circ C$ and incomplete removal is sustained at $200^\circ C$. The chloride content of the alumina in the fluid bed decreased from 0.77 w/o to 0.15 w/o at $200^\circ C$, from 0.15 w/o to 0.03 w/o at $275^\circ C$, and finally down to 0.006 w/o at $350^\circ C$. Incorporation of a hydrofluorination step in the reaction cycle does not appear to interfere with uranium recovery.

Fluid-Bed Behavior During Simulated "Emergencies"

Power failures simulated during each of the reaction steps in the runs made with fission product elements present (Runs Zr-40 and Al-4) were found to have no effect on bed behavior. A power failure consisted of turning off the heat supply and the main gas flow to the reactor; the latter, of course, resulted in a static bed. The entire reactor assembly was then rapidly cooled to room temperature. The reactor assembly was maintained at room temperature for two hours, then heated to the operating temperature, and the reaction step completed under fluidizing conditions. Gas flow failure was also simulated after each reaction step. The main gas supply was turned off, the reactor was rapidly heated to $600^\circ C$, maintained at that temperature for two hours, cooled back to the operating temperature for a similar period

*The reaction $Al + 3HCl \rightarrow AlCl_3 + 1\frac{1}{2} H_2$ is assumed

and then stabilized at the operating temperature of the next step. The behavior of the fluid bed during these runs was completely satisfactory. The bed was readily refluidized upon re-initiation of gas flow, remained free-flowing and was readily withdrawn at the end of each experiment.

Conclusions

Process operating conditions have now been established for recovering greater than 99% of the uranium from both uranium-aluminum and uranium-Zircaloy alloy charges. The concentration of uranium retained by alumina is reduced to less than 0.01 w/o by fluorination. Both sintered and fused grades of alumina were found to be suitable, inert bed materials.

The process offers considerable flexibility in the choice of operating conditions of temperature and reactant concentrations.

Future Work. Although the process appears to be reasonably well-established for both aluminum-based and Zircaloy-based fuels, investigations will be continued on methods of further decreasing the uranium losses due to retention by alumina. Also, feasibility of improving the overall efficiencies of HCl and fluorine utilization will be investigated; this work will be aimed at a scheme to obviate the need of recycle. Further correlation of the data obtained thus far is planned to aid in directing future efforts. Exploratory studies on a similar scheme for other fuels, for example, $\text{UO}_2\text{-ZrO}_2$ fuel clad in Zircaloy, will be carried out.

b. Pilot Plant for Demonstration of the Fluid-Bed Volatility Process for Enriched Uranium-alloy Fuels
(J. Holmes, J. Barghusen, N. Levitz, C. Schoffstoll, W. Kremsner)

Three shakedown experiments have been completed in the pilot-plant facility which will be used to demonstrate the fluid-bed volatility process for recovering uranium from enriched uranium-alloy fuels. The pilot plant is capable of batch processing plate-type assemblies of up to about 30 kg of uranium-zirconium alloy and up to about 14 kg of uranium-aluminum alloy.

The objectives of the initial experiments were (1) to gain operating experience with the equipment and instrumentation, (2) to demonstrate both the hydrochlorination and hydrofluorination steps with multiplate assemblies of Zircaloy or aluminum (no uranium present), (3) to determine the best method for the control of the hydrochlorination reaction rate; control by regulating flow, using fixed levels of reactant concentrations, and control by regulating the bed temperature were tested, (4) to determine the effect of HCl concentrations on alloy reaction rate, and (5) to demonstrate the operation of the hydrolysis reactor for zirconium-based and aluminum-based fuels.

The following sections include a description of the pilot plant equipment, instrumentation, and operating procedure, and a discussion of the results of the first three experiments.

Pilot Plant Equipment. The pilot plant equipment shown schematically in Figure II-33 consists of (1) a fluid-bed reactor, (2) a packed-bed filter, (3) a hydrolysis reactor, (4) uranium hexafluoride (UF_6) cold traps, (5) a disposal system for HCl and hydrogen fluoride (HF), (6) a fluorine disposal system, (7) a fluorine recycle pump (diaphragm compressor type), and (8) a number of auxiliary pieces of equipment. Since previous reports on this project gave little or no details of the major pieces of equipment, this information is now presented in summary form in Table II-19.

Figure II-33

SCHEMATIC FLOWSHEET OF URANIUM ALLOY FUEL PROCESSING
PILOT PLANT

108-5612 R.3

Power for heating is supplied by a two-wire, 240-volt system through twelve, 10-amp and seven 25-amp variable voltage transformers. Each of the larger transformers operates in conjunction with a proportioning-type temperature controller.

The valves used for dry HCl are bellows-sealed and constructed of stainless steel. The valves used for fluorine are constructed of Monel and are sealed by Monel bellows. Two all-nickel, double-bellows-sealed valves are used in the high-temperature region just downstream of the packed-bed filter.

Spiral-wound gaskets of nickel and asbestos are used in the primary reactor and packed-bed filter with the exception of the charge ports on both vessels where serrated gaskets of solid nickel are used. Spiral-wound gaskets of stainless steel and asbestos are used in the hydrolysis reactor.

Table II-19

PILOT PLANT EQUIPMENT SPECIFICATIONS

<u>Item of Equipment</u>	<u>Size</u>	<u>Material</u>	<u>Heated or Cooled</u>	<u>Special Features</u>
Preheater	2-in. ID, 3-ft long	nickel-200	3 kw	Internally finned
Reactor	6-in. Sched. 40 pipe, 70-in. long	nickel-200	25 kw, air-water cooled	Bubble-cap gas distributor ^a
Reactor Disengaging Section	12.5-in. ID, 20-in. long	nickel-200	12 kw	
Packed-Bed Filter	9.5-in. ID, 24-in. long	nickel-200	12 kw	Cone bottom and internally finned
Hydrolysis Reactor	6-in. Sched. 40 pipe, 36-in. long	304 stainless steel	16 kw	Bubble-cap gas distributor. ^a Product take-off at 21-in. bed level.
Hydrolyser Disengaging Section	11.75-in. ID, 28-in. long	304 stainless steel	---	
Hydrolyser Filters	2.75-in. OD, 18-in. long	sintered nickel or Inconel	---	Automatic blow-back with preheated 80 psig nitrogen
Off-gas disposal:				
Condenser	10.4 sq ft of surface area	impervious graphite	Water-cooled	
Scrubber	6-in. ID, 6-ft long	glass pipe	---	Recirculated water, ceramic saddle packing
UF ₆ Cold Traps	3/4-in. OD 16-ft length/coil 7.5 turns/coil	copper tubing	Individually cooled	Three coils in series
F ₂ Disposal Columns	6-in. Sched. 40, 83-in. long	Monel	---	Two columns in parallel
Recycle Pump	25-in. dia. heads 6 scfm fluorine	nickel process head, 304 SS secondary head	---	Double-diaphragm type (Model G-3, LAPP Insulator Co., Leroy, N.Y.), halo-carbon oil as an intermediate fluid
Piping:				
Dry HCl	1 or 1/2-in. Sched. 40	stainless steel	---	
F ₂	1 or 1/2-in. Sched. 40	nickel or Monel	---	
Aqueous waste	1-in.	PVC		

^aSee ANL-6342, page 12.

Instrumentation. The pilot-plant instrumentation consists of the following: (1) two temperature recorders and a temperature indicator, (2) temperature controllers, (3) pressure and differential pressure (Δp) transmitters and recorders, (4) flow recorders and controllers, (5) a reactor coolant controller, and (6) a thermal conductivity gas analyser.

The temperatures are monitored throughout the equipment with chromel-alumel thermocouples. Two multi-point strip chart instruments record the 36 most important temperatures. A manually operated temperature indicator is used to monitor as many as 48 other temperatures.

Proportioning-type temperature controllers are used to regulate the electrical power to the equipment heaters. The heaters are wired so that several of them may be used for a particular zone. Two heated zones are controlled on the primary reactor, one on the reactor disengaging section, one on the packed-bed filter, two on the hydrolysis reactor and one on the gas preheater. The controller for each zone operates by means of a signal from a thermocouple in contact with the walls of the respective vessels.

The following pressures and differential pressures (Δp) are measured by pneumatic transmitters and recorded on 4-in.-strip-chart recorders: (1) primary reactor bed Δp , (2) total system pressure, (3) packed-bed filter Δp , (4) hydrolyser gas distributor Δp , (5) hydrolyser bed Δp , (6) hydrolyser filter Δp , and (7) fluorine disposal column Δp .

The following flow rates are recorded using a pneumatic Δp transmitter with an integral orifice: (1) nitrogen flow rate, (2) HCl flow rate, (3) fluorine flow rate, (4) steam flow rate for the hydrolysis reactor, and (5) the total flow rate to the reactor. The HCl, fluorine and steam flows are all controlled by pneumatic valves using the signal from the respective flow orifice. The HCl flow can also be controlled directly by the temperature of the fluid bed. The nitrogen flow rate is controlled by the Δp measurement of total flow so that the total flow rate is maintained constant. During the recycle of fluorine, gas is bled from the system to maintain the total system pressure constant.

The wall of the main reactor is cooled by an air-water mixture which is circulated through a series of stainless steel coils wrapped around the reactor. A thermocouple attached to the wall of the reactor is the sensing element. The flow of coolant is regulated by a temperature controller which operates a system of pneumatic valves.

Thermal conductivity gas analysers are used to follow the hydrochlorination and fluorination steps of the reaction. During hydrochlorination, the extent of the reaction, reaction rate, and the required steam rate for the hydrolysis can be determined from the hydrogen production rate. The concentration of hydrogen produced during the alloy reaction is measured by comparing the thermal conductivity of a sample of the off-gas (a mixture of hydrogen and nitrogen) from the final scrubber with that of a reference gas (pure nitrogen). The thermal conductivity cell can be easily calibrated with

known mixtures of hydrogen and nitrogen and, therefore, provides accurate, quantitative information. The extent of the fluorination reaction is followed by comparing the thermal conductivity of the fluorine-nitrogen mixture entering the reactor (which is the reference gas, in this step) with that of the fluorine-nitrogen- UF_6 mixture leaving the reactor. Use of the cell as a method for determining the concentration of UF_6 in the gas stream awaits calibration of the system.

Experimental Procedure. A predetermined quantity of particulate material for the primary reactor bed, packed-bed filter and hydrolysis reactor are charged to the respective vessels. In the experiments carried out to date, high-fired alumina was used as bed material in the main reactor assembly and either alumina or sand in the hydrolysis reactor. The settled bed depth in the main reactor was about four feet, the packed-bed filter depth was about 0.5 ft and the settled bed depth in the hydrolyser was about 2.5 ft. The alloy charge is lowered onto the settled reactor bed and is then submerged by intermittently pulsing the bed with nitrogen. (Details of the fuel loading procedure are given in ANL-6687, p. 148). The entire reaction system is heated to the desired temperature while sufficient nitrogen is passed through the equipment to fluidize the alumina in the primary reactor and hydrolysis reactor. Steam is admitted to the hydrolysis reactor shortly before the flow of HCl is started to the primary reactor. The product from the hydrolysis reactor is periodically withdrawn through an electrically operated plug valve so as to maintain the bed level relatively constant. Hydrochlorination proceeds until the thermal conductivity analyser shows that hydrogen production has ceased. After the flow of HCl is shut off, the system is purged (for about 30 min) with nitrogen and the temperature is adjusted to that desired for the hydrofluorination step. The off-gas from the packed-bed filter is routed so that it will bypass the hydrolysis reactor; HF is then fed at the desired rate for 1 to 2 hr. The system is again purged for about 30 min and the temperature is adjusted to the desired fluorination conditions. The procedures for fluorine recycle and the hydrolysis of the UF_6 product are now being established and will be discussed in a later report.

Results and Discussion

The processing conditions and preliminary results of the recent shakedown experiments are given in Table II-20. Welded assemblies of Zircaloy plates weighing 17.75 kg and 13.6 kg were processed in the first two experiments (Runs 1 and 2). The third experiment (Run 3) involved a welded assembly of aluminum plates weighing 13.65 kg. In each experiment, the assembly was completely hydrochlorinated. Hydrofluorination was also carried out in all three runs. The hydrolysis column was operated in series with the main reactor in each of the runs for demonstration of the conversion of the volatile wastes (primarily zirconium and aluminum chlorides) to solids (oxides).

In general, the runs were considered satisfactory. Hydrochlorination periods were 8.25, 5.0, and 11.7 hr for Runs 1, 2, and 3, respectively, and were conducted with temperatures of the fluid bed at 400°C

Table II-20

PROCESS CONDITIONS AND RESULTS OF INITIAL PILOT PLANT RUNS ON ZIRCALOY AND
ALUMINUM MULTIPLATE ASSEMBLIES

		Run 1	Run 2	Run 3			
<u>Alloy Charge</u>							
Weight and Type		17.75 kg Zircaloy (welded)	13.6 kg Zircaloy (welded)	13.65 kg Aluminum (welded)			
No. of Plates		16	10	16 (0.125-in. thick, 2.5 in. wide); 1 (0.25-in. thick, 2.5-in. wide)			
<u>Overall Dimensions</u>							
(cross-section), in.		2.5 x 2.8	2.125 x 2.5	16 spaces (~0.1-in. wide)			
Length, in.		36	36	48			
<u>Beds</u>							
Reactor		40 kg, ~48-in. deep (static) alumina, 60 mesh (Type RR, Norton Co.)	40.6 kg, ~48-in. deep (static) alumina, 60 mesh (Type RR, Norton Co.)	38.0 kg, ~46-in. deep (static), alumina, 28-100 mesh (Type T61, Alcoa)			
Packed-Bed Filter		8.8 kg, ~5-in. deep alumina, 20 mesh (Type 38, Norton Co.)	9.0 kg, ~5-in. deep alumina, 20 mesh (Type 38, Norton Co.)	9.0 kg, ~5-in. deep alumina, 14-28 mesh (Type T61, Alcoa)			
Pyrohydrolyser		Sand ~20 kg (+40 mesh)	~20 kg, Sand and ZrO ₂ from Expt. 1	16.5 kg, 28-in. deep alumina, 28-100 mesh (Type T61, Alcoa)			
<u>Reactant Concentrations</u>							
HCl		0-95% in N ₂	46% in N ₂ (0-2.5 hr) 62% in N ₂ (2.5-5.0 hr)	55% in N ₂			
HF		- - -	15% in N ₂	8% in N ₂			
<u>Hydrochlorination</u>							
<u>Temperatures</u>							
(°C)		Average	Maximum	Average	Maximum		
Reactor Bed		400	450	400 (0-2.5 hr) 500 (2.5-5.0 hr)	420 545	300	320
Reactor Wall		375	380	395 (0-2.5 hr) 390 (2.5-5.0 hr)	405 460	270	295
Element Channel		---	625	430 (0-2.5 hr) 550 (2.5-5.0 hr)	600 710	330	335
Packed-bed Filter		380	---	390		300	
Pyrohydrolyser		375	---	360		300	
<u>Velocities (ft/sec)</u>							
Reactor		~0.6		0.66 (0-2.5 hr) 0.78 (2.5-5.0 hr)		0.52	
Packed-Bed Filter		~0.3		0.36 (0-2.5 hr) 0.37 (2.5-5.0 hr)		0.25	
Pyrohydrolyser		1.2		1.3		1.0	
<u>Reaction Rate (kg/hr)</u>							
Average		2.15		2.71		1.16	
Maximum		----		----		1.85	
<u>Reaction Time (hr)</u>							
Hydrochlorination		8.25		5.0		11.7	
Hydrofluorination		2.1		1.0 (at about 375°C)		1.8 (at about 330°C)	
<u>HCl Utilization Efficiency</u>							
Average		~40%		43%		55%	
Maximum		----		----		90%	

and 500°C when Zircaloy was being reacted and at about 300°C when the aluminum was being reacted. The respective hydrofluorinations were of 2.1-, 1.0- and 1.8-hr duration at bed temperatures of 330 (Run 3) and 375°C (Runs 1 and 2).

Thermocouples, spaced at 1-ft intervals (vertically) were inserted in the channels between the plates (one thermocouple in each of three spaces) of the fuel assembly in Experiments 2 and 3 in order to obtain a qualitative measure of the rate of reaction and an approximate temperature of the surface of the reacting metal. In both experiments, the lower thermocouple indicated generally higher temperatures than the other two thermocouples, thus showing that the highest reaction rates occur at the bottom of the metal charge (that is, at the reactant inlet region). The temperatures noted for the channels within the element and the temperature of the reactor bed indicated, qualitatively, that the reaction rate was greater when a higher concentration of HCl was used. In Run 2, the average temperatures of the element channel and bed were 430 and 400°C, respectively, for a 46% HCl stream as compared with 550 and 500°C for a 62% HCl stream. Quantitative reaction rate data were not obtained separately for these conditions owing to the malfunctioning of the nitrogen-hydrogen off-gas analysis system.

Although little reaction rate data were obtained in the first Zircaloy run (Run 1), it is interesting to note that the overall average hydrochlorination rate in this run was appreciably lower than in Run 2, even though the assembly processed in the first run had a larger metal cross section (16 plates in Run 1 as compared with 10 plates in Run 2). The rates were 2.7 kg/hr in Run 2 as compared with 2.1 kg/hr in Run 1. The higher reaction rate in Run 2 probably resulted from the method used for controlling the reactant input. A constant flow rate of HCl was used in Runs 2 and 3 whereas in Run 1 the HCl input was controlled by the reactor bed temperature. When the HCl input was controlled by bed temperature, wide variations in the HCl flow rate were experienced, since a rise in bed temperature resulted in complete shutoff of HCl flow. When the HCl input was controlled by flow rate, the temperatures in the element channels and in the bed were sustained at higher levels and resulted in higher reaction rates.

Although the hydrochlorination of aluminum proceeded at a rather low average rate, 1.16 kg/hr, when 55% HCl was used, a higher reaction rate can undoubtedly be achieved. The basis for this conclusion is the fact that the maximum temperature of the element channel in this case was only 335°C, a temperature well below the melting point (660°C) of aluminum, the temperature that is considered to be limiting for this system. In a subsequent experiment, conditions of higher bed temperature, higher HCl flow rate, and higher gas velocity will be tested in order to establish a practical limit for the reactor bed temperature.

The overall HCl utilization efficiency was high in all experiments. During the Zircaloy runs the efficiency averaged about 40%. The average efficiency during the aluminum run was 55% and was near 70% during the first two-thirds of the experiment.

The reactor cooling system, in which the coolant is an air-water mixture, operated satisfactorily and was found to have sufficient cooling capacity during all of the experiments. The wall temperature of the reactor was maintained between 265 and 275°C during the aluminum experiment and near 395°C during the Zircaloy experiments.

In these tests, the volatile chlorides produced during hydrochlorination were converted to oxides by reaction with steam in the fluid-bed hydrolysis reactor. The hydrolysis of zirconium tetrachloride was carried out at about 360°C (Runs 1 and 2) with a starting bed of -20+60 mesh sand. The final bed from the first run was used as the starting bed for the next run. It was observed that the zirconium dioxide product was, primarily, in the form of fine particles (-230 mesh) and there was little or no indication of any zirconium dioxide coating on the starting bed material.

The bed material employed in the hydrolysis reactor for the aluminum run was sintered alumina (Tabular T-61, Aluminum Co. of America) which had an average particle size of about 60 mesh. In this run, a bed temperature of 300°C was employed. Although a large proportion of the aluminum oxide formed as fines (-230 mesh), about one-third of the material appeared as +230 mesh particles. Screen analyses of the +230 mesh fraction indicated that the average particle size of the bed material increased from 278 μ to 304 μ during the 11.7 hours of processing time.

Although a large proportion of fines were produced in the hydrolysis reactor during the three runs, their presence did not appear to affect the operation of the reactor; bed temperatures remained uniform and no significant buildup of pressure across the sintered metal filters was noted. These data are consistent with results of earlier studies (ANL-6687, p. 146) which showed that, while most of the oxide produced in the hydrolysis reactor appeared as fine particles (-200 mesh), some of the oxide did form as a coating on the fluid-bed material. These earlier studies also showed that the operation of the hydrolysis reactor was not affected by the nature of the starting bed material or by the temperature at which the hydrolysis reaction was carried out.

Difficulties with the operation of the thermal conductivity cell were experienced in Runs 1 and 2 and were attributed to in-leakage of air and the carryover of excessive amounts of moisture from the final off-gas scrubber into the clean-up train located upstream of the cell. This was remedied by the installation of an improved sampling system and drying train prior to Run 3.

Another problem, which was readily solved, was the buildup of pressure (from 0.5 to 2.0 psig) across the packed-bed filter during the final hours of hydrochlorination in Runs 2 and 3. Relief of this pressure buildup was achieved by momentarily turning off the main fluidizing gas stream (the beds are static during this short time) and applying a reverse-flow pulse of nitrogen through the packed-bed filter.

Future Work

Future pilot plant operations will be directed toward: (1) testing the technique for trapping UF_6 and the establishment of a procedure for operating with fluorine recycle, (2) the demonstration of uranium recovery as UF_6 from unirradiated uranium-Zircaloy and uranium-aluminum fuel charges using conditions that are based on pilot-plant shakedown experience and on the results of work carried out in the 1.5-in. unit (see preceding section), (3) the demonstration of the operability of all components of the pilot plant, and (4) the determination of material balances on uranium and other key components, such as tin in Zircaloy.

c. High-activity-level Studies on Enriched Uranium Alloy Fuels (A. Chilenskas, K.S. Turner, J. Kincinas)

Work is continuing on the installation of a bench-scale facility for the study, at high activity levels, of the fluid-bed volatility process for highly enriched uranium alloy fuels. Irradiated specimens of uranium-Zircaloy and uranium-aluminum fuels will be used to investigate (1) the distribution of fission products throughout the various process steps, (2) decontamination factors that may be realized, and (3) the effect, if any, of irradiation and the presence of fission products on uranium recovery and reaction rates. The equipment and process steps will be similar to those previously described (see ANL-6569, pp. 114-118) for inactive studies, but, in addition, will include sodium fluoride (NaF) traps for additional uranium purification. The UF_6 which leaves the reactor during the fluorination step is collected in four NaF traps operated in series at temperatures between room temperature and 400°C . Desorption of the UF_6 using a mixture of nitrogen and fluorine at a controlled temperature will provide additional uranium hexafluoride decontamination from the fission products which form volatile hexafluorides. The unit will be installed in the Senior Cave facility of the Chemical Engineering Division.

The basic support frame for the equipment has been erected in the cave service area and installation of valves and instrumentation has commenced. Fabrication of the fluid-bed gas distributor, cold traps, HCl scrub tower, fluorine absorption tower, and some miscellaneous items is complete. The reactor assembly (includes the packed-bed filter section) and the ZrCl_4 condenser are awaiting final radiographic examination. The machining and some of the welding has been completed on the NaF traps.

The first components that were fabricated for the installation used the inert-gas-shielded arc process with nickel filler metal 61.* Due to the concern that the minor constituents (particularly titanium) present in this filler metal may have a deleterious effect upon the corrosion resistance of

* A product of International Nickel Company, Inc. with the following nominal composition (in percent): nickel (including cobalt); 93.00 min., titanium 2 to 3.5, aluminum 1.50, manganese 1.0, iron 1.0, silicon 0.75, carbon 0.15, sulfur 0.01, copper 0.25, other 0.50.

welds, the filler metal in later components was changed to nickel-200* in wire form. The final equipment will contain both types of filler metal. Further, the nickel corrosion testing program, which is described below, was revised to include welded specimens made with both filler metals.

Radiographs taken of the welds have shown that sound welds using the inert-gas-shielded arc process with either filler metal can be made provided that high standards of cleanliness are maintained. Some reworking of welds has been found to be necessary because of porosity or incomplete weld penetration. These welds were corrected by grinding and rewelding.

d. Corrosion Studies

(A.A. Chilenskas and G. Gunderson)

A supporting program for the evaluation of the suitability of nickel as a material of construction for the fluid-bed volatility processes has been initiated. The test conditions employed simulate those being used in the bench-scale and pilot-plant-scale studies on high-enriched and low-enriched fuels. These tests are being coordinated with in-column corrosion studies that are being conducted as a part of the process development work. In addition, other materials of interest are being exposed to corrosive environments and evaluated for possible use in the processes.

Nickel as a Material of Construction. The conditions for the test series underway are given below.

<u>Test Designation</u>	<u>Test Description</u>
5A	Continuous flow of 50% fluorine in nitrogen, furnace tube at 500°C.
2	Alternating flow of 50% HCl in nitrogen and 50% fluorine in nitrogen every 24 hours, furnace tube at 450°C.
6	Alternating flow of 50% oxygen in nitrogen and 50% fluorine in nitrogen every 24 hours, furnace tube at 500°C.

The test coupons are contained in nickel furnace tubes which are held at the desired operating temperature in resistance-heated furnaces. The test coupons which are being exposed consist of welded and non-welded specimens of nickel-200 plate. Two types of welded specimens are being tested: one type consists of specimens of nickel-200 welded with nickel-200 filler metal, the second type consists of specimens of nickel-200 welded with nickel filler metal 61. Standard metallographic evaluation techniques will be used to evaluate the rate and extent of corrosion exhibited by these specimens.

*Nickel-200 is a commercially pure wrought form which has the following composition (in percent): nickel (including cobalt), 99.4; copper, 0.1; iron, 0.15; manganese, 0.25; silicon, 0.05; carbon, 0.05; and sulfur, 0.005.

Armaflex 22 Insulation. Tests to determine the resistance of Armaflex 22* at room temperature to fluorine attack have been completed. These tests were performed to evaluate the safety aspects of the use of this material as a low temperature insulator for process condensers. The tests were conducted on small specimens of the material held in a nickel reactor at room temperature. Specimens were exposed to 10% fluorine in nitrogen, 50% fluorine in nitrogen and undiluted fluorine. Exposures for about 24-hr periods showed only a slight hardening of the exposed surfaces for the test with 10% fluorine, but increased hardening and increased penetration resulted during the 50% fluorine test. The specimen exposed to 100% fluorine reacted rapidly after an incubation period of about 2 hr and was converted to a powder in about 1/2 hr. On the basis of these tests, the material is judged to have adequate resistance to fluorine attack at room temperature and is being procured for process use.

e. Conversion of Uranium Hexafluoride to Uranium Dioxide:
Preparation of High-Density Particles
 (I. Knudsen, M. Jones, D. Raue)

A direct fluid-bed process for preparing high-density spheroidal particles of uranium dioxide (UO_2) from uranium hexafluoride (UF_6) is being studied. The results of these studies will be applied to subsequent work on the preparation of dense PuO_2 - UO_2 particles from mixed hexafluoride feeds. The process involves the reaction of the hexafluoride with a mixture of steam and hydrogen conducted in a fluidized bed of oxide particles at elevated temperatures. The work, to date, has been carried out at temperatures of 650°C and 700°C in a 3-in.-diameter Monel reactor described earlier (ANL-6379, page 183). At these respective temperatures, UO_2 particles with densities** as high as 9.6 g/cc and 9.8 g/cc (near 90% of theoretical density) were produced. Particle sizes ranged from 16 to 100 mesh. Final particle densities of 96.5% of theoretical density were obtained by sintering in hydrogen at 1725°C. This material would be intended for use in dispersion fuels or in bulk form in packed fuel elements.

In this process scheme, the reactions occur preferentially on the surface of the bed particles, the solid reaction products being deposited as a dense, adherent layer. As a result, the particles grow. Growth is offset to some extent as a normal consequence of "seed" particles being produced in the bed by the vapor-phase reaction of a portion, usually 5 to 10%, of the UF_6 feed; in addition, seed particles prepared by grinding a portion of the product are added. The run procedure includes periods of hexafluoride feed alternated with periods of fluoride cleanup when only steam and hydrogen are fed. The periods are usually of 30-min duration. Product is removed at the end of each cleanup period such that the bed weight remains approximately constant.

* This material is a solid, flexible, closed-cell plastic manufactured by the Armstrong Cork Co., Lancaster, Pennsylvania.

** As measured by mercury displacement.

In earlier work, the effects of process variables, such as reactant concentration, reactant rates, reactor temperature and bed height, on the density of the UO_2 product were evaluated. The amount of steam in the reactant stream was found to have the most pronounced effect, steam rates equivalent to about twice the UF_6 rate (in moles) resulting in the highest density UO_2 . Higher densities were achieved, also, by the use of: 1) lower UF_6 rates in the range 17 to 34 g/min (ANL-6596, page 159), and 2) greater bed depths, 18-in. vs. 8- to 10-in. (ANL-6648, page 174). A recent study (ANL-6725, pages 185 to 190) indicated it may be possible to use relatively low-density starting material and still produce a high-density product.

Preliminary to the current experiments, the equipment was modified so that the fines produced in the bed and carried out of the bed by entrainment could be returned directly to the bed during the run. Previously, these fines were trapped in a separate filter section (see Figure 51, ANL-6379, page 183). The filter vessel was relocated directly above the bed, thereby allowing the return of the fines to the bed during filter blowback. Experiments of 6- and 12-hr duration showed that satisfactory operation was obtained and that the UO_2 product was similar in density and purity to that of previous experiments. The advantages of the procedure of returning the fines to the bed is the elimination of the need to handle a separate product stream of fine material.

Current work investigated the possibility of: (1) increasing further the productivity of the unit; rates of UF_6 up to 50 g/min were employed as compared with the highest rate of 34 g/min used in previous runs; and (2) extending the range of particle sizes that could be produced; current efforts were directed to the production of particles in the -140 +170 mesh size; the previous range was -16 +100 mesh.

Tests with Increased UF_6 Rates

Tests at a higher rate of UF_6 feed, 50 g/min [87 lb U/(hr) (sq ft reactor cross section)] as compared to a previous high of 34 g/min were made at 650°C with 9- and 17-in. bed depths (static). In these tests the steam rate during the UF_6 feed period was increased to maintain the same proportion of steam/ UF_6 (mole ratio of 2.5/1) as used in previous work. The hydrogen rate was reduced accordingly to 0.87 scfm (hydrogen/ UF_6 mole ratio of about 8/1) to maintain the superficial gas velocity in the reactor at 1.0 ft/sec (exclusive of nitrogen purges and UF_6 flow). The duration of the UF_6 feed period and the cleanup period remained at 30 min each; however, during the cleanup period the steam and hydrogen rates were adjusted so that the steam concentration in the steam-hydrogen stream was increased from about 26 to 50 v/o.

The 9-in. deep bed (Run 75) consisted of 6.0 kg of UO_2 particles; the average diameter, D_{vs} (as defined by Dallavalle²⁷), of the

²⁷Dallavalle, J.M., Micromeritics, 2nd Ed., Pitman Publishing Corp., New York, 1948, p.47.

particles was $298\ \mu$ and the particle density was $9.3\ \text{g/cc}$. A batch of seed particles (D_{vs} of $152\ \mu$, particle density $9.2\ \text{g/cc}$) was prepared for use as needed, the requirements being determined by noting changes in size distribution of samples taken at regular intervals during the run. The duration of the run was 12 hr.

The starting bed for the run carried out with a 17-in. deep bed (Run 77A) was made by combining a number of product samples and the final bed from Run 75 and weighed 11.2 kg (D_{vs} of $273\ \mu$, particle density $8.8\ \text{g/cc}$).

The results of the tests with increased throughput were satisfactory in that no operating difficulties were encountered. The higher rate gave a product of slightly lower density; however, this effect of feed rate on density was found to be partially offset by the use of greater bed depth. During the run (Run 75) with the 9-in. deep bed, the density of the UO_2 decreased to $8.8\ \text{g/cc}$ (from a starting density of $9.3\ \text{g/cc}$). In the test with a 17-in. deep bed (Run 77A), the density of the UO_2 increased to $9.1\ \text{g/cc}$. An effect of bed depth on particle surface was also noted. The surfaces of the UO_2 particles produced in the run with the 9-in. deep bed were rough, whereas the surfaces of the particles produced in the run made with the deeper bed were smooth.

In spite of the higher UF_6 feed rate, the residual fluoride content of the UO_2 particles was reduced to a low value (from about 1.6% to 0.02% for the 9-in. bed and from 0.8% to 0.04% for the 17-in. bed) by the employment of an increased steam concentration during the cleanup period. The hexavalent uranium content and O/U ratio were lower in the run with the deeper bed, 0.53% U^{+6} and O/U ratio of 2.02 as compared with 2.2% U^{+6} and O/U ratio of 2.04, possibly, because of the longer solids residence time in the bed.

The use of deeper beds also appears to cause larger amounts of fines to form. In Run 77A (17-in. bed height), no separate seed fraction was added, yet the amount of fines produced (by the vapor-phase reaction) in the bed was sufficient to offset particle growth and allowed a uniform average particle size to be maintained. In contrast, in Run 75 (9-in. bed height), the addition of seed particles at a rate equivalent to 16% of the UF_6 feed rate was needed to offset particle growth. A similar effect of bed depth on the amount of fine particles formed was noted in earlier runs in which the separate filter vessel was used. The amounts of fines collected in runs with 9-in. and 16-in. deep beds were equivalent to 1.9% and 15.4%, respectively, of the UF_6 fed.

The effects of UF_6 rate and bed depth on particle density as determined in these and previous runs are summarized in Table II-21 and Figure II-34; higher densities are obtained when deeper beds and lower UF_6 rates are used. The density ranged from $9.6\ \text{g/cc}$ to $8.8\ \text{g/cc}$. The density appears to be a function of the thickness of the coating applied during the UF_6 feed period and, consequently, would be a function of the UF_6 feed rate and the total surface area (bed depth or bed inventory) available for coating.

Table II-21

EFFECT OF UF_6 RATE AND BED DEPTH ON THE DENSITY OF UO_2
PRODUCED BY REACTION OF UF_6 WITH STEAM AND HYDROGEN

<u>Run Conditions</u>			
Temperature:	650°C		
Steam/ UF_6 Mole Ratio:	~ 2.5/1		
Duration of UF_6 Feed Period:	30 min/hr		
<u>Run No.</u>	<u>UF_6 Rate (g/min)</u>	<u>Static Bed Depth (in.)</u>	<u>UO_2 Density^a (g/cc)</u>
66-Q ^b	17	9	9.5
66-I ^c	25	9	9.3
66-R ^d	26	17	9.6
66-N ^b	34	9	9.1
75	48	9	8.8
77A	50	17	9.1

^a Measured by mercury displacement

^b Conditions for last 6 hr of Run 66-Q and last 6 hr of Run 66-N (see ANL-6596, p. 159).

^c ANL-6569, p. 123.

^d ANL-6648, p. 173.

Figure II-34

EFFECT OF UF_6 RATE AND BED DEPTH ON DENSITY OF UO_2 PARTICLES
PRODUCED BY REACTION OF UF_6 WITH STEAM AND HYDROGEN

Run Conditions

Temperature: 650°C

Steam/ UF_6 mole ratio: 2.3-2.7/1

Duration of UF_6 feed period: 30 min/hr

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There appear to be no difficulties in operating this system at the higher throughputs. Further, the effect of bed height on fines formation may be useful in reducing the amount of seed particles required to offset particle growth.

Production of -140 Mesh Particles

In the interest of extending the range of particle sizes to which this fluid-bed process is applicable, the feasibility of preparing dense particles of about 140 mesh ($\sim 100\mu$) was demonstrated (Run 76); this particle size is one commonly used in coated-particle and other dispersion fuel elements. A starting bed of 3.7 kg (about 5-in. static bed height) of -170 +325 mesh particles (D_{vs} of 54μ , particle density of 8.6 g/cc) of UO_2 was used. No product was taken until the bed weight increased to 6.0 kg. The bed was completely withdrawn at 3- to 4-hr intervals to permit material balances on the individual particle size fractions. Total run time was 19 hr.

The UF_6 feed rate was held to 20 g/min during the first 11 hr of the run and was then increased to 25 g/min for the remaining 8 hr of the run. The superficial velocity of the gas in the column (exclusive of nitrogen purges and UF_6 flow) was increased from 0.50 to 0.75 ft/sec when the UF_6 rate was increased. During one 4-hr portion of the run, hydrogen alone was fed during the UF_6 feed period to determine the effect of this change in procedure on particle size distribution.

The product contained a high proportion (over 50%) of dense UO_2 particles in the desired size range, -140 +170 mesh (88 to 105μ). The density of the product was 9.8 g/cc, the highest value achieved to date at $650^\circ C$. Particle growth occurred (no seed particles were fed), although the formation of -325 mesh fines in varying amounts (2.7 to 13% of the UF_6 fed) was also noted. The particles were smooth but angular in shape similar to the starting bed material which had been prepared by grinding. Extending the period of operation would have allowed time for the application of a thicker coating on the particles and would have resulted in a more spherical product.

The material balances on the individual particle size fractions indicated that essentially no fines (-325 mesh particles) were formed during the portion of the run in which only hydrogen was fed with the UF_6 . A basis for this effect may be in the high activation energy requirements of the UF_6 -hydrogen reaction, which may allow reaction on a hot particle surface, but not in the gas phase. These data suggest that the generation of fine particles for the purpose of offsetting particle growth might be controlled by adjusting the amount of steam fed with the UF_6 .

Future Work

Design of a 2-in. dia. unit for the production of dense UO_2 - PuO_2 particles from mixed hexafluoride feeds is in progress. Feed for this unit will be obtained from the processing of the low-enriched uranium dioxide fuels. Additional studies will be carried out in the 3-in. dia. column on UF_6 only to provide such data as may be needed to facilitate the operation of the new unit.

III. HIGH TEMPERATURE FUELS AND MATERIALS DEVELOPMENT*

(R. K. Edwards)

A program directed toward the development of high temperature nuclear reactor fuels and materials is under way. The general area of study is concerned with the chemical stability and chemical reactions of potential fuels (such as oxides, phosphides, sulfides, arsenides, and nitrides of uranium and some of their solid solution alloys) with their possible reactor environments (such as hydrogen and possible contaminating gases) and supporting refractory components (such as tungsten, rhenium, molybdenum, tantalum and certain of their alloys).

The objective is to build up a reservoir of basic data from which needed information for evaluation may be drawn. The approach is to study the relevant chemical systems in a quantitative manner so as to obtain thermodynamic evaluations. Each selected fuel-refractory metal-gas system is to be studied in an integrated way, using several primary methods of high temperature investigations that are mutually supporting.

Program planning was initiated in March 1963, and the main efforts to date have been devoted to the planning, acquisition, installation, and adaptation of equipment for the projected measurements. Studies of the vapor-condensed state equilibria in the uranium-uranium dioxide system are in progress.

A. Estimation of the Nature of the High Temperature Phase Relations in the Uranium-Uranium Dioxide-Hydrogen System

From the data in the literature on uranium-uranium dioxide studies, the schematic representations in Figures III-1 and III-2 for two isothermal cross-sections are considered probable in form and useful for discussion and research planning purposes. The pressure-composition phase diagram at 1627°C, shown in Fig. III-1, is based primarily on a similar figure given by Ackermann and Thorn,¹ but Fig. III-1 also incorporates the concept of the probable existence of a substoichiometric range^{2,3} for uranium dioxide. Except for the points, a, d, and g, none of the phase boundaries have been

* A summary of this section is given on page 35.

¹ Thermodynamics of Nuclear Materials, Proceedings of the Symposium on Thermodynamics of Nuclear Materials, International Atomic Energy Agency, Vienna, May 1962, pp. 445-464.

² Rand, M.H. and Kubaschewski, O., The Thermochemical Properties of Uranium Compounds, Interscience Publishers, New York, 1963, p. 29.

³ Aitken, E.A., Brassfield, H.C. and McGurty, J.A., Transactions of the American Nuclear Society, June 1963, p. 153.

Figure III-1

SCHEMATIC DIAGRAM
FOR THE URANIUM-URANIUM
DIOXIDE SYSTEM AT 1627°C

(Only the points a, d and g can
be considered reliable.)

(Uranium dioxide is assumed to vary
in stoichiometry by $\pm x$.)

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Figure III-2

SCHEMATIC SPECULATIVE
DIAGRAM FOR THE
URANIUM-URANIUM
DIOXIDE SYSTEM AT 2400°C

(Points a, d and g are based on
reasonable extrapolations.)

(Uranium dioxide is assumed to
vary in stoichiometry by $\pm x$.)

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established. The pressure-composition phase diagram at 2400°C, shown in Fig. III-2, is speculative and is based on extrapolation of literature data¹ and discussions with Ackermann and Thorn⁴, particularly on the congruency of vaporization of uranium dioxide. The work of Ackermann, Gilles, and Thorn⁵ established that the vaporization of uranium dioxide at temperatures to 2200°C from effusion cells to vacuum yielded stoichiometric uranium dioxide residues within the cell. A few recent unpublished measurements⁴ show that this behavior prevails to 2400°C. Thus, the positioning of the points, g, in the two figures is considered reliable with regard to composition, although conflicting information² exists. The points a and d at 2400°C are reasonable estimates. The existence of hyperstoichiometric uranium dioxide is well established,⁶ but no reliable information for the phase boundary g-f exists for the temperature range under consideration (1627-2400°C).

It is apparent from Figs. III-1 and -2 that adequate reducing conditions would lead to the reduction of uranium dioxide to form liquid uranium-oxygen solutions. Because of the lack of thermodynamic data and knowledge of the true phase boundaries, the hydrogen pressures required to reach the c-d-e equilibria cannot be accurately calculated. However, if one considers the nonequilibrium situation in which hydrogen is passed over uranium dioxide and the reaction product, water vapor, is swept away, it is apparent that two competing processes would arise. (1) A reduction of the stoichiometric uranium dioxide solid would necessarily be initiated by the hydrogen and the composition of the solid would tend to change in the direction g→j. (2) Normal volatilization of the substoichiometric solid of composition, j, so produced, would tend to change the composition of the solid in the opposite direction j→g. If the first of these two processes is dominating, the reduction of the uranium dioxide along the path g-j-e-d-c could take place and lead to the formation of the liquid uranium-oxygen phase. Experiments by Aitken, Brassfield and McGurty³, in which hydrogen at one atmosphere was flowed slowly over uranium dioxide, demonstrate that reduction as far as an overall oxygen-to-uranium ratio of 1.88 was achieved at 2400°C. Their data suggest that this value is a limiting composition for the conditions of the experiment. They also performed one experiment in which a mixture of uranium and uranium dioxide having an oxygen-to-uranium ratio of 1.75 was made into a pellet. The pellet was subjected to prolonged heat treatment in the same type of flowing hydrogen atmosphere, but at 2600°C; and the final oxygen-to-uranium ratio of this pellet was 1.89. Metallographic examinations of all the

⁴Thorn, R.J. and Ackermann, R.J., Argonne National Laboratory, private communications, November 1963.

⁵Ackermann, R.J. Gilles, P.W. and Thorn, R.J., *J. Chem. Phys.* 25, 1089 (1956).

⁶Rand, M.H. and Kubaschewski, O., The Thermochemical Properties of Uranium Compounds, Interscience Publishers, New York, 1963, p.26.

specimens (cooled from 1500°C in helium to prevent possible hydriding of any free uranium) showed the presence of both uranium metal and uranium dioxide. It is to be assumed that the uranium precipitated out from a substoichiometric solid (such as along 3-j-g of Fig. III-2), yielding essentially stoichiometric² uranium dioxide.

The nature of the diagrams in Figs. III-1 and -2 indicates that any reduction of stoichiometric uranium dioxide leads to higher vapor pressures and greater volatility losses. The use of this material at high temperatures under reducing conditions would require cladding by some refractory material to inhibit volatility losses. Studies of interdiffusion between the fuels of interest and the refractory metals are a part of the program and will have importance with regard to experimentation containers and cladding problems.

B. Experimental Approaches

1. Effusion Vapor Pressure Studies

(M. Chandrasekharaiah, R. Edwards, P. Danielson)

Measurements of the rates of vaporization for substoichiometric uranium dioxide-liquid uranium compositions (c-d-e plateau) will be carried out as a function of temperature in the range 1600 to 2200°C. A Knudsen effusion apparatus will be used in the studies. Similar measurements are to be carried out for a series of compositions along the e-j-g substoichiometric boundary and also along the a-b''-b-c and a-c boundaries of Figs. III-1 and -2, respectively, if a suitable container technique can be devised.

Preparation of tungsten effusion cells is underway. Fabrication of uranium dioxide cups to contain the liquid uranium (to establish c-d-e within the cell) is in progress.

The above described studies are being done in collaboration with R.J. Ackermann and R.J. Thorn of the Chemistry Division using their equipment. Design work is in progress for a suitable experimental apparatus for the Chemical Engineering Division so that additional effusion studies can be carried out.

2. Mass Spectrometric Effusion Studies

(J. Reishus, R. Edwards, P. Danielson)

Mass spectrometric effusion studies paralleling the above described effusion measurements will be made to determine the gas phase boundaries with specific regard to the relative concentrations of the vaporizing gaseous species. In this general method, a Knudsen effusion cell containing the solid under investigation is heated to a high temperature and the effusion gas beam is then ionized by electron bombardment. The relative intensities of the various species in the gas are measured by the mass spectrometer. A second type of cell arrangement is also to be used in these studies. It will have a provision for introduction of gases directly to the cell

through a small tungsten capillary tube. Thus it should be possible to introduce either dry hydrogen or hydrogen-water vapor mixtures to the cell to influence the equilibria within. Initially, studies will be made of the isothermal reductions of uranium dioxide along the g-j-e boundary. The extent of reduction will be controlled by employing fixed gaseous ratios. The equilibrium condition will be identified by the attainment of constant concentrations of the various uranium-oxygen species. The composition of the residual material will be determined by chemical analysis. Thermodynamic evaluations should be possible from the data on the composition of the gas phase. A search for any new uranium-bearing species in the presence of the hydrogen-water vapor mixtures will be made. The existence of species of the type $U_a O_\beta H_\gamma$ (α, β and γ are undetermined integers) is considered possible.

Construction of the two Knudsen cell assemblies (Fig. III-3) is nearly complete. The mass spectrometer (Bendix-Time-of-Flight) has been installed and is functioning satisfactorily.

Figure III-3

BENDIX TIME-OF-FLIGHT MASS SPECTROMETER AND ACCESSORIES FOR HIGH TEMPERATURE KNUDSEN EFFUSION MEASUREMENTS

The effusion stack assembly is shown just as its top is being inserted within the mass spectrometer's port. The effusion cell, which is used to beam the vaporizing species to the ionizing zone of the mass spectrometer, is at the top of the stack surrounded by cylindrical tantalum radiation shields. Radiation shielding disks are visible at both the top and bottom of the effusion cell. Four tungsten posts, two of which are visible, support the top radiation shields. A tungsten filament (not visible) network is used to heat the cell by electron bombardment. The various other components are electrical leads and insulating spacers. Cell temperatures of 2900°C have been achieved.

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3. Transpiration Studies of Vaporization (M. Tetenbaum, C. Clifton)

Extension of the vapor pressure measurements to higher temperatures than those possible in the effusion measurements is to be carried out by use of the transpiration method. In this method, an inert carrier gas is passed slowly over preparations having uranium-oxygen compositions of interest. The transported material is collected through a small sample tube and analyzed. The data can yield equilibrium partial pressures of the various species when thermodynamic data for the species in the gas phase are adequate.

In particular, it is planned to study the volatility transport from uranium dioxide with hydrogen and hydrogen-water mixtures as reactant carrier gases. Alexander and Levy,⁷ in a single transpiration measurement at 1510°C, observed a decidedly enhanced volatility from uranium dioxide when the carrier gas was hydrogen at one atmosphere of pressure. A reduction of uranium dioxide by hydrogen along the path g-j-e would lead to such a result.

The principal equipment for the work should be on hand shortly. Container and sample tubes will be fabricated from tungsten metal. Measurements at temperatures as high as 2800°C are considered feasible.

4. Phase Diagram Studies (A. Martin, L. Yannopoulos, F. Mrazek)

Our knowledge of the uranium-uranium dioxide system is to be augmented by studies in the condensed state by the conventional thermal analysis and metallographic techniques. It is of particular interest to know what happens to the liquidus temperature of the uranium dioxide phase as that phase exceeds the saturation limit with respect to uranium. Some lowering of the liquidus temperature leading to a second liquid of a composition in the d-e range is considered probable. It is even conceivable that the oxygen-rich liquid phase region could penetrate through the c-d-e horizontal boundary presented in Fig. III-2. A search for a three-phase monotectic arrest could clarify this assumption. Duncan and Ferrari⁸, however, report an elevation of the liquidus temperature for the substoichiometric uranium dioxide. Further study is needed to clarify the behavior of the liquidus.

Preceding discussions have purposely neglected the role that a third component (refractory metal container) might play in the experiments. However, uranium liquid is known to dissolve appreciable quantities of the

⁷Alexander, C.A. and Levy, A., BMI-1546, p. L-26.

⁸Duncan, R.N. and Ferrari, H.M., Transactions of the American Nuclear Society, June 1963, p. 154.

most promising metals (those having the highest melting points and the lowest solubility for uranium), such as tungsten and tantalum. It is evident then that studies involving the presence of the liquid uranium phase must involve also the refractory metal container as a component. It is also evident that, if the assumption of the paragraph immediately above is correct, the additional refractory metal will interact with the uranium-uranium dioxide system whenever a liquid uranium phase is present and hence the ternary system requires consideration. Tungsten metal is to be used as the container material in most of the initial experimentation.

Prior to the initiation of the work with uranium dioxide, some exploratory experimentation was carried out with uranium monosulfide. Metal-uranium monosulfide mixtures were melted together by use of arc melting equipment. The metals used were tantalum, niobium, vanadium, tungsten, molybdenum, chromium, and rhenium. The low melting metals, chromium, vanadium, and niobium, were included because of generic relations to other metals in their respective columns in the periodic chart. Metallographic examinations of each of the quenched uranium monosulfide-metal melts revealed that two immiscible liquids (a metal-rich liquid and a uranium sulfide-rich liquid) had formed at the temperature of the arc melting. On freezing, each of the systems formed principally a uranium monosulfide phase and a metal phase. One or more additional phases were also formed. Results of X-ray diffraction examinations indicated that uranium sesquisulfide was the principal additional phase. The formation of uranium sesquisulfide is not expressible in terms of a simple binary phase diagram between the refractory metal and uranium monosulfide. A third component would be required to express the general phase relations. Thus, the interaction of uranium monosulfide with the refractory metals under consideration appears, from the exploratory arc melting experiments, to require studies in selected regions of the ternary systems, uranium-sulfur-refractory metal. Quantitative experimentation for those systems involving the most refractory metals is projected for some future date, dependent upon the progress of the uranium dioxide work described above.

High temperature vacuum furnace equipment is being assembled so that well defined conditions of heat treatment can be obtained for the general phase diagram studies. Equipment for other study techniques, such as differential thermal analysis, will be set up as time permits.

5. Interdiffusion Studies

(L. Yannopoulos, A. Martin, F. Mrazek)

Interdiffusion studies of the refractory metals and the refractory fuel materials are planned. The rate of diffusion of a high temperature fuel through potential refractory metal claddings is of obvious importance. Moreover, effective experimentation in the several studies discussed above requires knowledge of diffusion limitations, since the same refractory metals are being considered for use as container materials.

A preliminary experiment is being planned in which uranium monosulfide will be sealed (by electron beam welding) within a tungsten crucible, which will be held for an hour at a temperature slightly above the melting point of uranium monosulfide. Weight losses, if any, will be measured. Metallographic analysis will be carried out to assess the relative importance of attack at tungsten grain boundaries versus bulk diffusion. Studies of single crystals of tungsten, after controlled heat treatments in molten uranium monosulfide, are projected. Electron probe microanalyses will be carried out to determine the concentration gradients if they are in the measurable range.

A vacuum induction furnace is being assembled for the general interdiffusion studies.

IV. CALORIMETRY*

(W. N. Hubbard, H.M. Feder)

For many compounds of interest in high temperature chemistry, thermodynamic data are inaccurate or completely lacking. For some of the compounds, the reason for this has been the experimental difficulties involved in making the necessary measurements. For other compounds, the reason has been the difficulty in obtaining a well-characterized sample. A program has been undertaken here to determine some of the needed data. Emphasis has been placed both on the procurement of well-characterized samples and the development of adequate experimental techniques for the measurements.

The basic data needed are enthalpies of formation at 25°C. Part of the program of the group consists of determination of these enthalpies by the method of oxygen bomb calorimetry. However, many of the compounds of interest are difficult to burn in oxygen and, consequently, cannot be studied by oxygen bomb calorimetry. To study the compounds that are not amenable to oxygen bomb calorimetry, the techniques of the bomb calorimetric method (a method which has been developed to a high degree of precision and accuracy) have been modified so that fluorine can be used as the oxidant.

The accumulation of basic enthalpy of formation data for fluorides is a necessary preliminary adjunct to the general use of fluorine bomb calorimetry for the study of compounds and is a valuable program on its own merit. To date, enthalpy of formation values have been determined for the following fluorides: the difluorides of cadmium, magnesium, and zinc; the trifluorides of boron and aluminum; the tetrafluorides of titanium, zirconium, hafnium, and silicon; the pentafluorides of niobium, tantalum, and ruthenium; and the hexafluorides of molybdenum and uranium. The enthalpies of formation of several compounds, boron nitride, silicon dioxide, and the diborides of zirconium and niobium, have also been determined by fluorine bomb calorimetry.

To determine thermodynamic properties at high temperatures, the enthalpies of formation at 25°C from oxygen or fluorine bomb calorimetry will be combined with the high temperature enthalpy values measured by a drop calorimeter. A drop calorimeter system for making enthalpy increment measurements up to 1500°C has been designed and is being constructed and tested. Testing has shown where various improvements could be made.

A part of the drop calorimeter program has been the testing of design concepts for a drop calorimeter for making enthalpy increment measurements up to 2500°C. The use of electron bombardment heating for the furnace has been tested. The electronic components for the electron guns are on hand and a design of the complete calorimeter has been drawn.

* A summary of this section is given on page 36.

Table IV-1

RESULTS OF NIOBIUM COMBUSTIONS IN FLUORINE

Combustion No.	1	2	3	4	5	6
Mass, g	1.05270	1.05769	1.04740	1.04976	1.04358	1.04506
Δt_c , deg	1.36953	1.37599	1.36254	1.36601	1.35739	1.35935
ϵ (calor.) $(-\Delta t_c)$, cal	-4884.07	-4907.11	-4859.14	-4871.52	-4840.78	-4847.78
$\Delta E_{\text{contents}}$, cal	-9.81	-9.88	-9.81	-9.82	-9.75	-9.81
$\Delta E_{\text{ignition}}$, cal	0.52	0.66	0.73	0.79	0.98	0.76
ΔE_{gas} , cal	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10
$\Delta E_{\text{prefluorination}}$, cal	-1.9	-1.9	-1.9	-1.9	-1.9	-1.9
$\Delta E_{\text{impurities}}$, cal	-0.53	-0.53	-0.52	-0.52	-0.52	-0.52
$\Delta E_c^\circ/M$, cal g ⁻¹	-4650.79	-4650.57	-4650.31	-4651.60	-4649.45	-4649.83

Mean $\Delta E_c^\circ/M = -4650.4$ cal g⁻¹

Std. Dev. of Mean = ± 0.3 cal g⁻¹ or 0.007%

Table IV-2

RESULTS OF TANTALUM COMBUSTIONS IN FLUORINE

Combustion No.	8	9	11	12	13	14	15
Mass, g	2.72870	2.74600	2.72486	2.72652	2.72309	2.67219	2.73363
Δt_c , deg.	1.91390	1.92466	1.91106	1.91167	1.90853	1.87522	1.91716
ϵ (calor.) $(-\Delta t_c)$, cal	-6825.43	-6863.80	-6815.30	-6817.47	-6806.28	-6687.48	-6837.05
$\Delta E_{\text{contents}}$, cal ^a	-13.91	-13.97	-13.91	-13.90	-13.88	-13.59	-13.80
$\Delta E_{\text{ignition}}$, cal	1.02	0.58	0.58	0.52	0.77	0.79	0.58
ΔE_{gas} , cal	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18
$\Delta E_{\text{prefluorination}}$, cal	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0	-2.0
$\Delta E_{\text{impurities}}$, cal	-1.09	-1.10	-1.09	-1.09	-1.09	-1.07	-1.09
$\Delta E_c^\circ/M$, cal g ⁻¹	-2507.27	-2505.63	-2507.25	-2506.54	-2505.48	-2508.63	-2507.14

Mean $\Delta E_c^\circ/M = -2506.9$ cal g⁻¹

Std. Dev. of Mean = ± 0.4 or 0.01%

$$^a \Delta E_{\text{contents}} = \epsilon^i(\text{cont.}) (t_i - 25^\circ\text{C}) + \epsilon^f(\text{cont.}) (25^\circ\text{C} - t_f + \Delta t_{\text{corr.}})$$

A. Combustion of Niobium, Tantalum, and Ruthenium in Fluorine
(E. Greenberg, H.A. Porte, C.A. Natke)

Preliminary data for combustions of niobium and tantalum in fluorine (ANL-6687, p. 156) and more complete data for combustions of ruthenium in fluorine (ANL-6687, p. 159) have been reported. Standard state calculations have now been completed for these combustions. The results are summarized in Tables IV-1, IV-2, and IV-3. The data are subject to checking and revision. Derived data are presented for the enthalpies of formation of the three pentafluorides at 25°C. Because of improved experimental technique, the tantalum results reported herein are much more precise than the results of an earlier series (ANL-6687, p. 157) which are not being included in the final tabulation.

The entries in the table are defined as follows:

The mass of sample burned was determined by subtracting the mass of unburned metal recovered after combustion from the mass of metal initially charged to the bomb.

Δt_c is the observed increase in the calorimeter temperature, corrected for heat exchanged between the calorimeter and its surroundings.

ϵ (calor.) $(-\Delta t_c)$ is the energy equivalent of the calorimetric system minus the contents of the bomb, multiplied by the negative of the corrected temperature rise $(-\Delta t_c)$.

$\Delta E_{\text{contents}}$ represents the energy equivalents of the initial and final contents of the bomb, each multiplied by its appropriate portion of $-\Delta t_c$ to correct to the hypothetical isothermal process at 25°C.

$\Delta E_{\text{ignition}}$ is the electrical energy input for ignition of the fuse, measured with an integrating circuit.

ΔE_{gas} is the net correction for reducing the pressure of the bomb gas to standard state conditions.

ΔE_{fuse} is the correction in Table IV-3 for the energy supplied by combustion of the molybdenum fuse wire (which was used because of the unavailability of ruthenium wire). In the niobium and tantalum experiments, niobium and tantalum fuse wires were used; they were considered to be part of the samples and, therefore, no corrections for the wires were necessary.

$\Delta E_{\text{prefluorination}}$ is the correction in Tables IV-1 and IV-2 for fluorination of the sample prior to intentional ignition. Prior to the calorimetric experiments, trial exposures of weighed samples to fluorine indicated a definite spontaneous surface reaction in the case of niobium and tantalum. Therefore, in carrying out the calorimetric experiments, a special effort

Table IV-3

RESULTS OF RUTHENIUM COMBUSTIONS IN FLUORINE

<u>Combustion No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>7</u>	<u>8</u>
Mass, g	2.21296	2.36564	2.30691	2.63440	2.24632	2.27025
Δt_c , deg	1.31456	1.39981	1.36703	1.56054	1.32878	1.34577
$c(\text{calor.})(-\Delta t_c)$, cal	-4660.27	-4962.49	-4846.28	-5532.30	-4710.68	-4770.92
$\Delta E_{\text{contents}}$, cal	-11.35	-12.31	-11.98	-13.76	-11.66	-11.80
$\Delta E_{\text{ignition}}$, cal	1.09	0.82	1.09	0.94	0.97	0.88
ΔE_{gas} , cal	-0.42	-0.59	-0.59	-0.60	-0.59	-0.58
ΔE_{fuse} , cal	14.35	15.86	15.32	17.56	16.29	14.82
$\Delta E_{\text{impurities}}$, cal	4.51	4.83	4.71	5.37	4.58	4.63
$\Delta E_c^\circ/M$, cal g ⁻¹	-2102.20	-2094.10	-2097.06	-2096.41	-2092.80	-2097.99

Mean $\Delta E_c^\circ/M = -2096.8 \text{ cal g}^{-1}$

Std. Dev. of Mean = $\pm 1.5 \text{ cal g}^{-1}$ or 0.07%

was made to have the same elapsed time (between first filling the bomb with fluorine and initiating the combustion reaction in the calorimeter) for each run. At the conclusion of the calorimetric combustions, a series of blank experiments was run with each metal in which typical weighed samples were loaded and treated in a manner identical to the procedure employed for the calorimetric runs. After exposure to fluorine for the appropriate time interval, the bomb was evacuated and flushed with argon, and the sample was recovered and reweighed. Because of the interfering effects of moisture, the bomb was unloaded and the sample reweighed in an inert atmosphere glovebox. From the gain in weight of the sample, a thermal correction was applied for the prefluorination of the sample. Weighed samples of ruthenium showed no evidence of spontaneous reaction, and no correction was necessary.

$\Delta E_{\text{impurities}}$ is the net correction for fluorination of the impurities in the sample. The samples were analyzed for carbon, oxygen, hydrogen, and nitrogen, as well as for metallic impurities. To some extent the corrections cancel each other, leaving a relatively small net correction.

$\Delta E_c^\circ/M$ is the energy evolved per gram of metal burned. As can be seen from the data, nearly all of the measured energy is due to the heat of formation of the pentafluoride.

The precision shown for these combustions is typical of that obtained for the combustion of inorganic substances in either oxygen or fluorine. The standard deviation of the calibration experiments with benzoic acid varied from one-half to one-fifth that obtained for fluorine combustions.

The "uncertainty interval", equal to twice the combined standard deviations arising from known sources, is of the order of a few tenths of a kcal. mole⁻¹ in each case. For the niobium and tantalum measurements, this uncertainty is due primarily to the corrections for impurities and prefluorination of the sample. In the case of ruthenium, the largest uncertainty is the standard deviation of the calorimetric combustions, but this, in turn, is due largely to the difficulty in recovering the unburned metal to determine the mass of sample burned in the combustion experiment. This latter uncertainty is comparable to the uncertainty in the impurity corrections. As is usually the case in combustion calorimetry of inorganic substances, the actual calorimetric measurements can be carried out more precisely than one can define the combustion process.

Derived data for the formation of the pentafluorides from the respective elements at 25°C are summarized in Table IV-4. No Gibbs energy values are given for TaF₅ or RuF₅ because of the unavailability of entropy values at 25°C for these substances.

Table IV-4
DERIVED DATA^a FOR THE PENTAFLUORIDES
OF NIOBIUM, TANTALUM, and RUTHENIUM
(kcal mole⁻¹)

	<u>NbF₅</u>	<u>TaF₅</u>	<u>RuF₅</u>
Energy of formation, ΔE _f [°] = ΔE _c	-432.1	-453.6	-211.9
Enthalpy of formation, ΔH _f [°]	-433.5	-455.1	-213.4
Gibbs energy of formation, ΔG _f [°]	-406.2		

^aAt 25°C.

Comparison of the values of the heats of formation of the pentafluorides obtained in these experiments with literature values is not possible except in the case of niobium pentafluoride. No measurements or reliable estimates of the heat of formation are reported in the literature for either tantalum pentafluoride or ruthenium pentafluoride. However, Myers and Brady¹ have reported data for niobium pentafluoride. They carried out three different heat of solution measurements, with each of the thermochemical cycles involving estimation of unknown auxiliary data. The result of each cycle had an uncertainty of about 8 to 10 kcal mole⁻¹. The average value of the three results is -432 kcal mole⁻¹ which, considering the uncertainties involved, is in fortuitous agreement with the present measurements.

B. Combustion of Zirconium Diboride in Fluorine
(G. K. Johnson, E. Greenberg)

As part of a continuing program to determine the heats of formation of refractory substances by fluorine bomb calorimetry, zirconium diboride is being studied. An initial series of calorimetric combustions of zirconium diboride in fluorine was reported in ANL-6648, p. 181. Data are presented for an additional series of combustions, together with revised data for the earlier combustions. For both series the techniques described in ANL-6596, p. 173 were used.

As indicated in ANL-6648, the data presented previously were of a preliminary nature and did not include some of the standard state corrections which have since been calculated. One of these corrections arises from the free expansion of fluorine and the reaction of fluorine with the bomb walls when fluorine is expanded into the combustion bomb during the calorimetric experiment. The thermal correction for these two effects was determined by blank experiments in which fluorine was allowed to expand into an evacuated bomb.

The results of the new combustions are tabulated in Tables IV-5 and IV-6 together with revised data for the previously completed combustions. Results of Runs 1 and 5, reported previously, have been discarded because of the unusually severe attack on the zirconium support disc.

The entries in the tables are similar to those described for Tables IV-1, IV-2, and IV-3 with the following additions: ΔE_{sulfur} is the energy supplied by the combustion of the sulfur used to insure reproducible spontaneous ignition of the sample. The current value for this correction reflects a revision of the data previously presented (ANL-6648). $\Delta E_{\text{Zr disc}}$ represents the thermal correction for the loss in weight suffered by the zirconium support disc. ΔE_{blank} is the thermal correction for the reactions occurring when fluorine is admitted to the bomb.

¹Myers, O.E. and Brady, A.P., J. Phys. Chem. 64, 591 (1960).

Table IV-5
ZIRCONIUM DIBORIDE IN FLUORINE
RESULTS OF "A" SERIES COMBUSTIONS

	Run 3	Run 4	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12
Mass, g	0.63672	0.63609	0.63614	0.63953	0.63570	0.63469	0.62537	0.62837	0.62271
Δt_c , deg	1.65999	1.65660	1.66982	1.66864	1.65463	1.65504	1.64594	1.65715	1.64778
ϵ (calor.) $(-\Delta t_c)$, cal	-5629.82	-5618.33	-5663.16	-5659.16	-5611.64	-5613.04	-5529.95	-5567.61	-5536.13
$\Delta E_{\text{contents}}$, cal	-10.45	-10.54	-10.63	-10.49	-10.54	-10.39	-10.41	-10.59	-10.41
ΔE_{sulfur} , cal	446.64	455.46	497.12	453.12	442.86	453.75	440.79	471.39	475.44
$\Delta E_{\text{Zr disc}}$, cal	7.64	8.14	3.55	20.73	5.44	22.23	28.52	4.60	23.08
ΔE_{gas} , cal	-1.59	-1.59	-1.61	-1.60	-1.60	-1.59	-1.54	-1.49	-1.52
ΔE_{blank} , cal	15.54	15.54	15.54	15.54	15.54	15.54	7.98	7.98	7.98
$\Delta E_{\text{impurities}}$, cal	-10.33	-10.32	-10.32	-10.38	-10.32	-10.30	-10.15	-10.20	-10.11
$\Delta E_c^\circ/M$, cal g ⁻¹	-8139.21	-8114.63	-8126.39	-8118.84	-8133.19	-8104.40	-8114.82	-8125.69	-8112.39

Mean $\Delta E_c^\circ/M = -8121.1$ cal g⁻¹

Std. Dev. of Mean = ± 3.7 cal g⁻¹ or 0.045%

Table IV-6
ZIRCONIUM DIBORIDE IN FLUORINE
RESULTS OF "B" SERIES COMBUSTIONS

	Run B-1	Run B-2	Run B-3	Run B-4	Run B-5	Run B-6	Run B-7
Mass, g	0.72710	0.74806	0.75153	0.76394	0.39717	0.40029	0.39554
Δt_c , deg	1.86533	1.92336	1.92239	1.95920	1.07607	1.07838	1.06353
ϵ (calor.) $(-\Delta t_c)$, cal	-6267.04	-6462.01	-6458.75	-6582.42	-3615.33	-3623.09	-3573.19
$\Delta E_{\text{contents}}$, cal	-11.97	-12.18	-12.32	-12.40	-6.85	-6.78	-6.78
ΔE_{sulfur} , cal	367.91	387.26	350.28	384.83	384.02	366.92	354.87
$\Delta E_{\text{Zr disc}}$, cal	1.35	2.05	0.30	0.10	0.95	1.90	0.65
ΔE_{gas} , cal	-1.60	-1.58	-1.57	-1.57	-1.55	-1.54	-1.54
ΔE_{blank} , cal	7.98	7.98	7.98	7.98	7.98	7.98	7.98
$\Delta E_{\text{impurities}}$, cal	-24.74	-25.46	-25.57	-26.00	-13.52	-13.62	-13.46
$\Delta E_c^\circ/M$, cal g ⁻¹	-8153.05	-8159.68	-8169.58	-8154.38	-8168.57	-8164.66	-8169.81

Mean $\Delta E_c^\circ/M = -8162.8$ cal g⁻¹

Std. Dev. of Mean = ± 2.7 cal g⁻¹ or 0.033%

Table IV-5 represents the combustions with the original sample of zirconium diboride. The first six combustions in the table were reported previously in ANL-6648. The last three were completed more recently under conditions in which the value for the blank reaction was considered to be well known. The mean of the first six runs is approximately 5 cal g⁻¹ more negative than the last three. However, the spread in values of $\Delta E_c^\circ/M$ for the first six combustions completely overlaps the values obtained in the three latter experiments.

Table IV-6 summarizes the results of seven combustions with the new sample of zirconium diboride. The mean energy of combustion ($\Delta E_c^\circ/M$) of this series is 40 cal g⁻¹ more negative than that of the "A" series. The combustion results for the two series and the analytical data for the two samples are still being evaluated.

C: Combustion of Niobium Diboride in Fluorine
(G.K. Johnson, E. Greenberg)

The combustion of niobium diboride in fluorine is part of a continuing program to determine the heats of formation of the diborides of titanium, zirconium, hafnium, niobium, and tantalum, for which precise heat of formation values are not available. Seven combustions of niobium diboride in fluorine have been completed, using the technique previously described for zirconium diboride.

Table IV-7 summarizes the preliminary results obtained for this series of niobium diboride combustions. The entries in the table are similar to those described for Tables IV-5 and IV-6. However, since these are preliminary data, some of the standard state corrections have not yet been tabulated and included in the table.

Table IV-7

PRELIMINARY RESULTS OF NIOBIUM DIBORIDE COMBUSTIONS IN FLUORINE

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>	<u>Run 5</u>	<u>Run 6</u>	<u>Run 7</u>
Mass g	0.75057	0.73754	0.75212	0.73775	0.74794	0.40186	0.40859
Δt_c , deg	1.89009	1.87584	1.91054	1.87902	1.90729	1.08746	1.10411
ϵ (calor.) $(-\Delta t_c)$, cal	-6344.46	-6302.45	-6419.03	-6313.13	-6408.11	-3653.65	-3709.59
ΔE_{sulfur} , cal	466.89	546.43	554.88	560.73	560.64	515.02	517.63
$\Delta E_{\text{Zr disc}}$, cal	56.59	8.59	50.10	6.59	27.77	8.09	11.14
ΔE_{blank} , cal	13.38	7.98	7.98	7.98	7.98	7.98	7.98
$\Delta E_c^\circ/M$ (sample), cal g ⁻¹	-7737.59	-7781.88	-7719.61	-7777.47	-7770.40	-7770.26	-7765.34

Mean $\Delta E_c^\circ/M$ (sample) = -7760.4 cal g⁻¹

Runs 1 and 3, which show the greatest deviation from the mean, are also the runs in which the zirconium support disc suffered the greatest attack. This suggested the possibility of some unknown side reaction involving zirconium. An attempt was made to burn niobium diboride on a niobium disc. This was unsuccessful because of ignition of the niobium disc.

No further calorimetric combustions are planned at the present time. Additional analytical work is in progress to better characterize the sample used in order to make the standard state calculations as accurate as possible.

D. Combustion of Silicon Carbide in Fluorine
(E. Greenberg, C. Natke)

Discrepancies between literature values for the heat of formation of silicon carbide, recently pointed out by Chipman,² may be resolved by determining the heat of combustion of silicon carbide in fluorine since the heat of formation of silicon tetrafluoride has already been determined and the heat of formation of tetrafluoromethane is currently under study. Preliminary noncalorimetric experiments, directed at establishing a combustion technique for silicon carbide, were discussed in the previous quarterly (ANL-6687, p. 161). Continuation of these experiments led to the development of a combustion technique in which a 1/2-g sample of powdered silicon carbide (100-200 mesh) is burned on a 1/32-in. thick x 2-in. dia. nickel dish. For these experiments, the bomb is charged with 15 atm of fluorine. A short length of molybdenum fuse wire, placed directly over the silicon carbide, is used for ignition of the sample. The sample is confined to the center of the dish by means of a heavy-walled 3/4-in. dia. ring which is part of the dish. With this arrangement, approximately 95% of the sample is burned. The unburned portion is recovered and weighed after the combustion. Approximately 7.5 kcal is evolved in these combustions. Fluorination of the nickel dish appears to decrease with successive combustions and is of the order of a few tenths of a milligram.

In addition to CF_4 , which is the main fluorocarbon formed, several tenths of one percent of higher fluorocarbons (C_2F_6 , C_3F_8) are also formed. These side products are determined quantitatively by a gas chromatographic method.* All of the silicon appears to burn to SiF_4 , with no higher homologs being detected by mass spectrometry.

Three calorimetric combustions of silicon carbide in fluorine have been carried out using the technique described above. Additional combustion experiments are to be performed shortly.

²Chipman, J., J. Am. Chem. Soc. 83, 1762 (1961).

* Chemical Research Services, Inc., Addison, Illinois

E. Combustion of Carbon in Fluorine
(E. Greenberg, C. Natke)

Literature values for the heat of formation of tetrafluoromethane vary over a range of several kilocalories. Resolution of this discrepancy is being attempted. Preliminary noncalorimetric combustion experiments in which carbon was reacted with fluorine have been carried out in order to develop a suitable combustion technique. Initially, attempts were made to burn either graphite or diamond powder on a graphite disc. This system was unsatisfactory because ignition of the graphite disc usually occurred. Experiments were then tried with graphite rods in an attempt to work out a technique similar to that described for zirconium³ in which the graphite rod would serve as its own support. Successful ignitions could be achieved, but these combustions usually resulted in the formation of small amounts of incompletely fluorinated solid combustion products.

While combustion techniques for carbon were being sought, a suitable combustion technique for combustion of powdered silicon carbide on a nickel dish was developed, and it appeared that this same technique would also be satisfactory for combustion of carbon in fluorine to form tetrafluoromethane. Very favorable combustion reactions were obtained when this technique was used to burn about 0.4 g of graphite in 15 atm of fluorine. Gas chromatographic analysis of the combustion products in one of these test experiments was unable to detect any fluorocarbons other than CF_4 . About 95% of the sample was burned, and there did not appear to be any partially fluorinated solid combustion products. This combustion technique is the most successful approach tried so far and will probably be used for the calorimetric experiments.

Regardless of the form of graphite used (rods, powder, etc.), there is a substantial spontaneous weight gain when graphite is exposed to fluorine. The reaction apparently involves the addition of fluorine between the layers of graphite. Because of this spontaneous reaction, it will be necessary to keep the graphite and fluorine separated until it is desired to make the actual calorimetric measurements. The apparatus⁴ previously developed for combustion of spontaneously reacting substances is not well suited for achieving the desired 15-atm pressure in the combustion bomb. A new system utilizing the same principle is being designed for use with fluorine pressures of up to 25 atmospheres. An alternative approach also being investigated is the use of diamond powder instead of graphite for these combustions.

F. Combustion of Thorium in Fluorine
(E. Rudzitis)

Thorium and some of its compounds are of considerable importance in nuclear technology. Because most of the thorium compounds of interest

³Greenberg, E., Settle, J.L., Feder, H.M. and Hubbard, W.N., J. Phys. Chem., 65, 1168 (1961).

⁴Nuttall, R.L., Wise, S. S. and Hubbard, W. N., Rev. Sci. Instr., 32, 1402 (1961).

(borides, carbides and the like) are refractory in nature, fluorine combustion calorimetry appears to be the most promising method for the determination of their enthalpies of formation.

Knowledge of the enthalpy of formation of thorium tetrafluoride is a prerequisite to the determination of the enthalpy of formation of other thorium compounds by fluorine bomb calorimetry. Besides an early estimate by Brewer et al.⁵, the only published value of ΔH_f° (ThF_4) has been derived from equilibrium studies⁶ of the system: $\text{ThO}_2 + \text{SiF}_4 = \text{ThF}_4 + \text{SiO}_2$ at 627 and 727°C. Recalculation by the third law method and use of the recently obtained ΔH_f° values for SiF_4 ⁷ and SiO_2 ⁷ yielded ΔH_f° (ThF_4) = -500.0 ± 0.6 kcal mole⁻¹.

Values of the free energy function of ThF_4 , for which no high-temperature heat content data are available, were estimated by combining low-temperature heat capacity data of ThF_4 ⁸ with $H_T^\circ - H_{298}^\circ$ and $S_T^\circ - S_{298}^\circ$ data for UF_4 .⁹ Both ThF_4 and UF_4 are isostructural, and lattice dimensions of ThF_4 are about 2.5% larger than those of UF_4 . In view of the small relative differences in lattices and masses, it seems reasonable to assume that the heat capacities are also nearly equal.

Unpublished data of emf measurements on the systems: Mg , MgF_2 / CaF_2 / ThF_4 , Th and Al , AlF_3 / CaF_2 / ThF_4 Th at 527°C have been kindly made available by Dr. James J. Egan of Brookhaven National Laboratory. Third law calculations and the use of ΔH_f° (MgF_2) = -266.0 ± 0.5 and ΔH_f° (AlF_3) = -358.0 ± 0.5 ¹⁰ kcal mole⁻¹ yielded ΔH_f° (ThF_4) = -295.4 ± 1.4 and -497.4 ± 0.8 kcal mole⁻¹, respectively. These values compare with -500.0 ± 0.6 kcal mole⁻¹ calculated from the work of Darnell and -477 ± 10 kcal mole⁻¹ estimated by Brewer et al.⁵ Because of the existing uncertainty in values of the enthalpy of formation of ThF_4 , an attempt will be made to obtain the value calorimetrically by combustion of thorium in fluorine.

⁵Brewer, L., Bromlet, L.A., Gilles, P.W. and Lofgren, N.L., Paper 6 "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics" L.L. Quill, editor, McGraw-Hill Book Co., Inc., N.Y. (1950).

⁶Darnell, A.J., J. Inorg. Nucl. Chem. 15, 359 (1960).

⁷Wise, S.S., Margrave, J.L., Feder, H.M. and Hubbard, W.N., J. Phys. Chem., 65, 815 (1963).

⁸Lohr, H.R., Osborne, D.W. and Westrum, Jr., E.F., J. Am. Chem. Soc., 76, 3837 (1959).

⁹King, E.G. and Christensen, A.U., Bureau of Mines Rep. Inv. 5709 (1961).

¹⁰Preferred values based on results obtained at ANL by fluorine bomb calorimetry and evaluation of literature data.

Results of preliminary experiments by E. Greenberg of Argonne National Laboratory indicated that the "supported pin" technique, which has been successfully applied to metals having relatively volatile fluorides (such as ZrF_4 and UF_6), will not be directly applicable to the combustion of thorium owing to the ionic nature (low volatility) of ThF_4 . With this technique, the reaction product, ThF_4 , accumulates on the metal sample with two unfavorable effects: (1) inaccessibility of the metal surfaces to fluorine and (2) poor dissipation of heat, which results in melting of the metal. Both effects contribute to termination of the combustion at an early stage.

In order to achieve better cooling, the sample in the form of a triangle 30 to 50 mils thick was placed in a slit in a massive nickel block. Although a suitable mixture of fluorine and helium (1000 mm F_2 , 2500 mm He) was found in which ignition and burning of thorium occurred without melting the metal sample, a one-gram sample of thorium was only partially consumed, a large portion of the sample remaining unburned owing to the accumulation of molten ThF_4 around the metal. Use of the bomb in the inverted position to allow the molten salt to drop from the sample did not significantly improve the combustion yield. The hardness and adhesivity of the glassy-appearing ThF_4 prevented its mechanical separation from the unburned metal.

Combustion of nearly 100 percent of the thorium is necessary in order to achieve acceptable results, because no satisfactory analytical methods for the determination of unburned thorium are available. In order to obtain the necessary nearly complete combustion, a method was developed which combines the suspended sample and fluoride support techniques.¹¹ The metal sample in the form of a triangle was suspended by a short nickel wire from the top of the bomb. The bottom of the bomb cup was covered with an approximately 1/2-in. thick layer of slightly compacted metal fluoride powder. (Due to unavailability of ThF_4 , AlF_3 powder was used.) The sample was ignited by the usual wire-to-foil technique. Preliminary experiments in which an initial fluorine pressure of 170 psi was used showed that more than 90 percent of the thorium could be burned. It is possible that the combustion yield will improve when ThF_4 is used as the support since this will eliminate the possibility of the formation of a low-melting eutectic of ThF_4 and AlF_3 when the molten ThF_4 falls onto the AlF_3 support.

One of the desirable features of the method is the chance for the metal to get sufficiently hot during the initial stages of the combustion – the period of suspension and fall – to counteract the quenching effect when the sample falls to the support on the bottom of the bomb. It is hoped that the main drawback of the fluoride support technique – side reactions with impurities in the fluoride support – will be overcome by autoclaving the fluoride powder with liquid HF at elevated temperatures, a method which was successful in purifying CdF_2 and ZnF_2 .

¹¹Hubbard, W.N., Chapter 5 Experimental Thermochemistry Vol. II, H.A. Skinner, editor. Interscience Publishers, N.Y. (1962).

G. Thermochemistry of Uranium Compounds
(J. Settle, R. Terry)

This laboratory has undertaken a long-range program for the determination of the standard enthalpy of formation ($\Delta H_f^\circ_{298}$) of selected uranium compounds. There are on hand several compounds which were prepared and analyzed by H. Eding and E. Carr of Stanford Research Institute, Menlo Park, California. Table IV-8 is a listing of those compounds, giving their compositions as estimated from analytical data.

The enthalpy of formation of a compound can be obtained from the enthalpy of combustion of the compound and the enthalpies of combustion of its constituent elements. The following is an example of the method:

Table IV-8
COMPOSITION OF SELECTED URANIUM COMPOUNDS^a

Compound		Composition, w/o							
Nominal	Actual	UA _x	UO	UO ₂	UC	Free C	Al ₂ O ₃	B ₄ C	Other
UAl ₂	UAl _{1.84±0.01}	98.30±0.10	--- ^b	0.93±0.08	0.65±0.06	---	---	---	0.09±0.01
UAl ₃	UAl _{3.09±0.02}	98.82±0.1	---	0.06±0.06	0.65±0.06	---	0.26±0.02	---	0.16±0.03
UAl ₄	UAl _{4.28±0.02}	98.81±0.11	---	0.23±0.10	0.46±0.04	---	0.28±0.02	---	0.09±0.03
UB ₂	UB _{2.21±0.03}	89.40±0.34	---	4.14±0.08	6.25±0.33	---	---	0.09±0.01	0.13±0.02
UB ₄	UB _{4.54±0.04}	91.08±0.34	---	2.20±0.08	6.25±0.33	---	---	0.23±0.02	0.24±0.05
UC	UC _{1.036±0.002}	98.11±0.17	1.79±0.16	0.06±0.03	---	0.03±0.01	---	---	0.01±0.01
UC ₂	UC _{1.948±0.002}	95.87±0.17	3.78±0.16	0.02±0.02	---	0.32±0.02	---	---	0.01±0.01
UN	UN _{0.999±0.002}	98.97±0.16	0.70±0.15	0.08±0.03	0.25±0.04	---	---	---	---
U ₂ N ₃	UN _{1.719±0.002}	99.40±0.09	---	0.51±0.08	0.08±0.02	---	---	---	---
UP	UP _{1.012±0.003}	97.93±0.65	---	1.43±0.08	0.62±0.62	---	---	---	0.01±0.01
US	US _{1.027±0.005}	98.85±0.17	---	0.81±0.12	---	---	---	---	0.34±0.12
US ₂	US _{2.012±0.001}	99.89±0.04	---	0.05±0.02	---	---	---	---	0.06±0.02
USe	USe _{1.047±0.001}	94.52±0.65	---	4.22±0.08	1.25±0.62	---	---	---	0.01±0.01
USi ₂	USi _{1.90±0.01}	99.27±0.11	---	0.29±0.08	0.42±0.08	---	---	---	0.02±0.01
USi ₃	USi _{3.02±0.02}	98.95±0.15	---	0.26±0.08	0.73±0.12	---	---	---	0.06±0.03

^aThe first column gives the nominal formulas. The second column gives the actual formulas as estimated from the analytical data. The rest of the columns list the calculated composition, on a weight percent basis, of the samples. The A_x in the "UA_x" column denotes the stoichiometric proportion of the major constituent other than uranium in each compound. In the "Other" column are grouped the minor metallic impurities as determined by spectrochemical and calorimetric analyses.

^b--- means that no evidence was found for the compound.

Addition of Equations 1 and 2 and subtraction of Equation 3 yields

in which ΔH4 would be the value of the enthalpy of formation of the compound $\text{UB}_2(\text{c})$.

There are errors associated with each heat of reaction. Table IV-9, in which the compounds are listed by their nominal formulas, contains

Table IV-9

ERROR ANALYSIS FOR THE COMBUSTION IN FLUORINE
OF SELECTED URANIUM COMPOUNDS

Compound	Uncertainty Interval, kcal mole ⁻¹					
	Chemical	Calorimetric	$\Delta\text{Hf}^\circ(\text{UF}_6, \text{c})$	$\Delta\text{Hf}^\circ(\text{AF}_x)^a$	Combined	Literature
UAl_2	±1.56	±0.4	±0.43	±1.0	±1.7	±5.0
UAl_3	±1.88	±0.4	±0.43	±1.5	±2.5	±5.0
UAl_4	±3.52	±0.4	±0.43	±2.0	±4.1	±6.0
UB_2	±2.84	±0.4	±0.43	±0.48	±2.9	±3.0
UB_4	±6.24	±0.4	±0.43	±0.96	±6.3	±5.0
UC	±1.46	±0.4	±0.43	±1.0	±1.8	±1.0
UC_2	±2.36	±0.4	±0.43	±2.0	±3.1	±1.4
UN	±0.32	±0.4	±0.43	---	±0.7	±1.0
U_2N_3	±0.28	±0.7	±0.86	---	±1.1	±2.5
UP	±1.26	±0.4	±0.43	±0.38	±1.4	None Available
US	±1.50	±0.4	±0.43	±0.7	±1.7	±5.
US_2	±0.68	±0.4	±0.43	±1.4	±1.6	±10.
USe	±2.90	±0.4	±0.43	±5.0	±5.8	None Available
USi_2	±1.80	±0.4	±0.43	±0.50	±2.0	±0.6
USi_3	±2.94	±0.4	±0.43	±0.75	±3.1	±0.7

^aThe uncertainty interval arising from the value taken for the heat of formation of the fluoride of the major constituent element of the sample other than uranium. As no nitrogen fluoride is formed in the combustion of nitrogen compounds in fluorine, no value is necessary.

information concerning the errors expected if the enthalpies of formation of the compounds are determined by combustion in fluorine. For the purpose of making this error analysis, it is assumed that complete combustion of the compounds will be achieved and that the standard deviation of the mean of the calorimetric measurements will be less than 1 calorie per gram of sample reacted. All entries in the table are in the form of uncertainty intervals, defined¹² as being twice the combined standard deviations arising from known sources. The combined uncertainty interval is the square root of the sum of the squares of each uncertainty interval listed. The chemical error refers to uncertainties in the amounts of impurities, states of combination of impurities, and in the stoichiometry of the samples. The calorimetric error refers to the uncertainties in the calorimetric measurements, uncertainties in the weight of sample reacted, and uncertainties in the determination of the energy equivalent of the calorimetric system. The uncertainties in the enthalpies of formation of UF_6 ¹³, BF_3 ¹⁴, PF_5 ¹⁵, SF_6 ¹⁶, SeF_6 ¹⁷, and SiF_4 ¹⁸ were taken from the literature. The uncertainties in the enthalpies of formation of CF_4 ¹⁹ and AlF_3 ²⁰ were estimated. The last column in Table IV-9 lists the uncertainty intervals available in the literature for the standard enthalpies of formation of the aluminides,²¹ borides,²¹ carbides,^{22,23} nitrides,²¹

¹²Rossini, F.D., Ch. 14 in "Experimental Thermochemistry," F.D. Rossini, Ed., Interscience Publishers, Inc., New York, N.Y., 1956.

¹³Settle, J.L., Feder, H.M., and Hubbard, W.N., J. Phys. Chem., 67, 1892 (1963).

¹⁴Wise, S.S., Margrave, J.L., Feder, H.M., and Hubbard, W.N., ibid. 65, 2157 (1961).

¹⁵Gross, P., Hayman, C., Levi, D.L., and Stuart, M. C., Fulmer Research Institute Report R. 146/4/23, November 1960.

¹⁶Gross, P., Hayman, C. and Levi, D.L., XVIIth International Congress of Pure and Applied Chemistry, Abstracts, 1, 90 (1959).

¹⁷Yost, D.M. and Claussen, W.H., J. Am. Chem. Soc., 55, 885 (1933).

¹⁸Wise, S.S., Margrave, J.L., Feder, H.M. and Hubbard, W.N., J. Phys. Chem., 67, 815 (1963).

¹⁹Greenberg, E., private communication.

²⁰Rudzitis, E., private communication.

²¹Rand, M.H. and Kubaschewski, O., The Thermochemical Properties of Uranium Compounds, Oliver and Boyd, Ltd., London, U.K., 1963.

²²Huber, Jr., E.J., Holley, Jr., C.E. and Meierkord, E.H., J. Am. Chem. Soc., 74, 3406 (1952).

²³Huber, Jr., E.J., Head, Earl L. and Holley, Jr., C.E., J. Phys. Chem., 67, 1730 (1963).

sulfides,^{21,24} and silicides of uranium.²¹ There are no literature values available for the enthalpies of formation of the uranium phosphides and selenides.

The information in Table IV-9 can be regarded as a status report on the project for the preparation of uranium compounds of sufficiently high purity for calorimetric study. The data apply to the best preparations of each compound. Any substantial contribution to the existing body of thermochemical data on uranium compounds is of interest in reactor technology and is the goal of this project. It is apparent from the table that substantial contributions can be made with the present best preparations if satisfactory combustion techniques are developed for the determination of the enthalpies of formation of UP, USe, US, US₂, UAl₂, UAl₃ and, possibly, UAl₄ and U₂N₃. Consideration of the determination of the enthalpies of formation of the borides should be abandoned or further efforts be directed towards the preparation of a better sample. Consideration of the determination of the enthalpies of formation of the silicides falls in nearly the same category as the borides except that the small uncertainty reported in the literature is known to be only a measure of precision with no allowance for impurities being considered. A similar error analysis for the combustion in oxygen of the carbides and nitrides shows that, if the techniques are worked out to the same degree of precision as for the combustions in fluorine, the results of the oxygen bomb calorimetric study will be more accurate.

H. Combustion of Uranium Monosulfide in Fluorine (J. L. Settle)

Of the uranium compounds discussed in the previous section as being worthwhile studying by fluorine bomb calorimetry, the one chosen for first investigation was uranium monosulfide. Uranium monosulfide was chosen in preference to UAl₂ because both of the products of the combustion of uranium monosulfide are gaseous, a simplifying factor, in preference to UP because of the anticipated greater difficulty in burning phosphorous in fluorine than sulfur in fluorine, and in preference to USe because of the availability of a much better sample of uranium monosulfide.

Preliminary studies of the combustion of uranium monosulfide (US) in fluorine indicated that the extent of spontaneous reaction between US and fluorine was so great that the US would have to be protected from exposure to fluorine before intentional ignition. The preliminary studies also indicated that an auxiliary combustible substance significantly promoted the complete combustion of US to UF₆ and SF₆.

Three methods of protection against spontaneous reaction have been investigated and a fourth proposed. Bags made of Teflon FEP (fluorethylene-propylene polymer manufactured by E. I. duPont de Nemours and Co.) were

²⁴Cater, E. D., Gilles, P. W. and Thorn, R. J., J. Chem. Phys. 35, 608 (1961).

tested for their ability to prevent premature ignition of the samples. Sulfur was heat sealed into bags made of thin (0.002 in. thick or less) films of Teflon FLP. The spontaneous ignition of sulfur upon exposure to fluorine provided a test of the effectiveness of the seal. Approximately ninety percent of the bags failed to provide protection at their first exposure to fluorine. The rest of the bags provided protection on their first exposure but failed on their second exposure. It is not certain whether the failures were due to faulty sealing technique, to permeability of the thin films, or to a combination of both. This method of protection has been abandoned for the present.

It was found that fused silica bulbs, about 1 cm in diameter and weighing 0.3 to 0.5 g, will provide protection from fluorine. However, the great rush of fluorine into the bulb upon ignition scatters a powder sample over the inside of the combustion bomb, making impossible the quantitative recovery of unreacted or partially reacted material.

The two-chamber reaction vessel²⁵ for spontaneously combustible materials appears to be the most practical solution to the problem. It is necessary to redesign the vessel so that fluorine pressures of 10-15 atm can be attained in the reaction zone. In the meantime, attention will be shifted to finding the best means of obtaining complete combustion of US to UF_6 and SF_6 .

A fourth possibility is the use of a flow system for the combustion experiments. With such a system, the fluorine is introduced when it is desired to initiate the reaction and no protection of the sample is necessary. The system has the further advantage that near the end of the reaction, additional fluorine may be added to maintain the combustion. In a bomb, combustion might tend to stop as the supply of fluorine diminishes.

I. High Temperature Enthalpy Calorimetry — 1500°C
(D. R. Fredrickson, R. L. Nuttall, J. E. Brugger, A. T. Hu, R. Kleb)

A high precision, vacuum calorimetric system (ANL-6477, p. 164) for measuring changes in enthalpy up to 1500°C is under construction. The calorimeter is of the drop type and consists of a sample drop mechanism and tube that rest on a furnace where the sample is heated, a gate through which the heated sample passes when dropped, and an adiabatic calorimeter.

Copper Block Calorimeter

In view of the pressing need to make the system operational, a copper block calorimeter is being constructed so that preliminary data can

²⁵Nuttall, R. L., Wise, S. and Hubbard, W. N., Rev. Sci. Inst. 32, 1402 (1961).

Figure IV-1

COPPER BLOCK CALORIMETER

be obtained while the adiabatic calorimeter is being assembled and fully tested. The copper block calorimeter is shown in Figure IV-1. The temperature rise will be measured with a platinum resistance thermometer. The copper block is separated from a constant-temperature water bath by a 1-cm air space. This calorimeter may be used with either the 1500°C furnace or the 2500°C furnace. The calorimeter has been assembled and found to be vacuum tight. Associated equipment such as the system for circulating constant-temperature water, heaters for calibration, and the auxiliary equipment for electrical calibration are being assembled.

Furnace

Many requirements must be met in high-precision calorimetry. Two of the most crucial are that the temperature of the sample be known with both precision and accuracy and that the temperature of the sample be uniform. Special consideration was given to these factors in the design of the furnace. The attainment of uniform sample temperature is facilitated by the minimization of thermal gradients in the furnace heating zone. Low power input contributes to the minimization of gradients. At the same time, it is not desirable to use so large a quantity of insulation—thus insuring low equilibrium power input—that heatup time for the furnace is unreasonably long.

In the ANL design, a compromise was reached by building a multi-unit furnace (see ANL-6648, p. 184) and by installing a so-called dust shield, outside the heated furnace core units and inside a series of low thermal capacity radiation shields. The dust shield is equivalent to a number of very closely spaced radiation shields. The shield is formed by filling the annular space between two concentric tantalum cans with fine insulating grain. In the absence of furnace gas, heat transfer from grain to grain is chiefly by radiation, with a small contribution from conduction where the grains touch. Convection and gas conduction are absent. The very great efficiency of the dust shield—the temperature drops from 1350°C to 675°C across 2 cm of Morganite-brand 100 mesh alumina grain—makes it difficult to design a shield that will withstand thermal cycling. Stated simply, if the unit is constructed so sturdily that it does not deform, it is inefficient; if the unit is made of thin material, then the filling dust, during thermal cycling, flows in such a way as to reinforce the stresses set up by expansion of the metal shells, causing the inside wall of the shield to bulge inwards and the outer shell to bow outwards. Secondly, the quantity of dust at the top of the shield decreases and heat transfer through the top increases. These actions undoubtedly contributed to the furnace failure described in ANL-6725, p. 198.

A compromise design for the dust shield is being considered as well as a complete redesign of the entire radiation shield system to replace the dust shield if this is required.

Various dust materials have been tested in the dust shield. For these evaluations, the molybdenum heated core units have been replaced by a single ceramic core unit. In the first set of runs, a platinum wire wound, grooved Alundum core was used; in later sets, tantalum heater wire was cemented in place on a Morganite Triangle RR grade alumina core. Bubbled Alundum grain (Norton type E-163, 8 mesh) and Morganite RR grade 100 mesh alumina have been tested as filling dusts, and work is now under way with Carborundum high-purity silicon carbide (80 and 150 mesh). In all of these tests, the dust shield was surrounded by only 3 radiation shields (molybdenum) instead of by the original 11. In early runs, the cold surfaces of the furnace jacket became coated with a material which analyzed as sodium carbonate (presumably formed by carbon dioxide uptake by caustic soda). The alkali was apparently driven out of the bubbled alumina. Some deposition was also observed in the initial heatups of later runs. The deposit likely came from the furnace cements.

In theory, for a given power input to the core, the temperature of the outside of the dust shield and of the three radiation shields should be the same and independent of the dust material once thermal equilibrium has been attained. The results of tests with the shields do not conform to the theory. The discrepancy arises from at least four possible sources:

- (1) a failure to attain thermal equilibrium,

(2) the emissivities of the various radiating surfaces differed in different runs,

(3) thermal contact between the shields and supports may have changed with time or may have become irreproducible in reassembling the furnace,

(4) thermal contact between the shields and the thermocouples may have changed.

In the last of several heatups with the same filler dust, decreasing efficiency of the dust was generally shown. In all cases, there was a redistribution of dust and, in particular, a loss of dust from the top of the dust shield as a consequence of thermal cycling. For the alumina dusts, some sintering of the grains was observed. For a nominal core temperature of 1000°C, the core power requirements for 8-mesh bubbled Alundum grain, 100-mesh Morganite alumina grain, 80-mesh silicon carbide grain, and 150-mesh silicon carbide grain were, respectively, 375, 158, 263, and 239 watts. In a later heatup with 100-mesh alumina grain, the power requirement rose to 201 watts.

Gate

A control board for the motor-driven calorimeter shutter and the gas pressure-operated furnace gate has been built and tested. The control circuits are interlocked so that a drop cannot be made unless all components are ready. The gate has been installed on the furnace.

Drop Tube

In an enthalpy determination, the capsule containing the sample is brought to temperature equilibrium and then dropped through a cold zone into the calorimeter. It is desirable to minimize the heat loss occurring during the sample drop. In our apparatus, this is done by (1) providing a heated shield that maintains an isothermal zone at the top of the fall path where the capsule falls most slowly and (2) allowing the capsule to fall at an accelerated rate (approximately free fall). The capsule is attached by means of a wire to a drop weight (located in the drop tube which extends vertically above the furnace). The drop weight, held at the top of the drop tube during heatup, falls the length of the drop tube when released. This allows the sample to drop into the calorimeter chamber.

It is necessary to decelerate the capsule without subjecting the drop wire to too great a stress. In our apparatus, the drop weight falls in a vacuum and therefore cannot be decelerated by the usual technique of air damping in the drop tube. Rather, the drop weight is a permanent magnet which in falling induces a current in a solenoid wrapped around the drop tube and thereby triggers an electronic circuit which activates an eddy current brake magnet in the drop mechanism (see ANL-6477, p. 164). A

breadboard model of the control circuit for the drop mechanism has been built and tested. The circuit is now being assembled on a panel. The drop tube and drop mechanism will be installed on the furnace and a length of Lucite pipe placed below the furnace so that the fall of the capsule can be photographed (strobeflash technique or Fastax camera).

J. 2500°C Drop Calorimeter
 (R.L. Nuttall)

Tests with the mockup furnace using electron beam heating have led to the design of a furnace and drop mechanism for a 2500°C drop calorimeter (described in ANL-6687, p. 165). The design of a preliminary system is substantially complete, and construction has been started.

V. REACTOR SAFETY*

The program on reactor safety is comprised of two major areas of research: (1) the study of metal-water reactions and (2) the study of the oxidation and ignition processes of substances used in reactor technology.

In water-cooled reactors, coolant failure or a severe nuclear excursion could cause the reactor core metals to melt and disperse rapidly in the water. Chemical reactions between the metals and water could result in the release of energy approaching or exceeding the energy released by the fission process during a nuclear excursion. Studies of these reactions are being carried out to learn more about the selection of reactor conditions that would preclude the occurrence of a violent reaction of metal with water.

Laser-beam heating of specimens of zirconium, stainless steel, platinum, and aluminum while the specimens were submerged in water was utilized in one series of experiments. Studies of the kinetics of isothermal metal-steam reactions were made to extend the data to higher temperatures for uranium and molybdenum. Studies of the high-temperature combustion of aluminum and magnesium in water were carried out. Studies of metal-water reactions initiated by nuclear transients were continued with zirconium-uranium fuel. An experimental program was begun in which specimens of preirradiated fuel are melted and dispersed in water by a nuclear transient in the Transient Reactor Test Facility (TREAT). The purpose of this program is to determine the effect of preirradiation on the extent of metal-water reaction and on dispersion behavior during fuel meltdown.

Studies of the oxidation and ignition behavior of metals used in reactor technology are providing information needed to minimize the hazards associated with the handling of these materials. The study of the oxidation and ignition behavior of plutonium and alloys of plutonium were continued. The effect of moisture on the oxidation and ignition behavior of plutonium was studied. The ignition temperature in moist air was found to be nearly the same as that in dry air. The isothermal oxidation rate of plutonium in oxygen was found to be markedly affected by the presence of moisture.

Studies of the thermal conductivity of metal powders were initiated in order to achieve a better understanding of powder ignition phenomena. Nickel and uranium powders were used in the studies in which the effects of particle size, pressure, temperature and extent of oxidation on the thermal conductivity were evaluated.

Study of the aluminum- U_3O_8 thermite reaction was resumed.

*A summary of this section is given on pages 37-41.

A. Metal-Water Reactions
(L. Baker)

1. Studies of Metal-Water Reactions by the Laser Heating Method
(L. Leibowitz, R. E. Wilson, L. Mishler)

The laser heating experiment (see ANL-6725, p. 210) is an attempt to obtain fundamental data concerning the rates of chemical reaction and heat transfer between metal particles and water. In the experiment, an intense beam of light from a ruby laser is focused on a small particle of metal which is in a water environment. Nearly instantaneous heating of the particle simulates the rapid contacting of heated particles with water that would occur in a water-cooled nuclear reactor in the event of a violent meltdown. (Either a nuclear runaway or a sudden loss of coolant might result in the injection of heated particles of cladding or fuel into the water.) Knowledge of the rate of exchange of both chemical and thermal energy from individual particles to the water is of prime importance in the analysis of reactor accidents. Materials which cannot easily be examined by such techniques as condenser discharge (see ANL-6687, p. 178) or induction heating (see the following section on the volumetric method) may be studied in this way.

The experimental arrangement for study of metal-water reactions is shown in Figure V-1. The laser beam was aligned with the lens shown. The reaction cell, bearing optical flats at the top and bottom, was partially filled with water and a weighed sample of metal foil was placed in the cell.

Figure V-1

DIAGRAM OF EXPERIMENTAL ARRANGEMENT
FOR STUDIES OF METAL-WATER REACTIONS
BY THE LASER HEATING METHOD

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The cell was connected to a high vacuum system, and the water was degassed by repeated freezing, pumping, and thawing. The cell was then sealed off under vacuum. Before the reaction cell was placed in position, a small hole was made in the thin aluminum coating on the top surface of the prism by a low-energy laser pulse. The cell was then carefully aligned so that the metal sample was just above the hole. A high-energy laser pulse then heated the sample, initiating the reaction. The amount of hydrogen produced gives the extent of reaction. The cell was then reconnected to the vacuum system by means of the breakoff seal. Hydrogen analysis was performed using the method described by Stover, Partridge and Garrison.¹

The hydrogen analysis apparatus is shown diagrammatically in Figure V-2. The gas in the cell is passed by the Toepler pump through the

Figure V-2

SCHEMATIC OF HYDROGEN ANALYSIS APPARATUS

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two cold traps to remove water, and into the large bulb in the analysis unit. The gas is compressed into the calibrated volume and the pressure measured. The gas is then forced into the oxidation tube, where CuO at 300°C oxidizes the hydrogen to water. Water produced by this oxidation is removed by the Anhydron. The residual gas is removed from the pipette by expansion into the large bulb and is compressed again into the calibrated volume. The pressure is determined again and the amount of hydrogen found by difference.

Preliminary experiments have been carried out which have demonstrated the feasibility of the method and have already led to some interesting findings. In a typical experiment, a 2-mg sample of 5-mil

¹ Stover, Jr., C.N., Partridge, W.S. and Garrison, W.M., Anal. Chem., 21, 1013 (1949).

zirconium foil was exposed to an 18-joule laser pulse, and 0.21 ml H_2 (S.T.P.) was produced (reaction of 33 percent of the zirconium). Preliminary tests of this kind were carried out with zirconium, stainless steel, platinum, and aluminum. Aluminum has been difficult to heat because of the very low emissivity of the metal. It has been possible, however, to produce molten spheres from aluminum foil samples, 0.003 cm (1 mil) thick. Molten platinum particles have been produced from 0.1-cm squares of 0.008-cm (3-mil) foil, and molten spheres of zirconium and stainless steel have been produced from 0.1-cm squares of 0.013-cm (5-mil) foil.

In addition to the measurement of the extent of reaction by hydrogen analyses, the extent and character of the reactions will be determined by metallographic examination of the oxidized particles. A photomicrograph of a sectioned and polished zirconium sphere produced by heating a 0.1-cm square of 0.013-cm (5-mil) zirconium foil is shown in Figure V-3. The oxide film is clearly visible on the particle. Measurements of the oxide film thickness ($23\ \mu$) and the particle diameter ($440\ \mu$) indicate that 21% of the zirconium reacted.

Figure V-3

OXIDE COVERED ZIRCONIUM SPHERE; POLISHED SECTION

(Prepared by heating, under water, a 0.1-cm square by 0.013-cm thick foil with a laser pulse.)

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Hydrogen determinations and microscopic studies of the residue yield information concerning only the character and total extent of reactions. Two methods of studying the reaction rate are currently under development.

One of these methods involves a determination of the temperature vs. time behavior of the particles by means of a two-color optical pyrometer. This device consists simply of a lens to focus the image of the metal sample, a beam splitter and filter so that each of two RCA 7102 photomultiplier tubes receives light emitted at different wave length regions by the hot sample. A two-color instrument is necessary to reduce emissivity errors. The temperature of the sample is related to the ratio of intensities. The electronic components of the pyrometer have been operating well and the principal problems remaining are optical.

Scattered laser light must, of course, be removed. The filter required must be quite opaque to the laser light and still be unchanged after repeated exposures. In addition, optical alignment of the components must be precise for reproducible operation. The filters which have been used have proved to transmit too much of the scattered laser radiation, and new filters have been ordered.

The other method under development for obtaining information regarding the reaction rate is the use of high-speed motion pictures. It is expected that motion pictures taken with a Fastax camera at the rate of 5000 frames per second will allow measurement of the rate of growth of the steam-hydrogen film which rapidly develops around suddenly heated particles. Some photography has already been completed using a relatively large field of view. By means of these motion pictures, the large-scale dynamic behavior of the particle and the water column was observed. In the experiments, which were carried out in open tubes, 0.2-cm diameter pieces of 0.013-cm (5-mil) zirconium foil were heated by various energy pulses of the laser beam while submerged under 5-mm diameter water columns that were 2, 4, or 8 cm high. With a 2-cm height, the hydrogen-steam bubble simply blew by the water column. At 4 cm, the hot metal particle began to rise, following a bubble up the tube. About 10 msec after the laser pulse, however, the bubble collapsed, driving the metal to the bottom of the tube where it appeared to explode. The water column then began rising with increased violence. At a slightly lower laser energy with the same height, pulsations of the bubble were observed with roughly a 10-msec period. With water at the 8-cm level in the open tube, the bottom of the tube failed, perhaps as a consequence of a shock transmitted to it. Because of the importance of these observations to reactor safety problems, further examination of the water dynamics will be carried out.

2. Isothermal Studies of the Uranium-Steam Reaction by the Volumetric Method
(R.E. Wilson, C. Barnes)

A knowledge of the rates of reaction of metals with steam under isothermal conditions is necessary for the prediction of metal-water

reactions which might occur in the event of a reactor accident. A volumetric experiment (see ANL-6543, p. 183) was designed to study metal-steam reactions. When the metal surface is above the critical temperature (374°C) for water, steam and water are, in general, equivalent reactants at the same pressure.

Studies of the reaction of steam with uranium prepared at Argonne (see ANL-5974, p. 146, for a typical analysis) over the temperature range of 400 to 1200°C were reported earlier (ANL-6569, p. 148). This report describes experiments covering the temperature range from 1200 to 1600°C .

Experiments were not performed at temperatures greater than 1600°C because of the limits imposed by the platinum thermocouple and the softening point of the quartz support pedestal.

The sample, consisting of a cube of uranium about 1 cm on a side, was metallographically polished before exposure. After polishing, the sample area was measured with a micrometer. The apparatus was modified to allow study of the reaction at a higher temperature by providing a platform of quartz for support of the uranium sample. A thermocouple protruded through the platform to the center of the sample. After mounting in the apparatus, the uranium sample was heated inductively to the desired temperature in flowing steam at a pressure of about one atmosphere. In each of the experiments, the quartz pedestal and a strong, coherent oxide film which formed around the uranium supported the uranium even when it was molten (mp 1133°C). No cracks were apparent in the oxide during the course of the experiments. After the steam passed the sample, it was condensed and the hydrogen produced by the metal-steam reaction was collected over water and measured in a graduated vessel (for a detailed description of the apparatus and procedure, see ANL-6543, p. 185).

Typical results of an experiment at each of the temperatures studied are shown in Figure V-4. The slope of the lines shown in the log-log

Figure V-4

HYDROGEN EVOLUTION IN
THE REACTION OF STEAM
AT ONE ATMOSPHERE WITH
URANIUM

(1-cm uranium cubes, supported on
a quartz or urania pedestal)

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plot in this figure is nearly 0.5, indicating that from 1200 to 1600°C the kinetics of the uranium-steam reaction follows the parabolic rate law, which has the form:

$$V^2 = kt, \quad (1)$$

where V is the volume of hydrogen generated, t is time, and k is a constant.

The constants for the parabolic rate law were obtained by plotting the square of the volume of hydrogen reduced to standard conditions vs. time for each experiment. A plot of the results of two experiments at 1400°C is given in Figure V-5. The slope of the straight line in Figure V-5 is equal to the rate constant. The difference between the results of the duplicate runs was negligible.

Figure V-5

HYDROGEN EVOLUTION IN THE URANIUM-STEAM REACTION AT 1400°C

The parabolic rate law constants obtained from this and an earlier series of experiments are given in Table V-1; the average deviation for each temperature is also given in the table. The data from Table V-1 are plotted in Figure V-6 as a function of reciprocal temperature. The length of a datum point is equal to the average deviation given in the table. The Arrhenius equation for the lines drawn through the points are given in Figure V-6.

Table V-1

PARABOLIC RATE LAW CONSTANTS
FOR THE URANIUM-STEAM REACTION

Temperature (°C)	Parabolic Rate Constant, k [ml H ₂ (S. T. P.)/cm ²] ² /min
600	3.36 ± 0.33
700	15.6 ± 1.9
900	67 ± 14
1000	120 ± 11
1200	341 ± 1
1300	504 ± 49
1400	848 ± 18
1500	1335 ± 55
1600	1976 ± 122

To determine the possible effect of silicon diffusing into the uranium cube from the quartz support, some experiments were made with a disc of sintered UO₂ interposed between the quartz and the sample. No difference in the reaction rate could be detected. In addition, the steam flow rate was varied by a factor of ten with no change in the rate of reaction, although it took longer to reach the temperature at high steam flow rates.

Optical pyrometer measurements of the outer oxide surface during the course of several runs showed that the surface temperature was 100 to 400°C below the metal temperature as indicated by the central thermocouple. This resulted from the relatively poor thermal conductivity of the oxide and the very thick films developed during the oxidations.

Metal-gas reactions that follow the parabolic rate law are usually considered to be controlled by the diffusion of an ionic species through the oxide film. The existence of a significant temperature gradient through the oxide film, therefore, suggests that the rate law observed may not be representative of truly isothermal conditions. In particular, one

Figure V-6

EFFECT OF TEMPERATURE ON THE RATE OF HYDROGEN EVOLUTION
FOR THE REACTION OF STEAM WITH URANIUM

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would expect that the rate data developed in this study would give low results if extrapolated to very short reaction times when the temperature drop across the oxide film would be small. It does appear, however, that the parabolic rate law would apply and that only a minor change in the parabolic law constants would be required to describe the reaction at short times.

The temperature gradient across the oxide film in the previous studies below 1200°C was relatively minor.

The following rate equations summarize the results of the 600 to 1200°C and the 1200 to 1600°C studies:

$$600 \leq T < 1200^{\circ}\text{C}$$

$$V^2 = 1.95 \times 10^5 t \exp(-18,600/RT) \quad (2)$$

$$1200 \leq T \leq 1600^{\circ}\text{C}$$

$$V^2 = 1.59 \times 10^6 t \exp(-25,000/RT) \quad (3)$$

where V is the volume of hydrogen evolved in ml (S.T.P.)/cm²,
 t is the time, in min,
 R is the ideal gas constant, and
 T is absolute temperature, °K.

The change in reaction mechanism implied by the change of slope of the Arrhenius plot may be due to the melting of the metal at 1133°C. The state of the oxide is presumably the controlling factor in the parabolic oxidation and there is no change in the oxide at this temperature. This accounts for the change in rate caused by melting of the metal being relatively minor.

3. Reaction of Molybdenum with Steam (Martin Kilpatrick and S.K. Lott)

The study of the kinetics of reaction of steam with metals having melting points above 2000°C has a twofold purpose:

- 1) To determine the suitability of high melting metals for the fabrication of equipment so that metal-water studies may be carried out at higher temperatures.
- 2) To extend our knowledge of the kinetics and mechanisms of metal-water reactions so that by a reasonable extrapolation one can approximate the conditions of reaction with steam which exist at the moment of melting of a nonvolatile metal.

In previous work, the oxides resulting from the metal-water reaction have not been volatile. Among the high melting metals, however, are some which form at least one oxide whose melting point and boiling point lie below the corresponding melting point and boiling point of the parent metal. The study of the reaction of such metals with steam is expected to shed new light on the mechanism and rate laws of metal-water reactions. Table V-2 gives some pertinent data on the metals which were considered and their volatile oxides.

Molybdenum was chosen for the initial study since there is more information about the stability and volatility of molybdenum trioxide (MoO_3). Molybdenum trioxide is polymeric and consists of trimers, tetramers and pentamers, but may be mostly in the monomeric form in the presence of water vapor. The initial reaction of molybdenum with steam may form the dioxide (MoO_2), but the dioxide reacts with steam to give the volatile trioxide. Thus, the products of reaction are removed from the surface of a heated molybdenum specimen by volatilization, and may be swept rapidly away from the hot zone if a flow system is employed in conjunction with induction heating.

a. Experimental Method

Molybdenum samples of 1-cm length were prepared from rods of 5-mm or 13-mm diameter. Holes of 1/16-in. or 3/32-in. dia. were drilled in one face of the rods to a depth of 6 mm for mounting the weighed specimen on an alumina tube containing the thermocouple. Both of the

Table V-2
MELTING AND BOILING POINTS
OF METALS AND THEIR PRINCIPAL OXIDES

<u>Metal</u>	<u>M.P.</u> <u>(°C)</u>	<u>B.P.</u> <u>(°C)</u>	<u>Oxide</u>	<u>M.P.</u> <u>(°C)</u>	<u>B.P.</u> <u>(°C)</u>	<u>Remarks</u>
Tungsten	3380	(5900) ^a	WO ₃	α tp ^b 735 β 1473		oxide volatile above 1000°C
Rhenium	3100	(5600)	Re ₂ O ₇	296	362	oxide volatile above 300°C
Osmium	3000	(5500)	OsO ₄	41	131	oxide vapor is toxic
Tantalum	2996	6100	Ta ₂ O ₅	α tp 1350 β 1872		oxide nonvolatile below 1370°C
Molybdenum	2610	5500	MoO ₃	795	1100	oxide volatile above 600°C
Niobium	2470	4400	Nb ₂ O ₅	α unstable β 1495	decom- poses	oxide nonvolatile below 1495°C
Vanadium	1920	3350	V ₂ O ₅	675	decom- poses	oxide unstable below m.p. decomposition complete at 1700°C.

^a() indicates uncertainty

^b_{tp} = transition point

molybdenum rods were of high purity; the 5-mm rod material being 99.99 w/o molybdenum and the 13-mm rod material containing approximately the same amounts of trace impurities except for copper. The concentration of copper in the 13-mm sample was 0.01 w/o as compared with 0.001 w/o in the 5-mm sample. All specimens were descaled with 600 grit silicon carbide paper, washed with acetone, and rewashed with acetone before reweighing.

The experimental apparatus consisted of a steam boiler connected by ball joints to a quartz tube mounted vertically in the field of an induction furnace. The lower end of the quartz tube was connected by another ball joint to a metal cup which was connected to a condenser. A eudiometer tube was used for the collection of the hydrogen evolved. The alumina tube containing the Pt, Pt-10% Rh thermocouple was centered in the

metal cup and mounted so that the thermocouple junction was in the center of the field of the induction furnace. The thermocouple was connected to a recorder with suitable switches for direct reading on a potentiometer.

To carry out an experiment, the specimen was weighed, mounted on the alumina tube, and, after testing the apparatus for gas tightness, the apparatus was steamed out to remove air, and the appropriate gas burette or graduated cylinder for the collection of hydrogen was clamped in place. The induction furnace was then turned on and the volume of hydrogen evolved recorded at suitable time intervals. The volume of hydrogen collected varied from 100 to 500 ml depending on the rate of evolution which varied with temperature and sample size from less than 1 to 200 ml per minute. On completion of an experiment the metal sample was washed in acetone and weighed to determine the weight loss.

In addition to the determination of the temperature by the Pt, Pt-Rh thermocouple, the surface temperature of the reacting sample was measured by a two-color optical pyrometer and the brightness temperature by a standard Leeds and Northrup optical pyrometer.

b. Results

The stoichiometry of the reaction was determined from the ratio of the gram moles of hydrogen produced and the gram atoms of molybdenum reacted. The average value of this ratio for forty-one experiments was 2.96 indicating that the overall equation is

A value somewhat less than three is consistent with the observation that although the oxide vapor is white with a yellow tinge the aqueous condensate formed a colloidal blue solution characteristic of "moly blue" oxide which has an oxygen to molybdenum ratio somewhat less than three.

Experiments conducted in the range 1100-1700°C show that the reaction followed a linear rate law and that the experiments are quite reproducible especially with the larger samples. The velocity constant (k) expressed in g-atom molybdenum/(cm²)(min) varied from 6 x 10⁻⁴ at 1700°C to 2 x 10⁻⁶ at 1130°C.

Some discrepancy was noted between the thermocouple and pyrometer temperatures but this was considered to be caused by the light absorption of the slightly yellow volatile oxide. The logarithm of the velocity constant is presented as a function of the reciprocal temperature in Figure V-7. The equation obtained by least squares is

$$k = 6.58 \pm 1.54 \times 10^2 \exp \left(\frac{-54,000 \pm 700}{RT} \right) \quad (5)$$

Figure V-7

LINEAR RATE CONSTANTS FOR THE MOLYBDENUM-STEAM REACTION
(1100-1700°C)

108-7190 Rev.

The rapidity of the reaction even at the lowest temperature studied [0.2 mg Mo/(cm²)(min)] precludes the use of molybdenum in an environment of high temperature steam.

4. Study of the Combustion of Aluminum in Water
 (R.O. Ivins, R. Koonz)

The sustained combustion of aluminum pellets in water has been reported by Wilson and Martin (see ANL-6379, p. 208). In these studies, small pellets of aluminum were simultaneously levitated and heated in a radio-frequency field. It was discovered that ignition occurred when the pellet temperature reached 1750°C in air. The ignition resulted in a vigorous vapor phase burning in air, which continued when the pellets were dropped into water. Burning occurred beneath the surface of water and later at the water-air interface as the pellets were buoyed up to the surface by the evolving hydrogen.

Observation of the self-sustained vapor phase combustion process prompted the present study, in which the rate of metal consumption was determined as a function of pellet size. These studies were undertaken in order to provide a basis for estimating the rate of the aluminum-water reaction in the burning regime (metal temperature greater than 1750°C).

Samples of high-purity aluminum ranging in weight from 150 to 1000 mg were levitated, heated in air until they ignited, and then dropped into room temperature water. The time which elapsed from the moment of dropping until burning ceased was measured. The results of these measurements are plotted in Figure V-8. The data points were fitted to a straight line by the method of least squares. The equation of the line was as follows:

$$D_o = 0.160 t_c + 3.36 \quad (6)$$

where D_o is the original diameter of the particle, in mm, and t_c is the consumption time, in sec.

Figure V-8

CONSUMPTION OF ALUMINUM PELLETS BURNING IN WATER

(Water temperature: $\approx 25^\circ\text{C}$)

(Metal temperature: $\approx 2050^\circ\text{C}$)

108-7191

Initially, the drops of burning aluminum sank below the water surface and would rise and sink alternately as the hydrogen bubble surrounding it would grow and break off. As the drop became smaller, it would break the water surface, releasing the hydrogen, and then sink, form a bubble, and rise again. Eventually, when the size of the drop had become small enough, it would rise to the surface and float while continuing to burn. Once burning ended, the residual metal, enclosed in an irregular oxide coating, would sink to the bottom of the water container. While the drops were burning under water, they decreased in size and the condensation of fine alumina particles was evident as a particle spray from the burning surface of the drop. The size distribution of the fine particles given off during one run is shown in Figure V-9. The distribution data was obtained by microphotography of samples of the suspended particles.

Figure V-9

PARTICLE SIZE DISTRIBUTION OF Al_2O_3 RESIDUE
RESULTING FROM THE REACTION
OF ALUMINUM DROPLETS AND WATER

(Geometric Mean Particle Size = 2.69μ)

108-7192

Vapor phase burning of droplets of liquid fuels is often controlled by the rate of heat transfer from a cospherical flame front to the fuel sphere to provide the heat of vaporization and thus sustain burning.² The heat

²See, for example, Wise, H., Lorell, J. and Wood, B.J., The Effects of Chemical and Physical Parameters on the Burning Rate of a Liquid Droplet, Fifth Symposium (International) on Combustion, Reinhold Publishing Co., New York, 1955, p. 132.

transfer rate for hydrocarbon fuels is usually controlled by conduction and results in a consumption time which is proportional to the square of the original droplet diameter. It can be shown, however, that if the heat transfer rate occurs predominantly by thermal radiation, a linear relationship between the consumption time and the droplet diameter is expected. The linear character of the experimental results as expressed in Figure V-8 and Equation 6 is therefore consistent with a heat transfer rate controlled by radiation. This finding is consistent with the fact that aluminum has a higher temperature of combustion than those of liquid hydrocarbon fuels and forms a solid oxide product.

The data are consistent with a simple vapor burning model, except that the straight line in Figure V-8 does not pass through the origin. This occurred primarily because the aluminum droplets did not burn to completion in the water. An analysis of typical residue indicated that the equivalent of a 2.3-mm sphere remained unreacted. The experiment was also complicated by the fact that a small amount of burning occurred in air before the pellets were dropped and also that in the late stages of burning the sample was floating and therefore was in contact with both water and air. No quantitative significance, therefore, could be attached to the intercept in Figure V-8 or to the constant of 3.36 mm in Equation 6, since it could not be assumed that burning in air, under water, and at the water-air interface occurred at the same rate.

It could be assumed, however, that on the average the time of burning in air and at the water-air interface was constant for each run. This is equivalent to assuming that the droplets began burning at the water surface at a particular value of the diameter. The error incurred in including the surface burning time in the measurements, therefore, did not affect the slope of the line. It was, therefore, assumed that the slope (0.160 mm/sec) represents the burning rate of droplets submerged in room temperature water.

The calculation of the mass rate of consumption from the rate at which particle diameters decrease can be achieved as follows:

$$\frac{-dm}{A dt} = \frac{\rho}{\pi D^2} \frac{d \left(\frac{\pi}{6} D^3 \right)}{dt} \quad (7)$$

where $dm/A dt$ is the mass consumption rate in g aluminum/(cm²)(min),

ρ is density of aluminum at 2000°C, 2 g/cc,

D is the diameter of the aluminum drop at any time, in cm, and

t is time, in min.

Equation 7 reduces to the following:

$$\frac{-dm}{A dt} = \frac{\rho}{2} \frac{dD}{dt} = 0.96 \text{ g aluminum}/(\text{cm}^2)(\text{min}). \quad (8)$$

5. Study of the Magnesium-Water Reaction*
(R.C. Liimatainen)

The reaction of molten magnesium with water is of interest because it represents an example of a relatively low temperature reaction of water with a metal having a high vapor pressure.

Previously, two experiments had been reported on this reaction in which small batches of molten magnesium were dispersed in water with blasting caps.³ The two experiments each resulted in a sharp blast accompanied by a white flash, with 70 to 80% of the metal reacting.

Two studies have been published on the reaction of solid magnesium with water vapor. (The melting point of magnesium is 651°C, and its boiling point is 1103°C.) The first was an investigation of the magnesium-steam reaction, and results indicated that ignition occurred at 625°C, resulting in vapor-phase burning.⁴ The ignition temperature was approximately the same in oxygen and in hydrogen peroxide as it was in water vapor. The vapor pressure of magnesium at 625°C is 1.5 mm.

The second was a study of the reaction of magnesium with water vapor over the temperature range from 425 to 575°C using a manometric method to determine the rate of reaction. This investigation showed that the reaction followed a linear rate law after an induction period.⁵ Rate constants increased linearly with water vapor pressure between 31 and 208 mm Hg. Also, there was a gradual increase in activation energy with decreasing water vapor pressure in the 425 to 500°C range. In the 500 to 575°C range, the activation energy reached a limiting value of 33.7 kcal/mole, which is nearly identical with the heat of sublimation of magnesium (34.4 kcal/mole). The observations were explained on the basis of a change from a surface reaction at the lower temperature range to a vapor-phase reaction which

* Experiments performed at the Finland Institute of Technology, Otaneimi, Finland as part of a Fulbright Fellowship. Several people gave of their time and effort to help with this work; special thanks are given to Mr. Pauli Roiha and to Prof. Pekka Jauho for their contributions.

³Higgins, H.M., A Study of the Reaction of Metals and Water, AECD-3664, 1955.

⁴Kubaschewski, O. and Ebert, H., Reaction of Water Vapor and Hydrogen Peroxide Upon Light Metals at High Temperatures, Z. Metallk., 38, 232 (1947).

⁵Gibbs, D.S. and Svec, H.J., Kinetics of Reaction between Magnesium and Water Vapor, ISC-779, 1956.

appeared at higher temperature and lower water vapor pressures. The change in mechanism was believed to be the result of the increase in the vapor pressure of magnesium metal from 0.053 mm Hg at 500°C to 0.684 mm Hg at 600°C.

Since there were no quantitative data on the kinetics of the reaction between molten magnesium and water, and since the molten metal-water reaction, in general, is of more interest in reactor hazards analysis than the solid metal-water reaction, it seemed appropriate to obtain information at temperatures of about 700°C.

The experimental method in the study reported herein (see Figure V-10 for a diagram of the apparatus) consisted of first melting, with an induction heater, a known quantity (~1 g) of reagent grade magnesium in a

Figure V-10

DIAGRAM OF APPARATUS FOR Mg-H₂O REACTION STUDY

108-6558 Rev.

graphite crucible. Bottom-pour crucibles with holes of different diameters were used to study the effect of drop size on the extent of metal-water reaction. The molten magnesium was dropped into distilled water which was under one atmosphere of argon. The hydrogen produced from the reaction was measured as a function of time by taking motion pictures of the experiment. The photographs provided a record of the displacement of the water level in the gas burette as the hydrogen was evolved.

Figure V-11 gives the record from a typical test. The time, 0, corresponds to the moment when the molten magnesium hit the surface of the water. The slope of the curve is a measure of the kinetics of the reaction, and the total amount of hydrogen evolved indicates the percent reaction.

Figure V-11
TYPICAL Mg-H₂O REACTION DATA

Initial Conditions:

Mg at 700° C

H₂O at 20° C

108-6559 Rev.

Figure V-12 shows several photographs which indicate the general characteristics of the reaction. At 0.1 sec, the molten magnesium drop has just fallen into water and is completely submerged but not yet reacting appreciably. At 0.8 sec, the reaction is proceeding and the molten globule has broken up. Hydrogen and steam bubbles are apparent. At 1.5 and 1.8 sec, the reaction is vigorous, with emission of heat, light, and hydrogen. Other photographs showed that, after 2.5 sec, the reaction has stopped and the magnesium droplets are quenched. The reaction times for the experiments using various drop sizes ranged from 1.6 to 2.5 sec.

An effort was made to investigate both the influence of metal temperature and drop diameter on the rate and extent of reaction. However, because of the volatility of the magnesium at temperatures of 800°C or above, the temperature parameter could not be studied in this way. At the high temperatures, the magnesium would vaporize, a major fraction of the reaction would occur in the vapor phase, and the upper walls of the apparatus would be coated with magnesium oxide.

Data on the effect of the magnesium droplet diameter upon percent magnesium-water reaction are shown in Figure V-13. It is evident that the small particles undergo more reaction than the large ones. However, over the range of sizes studied, the dependence of extent of reaction on particle diameter is not great.

Both by direct observation and by analysis of the motion picture films, it was evident that magnesium reacts with water at 660 to 700°C in much the same manner as does aluminum at 1750°C or above. However,

Figure V-12

REACTION OF MOLTEN MAGNESIUM WITH WATER, SELECTED FRAMES
FROM MOTION PICTURE RECORD OF EXPERIMENT NO. 2

108-6692

0.1 sec

108-6693

0.8 sec

108-6694

1.5 sec

108-6695

1.8 sec

108-7193

there is one significant difference: Whereas the magnesium "reaction time" (defined as the time interval between the droplet hitting the water and the cessation of reaction, or quenching, as evidenced by the end of the hydrogen evolution) is, on the average, about 2 sec at 700°C, the aluminum reaction time is between 12 and 38 sec for droplet sizes from 5.3 to 9.6 mm (Figure V-8). The physical characteristics of magnesium at 700°C are very similar to those of aluminum at 1750°C. The vapor pressure of magnesium at 700°C is 5.5 mm, whereas that of aluminum at 1750°C is 7.0 mm. The heat of reaction with water for magnesium is -3570 cal/gram and that for aluminum is -4200 cal/gram.

Figure V-13

DEPENDENCE OF EXTENT OF
MAGNESIUM-WATER REACTION
ON PARTICLE SIZE

(Initial Magnesium
Temperature: 700°C)

108-6560 Rev.

To summarize, the high vapor pressures of magnesium and the relatively high heat of reaction results in a vigorous vapor-phase burning when magnesium is melted in the presence of water or steam. The course of the magnesium reaction generally parallels that of the aluminum-water reaction if the reactions are compared on the basis of metal vapor pressures.

6. Studies of the Reaction of Zirconium-Uranium Alloy with Water in TREAT

(R.O. Ivins, F.J. Testa, P. Krause, J. Hepperly)

The use of the TREAT (Transient REActor Test facility) reactor at the National Reactor Testing Station, Idaho, to study the reaction of various metals with water is continuing. The technique consists of subjecting fuel specimens immersed in water to a transient nuclear burst. The objectives of this program are:

1. To determine the extent of reaction between the metal and water,
2. To determine the fuel temperature and pressure history during the excursion, and
3. To determine the physical damage that occurs as a result of the transient; this is accomplished by such means as metallographic and particle size evaluations.

The results of five experiments in which unclad zirconium-10.65 w/o uranium (93% enriched) alloy plates were subjected to destructive transients in TREAT have been reported in previous summary reports (ANL-6569, p. 153 and ANL-6596, p. 195). In these experiments, nuclear energy inputs of 285, 344, 510, 628 and 785 cal/g gave 6.0, 5.2, 9.5, 11.5 and 67.2% zirconium-water reaction, respectively. Four additional experiments

have been conducted with the same type of plate. The nominal dimensions of each plate were 1 in. by 0.5 in. by 0.1 in., and individual plates weighed approximately 5.4 g.

In each of two experiments (CEN-163 and 164), a single plate submerged in room temperature water was subjected to a transient burst of neutrons while contained in an autoclave in which there was a 20 psia helium atmosphere. In the other two experiments (CEN-165H and 166H), single plates were subjected to similar transients while submerged in water in a heated autoclave at 285 °C with a 1000 psi overpressure of saturated steam. The results of these four experiments are summarized in Table V-3.

A bare junction chromel-alumel thermocouple was placed in a 1/16-in. hole drilled to a depth of 0.5 in. in each plate. The temperature history was recorded on an oscillograph in three of the four experiments. (The thermocouple failed to respond in experiment CEN-165H.)

The physical appearance of the plates after irradiation can be seen in Figures V-14, V-15, V-16, and V-17. Each figure contains a photograph

Table V-3

TREAT MELTDOWN EXPERIMENTS WITH ZIRCONIUM-URANIUM ALLOY PLATES

(Unclad, 89.35 w/o Zr, 10.65 w/o U, 93% enriched, 1.0 x 0.5 x 0.1 in.)

A bare junction chromel-alumel thermocouple was located in a 1/16-in. center hole in each plate.

TREAT Exp. CEN No.	Fuel Wt. (g)	Initial Water Temp. (°C)	Reactor Pulse		Calc. Energy Input (cal/g)	Calc. Peak Temp. Adiabatic ^a (°C)	Appearance of Fuel After Transient	Extent of Metal-Water Reaction (%)
			Period (msec)	Int. Power (Mw-sec)				
163	5.3895	25 (20 psia He)	104	113	155	1840 (partly melted)	Plate warped; a small quantity of molten material around the thermocouple.	5.3
164	5.4025	25 (20 psia He)	107	196	270	2500	Plate melted into a single large globule and a few small particles.	6.3
165H	5.3827	285 (1000 psi overpressure)	106	133	156 ^b	1840 (partly melted)	Plate bulged around the thermocouple.	2.3
166H	5.4120	285 (1000 psi overpressure)	104	263	289 ^b	3050	Plate melted into a single large globule and a few small particles.	13.1

^a These values are calculated from the energy input and thermodynamic data and are considerably higher than those actually reached by the samples due to heat losses.

^b The heat required to raise sample temperature from 25 to 285 °C was included in these energy values so that direct energy comparisons can be made with experiments at 25 °C.

Figure V-14

ZIRCONIUM-URANIUM ALLOY PLATE. TREAT EXPERIMENT CEN-163

(25°C water, 20 psia He)

Photograph of plate after irradiation
155 cal/g - 5.3% reacted

Plate temperature, reactor power, and
integrated power versus time

Figure V-15

ZIRCONIUM-URANIUM ALLOY PLATE. TREAT EXPERIMENT CEN-164

(25°C water, 20 psia He)

Photograph of plate after irradiation
 270 cal/g - 6.3% reacted

Plate temperature, reactor period,
 and integrated power vs time

Figure V-16

ZIRCONIUM-URANIUM ALLOY PLATE. TREAT EXPERIMENT CEN-165H

(285 °C water, 1000 psi overpressure)

Photograph of plate after irradiation
 156 cal/g - 2.3% reacted

108-6672-A

of the plate from the experiment and a graph of the temperature, reactor power, and integrated reactor power as a function of time, except that no graph is provided in Figure V-16.

The plates in experiments CEN-163 (room temperature) and 165H (285 °C) shown in Figures V-14 and V-16 were run at lower energy levels than the other two plates. They reached their melting point (approximately 1840 °C), as evidenced by their deformation. They retained their original shapes, apparently because of the strength of the oxide film. The plate in CEN-163 (initially in room temperature water) was more severely deformed, and some molten material was expelled from the thermocouple well. In both plates, more severe damage was apparent at the thermocouple well than at other locations, indicating a possible interaction between the thermocouple materials and the plate.

The two plates (CEN-164 and 166H) run at higher energy levels are shown in Figures V-15 and V-17. Both had melted and had formed a single large globule and two or three much smaller droplets.

The extent of reaction between the alloy plates and water was based on the quantity of hydrogen found in a gas sample taken from each autoclave. This determination was made by mass spectrometric analysis.

Figure V-17

ZIRCONIUM-URANIUM ALLOY PLATE. TREAT EXPERIMENT CEN-166H

(285°C water, 1000 psi overpressure)

Photograph of plate after irradiation
 289 cal/g - 13.1% reacted

Plate temperature, Reactor Power,
 integrated power versus time

108-7196

Figure V-18

TREAT ZIRCONIUM-URANIUM PLATE EXPERIMENTS.
PERCENT REACTION VERSUS NUCLEAR ENERGY INPUT

89.35 w/o zirconium-10.65 w/o uranium (93 percent enriched)
 alloy plates (1.0 in. x 0.5 in. x 0.1 in.)

108-7197

The extent of reaction is shown as a function of the nuclear energy input in Figure V-18. The data previously reported (ANL-6569 and ANL-6596) are included for comparison. The nuclear energy input is based on zero enthalpy at 25°C. In order to compare the experiments conducted in water heated to 285°C with those conducted in room temperature water, the sensible heat between 25°C and 285°C was added to the fission energy generated in the plates in the heated water experiments.

The plate in the heated water experiment (CEN-166H) at the higher energy input (289 cal/g) reacted with the water to the extent of 13.1%. At the same energy input, a plate subjected to a nuclear burst in room temperature water would have only reacted to the extent of 6.5%, as determined from the curve in Figure V-18.

At the lower energy input, the plate in 285°C water (CEN-165H) reacted to only 2.3 percent, as compared with 5.3 percent for the run in room temperature water (CEN-163). The material which exuded from the plate in CEN-163 but not in CEN-165H (Figures V-14 and V-16) probably accounts for this difference in percent reaction.

The increased extent of reaction of the zirconium-uranium alloy plate in heated water (CEN-165H and 166H) is probably due to a difference in the gas phase diffusion-controlled reaction rate. Similar results were obtained in a study of the zirconium-water reaction by the condenser discharge method (see ANL-6548). It is also possible that a difference in heat transfer due to the different initial water temperatures may have led to a

sufficiently different peak temperature for the similar energy inputs in the two types of experiments. Differences in peak temperature would then influence the extent of reaction achieved in the experiments. The results showed that, in general, there was only a minor effect of water temperature and steam overpressure.

A computer study of the heat transfer and reaction kinetics is in progress. It is anticipated that the effects resulting from heat transfer can be separated from those resulting from reaction kinetics. The plate temperature histories developed in the recent experiments will be used to guide the theoretical studies.

Additional experiments in high-temperature water (285°C) are also contemplated to better define the difference in behavior already noted.

7. Studies of Preirradiated Fuel Meltdown in TREAT
(R.C. Liimatainen, F.J. Testa, J. Hepperly)

Prior to this work, all of the meltdowns conducted in the TREAT metal-water program have been on unirradiated fuel. The main purpose of this new study is to compare data on the amount of molten metal-water reaction and the change in geometry for preirradiated fuel with previous data obtained in TREAT for unirradiated clean fuel samples.

In the first meltdown experiment with preirradiated fuel, summarized in Table V-4, a 93.5 w/o U (20% enriched)-5 w/o Zr-1.5 w/o

Table V-4

TREAT MELTDOWN EXPERIMENT WITH A PREIRRADIATED URANIUM-ZIRCONIUM-NIOBIUM ALLOY FUEL PIN

(93.5 w/o U (20% enriched)-5 w/o Zr-1.5 w/o Nb alloy pin,
0.2 in. diam. x 0.5 in. long, unclad)

(Preirradiated in MTR to 1.5% burnup of the U^{235} atoms present
and cooled for 2 yr.)

TREAT Exp. No.	CEN-167
Fuel Wt. (g)	4.2645
Initial Water Temp. (°C)	25 (20 psia He)
<u>Reactor Characteristics</u>	
Period (msec)	84
Int. Power (Mw-sec)	300
Peak Power (Mw)	917
Calc. Energy Input (cal/g)	270
Appearance of Fuel After Transient	Completely melted, with extensive particle formation
Extent of Reaction	22.6%

Nb alloy unclad fuel pin submerged in water was subjected to a reactor excursion in TREAT. The fuel was irradiated in MTR to 1.5% burnup of the U^{235} present and cooled for two years. It is estimated that the sample, weighing 4.2645 g, contained 0.32 cc of fission product gases, all of which were released in the meltdown. A hydrogen analysis, after the transient, indicated that 22.6% of the metal had reacted with the water. Post-irradiation examination and photographs of the fuel, shown in Figure V-19, indicated that the pin had been fully melted; the melted globules and particles appeared to be very similar to the fragments obtained in previous experiments with unirradiated fuel at a similar energy.

Figure V-19

PREIRRADIATED U-Zr-Nb ALLOY FUEL SAMPLE
AFTER MELTDOWN IN WATER .
TREAT TRANSIENT CEN-167

108-6699A

In Figure V-20 the extent of metal-water reaction observed in the preirradiated experiment is compared with previous runs with identical but unirradiated fuel. The previous data were reported in ANL-6250, p. 101 and later revised for publication.⁶ The revision involved changes in the values for

⁶Baker, Jr., L. and Liimatainen, R.C., Chemical Reactions, Chapter 8, Vol.I, Safety Information For the Technology Of Reactors (SIFTOR), MIT Press (in press).

Figure V-20

TREAT MELTDOWN EXPERIMENTS
WITH URANIUM-ZIRCONIUM-NIOBIUM
FUEL SAMPLES

108-7198

the fission energy input to the fuel in the light of recent refinements in calculations and measurements of neutron dose. Although it may be fortuitous that the point for the experiment with the preirradiated pin falls near the curve, a similarity in reaction for the two cases is indicated. Both the appearance of the fragmented fuel pin and the amount of metal-water reaction are very similar to those reported in runs with non-preirradiated fuel.

The tentative conclusion suggested by this preliminary experiment is that the meltdown behavior of fuel which contains fission products (from burnups to 1.5% of the U^{235}) is not markedly different from the behavior of unirradiated fuel. This conclusion appears to apply both to the physical aspects (change in geometry on meltdown) and chemical aspects (extent of reaction) of the meltdown of uranium fuel in water as a result of a reactor excursion. Further in-pile work will be done at other energies and with other fuel pins to check the validity of this tentative conclusion.

8. Development of Pressure Instrumentation for Experiments in TREAT

(R.C. Liimatainen, F.J. Testa, J. Hepperly)

In experiments to obtain precise rates of chemical reactions in TREAT, autoclave experiments with pressure transducers have been utilized (see ANL-6596, p. 192). These efforts have been frustrated by the strong response of commercial transducers to the neutron-gamma radiation pulse. TREAT experience with transducers was recently reviewed. This review

⁷Boland, J., DeForest, R.O., Ivins, R.O., Kirn, F.S., Lawroski, H., Liimatainen, R.C., Sensitivity of Pressure Transducers to Transient Neutron and Gamma Radiation, Trans. Amer. Nucl. Soc., 5 (1), 186 (1962).

and a more general discussion of the effects of radiation on transducers⁸ have indicated that there is little hope at present of developing a truly radiation-resistant pressure transducer having adequate time response.

As an alternative, studies were undertaken to evaluate the response of pressure transducers located outside the reactor core at a distance from the autoclave containing the reactants. The technique consists of connecting the autoclave chamber to the transducer with high-pressure tubing so that only the autoclave need be in the flux in the core of the reactor. A problem with this arrangement is attenuation of the pressure signal in the connecting tubing. Out-of-pile experiments were, therefore, performed to determine the degree and nature of the attenuation.

Figure V-21

AUTOCLAVE-TRANSDUCER
TEST ASSEMBLY

<u>Component</u>	<u>Volume (cc)</u>
autoclave:	225
piping:	25
connecting tubing:	
5 in.	2
3 ft.	17
15 ft.	84
65 ft.	362
115 ft.	640

Figure V-21 is a sketch of the test assembly in which pressure pulses from metal-water reactions were simulated. To simulate the release of hydrogen over approximately a 100-msec time interval, a rapid flow of helium into the autoclave is accomplished by opening a solenoid valve. There is no pressure regulator on the helium supply cylinder, and the full tank pressure can be applied directly to the autoclave. Transducer A senses the pressure inside the autoclave, and transducer B measures the pressures transmitted by 1/4-in. OD by 0.03-in. thick wall connecting tubing of the following lengths: 5 in., 3 ft, 15 ft, 65 ft, and 115 ft. Various lengths of tubing were used to determine how well transducer B would track transducer A at various distances.

⁸Chapin, W.E., Hamman, D.J., Wyler, E.N., The Effect of Nuclear Radiation on Transducers, Radiation Effects Information Center, Battelle Memorial Institute, Columbus, Ohio, p. 23, REIC No. 25 (1963).

Figures V-22 through V-26 give the results obtained. The figures are taken from oscilloscope traces of the pressure versus time, as recorded on Polaroid film. A comparison of Figures V-22 and V-23 indicates that there is no observable attenuation of the signal at either 5 in. or 3 ft of separation. However, when the transducer is 15 ft from the autoclave as shown in Figure V-24, there is an obvious delay time; nevertheless, the transducer still satisfactorily records pressure-time events with the time scale used in TREAT experiments. Finally, at 65 and 115 ft (Figures V-25

Figure V-22
TRANSDUCER RESPONSE:
PRESSURE VS. TIME,
5-in SEPARATION OF AUTOCLAVE
AND OUTSIDE TRANSDUCER

108-7200

Figure V-23
TRANSDUCER RESPONSE:
PRESSURE VS. TIME,
3-ft SEPARATION OF AUTOCLAVE
AND OUTSIDE TRANSDUCER

108-7201

Figure V-24
TRANSDUCER RESPONSE:
PRESSURE VS. TIME,
15-ft SEPARATION OF AUTOCLAVE
AND OUTSIDE TRANSDUCER

108-7202

Figure V-25
TRANSDUCER RESPONSE:
PRESSURE VS. TIME,
65-ft SEPARATION OF AUTOCLAVE
AND OUTSIDE TRANSDUCER

108-7203

Figure V-26

TRANSDUCER RESPONSE:
PRESSURE VS. TIME:
115-ft SEPARATION OF AUTOCLAVE
AND OUTSIDE TRANSDUCER

108-7204

Figure V-27

DELAY IN PRESSURE SIGNAL
VS. SEPARATION

108-7205

and V-26), the output signal from the outer transducer differs significantly from the true pressure inside the autoclave.

Figure V-27 shows the measured delay times as a function of the distance between the transducer and the autoclave. The delay time is defined as the time required for the signal to reach 10% of the full scale output. If the compression wave is propagated down the 0.19-in. ID connecting tubing to the outer transducer at the normal acoustic velocity, which is 3,182 feet/sec in helium gas, the pressure pulse would travel 115 feet in 36 msec; after this time interval, the diaphragm on the pickup would sense the pressure. The observed delay time for the 115 ft separation was 180 msec, however, suggesting that there were viscosity and frictional effects. The increase in volume as the tubing was lengthened also caused increased time to attain full pressure in the apparatus; however, this factor does not detract from the significance of the tests.

Reliable pressure data should be obtainable from in-pile metal-water experiments when the transducer is removed completely from the reactor core (to distances of 3 to 15 ft from the autoclave), and only small delay times should be experienced. By removing the transducer from the center of the reactor core, not only the radiation effect but also a thermal effect is eliminated, that is, the separated transducer will be in a cool, constant-temperature zone and will not undergo a change in output as a result of being heated by the surrounding reactor core, the temperature of which is sometimes as high as 200°C. Explosions can also be tracked with a remote

transducer since the frequency response (as measured by the rise time, which is the time to go from 10 to 90% of full scale output) is much faster than the delay time.

It is planned to select a transducer with a range which matches the requirement of the experiment, in which there may be only a few psi pressure rise; for example, a 4-g aluminum-uranium pin having an anticipated 25% reaction will generate 1,243 cc (S.T.P.) of H_2 , which will produce a pressure rise at 27°C of about 120 psi in an autoclave with a free gas volume of 150 cc. Thus, to obtain a sensitive record, a transducer with a range of 0 to 200 psi would be used, allowing a factor of about two for safety. The pressure ratings of autoclaves range as high as 4000 psi. Since strain gage transducers are generally rated at only twice the measurement range, the pressure transducer would be the weakest part of the assembly. If the pressure rating of the transducer fails to meet safety requirements, secondary containment will be provided for the transducer.

B. Metal Oxidation and Ignition Kinetics (L. Baker)

1. Plutonium Oxidation and Ignition Studies (J.G. Schnizlein and D.F. Fischer)

Appraisal of the pyrophoricity hazards associated with the handling of plutonium requires detailed knowledge concerning the oxidation and ignition characteristics of plutonium and plutonium alloys. Studies of the isothermal oxidation of plutonium between 140 and 450°C reported in ANL-6687, p. 171, have shown that the reaction is initially parabolic and subsequently becomes linear (paralinear rate law). It was also shown that there is a marked change in mechanism between 300 and 400°C. The mechanism change is reflected in the ignition behavior of plutonium (ANL-6725, p. 207). For samples of high specific area ($>5 \text{ cm}^2/\text{g}$), the ignition temperature is about 300°C, and for bulk material ($<1 \text{ cm}^2/\text{g}$), it is about 500°C.

This report includes information on (a) isothermal oxidation in the high-temperature regime, (b) effect of preoxidation in the high-temperature regime on oxidation at lower temperatures, (c) studies with ultrapure plutonium produced by electrolysis, (d) isothermal oxidation of a plutonium-2 a/o aluminum alloy which does not show ignition in the low-temperature regime, (e) influence of moisture on oxidation behavior of plutonium below 200°C, (f) effect of moisture on ignition temperatures, (g) ignition behavior of a series of plutonium alloys containing 2 a/o additives, and (h) ignition behavior of certain ternary uranium-plutonium alloys.

a. Isothermal Oxidation Kinetics in the High-Temperature Regime

Previous oxidation data for plutonium (ANL-6687, p. 171) established that a paralinear rate law was followed with activation energies

of 32 kcal/mole for the initial parabolic rate and 16 kcal/mole for the subsequent linear rate over the temperature range 140 to 300°C. Above 300°C, it appeared that a different process was involved which resulted in a minimum rate at 400°C. Previous experiments were performed at temperatures up to 480°C before self-heating became troublesome. Further knowledge of the kinetics of oxidation in the high-temperature regime was needed before a mathematical description of the ignition of plutonium and its alloys near 500°C could be achieved. An attempt was therefore made to extend the oxidation study to a higher temperature range while minimizing self-heating by use of a heat sink.

The heat sink was made in the form of two 5/8 x 1/4 x 1/8-in. thick stainless steel plates clamped on the sample which was in the form of a 1-cm cube. With pure plutonium and this heat sink, oxidations up to 557°C have been undertaken satisfactorily with only modest self-heating. A few experiments were performed at temperatures at which previous experiments were done which proved that the heat sink did not influence the oxidation.

The parabolic and linear rate constants for the high-temperature regime are presented in Table V-5. Figures V-28 and V-29 are

Table V-5

PLUTONIUM ISOTHERMAL OXIDATIONS AT HIGH TEMPERATURES

(In oxygen, except one run which was in air)

Temperature (°C)	Heat Sink Used	Parabolic Rate Const. [($\mu\text{g O}_2/\text{cm}^2$) ² /min] ($\times 10^4$)	Linear Rate Const. [($\mu\text{g O}_2/\text{cm}^2$)/min]
349	Yes	-	445
345	No	-	500
421	No	35.6	48.8
441	Yes	64.5	65.0
461	Yes	158	116
462	Yes	144	96
487	Yes	625	322
489	Yes	489 ^a	431 ^a
525	Yes	1467	368
557	Yes	4970	1188

^aIn air.

Figure V-28

INITIAL
PARABOLIC OXIDATION DATA
FOR PLUTONIUM -
HIGH TEMPERATURE REGIME

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Figure V-29

LINEAR OXIDATION DATA
FOR PLUTONIUM -
HIGH TEMPERATURE REGIME

108-7206

Arrhenius plots of the high-temperature regime. The initial parabolic oxidation process in the high-temperature regime (see Figure V-28) appears to have the same activation energy (32 kcal/mole) as the low-temperature regime. The subsequent linear process in the high-temperature regime, however, has a higher activation energy (29 kcal/mole) than does the low-temperature regime (16 kcal/mole).

b. Effect of Preoxidation at 440°C on the Isothermal Oxidation of Plutonium at Lower Temperatures

Previous isothermal oxidation studies have shown that a change of oxidation mechanism occurs for plutonium between 300 and 400°C to produce a minimum oxidation rate at approximately 400°C (see ANL-6687, p. 171). It has been proposed that above 400°C a second protective film is formed which is composed of the diphasic oxide (having an oxygen to plutonium ratio between 1.7 and 1.98) which was identified by Chikalla⁹ et al. in phase diagram studies. By measurements of electrical resistivity and thermal expansion of plutonium oxide they indicated that low-temperature transitions occur at temperatures ranging from 280 to 320°C. Perhaps if this oxide could be produced beforehand, its protective nature would cause decreased oxidation rates in the low-temperature regime.

An experiment was performed to test this hypothesis. A high-purity plutonium sample was oxidized at 440°C until 11,000 $\mu\text{g O}_2/\text{cm}^2$ was consumed and oxidation was proceeding at a linear rate of 63.0 $\mu\text{g}/(\text{cm}^2)(\text{min})$. Then, without removal of the oxygen, the temperature was decreased and controlled at a new lower temperature. After a new linear rate was determined, the temperature was reduced again. The linear rate observed at each temperature is compared in Table V-6 with the rate expected from previous data for the low-temperature regime. At 318°C, the rate was only 1.7% of that expected. These data are also compared with previously determined data on the Arrhenius plot in Figure V-30. It appears that if the preoxidation is performed, the high-temperature process can occur at temperatures lower than 400°C. Below 250°C, the linear oxidation rate was still considerably lower than in the absence of pre-oxidation, but when the sample was cooled to room temperature overnight and then reheated, a higher rate was again observed.

Similar experiments need to be performed to determine the reliability of these data and whether the same effect is obtained in air. The possibility of making plutonium more resistant to room-temperature oxidation by such a preoxidation would offer advantages in storage.

⁹Chikalla, T.D., McNeilly, C.E., and Skavdahl, R.E., The Plutonium-Oxygen System, HW-74802, 1962.

Table V-6

EFFECT OF PREOXIDATION AT 440°C
ON SUBSEQUENT OXIDATION OF PLUTONIUM

Temperature (°C)	Linear Rate Constant [$\mu\text{g O}_2 / (\text{cm}^2)(\text{min})$]	
	Expected from Previous Data ^a	After Preoxidation at 440°C
438	63.0	--b
400	21	18.5
346	118	3.44
318	94	1.60
301	65	1.28
278	37	1.20
257	21	1.10
229	9.0	0.27
200	3.5	0.18
149	0.45	0.05

^aANL-6687, p. 171.

^bThe observed rate of $63 \mu\text{g O}_2 / (\text{cm}^2)(\text{min})$ during preoxidation at this temperature is in excellent agreement with previously determined oxidation data.

Figure V-30
EFFECT OF PREOXIDATION
IN HIGH-TEMPERATURE REGIME
ON PLUTONIUM OXIDATION

108-7207

c. Oxidation of High-Purity Plutonium Produced by Electrolysis

Plutonium of extremely high purity is produced by electrolysis of a fused salt mixture. A few samples in the form of 9-mm cubes were obtained from the Metallurgy Division* for comparison of their oxidation behavior with that of the unalloyed plutonium from Hanford used in the studies reported in the preceding section. Impurity contents are presented in Table V-7. The

Table V-7

IMPURITIES IN PLUTONIUM MATERIALS

	Plutonium from Alloy Program, Hanford (ppm)	Electrolytic High-Purity Plutonium from Metallurgy Div., ANL (ppm)	
		CM 34	CM 33
Mg	180	- ^a	- ^a
Fe	198	40	20
Ca	100	- ^a	- ^a
Cu	50	- ^a	- ^a
Pb	50	- ^a	- ^a
Ni	23	20	15
Mn	20	1	1
Ag	10	- ^a	- ^a
Al	-	5	5
Cr	5	20	15
Sn	3	- ^a	- ^a
Si	2	20 ^b	12 ^b
Am	-	47 ^b	29 ^b
U	-	26 ^b	18 ^b
C	260 ^b	18 ^b	20 ^b
O ₂	110 ^b	4 ^b	6 ^b
N ₂	105 ^b	16 ^b	10 ^b
H ₂	3 ^b	1.2 ^b	1.4 ^b
Total	1119	218	152

^aBelow the limits of spectographic detection.

^bChemical analyses instead of spectographic.

*Through the courtesy of G.B. O'Keefe, Metallurgy Division, Argonne National Laboratory.

electrolytic plutonium is purer by one order of magnitude than the Hanford material. The electrolytic plutonium is 99.84 percent pure on an atomic basis.

Isothermal oxidations were performed at 151, 190, 192, 240, 300 and 438°C, and results showed the same characteristic behavior as was observed with unalloyed Hanford plutonium. All rate constants obtained were within the limits of deviations of the previous data.

d. Oxidation of Plutonium-2 a/o Aluminum Alloy

A nominal 2 a/o aluminum alloy of plutonium showed ignition temperatures approximately 70 degrees higher than the upper regime of ignition of pure plutonium (500°C) and showed no indication of a low regime of ignition (see subsection g). Because this is the most outstanding effect observed for any alloy additive, the aluminum alloy was chosen for some isothermal oxidation studies. The results might add to the understanding of the change of kinetics of oxidation between 300 and 420°C because 2 a/o aluminum stabilizes the delta phase of plutonium. The phase diagrams by investigators from the Soviet Union¹⁰ and from Los Alamos¹¹ indicate delta phase stability from 290 through 520°C and from 160 through 520°C, respectively.

Isothermal oxidations of 5-mm cubes have been performed at temperatures from 150 through 588°C on the thermobalance (see ANL-6413, p. 172). The results obtained in a few runs in air were not different from those obtained in oxygen. In general, a parabolic behavior was observed which was similar to that of unalloyed plutonium, but at all temperatures the rates for the alloy were lower. Oxidation data for plutonium-2 a/o aluminum are compared with data for unalloyed plutonium at a few selected temperatures in Figure V-31. The data for the initial portion of the reaction could be fitted to a cubic rate law as well as to a parabolic law. Parabolic, cubic, and subsequent linear rate constants obtained are presented in Table V-8. The parabolic rate constants for the plutonium-2 a/o aluminum alloy are compared with those for unalloyed plutonium in Figure V-32, while the linear constants for the alloyed and unalloyed metal are compared in Figure V-33.

In the high temperature region (above 420°C), the parabolic rate constants for the alloy are very similar to those for unalloyed plutonium. The linear rate constants are about a factor of two lower, but indicate the

¹⁰Bochvar, A.A. et al., Interaction of Plutonium and Other Metals in Connection with their Arrangement in Mendeleev's Periodic Table, Geneva Conf. 6, 184 (1958).

¹¹Schonfeld, F.W., "Plutonium Phase Diagrams," The Metal Plutonium, U. of Chicago Press (1961), p. 255.

Figure V-31

OXIDATION DATA FOR PLUTONIUM
AND PLUTONIUM-2 a/o
ALUMINUM IN OXYGEN

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Table V-8

OXIDATION DATA FOR 2 a/o ALUMINUM-PLUTONIUM ALLOY

($\mu\text{g O}_2/\text{cm}^2$)ⁿ/min

Run Number ^a	Temp. (°C)	Initial Oxidation		Subsequent Linear Rate Constant (n = 1)
		Parabolic Rate Constant (n = 2)	Cubic Rate Constant (n = 3)	
B-15	150	0.35 x 10 ⁴	3.94 x 10 ⁶	- ^b
B-7	188	0.38 x 10 ⁴	4.18 x 10 ⁶	- ^b
B-14	190	0.69 x 10 ⁴	11.4 x 10 ⁶	1.45
B-8	238	0.22 x 10 ⁴	3.0 x 10 ⁶	0.68
B-9	283	2.65 x 10 ⁴	19.4 x 10 ⁶	2.25
B-10	334	7.08 x 10 ⁴	260. x 10 ⁶	8.2
B-11	421	33.5 x 10 ⁴	4570. x 10 ⁶	22.8
BH-12	490	237. x 10 ⁴	60,000. x 10 ⁶	98.5
BH-22-A	500	265. x 10 ⁴	50,000. x 10 ⁶	146.
BH-16	539	1,764. x 10 ⁴	535,000. x 10 ⁶	333.
BH-13	572	IGNITION		
BH-23-A	588	4,726. x 10 ⁴	15,630,000. x 10 ⁶	1,555.

^aRuns performed with a heat sink are indicated by H in run number designation. Runs performed in air are indicated by A. All other runs were performed in oxygen.

^bNo meaningful data available. Total weight gain less than 1 mg, approaching the limit of sensitivity of the balance.

Figure V-32

PARABOLIC OXIDATION DATA FOR
PLUTONIUM AND 2 a/o
ALUMINUM-PLUTONIUM ALLOY

108-6921 Rev.

Figure V-33

LINEAR OXIDATION DATA FOR
PLUTONIUM AND 2 a/o
ALUMINUM-PLUTONIUM ALLOY

108-6923 Rev.

same activation energy. This is consistent with the observed ignition temperatures being approximately 70 degrees higher than the high temperature regime for unalloyed plutonium.

At lower temperatures (below 420°C), both parabolic and linear rates are very much lower and indicate different activation energies than for unalloyed plutonium. The activation energy for the parabolic process is about 14 kcal/mole and for the linear process about 13 kcal/mole.

An Arrhenius plot for the cubic rate constants is presented in Figure V-34. The rates for the two runs for unalloyed plutonium for which

Figure V-34

CUBIC OXIDATION DATA FOR PLUTONIUM AND 2 a/o
ALUMINUM-PLUTONIUM ALLOY

108-7208

cubic rate constants were obtained compare favorably. The results in Figure V-30 indicated that it was impossible to fit the data to a single activation energy; a break occurred at approximately 420°C. An activation energy of 52.7 kcal/mole would be indicated in the high temperature region and an activation energy of 22.8 kcal/mole in the low temperature region.

It is concluded that addition of aluminum to plutonium improves the oxidation resistance at all temperatures.

e. Effect of Moisture on the Oxidation of Plutonium

Numerous investigations^{12 16} have indicated pronounced increases in oxidation rate of plutonium in the presence of moisture at temperatures below 100°C. Comparison of the low temperature data obtained under moist conditions with those obtained under dry conditions and the extrapolation of higher temperature (140 to 300°C) data (ANL-6687, page 171) shows that the linear rate constants are increased 100- to 1000-fold by saturation of the oxidizing atmosphere with moisture. In a very recent publication Sachmann¹⁶ showed that the oxidation rate at 25°C in moist argon (95% relative humidity, RH) is between 4 and 25 times that in moist air. It was concluded that air oxidation produces a protective film and inhibits the reaction with moisture.

Results of experiments performed here recently with oxygen or air containing less than 5 ppm and up to 500 ppm moisture showed no discernible difference in oxidation kinetics above 240°C and compared favorably with data from experiments performed by Dempsey¹⁷ in air with 55% RH at 205°C. This leads to the conclusion that moisture has little or no effect at temperatures above 200°C.

In contrast, at 190°C and 150°C, marked effects upon isothermal oxidation of plutonium were observed with water contents of approximately 20, 180, and 510 ppm.

Figure V-35 illustrates the oxidation behavior of plutonium in oxygen at 190°C with four levels of moisture content, 510, 180, 21, and less than 5 ppm. It is now believed that the high oxidation rate, $\sim 20 \mu\text{g}/(\text{cm}^2)$ (min), previously called a third stage in the oxidation between 100 and 200°C (see ANL-6687, p. 171), is attributable to moisture. It is noteworthy that this high rate can be produced by a moisture content as low as 180 ppm.

¹²Kolodney, M., Protection of Plutonium Against Atmospheric Oxidation, LA-314, June 1945.

¹³Waber, J.T., Proceedings 2nd International Conf. on Peaceful Use of Atomic Energy 6, 204, Geneva (1958).

¹⁴Sachmann, J.F., Plutonium 1960, p. 222 (Cleaver Hume Press, London 1961).

¹⁵Pellissier-Tanon, Private Communication, A Commissariat a L' Energie Atomique, Paris, July 18, 1963.

¹⁶Sachmann, J.F., Nature 197, 587 (1963).

¹⁷Dempsey, E. and Kay, A.E., J. Inst. of Metals 86, 379 (1958).

Figure V-35

EFFECT OF MOISTURE
ON OXIDATION OF PLUTONIUM
AT 190°C IN OXYGEN

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Figure V-36

EFFECT OF CHANGE OF MOISTURE CONCENTRATION DURING OXIDATION
OF PLUTONIUM AT 190°C IN OXYGEN

108-7209

Figure V-36 illustrates the behavior when the moisture content was changed during the course of an oxidation. The oxidation rate increased quickly from 1.2 to 1.5 $\mu\text{g}/(\text{cm}^2)(\text{min})$ when the moisture content was increased from 21 ppm to 180 ppm; the oxidation rate increased to 3.4 with 510 ppm moisture content and decreased to 0.71 with 21 ppm moisture content.

It is concluded that below 200°C the presence of moisture causes partial breakdown of the protective layer of oxide formed in oxygen and a resulting increase in the oxidation rate which is higher than that which is obtained in the absence of moisture. The near absence of temperature dependence of the high oxidation rate of $\sim 20 \mu\text{g O}_2/(\text{cm}^2)(\text{min})$ may be a result of a balance between the formation of a protective layer by the oxygen reaction and the destruction of the protective layer by reaction with water vapor.

f. Effect of Moisture on Ignition Behavior of Plutonium and Plutonium-2 a/o Aluminum Alloy

To appraise the effect of moisture on the ignition of plutonium and its alloys, burning curves have been run in air saturated with moisture at room temperature ($>20,000$ ppm water). Isothermal studies (previous section) have shown that the presence of moisture increases the linear rate of oxidation at temperatures below 200°C, but has negligible effects at higher temperatures.

Although the burning curves indicate that ignition occurs in slightly shorter periods of time in moist air, the graphic method of defining ignition temperatures gives essentially identical ignition temperatures for experiments carried out in dry air as in moist air. These temperatures are tabulated below:

		Ignition Temperature	
		In Dry Air (°C)	In Wet Air (°C)
Pu	5-mm cube	524	522
Pu	0.11-mm foil	283	282
Pu-2 a/o Al	5-mm cube	585, 590	569

g. Plutonium Alloy Ignition Studies

Ignition data for plutonium samples ranging from 5-mm cubes to 0.1-mm thick foils in air and oxygen (see ANL-6725, p. 207) have shown the existence of two regimes of ignition. Samples with high specific area ignite at about 300°C, and bulk materials (5-mm cubes) at about 500°C.

A series of binary alloys of plutonium containing 2 a/o of various elements were prepared at Hanford.* Some of the elements were chosen because they are typical impurities; other elements were chosen to study the effect of valence. Additives of aluminum, carbon, cerium, chromium, cobalt, iron, manganese, nickel, and uranium were used to form 5-mm cubes of plutonium alloy and such foils as it was possible to fabricate. For one alloy, samples with thicknesses down to 0.07 mm (specific area 17.2 cm²/g) were available, whereas for one alloy only 5-mm cubes (specific area, 0.65 cm²/g) and foil 0.89 mm thick (specific area, 1.9 cm²/g) could be produced.

Burning curve and shielded ignition experiments were performed in both air and oxygen for most foil samples. In the burning curve experiment, the specimen is supported on a thermocouple and heated at a uniform rate (usually 10 deg/min) in a flowing oxidizing gas until ignition occurs. The ignition temperature is determined as the intersection of tangents to the preignition heating curve and the post-ignition self-heating curve. In the shielded ignition experiment, the sample is heated to a preset temperature in a protective atmosphere of helium. The oxidizing gas is then admitted suddenly, and it is determined whether or not ignition occurs. The ignition temperature is given as the range between the highest temperature at which ignition did not occur and the lowest temperature at which ignition did occur.

Results of ignition temperature determinations by both methods for various alloys and foil thicknesses are presented in Table V-9. Much of the data for cubes have previously been reported in ANL-6648, p. 192, but are repeated here for completeness. Some data for foils were previously presented in ANL-6183, p. 135. Ignition temperatures were plotted as a function of specific area, and a composite trace of the behavior in air for the various additives is presented in Figure V-37. Because the ignition temperatures fall in two regimes (consistent with two regimes observed in the isothermal oxidation), it is necessary to consider the influence of an additive in each regime and on the transition region.

In the high temperature regime the influence of the additives (using the behavior of pure plutonium as the standard for comparison) was as follows:

- (1) Increased resistance to ignition and oxidation: aluminum and silicon.
- (2) The same ignition and oxidation behavior as plutonium: nickel, chromium, uranium, cerium, and iron.

* Preparations were under the supervision of R.R. King, P.G. Palmer, T. Nelson and O.J. Wick, General Electric Co., Hanford Atomic Products Division, Richland, Washington.

Table V-9

IGNITION DATA FOR PLUTONIUM ALLOYS

Alloy	Foil Thickness (mm)	Specific Area (sq cm/g)	Burning Curve Ignition Temperature (°C)		Shielded Ignition ^a Temperature (°C)	
			Air	O ₂	Air	O ₂
Al	5 (cube)	0.79	588,590	576		
	0.26	4.4	554	555		350-388
	0.26	4.8	557	546	250-388	375-407
Ce	5 (cube)	0.64	510	485		
	0.96	1.6	488	478	398-436	406-442
	0.11	11.0	478	481	325-351	299-342
C	5 (cube)	0.65	498	486		
	5 x 5.6 dia. rod	0.63	295,459	208,447,455		
	0.97	1.6	474	478	401-440	287-328
	0.28	4.1				270-300
	0.16	7.8	469	466	386-428	275-309
Co	5 (cube)	0.67	474	462		
	0.93	1.7	456	465	410-477	380-413
	0.23	5.2	465	462	346-389	340-390
Cr		0.65				
	5 (cube)	0.65	512,514	498,507		
	1.01	1.70	513	503	325-375	
	0.15	7.5	575	527	380-421	268-380
	0.08	14.5	No Ignition	517	243-292	
	0.21	5.8	380	No Ign, 320		275-307
Fe	5 (cube)	0.65	548	515		
	0.85	1.71	596	266		
	0.39	3.33	589	567	327-377	
	0.21	5.7	602	289	271-315	243-287
			No Ignition			
	0.11	11.5	352	253	246-288	
	5 x 5.7 dia. rod	0.60	476,485	520		
			490,516			
	0.26	4.88	372	330		
	0.25	5.16	358	310		
	0.22	5.66				307-348
	0.19	6.60	550	532,537,539		

(Contd.)

Table V-9 (Continued)

IGNITION DATA FOR PLUTONIUM ALLOYS

Alloy	Foil Thickness (mm)	Specific Area (sq cm/g)	Burning Curve Ignition Temperature (°C)		Shielded Ignition ^a Temperature (°C)	
			Air	O ₂	Air	O ₂
Mn	5 (cube)	0.66	499	477		
	1.0	1.6	496	483	362-406	249-294
	0.53	2.7	293	320	221-258	240-288
	0.24	5.3	365 ^b , 598 ^b	293	257-288	276-300
	0.21	5.6	330	247		214-230
	0.10	12.1	No Ignition ^c	289	282-317	242-278
	0.07	17.2	No Ignition ^c	279	251-258	251-282
Ni	5 (cube)	0.66	490-529	468		
		0.64		489-509		
	1.05	1.55	486	470	420-263	367-422
	0.24	5.1	325	316		297-317
	0.24	5.4	No Ignition ^d	288		
	0.25	5.4	302			
	0.15	7.6	No Ignition	467	282-335	238-282
Si	5 (cube)	0.62	544	537		
	5 (cube)	0.65	548	537		
	5 (cube)	0.67	548	525	462-511	412-467
	5 (cube)	0.72	553	540		
	0.95	1.67	528	515		
	0.28	4.29	202, 286, 295	318		
	0.20	5.85	537	310	281-325	265-297
U	5 (cube)	0.65	510, 513	490		
	0.89	1.9	252, 550	242	(e)-443	(e)-233

^aIndicated as the highest temperature at which ignition did not occur and the lowest temperature at which ignition did occur.

^bThis particular foil was observed to ignite at 598°C in air with the usual self heating. However, when the experiment was repeated, ignition was observed in the region of 365°C but without the usual temperature rise.

^cSample completely oxidized or disintegrated before ignition occurred.

^dThere was a thermal spike of 150 degrees at 309°C with no visual ignition. Another spike of 80 degrees was observed at 610°C with no visual ignition.

^eInsufficient sample to determine lower limit of shielded ignition range.

Figure V-37

EFFECT OF ADDITIVES ON IGNITION BEHAVIOR IN AIR
OF PLUTONIUM FOILS

Concentration of each additive is 2 a/o

- (3) Decreased resistance to ignition and oxidation: cobalt, carbon, and manganese.

In the low temperature regime, the influence of the additives was as follows:

- (1) Increased resistance to ignition and oxidation: aluminum, cerium, carbon, cobalt, manganese, and possibly chromium.
- (2) The same ignition and oxidation behavior as plutonium: nickel and silicon.
- (3) Decreased resistance to ignition and oxidation: iron and uranium.

The transition from the high regime to the low regime does not occur in air for alloys of aluminum, cerium, carbon, and cobalt for specimens with specific areas of up to approximately 10 cm²/g. The addition of silicon to plutonium causes a shift of the transition from a specific area of 2 cm²/g for pure plutonium to 4 cm²/g for the alloy. Additions of nickel, manganese, and uranium to plutonium caused no change in the transition region, which occurs at 2 cm²/g for pure plutonium.

h. Uranium-Plutonium Alloy Ignition Studies

In order to obtain nuclear data, zero power critical experiments with U-Pu alloys are being planned by the Reactor Engineering Division. Alloys having an atom ratio of U^{238} to Pu^{239} of about 2:1 are preferred to avoid a positive Doppler temperature coefficient. Unfortunately, previous experience indicates that alloys in this composition range are extremely pyrophoric.

An alloy which has been shown to be relatively nonpyrophoric is one containing an additive of 1.5 w/o iron. The French have conducted some studies on a 73.5 w/o U-25 w/o Pu-1.5 w/o Fe alloy based on a U.S. Patent.¹⁸ In these studies, samples were exposed to moist air at 25°C for extended periods of time. The ternary alloy was more resistant to oxidation than binary alloys containing only plutonium and uranium. The French plan to use the fuel in their Mazurka facility. Under a plan by Euratom, such a fuel might also be used for Karlsruhe experiments.

A program has been proposed¹⁹ to develop a nonpyrophoric U-Pu fuel, and tests of ternary alloys containing Al, C, Cu, Mo, and Zr as well as tests of ternary iron alloy are underway.

Speculations as to how these additives might influence the U-Pu system so as to avoid the formation of the zeta phase (U-Pu), which is thought to cause the crumbling and pyrophoricity, are as follows:

- (a) Iron should complex enough plutonium to form $(Pu, U)_6Fe$ and move from the zeta phase region into the region of alpha uranium with less than 11 a/o Pu in solution and inclusions of $(Pu, U)_6Fe$.
- (b) Zirconium might behave similarly to form Pu_6Zr , (U_6Zr is not formed, but UZr_2 is formed) and in addition the delta plutonium field is enlarged.
- (c) Molybdenum forms no compounds with plutonium but stabilizes gamma uranium (U_2Mo stable to 565°C) which is in complete solution with delta plutonium.
- (d) Copper forms UCu_5 and probably $PuCu_5$. It has also been shown to decrease uranium oxidation at temperatures above 450°C.
- (e) Aluminum forms Pu_3Al and stabilizes delta plutonium (below room temperature at 8 a/o Pu). The compound UAl_2 is also produced. Aluminum has been shown to cause decreased oxidation of plutonium in the low temperature regime (up to

¹⁸ U.S. Patent 2,902,362, Sept. 1, 1959.

¹⁹ Metallurgy Division Annual Report for 1963, ANL-6868 (in preparation).

300°C), and increased oxidation of uranium in the high temperature regime (above 450°C).

Burning curve experiments, wherein the sample (6 x 6 mm-dia. right cylinder) is heated in flowing dry air (1200 cc/min) at a programmed rate of 10 degrees per min have been performed. The temperature of the sample, indicated by a thermocouple in a hole in the sample or in contact with the sample, is recorded. As the sample temperature increases, the heat of oxidation causes the temperature of the sample to exceed the furnace temperature slightly until a sharp increase in the temperature of the sample occurs at ignition. Ignition is dependent upon the rate of heat generated by oxidation and the rate of heat loss from the sample, which in turn is dependent upon the temperature of the surroundings. In these experiments, the surrounding temperature is defined by the furnace which is programmed to increase at 10 degrees per minute. The ignition temperature in these experiments is defined by the intersection of two straight lines through the two branches of the curve.

Time-temperature traces for ternary alloys of uranium-30 a/o plutonium containing 6 a/o aluminum, copper, carbon, or zirconium are compared with traces for uranium-30 a/o plutonium binary alloy and plutonium and uranium in Figure V-38. The curves indicate that these ternary

Figure V-38

BURNING CURVES FOR
U-30 Pu, U-30 Pu-6Al, U-30 Pu-6Cu, U-30 Pu-6C, U-30 Pu-6 Zr, Pu, and U
 (numbers are in atom percent)
 (6 x 6 mm dia. right cylinders in dry air)

108-7210

alloys have undesirable oxidation behavior. The ternary alloys containing aluminum and copper ignite in 18 and 19.5 min at 213 and 211°C, respectively. The binary uranium-plutonium alloy, which ignited in 13 min at 157°C may be slightly more susceptible to ignition because of possible porosity and increased surface area. The ternary alloy containing carbon shows a marked temperature rise (from 250 to 550°C) at 21 min and is considered to ignite at 674°C in 51 minutes. The zirconium ternary alloy does not ignite (although heated through 800°C) but undergoes marked self-heating from 250 to 500°C at 22 min that is similar to the self-heating for the carbon alloy.

Figure V-39

BURNING CURVES FOR
U-30 a/o Pu-6 a/o Fe, U-30 a/o Pu-6 a/o Mo, Pu, U, and U-30 a/o Pu
 (6 x 6 mm dia. right cylinders in dry air)

108-7211

Burning curves in dry air for the two ternary alloys which show promise of being less pyrophoric alloys, contain iron and molybdenum and are compared with curves for plutonium, uranium and U-30 a/o Pu binary alloy in Figure V-39. The iron alloy did not ignite although heated to 820°C. It shows slightly greater self-heating than pure plutonium just above 300°C and inflections at 585°C and 705°C. These inflections probably correspond to transformation and melting points which were reported by the French at 590°C and 680°C for a uranium-25 a/o plutonium-6 a/o iron alloy. The molybdenum alloy undergoes slightly less self-heating than the iron alloy from 350°C to 603°C at which temperature the molybdenum alloy ignites.

Perhaps additional molybdenum content or heat treating to stabilize gamma uranium would improve the ignition behavior of the alloy. Pure plutonium ignites at 524°C and uranium (from which the alloys were made) at 617°C.

Figure V-40

BURNING CURVES FOR U-Pu-Mo AND U-Pu-Fe ALLOYS
IN WET AND DRY AIR

(6 x 6-mm dia. right cylinders)

108-7212

To appraise the effect of moisture on the ignition behavior of the alloys, burning curve oxidation experiments were also performed in wet air (saturated at room temperature to contain greater than 20,000 ppm moisture) on three ternary alloys. The time-temperature traces for the U-30 a/o Pu-6 a/o Mo and U-30 a/o Pu-6 a/o Fe alloys in wet and dry air are reproduced in Figure V-40. The ternary alloy containing molybdenum ignites at essentially the same temperature whether in wet or dry air but undergoes increased oxidation rates in wet air near 200°C, where a small amount of self-heating is observed. After ignition, the reaction sustains a higher temperature in wet air than in dry air. The ternary alloy containing iron shows a much greater self-heating near 300°C in wet air than in dry air. The reaction continues at a sufficiently high rate that the continued increase of furnace temperature soon causes ignition. Although a well defined ignition temperature is not possible from the burning curve for the iron ternary alloy in wet air, the intersection of extensions of the two branches (immediately after ignition and prior to the marked self-heating) occurs at 480°C after 38 minutes.

A slight thermal arrest is observed at 455°C during the self-heating of the ternary alloy containing iron in wet air, which may be an indication of another transformation in addition to the one observed at 545°C (also observed in dry air at 585°C). In dry air, it should be noted that the maximum temperature of the hump at about 30 minutes is at the same temperature.

Figure V-41
BURNING CURVES FOR U-30 a/o
Pu-6 a/o Al IN WET AND DRY AIR

(6 x 6-mm dia. right cylinders)

The U-Pu-Al ternary alloy was also run, as representatives of the more readily ignitable ternary alloys, in wet air. The time-temperature traces in wet and in dry air, which are compared in Figure V-41, indicate that the ignition temperatures are nearly the same, 206°C in wet air and 213°C in dry air.

Ignition temperatures, times to ignition, and maximum burning temperatures of the uranium-plutonium alloys studied in wet and dry air are summarized in Table V-10.

The extent of reaction of the samples during the burning curve experiments is shown in Figure V-42. The extent of reaction is based on the weight gain of the specimen, assuming formation of U_3O_8 , PuO_2 and the most probable additive oxide. The data further illustrate the relatively low reactivity of the iron and the molybdenum ternary alloys with dry air. Comparisons of the extent of reaction during the burning curve experiments for the molybdenum and iron ternaries in wet and dry air are shown in Figure V-43. These data further indicate that the oxidation behavior of the molybdenum ternary in wet air is better than that of the iron ternary. The lowest extent of reaction, 0.1 percent, indicated in the figure corresponds to approximately 1 micron penetration.

Table V-10

IGNITION CHARACTERISTICS OF CERTAIN URANIUM-PLUTONIUM ALLOYS

(30 atom percent Pu, 6 atom percent other element, and balance U)

(6 mm by 6 mm right cylinders in 1200 cc/min gas flow)

<u>Alloy</u>	<u>Time^a (min)</u>	<u>Ignition Temp. (°C)</u>	<u>Max. Burning Temp. (°C)</u>
<u>In air dried to contain less than 5 ppm moisture</u>			
U	55	716	1400
Pu	45	524	990
U-Pu	13	157	820
U-Pu-Al	18	213	770
U-Pu-Cu	19.5	211	890
U-Pu-C	51	674 ^b	905
U-Pu-Mo	54	603	950
U-Pu-Zr	-	no ignition to 820 ^c	-
U-Pu-Fe	-	no ignition to 820 ^d	-
<u>In air saturated at room temperature to contain >20,000 ppm moisture</u>			
U-Pu-Al	16	206	820
U-Pu-Fe	38	480 ^e	880
U-Pu-Mo	54	603	930

^aTime of heating at 10°/min prior to the occurrence of ignition.^bSelf-heats from 250 to 550°C at 21 min.^cSelf-heats from 250 to 500°C at 22 min.^dSlight self-heating from 350 to 450°C at 27 min.^eMarked self-heating from 300 to 525°C at 27 min.

Figure V-42

EXTENT OF REACTION DURING BURNING CURVES. 6 mm BY 6 mm RIGHT CYLINDERS IN DRY AIR. TERNARY URANIUM ALLOYS CONTAINING 30 a/o Pu AND 6 a/o OTHER ELEMENT

(Extent of reaction is based on weight gain of specimen, assuming formation of U_3O_8 , PuO_2 , and most probable additive oxide.)

108-7214

Of the alloys tested, the U-Pu-Fe and U-Pu-Mo show the least susceptibility to ignition. The 6 a/o iron ternary is least apt to ignite in dry air when subjected to a uniform heating rate up to 800°C. However, in wet air increased reaction above 300°C resulted in ignition at about 480°C. The 6 a/o molybdenum alloy ignited sharply at 600°C in either wet or dry air. Their behavior, when suddenly exposed to an oxidizing atmosphere at a temperature above 300°C, has not been determined. It must be recognized that increasing the specific area (area-to-mass ratio), as would occur if a sample crumbled, would make the material much more susceptible to ignition.

Because the mechanical properties of the ternary alloys appear to be dependent on the method of fabrication, further ignition experiments will be postponed until the method of fabrication has been selected.

Figure V-43

EXTENT OF REACTION DURING BURNING CURVE EXPERIMENTS
FOR U-Pu-Mo AND U-Pu-Fe IN WET AND DRY AIR

(Extent of reaction is based on weight gain of specimen, assuming formation of U_3O_8 , PuO_2 , and most probable additive oxide.)

108-7215

2. Thermal Conductivity of Metal Powders
 (D. Swift, P. Krause)

An investigation of the thermal conductivity of metal powders has been initiated to better understand powder ignition phenomena. The increased use of reactive metal powders in metallurgical processes has increased the importance of understanding the mechanism of air ignition. Previous ignition studies with uranium,²⁰ zirconium (ANL-6569, p. 145), and uranium monocarbide powders (ANL-6379, p. 192) have been reported. The results of the uranium experiments have been interpreted in terms of the Frank-Kamenetskii theory of thermal explosion.²⁰ This theory defines a criterion for ignition in terms of the geometry of the system, the rate and heat of reaction, and the thermal conductivity. It is thus desirable to know how thermal conductivity of powder depends on particle size, temperature, and the extent of oxidation on the surface of the particles. The effect of pressure is important in determining the contribution of gas and solid to the

²⁰ Tetenbaum, M., Mishler, L., and Schnizlein, G., Nuclear Sci. and Eng. 14, 230 (1962).

overall conductivity. Experiments performed thus far have included a preliminary series with nickel powder and studies with three sieved fractions of spherical uranium powders.

a. Experimental

A number of methods are described in the literature to determine thermal conductivity; some are absolute methods and others comparative. Some of these methods require elaborate insulation or careful placement of thermocouples. The transient line source method was chosen for this investigation because it is a rapid, absolute method, which is suitable for measuring powder conductivities at varying temperatures and pressures. This method makes use of the fact that the rate at which heat is conducted away from the line source is a function of the thermal properties of the medium. It is unique among transient methods in that the experiment yields thermal conductivity directly, not thermal diffusivity. It was first used to measure the thermal conductivity of soil,²¹ and has since been used for insulating materials,²² polymers,²³ and various liquids.^{24 25}

For a true line source of infinite length in a medium of infinite extent, the temperatures at any two times are related by the following:²⁵

$$T_2 - T_1 = \frac{q}{4\pi k} \ln \frac{\theta_2}{\theta_1} \quad (9)$$

where T = temperature of the line,

q = heating rate,

k = thermal conductivity, and

θ = time.

In practice, the source is of finite length and has a finite diameter, but it has been shown²⁵ that this can be compensated for by the

²¹Stalhane, B. and Pyk, S., Tek. Tidskr., 61, 289 (1931).

²²Vos, B. H., App. Sci. Res., 45, 425 (1954).

²³Underwood, W. M., and McTaggart, R. B., CEP Symp. (Heat Trans.), 56, 261 (1959).

²⁴Van der Held, E. F. M. and van Drunen, F. G., Physica, 15, 865 (1949).

²⁵Horrocks, J. K. and McLaughlin, E., Proc. Roy. Soc. A273, 259 (1963).

introduction of a zero time correction, θ_0 , giving

$$T_2 - T_1 = \frac{q}{4\pi k} \ln \frac{\theta_2 - \theta_0}{\theta_1 - \theta_0} \quad (10)$$

The value of θ_0 is determined by plotting temperature vs log time and finding by trial the θ_0 which gives a straight line. The slope of this line is then $q/4\pi k$. Equation (10) correctly describes the time-line temperature relationship for a medium of finite extent as long as the temperature change at the boundary is negligible. It has been shown that the time at which the temperature change is no longer negligible is given by the equation

$$\frac{d^2}{4a\theta_c} = 0.6 \quad (11)$$

where d = distance from line source to boundary,

a = thermal diffusivity, and

θ_c = time after which Equation 10 is not applicable.

In this investigation, the powder is contained in a cylindrical cell with the heating source along the axis. A schematic drawing of the apparatus is shown in Figure V-44. The inside diameter of the cell is 0.75 in. so that $d = 0.375$ in. and, for the powders investigated, θ_c is approximately one minute.

Figure V-44

The cell is constructed of stainless steel and is 2 in. long. A hypodermic tubing having a 25-mil outside diameter is soldered in place along the axis and contains the heating wire, 36 gauge constantan wire. It also contains two

40 gauge iron-constantan thermocouples, the junctions being placed midway in the tube. Two reference iron-constantan couples are embedded in cement on the outside of the cell, and the thermocouples are connected as a thermopile. The heating wire is powered by a d-c source with a maximum output of 0.5 amp at 40 volts. The current through this wire is computed from the voltage drop across a 3-ohm precision resistor in series with the wire. The potential drop is measured with a potentiometer. The resistance of the heating wire is measured independently with a bridge. Knowing the current and resistance, it is possible to compute q , and thus to determine k from the temperature-log time plot.

The cell is connected to a manifold by a stainless steel tube. The manifold can be connected to a vacuum pump or a pressurized gas cylinder and is connected to pressure measuring instruments. High pressures are measured by the regulator gauge in the gas cylinder, moderate pressures and vacuums by a mercury manometer, and higher vacuums by a McLeod Gauge. Thermal conductivities have been measured using air, nitrogen, helium, and argon.

Since powder thermal conductivity is sensitive to the extent of mechanical packing, it was necessary to standardize the method of loading the cell so that reproducible results could be obtained. It was found that if the cell was gently tapped following loading, the powder contained 36% volume voids, in agreement with other random packing experiments with spheres. This procedure, which was used in the ignition experiments, was used in all the conductivity experiments.

b. Results with Nickel Powder

Preliminary experiments with nickel powder (-230 +325 mesh) were carried out to test the measurement and oxidation procedures. The conductivity was measured in helium, nitrogen, and argon at 24°C and at various pressures to determine how the gas influenced the effective conductivity of the powder. As shown in Figure V-45, the effective powder conductivity at atmospheric pressure is strongly dependent upon the gas used and has the same order as the gas conductivities, i.e., $k_{\text{He}} > k_{\text{N}} > k_{\text{Ar}}$.

The nickel powder was then oxidized in air for twelve hours at 400°C and the weight gain indicated that approximately 0.2% of the nickel had oxidized. There was a notable change in the appearance of the powder and some evidence of local sintering, but there was no difficulty in breaking the agglomerates. The thermal conductivity of the oxidized nickel powder was 5% less than that of the unoxidized powder at gas pressures above 10 mm.

c. Results with Uranium Powders

Experiments with uranium powders have been conducted using three size fractions, -16 +20, -70 +80, and -230 +325 mesh. The

Figure V-45

THERMAL CONDUCTIVITY OF NICKEL POWDER(-230 +325 mesh) AT 24°C

thermal conductivities of the unoxidized powders in nitrogen gas at 24°C are shown in Figure V-46. The increase in thermal conductivity with particle size is consistent with other measurements of powder thermal conductivity.²⁶ The conductivity of the unoxidized, medium-size powder, -70 +80 mesh, at 24, 150, and 280°C is shown in Figure V-47 as a function of the nitrogen pressure. The residual conductivity as the pressure approaches zero is slightly higher at 280°C than at 24°C. This was probably due to the fact that the powder was packed at 24°C and the temperature of the cell was then

Figure V-46

THERMAL CONDUCTIVITY OF
UNOXIDIZED URANIUM POWDERS
IN NITROGEN AT 24°C

108-7218

²⁶ Masamuni, S. and Smith, J. M., Ind. Eng. Chem. (Fund.) 2, 136 (1963).

Figure V-47

THERMAL CONDUCTIVITY
OF UNOXIDIZED URANIUM POWDER
(-70 +80 mesh) IN NITROGEN

108-7219

raised to 280°C, so that the thermal expansion of the particles resulted in somewhat better contact.

At present, thermal conductivity measurements with oxidized uranium powder in nitrogen have been carried out only with the -70 +80 fraction powder. The powder was placed in a Petri dish and weighed. It was then oxidized in an oven at 150°C, and reweighed to determine the percent reaction to UO₂. After the thermal conductivity was measured, the powder was further oxidized. The rate of oxidation for the powder is shown in Figure V-48; from 200 to 700 minutes the rate is approximately linear, but after 700 minutes there is an increase in the rate.

Figure V-49 shows the effect of oxidation upon the thermal conductivity at 24°C for powders in which as much as 11.8% of the uranium

Figure V-48

RATE OF OXIDATION
OF -70 +80 MESH
SPHERICAL URANIUM POWDER
AT 150°C

108-7220

has been oxidized. The initial oxidation has a greater effect in reducing the thermal conductivity than subsequent incremental oxidation. It has been observed that the oxidation of uranium powders is marked by the appearance of oxide nodules on the surface of the spherical particles (ANL-6333, p. 201). It appears that the onset of nodule formation may have a greater effect on the thermal conductivity than subsequent growth of nodules as more oxide is produced. Nodule formation very likely changes the nature of the particle to particle contact.

The effect of oxidation upon the thermal conductivity of the -70 +80 powder at 280°C is shown in Figure V-50. The effect of oxidation is even less marked at 280°C than at 24°C. The bulk conductivities of gases increase approximately as the square root of the temperature, whereas, in general, conductivities of solids decrease with temperature. This means that, as the temperature increases, the contribution from the gas to the effective powder conductivity increases, so that changes in the solid properties will likely have less effect on the effective powder conductivity. The effect of oxidation on the thermal conductivity of the fine uranium powder, -230 +325 mesh, is currently being investigated.

A literature survey has revealed a number of theories for powder thermal conductivity expressed in terms of particle size, gas pressure, bulk solid and gas conductivities, and state of compaction. The theory of heat conduction in powders is being studied in order to choose the most appropriate model to describe the results of this study.

Figure V-49

THERMAL CONDUCTIVITY
OF -70 +80 MESH
SPHERICAL URANIUM POWDER
IN NITROGEN AT 24°C

108-7221

Figure V-50

THERMAL CONDUCTIVITY
OF -70 +80 MESH
SPHERICAL URANIUM POWDER
IN NITROGEN AT 280°C

108-7222

3. Aluminum-U₃O₈ Thermite Reaction (L. Baker, J.D. Bingle, R. Warchal, C. Barnes)

The need for aluminum-base dispersion fuel elements for high flux reactors has led to the development of aluminum-uranium oxide cermet. The 1955 Geneva Conference Reactor (GCR) used an Al-UO₂ fuel. Great difficulty was experienced during manufacture of the GCR fuel elements because of abnormal dimensional growth during elevated temperature fabrication procedures. The growth of the fuel plates was traced to volume changes accompanying the following reaction:²⁷

The reaction reached 90 to 100 percent completion in 10 hr at 600°C in 52 w/o UO₂ fuel plates.

Attempts to improve upon the UO₂-Al cermet led to the discovery that the reaction of U₃O₈ with aluminum was much slower at the temperatures needed for fabrication.²⁸ It has been shown that 3000 hr were required for complete reaction at 600°C.²⁹ Fuel plates could, therefore, be fabricated from U₃O₈ and aluminum with relatively little difficulty arising from dimensional changes attending reaction between the components. This process, however, leads to a fuel element in which remains the potential for an exothermic "thermite" reaction between the components.

A brief study of the reaction was reported in a previous progress report (see ANL-6333, p. 221) in which cold-pressed compacts containing 10 and 50 w/o U₃O₈ were subjected to differential thermal analysis. The results of this study indicated that there was no perceptible heat evolved in the 10 w/o U₃O₈ specimen over the range 25 to 1200°C. A definite exothermic reaction occurred between 900 and 950°C with the specimen containing 50 w/o U₃O₈. The rise in temperature of the specimen was only about 30°C and the area under the differential temperature-time curve indicated that the heat evolution was between 60 and 90 cal/g.

²⁷Waugh, R.C., The Reaction and Growth of Uranium Dioxide - Aluminum Fuel Plates and Compacts, ORNL-2701 (1959).

²⁸Beaver, R.J. and Cunningham, J.E., Recent Developments in Aluminum-Base Fuel Elements for Research Reactors, Fuel Elements Conference held at Gatlinburg, Tenn., May 14-16, 1958, TID-7559 (part 1), p. 40 (1959).

²⁹Belle, J., (Ed.) Uranium Dioxide: Properties and Nuclear Applications, USGPO (1961), p. 369.

It has been reported in a more recent publication³⁰ that violent reactions occurred with mixtures containing from 74.5 to 89.8 w/o U_3O_8 . The differential thermal analysis method was used in these studies and peak heights up to 4.56 mv (Pt, Pt-13% Rh) were reported, which corresponded to a spontaneous temperature rise of about 330°C. The reactions were initiated at specimen temperatures of 820 to 1050°C, depending upon the particle sizes of powders used to prepare the pressed compacts. It was also reported in this study that surface temperatures reached as high as 2200°C during ignition. The reported violence of the reaction prompted a further study of the reaction over a wider composition range and these are reported below.

a. Experimental

A series of cold-pressed compacts were prepared which contained 30, 45, 60, 75, and 90 w/o U_3O_8 . The U_3O_8 was prepared from commercial UO_2 by calcining at 1200°C for 15 hr. The U_3O_8 was sieved and only the -400 mesh fraction was used in preparing specimens. The particle size distribution was determined using a Coulter Counter* and the shapes of the particles were observed by means of photomicrographs. The particle size distribution of the U_3O_8 powder is shown in Figure V-51 and indicates

Figure V-51

PARTICLE SIZE MEASUREMENTS OF -400 MESH U_3O_8 AND ALUMINUM POWDERS (Determined by means of a Coulter Counter)

108-7223

³⁰Fleming, J.D. and Johnson, J.W., Aluminium- U_3O_8 Exothermic Reactions, Nucleonics 21 (5), 84 (1963).

*Analyses performed by J. Gabor and L. Marek.

the median particle size to be 12μ . A typical photomicrograph of the U_3O_8 is shown in Figure V-52. The aluminum was Alcoa 120 powder (2S aluminum) and only a -400 fraction was used. The particle size distribution of this powder is included in Figure V-51.

Figure V-52

TYPICAL PHOTOMICROGRAPH OF -400 MESH U_3O_8 POWDER

108-7224

The powders were stored in a desiccator over Drierite for several days followed by dry mixing on a ball mill in several flasks containing rubber impactors. Pellets were then formed by dry pressing in a 5/8-in. diameter die at 10,000 lb force. Some of the pellets were pressed in a 3/4-in. diameter die at 20,000 lb. Pellets were nominally 3/4 in. long. After pressing, an axial hole 1/8 in. in diameter was drilled more than half way through each pellet to serve as a thermocouple well. A platinum-platinum, 10 w/o rhodium thermocouple, enclosed in an alumina sheath was inserted in the holes.

Some of the pellets were prepared with 3% water added to the powder mixture just before pressing. Two experiments were performed with

unenriched Argonaut fuel plates. These are about 0.17 in. thick and are composed of a 39 w/o U_3O_8 - 61 w/o aluminum cermet which is pressed, sintered, and clad with a few mils of aluminum. Specimens were prepared by stacking five 3/4-in. diameter discs of the plate material in an alumina crucible. The clad was not removed, and the effective U_3O_8 concentration was, therefore, somewhat less than 39 w/o.

Two different furnaces were used for the heating experiments. One was a 300 kc, 20 kw induction heater, which was coupled to a covered graphite container 1 3/4 in. in diameter by 5 in. long, while the other was a platinum wound Marshall Furnace.

The container used with the induction heater was completely enclosed within a 2-in. diameter quartz tube through which slowly flowing tank argon gas was passed. A chromel-alumel control thermocouple was imbedded near the external surface of the graphite crucible. The crucible was supported in the quartz tube on a bed of alundum beads. The specimen pellet was inserted in an alumina crucible 3/4-in. ID by 3/4 in. in depth. The alumina crucible was then supported at the center of the graphite enclosure by means of a structure of stainless steel foil and wire. Leads from the control thermocouple, the sample thermocouple, and another thermocouple located within the graphite enclosure were brought out through sealing wax at a cooled end of the quartz tube several feet above the graphite container.

Two series of experiments were performed in the induction heated graphite furnace. In one series of tests, furnace temperature, as indicated by the control thermocouple, was programmed to increase at approximately 25°C/min. This was accomplished by means of a recorder-controller which was fed from the chromel-alumel control thermocouple. The differential signal from the controller was used to determine the direction of drive of the large autotransformers controlling the power of the induction generator. Temperature-time behavior of the specimen pellet was recorded on a millivolt recorder having 1/4-sec full scale response time. In the other series of tests, the induction heater was preset to generate an equilibrium temperature of 1250°C. After loading the specimen, assembling the apparatus, and displacing the air with argon, the induction heater was turned on to high power so that the desired temperature could be rapidly attained. The graphite container reached the equilibrium temperature of 1250°C in less than a minute because of the direct induction heating.

The platinum-wound Marshall Furnace was used in a series of tests in which the heating was performed in an air environment. These tests were of the plunging type in which sample pellets contained in the alumina crucibles were manually thrust into the core of the furnace which was preheated to about 1250°C. The pellets used in these experiments were 3/4 in. in diameter. The apparatus was nearly identical to that used previously in the determination of ignition temperatures of metals by the shielded method (see ANL-5974, p. 87). In these tests, the sample

temperature was measured by means of the imbedded thermocouple and also by means of a transient recording two-color optical pyrometer. The pyrometer has been previously described in detail (see ANL-6101, p. 144).

Chemical analyses of the residues from the heated pellets were performed for most of the pellets studied. A weighed sample of the residue was contacted with an iodine-methanol solution according to the method of Pryor and Keir.³¹ It has been shown that this treatment causes the dissolution of aluminum while leaving aluminum oxide films intact. It was anticipated that the treatment would also cause the dissolution of aluminum-uranium intermetallic compounds as well as aluminum itself, while the oxides of uranium would not be dissolved. Samples of both the dissolved material and the undissolved residue were then submitted for the quantitative determination of the uranium and aluminum present in each fraction. The results of the analysis are discussed later.

b. Results of Heating Experiments

In the experiments utilizing the induction-heated apparatus, duplicate runs were made in which the aluminum- U_3O_8 samples were heated at $25^\circ\text{C}/\text{min}$ in an argon environment. The concentration of U_3O_8 in the aluminum- U_3O_8 compacts tested was as follows (in weight percent): 30, 45, 60, 75, and 90. A typical temperature-time curve is shown in Figure V-53

Figure V-53

TEMPERATURE - TIME CURVES FOR ALUMINUM- U_3O_8 COMPACTS HEATED AT THE RATE OF 25°C PER MINUTE

108-7225

³¹Pryor, J.J. and Keir, D.S., J. Electrochem. Soc. 102, 370 (1955).

Figure V-54

TYPICAL RESIDUES OF U_3O_8 -ALUMINUM MIXTURES
HEATED TO 1250°C AT 25 DEGREES PER MINUTE

(Numbers indicate weight percent U_3O_8)

(Portions of crucible remain attached to 30 and 45 w/o U_3O_8 specimens;
center thermocouple well visible in all samples)

108-6380 A

for each composition, while Figure V-54 shows typical specimen pellets after heating. The duplicate experiments showed that the results were closely reproducible. The temperature-time curves showed that no exothermic reaction was apparent in the 30 w/o U_3O_8 pellet but that marked self-heating occurred in the pellets containing 45 w/o or more U_3O_8 . Noticeable self-heating was initiated when the furnace temperature reached about 900°C.

The maximum self-heating occurred in pellets containing 60 w/o U_3O_8 ; the peak specimen temperature was about 1300°C , which was about 400°C above the furnace temperature.

Experiments in the induction heated apparatus were also performed with one aluminum- U_3O_8 pellet of each of the following compositions: 30, 45, 60, 75, and 90 w/o U_3O_8 which contained, in addition, 3 w/o of water. The water was added at the time of pressing and the heating experiments were performed within a few hours of pressing. The temperature-time curves obtained with the moist pellets did not differ significantly from those obtained with the dry pellets. This result eliminated the possibility that the heat effects originated from a metal-water reaction.

Another series of single experiments with each of the five compositions was performed by the rapid heating method. The temperature-time traces obtained in these experiments are plotted in Figure V-55. The curves in the figure are displaced successively one minute to the right for clarity of presentation. On the far left of the figure is a heating curve for an inert sample (stainless steel) having the same dimensions as the experimental samples. The heating curve of the inert sample indicated that about 5 min were required for the temperature to rise from 600 to 1200°C . The endothermic melting of aluminum (m.p. 660°C) can be seen as inflections in the heating curve for aluminum-rich specimens. Comparison of the heating

Figure V-55

TEMPERATURE TRACES FROM RAPID HEATING OF
ALUMINUM- U_3O_8 CERMETS

curves of the cermet pellets with the curve of the inert sample shows that exothermic reaction began at temperatures only slightly above the aluminum melting point. It can be seen that rapid self-heating occurred in all of the cermet specimens, with the maximum effect occurring in the 75 w/o U_3O_8 composition. The peak temperature recorded by the thermocouple in the 75 w/o U_3O_8 pellet was about $1600^{\circ}C$, which was about $400^{\circ}C$ higher than the temperature of the graphite container.

Only a few experiments thus far have been conducted in air environment in the Marshall Furnace apparatus by the plunging method. These were performed with 3/4-in. diameter aluminum-75 w/o U_3O_8 specimens. The temperature-time curves recorded by the thermocouples were nominally identical with those plotted in Figure V-55 suggesting that the presence of air or differences between the two methods had no measurable effect on the reaction. The transient surface temperature was measured with the two-color pyrometer in these experiments. The temperature-time curves in the region of the peak temperature are given in Figure V-56 for the two

Figure V-56

TEMPERATURE-TIME RECORD OF 75 w/o U_3O_8 -ALUMINUM
PRESSED POWDER SPECIMENS
PLUNGED INTO FURNACE PREHEATED TO $1250^{\circ}C$

(temperature measured with an electronic two-color pyrometer)

108-7266

runs. The pyrometer has a time resolution of about 50 msec, suggesting that the rise, peaking, and the decrease of temperature were faithfully reproduced. The temperature peaks of $1730^{\circ}C$ and $1830^{\circ}C$ indicated some lack of reproducibility for the two runs. The values for the transient peak temperatures were somewhat higher than the highest peak temperature, $1600^{\circ}C$ (measured by a

thermocouple), in Figure V-55. The maximum rate of temperature rise deduced from the pyrometer traces was about $150^{\circ}\text{C}/\text{sec}$.

Two experiments were also conducted with the Argonaut fuel plate material. The experiments were performed in air in the Marshall furnace by the plunging technique. The transient temperature was measured by the two-color pyrometer and by an imbedded thermocouple. In each of the runs, both measurement methods yielded a peak temperature of 1350°C . The temperature-time curve for one of the runs is given in Figure V-57 and indicates a behavior intermediate between that found for aluminum-30 w/o U_3O_8 and aluminum-45 w/o U_3O_8 pellets, as shown in Figure V-55.

Figure V-57

TEMPERATURE-TIME RECORD
OF UNENRICHED ARGONAUT FUEL PLATE SPECIMENS
PLUNGED INTO FURNACE PREHEATED TO 1250°C

108-7227

c. Results of Chemical Analyses

Specimens of the aluminum- U_3O_8 mixtures submitted for chemical analysis included those heated to 1250°C at $25^{\circ}\text{C}/\text{min}$ and those heated rapidly to 1250°C . (In the rapid heating experiments, pellets were allowed to remain at 1250°C for about one-half hour.) The results of analytical chemical studies of the 75 w/o U_3O_8 specimens are given in Table V-11. The percentages of the original 75 w/o U_3O_8 pellets that were insoluble in the iodine-methanol solution ranged from 37.8 to 44.0 w/o. It is assumed that this material consisted of the oxide phases, U_3O_8 , UO_2 , and Al_2O_3 . The

Table V-11

SUMMARY OF ANALYTICAL RESULTS
FOR 75 w/o U₃O₈ -ALUMINUM SPECIMENS

(Basis 1 gram of sample)

Run ^a	Oxide (Insoluble)			Metal (Soluble)		
	Percent Oxide	U found as UO ₂ (g)	Al found as Al ₂ O ₃ (g)	U found (g)	Al found (g)	Al/U Atom Ratio
1	41.3	-	-	0.464	0.139	2.7
2	40.5	-	-	0.450	0.133	2.6
3	44.0	0.232	0.204	0.421	0.131	3.1
4	43.2	0.230	0.213	0.430	0.130	3.0
9	42.0	0.211	0.207	0.447	0.138	2.7
15	39.9	0.143	0.244	0.469	0.149	2.8
16	43.0	0.204	0.194	0.429	0.151	3.1
29 ^b	37.8	0.182	0.198	0.483	0.142	2.9
Eqn. 13	40.7	0.217	0.190	0.442	0.151	3.0

^aResidue from one run could not be dissolved satisfactorily.

^bContained 3% H₂O originally.

soluble material was assumed to be the metallic phases, aluminum and the aluminum-uranium intermetallic compounds. These assumptions were based on the demonstrated ability of the iodine-methanol solution to dissolve aluminum without affecting aluminum oxides.³¹ From eight individual analyses of the quantity of uranium and aluminum in the soluble material (see Table V-11), an aluminum to uranium atom ratio of 2.86 was obtained with a standard deviation of 0.18. This suggested that the main, overall reaction may be described by the following equation

Calculations based on Equation 13 are included in Table V-11 and indicate that all of the experimental values are consistent with the equation within the experimental scatter.

Equation 13 corresponds to a stoichiometric mixture consisting of 68.5 w/o U₃O₈ and 31.5 w/o Al. The 30, 45, and 60 w/o U₃O₈

compositions studied in the heating experiments contain excess aluminum relative to the stoichiometric amount. Complete reaction, therefore, would result in the complete removal of uranium from the oxide (insoluble) phase. The analytical results were examined from this point of view and are presented in Table V-12. The results show that 1.0% or less of the uranium remained in the oxide phase for the pellets that originally contained 30 and 45 w/o U_3O_8 . A maximum of 3.4% of the uranium initially present remained as oxide in the 60 w/o U_3O_8 pellets. Experimental values for the percentage of oxide in the heated pellets are in good agreement with values calculated from Equation 13 as shown in Table V-12.

Table V-12

ANALYTICAL RESULTS FOR COLD-PRESSED U_3O_8 -ALUMINUM COMPACTS
CONTAINING EXCESS ALUMINUM AFTER HEATING TO 1300°C

Run No.	Original Composition (w/o U_3O_8)	Final Composition			
		Insoluble (oxides)(w/o) ^a		Uranium Found in Insoluble Material (g U/g Sample)	Percent of Uranium in Oxide Form
		Exp.	Calc.		
6	30	9.7	9.69	0.0009	0.3
12	30	10.8	9.69	0.0002	0.1
17	30	10.9	9.69	0.0016	0.6
7	45	15.3	14.52	0.0013	0.3
13	45	15.5	14.52	0.0011	0.3
28	45	15.7	14.52	0.0023	0.6
18	45	15.8	14.52	0.0038	1.0
22	45	15.5	14.52	0.0030	0.8
8	60	23.5	19.4	0.0055	1.0
14	60	20.9	19.4	0.0042	0.8
25	60	22.3	19.4	0.0154	3.0
19	60	24.3	19.4	0.0175	3.4
23	60	21.4	19.4	0.0038	0.7
24	60	21.7	19.4	0.0139	2.7
27	60	21.7	19.4	0.0121	2.4

^aCalculated according to Equation 13.

Analytical chemical results for the pellets containing 90 w/o U_3O_8 were unsatisfactory. The pellets after heating were a hard refractory material and were not attacked readily by the iodine-methanol solution. The soluble intermetallic compounds apparently could not be dissolved because of a protective insoluble oxide matrix. No useful results could be obtained.

d. Discussion and Future Program

The results of the chemical analyses indicate that the iodine-methanol dissolution method, developed by Pryor and Keir³¹ for aluminum-aluminum oxide separations, is useful in analyses involving aluminum-uranium intermetallic compounds and aluminum and uranium oxides. The results also indicate that UAl_3 is the favored reaction product and that the thermite reaction went to completion in each heating experiment. The former finding is consistent with the fact that UAl_4 has no region of stability above 730°C . The UAl_3 compound is stable up to 1350°C and is probably favored thermodynamically over UAl_2 .

X-ray diffraction analyses were performed in the previous study (see ANL-6333, p. 221) and by Fleming and Johnson.³² These results have shown the presence of UO_2 , Al_2O_3 , UAl_4 , UAl_3 , UAl_2 , and Al. Uranium, however, is not formed. The intermetallics UAl_2 and UAl_4 are probably formed by disproportionation of some of the UAl_3 as the specimens are cooled below 730°C , where UAl_4 can form.

The greatest thermal effects were noted with the 60 w/o U_3O_8 specimens in the slow-heating experiments and with the 75 w/o U_3O_8 specimens in the rapid-heating experiments. This is consistent with the conclusion that the stoichiometric mixture contains 68.5 w/o U_3O_8 . The violent ignitions and the peak temperature of 2200°C reported by Fleming and Johnson³⁰ for specimens containing 85 w/o U_3O_8 were not observed with any of our pellets. One possibility for the difference in results, suggested by J.D. Fleming,³³ was that our U_3O_8 powder ($12\text{-}\mu$ av. particle size) was finer than his ($44\text{-}\mu$ av. particle size). Reaction may begin slowly at lower temperatures with the finer material so that less energy remains to be

³²Fleming, J.D. and Johnson, J. W., "Materials for High Temperature Nuclear Engineering Applications", Progress Report No. 3, Aug. 15, 1960 to Aug. 15, 1961, Engineering Experiment Station, Georgia Institute of Technology.

³³Fleming, J.D., Georgia Institute of Technology, Personal Communication.

liberated rapidly at higher temperatures. With the coarser U_3O_8 , Fleming reported a violent reaction which appeared to be triggered at about 1000°C . Self-heating rates, as Fleming deduced from high-speed motion pictures of ignitions of the coarse material, were several thousand degrees per second, whereas the greatest self-heating rate noted in this study was $150^\circ\text{C}/\text{sec}$.

Studies with coarse U_3O_8 powder will be undertaken in an effort to resolve the apparent differences in results. Studies will be performed to account quantitatively for the energy of the reaction. It may be possible to simulate the reaction rate and heat loss rates mathematically and thereby describe the heating curves found experimentally. It would then be possible to calculate the rate of chemical energy release that would occur as a result of a rapid nuclear excursion in an aluminum- U_3O_8 fuel material.

VI. ENERGY CONVERSION*

Methods of directly converting nuclear energy into electricity are being studied. The main effort is being directed toward the development of regenerative emf cells. The thermocouple effect has also been investigated in a limited program. Current work on this method consisted mainly of collecting data needed to round out the program, which is being terminated.

A. Regenerative Emf Cells (C.E. Crouthamel)

Work was continued on the development of regenerative emf cells for the conversion of reactor heat into electrical energy. Such devices should operate continuously in a closed Carnot cycle, subject to Carnot efficiency limits for the overall conversion of heat to useful energy. The maximum Carnot efficiency, Eff, is given by the equation

$$\text{Eff} = \frac{T_2 - T_1}{T_2}$$

where T_1 is the cell operating temperature at which the isothermal and, as nearly as possible, reversible formation of the cell products occurs and T_2 is the high temperature at which isothermal regeneration of the cell reactants from the cell product is accomplished. In one of the two adiabatic steps of the Carnot cycle, the cell product is transferred to the regenerator; in the other adiabatic step, the cell reactants are returned to the emf cell. The cell products regenerated at the high temperature T_2 must be separated before they are returned to temperature T_1 , where spontaneous recombination would otherwise occur with the resulting loss of all useful electrical energy. The upper practical limit of T_2 is generally considered to be about 1000°C. This limit, however, is subject to continuous re-evaluation, since it merely reflects the availability of suitable container material.

Two main types of regenerative emf cells are being studied. These are bimetallic concentration cells and the hydride cell.

The bimetallic cells have two liquid metal electrodes in contact with a molten salt electrolyte which contains only the salts of the anode metal. The anode metals under consideration are lithium and sodium. The overall reaction of these cells is

Molten Anodic metal A $\rightarrow$ A dissolved in molten cathodic metal B

* A summary of this section is given on pages 41-42.

The hydride cell consists of an anode of molten metal, an electrolyte of molten salts containing the anode metal ion, and a hydrogen gas cathode. In cell operation, the liquid anode metal is oxidized to ions of the metal and the hydrogen gas is reduced to hydride ions. Currently, only two hydrides, lithium hydride and calcium hydride, are of interest as possible reactants in regenerative cells.

The known bimetallic cells offer a wide range of atomic interaction energies so that it is possible to select systems with regeneration temperatures from about 2000°C to about 800°C for cells with voltages ranging from about 2.0 volts to about 0.5 volt. The hydride cells do not offer this flexibility in operating range.

Work was continued on the lithium-bismuth cell. The emf-temperature-composition data were obtained for the cell in the temperature range 775-1150°K and for concentrations of lithium in the cathode up to saturated solutions of Li_3Bi in bismuth. The analysis of these data has been completed. In addition, an effort was made to obtain emf data on saturated lithium-bismuth cells at temperatures in the range from 1150°K to about 1273°K; this effort has not been successful with the cell design used at the lower temperatures. The reason for this is being investigated in more detail. However, this difficulty does not seem likely to be a problem for the practical operation of the cell since it would be expected that the cell would operate at about 775°K. The above data are being collected to furnish thermodynamic information on this system.

Because of its unusual physical properties, tin is very attractive as a cathodic liquid metal for a thermally regenerative cell. Liquid tin has very low equilibrium vapor pressures at high temperatures (e.g., at 1000°C, tin vapor pressure is about 2×10^{-4} mm Hg, whereas bismuth vapor pressure is about 2 mm Hg). In addition, tin is a liquid at a relatively low temperature, m.p. 232°C. The low melting point of tin allows a liquid metal cathode to be operated at low cell temperatures and the liquid cathode with dissolved alkali metal to be transported to the high-temperature, regenerative portion of the cycle. The low vapor pressure of tin is important in that it permits regeneration of the lithium-tin binary with virtually pure lithium in the vapor phase at relatively high temperature. The experimental studies on the lithium-tin binary system (emf-temperature-composition data) are completed, and the data are reported graphically. Thermodynamic analysis of the data, similar to that reported for the lithium-bismuth system, is in progress.

The design of both the bimetallic and hydride cells requires a fused salt electrolyte that will allow relatively low temperature cell operation with electrolyte which is thermodynamically stable with respect to the molten metal anode. Solid-liquid equilibria for most fused salts with lithium hydride are not known. The phase diagram for the lithium hydride-lithium chloride system has been reported previously (ANL-6687, p. 195 and ANL-6725, p. 228). In this report lithium hydride-lithium bromide experimental data and

thermodynamic calculations are given. Also, there has been considerable disagreement in the literature on the latent heat of fusion of lithium hydride; values range from 7000 ± 2000 cal/mole to 4900 ± 700 cal/mole. This has been redetermined as 5240 cal/mole by calibrating the length of the thermal arrests during fusion under a pure hydrogen atmosphere.

Special studies of the high temperature regeneration of lithium-bismuth, lithium-tin and sodium-tin binary alloys have been completed. Mass spectrometric data yielded ΔF° (1120°K) for the formation of $\text{Li}_3\text{Bi(s)}$ of -46.0 kcal/mole, compared to -43.2 ± 0.9 kcal/mole for the emf studies. Regeneration of the lithium-bismuth system did not appear too favorable, however, because of the relatively high bismuth content in the vapor phase. Regeneration of both sodium-tin and lithium-tin systems appears very favorable. In each case, the original alloy was 50 a/o and the undistilled alloy after distillation was 1.6 a/o sodium in tin with 90% of the sodium distilling and 36.0 a/o lithium in tin with 17% of the lithium distilling.

1. Bimetallic Cells (M. S. Foster and R. Eppley)

Thermodynamics of the Lithium-Bismuth System

Systematic studies to determine the thermodynamic properties of lithium-bismuth alloys in the temperature region between 775 and 1150°K have been concluded and data analysis has been completed.

Information used for the calculation of thermodynamic properties came from temperature-cell potential-composition studies reported previously (ANL-6687, p. 188, and ANL-6725, p. 225) and concerned three types of cells:

type 1: $\text{Li(l)}/\text{LiCl-LiF}/\text{Li in Bi(l)}$ (X_{Li} = atom fraction Li)

type 2: $\text{Li(l)}/\text{LiCl-LiF}/\text{Bi(l)}$ saturated with $\text{Li}_3\text{Bi(s)}$ and

type 3: Bi(l) saturated with $\text{Li}_3\text{Bi(s)}/\text{LiCl-LiF}/\text{Li in Bi}$ (X_{Li} = atom fraction Li).

The characteristic properties of the cell of type 1 were calculated from data obtained from laboratory studies of cells of type 2 and type 3.

For the derivation of partial molar quantities from the calculated data for the cell of type 1, the cell reaction is written

Data at various temperatures between 810 and 1150°K for $X_{\text{Li}} = 0.05, 0.20, 0.30, \text{ and } 0.40$ were used. It was desirable to derive the surface function which best fits the data according to the least squares method.

Initially, an arbitrary choice of

$$\frac{\Delta\mu_{\text{Li}}^{\text{E}}}{X_{\text{Bi}}^2} = \frac{-FE - RT \ln X_{\text{Li}}}{X_{\text{Bi}}^2} \quad (2)$$

was made for the fitting function, where $\Delta\mu_{\text{Li}}^{\text{E}}$ is the excess chemical potential of lithium in bismuth, X_{Bi} is the atom fraction of bismuth in the alloy, F is the value of the Faraday, E is the calculated cell potential versus a pure lithium anode, R is the gas constant, and T is the absolute temperature. It was found that, at constant composition, this function was fit by a quadratic function of temperature, i.e., $A + BT + CT^2$. In general, A , B , and C are functions of X_{Li} , and a plot of these coefficients versus X_{Li} suggested that A was linear in X_{Li} , while B and C were quadratic in X_{Li} . A fit of the data to the function

$$\begin{aligned} \frac{\Delta\mu_{\text{Li}}^{\text{E}}}{X_{\text{Bi}}^2} = & (a_1 + a_2 X_{\text{Li}}) + (a_3 + a_4 X_{\text{Li}} + a_5 X_{\text{Li}}^2) T \\ & + (a_6 + a_7 X_{\text{Li}} + a_8 X_{\text{Li}}^2) T^2 \end{aligned} \quad (3)$$

was made using a generalized least squares program and the IBM 704F computer. The resulting standard deviation in $\Delta\mu_{\text{Li}}^{\text{E}}/X_{\text{Bi}}^2$ was 177 cal/mole. The coefficients were used to calculate $\Delta\mu_{\text{Li}}^{\text{E}}$ as a function of temperature and composition. The region of validity of $\Delta\mu_{\text{Li}}^{\text{E}}$ so calculated extends only over the portion of the phase diagram in which bismuth-rich, unsaturated alloys are found.

The data reported previously for the cell of type 2

when combined with the phase diagram given by Hansen and Anderko,¹ may conveniently be compared with the extrapolation of the data from unsaturated cells of type 1 used in the initial calculation both in terms of the composition of the saturated alloy and in terms of the extrapolated $\Delta\mu_{\text{Li}}^{\text{E}}$. The comparison of $\Delta\mu_{\text{Li}}^{\text{E}}$ for temperatures of 850 and 1000°K is seen in Figure VI-1 and of the composition of the saturated alloy in Figure VI-2. The curves in Figure VI-1 represent the results of calculations using the least squares derived coefficients; the circles represent data calculated for a type 1 cell, and the squares indicate the values derived from the saturated composition as given by Hansen and Anderko combined with data from the type-2 cell. The extrapolation of the partial molar quantity as derived by the least squares method to the region of saturation is seen to be poor. The curves fit reasonably well in the region of the data, but deviate upward rapidly for alloy compositions

¹Hansen, M. and Anderko, K., Constitution of Binary Alloys, McGraw-Hill, 1958.

Figure VI-1

EXCESS CHEMICAL POTENTIAL OF LITHIUM IN LITHIUM-BISMUTH ALLOYS

108-7260

Figure VI-2

PHASE DIAGRAM¹ OF LITHIUM-BISMUTH SYSTEM COMPARED WITH CALCULATED COMPOSITIONS OF ALLOYS SATURATED WITH Li_3Bi

108-7252

more nearly saturated with $\text{Li}_3\text{Bi(s)}$. The same behavior is exhibited in Figure VI-2, where the curve represents the region of interest on the phase diagram as given by Hansen and Anderko and the points in circles represent the saturated compositions calculated from the least squares coefficients and the data from the type 2 cell.

It was decided that this behavior was forced on the least squares result by the inclusion of the X_{Bi}^2 term in Equation 2. The inclusion of this term was originally suggested by Margules and has been derived by others using the methods of statistical mechanics (as reported by Darken and Gurry²). This term should be included in any treatment of alloys over the entire composition range of $0 \leq X_{\text{Li}} \leq 1$. However, since this study was concerned only with alloys which were bismuth-rich, the inclusion of this term will not necessarily yield the best fit to the data over a limited composition range. An attempt was then made to fit the excess chemical potential data by means of the least squares method to the equation

$$\Delta\mu_{\text{Li}}^{\text{E}} + A + B X_{\text{Li}} \quad (4)$$

where A and B are now independent quadratic functions of temperature. This was accomplished by using the function

$$\frac{\Delta\mu_{\text{Li}}^{\text{E}}}{X_{\text{Bi}}^2} = \frac{(b_1 + b_2T + b_3T^2) + (b_4 + b_5T + b_6T^2) X_{\text{Li}}}{X_{\text{Bi}}^2} \quad (5)$$

The standard deviation of $\Delta\mu_{\text{Li}}^{\text{E}}/X_{\text{Bi}}^2$ in this case was 127 cal/mole; the extrapolations of $\Delta\mu_{\text{Li}}^{\text{E}}$ are shown in Figure VI-3. The calculated phase diagram based on the use of Equation 5 is shown in Figure VI-4. The use of Equation 5 is judged to be better than the use of Equation 3 in that the experimentally derived values for a type 1 cell fit the curve more closely and the extrapolated portion of the curve shows better agreement with values calculated from data obtained from a type 2 cell and the phase diagram.¹ For these reasons, the equation used in calculating other thermodynamic quantities for the one-phase liquid region of the lithium-bismuth system between the composition limits of pure bismuth and a lithium-bismuth solution saturated with $\text{Li}_3\text{Bi(s)}$ and between the temperature limits of 775 and 1150°K is given by

$$\frac{\Delta\mu_{\text{Li}}^{\text{E}}}{X_{\text{Bi}}^2} = \frac{(9397 + 18.16T - 0.0109T^2) + (7103X_{\text{Li}} - 19.44TX_{\text{Li}} + 0.0068T^2X_{\text{Li}})}{X_{\text{Bi}}^2} \quad (6)$$

²Darken, L.S. and Gurry, R.W., Physical Chemistry of Metals, p. 265, McGraw-Hill, 1953.

Figure VI-3

EXCESS CHEMICAL POTENTIAL OF LITHIUM IN THE LITHIUM-BISMUTH SYSTEM

108-7258

Figure VI-4

COMPOSITIONS OF LITHIUM-BISMUTH ALLOYS SATURATED WITH Li_3Bi COMPARED WITH PHASE DIAGRAM¹

108-7253

Applying the Gibbs-Duhem relationship, it was possible to calculate the activity of bismuth in the solution for the region $0 \leq X_{\text{Li}} \leq$ saturated with Li_3Bi and $775^\circ\text{K} \leq T \leq 1150^\circ\text{K}$ and thus it was also possible to calculate the standard free energy of formation of $\text{Li}_3\text{Bi(s)}$ using data from the cell of type 2 in which the reaction may be written as:

If Li(l) and $\text{Li}_3\text{Bi(s)}$ are said to be in their standard states in the cell environment, then ΔF for the reaction is:

$$\Delta F = -\mathfrak{S}E = 1/3 \Delta F_f^\circ, \text{Li}_3\text{Bi(s)} - RT \ln a_{\text{Bi (in alloy)}}^{1/3} \quad (8)$$

This equation has been used to calculate ΔF_f° for various temperatures. The results are shown in Figure VI-5.

Using the calculated partial molar properties of lithium and bismuth, it is possible to make some estimation of the partial vapor pressures of lithium and bismuth over an alloy at higher temperatures. Assuming that such an extrapolation may be made outside the region of reliability, the partial pressure of lithium over a 0.60 atom fraction lithium alloy with bismuth at 1273°K is estimated as 0.24 mm Hg and the partial pressure of bismuth over the same alloy is estimated as 0.15 mm Hg. This indicates that the partial pressure of lithium is so low that separation of any substantial

Figure VI-5

CALCULATED STANDARD FREE ENERGY OF FORMATION OF
 $\text{Li}_3\text{Bi(s)}$

quantity of lithium vapor would be difficult. Further, the vapor separated would contain considerable bismuth. Since the lithium-bismuth cell would be difficult to regenerate thermally, other systems which might be easier to regenerate are being investigated. Some of these systems are described below.

Lithium-Tin Cell Experiments

Previous studies (ANL-6725, p. 225) of the cell of type 4:

with an overall cathode composition of 0.70 atom fraction Li have produced cell potential-temperature data which in turn have indicated a higher liquidus temperature (1003°K) than that obtained from the published phase diagram (982°K)¹.

Further studies designed to resolve this temperature difference and to elucidate the thermodynamic properties of the binary lithium-tin system have been completed. Thermal analysis of a 0.70 atom fraction lithium sample indicates a solid-liquid equilibrium temperature of 991°K. Potential measurements with the cell of type 5

indicate the liquidus equilibrium (overall composition 0.70 atom fraction Li) temperature of 993°K. These are considered to agree satisfactorily, but are lower than reported previously from studies of a type 4 cell. The liquidus temperature reported previously is probably high due to an irreversible transfer of lithium from the anode to the cathode.

Other cells of type 6

have been operated at various values of X_{Li} between 0.10 and 0.70. At the higher concentration of lithium in the anode, solid Li_5Sn_2 was present at temperatures below 993°K. The cell potential was measured for each composition at various temperatures between 767 and 1117°K. Using the voltage-temperature curve previously determined for the type 2 cell,

data from cells of type 6 were treated to yield values which would be applicable to cells of type 7:

Curves were plotted from these values and are shown in Figure VI-6. The

Figure VI-6

TEMPERATURE-POTENTIAL CURVES FOR CELLS OF TYPE 7:

Li(1)/LiCl-LiF(1)/Li in Sn (X_{Li} = atom fraction Li)

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derived standard deviation (σ) of the individual data points and the number (N) of raw data points used in deriving the curve (N) are shown near each curve. A thermodynamic analysis of these data is in progress.

High Temperature Reference Electrode Studies

Cells of type 2 have previously been operated successfully in the temperature region between 775 and 1100°K. In view of the potential utility of the cathode as a reference electrode in the study of alloys involving lithium as a component, it is desirable to extend the temperature range of successful operation to 1273°K. Two attempts to operate cells of type 2 in this higher temperature region were unsuccessful; the cell emf decreased in an irregular manner, evidently because of massive transfer of lithium from the anode.

To determine whether transfer of lithium from the anode was the cause of the unsuccessful operation of the cell at higher temperatures, several samples of LiCl-LiF eutectic over 0.70 atom fraction lithium in bismuth, taken with stainless steel sampling buckets, have been analyzed for lithium and bismuth at temperatures between 973 and 1273°K. Lithium analysis consisted of an acid titration in aqueous solution, while bismuth was determined by a tracer technique. The average ratio Li/Bi was determined as 2.7 ± 0.3 . This result suggests that Li_3Bi may be the species in solution. However, a conclusive distinction between molecular dissolution of Li_3Bi in the melt, suspension of solid particles of Li_3Bi in the melt or individual dissolution of lithium and bismuth in the melt does not seem possible at present. Further experimental work is in progress.

2. Lithium Hydride-Lithium Halide Solid-Liquid Equilibrium Studies (Carl E. Johnson and John W. Allen)

In operating a lithium hydride emf cell through a regenerative cycle, it is important to keep the cell operating temperature as low as possible in order to maximize the Carnot cycle efficiency. Therefore, thermal analysis studies are being made of several lithium salt systems in a search for lower melting eutectics. All components in the fused salt electrolyte must, of course, be thermodynamically stable with respect to lithium metal.

The solid-liquid equilibrium data for the lithium hydride-lithium bromide binary system have been completed. These data were obtained using the apparatus previously described in ANL-6596, p. 203. The lithium hydride-lithium bromide system has a eutectic melting point of 452.3°C and a eutectic composition of 29.7 m/o lithium hydride. The liquid-solid equilibrium data are plotted in Figure VI-7. Within the limits of the compositions sampled, 5 and 95 m/o lithium hydride, solid solution formation was not observed in either the X-ray powder patterns or the heating-cooling curves.

An excellent outline is given by Wagner³ for the method of calculating thermodynamic functions for each component from the liquid-solid equilibrium data. In this type of analysis, only the heterogeneous

Figure VI-7

PHASE DIAGRAM FOR THE LiH-LiBr SYSTEM

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³Wagner, C., Thermodynamics of Alloys, Addison Wesley Press, Cambridge, Mass. (1952).

equilibrium between pure solid and the binary liquid mixture is considered. These data are given in Tables VI-1 and VI-2. An integrated form of the Gibbs-Duhem equation was used to calculate the excess chemical potential of one component in the region of the other as given in Figure VI-8.

The lithium hydride-lithium bromide system is very similar to the lithium hydride-lithium chloride system (ANL-6725, p. 228) in that deviations from ideal solution behavior are not great. However, the activity coefficient exhibits anomalous behavior near the eutectic for both components. Peritectic dissociation of some compound close to the eutectic composition would explain this anomaly. However, X-ray diffraction analysis of material from either side of the eutectic composition did not disclose any unusual distortions in the crystal lattice and therefore appears to rule out peritectic formation.

Table VI-1

THERMODYNAMIC DATA FOR LiH IN LiH-LiBr SYSTEM

<u>LiH</u> <u>(mole fraction)</u>	<u>Te^a</u> <u>(°K)</u>	<u>$\bar{F}^M{}^b$</u> <u>(cal/mole)</u>	<u>$\bar{F}^E{}^c$</u> <u>(cal/mole)</u>	<u>γ^d</u>
1.0	859.0	-	-	1.0
0.897	935.9	-127.3	74.9	1.038
0.800	912.2	-259.5	145.0	1.075
0.749	899.8	-329.1	187.7	1.099
0.700	886.7	-403.6	224.9	1.120
0.601	860.3	-554.6	315.9	1.172
0.550	843.2	-653.2	348.6	1.192
0.486	820.4	-786.0	390.4	1.217
0.406	786.4	-986.1	422.6	1.237
0.351	758.1	-1153.7	423.7	1.238
0.297 ^e	725.5	-1348.0	402.4	1.224

^aTe Liquidus-solidus equilibrium temperature.

^b $\bar{F}^M$ Relative partial molar free energy.

^c $\bar{F}^E$ Excess partial molar free energy.

^d γ Activity coefficient.

^e Eutectic composition.

Table VI-2

THERMODYNAMIC DATA FOR LiBr IN LiH-LiBr SYSTEM

LiBr (mole fraction)	T_e^a (°K)	$\bar{F}^M{}^b$ (cal/mole)	$\bar{F}^E{}^c$ (cal/mole)	γ^d
1.00	820.8	-	-	1.0
0.950	811.4	-48.1	34.7	1.017
0.902	800.4	-104.1	60.0	1.031
0.850	786.7	-173.6	80.6	1.042
0.804	772.4	-245.8	88.9	1.046
0.750	751.7	-348.9	80.7	1.042
0.703 ^e	725.5	-477.6	30.7	1.016

^a T_e Liquidus-solidus equilibrium temperature.

^b $\bar{F}^M$ Relative partial molar free energy.

^c $\bar{F}^E$ Excess partial molar free energy.

^d γ Activity coefficient.

^e Eutectic composition.

Figure VI-8
EXCESS FREE ENERGY IN THE LiH-LiBr SYSTEM

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Latent Heat of Fusion of Lithium Hydride

The heat of fusion of lithium hydride is the least accurately known parameter being used in the calculation of thermodynamic functions for each component in the lithium hydride-lithium chloride and the lithium hydride-lithium bromide systems. In an early report,⁴ Messer et al. made an estimate of the heat of fusion of lithium hydride as being 7000 ± 2000 cal/mole, based on time-temperature curves of the fusion process. In a subsequent report,⁵ Messer calculated a cryogenic value from the lowering of the freezing point of lithium hydride by the solutes lithium oxide and calcium hydride. This value is $\Delta H_f = 4900 \pm 700$ cal/mole. More recently, a value of $\Delta H_f = 5237$ cal/mole was reported⁶ by a group from Thompson, Ramo, Wooldridge. This measurement was made using a drop-type adiabatic calorimeter. Included in this report were references to private communications concerning two other calorimetric values: Hoffman of ORNL reported a value of 5518 cal/mole, and Wilson, Boehn and Cooper reported a value of 4967 cal/mole. The average of these three calorimetric determinations is $\Delta H_f = 5240 \pm 225$ cal/mole. With a melting point of 959.0°K , this value yields an entropy of fusion for lithium hydride of 5.46 cal/mole deg, which agrees favorably with the range shown by the lithium halides.⁷ The heat of fusion being such an important parameter, it was decided that a check should be made using the thermal analysis apparatus (see ANL-6596, p. 203).

Before quantitative heat measurements could be made with this equipment, it was necessary to calibrate the apparatus by determining the rate of heat loss of the apparatus while carrying out fusions of such compounds as potassium chloride, sodium iodide, magnesium chloride, and lithium chloride. The heats of fusion of these compounds are reasonably well known and their melting points bracket a temperature range about that of the salt (LiH) in question.

The rate of heat flow through the sample container is equal to the product of its thermal conductivity, a constant depending on the size and shape of the container, and the temperature difference between its inner and outer surfaces. With a given container, the first two factors are constant; the temperature difference is fixed and maintained constant by instrumental control. The resulting constant heat flow serves to supply the specific heat of the sample, its heat of transformation, and the specific heat of an intermediate part of the container itself; i.e.,

$$C\Delta t = \Delta T_1 Q_1 W_1 + L_1 W_1 + \Delta T_1 Q_r W_r$$

⁴Messer, C.E., Damon, E.B., Maybury, P.C., NYO-3958 (1957).

⁵Messer, C.E., NYO-8027.

⁶Vogt, J.W., NP-11888 (1961).

⁷Dworkin, A.S., and Bredig, M.A., J. Phys. Chem. 64, 269 (1960).

where C is the heat flow per unit time; Q_1 , Q_r , and W_1 , W_r are the specific heats and masses of the sample and of the effective part of the container, respectively; ΔT is the temperature change in time Δt ; and L_1 is the latent heat of any transformation that may occur in the temperature range ΔT .

The latent heat of a transformation causing an arrest at constant temperature is directly proportional to the duration of this arrest. With the temperature constant, the above equation reduces to

$$C\Delta t = L_1 W_1$$

Therefore, once C has been determined, it is possible to determine the heat of fusion of any unknown salt.

For all experiments, enough material was used to give about 8 cc of melt in the sample cup, which was enough to cover the heat conduction fins of the center thermowell. That it was important to use this volume of liquid in each experiment is evident from the data. The rate of heat loss for one sample of sodium iodide consisting of only 5.39 cc of material differed considerably from the rate for 8-cc samples of sodium iodide.

At temperatures at or above its melting point, lithium hydride must be handled in hydrogen gas to prevent decomposition; therefore, all experiments were carried out in a hydrogen atmosphere. No observable reactions occurred with any of the salts when they were heated in a hydrogen atmosphere.

Experimental data are given in Table VI-3 and are plotted in Figure VI-9. Two values of the latent heat of transformation were calculated for lithium hydride from the experimental data. One value was calculated using 7000 cal/mole⁴ for the heat of fusion of lithium hydride; the other value was calculated using 5240 cal/mole⁶ for the heat of fusion. Excellent agreement with the other materials was obtained when 5240 cal/mole was used for the heat of fusion of lithium hydride, indicating that this value should be used in all subsequent calculations.

In constructing the curve in Figure VI-9, the datum for lithium chloride was not used because the value was unreliable. Three experiments were run with lithium chloride, and these varied from about 2 cal/min to the tabulated 8.6 cal/min. It would also seem more reasonable to expect that the transition from the radiative heat loss to a convective heat loss would be smoother than the abrupt change required by the data. Lithium chloride appears to have some unusual thermal conductivity characteristics, as attested to by our own experience.⁸

⁸Johnson, C.E., Crouthamel, C.E. and Wood, S.E., *Nature* 201, 293 (1964).

Table VI-3

RATE OF LOSS OF HEAT FOR VARIOUS SALTS

<u>Salt</u>	<u>T_m^a (°K)</u>	<u>Mole</u>	<u>ΔH_f^b (cal/mole)</u>	<u>Time Duration of Arrest (min)</u>	<u>cal/min</u>
LiH	959.0	0.8365	5,240	378.0	11.56
NaI	933.0	0.2011	5,640	120.0	9.45
NaI	933.0	0.2005	5,640	129.0	8.77
KCl	1043.0	0.2690	6,280	72.0	23.46
LiCl	881.0	0.3995	4,740	217.5	8.67
MgCl ₂	987.6	0.3474	10,300	213.0	16.80
NaI ^c	933.0	0.1318	5,640	73.5	10.13

^aT_m - melting point

^bΔH_f - latent heat of fusion

^cOnly 5.39 cc of sample

Figure VI-9

CALIBRATION CURVE FOR THE
LATENT HEAT OF FUSION
OF LiH

108-7290

3. Regeneration Studies (Albert K. Fischer and S. Johnson)

Some aspects of the regeneration of a number of bimetallic systems have been surveyed. The particular kind of regeneration which has been of concern is thermal regeneration. In principle, in this mode of regeneration, the cathodic alloy product from the cell is thermally decomposed at a temperature higher than the cell current-generating temperature. The more volatile component, which is preferably the more electropositive anode component, is distilled out from the cathodic alloy, condensed, and returned to the anode; the residue is returned to the cathode.

The Lithium-Bismuth System

Several bimetallic systems have been examined in regard to the feasibility and extent of regeneration. First to be studied was the Li-Bi system in the form of the compound Li_3Bi . This material was studied mass spectrographically in cooperation with J. Berkowitz and W. Chupka in the Physics Division. From the mass spectrographic data, the amounts and identities of vapor species in equilibrium with Li_3Bi were determined. It was found that Li^+ and Bi^+ were the predominant vapor species. The compound Li_3Bi was, however, found not to vaporize congruently since the ratio of Li^+ to Bi^+ did not have a constant value of 3 over the course of the experiment. However, this did not preclude the calculation of an equilibrium constant for the reaction since $\text{Li}_3\text{Bi(s)}$ remained in the Knudsen cell.

This equilibrium constant was found to be $K_{1120^\circ\text{K}} = 1.92 \times 10^{-21}$. From this value, the free energy of reaction $\Delta F^\circ_{1120^\circ\text{K}}$ was calculated to be 93.9 kcal/mole. Using established thermodynamic data, this value for ΔF° for the above reaction was converted to $\Delta F^\circ_{1120^\circ\text{K}} = +46.0$ kcal/mole for the reaction

This is regarded as favorable agreement with a value of $+43.2 \pm 0.9$ kcal/mole obtained from extrapolated emf data (see Figure VI-5).

Other mass peaks corresponding to LiBi^+ , Bi_2^+ and LiBi_2^+ were observed in very minor proportions. In view of the preponderance of Li^+ and Bi^+ in approximately comparable proportions, the chance of separating Li and Bi in the vapor phase in a thermal regeneration step of a regenerative cell did not appear good.

At least one other mass spectrometric study of an alkali metal-bismuth system is planned. Work has started on the Rb-Bi system as represented by the compound Rb_3Bi . In addition to providing information for the regeneration problem, the mass spectrographic studies also will permit evaluation of the relative cross sections of the alkali metals toward ionization by electron impact. This aspect is of interest to the cooperating group in the Physics Division.

The Lithium-Tin and Sodium-Tin Systems

Preliminary evaluation of the regeneration potentialities of the Li-Sn and Na-Sn systems was obtained by equilibrating a 50 a/o alloy at about 950°C with a lower temperature zone. Each alloy was contained in a sealed stainless steel tube. The more volatile alkali metal condensed on a stainless steel sponge in the cooler zone to the extent that the activity of the cooler, purer alkali metal became equal to the activity of the alkali metal in the residual alloy at the high temperature. In the case of Na-Sn alloy, 90% of the sodium condensed in a zone at 550°C. In the case of Li-Sn alloy, 16.7% of the total lithium condensed in a zone at a temperature intermediate between the extremes of 950° and 450°C provided in the equilibration tube. From this information, the Na-Sn system appears capable of a greater degree of regeneration than does the Li-Sn system. However, for the eventual selection of a system for a regenerative cell, other factors, such as the emf delivered by the cell and the corrosiveness of the system, will have to be considered also. Work on the Na-Sn and Li-Sn systems will be continued with a refined apparatus to get accurate activity data.

Other systems of a relatively noble metal with an alkali metal may provide an alternative. One such system which will be examined by the equilibration technique just described is the Na-Bi system.

B. Thermoelectricity Research (R. K. Edwards)

Studies in thermoelectricity have been underway in an effort to contribute to the future technological development of a method for the direct conversion of heat generated in a nuclear reactor to electrical power by means of the thermocouple effect.

This program is being discontinued, and present studies are mainly concerned with measurements needed to conclude some of the investigations that had been undertaken. A number of measurements were carried out on refractory solid systems, primarily uranium monosulfide and certain solid solutions containing this material.

Refractory Thermocouple Systems (M. Tetenbaum, F. Mrazek)

Electrical Resistivity Measurements of US and US-ThS Solid Solutions

Resistivity measurements as a function of temperature have been made on sintered specimens of US and solid solutions having the following compositions: 25 mole percent US-75 ThS and 75 US-25 ThS. With US, X-ray analysis showed only single phase material. Secondary phases were found to be less than 0.1% based on chemical analysis; with the solid

Figure VI-10

RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR SINTERED SPECIMENS OF URANIUM MONOSULFIDE, THORIUM MONOSULFIDE, AND US-ThS SOLID SOLUTIONS

108-6902

solutions, the secondary phase (ThOS) was found to be approximately 5%. The results are shown in Figure VI-10, along with previous resistivity measurements (ANL-6725) obtained with ThS and a solid solution of composition 50 US-50 ThS. It is apparent from Figure VI-10 that US and the US-ThS solid solutions show, in general, a very weak temperature dependency of resistivity. In addition, except for initial disordering effects, the resistivity of US decreases with increasing ThS content. This is shown in Figure VI-11, where the room temperature resistivity is plotted as a function of composition. The shape of the curve is somewhat typical of the resistance of disordered alloys in which a continuous range of solid solutions is formed from pure components that differ considerably in their resistivity.

Figure VI-11

ROOM TEMPERATURE RESISTIVITY VERSUS COMPOSITION FOR US-ThS SYSTEM

(Sintered specimens - 85% Theoretical Density)

108-6900

With the 75 US-25 ThS composition, a minimum in the resistivity curve was found to occur at approximately 600°C. A rerun with the sample confirmed the existence of the minimum. The significance of the minimum is not clear to us at the present time.

It has been suggested⁹ that the weak temperature dependence of resistivity of US and US-ThS solid solutions might arise from compensating effects. Thus, an increase in the number of phonons with temperature would lead to increased resistivity, whereas an increase in the number of charge carriers (a temperature-dependent Hall coefficient has been noted for US from room temperature to approximately 90°C¹⁰) and a shift of the Fermi level toward a region of a lowered density of states (leading to a decrease in carrier scattering in the 'f' band) would contribute to a decreased resistivity.

Temperature Dependency of the Figure of Merit for US

Using recent thermal conductivity values obtained by R. Dunworth (Metallurgy Division) on a sintered specimen of uranium monosulfide (97% theoretical density), figure of merit values were estimated as a function of temperature using resistivity and Seebeck coefficient values. The results are summarized in Table VI-4. Although the figure of merit values do not change appreciably in the temperature range investigated, these values seem too low for useful high temperature thermoelectric power generation by a factor of approximately ten.

Table VI-4

FIGURE OF MERIT AS A FUNCTION OF TEMPERATURE FOR URANIUM MONOSULFIDE

Temp (°C)	Seebeck Coefficient ($\mu\text{V}/^\circ\text{C}$)	Resistivity ($\mu\text{ ohm-cm}$)	Thermal ^a Conductivity (watts/cm deg)	Figure of Merit (deg ⁻¹)
25	50.0	286	0.0979	0.89×10^{-4}
100	55.6	298	0.0982	1.1×10^{-4}
200	58.8	310	0.1035	1.1×10^{-4}
300	59.2	318	0.1095	1.0×10^{-4}
400	58.4	323	0.1170	0.90×10^{-4}
500	56.6	325	0.1252	0.79×10^{-4}
600	54.4	327	0.1331	0.68×10^{-4}
700	52.0	328	0.1395	0.59×10^{-4}
800	49.4	328	0.1432	0.52×10^{-4}
900	46.6	328	0.1472	0.45×10^{-4}
1000	43.5	328	0.1490	0.41×10^{-4}

^aData of R. Dunworth, Metallurgy Division, ANL, corrected to 85% theoretical density.

⁹Professor F. Blatt (Michigan State University), Private communication.

¹⁰M. Kanter and C. W. Kazmierowicz, Solid State Science Division, ANL, Private communication.

Lattice Thermal Conductivity for Uranium Monosulfide

A range estimate of the lattice contribution to the thermal conductivity of uranium monosulfide can be made from the resistivity and thermal conductivity values shown in Table VI-4. The thermal conductivity can be expressed as follows:

$$k = k_e + k_L \quad (1)$$

where k_e is the carrier and k_L the lattice thermal conductivity. It should be pointed out that k_e and k_L are not independent, since the carriers provide a mechanism for scattering the lattice vibrations. Assuming a Wiedemann-Franz ratio of 2.45×10^{-8} (volt/deg)², k_e and then k_L can be estimated from Equation 1. The results are summarized in Figure VI-12. It is apparent from Figure VI-12 that the lattice vibrations make a significant contribution to the thermal conductivity of uranium monosulfide which can be considered degenerate. The observed increase of thermal conductivity with temperature appears to be consistent with the increase in carrier density with temperature, as indicated by the trend in Hall measurements of Kanter and Kazmierowicz.¹⁰

Figure VI-12

THERMAL CONDUCTIVITY OF URANIUM MONOSULFIDE

108-6901

VII. NUCLEAR CONSTANTS*

(D. C. Stupégia)

One of the most important numbers used in the description of the behavior of a nuclear reactor is the quantity $\eta = \nu / 1 + \alpha$, which is the number of neutrons formed per neutron absorbed in the fissile material. Here ν is the average number of neutrons produced per fission, and α is the ratio of the capture and fission cross sections of the fissile nucleus. The net result of capture and fission is the production of $\eta - 1$ neutrons; that is, there are at most $\eta - 1$ neutrons available for breeding. The breeding ratio actually obtained is a fraction of $\eta - 1$, the value of the fraction depending upon the geometry of the reactor and the presence of neutron absorbing materials in its structure. Taking these variables into account, the breeding ratio can be written.

$$R = \eta - 1 - \frac{A + \Lambda - F(\nu' - 1)}{1 + \alpha},$$

where, for each fissile atom fissioned, A is the number of neutrons captured by parasites, Λ is the number leaking out of the system, and F is the number of fertile nuclei fissioned; ν' is the average number of neutrons per fission in the fertile species. Therefore, besides ν and α , and the fission parameters of the fertile species, the breeding ratio is a function of the cross sections which remove neutrons unproductively from the system. These are the cross sections for radiative capture and for the (n, p) and (n, α) reactions. Further, a knowledge is needed of the cross sections for reactions which degrade the neutron energy spectrum of the reactor, that is, the inelastic and elastic neutron scattering processes. All of these reactions are functions of neutron energy, which in fast reactors, ranges from one kev or less to several Mev.

In the present program, many of the above types of neutron reactions have been studied for fissile and fertile species and for other materials used in the construction of reactors. Radiative capture cross sections of rhenium-187 and gadolinium-158 and the neutron total cross sections of rhenium have been recently measured. Preparations are also being made to obtain information which will allow the estimation of the breeding ratios for various fast reactor systems. The ratio of capture and fission cross sections will be measured as a function of position in EBR-II. Samples of Pu^{239} , Pu^{240} , Pu^{242} , U^{233} , U^{235} , and U^{238} will be used in the initial studies.

A. Neutron Capture

(D. C. Stupégia, A. A. Madson, M. Schmidt)

Monoenergetic neutrons are produced by the reaction $\text{Li}^7(p, n) \text{Be}^7$, resulting from the bombardment of a lithium target with protons from the

*A summary of this section is given on page 42.

Van de Graaff accelerator. Irradiation of a sample of the material being studied produces a neutron capture product whose gamma ray spectrum is analyzed with a NaI scintillation spectrometer. The absolute disintegration rate corresponding to the gamma ray spectrum of the irradiated target is determined by comparing this spectrum to the spectrum of a known activity of the same species counted in the same geometry, the activity of the latter having been determined by absolute beta counting. The neutron flux is measured with a fission chamber, which counts fissions in a sample of uranium. Results are given below for the capture cross sections of rhenium-187 and gadolinium-158.

1. Rhenium

Rhenium has recently been considered as a component in structural materials for reactors because of its metallurgical properties and its high-temperature characteristics. Its metallurgy resembles that of tantalum and tungsten, and its alloys with the latter are highly ductile. The use of such alloys as structural materials for fast reactors has been suggested. The disadvantages of rhenium are its high cost and its low resistance to high temperature oxidation in air. In these respects, rhenium is again like tungsten.

The present studies, however, are concerned only with the nuclear properties of rhenium. Rhenium consists of two isotopes, Re^{185} and Re^{187} , which are present in concentrations of 37.07% and 62.93%, respectively. Neutron irradiation of rhenium produces the following three capture reactions:

Preliminary results on the capture cross section of Re^{187} were reported in ANL-6725, p. 243. These data and the results of more recent measurements are combined in Figure VII-1. These capture cross section values represent the sum of the cross sections for the production of Re^{188m} and Re^{188} . The values are accurate to about $\pm 8\%$, and the neutron energy spread about each point is about ± 20 kev. When calculations are complete, it will be possible to state the cross sections for Re^{185} and for the production of each state of Re^{188} , separately.

Figure VII-1

CAPTURE CROSS SECTION
OF RHENIUM-187

108-7301

2. Gadolinium

The possible use of several of the rare earth elements as components of ceramic fuel elements and control rods has been discussed previously (see ANL-6379, p. 226). Recently, neutron total cross sections of some of the naturally occurring rare earths and the neutron capture cross sections of some of their isotopes have been determined. Capture cross section data for Gd^{158} can now be reported. Figure VII-2 shows the radiative

Figure VII-2

NEUTRON CAPTURE CROSS SECTION OF GADOLINIUM-158

108-7150

capture cross section of Gd^{158} for neutron energies between 0.05 and 2 Mev. The cross section values are accurate to about $\pm 8\%$; the neutron energy spread is about ± 25 kev at each point. The rise in the cross section near 1 Mev resembles the behavior of many other nuclides whose atomic number and mass number are even.

3. Lower Energy Neutron Capture

In the capture work to date, the lower limit of the neutron energy has been about 0.15 Mev. This is the energy below which it is not possible to get a useful neutron beam from the $\text{Li}^7(\text{p}, \text{n}) \text{Be}^7$ reaction at 0° with respect to the proton beam. Other neutron-producing reactions suffer from the limitation that their neutron intensity is quite low. It is possible, however, to get reasonable neutron intensities of low energy from the lithium reaction by using the neutrons at angles greater than zero degree with respect to the direction of the proton beam. By taking neutrons at an angle somewhat greater than 90° , measurements of capture cross sections at neutron energy as low as about 5 kev will be attempted. For this work, targets have been obtained in the form of thin ribbons which will be placed in the neutron beam in such a way as to be in the path of all neutrons being emitted within the desired polar angle.

B. Neutron Total Cross Sections of Rhenium

The total cross section of rhenium is obtained by measuring the total attenuation of a neutron beam by the sample. This work has been carried out with the neutron collimation and detection apparatus associated with the Physics Division's Van de Graaff accelerator. Using the $\text{Li}^7(\text{p}, \text{n}) \text{Be}^7$ reaction, and taking neutrons at 45° and at 135° with respect to the proton beam, one can measure the cross sections between a few kev and 2 Mev.

Figure VII-3

The neutron total cross section of rhenium has been measured for neutron energies between 3 kev and 2 Mev, and the results are shown in Figure VII-3. The cross section values are in general accurate to about $\pm 2\%$

or less. The neutron energy spreads about each point range from ± 0.5 kev for the lowest energies to about ± 20 kev for the highest energies. Nuclear energy level structure is evident in the low energy region, but at the higher energies such structure can no longer be resolved. At the low energy end of the curve, the fast chopper data of Melkonian, Havens, and Rainwater¹ are also shown. The figure makes apparent the upper limit of usefulness of the fast chopper and the lower limit of the present method. The two sets of data can be compared only roughly, since the number of data points is limited in this region.

C. Capture to Fission Ratios in EBR-II

To make calculations on the breeding gain of fast reactors, it is necessary to know (1) the capture and fission cross sections of the fissile and fertile species, and (2) the neutron spectrum of the reactor. Of main interest are the properties of U^{233} , U^{235} , and U^{238} , and the plutonium isotopes of mass 239 to 242. For many of these nuclides, much of the data are not known, and present techniques and availability of isotopes do not allow for their measurement in a reasonable length of time. As an alternate approach to this problem, preparations are being made to obtain information on the breeding gain of nuclear fuels in EBR-II by measuring the ratio of the capture and fission rates of the uranium and plutonium isotopes as a function of position in EBR-II. Samples of Pu^{239} , Pu^{240} , Pu^{242} , U^{233} , U^{235} , and U^{238} of sufficient quantity and purity for these measurements are now available to us. Enough material is available to place 6 or more samples of each isotope at various positions in EBR-II.

Following irradiations of several months in EBR-II, the samples will be analyzed for the number of fissions and captures. The numbers of fissions will be determined by separation and counting of the fission product cesium-137, and the number of captures will be measured by a mass spectrometric analysis of the capture product.

¹Melkonian, E., Havens, Jr., W. W. and Rainwater, L. J., Phys. Rev. 92, 702 (1953).